## Amine Functionalised Metal-Organic Frameworks for Carbon Dioxide Capture

A thesis submitted to the Faculty of Science, Monash University, in fulfilment of the requirement for the degree of

## **Doctor of Philosophy**

Christin Patzschke

M.Sc. Chemistry, University of Leipzig, Germany

School of Chemistry

Monash University

Australia





#### Notice 1

Under the Copyright Act 1968, this thesis must be used only under the normal conditions of scholarly fair dealing. In particular no results or conclusions should be extracted from it, nor should it be copied or closely paraphrased in whole or in part without the written consent of the author. Proper written acknowledgement should be made for any assistance obtained from this thesis.

#### Notice 2

I certify that I have made all reasonable efforts to secure copyright permissions for thirdparty content included in this thesis and have not knowingly added copyright content to my work without the owner's permission.

## Declaration

### Monash University

### Monash Research Graduate School

# Declaration for thesis based or partially based on conjointly published or unpublished work

### **General Declaration**

In accordance with Monash University Doctorate Regulation 17 Doctor of Philosophy and Research Master's regulations the following declarations are made:

I hereby declare that this thesis contains no material which has been accepted for the award of any other degree or diploma at any university or equivalent institution and that, to the best of my knowledge and belief, this thesis contains no material previously published or written by another person, except where due reference is made in the text of the thesis.

This thesis includes <u>one</u> original paper published in a peer reviewed journal and <u>six</u> unpublished publications. The core theme of the thesis is "Amine functionalised metalorganic frameworks for carbon dioxide capture". The ideas, development and writing up of all the papers in the thesis were the principal responsibility of myself, the candidate, working within the <u>School of Chemistry</u> under the supervision of <u>Prof. Alan L. Chaffee and Prof. Stuart R. Batten</u>.

The inclusion of co-authors reflects the fact that the work came from active collaboration between researchers and acknowledges input into team-based research

In the case of seven subchapters, as outlined in the following table, my contribution to the work involved the following:

Thesis	Publication title	Publication	Nature and extent of
chapter		status*	candidate's contribution
3.3	Postsynthetic modification of MIL-100(Fe): an adsorption study	Fully written, to be adjusted for submission to J Mater Chem A	Proposed original idea, prepared and analysed samples, developed interpretations, fully drafted paper and conclusion.
3.4	CO <sub>2</sub> adsorption in postsynthetically modified MIL-101(Cr)-NH <sub>2</sub>	Fully written, to be adjusted for submission to J Mater Chem A	Proposed original idea; prepared and analysed samples; developed interpretations; fully drafted paper and conclusion.

3.5	Postsynthetic modification of MIL-101(Al)-NH <sub>2</sub> for CO <sub>2</sub> capture	Fully written, to be adjusted for submission to J Mater Chem A	Proposed original idea, prepared and analysed samples, developed interpretations, fully drafted paper and conclusion.
3.6	Adsorption study on STA- 16(Co)	Fully written, to be adjusted for submission to J Mater Chem A	Proposed original idea, prepared and analysed samples, developed interpretations, fully drafted paper and conclusion.
5.2	Effect of flue gas contaminants on the stability and the post-combustion CO <sub>2</sub> capture in MIL-101 frameworks	Fully written, to be adjusted for submission to Energy Environ. Sci.	Proposed original idea, prepared and analysed samples, developed interpretations, fully drafted paper and conclusion.
5.3	Adsorption of flue gas contaminants in MIL- 100(Fe), MIL-53(Al)-NH <sub>2</sub> and STA-16(Co) and their effect on the framework stability and CO <sub>2</sub> uptake	Fully written, to be adjusted for submission to Energy Environ. Sci.	Proposed original idea, prepared and analysed samples, developed interpretations, fully drafted paper and conclusion.
6.2/6.3	Formation of a Non-Porous Cobalt-Phosphonate Framework by small pH Change in the Preparation of the Microporous STA-16(Co)	Published in CrystEngComm	Proposed original idea, prepared and analysed sample (except single- crystal XRD), drafted paper.

I have / have not (circle that which applies) renumbered sections of submitted or published papers in order to generate a consistent presentation within the thesis.

Signed: .....

Date: .....

## Abstract

Adsorption-based methods, such as pressure swing adsorption (PSA) or vacuum swing adsorption (VSA), are promising for capturing  $CO_2$  from natural gas or flue gas.  $CO_2$  adsorbents take a variety of forms, but one approach is the use of metal-organic frameworks (MOFs). These have attracted tremendous attention over the past decade due their porosity, high surface area, high pore volume, tuneable pore sizes and topologies. Previous studies on adsorbents of this type, such as CPO-27(Mg), HKUST-1, MOF-177 or MIL-101, have reported good  $CO_2$  adsorption capacities. Moreover, through introducing specific polar groups onto the organic linker or by grafting components onto coordinatively unsaturated sites (CUS) of specific MOFs, increases in the  $CO_2$  affinity have been observed, particularly at low pressure.

This project investigated the potential of MOFs for post-combustion carbon capture and high pressure separation processes. Two classes of MOFs were chosen:

- 1) MOFs containing CUS, which allow further postsynthetic modification (PSM) by grafting/impregnating these materials with amines.
- 2) Flexible MOFs, due to their good selectivities and high  $CO_2$  capacities.

Enhanced CO<sub>2</sub> capacities were sought by two approaches or a combination of both: (i) prefunctionalisation of MIL-53 and MIL-101 (where substituent groups are incorporated into the linker unit before MOF construction) and (ii) postsynthetic modification (PSM) of MIL-100 and MIL-101 (where substituents like ethylenediamine (ED), diethylenetriamine (DETA), 2<sup>nd</sup> generation polypropylenimine actamine dendrimer (DAB-AM-8) and polyethyleneimine (PEI) are added after MOF construction).

In the first part of this study, MIL-100/MIL-110(Al), MIL-100(Fe), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub>, MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) were synthesised and characterised by Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (PXRD), elemental analysis, N<sub>2</sub> sorption at -196 °C, helium density, scanning electron microscopy (SEM) and thermal decomposition. Despite the highly acidic environment during the preparation of MIL-100(Al), a 60:40 mixture with MIL-110(Al) was obtained in all cases. The formation of STA-16 was found to be strongly dependent on the pH. Slight changes in the pH resulted in the formation of a mixture with or pure phase of a new polymorphous MOF, denoted here as CoMOF. In contrast to the microporous character of STA-16(Co),

CoMOF is non-porous and therefore not applicable for  $CO_2$  capture. For this reason, no PSM on the CUS of MIL-100/MIL-110(Al) and STA-16(Co) were conducted.

In the second part of this study, all MOFs (except CoMOF) were evaluated for their ability to capture  $CO_2$  by measuring adsorption equilibria in the temperature range of 25 to 75/105 °C and a pressure range of 0 to 0.5 bar which is appropriate to the VSA process for post-combustion capture. Among them, MIL-53(Al)-NH<sub>2</sub> was found to have the highest  $CO_2$  adsorption capacity in the studied pressure and temperature range, while the MOFs containing CUS showed lower adsorption capacities.

In order to improve the capacities of MOFs containing CUS, PSM of MIL-100(Fe) and MIL-101(Cr/Al)-NH<sub>2</sub> were performed. Despite slower kinetics after the modification of the MIL-101-NH<sub>2</sub> frameworks, higher adsorption capacities were observed at pressures below 0.15 bar over the entire temperature range evaluated. A smaller impact of ED and DETA relative to PEI and DAB-AM-8 was expected due to the lower amine densities. However in comparison with the MOFs prior to PSM, the adsorption capacities were mostly lower or similar, suggesting that most of the amine groups inside the pores are not accessible for CO<sub>2</sub>. In other words, the results suggest that most of the pores were blocked. The maximum loadings of the amines used in this work were 150 wt% and 100 wt% for MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub>, respectively. The best performing materials were MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 and MIL-101(Al)-NH<sub>2</sub>-PEI-96. Despite the promising results for MIL-101(Al)-NH<sub>2</sub> containing 96 wt% PEI, the similar loadings of DAB-AM-8 (94 wt%) and DETA (88 wt%) resulted in complete pore filling and consequent reductions in CO<sub>2</sub> adsorption capacities at low pressures. While PSM of MIL-101 frameworks showed promising results, the increase in CO<sub>2</sub> adsorption capacity in PSM MIL-100(Fe) was relatively limited. One reason for this is the lower pore volume of the latter MOF, which decreases the amount of amine that can be incorporated. It was also found that the ED modified MIL-100(Fe) performed better than the PEI modified analogue; this result is probably due to the smaller size of ED in comparison with PEI. The comparison with the adsorption capacities of DAB-AM-8, DETA and PEI revealed that only MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 and MIL-101(Al)-NH<sub>2</sub>-PEI-96 showed higher CO<sub>2</sub> capacities than those of the neat amines and the parent MOF.

In the third part of this study, the stability of these MOFs under cycling conditions and in the presence of moisture (1 vol%  $H_2O$ ) was tested, since this would be essential for

industrial applications. Instability in the presence of  $H_2O$  is a known problem for many MOFs, since phase transformations and/or decomposition of the framework structure can occur. Due to the slower CO<sub>2</sub> adsorption/desorption kinetics at lower temperatures on MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 MIL-101(Cr)-NH<sub>2</sub>-PEI-68/88/130, and amine modified MIL-101(Al)-NH<sub>2</sub>, the cycling experiments were performed at 75 or 105 °C. The cycling temperature of DETA and ED modified MIL-101(Cr)-NH<sub>2</sub> was set to 45 °C. Other materials were cycled at 25 °C. The working capacities in each cycle of the PSM materials were lower or similar to those of the parent materials. One exception was MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 which outperformed MIL-101(Cr)-NH<sub>2</sub>. The improvement in working capacity and cycling at somewhat elevated temperature can be beneficial for postcombustion capture, since the temperature of the flue gas to be treated is often elevated also. The presence of amines resulted in decreased H<sub>2</sub>O capacities due to the lower pore volumes. Significant decreases in the performance of MIL-100(Fe) were found during the wet cycling processes due the progressive filling of the pores by H<sub>2</sub>O. PXRD studies showed that MIL-101(Cr)-NH<sub>2</sub>, MIL-100(Fe), MIL-100(Fe)-ED and MIL-100(Fe)-PEI remained stable in the presence of H<sub>2</sub>O. In contrast to this, MIL-101(Al)-NH<sub>2</sub> remained stable during the wet cycling experiments, but exhibited partial decomposition when H<sub>2</sub>O desorbed upon heating at 110 °C in Ar atmosphere.

While MIL-53(Al)-NH<sub>2</sub> exhibited a working capacity of 2.88 wt% under dry conditions,  $H_2O$  was found to almost completely disable the  $CO_2$  adsorption/desorption during cycling. Improvements were sought by PSM with benzoic anhydride. Due to the size of the anhydride, the working capacity was reduced to 0.37 wt% under dry conditions. The presence of  $H_2O$  resulted in further reduction of the working capacity to 0.08 wt% in the PSM material. Despite the decrease in working capacities both neat and PSM materials were stable during the wet cycling process.

In the third part of this study, high pressure CO<sub>2</sub> and N<sub>2</sub> adsorption/desorption experiments were performed on MIL-100/MIL-110(Al), MIL-100(Fe), MIL-101(Cr/Al)-NH<sub>2</sub> and STA-16 frameworks in the temperature range of 25 to 105 °C and pressure range of 0 to 40 bar. All materials were found to selectively adsorb CO<sub>2</sub>, with relatively high CO<sub>2</sub> adsorption capacities observable in the MIL-101 frameworks. The hydrothermal stability of selected MOFs was evaluated by measuring CO<sub>2</sub> isotherms before and after the treatment with H<sub>2</sub>O vapour (30, 60 and 90 % RH). While MIL-100/MIL-110(Al) and MIL-101(Al)-NH<sub>2</sub> showed decreases in the CO<sub>2</sub> uptake after the treatment with H<sub>2</sub>O at 30 % RH, the

phosphonate framework STA-16(Co) remained stable up to 60 % RH. PXRD studies revealed that the lower CO<sub>2</sub> adsorption capacities are due to the collapse of the MIL-110(Al) and MIL-101(Al)-NH<sub>2</sub> frameworks. In contrast to MIL-110, the diffraction pattern of MIL-100(Al) remained unchanged. Structural changes were observed in STA-16(Co) after the adsorption of H<sub>2</sub>O at 90 % RH; and this also resulted in a small decrease in CO<sub>2</sub> capacity from 13.2 wt% to 12.5 wt% at 25 °C and 5 bar.

In the last part of this study, the effect of flue gas impurities on the stability and the  $CO_2$  uptake of MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub>, MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) were evaluated by performing PXRD and FTIR studies, screening tests and a series of cycling experiments using NO, NO<sub>2</sub> and SO<sub>2</sub>. The MOFs were chosen in order to determine the effects of the CUS, flexible vs rigid frameworks, the type of metal cation and the nature of the organic linker molecule.

In order to determine the effect of NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability of the MOFs, PXRD studies were conducted after the materials had been subjected to 10000 ppm contaminant at 25 °C and at elevated temperatures (50, 80 °C). Decreased crystallinities and therefore partial loss in long-range crystallographic ordering or partially collapsed structures were observed in all MOFs. This suggests that the frameworks might ultimately collapse upon prolonged exposure to all contaminants examined. MIL-53(Al)-NH<sub>2</sub> was found to be flexible upon NO<sub>2</sub> adsorption, with a transformation from narrow pore (np) to large pore (lp) form taking place. STA-16(Co) was partially transformed into CoMOF after NO and SO<sub>2</sub> exposure, while NO<sub>2</sub> resulted in a complete collapse of the framework. FTIR studies of the samples after the exposure indicated that NO<sub>2</sub> is strongly interacting with the CUS in MIL-100(Fe), MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub> and STA-16(Co).

During the screening tests, the MOFs were subjected to 5000 ppm of contaminant over a heat ramp from 20 to 110 °C with a heating rate of 2 °C min<sup>-1</sup>. The peak mass change in the majority of the MOFs was found at 50 °C for NO and SO<sub>2</sub> and at 80 °C for NO<sub>2</sub>. The effect of contaminant concentration was investigated by exposing the samples to the contaminants by varying the partial pressures between 0 and 500 ppm (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>) or 5000 ppm (NO, NO<sub>2</sub>, SO<sub>2</sub>) until five cycles of adsorption and desorption were conducted at 25 °C. With increasing concentration of the contaminants an increase in mass uptake was observed. The presence of CUS in MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub>, MIL-100(Fe) and STA-16(Co) resulted in a strong

interaction with 5000 ppm NO<sub>2</sub> and irreversible adsorption. In contrast to this, the adsorption of NO<sub>2</sub> in MIL-53(Al)-NH<sub>2</sub> was completely reversible due to the flexibility of the framework. The impact of the contaminants on the ability to capture CO<sub>2</sub> was investigated by varying the CO<sub>2</sub> partial pressures between 0.05 and 0.15 bar while simultaneously varying the contaminant partial pressures between 0 and 500 ppm (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>) during five cycle experiments at 25 °C. The CO<sub>2</sub> working capacities in the presence of the contaminants were diminished in most cases, suggesting that the removal of NO, NO<sub>2</sub> and SO<sub>2</sub> is required prior to the capture process.

In summary, a series of MOFs were synthesised, characterised and evaluated for their utility in CO<sub>2</sub> capture processes. Amine modifications were shown to increase the CO<sub>2</sub> adsorption capacities; however the impact of the amine groups varied between the studied MOFs. It was found that an improvement in CO<sub>2</sub> adsorption capacities in MOFs with smaller pore volumes can be achieved by introducing smaller amines (ED), while PEI and/or DAB-AM-8 had a bigger impact on the MOFs with a larger pore volume. Decreases in working capacities were observed in the majority of the materials tested, although the stability of most materials was confirmed by PXRD measurements after wet cycling. Furthermore, the presence of flue gas contaminants was found to have a big impact on the CO<sub>2</sub> uptakes and the stability of the frameworks. Therefore, the application of the MOFs studied here for post-combustion capture is seen to be limited. However, the high H<sub>2</sub>O uptakes in MIL-100(Fe), MIL-101(Cr)-NH<sub>2</sub> and STA-16(Co) suggest that these materials might be useful as H<sub>2</sub>O sorbents. Furthermore, the good performance during high pressure CO<sub>2</sub> sorption experiments makes the MOFs good candidates for applications where high pressure separation processes can be utilised.

## Acknowledgements

Firstly I would like to acknowledge the funding provided by the Australian Government through its CRC Program to support this CO2CRC research project. Without the support from the Faculty of Science, Monash University, it wouldn't have been possible for me to undertake my PhD in Australia, so I would like to thank them for the financial support.

I would like to thank my supervisors, Professor Alan L. Chaffee and Professor Stuart R. Batten, for their help throughout this project in so many ways. Their assistance, discussions, encouragement, guidance and patience were essential in finishing my studies. A special thanks to Professor Alan L. Chaffee for giving me the opportunity to do my PhD at Monash University.

I owe my deepest gratitude to Dr. Marc Marshall and Dr. Gregory Knowles for their invaluable feedback, discussions, comments and suggestions on my papers. I also would like to thank Marc for conducting the high pressure adsorption measurements using an Intelligent Gravimetric Analyser (IGA-1 series, Hiden Analytical Ltd.) and guidance in data analysis. I sincerely thank Greg for the training he provided on most of the instruments as well as for the help and support in data analysis.

I acknowledge the use of facilities within the Monash Centre for Electron Microscopy. This research used equipment whose purchase was supported under the Australian Research Council's *Centres of Excellence* funding scheme (COE for Design in Light Metals).

I would like to thank Dr. Peter Nichols for his assistance with the NMR experiments, Craig Forsyth for conducting the single-crystal XRD, Dr. Martin Duriska and Craig Forsyth for their assistance with the PXRD, Dr. Xi-ya Fang for assistance in SEM, Campbell Microanalytical Laboratory at the University of Otago, New Zealand, for the elemental analysis. A special thanks goes to Bruce Dobney and Maria Triantis for giving me access to the IR facilities and letting me use and borrow the centrifuge from the 2<sup>nd</sup> year labs especially during the stressful weeks when finishing up my experimental work.

Thanks to all past and present members of the Alan Chaffee group, including Dirgarini J.N. Subagyono, Dr. Christian Vogt, Lachlan Ciddor, Anita D'Angelo, Brad Wells, Dr.

Jamileh Moghaddam, Mamun Mollah Mohammad Parsa, Dr. Anthony Auxilio, Dr. Mohammad Amer and Dr. Fei Yi, for creating such a friendly and supportive environment.

The support of my family has been invaluable in helping me to complete my studies, especially during difficult times when nothing seemed to work out the way it was planned or when I spent most of my days at work. Last but not least, I would like to thank my partner Quentin for his support, patience, reassurance and love over the last 2 years. Thank you for believing in me!

# **Table of Contents**

	Declaration	i
	Abstract	iii
	Acknowledgements	viii
	Table of Contents	X
	List of Figures	xx
	List of Tables	.xxxi
	List of Abbreviations	xxxii
1	Introduction	1
	1.1 Research motivation: The need to reduce greenhouse gas emissions	1
	1.2 The CCS process	2
	1.2.1 Carbon capture technologies	2
	1.2.1.1 Post-combustion	3
	1.2.1.2 Pre-combustion	3
	1.2.1.3 Oxy-fuel combustion	4
	1.2.1.4 Chemical looping combustion	5
	1.2.2 Carbon capture techniques	6
	1.2.2.1 Absorption	6
	1.2.2.2 Membranes	7
	1.2.2.3 Cryogenic separation	10
	1.2.2.4 Adsorption	10
	1.3 Metal-organic frameworks (MOFs)	14
	1.3.1 Carbon dioxide capture in MOFs	15
	1.3.2 Amine modification of MOFs	17
	1.3.2.1 Amine modification of MOFs via "prefunctionalisation" approach	18
	1.3.2.2 Amine modification of MOFs via postsynthetic modification (PSM)	26
	1.3.2.2.1 Covalent PSM	27
	1.3.2.2.2 Dative PSM	28
	1.3.2.2.3 Postsynthetic deprotection (PSD)	32
	1.3.3 Phosphonate MOFs	33
	1.3.4 Water stability in MOFs	35
	1.3.5 Effect of flue gas and syngas impurities on the stability of MOFs	37
	1.4 Research objective	38

	1.5	Res	earch hypothesis	39
	1.6	Ref	erence	40
2	Exj	perin	nental details and characterisation techniques	53
	2.1	Che	emicals	53
	2.2	Syn	thesis and characterisation of ligands	54
	2.2	2.1	Synthesis and characterisation of trimethyl-1,3,5-benzenetricarboxylat	e54
	2.2 pho	2.2 Ospho	Synthesis and characterisation of $N,N'-4,4'$ -bipiperidinebis(methonic acid) tetrahydrate (H <sub>4</sub> LL)	hylene- 56
	2.3	Syn	thesis of MOFs	60
	2.4	Cha	aracterisation techniques	61
	2.4	.1	Infrared spectroscopy	61
	2.4	.2	Nuclear Magnetic Resonance Spectroscopy (NMR)	62
	2.4	.3	Melting point measurement	63
	2.4	.4	Elemental analysis	63
	2.4	.5	Powder X-ray diffraction and Single crystal X-ray diffraction	63
	2	.4.5.	1 Powder X-ray diffraction (PXRD)	64
	2	2.4.5.2	2 Single crystal X-ray diffraction	65
	2.4	.6	Helium pycnometry	66
	2.4	.7	Textural property measurement	66
	2.4	.8	Scanning electron microscopy (SEM)	67
	2.4	.9	Thermal stability measurement	69
	2.5	Sor	ption measurements	71
	2.5	5.1	CO <sub>2</sub> sorption at low pressure	71
	2.5	5.2	Gas sorption at high pressure	72
	2.5	5.3	CO <sub>2</sub> cycling experiments	73
	2.5	5.4	Sorption of flue gas contaminants	75
	2.6	Ref	erences	75
3	MO	OFs v	vith coordinatively unsaturated sites for carbon capture	78
	3.1	Cha	apter overview	78
	3.2	Syn	thesis and characterisation of MIL-100/MIL-110(Al): an adsorption stu	dy79
	3.2	2.1	Introduction	79
	3.2	2.2	Experimental section	80
	3	.2.2.	1 Chemicals	80

3.2.2.2 Synthesis of MIL-100/MIL-110(Al)	81
3.2.3 Results and discussion	81
3.2.3.1 Characterisation of MIL-100/MIL-110(Al)	81
3.2.3.2 Low pressure gas sorption measurements	
3.2.3.3 Cycling experiments	
3.2.3.4 High pressure gas sorption measurements	87
3.2.4 H <sub>2</sub> O stability of MIL-100(Al)/MIL-110(Al)	89
3.2.5 Conclusion	90
3.2.6 References	91
3.3 Postsynthetic modification of MIL-100(Fe): an adsorption study	94
3.3.1 Abstract	94
3.3.2 Introduction	94
3.3.3 Experimental section	96
3.3.3.1 Chemicals	96
3.3.3.2 Preparation of MOFs	97
3.3.3.2.1 Synthesis of Me <sub>3</sub> BTC	97
3.3.3.2.2 Synthesis of MIL-100(Fe)	97
3.3.3.2.3 PSM of MIL-100(Fe)	97
3.3.3.3 Characterisation of MIL-100(Fe) before and after PSM	
3.3.3.4 Low pressure gas sorption experiments on MIL-100(Fe) before PSM	re and after
3.3.3.5 Cycling experiments on MIL-100(Fe) before and after PSM	
2.2.2.6 High pressure as comption experiments on MIL 100(Fe)	
5.5.5.0 High pressure gas sorption experiments on Mill-100(Fe)	
3.3.4       Results and discussion	
<ul> <li>3.3.4 Results and discussion</li></ul>	

References	116
ntary material	121
SEM images	121
Experimental and theoretical PXRD	121
Thermal decomposition	
FTIR spectra	
DTA profiles	
CO <sub>2</sub> adsorption in MIL-100(Fe)-PEI-50	
Impact of H <sub>2</sub> O – PXRD after wet cycling	124
References supplementary information	
2 adsorption in postsynthetic modified MIL-101(Cr)-NH2	127
Abstract	127
Introduction	127
Experimental section	130
1 Chemicals	130
2 Synthesis of MIL-101(Cr)-NH <sub>2</sub>	131
3 PSM of MIL-101(Cr)-NH <sub>2</sub>	131
4 Characterisation of MIL-101(Cr)-NH <sub>2</sub> before and after PSM	
5 Low pressure gas sorption measurements on MIL-101(Cr)-NH <sub>2</sub> PSM	before and 133
6 Cycling experiments on MIL-101(Cr)-NH <sub>2</sub> before and after PSI	M134
7 High pressure gas sorption on MIL-101(Cr)-NH <sub>2</sub>	134
Results and discussion	
1 Characterisation of MIL-101(Cr)-NH <sub>2</sub> before and after PSM	
2 Low pressure gas sorption measurements on MIL-101(Cr)-NH <sub>2</sub>	before and
PSM	140
.4.2.1 Effect of PEI loading	140
.4.2.2 Effect of different amines on the CO <sub>2</sub> uptakes	142
.4.2.3 Effect of different amines on the sorption kinetics	144
.4.2.4 Comparison to neat DAB-AM-8, DETA and PEI	146
3 Cycling experiments on MIL-101(Cr)-NH <sub>2</sub> before and after PSI	M149
4 High pressure gas sorption on MIL-101(Cr)-NH <sub>2</sub>	
Conclusion	154
Acknowledgements	
	References         ntary material         SEM images.         Experimental and theoretical PXRD         Thermal decomposition         FTIR spectra         DTA profiles         CO2 adsorption in MIL-100(Fe)-PEI-50         Impact of H2O – PXRD after wet cycling         References supplementary information         2 adsorption in postsynthetic modified MIL-101(Cr)-NH2         Abstract         Introduction         Experimental section         1 Chemicals.         2 Synthesis of MIL-101(Cr)-NH2         3 PSM of MIL-101(Cr)-NH2         4 Characterisation of MIL-101(Cr)-NH2 before and after PSM         5 Low pressure gas sorption measurements on MIL-101(Cr)-NH2         PSM.         6 Cycling experiments on MIL-101(Cr)-NH2 before and after PSM         7 High pressure gas sorption on MIL-101(Cr)-NH2         PSM         1 Characterisation of MIL-101(Cr)-NH2 before and after PSM         2 Low pressure gas sorption measurements on MIL-101(Cr)-NH2         PSM         4.2.1 Effect of PEI loading         4.2.2 Effect of different amines on the CO2 uptakes         4.2.3 Effect of different amines on the sorption kinetics         4.2.4 Comparison to neat DAB-AM-8, DETA and PEI         3 Cycling experiments on MIL-101(Cr)-NH2 bef

3.4.7	References	55
Supplemen	tary material15	59
3.4.8	Thermal decomposition, PXRD and DTA profiles15	59
3.4.9	Comparison of PXRD results before and after wet cycling16	50
3.5 Post the CO <sub>2</sub> so	synthetic modification of MIL-101(Al)-NH <sub>2</sub> with amines and their effect or rption	on 53
3.5.1	Abstract	53
3.5.2	Introduction	53
3.5.3	Experimental section	55
3.5.3.1	Chemicals16	55
3.5.3.2	2 Synthesis of MIL-101(Al)-NH <sub>2</sub> 16	56
3.5.3.3	Amine modification of MIL-101(Al)-NH <sub>2</sub> 16	56
3.5.3.4	Characterisation of MIL-101(Al)-NH <sub>2</sub> before and after PSM16	57
3.5.3.5 after P	Low pressure gas sorption measurements on MIL-101(Al)-NH <sub>2</sub> before an SM	ıd 58
3.5.3.6	Cycling experiments on MIL-101(Al)-NH <sub>2</sub> before and after PSM16	58
3.5.3.7	High pressure gas sorption on MIL-101(Al)-NH <sub>2</sub>	59
3.5.4	Results and discussion	59
3.5.4.1	Characterisation of MIL-101(Al)-NH <sub>2</sub> before and after PSM16	59
3.5.4.2 after P	Low pressure gas sorption measurements on MIL-101(Al)-NH <sub>2</sub> before an SM	ıd 75
3.5.4	4.2.1 MIL-101(Al)-NH <sub>2</sub> before PSM	75
3.5.4	4.2.2 Effect of PEI loading	76
3.5.4	4.2.3 Effect of DAB-AM-8 and DETA17	78
3.5.4	4.2.4 Effect of different amines on the sorption kinetics	31
3.5.4.3	Cycling experiments on MIL-101(Al)-NH <sub>2</sub> before and after PSM	34
3.5.4.4	High pressure gas sorption on MIL-101(Al)-NH <sub>2</sub>	36
3.5.4	4.4.1 High pressure $CO_2$ and $N_2$ sorption	37
3.5.4	1.4.2 Hydrothermal stability	38
3.5.5	Conclusion	39
3.5.6	Acknowledgements	<del>)</del> 0
3.5.7	References	<del>)</del> 0
Supplemen	tary material	<del>)</del> 4
3.5.8	Theoretical and experimental PXRD of MIL-101(Al)-NH <sub>2</sub> 19	<b>)</b> 4

3.5.9	Thermal decomposition and DTA profiles	
3.5.10	High pressure adsorption $-CO_2/N_2$ selectivities and heat of adsorption	ption195
3.5.11	Impact of H <sub>2</sub> O – PXRD	196
3.5.12	References supplementary information	
3.6 An	adsorption study on STA-16(Co)	
3.6.1	Abstract	
3.6.2	Introduction	
3.6.3	Experimental section	
3.6.3.	1 Chemicals	
3.6.3.	2 Synthesis of STA-16(Co)	
3.6.3.	3 Characterisation of STA-16(Co)	
3.6.3.	4 Low pressure gas sorption	
3.6.3.	5 Cycling experiments	
3.6.3.	6 High pressure gas sorption	
3.6.4	Results and discussion	
3.6.4.	1 Characterisation of STA-16(Co)	
3.6.4.	2 Low pressure gas sorption	
3.6.4.	3 Cycling experiments	
3.6.4.	4 High pressure $CO_2$ and $N_2$ sorption	
3.6.4.	5 Hydrothermal stability of STA-16(Co)	
3.6.5	Conclusion	
3.6.6	Acknowledgements	
3.6.7	References	
4 Flexible	e MOFs for carbon capture	
4.1 Cha	apter overview	
4.2 MI	L-53(Al)-NH <sub>2</sub> and MIL-53(Al)-AM for carbon capture	
4.2.1	Introduction	
4.2.2	Experimental section	
4.2.2.	1 Chemicals	
4.2.2.	2 Synthesis of MIL-53(Al)-NH <sub>2</sub>	
4.2.2.	3 PSM of MIL-53(Al)-NH <sub>2</sub>	
4.2.3	Results and discussion	
4.2.3.	1 Characterisation of MIL-53(Al)-NH <sub>2</sub> and MIL-53(Al)-AM	

	4.2.3.	.2 Low pressure gas sorption measurements	225
	4.2.3.	.3 Material stability during cycling processes under dry and wet conditio	ns
			227
	4.2.4	Conclusion	230
	4.2.5	References	230
5	Effect o	of flue gas contaminants	233
	5.1 Cha	apter overview	233
	5.2 Effective capture in	ect of flue gas contaminants on the stability and the post-combustion MIL-101 frameworks	CO <sub>2</sub> 235
	5.2.1	Abstract	235
	5.2.2	Introduction	235
	5.2.3	Experimental section	239
	5.2.3.	.1 Synthesis of MOFs	239
	5.2	.3.1.1 Chemicals	239
	5.2	.3.1.2 Synthesis of MIL-101(Cr)	239
	5.2	.3.1.3 Synthesis of MIL-101(Cr)-NH <sub>2</sub>	240
	5.2	.3.1.4 Synthesis of MIL-101(Al)-NH <sub>2</sub>	240
	5.2.3.	.2 Characterisation of the MOFs	240
	5.2.3.	.3 Exposure to concentrated flue gas contaminants	240
	5.2	.3.3.1 Flue gas contaminant screening test	240
	5.2	.3.3.2 PXRD and FTIR studies after the exposure to 10000 ppm of	
	con	ntaminant	241
	5.2.3.	.4 Sorption of flue gas contaminants	242
	5.2	.3.4.1 Flue gas contaminant cycling experiments	242
	5.2	.3.4.2 Flue gas contaminant cycling in the presence of $CO_2$	242
	5.2.4	Results and discussion	243
	5.2.4.	.1 Exposure to concentrated flue gas contaminants	243
	5.2	.4.1.1 Flue gas contaminant screening tests	243
	5.2	.4.1.2 FTIR studies	246
	5.2	.4.1.3 PXRD studies	249
	5.2.4.	.2 Sorption of flue gas contaminants	251
	5.2	.4.2.1 Flue gas contaminant cycling experiments	251
	5.2	.4.2.2 Flue gas contaminant cycling in the presence of CO <sub>2</sub>	256
	5.2.5	Conclusion	260

5.2.6	Acknowledgements	
5.2.7	References	
Supplemen	ntary material	
5.2.8	Characterisation of MIL-101(Cr)	
5.2.9	FTIR of MIL-101(Cr) after contaminant sorption – TGA	
5.2.10	FTIR of MIL-101(Cr)-NH <sub>2</sub> after contaminant sorption – TGA	
5.2.11	FTIR of MIL-101(Al)-NH <sub>2</sub> after contaminant sorption – TGA	
5.2.12	PXRD of MIL-101(Cr) after contaminant sorption- TGA	
5.2.13	PXRD of MIL-101(Cr)-NH <sub>2</sub> after contaminant sorption – TGA	
5.2.14	PXRD of MIL-101(Al)-NH <sub>2</sub> after contaminant sorption – TGA	
5.2.15	References	272
5.3 Ads	sorption of flue gas contaminants in MIL-100(Fe), MIL-53(Al)-NH <sub>2</sub> a	and STA-
16 and the	ir effect on the framework stabilities and CO <sub>2</sub> uptakes	
5.3.1	Abstract	
5.3.2	Introduction	
5.3.3	Experimental section	
5.3.3.	1 Synthesis of MOFs	
5.3.	3.1.1 Chemicals	
5.3.	3.1.2 Synthesis of MIL-100(Fe)	
5.3.	3.1.3 Synthesis of MIL-53(Al)-NH <sub>2</sub>	
5.3.	3.1.4 Synthesis of STA-16(Co)	
5.3.3.2	2 Characterisation of the MOFs	279
5.3.3.	3 Exposure to concentrated flue gas contaminants	
5.3.	3.3.1 Screening tests of flue gas contaminants	279
5.3. and	3.3.2 PXRD and FTIR studies after the exposure to 10000 ppm of N SO <sub>2</sub>	O, NO <sub>2</sub>
5.3.3.4	4 Sorption of flue gas contaminants and CO <sub>2</sub>	
5.3.	3.4.1 Flue gas contaminant cycling experiments	
5.3.	3.4.2 Flue gas contaminant cycling experiments in the presence of C	CO <sub>2</sub> 281
5.3.4	Results and discussion	
5.3.4.	1 Exposure to concentrated flue gas contaminants	
5.3.	4.1.1 Screening test of flue gas contaminants	
5.3.	4.1.2 PXRD studies after the exposure to 10000 ppm of NO, NO <sub>2</sub> ar	1d SO <sub>2</sub>
	· · · · · ·	

	5.3	.4.1.3 FTIR studies after the exposure to 10000 ppm of NO, $NO_2$ and $SO_2287$
	5.3.4	2 Sorption of flue gas contaminants and CO <sub>2</sub> 290
	5.3	.4.2.1 Flue gas contaminant cycling experiments
	5.3	.4.2.2 Flue gas contaminant cycling experiments in the presence of $CO_2294$
	5.3.5	Conclusion
	5.3.6	Acknowledgement
	5.3.7	References
	Suppleme	ntary material
	5.3.8	Structure validation of MIL-53(Al)-NH <sub>2</sub>
	5.3.9	FTIR of MIL-100(Fe) after contaminant sorption – TGA
	5.3.10	FTIR of MIL-53(Al)-NH <sub>2</sub> after contaminant sorption – TGA
	5.3.11	FTIR of STA-16(Co) after contaminant sorption – TGA
	5.3.12	PXRD of MIL-100(Fe) after contaminant sorption – TGA
	5.3.13	PXRD of MIL-53(Al)-NH <sub>2</sub> after contaminant sorption – TGA
	5.3.14	PXRD of STA-16(Co) after contaminant sorption – TGA
	5.3.15	References supplementary information
6	Non-po	rous MOF
	6.1 Ch	apter overview
	6.2 For the prepar	rmation of a non-porous cobalt-phosphonate framework by small pH change in ration of the microporous STA-16(Co)
	6.2 For the prepar Supportin	rmation of a non-porous cobalt-phosphonate framework by small pH change in ration of the microporous STA-16(Co)
	6.2 For the prepar Supportin 6.2.1	rmation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
	<ul><li>6.2 For the prepare</li><li>Supportine</li><li>6.2.1</li><li>6.2.2</li></ul>	rmation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
	<ul> <li>6.2 For the prepare support in 6.2.1</li> <li>6.2.2</li> <li>6.2.3</li> </ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
	<ul> <li>6.2 For the prepare support in 6.2.1</li> <li>6.2.2</li> <li>6.2.3</li> <li>6.2.4</li> </ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
	<ul> <li>6.2 For the preparent of the pr</li></ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
	<ul> <li>6.2 For the preparent of the pr</li></ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
	<ul> <li>6.2 For the preparent of the pr</li></ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
7	<ul> <li>6.2 For the preparent of the pr</li></ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
7	<ul> <li>6.2 For the preparent of the pr</li></ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
7	<ul> <li>6.2 For the preparent of the pr</li></ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)
7	<ul> <li>6.2 For the preparent of the pr</li></ul>	mation of a non-porous cobalt-phosphonate framework by small pH change in ation of the microporous STA-16(Co)

References	
Appendix 2: About the author	

## **List of Figures**

Figure 1.1: A simplified overview of the CCS process [16]. Copyright CO2CRC2
Figure 1.2: Conceptual scheme of post-combustion [19]. Copyright CO2CRC
Figure 1.3: Conceptual scheme of pre-combustion process [19]. Copyright CO2CRC4
Figure 1.4: Conceptual scheme of oxy-fuel combustion [19]. Copyright CO2CRC
Figure 1.5: Conceptual scheme of chemical looping combustion. Reprinted from [12], Copyright 2008, with permission from Elsevier
Figure 1.6: Mass transfer steps in a chemical absorption process. Reproduced from [22] with permission of The Royal Society of Chemistry
Figure 1.7: Carbon capture process using supported liquid membranes [36]. Copyright CO2CRC
Figure 1.8: Transport mechanism through membranes [40, 41]. Adapted from a CO2CRC picture [40]. Reprinted from [41], Copyright 1995, with permission from Elsevier
Figure 1.9: Principles of CO <sub>2</sub> capture via adsorption [35]. Copyright CO2CRC11
Figure 1.10: A general scheme of MOF synthesis. From left to right: trimers of aluminium octahedral and trimesic acid, the resulting hybrid supertetrahedra of MIL-100(Al) and one unit cell of MIL-100(Al) [60]. Ball and stick view (Al octahedral: pink, C: grey, O: red). Hydrogen atoms have been omitted. Adapted from [61] with permission of The Royal Society of Chemistry
Figure 1.11: A general scheme illustrating the concept of "prefunctionalisation" of porous MOFs. Reproduced from [87] with permission of The Royal Society of Chemistry
Figure 1.12: Examples of amine functionalised ligands [30, 71, 78, 91-100]19
Figure 1.13: Optimised structures and relative energies of parent MIL-53 (left) and amino- functionalised MIL-53(Al)-NH <sub>2</sub> materials and their complexes with CO <sub>2</sub> . Reprinted with permission from [101] (E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon, and F. Kapteijn, "Complexity behind CO <sub>2</sub> Capture on NH <sub>2</sub> -MIL-53(Al)," <i>Langmuir</i> , vol. 27, pp. 3970-3976, 2011). Copyright 2011 American Chemical Society
Figure 1.14: The sequence of events during the crystallisation of terephthalate based Aluminium MOFs in different media: Low precursor concentrations (DMF); high precursor concentrations (H <sub>2</sub> O/DMF or H <sub>2</sub> O). Reproduced from [103], Copyright 2011, with the permission of WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim22
Figure 1.15: Sorption isotherms of $Zn(ad)(ain) \cdot (DMF)$ : CO <sub>2</sub> adsorption/desorption isotherms at 25 °C ( $\bullet$ ) and N <sub>2</sub> isotherm at 25 °C ( $\blacksquare$ ). Closed symbols ( $\bullet$ ): adsorption.

Figure 1.17: Structure and Staudinger reduction of AzM-BP and concept of surface modification. Reproduced from [116] with permission of The Royal Society of Chemistry.

Figure 1.18: CO<sub>2</sub> (•) and N<sub>2</sub> ( $\blacktriangle$ ) adsorption isotherms at 25 °C in H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>] (black), in the ED modified MOF (green) [64] and in the MMEN amine modified MOF (blue) [117]. Reprinted with permission from [64] (A. Demessence, D. M. D'Alessandro, M. L. Foo, and J. R. Long, "Strong CO<sub>2</sub> Binding in a Water-Stable, Triazolate-Bridged Metal-Organic Framework Functionalized with Ethylenediamine," *Journal of the American Chemical Society*, vol. 131, pp. 8784-8786, 2009.). Copyright (2009) American Chemical Society. Reproduced from [117] with permission of The Royal Society of Chemistry.

Figure 1.25: Structure of DAB-AM-8, DETA, ED, linear PEI and branched PEI. ......40

Figure	2.1:	<sup>1</sup> H-NMR	of	trimethyl-1,3,5-benzenetricarboxylate	in	$CDCl_3$	recorded	at
400.17	MHz.				•••••			55

Figure 2.2: <sup>13</sup> C-NMR of trimethyl-1,3,5-benzenetricarboxylate in CDCl <sub>3</sub> recorded at 100.62 MHz.
Figure 2.3: FTIR spectra of trimethyl-1,3,5-benzenetricarboxylate
Figure 2.4: <sup>13</sup> C-NMR of H <sub>4</sub> LL in solid state at 100.62 MHz58
Figure 2.5: <sup>31</sup> P-NMR of H <sub>4</sub> LL in the solid state recorded at 161.98 MHz59
Figure 2.6: FTIR spectra of H <sub>4</sub> LL60
Figure 2.7: Components of an FTIR spectrometer [5]61
Figure 2.8: Illustration of Bragg's law [12]64
Figure 2.9: General components of Bruker D8 Focus Bragg-Brentano powder diffractometer and sample holders used in this work
Figure 2.10: General components of the Oxford Gemini Ultra CCD diffractometer
Figure 2.11: Basic components of the SEM [4]68
Figure 2.12: Scanning electron microscope (JEOL 7001F), equipped with a Bruker X-flash EDX detector
Figure 2.13: Temperature program for thermal stability measurements70
Figure 2.14: Gas and temperature program of adsorption/desorption measurement in Ar/CO <sub>2</sub>
Figure 2.15: System schematic of the HPVA-200 from Micromeritics73
Figure 2.16: Gas and temperature program of cycling experiments under dry conditions (Ar/CO <sub>2</sub> )
Figure 2.17: Gas and temperature program of cycling experiments under wet conditions (Ar/CO <sub>2</sub> /H <sub>2</sub> O)
Figure 3.1: Crystal structure of MIL-100 (Al): (a) Hybrid supertetrahedra of MIL-100(Al). (b) One unit cell of MIL-100(Al) presenting both cages. Ball and stick view (Al octahedra: pink, C: grey, O: red, H: white)
Figure 3.2: Crystal Structure of MIL-110(Al): (a) View along the c axis showing the channels delimited by the discrete Al8 clusters and the trimesate group in MIL-110(Al). (b) View along the c axis showing the connection mode of the Al8 clusters in MIL-110(Al) with the trimesate species parallel to the walls of the channels. Ball and stick view (Al octahedra: pink (Al1) and orange (Al2), C: grey, O: red, H: white)
Figure 3.3: SEM images of MIL-100(Al)/MIL-110(Al) showing the typical octahedral shape crystals of MIL-100(Al) and the rod shaped crystals of MIL-110(Al). On the right, a selected crystal of MIL-100(Al) is presented at higher magnification

Figure 3.4: (a) XRD patterns of the samples of the MIL-100(Al)/MIL-110(Al) after activation compared to the simulated pattern for the crystal structures of MIL-100(Al) [2]

Figure 3.8: High pressure (a) CO<sub>2</sub> isotherms at 25 ( $\blacksquare$ ), 45 ( $\blacklozenge$ ), 75 ( $\blacktriangle$ ) and 105 °C ( $\bullet$ ).and (b) N<sub>2</sub> isotherm at 25 °C. Closed symbols ( $\blacksquare$ ): adsorption, open symbols ( $\square$ ): desorption.89

Figure 3.13: CO<sub>2</sub> pseudo-isotherms of MIL-100(Fe) before and after ED modification (left) at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ) and 75 °C ( $\blacktriangle$ ). TGA profiles of the low pressure CO<sub>2</sub> sorption (right). Closed symbols ( $\blacksquare$ ): adsorption and open symbols ( $\square$ ): desorption. .....107

Figure 3.16: High pressure (a, b)  $CO_2$  and (c)  $N_2$  isotherms of MIL-100(Fe) at 25 (**n**), 45 (**4**), 75 (**A**) and 105 °C (**•**). (d)  $CO_2/N_2$  selectivities as a function of pressure at 25 (black), 45 (red), 75 (blue) and 105 °C (green). Closed (**n**) and open (**a**) symbols represent adsorption and desorption, respectively. 114

Figure 3.18: Comparison of simulated [1] and experimental XRD pattern of MIL-100(Fe).

Figure 3.19: Thermal decomposition of MIL-100(Fe) before and after PSM122
Figure 3.20: FTIR spectra of MIL-100(Fe) before and after PSM122
Figure 3.21: DTG profiles at 25 °C of MIL-100(Fe) before and after PSM123
Figure 3.22: (a) CO <sub>2</sub> pseudo-isotherms of MIL-100(Fe)-PEI-50 at 25 ( $\blacksquare$ ), 45 ( $\blacklozenge$ ) and 75 °C ( $\blacktriangle$ ). (b) TGA profiles of the low pressure CO <sub>2</sub> sorption at 25 (black), 45 (red) and 75 °C (blue). Closed ( $\blacksquare$ ) and open ( $\Box$ ) symbols represent adsorption and desorption, respectively.
Figure 3.23: PXRD of MIL-100(Fe) and its amine modifications before (black) and after (blue) the sorption of $H_2O$
Figure 3.24: $N_2$ isotherms measured at -196 °C on MIL-101(Cr)-NH <sub>2</sub> before and after PSM. The right graph shows the isotherms of the amine modified materials on an enlarged scale for better comparison
Figure 3.25: SEM images of (a) MIL-101(Cr)-NH <sub>2</sub> , (b) MIL-101(Cr)-NH <sub>2</sub> -DETA-88, (c) MIL-101(Cr)-NH <sub>2</sub> -PEI-68 and (d) MIL-101(Cr)-NH <sub>2</sub> -PEI-88138
Figure 3.26: FTIR spectra of MIL-101(Cr)-NH <sub>2</sub> before and after the PSM with (a) PEI, (b) DAB-AM-8, (c) ED and (d) DETA. The spectra are compared to the spectra of the neat amines
Figure 3.27: CO <sub>2</sub> adsorption ( $\blacksquare$ )/desorption ( $\square$ ) pseudo-isotherms for MIL-101(Cr)-NH <sub>2</sub> before and after PEI modification at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\bullet$ )142
Figure 3.28: CO <sub>2</sub> adsorption ( $\blacksquare$ )/desorption ( $\Box$ ) pseudo-isotherms for MIL-101(Cr)-NH <sub>2</sub> before and after amine modification at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\bullet$ ). 144
Figure 3.29: TGA profiles of MIL-101(Cr)-NH <sub>2</sub> before and after amine modification at (a) 25 °C, (b) 45 °C, (c) 75 °C and (d) 105 °C145
Figure 3.30: (a) CO <sub>2</sub> adsorption ( <b>■</b> ) pseudo-isotherms for DAB-AM-8 (red), DETA (black) and PEI (green) at 25 °C ( <b>■</b> ), 45 °C ( <b>♦</b> ), 75 °C ( <b>▲</b> ) and 105 °C ( <b>●</b> ). TGA profiles of DAB-AM-8 (b), DETA (c) and PEI (d) at 25 °C (black), 45 °C (red), 75 °C (blue) and 105 °C (green). Between t=220 min and t~250 min the amines were heated to 90 °C (DETA) or 110 °C (PEI, DAB-AM-8) and then cooled under flowing Ar
Figure 3.31: Comparison of $CO_2$ adsorption pseudo-isotherms for MIL-101(Cr) modified frameworks with neat DAB-AM-8, DETA and PEI at 25 °C ( <b>•</b> ), 45 °C ( <b>•</b> ), 75 °C ( <b>•</b> ) and 105 °C ( <b>•</b> )
Figure 3.32: TGA profiles of MIL-101(Cr)-NH <sub>2</sub> before and after amine modification under (a) dry and (b) wet (1 vol% H <sub>2</sub> O) conditions
Figure 3.33: (a) High pressure $CO_2$ and (b) high pressure $N_2$ adsorption isotherms on MIL-101(Cr)-NH <sub>2</sub> . (c) $CO_2/N_2$ selectivities calculated from the single component isotherms at 25 °C. ( <b>■</b> ), 45 °C ( <b>♦</b> ), 75 °C ( <b>▲</b> ) and 105 °C ( <b>●</b> ). (d) Isosteric heat of adsorption determined by fitting the Tóth isotherm model to the $CO_2$ isotherms

Figure 3.34: (a) TGA decomposition profiles on MIL-10(Cr)-NH<sub>2</sub> before and after PSM. (b) PXRD on MIL-101(Cr)-NH<sub>2</sub> before and after PSM. For a better clarity of the results obtained, the intensities of the diffraction patterns of the amine modified materials were multiplied by 5. (c) DTA profiles of MIL-101(Cr)-NH<sub>2</sub> before and after amine Figure 3.35: PXRD of MIL-101(Cr)-NH<sub>2</sub> and its PEI and DAB-AM-8 modifications before (black) and after (blue) the wet cycling experiments......160 Figure 3.36: PXRD of DETA and ED modified MIL-101(Cr)-NH<sub>2</sub> before (black) and after Figure 3.37: N<sub>2</sub> isotherms measured at -196 °C on MIL-101(Al)-NH<sub>2</sub> before and after PSM. The right graph expands the isotherms of the amine modified materials for a better Figure 3.38: (a) FTIR spectra and (b) PXRD of MIL-101(Al)-NH<sub>2</sub> before and after PSM. Figure 3.39: SEM images of (a) MIL-101(Al)-NH<sub>2</sub>, (b) MIL-101(Al)-NH<sub>2</sub>-PEI-48, (c) MIL-101(Al)-NH<sub>2</sub>-PEI-96, (d) MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 and (e) MIL-101(Al)-NH<sub>2</sub>-DETA-89......174 Figure 3.40: Comparison of CO<sub>2</sub> pseudo-isotherms of MIL-101(Al)-NH<sub>2</sub> and its PEI modifications with neat PEI at 25 °C (■), 45 °C (♦), 75 °C (▲) and 105 °C (●).Closed symbols ( $\blacksquare$ ) and open symbols ( $\Box$ ) represent the adsorption and desorption of CO<sub>2</sub>, Figure 3.41: CO<sub>2</sub> pseudo-isotherms on MIL-101(Al)-NH<sub>2</sub> before and after modification with DAB-AM-8 and DETA in comparison with the neat amines at 25 °C (■), 45 °C (♦), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\bullet$ ).Closed symbols ( $\blacksquare$ ) and open symbols ( $\square$ ) represent the Figure 3.42: CO<sub>2</sub> sorption TGA profiles of MIL-101(Al)-NH<sub>2</sub>, its PEI modifications and neat PEI at 25 °C (black), 45 °C (red), 75 °C (blue) and 105 °C (green)......182 Figure 3.43: CO<sub>2</sub> sorption TGA profiles of MIL-101(Al)-NH<sub>2</sub>-DETA-89, MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94, DETA and DAB-AM-8 at 25 °C (black), 45 °C (red), 75 °C (blue) Figure 3.44: TGA profiles of MIL-101(Al)-NH<sub>2</sub> before and after amine modifications under dry (a) and wet (b) conditions. Working capacities during the 10 cycles under dry (c) and wet (d) conditions. The line and marker colours correspond to the MOF and the symbols to the cycling temperature (25 °C (■) and 105 °C (●)).....185 Figure 3.45: High pressure (a) CO<sub>2</sub> isotherms at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\bullet$ ) and (b) N<sub>2</sub> isotherms at 25 °C ( $\blacksquare$ ) and 105 °C ( $\bullet$ ) on MIL-101(Al)-NH<sub>2</sub> recorded on the HPVA in the pressure range of 0 to 40 bar. Closed symbols (**■**) and open symbols () represent the adsorption and desorption of the adsorbates, respectively. .....188 Figure 3.46: (a) CO<sub>2</sub> isotherms before (black) and after (red) H<sub>2</sub>O adsorption/desorption at 25 °C (b) H<sub>2</sub>O isotherm at 30 % RH and 25 °C. The measurements were conducted on the

IGA. Closed symbols ( $\blacksquare$ ) and open symbols ( $\Box$ ) represent the adsorption and desorption of the adsorbates, respectively
Figure 3.47: Comparison of the theoretical PXRD calculated from the crystal structure of MIL-101(Cr) [1](red) and the PXRD of MIL-101(Al)-NH <sub>2</sub> (black)
Figure 3.48: (a) Thermal decomposition of MIL-101(Al)-NH <sub>2</sub> before and after amine modification. (b) DTA profiles of MIL-101(Al)-NH <sub>2</sub> before and after amine modification at 25 °C
Figure 3.49: (a) $CO_2/N_2$ selectivities at 25 (black) and 105 °C (red). (b) Isosteric heat of adsorption determined by fitting the Tóth isotherm model to the $CO_2$ isotherms195
Figure 3.50: PXRD of MIL-101(Al)-NH <sub>2</sub> and its amine modifications before (black) and after (blue) the sorption of H <sub>2</sub> O
Figure 3.51: The hexagonal array of channels in STA-16(Co) (Phosphonate tetrahedral: green, Co(II) octahedra: blue, C: grey, N: dark blue, O: red). The lattice $H_2O$ molecules and the hydrogen atoms have been omitted [31]
<b>Figure 3.52</b> : SEM images of STA-16(Co) at a magnification of 10000 (a) and 20000 (b). 205
Figure 3.53: (a) Comparison of experimental (black, 25 °C) and the calculated diffractogram of STA-16(Co) (red, -173 °C). (b) IR spectrum of STA-16(Co). (c) Thermal decomposition of STA-16(Co) compared to literature data [31]
Figure 3.54: Low pressure $CO_2$ pseudo-isotherms (a) and TGA profiles (b) on STA-16(Co). The closed symbols ( $\blacksquare$ ) represent the adsorption of $CO_2$ and the open symbols ( $\Box$ ) represent the desorption
Figure 3.55: TGA profiles of dry (a) and wet (b) cycling experiments at 25 $^{\circ}$ C and CO <sub>2</sub> working capacities in 10 cycles under dry (c) and wet (d) conditions209
Figure 3.56: (a) High pressure $CO_2$ (•) and (b) high pressure $N_2$ sorption isotherms ( <b>■</b> ) on STA-16(Co). The closed symbols (•, <b>■</b> ) represent the adsorption of the adsorbates and the open symbols ( $\circ$ , $\Box$ ) represent the desorption. (c) $CO_2/N_2$ selectivity at 25/30 °C. (d) Isosteric heat of adsorption for $CO_2$ on STA-16(Co)
Figure 3.57: (a) $H_2O$ isotherms of 30 %RH (black), 60 % RH (red) and 90 %RH (green) at 25 °C. (b) $H_2O$ isotherms of 30 %RH (black), 60 % RH (red) and 90 %RH (green) at 25 °C on an enlarged scale. (c) $CO_2$ isotherms before (black) and after adsorption of 30 % RH (red), 60 % RH (green) and 90 % RH (blue) at 25 °C and 0 to 5 bar. Closed ( <b>■</b> ) and open ( $\Box$ ) symbols denote adsorption and desorption respectively. (d) PXRD before (black) and after 90 % RH treatment (blue)
Figure 4.1: Schematic view of the breathing phenomenon of MIL-53(Al)-NH <sub>2</sub> upon adsorption/desorption of CO <sub>2</sub> . Ball and stick view (Al octahedra: pink, C: grey, O: red, N: blue) [10]

Figure 4.2: IR spectra of MIL-53(Al)-NH<sub>2</sub> before and after modification with benzoic anhydride.

Figure 4.3: Comparison of the PXRD pattern of MIL-53(Al)-NH <sub>2</sub> , MIL-53(Al)-AM and the simulated diffraction patterns [10] for MIL-53(Al)-NH <sub>2</sub> <i>np</i> and MIL-53(Al)-NH <sub>2</sub> <i>lp</i> . 223
Figure 4.4: SEM images of MIL-53(Al)-NH <sub>2</sub> (left) and MIL-53(Al)-AM (right)224
Figure 4.5: (a) Comparison of the thermal decomposition of MIL-53(Al)-NH <sub>2</sub> and MIL-53(Al)-AM with literature data [9]. (b) N <sub>2</sub> isotherm on MIL-53(Al)-AM at -196 °C225
Figure 4.6: CO <sub>2</sub> adsorption ( $\blacksquare$ )/desorption ( $\Box$ ) isotherms on (a) MIL-53(Al)-NH <sub>2</sub> and (b) MIL-53(Al)-AM. CO <sub>2</sub> adsorption/desorption profile of (c) MIL-53(Al)-NH <sub>2</sub> and (d) MIL-53(Al)-AM. 226
Figure 4.7: CO <sub>2</sub> working capacity at 25 °C and TGA profiles of MIL-53(Al)-NH <sub>2</sub> and of MIL-53(Al)-AM under dry conditions
Figure 4.8: CO <sub>2</sub> working capacity at 25 °C and TGA profiles of MIL-53(Al)-NH <sub>2</sub> and of MIL-53(Al)-AM under wet conditions
Figure 4.9: PXRD pattern of (a) MIL-53(Al)-NH <sub>2</sub> and (b) MIL-53(Al)-AM before (black) and after (blue) the wet cycling experiments
Figure 5.1: Crystal structure of MIL-101(Cr). Hybrid supertetrahedra (left) and one unit cell of MIL-101(Cr) presenting both cages (right). Ball and stick view (Cr octahedra: green, C: grey and O: red, H: omitted) [38]
Figure 5.2: Thermo-gravimetric analysis process conditions for the flue gas contaminant screening tests
Figure 5.3: Thermo-gravimetric analysis process conditions used for the (a) Flue gas contaminant cycling experiments, and the (b) Flue gas contaminant cycling in the presence of $CO_2$ experiments
Figure 5.4:TGA of exposure of MIL-101(Cr) (red), MIL-101(Cr)-NH <sub>2</sub> (green) and MIL-101(Al)-NH <sub>2</sub> (blue) to atmospheres comprising 5000 ppm of (a) NO, (b) NO <sub>2</sub> and (c) SO <sub>2</sub> over a heat ramp from 20 to 110 °C with a heating rate of 2 °C min <sup>-1</sup> 245
Figure 5.5: FTIR spectra of (a) MIL-101(Cr), (b) MIL-101(Cr)-NH <sub>2</sub> and (c) MIL-101(Al)-NH <sub>2</sub> before and after treatment with 10000 ppm of contaminant at room (RT) and more elevated temperature. (d) Comparison of FTIR spectra before and after NO <sub>2</sub> treatment on MIL-101(Cr)-NH <sub>2</sub> and MIL-101(Al)-NH <sub>2</sub> with BDC-NH <sub>2</sub>
Figure 5.6: PXRD of (a) MIL-101(Cr), (b) MIL-101(Cr)-NH <sub>2</sub> and (c) MIL-101(Al)-NH <sub>2</sub> before and after the treatment with 10000 ppm at room (RT) and more elevated temperature.
Figure 5.7: TGA profile (left) and mass uptakes (right) of different concentrations of NO, NO <sub>2</sub> and SO <sub>2</sub> on MIL-101(Cr) during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm253
Figure 5.8: TGA profile (left) and mass uptakes on a molar basis (right) of different concentrations of NO, NO <sub>2</sub> and SO <sub>2</sub> on MIL-101(Cr)-NH <sub>2</sub> during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm
xxvii

Figure 5.11: TGA profile (left) and the calculated mass loss (right) of  $CO_2$  with and without NO,  $SO_2$  and  $NO_2$  on MIL-101(Cr)-NH<sub>2</sub> at 25 °C. Cycling experiments were conducted by varying the  $CO_2$  partial pressure between 0.05 and 0.15 bar and the contaminant partial pressure between 0 ppm and 500 (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>).....258

Figure 5.14: FTIR spectra of MIL-101(Cr) before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>......266

Figure 5.15: FTIR spectra of MIL-101(Cr)-NH<sub>2</sub> before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.......267

Figure 5.16: FTIR spectra of MIL-101(Al)-NH<sub>2</sub> before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.......268

Figure 5.17: PXRD of MIL-101(Cr) before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.....269

Figure 5.18: PXRD of MIL-101(Cr)-NH<sub>2</sub> before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>......270

Figure 5.19: PXRD of MIL-101(Al)-NH<sub>2</sub> before and after screening tests, contaminant and CO<sub>2</sub>/contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>......271

Figure 5.22: TGA of exposure of MIL-100(Fe) (black), MIL-53(Al)-NH<sub>2</sub> (yellow) and STA-16(Co) (purple) to atmospheres comprising 5000 ppm of (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub> over a heat ramp from 20 to 110 °C with a heating rat of 2 °C min<sup>-1</sup>......284

Figure 5.25: TGA profile (left) and the mass gain (right) of different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-100(Fe) during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm.......292

Figure 5.31: Powder X-ray diffractogram of MIL-53(Al)-NH<sub>2</sub> (black) in comparison with the calculated diffraction pattern for MIL-53(Al)-NH<sub>2</sub> *np* (red) [1]......305

## **List of Tables**

Table 1.1: $CO_2$ adsorption capacities for various adsorbents (black) and the amount of $CO_2$ adsorbed near ambient conditions (red) [65, 66, 75-77]
Table 1.2: Specific surface areas (SSA) and pore volumes (PV) [91, 92]21
Table 1.3: Predicted selectivities and working capacities in the UiO-66(Zr) series at 30 °C      [106].
Table 1.4: CO2 and CH4 adsorption capacities in UHM-30 and HKUST-1 at 25 °C and 1 bar.
Table 2.1: Chemicals for the synthesis of the ligands and gases used in this work
Table 2.2: Elemental chemical analysis of H4LL.    57
Table 2.3: Summary of MOFs prepared in this work60
Table 2.4: Activation temperatures for MOFs.    67
Table 3.1: Elementary chemical analysis of MIL-100(Al)/MIL-110(Al) as, MIL-100(Al)/MIL-110(Al) activated, MIL-100(Al) and MIL-110(Al) with empty pores
Table 3.2: An overview of the theoretical amine loadings, the loadings after vacuum activation (evac) and the corresponding molar loadings of the CUS
Table 3.3: Comparison of results obtained by Elemental analysis, $N_2$ physisorption at - 196 °C and helium density measurements
Table 3.4: Overview of the theoretical amine loadings (wt%), the amine loadings after vacuum activation (evac) and the corresponding molar loadings of the CUS
Table 3.5: Elemental composition, BET surface area, total pore volume and helium densityof MIL-101(Cr)-NH2 and its modifications
Table 3.6: Summary of cycling conditions and results.    149
Table 3.7: Overview of the targeted loading and the actual loading after vacuum activation.
Table 3.8: Elemental composition, BET surface area and total pore volume of MIL- 101(Al)-NH2 and its modifications
Table 3.9: Elementary chemical analysis of STA-16(Co)
Table 4.1: Elemental analysis of MIL-53(Al)-NH <sub>2</sub> and MIL-53(Al)-AM223
Table 5.1: Comparison of experimental and theoretical C, H and N contents of MIL-      53(Al)-NH2 np.

# **List of Abbreviations**

### Used abbreviations

Term	Definition
ad	adeninate
ADC	Azobenzene-4,4'-dicarboxylate
ain	2-aminoisonicotinate
APTS	Aminopropyltrimethoxysilane
Atz	3-amino-1,2,4-triazole
AzM	Azide modified Metal-Organic Framework
BDC	1,4-Benzene-dicarboxylic acid
BET	Brunauer-Emmett-Teller method
Boc	tert-butyloxycarbonyl
BP	2,2 '-bis(azidomethyl)biphenyl-4,4 '-dicarboxylic acid
BTB	1,3,5-benzenetrisbenzoate
BTC	1,3,5-Benzene-tricarboxylic acid
H <sub>3</sub> BTTri	1,3,5-tris(1H-1,2,3-triazol-5-yl)benzene
CALF	Calgary Framework
CCD	Charge Coupled Device
CCS	Carbon Capture and Storage
СРО	Coordination Polymer of Oslo
CUS	Coordinatively Unsaturated Sites
DAB-AM-8	polypropylenimine octaamine dendrimer, $2^{nd}$ generation
DABCO	1,4-diazabicyclo[2.2.2]octane
DEA	Diethanolamine
DEF	N,N-diethylformamide
DETA	Diethylenetriamine
DMF	N,N-dimethylformamide
DMOF	DABCO Metal-Organic Framework

DOBDC	2,5-dioxido-1,4-benzenedicarboxylate
ED	Ethylenediamine
EDS	Energy X-ray Dispersive Spectroscopy
FGD	Flue Gas Desulphurisation
FTIR	Fourier Transform Infrared Spectroscopy
GCMC	Grand Canonical Monte Carlo
H <sub>3</sub> BTATB	4,4',4"-(benzene-1,3,5-triyltris(azanediyl)tribenzoic acid
HKUST	Hong Kong University of Science and Technology
HMS	Hexagonal Mesoporous Silica
HRGS	Heat Recovery Steam Generator
H <sub>3</sub> TATAB	4,4',4"-(2,4,6-trimethylbenzene-1,3,5-triyl)tribenzoic acid
H <sub>3</sub> trencba	tris (2-(4-carboxy pheny lmethyl) aminoethyl) amine
IGA	Intelligent Gravimetric Analyser
IGCC	Integrated Gasification Combined Cycle
IPCC	International Panel on Climate Change
IRMOF	Isoreticular Metal-Organic Framework
IUPAC	International Union of Pure and Applied Chemistry
LIC	Leiden Institute of Chemistry
lp	large pore
MCF	Mesostructured Cellular Foam
MEA	Monoethanolamine
MIL	Matériaux Institute Lavoisier
MMEN	N,N'-dimethylethylenediamine
MOF	Metal-Organic Framework
NH <sub>2</sub> IN	3-aminoisonicotinate
NMR	Nuclear Magnetic Resonance Spectroscopy
np	narrow pore
OX	oxalate
PBI	Polybenzimidazole

PCN	Porous Coordination Network
РЕНА	Pentaethylenehexamine
PEI	Polyethylenimine
PSA	Pressure Swing Adsorption
PSD	Postsynthetic Deprotection
PSM	Postsynthetic Modification
PXRD	Powder X-ray diffraction spectroscopy
RH	Relative Humidity
SBA-15	Santa Barbara Acid-15
SBU	Secondary Building Unit
SEM	Scanning Electron Microscopy
SNU	Seoul National University
SSA	Specific Surface Area
STA	St. Andrews porous material
STP	Standard Temperature Pressure
TED	Triethylenediamine
TGA	Thermogravimetric analysis
TSA	Temperature Swing Adsorption
UHM	University of Hamburg Materials
UiO	University of Oslo
UMCM	University of Michigan Crystalline Material
USO	University & SINTEF in Oslo
VSA	Vacuum swing adsorption
XRD	X-ray Diffraction Spectroscopy
ZIF	Zeolite Imidazolate Framework

### Used formula symbols

Latin symbols

Symbol	Unit	Term
b	bar	Langmuir parameter
d <sub>hkl</sub>	Å	Interatomic spacing
-------------------	----------------------	--
$-\Delta H_{iso}$	kJ mol <sup>-1</sup>	Isosteric heat of adsorption
n	-	Integer in Bragg's Law
Ν	mol g <sup>-1</sup>	Loading
N <sub>max</sub>	mol g <sup>-1</sup>	Maximal loading
Р	bar	Pressure
R	$J K^{-1} mol^{-1}$	Universal gas constant
t	-	Heterogeneity of adsorbent-adsorbate system (Tóth)
Т	Κ	Temperature

# Greek symbols

Symbol	Unit	Term
Δ	Å	Path difference
λ	Å	Wavelength
θ	0	Diffraction angle in XRD
θ	-	Surface coverage in Clausius-Calpeyron and Tóth equation

## **1** Introduction

#### **1.1** Research motivation: The need to reduce greenhouse gas emissions

One of the most pressing environmental concerns of our age is the escalating level of atmospheric CO<sub>2</sub>, which is believed to be a primary factor in global warming and climate change [1, 2]. The carbon cycle was in balance for centuries, before the onset of the industrial revolution, which appears to have led to an increase of the CO<sub>2</sub> concentration in the atmosphere from 280 ppm in 1750 to above 395 ppm in March 2012 [3-5]. As a result, the outward transmission of heat from the surface of the earth into space is reduced, producing a rise in average global temperature, a rise in average sea level and melting of glaciers [5]. The International Panel on Climate Change (IPCC) predicts that CO<sub>2</sub> concentrations in the atmosphere may reach 570 ppm in 2100, resulting in a mean global temperature rise of  $1.9 \,^{\circ}$ C, a mean sea level increase of 1 m, extinction of species and increasing desertification [6].

 $CO_2$  comprises approximately 77 % of global greenhouse gas emissions, which stems predominantly from the combustion of coal, oil and natural gas ( $30x10^{12}$  kg CO<sub>2</sub> per year) [7-9]. Due to the expected continued use of fossil fuels as the backbone of the worldwide electricity production in the near future, strategies to reduce CO<sub>2</sub> emissions are urgently required [10].

The use of renewable energy forms is one possibility to decrease our  $CO_2$  emissions; however they currently account for only 12.88 % of all global energy [5]. Further development of these technologies would be necessary in order to facilitate large scale implementation and therefore allow a complete transition from carbon-based sources to cleaner alternatives [11, 12]. Although strategies like the introduction of cleaner industrial processes and the increase in energy efficiency can contribute towards reducing greenhouse gas emissions, the  $CO_2$  produced from coal-fired power plants will still be a major challenge [13, 14]. The utilization of  $CO_2$  for the production of bulk chemicals, polymers and fine chemicals can be applied in order to reduce our emissions; however it is not regarded as an overall solution due to the huge amounts of  $CO_2$  currently emitted (Teraton challenge) [6, 11]. One promising near future solution is the application of carbon capture and storage (CCS), which could reduce the  $CO_2$  emissions from power stations by 90 % [14]. A more detailed description of CCS is given in the following sub-chapters.

## **1.2 The CCS process**

One option for reducing anthropogenic  $CO_2$  emissions is carbon capture and storage (CCS) from large point sources (Figure 1.1). The first step in the CCS is the capture and concentration of  $CO_2$  from a power plant, industrial process or other source. After the transportation to a storage site, the  $CO_2$  is injected into suitable geologic formation, such as depleted oil and gas fields, saline formations and unmineable coal seams, where it can be stored indefinitely. The downside is that CCS increases the electricity production cost by 50 %. The  $CO_2$  capture and concentration is purported to account for about 75 % of the overall cost of CCS. Additionally, due to the higher energy requirement for power plants with CCS, more fuel needs to be burned for the same electrical output, which in turn results in larger and more expensive plants. Although numbers may vary with different CCS schemes, cutting the capture cost appears to be the most important challenge to make the CCS process economically viable for implementation within the energy industry [1, 4, 12, 15].





## **1.2.1** Carbon capture technologies

The most promising principles for reducing  $CO_2$  emissions to the atmosphere are postcombustion capture ( $CO_2/N_2$  separation), pre-combustion capture ( $CO_2/H_2$  separation) oxy-fuel combustion ( $CO_2/N_2$  separation) and chemical looping combustion. In the following sections an overview of the different capture strategies is given.

#### 1.2.1.1 Post-combustion

In the post-combustion approach (Figure 1.2), the  $CO_2$  is separated from other flue gas constituents, which are either originally present in the air or produced by combustion. Existing power plants use air for combustion and generate a flue gas that is at atmospheric pressure and typically has a CO<sub>2</sub> concentration of less than 15 %. In conventional coal plants, the coal is first pulverised and then burned with hot air. The heat generated in this process is used to produce steam from H<sub>2</sub>O, which is piped into a turbine and turns the shaft of the turbine generator to produce electricity. The hot coal fired flue gas of the boiler typically contains 75-80 % N<sub>2</sub>, 12 -15 % CO<sub>2</sub>, 5-7 % H<sub>2</sub>O, 3-4 % O<sub>2</sub> and trace amounts of CO (<100 ppm), SO<sub>2</sub> (1800 ppm) and NO<sub>x</sub> (500 ppm) [14, 17]. These impurities can impede with the capture system and need to be removed. The fuel type used and the location of the combustion unit in the power plant determine the flue gas composition. After flue gas desulphurisation (FGD) the gas stream temperature is around 40 to 80 °C. A technical challenge for the development of cost effective advanced capture processes is created due to the low thermodynamic driving force for CO<sub>2</sub> capture from flue gas. Nevertheless post-combustion carbon capture has the greatest near-term potential for reducing green house gas emissions, because it can be retrofitted to existing units and high CO<sub>2</sub> purities can be achieved (>99.99 %) [1, 12, 15, 18].



Figure 1.2: Conceptual scheme of post-combustion [19]. Copyright CO2CRC.

## 1.2.1.2 Pre-combustion

The recovery of CO<sub>2</sub> from a process stream (containing 35.5 % CO<sub>2</sub>) before burning the fuel is called pre-combustion (Figure 1.3). The integrated gasification combined cycle (IGCC) process operates at pressures between approximately 35 and 50 bar. The first step is usually the separation of O<sub>2</sub> from air in an air separation unit. The O<sub>2</sub> is then used to gasify the coal at temperatures above 1260 °C to produce syngas, which is sent to a shift converter where the H<sub>2</sub>O gas shift reaction takes place (Eq.1.1).

$$\mathrm{CO} + \mathrm{H}_2\mathrm{O} \to \mathrm{CO}_2 + \mathrm{H}_2 \tag{1.1}$$

The conversion increases with decreasing temperature due to the equilibrium limitation of the reaction. After the removal of sulphur compounds in order to avoid the corrosion of the turbine and cooling the syngas to approximately 315 to 445 °C, the CO<sub>2</sub> is separated from H<sub>2</sub>. In some industrial approaches, the syngas is sent to a low temperature shift reactor which operates at 200 to 250 °C before the separation process takes place [20]. The H<sub>2</sub> rich gas, which is mixed with N<sub>2</sub> and steam, is then burnt and the hot exhaust gas from the combustion turbine is passed through a gas turbine to produce energy. The recovered heat is sent to a recovery steam generator (HRGS) to produce steam for the steam turbine that generates additional power and increases the overall power system efficiency (37-44 % for an IGCC plant) [1, 4, 12, 15, 18, 20]. Due to the greater difference in molecular weights and molecular kinetic diameters for CO<sub>2</sub> versus H<sub>2</sub> compared to CO<sub>2</sub> versus N<sub>2</sub>, the separation is easier than in a post-combustion capture process [21]. Absorption using physical solvents is currently the most commercially developed technology for the separation of CO<sub>2</sub> from H<sub>2</sub> [5]. The main advantages of pre-combustion are the lower energy requirements for the capture and compression of CO<sub>2</sub>. However, temperature and efficiency issues with the H<sub>2</sub>-rich gas turbine fuel need to be resolved [17].



Figure 1.3: Conceptual scheme of pre-combustion process [19]. Copyright CO2CRC.

## 1.2.1.3 Oxy-fuel combustion

Oxy-fuel technology is designed to solve the problem of the small content of  $CO_2$  in the flue gas from conventional plants. Oxy-fuel combustion (Figure 1.4) followed by carbon capture can be adapted to both existing and new coal-fired power stations [22]. In an oxy-fuel process, the fuel, which contains mainly  $CO_2$  and steam, is burned in a nearly pure  $O_2$  environment instead of air which results in a higher combustion temperature. The  $O_2$  for the combustion process is delivered in form of a gas stream, which is produced by the cryogenic separation of  $O_2$  from air (T<-182 °C), or as a solid oxide in a chemical looping process. The air separation unit removes the  $N_2$  from the air by cooling it to a liquid. However, more energy efficient and cost effective strategies, e.g. membranes or a bed of  $O_2$ -separating minerals may be implemented in the future. Due to the high  $CO_2$  content of up to 90 % in the exhaust gas, no separation of  $CO_2$  is required. After the dehydration and compression, the raw exhaust gas may be stored directly without the need of further

purification if permitted by regulations, but in most cases removal of impurities (e.g.  $O_2$ ,  $N_2$ , Ar) is required. The recycling of approximately 70 % of the flue gas stream prevents the overheating of the boiler by diluting the  $O_2$  enriched environment. The first electricity production plant to implement this capture scheme became operational at Schwarze Pumpe in 2008. After 1200 operating hours 1000 t of  $CO_2$  were captured with a purity of 99.7 % [5, 11].



Figure 1.4: Conceptual scheme of oxy-fuel combustion [19]. Copyright CO2CRC.

## 1.2.1.4 Chemical looping combustion

A more recent capture technology is chemical looping (Figure 1.5), in which carboncontaining fuels are combusted in the presence of small particles of metal oxides (e.g.  $Mn_2O_3$ , NiO, CuO, Fe<sub>2</sub>O<sub>3</sub>). In this reaction, the fuel is oxidised to H<sub>2</sub>O and CO<sub>2</sub>, while the metal oxide is reduced (Eq. 1.2). The H<sub>2</sub>O vapour is then condensed and CO<sub>2</sub> is released in high purity. The metal oxide is regenerated (Eq. 1.3) via oxidation, passes through a cyclone for the separation from hot N<sub>2</sub> and O<sub>2</sub> and is then re-circulated into the fuel reactor [20, 23].

$$C_nH_m + (2n+0.5m) \text{ MeO} \rightarrow nCO_2 + 0.5mH_2O + (2n+0.5m)Me$$
 (1.2)

$$O_2 + 2Me \rightarrow 2MeO$$
 (1.3)



**Figure 1.5:** Conceptual scheme of chemical looping combustion. Reprinted from [12], Copyright 2008, with permission from Elsevier.

The exhaust gas contains  $N_2$  and unreacted  $O_2$ , which can be released into the atmosphere with minor impact on the environment. The advantage of this process is the lower energy requirement compared to post-combustion, the improvement of the overall efficiency due to the use of the heat generated during the oxidation of the metal as well as the generation of a concentrated  $CO_2$  stream without the need of an air separation unit, in addition to minimisation of  $NO_x$  formation [15, 20, 24].

## **1.2.2** Carbon capture techniques

Several techniques for the separation of  $CO_2$  from flue gas, syngas and natural gas, such as absorption, cryogenic distillation, membrane separation and adsorption are currently under investigation. The following sub-sections give an overview of these techniques with their advantages and disadvantages.

## 1.2.2.1 Absorption

Traditional technologies for capturing  $CO_2$  include absorption by aqueous amines (e.g. monoethanolamine (MEA), diethanolamine (DEA), etc.). The chemical absorption is typically a four step process, in which  $CO_2$  diffuses in the gas phase of a given mixture, before it is dissolved into the liquid film, in which the separation takes place. The process is shown in Figure 1.6 [25].

Gas	Liquid Film	Liquid	
Step 1	Step 2	Step 3	Step 4
CO <sub>2</sub> ———	$\rightarrow$ CO <sub>2</sub> $\rightarrow$	$\rightarrow$ CO <sub>2</sub> +2B	$\longrightarrow$ BCO <sub>2</sub> + B
diffusion diss	olution	diffusion	chemical reaction

**Figure 1.6:** Mass transfer steps in a chemical absorption process. Reproduced from [22] with permission of The Royal Society of Chemistry.

Three possible reaction mechanisms for the chemical reaction of  $CO_2$  with alkanolamines have been proposed in the literature [17, 25]. The first mechanism is a two-step process and involves the formation of a zwitterion (carbamate). In a second step, this transition complex reacts with H<sub>2</sub>O [26, 27].

**Mechanism 1:** 
$$CO_2 + 2 R_2 NH \leftrightarrows [R_2 NHCO_2] + R_2 NH_2^+$$
 (1.4)

$$[R_2HNCO_2]^- + H_2O \rightarrow R_2NCO_2^- + H_3O^+$$
 (1.5)

The termolecular mechanism (mechanism 2) is a direct molecular reaction involving the reaction of  $CO_2$ ,  $H_2O$  and the primary or secondary amine in a single step. The amine

protonation in the solution is a direct result of the hydronium ions formed, which can result in the formation of carbamate species (Eq. 1.7) [27, 28].

Mechanism 2: 
$$CO_2 + R_2NH + H_2O \leftrightarrows R_2NCO_2^- + H_3O^+$$
 (1.6)

$$\mathbf{R}_{2}\mathbf{N}\mathbf{H} + \mathbf{H}_{3}\mathbf{O}^{+} \leftrightarrows \mathbf{R}_{2}\mathbf{H}_{2}\mathbf{N}^{+} + \mathbf{H}_{2}\mathbf{O}$$
(1.7)

The third mechanism occurs in the presence of tertiary amines. As a result of the steric hindrance of the three "R" groups, no direct bond to the carbon atom in  $CO_2$  can be formed. Due to the lower stability of the bicarbonate species, more readily  $CO_2$  absorptions have been observed [17, 27].

Mechanism 3: 
$$CO_2 + R_3N + H_2O \leftrightarrows R_3HN^+ + HCO_3^-$$
 (1.8)

While primary amines interact with  $CO_2$  in a 2 to 1 ratio, secondary and tertiary amines react in a 1:1 ratio. Hence, higher absorption capacities are anticipated for secondary and tertiary amines. The required energy for the regeneration decreases in the order primary>secondary>tertiary amine [7].

The industrial employment of the primary alkanolamine MEA for "wet-scrubbing" processes involves the supply of the flue gas through the bottom of the absorber and the addition of the solvent through the top. The reaction of the amine with the CO<sub>2</sub> takes place at 40 °C. The regeneration of the CO<sub>2</sub> rich solvent occurs via the addition of steam in a stripping tower at temperatures between 100 to 140 °C. The solvent is then cycled back into the absorber column. 30 wt% MEA solutions have a working capacity in the range of 2.1 and 5.5 wt% depending on the configuration of the scrubbing process [1, 17].

However, aqueous alkanolamines possess some disadvantages. For example, there is a higher energy requirement for regenerating the absorbents, a loss of effectiveness over time due to low thermal stability, material losses due to evaporation, a tendency to induce corrosion and the formation of heat stable salts [6, 29-33].

## 1.2.2.2 Membranes

Membrane technologies offer an alternative to traditional solvents and are considered an attractive technology for pre-combustion [34]. Different strategies have been proposed for the use of membranes in carbon capture, which include supported liquid membranes and gas separation membranes [17, 35].

One possible approach is the use of supported liquid membranes, which acts as a barrier between the gas and liquid phase (Figure 1.7). The gas mixture diffuses through the pores of the membrane into the liquid phase, in which the  $CO_2$  is absorbed. The membrane impedes the passage of impurities and therefore prevents the formation of stable salts resulting in a decrease in solvent loss. The regeneration of the solvent is achieved by the application of vacuum or the introduction of sweep gas. This process eliminates flow problems, which are observed in absorption processes without membranes, but maintains the disadvantages of a pure absorption process, like the evaporation and the required regeneration of the solvent [17].



Figure 1.7: Carbon capture process using supported liquid membranes [36]. Copyright CO2CRC.

Gas separation membranes on the other hand are space efficient, easy to integrate into a power plant, contain no hazardous chemicals and are less energy extensive. However, a sufficient driving force is necessary for an effective separation process, which presents a challenge for post-combustion and natural gas separation due the low concentrations of  $CO_2$  [12, 17, 37].

Five possible mechanisms (Figure 1.8) for gas separation processes are:

- Knudsen diffusion: Gas molecules are separated by the difference in mean path through the pores.
- Molecular sieving: Gas molecules are separated based on differences in kinetic diameter.

- Solution diffusion: Gas molecules are separated by different solubilities in the membrane.
- Surface diffusion: Adsorption of highly polar gas molecules onto the membrane surface and transport through the membrane by moving from one adsorption site to the next.
- Capillary condensation: Separation based on differences in vapour pressure [38-40]



**Figure 1.8:** Transport mechanism through membranes [40, 41]. Adapted from a CO2CRC picture [40]. Reprinted from [41], Copyright 1995, with permission from Elsevier.

The most common mechanisms are molecular sieving and solution diffusion, which can be found in most gas separation membranes [39]. Various membranes are tested for their applicability in carbon capture including porous inorganic membranes, palladium membranes and polymeric membranes[17].

The use of palladium membranes for the separation of  $H_2$  from various gas streams has been studied extensively. While palladium membranes are highly selective towards  $H_2$ , undesirable phase changes at high temperatures have been observed. Furthermore, the membrane is not applicable for gas streams containing  $O_2$ , as palladium is a known oxidation catalyst [42].

Porous inorganic membranes show a good long-term stability at high temperatures, resistance to harsh environments and high pressure drops, as well as an easy-cleaning ability after fouling. The high hydrothermal stability makes these membranes promising for pre-combustion carbon capture, because cooling the syngas can be avoided, resulting in lower energy costs. However their major drawbacks are the high capital costs, the brittleness, the low membrane surface per module volume, the low selectivities in large

scale applications and the low permeability of dense membranes at medium temperatures [43].

Polybenzimidazole (PBI) based membranes are one of the best candidates for the use in extreme chemical and thermal environments due to their long-term hydrothermal stability up to 400 °C, sulphur tolerance and durability in simulated coal-derived syngas for 400 days at 250 °C. The high operating temperature is an advantage compared to conventional polymeric membranes, which only operate up to 150 °C and require cooling of the syngas. Furthermore, the concentrated CO<sub>2</sub> stream is at elevated pressures, which results in a reduction of the energy required for the compression [17, 37].

#### 1.2.2.3 Cryogenic separation

Cryogenic distillation involves the separation of a gas mixture based upon differences in boiling points and volatilities of different gases in a mixture. The technology produces liquid  $CO_2$  in high purity and is widely applied in the separation of oxygen from air. Another potential application is pre-combustion carbon capture in IGCC plants [13, 44, 45].

In a first step the gas mixture is compressed and impurities (e.g.  $H_2O$ , acid gases) are removed, before the mixture flows through a number of heat exchangers in order to cool the feed gas until the  $CO_2$  is condensed. Due to the sublimation of  $CO_2$ , the condensation takes place at temperatures above the triple point temperature of -56.6 °C [44].

The main disadvantages of the process are the high energy requirements for the cooling process and pressurisation, the need to remove impurities prior to the cooling process as they could freeze and cause a blockage of the equipment, and the high capital costs. The application in post-combustion capture is limited due to the low  $CO_2$  concentration in the flue gas [44, 46].

#### 1.2.2.4 Adsorption

The separation of  $CO_2$  using porous, solid adsorbents as an alternative to amine-based absorption/stripping processes, has received much attention during the past decade. The first step is the selective adsorption from  $CO_2$  from the feed gas, while the other components pass through the adsorbent bed. Once the bed is saturated with  $CO_2$  it must be desorbed back into the gas phase (Figure 1.9).



Figure 1.9: Principles of CO<sub>2</sub> capture via adsorption [35]. Copyright CO2CRC.

The interaction of the adsorbate with the adsorbent can either be due to Van der Waals and electrostatic forces (physisorption) or to the formation of a covalent bond (chemisorption). The mechanisms differ in the amount of heat released during the adsorption process. While heats of adsorption smaller than 50 kJ mol<sup>-1</sup> are characteristic for physisorption, these values are much higher for chemisorption. Therefore, adsorption via physisorption is often preferred due to the lower energy requirement for the regeneration of the adsorbent [47].

The regeneration of the adsorbent in a fixed-bed reactor can be achieved by either increasing the temperature (TSA) or decreasing the pressure (VSA or PSA). Adsorptionbased methods such as pressure swing adsorption (PSA) or vacuum swing adsorption (VSA) are promising because of their simple and easy control, low operating and capital costs, and superior energy efficiency [35]. In a PSA process the inlet gas is pressurised and flows through the column until saturation is achieved. Closing the inlet valve, results in the removal of adsorbent out of the column due to the decrease in column pressure towards ambient pressure. The main disadvantage of PSA is the cost associated with the compression due to the large flow rates in a post-combustion process. However, this is not the case for the use of PSA in pre-combustion capture as the gas stream is at elevated pressures. In contrast to a PSA process, the pressure in a VSA process is lowered to sub-atmospheric pressure by applying vacuum. The regeneration of the adsorbent in a TSA process is achieved by increasing the temperature of the bed using an external heat exchanger or directly with a hot gas purge. The released gas molecules leave the bed due to the increased pressure at the higher temperature. After reaching equilibrium, residual gas in void spaces is removed by purging the column until the desired purity of the eluted gas is reached. The bed is then cooled for the next adsorption step. A possible source of energy required for the regeneration in a TSA process, is the low-grade heat from the power plant [7, 47]. The selection of a highly selective adsorbent with a high  $CO_2$  capacity presents the key step in the design of PSA, VSA and TSA processes for the separation and purification of  $CO_2$  [10, 48, 49]. Porous materials, such as activated carbons, zeolites, amine modified siliceous materials and MOFs as well as non-porous materials such as metal carbonates have attracted tremendous attention for carbon capture.

The robust nature of zeolites coupled with their low cost, makes them an attractive target for carbon capture applications. The  $CO_2$  capacities are affected by the pore size and architecture as well as the chemical composition. The most promising zeolites are characterised by a low Si/Al ratio, as aluminium introduces negative framework charges that are compensated by exchangeable cations. Studies have shown that the replacement of the cation in NaX results in a decline in CO<sub>2</sub> adsorption capacity at 0.1 bar in the order Cs<Rb~K<Li~Na. In contrast, dominant CO<sub>2</sub>-framework oxygen interactions over the polarising effect for Y faujasite containing Cs or K result in a higher uptake compared to NaY [50]. Among them, zeolite 13X has shown great potential with a CO<sub>2</sub> adsorption capacity 20.7 wt% at 25 °C and 1 bar [51]. In comparison with aqueous alkanolamine absorbents, zeolites used in small scale pilot plants showed more rapid CO<sub>2</sub> adsorption and lower energy penalties. However, the major drawback of zeolites are their diminished CO<sub>2</sub> adsorption capacities in the presence of H<sub>2</sub>O, their energy extensive regeneration, due to the large heat of adsorptions, and their low selectivity [9, 17, 47]. Amine modifications of zeolite 13X with MEA have shown to enhance the CO<sub>2</sub> adsorption capacity from 4 to 14 mL g<sup>-1</sup> at 120 °C and improvements in performance under humid conditions have been observed [52].

The preparation of activated carbons from carbon containing resins, fly ash and biomass makes them low cost adsorbents [17]. Additionally, activated carbons possess a hydrophobic nature and a low energy requirement for regeneration, which are advantageous properties for carbon capture [7]. They show potential for pre-combustion capture, due to their high surface areas and hence high  $CO_2$  adsorption capacities at high pressure with a upper limit of 60 to 70 wt% [53]. In comparison with zeolites, the  $CO_2$  adsorption capacities were found to be lower at low pressures with a limit of 10 to 11 wt% owing their uniform electric potential on the surface [47]. Depending on the diffusion

mechanism and the heterogeneity of the surface, comparable adsorption kinetics to zeolites can be obtained. The low enthalpies of activated carbons allow a complete regeneration. However, the presence of functional groups can lead to incomplete desorption [50].

High adsorption capacities have also been reported for amine modified siliceous materials (e.g. MCM-41 and SBA-15). While primary and secondary amines react with CO<sub>2</sub> under dry conditions to carbamate, tertiary amines act as proton acceptors. The reaction 1.9 shows, that 1 mol CO<sub>2</sub> react with 2 moles of amine. In the presence of H<sub>2</sub>O bicarbonate is formed and the stoichiometry changes to 1 mol CO<sub>2</sub> per 1 mol of amine. Due to the reversibility of these reactions PSA, VSA and TSA processes are possible [54].

 $\operatorname{CO}_2 + 2\operatorname{R-NH}_2 \leftrightarrows \operatorname{R-NH}_3^+ + \operatorname{R-NHCO}_2^-$  (1.9)

$$CO_2 + R - NH_2 + H_2O \leftrightarrows R - NH_3^+ + R - NH_3^+ HCO_3^-$$
(1.10)

Under dry conditions SBA-15-PEI (50 wt% loading) adsorbs 9.2 wt% under a flow of 15 % CO<sub>2</sub> and 14.0 wt% in the presence of 10 % H<sub>2</sub>O vapour and 13 % CO<sub>2</sub> at 75 °C. In comparison, MCM-41 with the same loading captures 8.8 wt% under dry conditions and 12.5 wt% under wet conditions [50]. However, the presence of H<sub>2</sub>O vapour does not always enhance the CO<sub>2</sub> capacity. An example is the decline in CO<sub>2</sub> capacity under humid conditions from 3.90 to 2.00 wt% on heaxagonal mesoporous silica (HMS) grafted with aminopropyltrimethoxysilane (APTS) [55]. Higher temperatures improve the adsorption/desorption kinetics and reduce the energy required for cooling the flue gas [54].

Metal carbonates have been studied for their potential application in pre-combustion carbon capture. Vogt et al. have prepared and tested a series of sodium iodide doped cadmium carbonate samples and found that the addition of sodium iodide is necessary in order to promote the sorption of  $CO_2$ . Doping at levels of 20 wt% and higher has a negative impact on the sorption performance, whereas a minimum of 7.5 wt% in the uncalcined sample is required to trigger adsorption. In the temperature range of 250 to 300 °C, cadmium oxide doped with 17.5 wt% sodium iodide has a  $CO_2$  uptake of 24 wt%. The carbonation and decarbonisation takes place at the same temperature and makes these materials viable for use in a PSA process [56].

# 1.3 Metal-organic frameworks (MOFs)

MOFs have attracted tremendous attention during the past decade as a class of very promising organic-inorganic hybrid materials for diverse applications like gas storage, gas/vapour separation, catalysis and drug storage and delivery [57, 58]. These porous crystalline materials have structures consisting of metal ions (e.g.  $Al^{3+}$ ,  $Cr^{3+}$ ,  $Zn^{2+}$  or  $Cu^{2+}$ ) that are linked by organic molecules through specific functional groups (e.g., carboxylate, phosphonate). These two main components are connected to each other by coordinative bonds, together with other intermolecular interactions, to afford a network having definite topology with pores usually occupied by solvent molecules [3, 59] (Figure 1.10).



**Figure 1.10:** A general scheme of MOF synthesis. From left to right: trimers of aluminium octahedral and trimesic acid, the resulting hybrid supertetrahedra of MIL-100(Al) and one unit cell of MIL-100(Al) [60]. Ball and stick view (Al octahedral: pink, C: grey, O: red). Hydrogen atoms have been omitted. Adapted from [61] with permission of The Royal Society of Chemistry.

With the nature of the bonding being weaker than that in metal oxides, solvated pores, which are observed in crystal structures, will not necessarily be stable upon solvent removal. This fact has led to a classification of these materials into three generations: those that collapse irreversibly and are not porous (first generation); those that retain their structures and show reversible gas sorption isotherms (second generation); and a final category where the material behaves more like a sponge and changes structure reversibly with guest molecules (third generation) [62].

Based on the flexibility, MOFs can be distinguished into two types: rigid and flexible MOFs. While the framework structure of rigid MOFs (found in 3D structured MOFs) remains intact after guest accommodation/removal, flexible MOFs (found in 1D, 2D and 3D MOFs) are characterised by a structural flexibility upon accommodation/removal of guest molecules. An example for a rigid framework is MOF-5, which shows high adsorption capacities of CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>. Upon removal of the guest molecules from the

pores, the integrity of the MOF-5 framework is fundamentally retained.  $Cu(bpy)_2(BF_4)_2$  on the other hand is an example for a flexible MOF. The framework shows a gate adsorption phenomena for various gases through clathrate formation between host frameworks and guest molecules accompanied by structural transformation [63].

An overview of the MOFs mentioned in this chapter is given in Appendix 1 including possible metal centres, their ligands, their empirical formula and references providing structural details.

#### 1.3.1 Carbon dioxide capture in MOFs

MOFs are attracting increasing attention in  $CO_2$  capture owing to their very high porosity and surface area, ordered and well characterised porous structure, and adjustable chemical functionality [64]. In order to be applicable to realistic flue streams  $CO_2$  adsorbents should fulfil the following requirements:

- high CO<sub>2</sub> capture capacity,
- high selectivity for CO<sub>2</sub> over other components in the flue gas,
- moderate or low heat of adsorption,
- high stability and regenerability under cyclic conditions,
- high thermal and hydrothermal stability.

In Table 1.1 the CO<sub>2</sub> adsorption capacities reported for a number of adsorbent types are given. In comparison to silicate and both zeolite samples, the MOF materials exhibit higher maximal loadings, while the activated carbons are comparable or even show a greater maximal loading than some of the MOFs. To date the record capacity for CO<sub>2</sub> capture of 176 wt% was obtained by Llewellyn et al. with MIL-101(Cr) at 50 bar and 31 °C [65]. In terms of CO<sub>2</sub> adsorption uptakes and heat of adsorption obtained near Standard Temperature Pressure (STP) conditions, the most promising MOFs are CPO-27, HKUST-1, bio-MOF-11, MIL-53, MOF-5, MIL-100, MIL-101 and YO-MOF [66].

While the majority of  $CO_2$  adsorption isotherms obtained from rigid MOFs present a type-I shape after IUPAC [67], sigmoidal isotherms in rigid MOFs (e.g. MOF-5 and MOF-177 [68]) were also reported [69]. Molecular simulations conducted by Walton et al. suggested that the cause of this phenomenon is the interstatic interaction between  $CO_2$  molecules resulting in their bulk condensation [70]. On the other hand, the  $CO_2$  isotherms of flexible MOFs usually exhibit distinct adsorption steps and/or hysteresis during desorption. This

flexibility is a unique feature of these materials and provides for an additional means of controlling the selective adsorption and separation of gases [63, 71-73]. Novel MOFs like MIL-53(Al, Cr) exhibit a breathing framework with flexible and dynamic properties, which may greatly benefit the capture and release performance of gaseous molecules while maintaining their crystallinity and thus their long range order [2, 74].

Adsorbent	Conditions	Amount adsorbed /
		wt%
silicate	302 K / 30 bar	11.0
zeolite NaX	302 K / 30 bar	34.3
zeolite 13X	298 K / 32 bar	32.6
activated carbon NORIT R1	298 K / 30 bar	44.0
activated carbon Maxsorb	298 K / 35 bar	110.0
<b>MIL-53</b> (Cr)	302 K / 25 bar	44.0
	303 K / 1 bar	10.5
HKUST-1	298 K / 42 bar	47.1
	298 K / 1 bar	17.9
<b>MIL-47(V)</b>	302 K / 20 bar	48.4
	298 K / 1 bar	8.80
IRMOF-1	298 K / 35 bar	95.5
	296 K / 1bar	9.24
<b>MOF-177</b>	298 K/ 42 bar	147.4
MIL-100(Cr)	304 K / 50 bar	79.2
<b>MIL-101(Cr)</b>	304 K / 50 bar	176.0
<b>CPO-27(Mg)</b>	298 K / 1 bar	37.3
<b>CPO-27(Co)</b>	298 K / 1 bar	33.2
<b>CPO-27(Ni)</b>	298 K / 1 bar	31.5
Bio-MOF-11	273 K / 1 bar	26.4
YO-MOF	273 K / 1 bar	14.9

**Table 1.1:**  $CO_2$  adsorption capacities for various adsorbents (black) and the amount of  $CO_2$  adsorbed near ambient conditions (red) [65, 66, 75-77]

The highest gravimetric adsorption for  $CO_2$  has been reported in frameworks with high surface areas and pore diameters of greater than 1.5 nm [1]. However, the synthesis of mesoporous MOFs is still challenging due to the fact that open frameworks constructed from large ligands tend to disintegrate after the removal of guest molecules. Another problem is the interpenetration of the framework, which adds stability but drastically reduces the size of the channels or cavities. Thus, the preparation of new mesoporous MOFs should focus on ligand extension to produce stable frameworks, while preventing interpenetration [78].

Although high  $CO_2$  capture capacities under equilibrium conditions have been reported, the selective capture of  $CO_2$  from industrial emission streams that contain other gases such as  $N_2$ ,  $CH_4$  and  $H_2O$  still remains challenging. Due to the fact, that most MOF materials show little uptake in the pressure regime of 0.1-0.2 bar, their application for postcombustion capture is seen to be limited. Tremendous efforts have been undertaken to increase the CO<sub>2</sub> selectivity, while maintaining or increasing the capture capacities of these materials [79-81]. High selectivity for CO<sub>2</sub> adsorption was observed for MOFs, which are characterised by coordinatively unsaturated sites (CUS) and functional groups [2, 49, 82, 83]. CUS can be obtained by introducing solvent molecules during the synthesis as terminal ligands, which can then be removed at elevated temperatures and/or vacuum. These charge-dense binding sites can induce strong local interactions with CO<sub>2</sub> and H<sub>2</sub> adsorbates resulting in higher binding energies and enthalpies of adsorption [13]. In the context of post-combustion capture from flue gas, CUS interact more strongly with CO<sub>2</sub> compared with N<sub>2</sub>, due to the higher quadrupole moment and polarisibility of CO<sub>2</sub> [7, 49].

Ye and co-workers investigated the potential of HKUST-1 for post-combustion  $CO_2$  capture using either TSA or VSA. While the regeneration of the MOF was easily achieved by increasing the temperature to 100 °C under N<sub>2</sub> purge, vacuum was found to be insufficient for the regeneration of the material. Different temperatures were tested (80-120 °C), which had no impact on the regeneration in a TSA process, although higher temperatures result in a shorter regeneration time [84].

The very wide chemical flexibility of possible ligands and functional groups, and the high accessibility of the functional groups to the adsorbates, makes ligand functionalisation a promising strategy to enhance  $CO_2$ -framework interactions [85, 86]. Two methods have been employed to incorporate Lewis basic sites into a MOF structure, the "prefunctionalisation approach" and the post synthetic modification as described in Chapter 1.3.2.

## 1.3.2 Amine modification of MOFs

Two major strategies have been envisaged to produce highly efficient capture materials by virtue of the affinity of alkylamines for CO<sub>2</sub>:

- 1. the "prefunctionalisation" approach and
- 2. postsynthetic modification (PSM).

## 1.3.2.1 Amine modification of MOFs via "prefunctionalisation" approach

The "prefunctionalisation" approach has resulted in MOFs with pendant groups such as -Br, -NH<sub>2</sub> and -CH<sub>3</sub> [87]. The generic scheme for the preparation of functionalised MOFs by using direct solvothermal synthesis is shown in Figure 1.11.



**Figure 1.11:** A general scheme illustrating the concept of "prefunctionalisation" of porous MOFs. Reproduced from [87] with permission of The Royal Society of Chemistry.

Three strategies have been employed to achieve functionalisation prior to or during MOF synthesis [88]:

- The use of functional properties associated with metal ions (e.g. the use of metalloligands as the 'organic' building block).
- The use of a functionalised ligand as the organic building block.
- The incorporation of functional 'cartridge molecules' that are non-covalently bound within MOFs. For instance, Kawano et al. have synthesised a porous coordination network composed of two interpenetrating networks in which the pores are surrounded by aromatic bricks. These bricks consist of alternatively layered 2,4,6-tris(4-pyridyl)-1,3,5-triazine and triphenylene. 2,4,6-tris(4-pyridyl)-1,3,5-triazine forms an infinite 3D network via coordination to ZnI<sub>2</sub>, whereas triphenylene is involved in the 3D framework without forming any covalent or coordination bonds with other components. The intercalated triphenylenes are regarded as the cartridge molecules [89].

Although diverse functionalised MOFs have been prepared via direct solvothermal synthesis, the range of functional groups placed within the pores has remained limited. This is due to the fact that these groups can either interfere with the formation of the desired MOF, or they are not compatible with or stable to the synthetic conditions like high temperature and pressure [90].

Ligands which have been used for synthesising amine functionalised MOFs are shown in Figure 1.12. Primary amines as well as secondary amines have been reported. In the



following a short overview about amine functionalised MOFs and their  $CO_2$  capture capacities (where available) is presented.

Figure 1.12: Examples of amine functionalised ligands [30, 71, 78, 91-100].

Gascon et al. found that through the presence of amino groups on the aromatic rings of the terephthalic acid linker in MIL-53(Al)-NH<sub>2</sub> the number of apolar adsorption sites is reduced. This, in turn, led to a reduced CH<sub>4</sub> uptake relative to the unfunctionalised analogue [71, 92]. The separation performance of MIL-53(Al)-NH<sub>2</sub> was tested in breakthrough experiments at 30 °C using an equimolar CO<sub>2</sub>/CH<sub>4</sub> mixture. It was found, that essentially no CH<sub>4</sub> was adsorbed while 0.83 mmol of CO<sub>2</sub> was adsorbed per gram of adsorbent. Therefore the selectivity was improved from ~7 (MIL-53(Al)) to almost infinity (MIL-53(Al)-NH<sub>2</sub>) at 1 bar [71]. In the absence of adsorbate, the large pore form (*lp*) of unfunctionalised MIL-53(Al) is energetically preferred over the narrow pore (*np*) form by 3 kJ mol<sup>-1</sup>. The CO<sub>2</sub> adsorption on MIL-53(Al) is directed by the formation of rather weak hydrogen bonds between CO<sub>2</sub> and bridging hydroxyl groups of the lattice (Figure 1.13).

MIL-53(Al)-NH<sub>2</sub> on the other hand favours the narrow pore over the large pore form by 14 kJ mol<sup>-1</sup> due to more efficient hydrogen bonding involving the amine moieties and the  $[AlO_6]_{\infty}$ . This enhancement of hydrogen bonding is caused by a variety of van der Waals contacts between organic structural fragments evident and by the breakage of the CH·····Π interaction network after amine modification. The result is a higher relative stability of MIL-53(Al)-NH<sub>2</sub> *np*. The basic amino groups in the framework influence the intrinsic properties of CO<sub>2</sub> adsorption sites. While N<sub>2</sub> is only adsorbed in small amounts up to 2 bar, CH<sub>4</sub> is not adsorbed at all under 1 bar. The preference for the *np* form reduces the adsorption of larger molecules such as CH<sub>4</sub> and therefore increases the selectivity for CO<sub>2</sub>. For the transition from the *np* to the *lp* form higher partial pressures of CO<sub>2</sub> (10 bar) are needed due to the NH<sub>2</sub>-OH interaction [101]. Because of the high selectivity of CO<sub>2</sub>/N<sub>2</sub>, MIL-53(Al)-NH<sub>2</sub> is a promising material for post-combustion carbon capture.



**Figure 1.13:** Optimised structures and relative energies of parent MIL-53 (left) and aminofunctionalised MIL-53(Al)-NH<sub>2</sub> materials and their complexes with CO<sub>2</sub>. Reprinted with permission from [101] (E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon, and F. Kapteijn, "Complexity behind CO<sub>2</sub> Capture on NH<sub>2</sub>-MIL-53(Al)," *Langmuir*, vol. 27, pp. 3970-3976, 2011). Copyright 2011 American Chemical Society.

Arstad et al. have prepared three different highly porous MOF structures with and without amine functionalities and have determined the capture capacities to study the effect of such functionalities upon sorption behaviour. The amine modified MOFs were synthesised by using 2-aminoterephthalic acid (BDC-NH<sub>2</sub>) as the organic building block. Although MIL-53(Al)-NH<sub>2</sub>, USO-2(Ni)-NH<sub>2</sub> and MIL-68(In)-NH<sub>2</sub> possess lower specific surface areas (Table 1.2) relative to their mother compounds, their CO<sub>2</sub> adsorption capacities were found to be higher at 25 °C and up to 1 bar [92, 95].

<b>*</b>	$\overline{SSA[m^2g^{-1}]}$	PV [mL g <sup>-1</sup> ]
MIL-53(Al)	1300	0.42
<b>MIL-53(Al)-NH</b> <sub>2</sub>	960	0.25
USO-2(Ni)	1925	0.74
USO-2(Ni)-NH <sub>2</sub>	1530	0.50
<b>MIL-68(In)</b>	930	0.34
<b>MIL-68(In)- NH</b> <sub>2</sub>	16	-
$Zn_2(Atz)_2(ox)$	782	0.19

Table 1.2: Specific surface areas (SSA) and pore volumes (PV) [91, 92].

The synthesis and CO<sub>2</sub> adsorption of  $Zn_2(Atz)_2(ox)$  has been reported by Vaidhyanathan et al. The MOF is characterised by a rapid uptake of CO<sub>2</sub> at low pressure. At 0 °C and 1.2 bar the CO<sub>2</sub> adsorption capacity was determined to be 19.1 wt%. The cycle was repeated eight times with complete reversibility [30, 91]. To be applicable for CO<sub>2</sub> post-combustion capture, the sorbent also has to be H<sub>2</sub>O stable. Information about the hydrothermal stability of this material has not been published yet.

MIL-101(Al)-NH<sub>2</sub> was prepared and characterised by Serra-Crespo et al. and is assembled by using aluminium chloride hexahydrate as the metal source and 2-aminoterephthalic acid as the ligand. The amine functionalised framework shows a CO<sub>2</sub> adsorption capacity of 61.6 wt% at 30 bar, which is lower in comparison to 88.0 wt% for MIL-101(Cr). To date, the synthesis of unfunctionalised MIL-101(Al)-NH<sub>2</sub> hasn't been successful. The inclusion of amine moieties prevents to a large extent the hydrolysis of some frameworks and therefore stabilises the structure [102]. The complexity of the crystallisation process of MIL-101(Al)-NH<sub>2</sub> and MIL-53(Al)-NH<sub>2</sub> was reported by Stavitski et al. (Figure 1.14). They found that, after 2-aminoterephthalic acid is dissolved completely, the formation of the disordered MOF-235 phase rapidly occurs in the intermediate temperature regime. In an aprotic solvent the assembly of MOF-235 clusters into MIL-101 phase follows as temperature rises. However, in the presence of H<sub>2</sub>O, MOF-235 is hydrolysed as temperature rises and MIL-53, the thermodynamically favourable phase, is assembled. For a successful synthesis of MIL-101(Al)-NH<sub>2</sub>, the stabilisation of the metastable MOF-235 phase by DMF is therefore essential [103].

Although some amino-functionalised MOFs (e.g. MIL- $101(Al)-NH_2$ ) can be obtained by directly replacing the unfunctionalised ligand by the corresponding functionalised ligand (e.g. terephthalic acid by 2-aminoterephthalic acid), this is not always easily accomplished. The high temperature of 200 °C used for synthesising MIL-101(Cr), leads to the decomposition of 2-aminoterephthalic acid. However, by decreasing the reaction

temperature and adding sodium hydroxide, the preparation of MIL-101(Cr)-NH<sub>2</sub> using the "prefunctionalisation" approach is possible and was first reported by Lin and co-workers [104]. Owing to the synergetic effect of the high surface area and Lewis basic amine groups, the MOF displays an excellent CO<sub>2</sub> capture ability. The "ideal" CO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivities (ratio of the single component adsorption capacities) at 25 °C were reported to be 8-16 and 3-5. The amine functionalised framework shows a CO<sub>2</sub> adsorption capacity of 66.0 wt% at 25 bar.



**Figure 1.14:** The sequence of events during the crystallisation of terephthalate based Aluminium MOFs in different media: Low precursor concentrations (DMF); high precursor concentrations (H<sub>2</sub>O/DMF or H<sub>2</sub>O). Reproduced from [103], Copyright 2011, with the permission of WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

A number of MOFs containing trivalent metal atoms and 2-aminoterephthalic acid can be found in the literature (e.g. MIL-53(Al)-NH<sub>2</sub>, MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub>, MIL-101(Fe)-NH<sub>2</sub>). However, the use of divalent metal salts and BDC-NH<sub>2</sub> in the construction of MOFs is scarce. The only publication to date by Liang et al. describes the assembly of a non-porous Ca-MOF which possesses an extended 3D framework in which the asymmetric unit contains one calcium atom, one BDC-NH<sub>2</sub> ligand, and two DMF molecules [105]. However, due to the lack of porosity the material is not applicable for CO<sub>2</sub> capture. The synthesis and characterisation of a novel 3D porous MOF,  $[Zn_5(trencba)_2(OH)_2Cl_2\cdot 4H_2O]$  (H<sub>3</sub>trencba=N, N, N'N'N''-tris[(4-carboxylate-2-yl) methyl] tris(2-aminoethyl)amine) with an unprecedented penta-nuclear zinc cluster fragment was described by Wen and co-workers. Due to the photoluminescence properties, the material appears to be a good candidate for blue-light-emitting diode devices [94].

The MOF  $[(In_3O)(OH)(ADC)_2(NH_2IN)_2]\cdot 2.67H_2O$ , which is assembled by using  $In_3O(O_2CR)_6X_3$  as metal cluster, azobenzene-4,4'-dicarboxylate (ADC) as large linker, and 3-aminoisonicotinate (NH<sub>2</sub>IN) as an apical bridging ligand of trimer, was synthesised by Gu et al. The maximum CO<sub>2</sub> adsorption capacity for the mesoporous mother compound  $[(In_3O)(OH)(ADC)_2(IN)_2]\cdot 4.67H_2O$  was determined to be 69.98 wt% at -78 °C. Grafting of basic amine groups onto the surface of porous materials leads to an increase in the adsorption capacity (78.82 wt%) [98].

PCN-100 and PCN-101 were prepared and characterised by Fang et al. and are two of only a few mesoporous MOFs that have been reported so far. The use of extended trigonal planar ligands containing amino functional groups as secondary building units (SBUs) (TATAB=  $4,4^{\circ},4^{\circ}$ -s-triazine-1,3,5-triyltri-*p*-aminobenzoate, BTATB=  $4,4^{\circ},4^{\circ}$ -(benzene-1,3,5-triyltris (azanediyl)tribenzoate)) lead to mesoporous materials which are stabilized by hydrogen bonding. Both materials have been tested as catalysts in Knoevenagel condensation reactions. Additionally PCN-100 has been found to capture metal ions (Co(II), Cd(II), Hg(II)) [78]. For both materials CO<sub>2</sub> adsorption data are not available in the literature.

Materials	CO <sub>2</sub> /CH <sub>4</sub> Selectivity		Working Capacity
	1 bar	10 bar	cm <sup>3</sup> (STP) cm <sup>-3</sup>
<b>UiO-66</b> ( <b>Zr</b> )	9.4	8.9	78.8
UiO-66(Zr)-Br	9.8	10.3	52.8
<b>UiO-66(Zr)-NO</b> <sub>2</sub>	12.7	14.4	57.7
UiO-66(Zr)-NH <sub>2</sub>	14.8	14.7	86.2
UiO-66(Zr)-COOH	19.2	23.2	57.0

**Table 1.3:** Predicted selectivities and working capacities in the UiO-66(Zr) series at 30 °C [106].

Yang and co-workers investigated the effect of different polar functional groups grafted onto the ligand (terephthalic acid) of UiO-66(Zr) by Grand Canonical Monte Carlo simulations (GCMC) in order to predict the  $CO_2/CH_4$  separation performance of these materials in their hydroxylated versions. The grafting of polar groups on the MOF leads to an enhancement of its affinity for  $CO_2$  and to a significant improvement of its  $CO_2/CH_4$  separation performance (Table 1.3). The increase in the polarity of the functional groups resulted in a rise in the heat of adsorption for  $CO_2$  (except for UiO(Zr)-NO<sub>2</sub>). Among the studied modifications UiO-66(Zr)-COOH not only exhibited good  $CO_2/CH_4$  selectivities and good working capacities, but also a medium range heat of adsorption values for  $CO_2$  (33 kJ mol<sup>-1</sup> at low coverage). UiO-66(Zr) materials are predicted to be an excellent alternative solution to the conventional zeolite 13X adsorbent used in PSA applications due to its resistance towards humidity [106, 107].

The preparation of DMOF-1-NH<sub>2</sub> and the effect of the amine group on the CO<sub>2</sub> adsorption capacity were described by Zhao et al. The enhancement of CO<sub>2</sub> capacity from 7.4 wt% (unmodified MOF) to 9.4 wt% (amine modified MOF) at 1 bar and 25 °C can be attributed primarily to the strong electron donor-acceptor interaction between the framework and CO<sub>2</sub> molecule, in which the nitrogen atoms containing lone pairs of electrons from amino groups serve as the electron donor centres [108].

An et al. described the preparation and adsorption properties of a bio-MOF-11 exhibiting pyrimidine- and amino-decorated pores. The CO<sub>2</sub> adsorption capcity at 25 °C was found to be 18.0 wt% at 1 bar, while under the same conditions only 0.4 wt% of N<sub>2</sub> was adsorbed. The calculated CO<sub>2</sub>/N<sub>2</sub> selectivity from this data is 75:1. Due to the high CO<sub>2</sub> selectivity of bio-MOF-11 over all other gases and the negligible effect of H<sub>2</sub>O on the adsorption capacity, the material presents promising properties for the application in CO<sub>2</sub> capture [77, 109, 110].

Peikert et al. reported the synthesis of UHM-30, which is assembled by using 2-amino-1,3,5-tricarboxylic acid as ligand and copper nitrate trihydrate as metal source. The  $CO_2$ and  $CH_4$  adsorption capacities were measured and compared to the isostructural HKUST-1. In both cases the amine functionality on the ligand leads to an increase in uptake at 25 °C and 1 bar (Table 1.4) [100].

	CO <sub>2</sub> adsorption capacity /	CH4 adsorption capacity /	
	wt%	wt%	
HKUST-1	20.6	1.6	
<b>UHM-30</b>	23.1	1.7	

**Table 1.4:**  $CO_2$  and  $CH_4$  adsorption capacities in UHM-30 and HKUST-1 at 25 °C and 1 bar.

The generation of a porous tetrahedral framework material,  $Zn(ad)(ain) \cdot (DMF)$  (ain=2aminoisonicotinate, ad=adeninate, DMF=*N*,*N*-dimethylformamide), was reported by Yang et al. The amino-functionalised MOF shows a high CO<sub>2</sub> adsorption capacity of 4.9 wt% at 0.1 bar and 25 °C, a high CO<sub>2</sub> adsorption enthalpy (40 kJ mol<sup>-1</sup>) and an excellent adsorption selectivity of 259 for CO<sub>2</sub> over N<sub>2</sub> under ambient conditions [111].



**Figure 1.15:** Sorption isotherms of  $Zn(ad)(ain) \cdot (DMF)$ : CO<sub>2</sub> adsorption/desorption isotherms at 25 °C (•) and N<sub>2</sub> isotherm at 25 °C (•). Closed symbols (•): adsorption. Open symbols (•): desorption. Reproduced from [111] with permission of The Royal Society of Chemistry.

There are also different approaches available in the literature for synthesising amine modified MOFs for further PSM [112]. For instance, Costa et al. reported the synthesis of MOF-LIC-1 using gadolinium(III) nitrate and BDC-NH<sub>2</sub>. The framework is characterised through amino functional groups which are oriented inside the pores and offer the possibility of further modification with ethylisocyanate or acetic acid by using PSM [97]. In order to allow PSM of the MIL-101(Fe) nanoparticles, Taylor-Pashow et al. prepared MIL-101(Fe)-NH<sub>2</sub> by incorporating BDC-NH<sub>2</sub>. They found that particles with low BDC-NH<sub>2</sub> incorporation exhibited the same MIL-101 structure, but particles with higher BDC-NH<sub>2</sub> incorporation adopted the MIL-88b structure [99]. Wang et al. have prepared and

modified DMOF-1-NH<sub>2</sub> ([Zn(BDC-NH<sub>2</sub>)(DABCO)]) and UMCM-41-NH<sub>2</sub> [Zn4O(BDC) (BTB)4/3] (BTB=1,3,5-benzenetrisbenzoate). Both materials were used to evaluate the effects of structural variation and pore dimension on PSM [95].

## 1.3.2.2 Amine modification of MOFs via postsynthetic modification (PSM)

In 1990 Hoskins and Robson suggested the principle of PSM [113], but it was formally introduced by Wang and Cohen [90]. It can be defined as the modification of a framework after it has been synthesised and can be divided into three areas: (a) covalent PSM, (b) dative PSM and (c) postsynthetic deprotection (PSD) (Figure 1.16).



**Figure 1.16:** A general scheme illustrating the concept for (a) covalent PSM, (b) dative PSM, and (c) PSD. Adapted from with permission from [114] ("Postsynthetic Methods for the Functionalization of Metal–Organic Frameworks," *Chemical Reviews*, vol. 112, pp. 970-1000, 2012/02/08 2011). Copyright (2011) American Chemical Society.

One advantage of PSM over "prefunctionalisation" is the greater control over the type and number of functional groups that can be incorporated into the framework. PSM offers the possibility to modify the metal or organic components without affecting the overall stability of the framework and is therefore an excellent tool for preparing topologically identical, but functional diverse frameworks. Another advantage is the facileness of purification and isolation of modified products due to the direct performance of the chemical derivatisation on crystalline solids [87, 88].

Wang et al. identified several key concepts that are of particular importance in the process of postsynthetic modification by using six linear alkyl anhydrides ( $[CH_3(CH_2)_nCO]_2O$ , where n=0, 2, 4, 8, 12, 18) and two branched anhydrides (trimethylacetic anhydride and isobutyric anhydride) to modify UMCM-1-NH<sub>2</sub>, IRMOF-3 and DMOF-1-NH<sub>2</sub>:

- 1. the overall porosity of MOFs largely determines the degree of modification and the range of reagents that can be accessed,
- 2. the framework connectivity and in particular, the local environment surrounding the targeted reactive groups (e.g. NH<sub>2</sub>) play an important role that affects the reactivity and,
- 3. the size and shape of reagent molecules play a critical role in influencing the modification outcome [96].

## 1.3.2.2.1 Covalent PSM

The use of a reagent to modify a component of the MOF in a heterogenous, postsynthetic manner to form a new covalent bond is called covalent PSM. This type of PSM is the most extensively investigated of the postsynthetic methods and the target is generally the organic ligand of the MOF. Occasionally, such modification to the SBUs have also been described [114]. Examples for the covalent PSM on unfunctionalised ligand molecules in MOFs are discussed below.

Bernt and co-worker reported the PSM of MIL-101(Cr) by modifying the terephthalate ligands. The nitration of MIL-101(Cr) to MIL-101(Cr)-NO<sub>2</sub> using nitrating acid, is followed by a subsequent reduction to the amino functionalised MIL-101(Cr)-NH<sub>2</sub>. The schematic representation of the postsynthetic modification of MIL-101(Cr) is shown in Eq. 1.11. Expanding the nitration time from 5 to 48 h, no multiple nitration of the aromatic system was observed due to the -M and -I (resonance (M) and inductive (I) effect: NO<sub>2</sub> group withdraws electrons from aromatic ring) effect of the nitro group which deactivates the system and prevents a second electrophilic substitution reaction [115].



The facile conversion of azide to primary amine MOFs using Staudinger reduction was reported by Nagata et al. In a first step AzM-BP was synthesised and characterised, before reducing the azide groups by using triphenylphosphine and  $H_2O$  as reducing agents (Figure 1.17). Depending on the reaction time a partial (1 day) or a complete (1 week) conversion of the azide groups was observed. In the case of partial conversion, the primary amines were located near the surface and the azide groups at the core of the crystals, thus achieving a core-shell structure. The utilisation of both groups for further chemical modifications with different functional moieties for preparation of multi-component complex MOFs could pave the way to microfabricated porous materials for medical or optoelectrical applications [116].



**Figure 1.17:** Structure and Staudinger reduction of AzM-BP and concept of surface modification. Reproduced from [116] with permission of The Royal Society of Chemistry.

## 1.3.2.2.2 Dative PSM

Dative PSM is defined as the use of a reagent that forms a dative (e.g. metal-ligand) bond with a component of the MOF. Examples for dative PSM are the coordination of additional ligands to the SBU of the MOF or adding metal sources to the MOF, which will then bind to the organic ligand [114].

Demessence et al. reported the functionalisation of the coordinatively unsaturated  $Cu^{II}$  sites of the H<sub>2</sub>O stable MOF H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>] (H<sub>3</sub>BTTri=1,3,5-tris(1*H*-1,2,3-triazol-

5-yl)benzene) by using ethylenediamine (ED). In Figure 1.18 the CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms for the functionalised and non-modified MOF at 25 °C are compared. At low pressure (up to 0.06 bar) the attraction of CO<sub>2</sub> is greater for the more basic amine sites which leads to a CO<sub>2</sub> adsorption capacity of 1.6 wt % for the amine modified MOF compared to 1.2 wt% for the non-modified MOF. Due to the fact that CO<sub>2</sub> is filling the available pore volume at pressures above 0.1 bar, the adsorption capacity for the non-modified MOF is 14.3 wt % at 1 bar, greater than that for the amine modified compound which is 5.5 wt %. While amine grafting does lead to a steeper rise in the CO<sub>2</sub> isotherm at low pressure, the pore size of H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>] appears to be too small to permit complete exposure of the resulting terminal alkylamines. On the other hand, the alkylamine functionalities endow the material with a higher CO<sub>2</sub>/N<sub>2</sub> selectivity over the entire pressure range measured. At 25 °C the CO<sub>2</sub>/N<sub>2</sub> selectivity for the amine functionalised MOF is 13:1 at 0.1 bar and 25:1 at 1 bar [64].



**Figure 1.18:**  $CO_2(\bullet)$  and  $N_2(\blacktriangle)$  adsorption isotherms at 25 °C in  $H_3[(Cu_4Cl)_3(BTTri)_8]$  (black), in the ED modified MOF (green) [64] and in the MMEN amine modified MOF (blue) [117]. Reprinted with permission from [64] (A. Demessence, D. M. D'Alessandro, M. L. Foo, and J. R. Long, "Strong CO<sub>2</sub> Binding in a Water-Stable, Triazolate-Bridged Metal-Organic Framework Functionalized with Ethylenediamine," *Journal of the American Chemical Society*, vol. 131, pp. 8784-8786, 2009.). Copyright (2009) American Chemical Society. Reproduced from [117] with permission of The Royal Society of Chemistry.

However, McDonald and co-workers observed a CO<sub>2</sub> working capacity of approximately 7 wt% between 0.15 and 0.02 bar at 25 °C in H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>] functionalised with N,N'-dimethylethylenediamine (MMEN). It therefore shows the highest binding strength for CO<sub>2</sub> of any MOF reported to date. The cycling capacity of the MOF under dry

conditions is comparable or even greater than the working capacity of a 30 % MEA solution, which is frequently reported as 5.5 wt% [117].

The grafting of an alkylamine or poly-alkyamine functionality onto the CUS of MIL-101(Cr) was reported by Hwang et al. [118], Kim et al. [119], Anbia et al. [120] and Lin et al. [121]. For the selective functionalisation of the CUS, ED as an effective grafting reagent with multifunctional chelating groups was chosen. As illustrated in Figure 1.19, if one amine group of ED is grafted to the CUS of MIL-101 by direct ligation, the other amine group can play the role of immobilised base catalyst [118].



**Figure 1.19:** Site-selective functionalisation of MIL-101 through selective grafting of amine molecules (i.e. ethylenediamine) onto coordinatively unsaturated sites. Reprinted with permission from [114] (S. M. Cohen, ("Postsynthetic Methods for the Functionalization of Metal–Organic Frameworks," *Chemical Reviews*, vol. 112, pp. 970-1000, 2012/02/08 2011). Copyright (2012) American Chemical society.

Kim et al. suggested the use of diethylenetriamine (DETA) as a grafting agent due to the increased number of electron rich N sites, which are more shielded from the electrondeficient Lewis acidic CUS in MIL-101. Pressures lower than 0.15 bar showed higher adsorption capacities than the unmodified MIL-101 framework. At higher pressures however, the adsorption capacity decreases from 7.9 wt% to 3.1 wt% at 25 °C and 1 bar due to the significant decrease in surface area after the modification [119]. The modification of MIL-101 with pentaethylenehexamine (PEHA) resulted in an improvement of the CO<sub>2</sub> capacity at 25 °C and 10 bar from 3.74 wt% before the modification to 5.72 wt% after the incorporation [120]. On the other hand, polyalkylamines (e.g. PEI) offer a high amine density and accessible primary amine sites on the chain ends, resulting in a strong interaction with CO<sub>2</sub>. Lin et al. reported the use of linear PEI with an average molecular weight of 300 g mol<sup>-1</sup> for the dative PSM of MIL-101(Cr), which afforded a high-performance sorbent for post-combustion capture. A number of different PEI loadings were studied and an increase in  $CO_2$  capacity was found in all cases. For example, a 100 wt% loading with PEI increases the  $CO_2$  adsorption capacity from 1.5 wt% before modification to 1.8 wt% after modification at 0.15 bar and 25 °C [121].

A similar approach was reported by Choi et al., in which ED was employed as a grafting reagent to functionalise the coordinative unsaturated sites of CPO-27-Mg (Mg-DOBDC). The modified MOF exhibited an improved  $CO_2$  working capacity at ultradilute  $CO_2$  partial pressures and an increased stability/regenerability (Figure 1.20) [122].



**Figure 1.20:** Changes in the  $CO_2$  working capacity of Mg/DOBDC and ED modified Mg/DOBDC. The working capacities were determined from multicycle TGA adsorption experiments in which dry 400 ppm  $CO_2$  in Ar was used as the test gas at room temperature. Adapted from [122] (S. Choi, T. Watanabe, T.-H. Bae, D. S. Sholl, and C. W. Jones, "Modification of the Mg/DOBDC MOF with Amines to Enhance  $CO_2$  Adsorption from Ultradilute Gases," *The Journal of Physical Chemistry Letters*, vol. 3, pp. 1136-1141, 2012/05/25 2012.). Copyright (2012) American Chemical Society.

The postsynthetic incorporation of piperazine onto the CUS of CPO-27-Ni for an enhanced ability of the framework to selectively separate  $CO_2$  from a  $CO_2/N_2$  mixture was described by Das et al. (Figure 1.21). After the modification with secondary amines, a decrease in  $CO_2$  adsorption capacity from 25.5 to 14.1 wt% at 1 bar and 25 °C was observed. However, the  $CO_2/N_2$  selectivity factor was improved from 30 to 51. The performance of the material in a 40-80 °C temperature swing process over 10 cycles indicated good stability and reversibility of the material with a  $CO_2$  working capacity of 10 wt% [123, 124].



**Figure 1.21:** Left: "Honeycomb" structure of CPO-27-Ni framework viewed along the one dimensional channels (Ni: blue, O: red, C: grey). Right: CO<sub>2</sub> adsorption isotherm at 25 °C before (•) and after (•) modification of CPO-27-Ni with piperazine, ( $\blacktriangle$ ) N<sub>2</sub> adsorption isotherm at 25 °C for amine modified CPO-27-Ni. Reproduced from [123] with permission of The Royal Society of Chemistry.

## 1.3.2.2.3 Postsynthetic deprotection (PSD)

PSD results in the cleavage of a chemical bond within an intact framework. In principle any kind of chemical bond (e.g. covalent, dative, etc.) can be broken during a PSD reaction to reveal a chemical functionality and produce materials with different properties. Although it is the least explored PSM method, it has already been shown to be a distinct and useful approach for modifying MOFs [114].



**Figure 1.22:** Thermally induced PSD on  $Zn_4O(2)_3$ . Reprinted with permission from [114] ("Postsynthetic Methods for the Functionalization of Metal–Organic Frameworks," *Chemical Reviews*, vol. 112, pp. 970-1000, 2012/02/08 2011). Copyright (2011) American Chemical Society.

Deshpande and co-worker reported the preparation of  $Zn_4O(2)_3$ . After protecting the amine group of the ligand 2-aminobiphenyl-4,4'-dicarboxylate (H<sub>2</sub>2) with a bulky *tert*butylcarbamate (Boc) group, the MOF was assembled by heating the ligand,  $Zn(NO_3)_2$ ·4H<sub>2</sub>O in DEF (DEF=*N*,*N*-diethylformamide) at 85 °C. The protection of the amine group is essential in order to prevent the preclusion of the MOF growth. The removal of the *tert*-butyl groups by thermolysis at 150 °C in DMF resulted in the generation of an IRMOF-10 analogue with free amine groups and a clear absence of interpenetration (Figure 1.22) [125].

## 1.3.3 Phosphonate MOFs

Although metal phosphonates were among the first microporous inorganic hybrid adsorbents to be investigated, the development of new phosphonate and sulfonate based MOFs has not progressed as rapidly as the systems described above [126-130]. One explanation for this is the strong affinity and chelation of phosphonate groups to metal ions, which results in the predisposition of simple metal phosphonates to form a dense layered motif and therefore makes the formation of high surface area materials challenging. The second reason is the rapid precipitation of phosphonate MOFs as less ordered, insoluble phases, which makes the growth of single crystals more difficult. Furthermore, the higher number of ligating modes and the three possible states of protonation, makes the prediction of the coordination chemistry of these materials more difficult [131, 132].

However, research groups of Clearfield and Zubieta are regarded as pioneers in transition metal chemistry involving the solvothermal synthesis of phosphonate MOFs [133-145]. Possible applications of metal phosphonates include cation exchange, sorption, catalysis, catalyst supports, sensors as well as non-linear optics [146]. There is a rich variety of phosphonate building units that can be used as reagents (as acids or esters, for example) that are either commercially available or readily synthesises by Michaelis-Arbuzov- or Mannich-type reactions.



**Figure 1.23:** Michaelis-Arbuzov reaction mechanism. Reproduced from [147], Copyright Elsevier (2005).

The Michaelis-Arbuzov reaction was invented by Michaelis and investigated and developed by Arbuzov. The reaction mechanism consists of two nucleophilic substitutions and is shown in Figure 1.23. The first step is the nucleophilic attack of a trialkyl phosphate on the  $\alpha$ -carbon of the alkyl halide, resulting in the formation of a quasi phosphonium salt.

The nucleophilic halide anion is then attacking the carbon atom of one of the alkoxy groups directly connected to the oxygen atom. A new C-X bond is formed after electron pair reorganisation and the simultaneous cleavage of C-O bond. The by-product is a new alkyl halide in which the alkyl group comes from the trialkyl phosphite.

The first step in an acid catalysed Mannich reaction is the protonation of formaldehyde, followed by the nucleophilic attack of the nitrogen atom of ammonia, a primary or a secondary amine at the carbon atom of formaldehyde, which results in the formation of an iminium ion. The phosphorous atom of phosphorous acid can then attack the carbon atom of the iminium ion and a phosphonate is obtained (Figure 1.24).



**Figure 1.24:** Mannich reaction mechanism. Reproduced from [147], Copyright Elsevier (2005).

Like carboxylic acids, phosphonic acids are not prone to self condensation. Phosphonates form strong P-O-metal bonds with a range of metal cations, to which they can bind through one, two or three of these oxygen atoms per phosphonate group [148, 149]. Metal phosphonates are typically synthesised in aqueous solution, so it is not surprising that  $H_2O$ is commonly found in their lattice, participating in extensive hydrogen bonding, which is predominant in these architectures resulting in 1D, 2D and 3D supramolecular networks. Unlike trivalent and tetravalent metal phosphonates, which are highly insoluble and tend to precipitate as poorly ordered layered materials, the solubility of divalent metal phosphonates is high enough to obtain single crystals by hydrothermal or solvothermal techniques.

The application of most metal phosphonates in adsorption processes is limited, due to small pore sizes of 0.6 nm and less. Possible routes for the formation of porous structures

include the incorporation of co-ligands/templates or a direct reaction of metal salts with the phosphonic acids [150, 151]. One example is use of N,N'piperazinebis(methylenephosphonic acid), which resulted in phosphonate MOFs with large pores and high adsorption capacities [152]. Groves et al. reported the synthesis of the first fully crystalline metal phosphonate MOF (STA-12) with pores approaching 1 nm [126]. The dehydrated STA-12(Ni) showed a CO<sub>2</sub> uptake of 26.4 wt% at 15 bar. At 1 bar the uptake was reported to be 10 times that of CH<sub>4</sub>, which is higher than that observed for adsorption on other large pore MOFs, such as MIL-100 and MIL-101 [153]. The use of N,N'-4,4'-bipiperidinebis(methylenephosphonic acid) lead to the formation of STA-16, which showed an extension of the pore size towards the mesoporous regime (1.8 nm) [154].

Furthermore, hydrothermal phosphonate MOFs containing phosphonate monoesters, e.g. CALF-25, have shown to be stable upon treatment with 95 % RH at 45 °C due to the protective shielding of alkyl groups (ethyl groups) lining the pores [155].

## 1.3.4 Water stability in MOFs

In order to be applicable for industrial purposes, a good hydrothermal stability of sorbent materials is required in order to prevent additional costs for removing the  $H_2O$  from the flue gas prior to the separation of  $CO_2$ . However, one of the major drawbacks of MOFs is their hydrothermal stability due to the weak M-O-coordination, which allows the attack of  $H_2O$  molecules. The result is a phase transformation, a decomposition of the framework and finally a poor reproducibility and a decrease in gas sorption capacities [156-158].

The reaction of  $H_2O$  with the metal oxide cluster in MOFs can involve ligand displacement and/or hydrolysis. During the ligand displacement a  $H_2O$  molecule is inserted into a metalligand bond as shown in Eq. 1.12:

$$M-L + H_2O \rightarrow M-(OH_2)\cdots L$$
 (1.12)

After the metal-ligand bond is broken and  $H_2O$  dissociates into a hydroxide anion and proton, the hydroxide anion binds to the metal, and the proton binds to the displaced ligand (Eq. 1.13)

$$M-L + H_2O \rightarrow M-(OH) + LH$$
(1.13)

Recently the H<sub>2</sub>O stability of some MOFs, such as MOF-5, MOF-177, HKUST-1, ZIF-8, MIL-100(Fe) and MIL-101 has been investigated [32, 159-164]. Among them, only ZIF-8,
MIL-100 and MIL-101 were found to be H<sub>2</sub>O stable. The level of relative humidity (RH) has shown to have a big impact on the stability of MOFs. Liang and co-workers showed that the CO<sub>2</sub> capacities of conventional and HF-free MIL-101(Cr) were retained after the exposure to different relative humidities (30, 60 and 90% RH) [165]. In contrast to this, CPO-27(Zn) and CPO-27(Ni) were stable under 30 % RH, but collapsed under 60 % RH [160]. Although, CPO-27(Mg) is known for its superior CO<sub>2</sub> capacities under dry condition, the coordination of H<sub>2</sub>O results a reduction of the CO<sub>2</sub> uptake by 90 % upon exposure to 70 % RH at 25 °C [166]. Additionally, the metal incorporated into the SBU of any particular MOF can have an impact on the hydrothermal stability as is the case for the CPO-27 family (Co>Ni>Zn≈Mg). This trend can be explained with the reduction in the density of CUS for MOFs containing more readily oxidisable metals [167, 168].

A promoting effect of  $H_2O$  on the CO<sub>2</sub> capacity has been reported for HKUST-1, MIL-100(Fe) and MIL-101(Cr) [82, 169, 170]. While HKUST-1 decomposes in the presence of high relative humidity, Yazaydin et al. reported a 45 % increase in CO<sub>2</sub> uptake after loading the MOF with 4 wt% H<sub>2</sub>O at 1bar and 25 °C [82]. Liu and co-worker observed a small increase in CO<sub>2</sub> capacity from 2.16 wt% to 2.24 wt% after the treatment of MIL-101(Cr) with 10 % RH, which can be explained with the electrostatic interaction between H<sub>2</sub>O bound to the CUS and the quadrupole moment of CO<sub>2</sub>. However higher RHs were found to result in a decrease in CO<sub>2</sub> capacity due to competitive adsorption between H<sub>2</sub>O and CO<sub>2</sub> [169]. The formation of microporous pockets after the pre-equilibration with H<sub>2</sub>O in the mesopores of MIL-100(Fe) was described by Soubeyrand-Lenoir et al. [170]. The treatment of the MOF with 40 % RH resulted in a 5fold increase of the CO<sub>2</sub> uptake at low pressures.

Different approaches are available in the literature to improve the  $H_2O$  stability of MOFs by introducing hydrophobic groups. For instance, Yang et al. found that by synthesising MOF-5 with 2-methylterephthalic acid or 2,5-dimethylterephthalic acid, the moisturestability had been improved. MOF-5 is known to be unstable when exposed to more than 4 wt% H<sub>2</sub>O. But with increasing the concentration of CH<sub>3</sub> functionalities, the H<sub>2</sub>O uptake decreases and stays well below 4 wt% [157]. Another example for building H<sub>2</sub>O resistant MOF structures by introducing H<sub>2</sub>O repellent functional groups into the framework, was demonstrated by Wu et al. Banasorb-22 (a modification of MOF-5) contains the trifluoromethoxy group, which is known for its strong H<sub>2</sub>O repelling effects in polymer chemistry. To test the H<sub>2</sub>O stability, Banasorb-22 was exposed to the steam over boiling H<sub>2</sub>O for one week and BET surface areas were measured. While the structure of MOF-5 collapsed under the same conditions in just a few minutes from 2365 m<sup>2</sup> g<sup>-1</sup> to 50 m<sup>2</sup> g<sup>-1</sup>, Banasorb-22 showed a decrease from 1113 m<sup>2</sup> g<sup>-1</sup> to 210 m<sup>2</sup> g<sup>-1</sup> after 1 week [171]. Nguyen and co-worker introduced hydrophobic alkylchains in amine functionalised IRMOF-3 and MIL-53(Al)-NH<sub>2</sub> by using different anhydrides (e.g., palmitic anhydride, valeric anhydride) and studied their influence on moisture stability by using contact angle measurements after exposing the MOFs to ambient air or immersing them in H<sub>2</sub>O. They demonstrated, that medium to long alkyl groups shield the moisture sensitive IRMOF-3 by turning it into a hydrophobic material, but MIL-53(Al)-NH<sub>2</sub> was transformed into a MOF with superhydrophobic properties [172].

#### 1.3.5 Effect of flue gas and syngas impurities on the stability of MOFs

The presence of flue gas  $(SO_x, NO_x)$  and syngas  $(H_2S)$  impurities greatly affect the performance of adsorbents and the stability of MOFs. Only limited experimental studies on the impact of these impurities on the stability of MOFs and their CO<sub>2</sub> uptake are available.

Ding et al. performed computational studies on the effect of flue gas impurities on the CO<sub>2</sub> uptake in MOFs containing CUS (CPO-27(Mg, Ni, Co)), MOFs containing amine modified linker molecules (Bio-MOF-11, Zn-Atz-Ox) and HKUST-1, which has small side pockets that are connected to large central cages. GCMC simulations of five different ternary gas mixtures ((1) CO<sub>2</sub>, N<sub>2</sub>, CO; (2) CO<sub>2</sub>, N<sub>2</sub>, NO<sub>2</sub>; (3) CO<sub>2</sub>, N<sub>2</sub>, NO; (4) CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>; (5) CO<sub>2</sub>, N<sub>2</sub> SO<sub>2</sub>) indicated no change in CO<sub>2</sub> capacity with increasing concentrations (0.0001 to 10 %) of NO<sub>2</sub>, NO, CO and O<sub>2</sub>, but a slight decrease in N<sub>2</sub> capacity was observed. In the case of SO<sub>2</sub>, both N<sub>2</sub> and CO<sub>2</sub> uptakes declined with increasing impurity concentrations. In all MOFs the adsorption capacity of SO<sub>2</sub> was found to be higher than the CO<sub>2</sub> uptake, which suggests that the occupancy of preferred adsorption sites and the exclusion of CO2 and N2 molecules is likely. Additionally, an initial increase in CO2 capacity was reported, which was more pronounced in the CPO-27 frameworks due to the larger pores [173]. Allan et al. studied the effect of H<sub>2</sub>S on the crystalline structure of CPO-27(Ni). Although the MOF was highly stable over a period of six months, Chavan et al. found, that the formation of stable adducts at the nickel sites make a thermal activation at 200 °C necessary in order to remove the adsorbed H<sub>2</sub>S completely [174, 175].

The influence of  $SO_2$  on the performance of HKUST-1 in a post-combustion process was evaluated using molecular modelling by Yu and co-worker. Higher binding energies of

 $SO_2$  to the HKUST-1 framework were calculated than for  $CO_2$ , which result in a smaller  $CO_2$  capacity and  $CO_2/N_2$  selectivity [176].

Liu and co-worker investigated the effect of NO and  $SO_2$  on the adsorption capacity of MIL-101(Cr). While they observed a gradual decrease in  $CO_2$  aqdsorption capacity with increasing the NO concentrations from 0 to 2000 ppm,  $SO_2$  only had a slight impact in the same concentration range. A possible explanation for the relatively small effect of the flue gas impurities on the  $CO_2$  adsorption capacities is the lack of functional groups, which leads to a replacement of these trace impurities by the much higher concentrated  $CO_2$  [169].

Xiao et al. studied the NO adsorption properties of HKUST-1 and found that the material is a suitable storage material due to the high NO uptake of 9.0 wt% at 25 °C and 1 bar. By lowering the NO pressure to almost 0 bar, approximately 6.6 wt% of NO remained trapped inside the material. IR studies showed that this is due to the coordination of NO to the CUS lining the pore walls of HKUST-1 [177].

 $H_2S$  adsorption isotherms (30 °C, 20 bar) on MIL-47(V), MIL-53(Al, Cr, Fe), MIL-100(Cr) and MIL-101(Cr) were reported by Hamon et al. The breathing effect was observed in MIL-53(Al, Cr, Fe), which could be explained by the strong interaction of polar  $H_2S$  with the OH group of the linker molecules resulting in a closure of the pores at low loadings (Cr: 13.3 wt%; Al: 14.3 wt%; Fe: 5.2 wt%). At higher loadings these interactions will break and the framework will reopen. CH<sub>4</sub> isotherms were measured before and after  $H_2S$  treatment and indicated that small pore MOFs (MIL-47(V) and MIL-53(Cr, Al)) are stable towards  $H_2S$  with the exception of MIL-53(Fe). In contrast to this, large pore MOFs (MIL-100(Cr) and MIL-101(Cr)) showed a decrease in CH<sub>4</sub> capacity due to the strong interaction of  $H_2S$  with the CUS in both frameworks [178].

#### 1.4 Research objective

The objective of this project is to evaluate a series of MOFs for their ability to capture  $CO_2$  at pressures up to 0.5 bar. Enhanced  $CO_2$  capacities are being sought by two approaches or a combination of both: (i) "prefunctionalisation" and (ii) postsynthetic modification of MOFs containing CUS. Although previous studies of  $CO_2$  adsorption in DETA and PEI modified MIL-101(Cr) have been reported, the modification of MIL-100(Fe), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> have not been previously examined.

The primary focus is to consider their potential application in a post-combustion process. A particular emphasis of the study is to determine the capabilities of the MOFs to operate under simulated vacuum swing condition in which the  $CO_2$  partial pressures are varied between 0.05 and 0.15 bar in order to determine the stability and regenerability over ten cycles. The effect of H<sub>2</sub>O is determined by saturating the MOFs with H<sub>2</sub>O vapour prior to the cycling experiments and measuring the PXRD before and after the exposure. Furthermore, the effects of NO<sub>2</sub>, NO and SO<sub>2</sub> on the framework stability as well as the  $CO_2$  uptake are assessed. High pressure adsorption isotherms were measured for MOFs prior to the PSM, in order to evaluate the potential for pre-combustion carbon capture.

#### **1.5 Research hypothesis**

The following hypotheses are examined in this project:

- It is hypothesised that metal phosphonates offer an alternative set of chemical and structural possibilities to the known carboxylates for CO<sub>2</sub> capture. Until now only a few examples of metal phosphonates are known, and even fewer have been studied for their adsorption properties, probably because of their small pores and/or their lack of permanent porosity. Simple monophosphonate or linear diphosphonate ligands have been found to pack too efficiently to enable the formation of void space between the pillaring groups of the ligands. Therefore structures with larger pores and adsorption capacities are required. Triphosphonic acid might function as a robust synthon for the construction of two/threedimensional networks through the formation of strong hydrogen bonds.
- It is hypothesised that modifications of MOFs with polar groups (i.e. -NH<sub>2</sub>, -COOH) can lead to higher CO<sub>2</sub> capacities and improved selectivities. Therefore postsynthetic modification (using polyethyleneimine, ethylenediamine, diethylamine, polypropylenimine octaamine dendrimer (2<sup>nd</sup> generation)) or "prefunctionalisation" of MOFs (using 2-aminoterephthalic acid) are tested. The structures of DAB-AM-8, DETA, ED, branched PEI and linear PEI are illustrated in Figure 1.25. It is anticipated that postsynthetic modifications with ED, DAB-AM-8, DETA and PEI will have a bigger impact on the CO<sub>2</sub> capacity than the "prefunctionalisation", due to the introduction of more active amine groups. Based on the literature review (Section 1.2.2.4), higher operation temperatures can be achieved after amine modifications, resulting in lower capture costs.

• It is hypothesised that, for practical applications, H<sub>2</sub>O stable MOFs are required which exhibit high CO<sub>2</sub> capacity, high thermal stability and good long-term stability. This is necessary in order to facilitate handling and reduce costs. Unfortunately H<sub>2</sub>O sorption studies on MOFs are still scarce. It is therefore necessary to investigate their framework stability on H<sub>2</sub>O sorption because flue gas contains H<sub>2</sub>O vapour.



Figure 1.25: Structure of DAB-AM-8, DETA, ED, linear PEI and branched PEI.

• It is hypothesised that, for lowering the capture costs, MOFs are required that are stable in the presence of flue gas impurities. However, adsorption studies of these impurities in MOFs are very scarce. It is therefore necessary to investigate the framework stability and the impact this has on CO<sub>2</sub> uptake, as these data are essential for process design.

### **1.6 Reference**

- [1] D. M. D'Alessandro, B. Smit, and J. R. Long, "Carbon Dioxide Capture: Prospects for New Materials," *Angewandte Chemie International Edition*, vol. 49, pp. 6058-6082, 2010.
- [2] G.-P. Hao, W.-C. Li, and A.-H. Lu, "Novel porous solids for carbon dioxide capture," *Journal of Materials Chemistry*, vol. 21, pp. 6447-6451, 2011.
- [3] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, pp. 1791-1823, 2011.

- [4] S. I. Plasynski, J. T. Litynski, H. G. McIlvried, and R. D. Srivastava, "Progress and New Developments in Carbon Capture and Storage," *Critical Reviews in Plant Sciences*, vol. 28, pp. 123-138, 2009.
- [5] R. Guerrero-Lemus and J. Martínez-Duart, "Carbon Capture and Storage," in *Renewable Energies and CO*<sub>2</sub>. vol. 3, ed: Springer London, 2013, pp. 353-373.
- [6] M. Mikkelsen, M. Jorgensen, and F. C. Krebs, "The teraton challenge. A review of fixation and transformation of carbon dioxide," *Energy & Environmental Science*, vol. 3, pp. 43-81, 2010.
- [7] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, and J. R. Long, "Carbon Dioxide Capture in Metal–Organic Frameworks," *Chemical Reviews*, vol. 112, pp. 724-781, 2012/02/08 2011.
- [8] R. K. Pachauri and A. Reisinger, "IPCC Fourth Assessment Report," *Intergovernmental Panel on Climate Change*, 2007.
- [9] N. Hedin, L. Andersson, L. Bergström, and J. Yan, "Adsorbents for the postcombustion capture of CO<sub>2</sub> using rapid temperature swing or vacuum swing adsorption," *Applied Energy*, vol. 104, pp. 418-433, 2013.
- [10] H. Wu, R. S. Reali, D. A. Smith, M. C. Trachtenberg, and J. Li, "Highly Selective CO<sub>2</sub> Capture by a Flexible Microporous Metal–Organic Framework (MMOF) Material," *Chemistry – A European Journal*, vol. 16, pp. 13951-13954, 2010.
- [11] P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber, and T. E. Muller, "Worldwide innovations in the development of carbon capture technologies and the utilization of CO<sub>2</sub>," *Energy & Environmental Science*, vol. 5, pp. 7281-7305, 2012.
- [12] H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, and I. Wright, "Progress in carbon dioxide separation and capture: A review," *Journal of Environmental Sciences*, vol. 20, pp. 14-27, 2008.
- [13] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, pp. 1791-1823, 2011.
- [14] T. C. Drage, C. E. Snape, L. A. Stevens, J. Wood, J. Wang, A. I. Cooper, R. Dawson, X. Guo, C. Satterley, and R. Irons, "Materials challenges for the development of solid sorbents for post-combustion carbon capture," *Journal of Materials Chemistry*, vol. 22, pp. 2815-2823, 2012.
- [15] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, and R. D. Srivastava, "Advances in CO<sub>2</sub> capture technology--The U.S. Department of Energy's Carbon Sequestration Program," *International Journal of Greenhouse Gas Control*, vol. 2, pp. 9-20, 2008.
- [16] <u>http://www.co2crc.com.au/aboutccs.html</u>, (accessed 14.08.2014).
- [17] S. D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A. G. Russell, Q. Wei, and M. Fan, "Review of recent advances in carbon dioxide separation and capture," *RSC Advances*, 2013.
- [18] R. Dawson, D. J. Adams, and A. I. Cooper, "Chemical tuning of CO<sub>2</sub> sorption in robust nanoporous organic polymers," *Chemical Science*, vol. 2, pp. 1173-1177, 2011.
- [19] <u>http://www.co2crc.com.au/imagelibrary3/capture.php?screen=3</u>, (accessed 14.08.2014).
- [20] J. Wilcox, "Introduction to Carbon Capture," in *Carbon Capture*, ed: Springer New York, 2012, pp. 1-34.

- [21] S. A. Rackley, "Chapter 4 Carbon Capture from Power Generation," in *Carbon Capture and Storage*, S. A. Rackley, Ed., ed Boston: Butterworth-Heinemann, 2010, pp. 65-93.
- [22] B. J. P. Buhre, L. K. Elliott, C. D. Sheng, R. P. Gupta, and T. F. Wall, "Oxy-fuel combustion technology for coal-fired power generation," *Progress in Energy and Combustion Science*, vol. 31, pp. 283-307, 2005.
- [23] L.-S. Fan, L. Zeng, W. Wang, and S. Luo, "Chemical looping processes for CO<sub>2</sub> capture and carbonaceous fuel conversion prospect and opportunity," *Energy & Environmental Science*, vol. 5, pp. 7254-7280, 2012.
- [24] M. M. Hossain and H. I. de Lasa, "Chemical-looping combustion (CLC) for inherent separations—a review," *Chemical Engineering Science*, vol. 63, pp. 4433-4451, 2008.
- [25] J. Wilcox, "Absorption," in *Carbon Capture*, ed: Springer New York, 2012, pp. 53-113.
- [26] M. Caplow, "Kinetics of carbamate formation and breakdown," *Journal of the American Chemical Society*, vol. 90, pp. 6795-6803, 1968/11/01 1968.
- [27] P. D. Vaidya and E. Y. Kenig, "CO<sub>2</sub>-Alkanolamine Reaction Kinetics: A Review of Recent Studies," *Chemical Engineering & Technology*, vol. 30, pp. 1467-1474, 2007.
- [28] E. F. da Silva and H. F. Svendsen, "Ab Initio Study of the Reaction of Carbamate Formation from CO<sub>2</sub> and Alkanolamines," *Industrial & Engineering Chemistry Research*, vol. 43, pp. 3413-3418, 2004/06/01 2004.
- [29] A. Torrisi, R. G. Bell, and C. Mellot-Draznieks, "Functionalized MOFs for Enhanced CO<sub>2</sub> Capture," *Crystal Growth & Design*, vol. 10, pp. 2839-2841, 2010.
- [30] R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi, and T. K. Woo, "Direct Observation and Quantification of CO<sub>2</sub> Binding Within an Amine-Functionalized Nanoporous Solid," *Science*, vol. 330, pp. 650-653, October 29, 2010 2010.
- [31] C. Lastoskie, "Caging Carbon Dioxide," *Science*, vol. 330, pp. 595-596, October 29, 2010 2010.
- [32] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X)," *Energy & Fuels*, vol. 23, pp. 2785-2789, 2009.
- [33] K. A. Mumford, K. H. Smith, C. J. Anderson, S. Shen, W. Tao, Y. A. Suryaputradinata, A. Qader, B. Hooper, R. A. Innocenzi, S. E. Kentish, and G. W. Stevens, "Post-combustion Capture of CO<sub>2</sub>: Results from the Solvent Absorption Capture Plant at Hazelwood Power Station Using Potassium Carbonate Solvent," *Energy & Fuels*, vol. 26, pp. 138-146, 2012/01/19 2011.
- [34] S.-K. Ryi, J.-S. Park, K.-R. Hwang, C.-B. Lee, and S.-W. Lee, "The property of hydrogen separation from CO<sub>2</sub> mixture using Pd-based membranes for carbon capture and storage (CCS)," *International Journal of Hydrogen Energy*, vol. 38, pp. 7605-7611, 2013.
- [35] <u>http://www.co2crc.com.au/aboutccs/cap\_adsorption.html</u>, (accessed 20.09.2013).
- [36] <u>http://www.co2crc.com.au/imagelibrary3/capture.php</u>, (accessed 14.08.2014).
- [37] J. Wilcox, "Membrane Technology," in *Carbon Capture*, ed: Springer New York, 2012, pp. 177-218.
- [38] P. Pandey and R. S. Chauhan, "Membranes for gas separation," *Progress in Polymer Science*, vol. 26, pp. 853-893, 2001.
- [39] A. A. Olajire, "CO<sub>2</sub> capture and separation technologies for end-of-pipe applications A review," *Energy*, vol. 35, pp. 2610-2628, 2010.

- [40] <u>http://www.co2crc.com.au/aboutccs/cap\_membranes.html</u>, (accessed 14.08.2014).
- [41] M. H. Hassan, J. Douglas Way, P. M. Thoen, and A. C. Dillon, "Single component and mixed gas transport in a silica hollow fiber membrane," *Journal of Membrane Science*, vol. 104, pp. 27-42, 1995.
- [42] E. J. Granite and T. O'Brien, "Review of novel methods for carbon dioxide separation from flue and fuel gases," *Fuel Processing Technology*, vol. 86, pp. 1423-1434, 2005.
- [43] J. Caro, M. Noack, P. Kölsch, and R. Schäfer, "Zeolite membranes state of their development and perspective," *Microporous and Mesoporous Materials*, vol. 38, pp. 3-24, 2000.
- [44] J. Wilcox, "Cryogenic Distillation and Air Separation," in *Carbon Capture*, ed: Springer New York, 2012, pp. 219-229.
- [45] A. D. Ebner and J. A. Ritter, "State-of-the-art Adsorption and Membrane Separation Processes for Carbon Dioxide Production from Carbon Dioxide Emitting Industries," *Separation Science and Technology*, vol. 44, pp. 1273-1421, 2009/04/03 2009.
- [46] M. J. Tuinier, H. P. Hamers, and M. van Sint Annaland, "Techno-economic evaluation of cryogenic CO<sub>2</sub> capture—A comparison with absorption and membrane technology," *International Journal of Greenhouse Gas Control*, vol. 5, pp. 1559-1565, 2011.
- [47] J. Wilcox, "Adsorption," in *Carbon Capture*, ed: Springer New York, 2012, pp. 115-175.
- [48] Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, and R. Q. Snurr, "Separation of CO<sub>2</sub> from CH<sub>4</sub> Using Mixed-Ligand Metal-Organic Frameworks," *Langmuir*, vol. 24, pp. 8592-8598, 2008.
- [49] Y.-S. Bae, O. K. Farha, J. T. Hupp, and R. Q. Snurr, "Enhancement of CO<sub>2</sub>/N<sub>2</sub> selectivity in a metal-organic framework by cavity modification," *Journal of Materials Chemistry*, vol. 19, pp. 2131-2134, 2009.
- [50] A. Sayari, Y. Belmabkhout, and R. Serna-Guerrero, "Flue gas treatment via CO<sub>2</sub> adsorption," *Chemical Engineering Journal*, vol. 171, pp. 760-774, 2011.
- [51] S. Keskin, T. M. van Heest, and D. S. Sholl, "Can Metal–Organic Framework Materials Play a Useful Role in Large-Scale Carbon Dioxide Separations?," *ChemSusChem*, vol. 3, pp. 879-891, 2010.
- [52] P. D. Jadhav, R. V. Chatti, R. B. Biniwale, N. K. Labhsetwar, S. Devotta, and S. S. Rayalu, "Monoethanol Amine Modified Zeolite 13X for CO<sub>2</sub> Adsorption at Different Temperatures," *Energy & Fuels*, vol. 21, pp. 3555-3559, 2007/11/01 2007.
- [53] C. F. Martín, M. G. Plaza, J. J. Pis, F. Rubiera, C. Pevida, and T. A. Centeno, "On the limits of CO<sub>2</sub> capture capacity of carbons," *Separation and Purification Technology*, vol. 74, pp. 225-229, 2010.
- [54] D. J. N. Subagyono, M. Marshall, G. P. Knowles, and A. L. Chaffee, "CO<sub>2</sub> adsorption by amine modified siliceous mesostructured cellular foam (MCF) in humidified gas," *Microporous and Mesoporous Materials*, vol. 186, pp. 84-93, 2014.
- [55] G. P. Knowles, J. V. Graham, S. W. Delaney, and A. L. Chaffee, "Aminopropylfunctionalized mesoporous silicas as CO<sub>2</sub> adsorbents," *Fuel Processing Technology*, vol. 86, pp. 1435-1448, 2005.
- [56] C. Vogt, G. P. Knowles, S. L. Y. Chang, and A. L. Chaffee, "Cadmium oxide/alkali metal halide mixtures a potential high capacity sorbent for pre-combustion CO<sub>2</sub> capture," *Journal of Materials Chemistry A*, vol. 1, pp. 10962-10971, 2013.

- [57] R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, and H. C. Zhou, "Potential applications of metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 253, pp. 3042-3066, 2009.
- [58] W. Xuan, C. Zhu, Y. Liu, and Y. Cui, "Mesoporous metal-organic framework materials," *Chemical Society Reviews*, vol. 41, pp. 1677-1695, 2012.
- [59] H.-L. Jiang and Q. Xu, "Porous metal-organic frameworks as platforms for functional applications," *Chemical Communications*, vol. 47, pp. 3351-3370, 2011.
- [60] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.
- [61] R. Canioni, C. Roch-Marchal, F. Secheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Ferey, J.-M. Greneche, F. Lefebvre, J.-S. Chang, Y.-K. Hwang, O. Lebedev, S. Turner, and G. Van Tendeloo, "Stable polyoxometalate insertion within the mesoporous metal organic framework MIL-100(Fe)," *Journal of Materials Chemistry*, vol. 21, pp. 1226-1233, 2011.
- [62] A. Samanta, A. Zhao, G. K. H. Shimizu, P. Sarkar, and R. Gupta, "Post-Combustion CO<sub>2</sub> Capture Using Solid Sorbents: A Review," *Industrial & Engineering Chemistry Research*, vol. 51, pp. 1438-1463, 2012/01/26 2011.
- [63] R. Kotani, A. Kondo, and K. Maeda, "Gate adsorption of CO<sub>2</sub> on a flexible onedimensional copper-based coordination polymer crystal," *Chemical Communications*, vol. 48, pp. 11316-11318, 2012.
- [64] A. Demessence, D. M. D'Alessandro, M. L. Foo, and J. R. Long, "Strong CO<sub>2</sub> Binding in a Water-Stable, Triazolate-Bridged Metal-Organic Framework Functionalized with Ethylenediamine," *Journal of the American Chemical Society*, vol. 131, pp. 8784-8786, 2009.
- [65] P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jhung, and G. Férey, "High Uptakes of CO<sub>2</sub> and CH<sub>4</sub> in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101," *Langmuir*, vol. 24, pp. 7245-7250, 2008.
- [66] G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi, and J.-S. Chang, "Why hybrid porous solids capture greenhouse gases?," *Chemical Society Reviews*, vol. 40, pp. 550-562, 2011.
- [67] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, and T. Siemieniewska, "Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity," *Pure & Appl. Chem.*, vol. 57, pp. 603-619, 1985.
- [68] A. R. Millward and O. M. Yaghi, "Metal-Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature," *Journal of the American Chemical Society*, vol. 127, pp. 17998-17999, 2005.
- [69] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, pp. 1791-1823, 2011.
- [70] K. S. Walton, A. R. Millward, D. Dubbeldam, H. Frost, J. J. Low, O. M. Yaghi, and R. Q. Snurr, "Understanding Inflections and Steps in Carbon Dioxide Adsorption Isotherms in Metal-Organic Frameworks," *Journal of the American Chemical Society*, vol. 130, pp. 406-407, 2007.

- [71] S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, and F. Kapteijn, "An Amine-Functionalized MIL-53 Metal-Organic Framework with Large Separation Power for CO<sub>2</sub> and CH<sub>4</sub>," *Journal of the American Chemical Society*, vol. 131, pp. 6326-6327, 2009.
- [72] S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, and G. Férey, "Different Adsorption Behaviors of Methane and Carbon Dioxide in the Isotypic Nanoporous Metal Terephthalates MIL-53 and MIL-47," *Journal of the American Chemical Society*, vol. 127, pp. 13519-13521, 2005.
- [73] J. Seo, R. Matsuda, H. Sakamoto, C. Bonneau, and S. Kitagawa, "A Pillared-Layer Coordination Polymer with a Rotatable Pillar Acting as a Molecular Gate for Guest Molecules," *Journal of the American Chemical Society*, vol. 131, pp. 12792-12800, 2009/09/09 2009.
- [74] U. M. Baba, K. S. N. Kamarudin, and N. Alias, "Separation of Carbon Dioxide Using Selected Porous Materials: A Review," *International Journal of Chemical* and Environmental Engineering, vol. 1, pp. 40-46, 2010.
- [75] A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, "Screening of Metal-Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach," *Journal of the American Chemical Society*, vol. 131, pp. 18198-18199, 2009.
- [76] K. L. Mulfort, O. K. Farha, C. D. Malliakas, M. G. Kanatzidis, and J. T. Hupp, "An Interpenetrated Framework Material with Hysteretic CO<sub>2</sub> Uptake," *Chemistry – A European Journal*, vol. 16, pp. 276-281, 2010.
- [77] J. An, S. J. Geib, and N. L. Rosi, "High and Selective CO<sub>2</sub> Uptake in a Cobalt Adeninate Metal–Organic Framework Exhibiting Pyrimidine- and Amino-Decorated Pores," *Journal of the American Chemical Society*, vol. 132, pp. 38-39, 2010/01/13 2009.
- [78] Q.-R. Fang, D.-Q. Yuan, J. Sculley, J.-R. Li, Z.-B. Han, and H.-C. Zhou, "Functional Mesoporous Metal-Organic Frameworks for the Capture of Heavy Metal Ions and Size-Selective Catalysis," *Inorganic Chemistry*, vol. 49, pp. 11637-11642, 2010.
- [79] H.-S. Choi and M. P. Suh, "Highly Selective CO<sub>2</sub> Capture in Flexible 3D Coordination Polymer Networks," *Angewandte Chemie International Edition*, vol. 48, pp. 6865-6869, 2009.
- [80] P. K. Thallapally, J. Tian, M. Radha Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, and J. L. Atwood, "Flexible (Breathing) Interpenetrated Metal-Organic Frameworks for CO<sub>2</sub> Separation Applications," *Journal of the American Chemical Society*, vol. 130, pp. 16842-16843, 2008.
- [81] Q. Wang, J. Luo, Z. Zhong, and A. Borgna, "CO<sub>2</sub> capture by solid adsorbents and their applications: current status and new trends," *Energy & Environmental Science*, vol. 4, pp. 42-55, 2011.
- [82] A. Ö. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis, and R. Q. Snurr, "Enhanced CO<sub>2</sub> Adsorption in Metal-Organic Frameworks via Occupation of Open-Metal Sites by Coordinated Water Molecules," *Chemistry of Materials*, vol. 21, pp. 1425-1430, 2009.
- [83] D. Britt, H. Furukawa, B. Wang, T. G. Glover, and O. M. Yaghi, "Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites," *Proceedings of the National Academy of Sciences*, vol. 106, pp. 20637-20640, December 8, 2009 2009.

- [84] S. Ye, X. Jiang, L.-W. Ruan, B. Liu, Y.-M. Wang, J.-F. Zhu, and L.-G. Qiu, "Postcombustion CO<sub>2</sub> capture with the HKUST-1 and MIL-101(Cr) metal–organic frameworks: Adsorption, separation and regeneration investigations," *Microporous and Mesoporous Materials*, vol. 179, pp. 191-197, 2013.
- [85] A. Torrisi, R. G. Bell, and C. Mellot-Draznieks, "Predicting the impact of functionalized ligands on CO<sub>2</sub> adsorption in MOFs: A combined DFT and Grand Canonical Monte Carlo study," *Microporous and Mesoporous Materials*, vol. 168, pp. 225-238, 2013.
- [86] Z. Zhang, Y. Zhao, Q. Gong, Z. Li, and J. Li, "MOFs for CO<sub>2</sub> capture and separation from flue gas mixtures: the effect of multifunctional sites on their adsorption capacity and selectivity," *Chemical Communications*, vol. 49, pp. 653-661, 2013.
- [87] K. K. Tanabe and S. M. Cohen, "Postsynthetic modification of metal-organic frameworks-a progress report," *Chemical Society Reviews*, vol. 40, pp. 498-519, 2011.
- [88] Z. Wang and S. M. Cohen, "Postsynthetic modification of metal-organic frameworks," *Chemical Society Reviews*, vol. 38, pp. 1315-1329, 2009.
- [89] M. Kawano, T. Kawamichi, T. Haneda, T. Kojima, and M. Fujita, "The Modular Synthesis of Functional Porous Coordination Networks," *Journal of the American Chemical Society*, vol. 129, pp. 15418-15419, 2007.
- [90] Z. Wang and S. M. Cohen, "Postsynthetic Covalent Modification of a Neutral Metal-Organic Framework," *Journal of the American Chemical Society*, vol. 129, pp. 12368-12369, 2007.
- [91] R. Vaidhyanathan, S. S. Iremonger, K. W. Dawson, and G. K. H. Shimizu, "An amine-functionalized metal organic framework for preferential CO<sub>2</sub> adsorption at low pressures," *Chemical Communications*, pp. 5230-5232, 2009.
- [92] B. Arstad, H. Fjellvåg, K. Kongshaug, O. Swang, and R. Blom, "Amine functionalised metal organic frameworks (MOFs) as adsorbents for carbon dioxide," *Adsorption*, vol. 14, pp. 755-762, 2008.
- [93] T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey, and N. Stock, "Synthesis and Modification of a Functionalized 3D Open-Framework Structure with MIL-53 Topology," *Inorganic Chemistry*, vol. 48, pp. 3057-3064, 2009.
- [94] L. Wen, D. e. Wang, C. Wang, F. Wang, D. Li, and K. Deng, "A 3D porous zinc MOF constructed from a flexible tripodal ligand: Synthesis, structure, and photoluminescence property," *Journal of Solid State Chemistry*, vol. 182, pp. 574-579, 2009.
- [95] M. Savonnet, D. Bazer-Bachi, N. Bats, J. Perez-Pellitero, E. Jeanneau, V. Lecocq, C. Pinel, and D. Farrusseng, "Generic Postfunctionalization Route from Amino-Derived Metal-Organic Frameworks," *Journal of the American Chemical Society*, vol. 132, pp. 4518-4519, 2010.
- [96] Z. Wang, K. K. Tanabe, and S. M. Cohen, "Accessing Postsynthetic Modification in a Series of Metal-Organic Frameworks and the Influence of Framework Topology on Reactivity," *Inorganic Chemistry*, vol. 48, pp. 296-306, 2008.
- [97] J. S. Costa, P. Gamez, C. A. Black, O. Roubeau, S. J. Teat, and J. Reedijk, "Chemical Modification of a Bridging Ligand Inside a Metal–Organic Framework while Maintaining the 3D Structure," *European Journal of Inorganic Chemistry*, vol. 2008, pp. 1551-1554, 2008.
- [98] X. Gu, Z.-H. Lu, and Q. Xu, "High-connected mesoporous metal-organic framework," *Chemical Communications*, vol. 46, pp. 7400-7402, 2010.

- [99] K. M. L. Taylor-Pashow, J. D. Rocca, Z. Xie, S. Tran, and W. Lin, "Postsynthetic Modifications of Iron-Carboxylate Nanoscale Metal-Organic Frameworks for Imaging and Drug Delivery," *Journal of the American Chemical Society*, vol. 131, pp. 14261-14263, 2009.
- [100] K. Peikert, F. Hoffmann, and M. Froba, "Amino substituted Cu<sub>3</sub>(btc)<sub>2</sub>: a new metal-organic framework with a versatile functionality," *Chemical Communications*, vol. 48, pp. 11196-11198, 2012.
- [101] E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon, and F. Kapteijn, "Complexity behind CO<sub>2</sub> Capture on NH<sub>2</sub>-MIL-53(Al)," *Langmuir*, vol. 27, pp. 3970-3976, 2011.
- [102] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, and F. Kapteijn, "Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties," *Chemistry of Materials*, vol. 23, pp. 2565-2572, 2011.
- [103] E. Stavitski, M. Goesten, J. Juan-Alcañiz, A. Martinez-Joaristi, P. Serra-Crespo, A. V. Petukhov, J. Gascon, and F. Kapteijn, "Kinetic Control of Metal–Organic Framework Crystallization Investigated by Time-Resolved InSitu X-Ray Scattering," *Angewandte Chemie International Edition*, vol. 50, pp. 9624-9628, 2011.
- [104] Y. Lin, C. Kong, and L. Chen, "Direct synthesis of amine-functionalized MIL-101(Cr) nanoparticles and application for CO<sub>2</sub> capture," *RSC Advances*, vol. 2, pp. 6417-6419, 2012.
- [105] P.-C. Liang, H.-K. Liu, C.-T. Yeh, C.-H. Lin, and V. t. z. Zima, "Supramolecular Assembly of Calcium Metal–Organic Frameworks with Structural Transformations," *Crystal Growth & Design*, vol. 11, pp. 699-708, 2011/03/02 2011.
- [106] Q. Yang, A. D. Wiersum, P. L. Llewellyn, V. Guillerm, C. Serre, and G. Maurin, "Functionalizing porous zirconium terephthalate UiO-66(Zr) for natural gas upgrading: a computational exploration," *Chemical Communications*, vol. 47, pp. 9603-9605, 2011.
- [107] Q. Yang, A. D. Wiersum, H. Jobic, V. Guillerm, C. Serre, P. L. Llewellyn, and G. Maurin, "Understanding the Thermodynamic and Kinetic Behavior of the CO<sub>2</sub>/CH<sub>4</sub> Gas Mixture within the Porous Zirconium Terephthalate UiO-66(Zr): A Joint Experimental and Modeling Approach," *The Journal of Physical Chemistry C*, vol. 115, pp. 13768-13774, 2011/07/21 2011.
- [108] Y. Zhao, H. Wu, T. J. Emge, Q. Gong, N. Nijem, Y. J. Chabal, L. Kong, D. C. Langreth, H. Liu, H. Zeng, and J. Li, "Enhancing Gas Adsorption and Separation Capacity through Ligand Functionalization of Microporous Metal–Organic Framework Structures," *Chemistry A European Journal*, vol. 17, pp. 5101-5109, 2011.
- [109] E. Atci, I. Erucar, and S. Keskin, "Adsorption and Transport of CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub> Mixtures in a Bio-MOF Material from Molecular Simulations," *The Journal of Physical Chemistry C*, vol. 115, pp. 6833-6840, 2011/04/14 2011.
- [110] Y. Chen and J. Jiang, "A Bio-Metal–Organic Framework for Highly Selective CO<sub>2</sub> Capture: A Molecular Simulation Study," *ChemSusChem*, vol. 3, pp. 982-988, 2010.
- [111] E. Yang, H.-Y. Li, F. Wang, H. Yang, and J. Zhang, "Enhancing CO<sub>2</sub> adsorption enthalpy and selectivity via amino functionalization of a tetrahedral framework material," *CrystEngComm*, vol. 15, pp. 658-661, 2013.

- [112] C. Janiak and J. K. Vieth, "MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs)," *New Journal of Chemistry*, vol. 34, pp. 2366-2388, 2010.
- [113] B. F. Hoskins and R. Robson, "Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related frameworks [N(CH<sub>3</sub>)<sub>4</sub>][CuIZnII(CN)<sub>4</sub>] and CuI[4,4',4'',4'''tetracyanotetraphenylmethane]BF<sub>4</sub>.xC<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>," *Journal of the American Chemical Society*, vol. 112, pp. 1546-1554, 1990.
- [114] S. M. Cohen, "Postsynthetic Methods for the Functionalization of Metal–Organic Frameworks," *Chemical Reviews*, vol. 112, pp. 970-1000, 2012/02/08 2011.
- [115] S. Bernt, V. Guillerm, C. Serre, and N. Stock, "Direct covalent post-synthetic chemical modification of Cr-MIL-101 using nitrating acid," *Chemical Communications*, vol. 47, pp. 2838-2840, 2011.
- [116] S. Nagata, H. Sato, K. Sugikawa, K. Kokado, and K. Sada, "Conversion of azide to primary amine via Staudinger reaction in metal-organic frameworks," *CrystEngComm*, vol. 14, pp. 4137-4141, 2012.
- [117] T. M. McDonald, D. M. D'Alessandro, R. Krishna, and J. R. Long, "Enhanced carbon dioxide capture upon incorporation of N,N'-dimethylethylenediamine in the metal-organic framework CuBTTri," *Chemical Science*, vol. 2, pp. 2022-2028, 2011.
- [118] Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, and G. Férey, "Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation," *Angewandte Chemie International Edition*, vol. 47, pp. 4144-4148, 2008.
- [119] S.-N. Kim, S.-T. Yang, J. Kim, J.-E. Park, and W.-S. Ahn, "Post-synthesis functionalization of MIL-101 using diethylenetriamine: a study on adsorption and catalysis," *CrystEngComm*, vol. 14, pp. 4142-4147, 2012.
- [120] M. Anbia and V. Hoseini, "Enhancement of CO<sub>2</sub> adsorption on nanoporous chromium terephthalate (MIL-101) by amine modification," *Journal of Natural Gas Chemistry*, vol. 21, pp. 339-343, 2012.
- [121] Y. Lin, Q. Yan, C. Kong, and L. Chen, "Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO<sub>2</sub> Capture," *Sci. Rep.*, vol. 3, pp. 1-7, 2013.
- [122] S. Choi, T. Watanabe, T.-H. Bae, D. S. Sholl, and C. W. Jones, "Modification of the Mg/DOBDC MOF with Amines to Enhance CO<sub>2</sub> Adsorption from Ultradilute Gases," *The Journal of Physical Chemistry Letters*, vol. 3, pp. 1136-1141, 2012/05/25 2012.
- [123] A. Das, P. D. Southon, M. Zhao, C. J. Kepert, A. T. Harris, and D. M. D'Alessandro, "Carbon dioxide adsorption by physisorption and chemisorption interactions in piperazine-grafted Ni2(dobdc) (dobdc = 1,4-dioxido-2,5-benzenedicarboxylate)," *Dalton Transactions*, vol. 41, pp. 11739-11744, 2012.
- [124] S. R. Caskey, A. G. Wong-Foy, and A. J. Matzger, "Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores," *Journal of the American Chemical Society*, vol. 130, pp. 10870-10871, 2008/08/01 2008.
- [125] R. K. Deshpande, J. L. Minnaar, and S. G. Telfer, "Thermolabile Groups in Metal-Organic Frameworks: Suppression of Network Interpenetration, Post-Synthetic

Cavity Expansion, and Protection of Reactive Functional Groups," *Angewandte Chemie International Edition*, vol. 49, pp. 4598-4602, 2010.

- [126] J. A. Groves, S. R. Miller, S. J. Warrender, C. Mellot-Draznieks, P. Lightfoot, and P. A. Wright, "The first route to large pore metal phosphonates," *Chemical Communications*, pp. 3305-3307, 2006.
- [127] S. S. Iremonger, J. Liang, R. Vaidhyanathan, and G. K. H. Shimizu, "A permanently porous van der Waals solid by using phosphonate monoester linkers in a metal organic framework," *Chemical Communications*, vol. 47, pp. 4430-4432, 2011.
- [128] K. Maeda, J. Akimoto, Y. Kiyozumi, and F. Mizukami, "Structure of aluminium methylphosphonate, AIMepO-[small beta], with unidimensional channels formed from ladder-like organic-inorganic polymer chains," *Journal of the Chemical Society, Chemical Communications*, pp. 1033-1034, 1995.
- [129] K. Maeda, J. Akimoto, Y. Kiyozumi, and F. Mizukami, "AlMepO-α: A Novel Open-Framework Aluminum Methylphosphonate with Organo-Lined Unidimensional Channels," *Angewandte Chemie International Edition in English*, vol. 34, pp. 1199-1201, 1995.
- [130] K. Maeda, Y. Kiyozumi, and F. Mizukami, "Synthesis of the First Microporous Aluminum Phosphonate with Organic Groups Covalently Bonded to the Skeleton," *Angewandte Chemie International Edition in English*, vol. 33, pp. 2335-2337, 1994.
- [131] G. K. H. Shimizu, R. Vaidhyanathan, and J. M. Taylor, "Phosphonate and sulfonate metal organic frameworks," *Chemical Society Reviews*, vol. 38, pp. 1430-1449, 2009.
- [132] F. Zhai, Q. Zheng, Z. Chen, Y. Ling, X. Liu, L. Weng, and Y. Zhou, "Crystal transformation synthesis of a highly stable phosphonate MOF for selective adsorption of CO<sub>2</sub>," *CrystEngComm*, vol. 15, pp. 2040-2043, 2013.
- [133] J. D. Wang, A. Clearfield, and P. Guang-Zhi, "Preparation of layered zirconium phosphonate/phosphate, zirconium phosphonate/phosphite and related compounds," *Materials Chemistry and Physics*, vol. 35, pp. 208-216, 1993.
- [134] B. Zhang and A. Clearfield, "Crown Ether Pillared and Functionalized Layered Zirconium Phosphonates:  A New Strategy to Synthesize Novel Ion Selective Materials," *Journal of the American Chemical Society*, vol. 119, pp. 2751-2752, 2012/02/07 1997.
- [135] C. V. K. Sharma, A. Clearfield, A. Cabeza, M. A. G. Aranda, and S. Bruque, "Deprotonation of Phosphonic Acids with M<sup>2+</sup> Cations for the Design of Neutral Isostructural Organic-Inorganic Hybrids," *Journal of the American Chemical Society*, vol. 123, pp. 2885-2886, 2001.
- [136] F. Fredoueil, D. Massiot, P. Janvier, F. Gingl, M. Bujoli-Doeuff, M. Evain, A. Clearfield, and B. Bujoli, "Synthesis and X-ray Powder Structure of a New Pillared Layered Cadmium Phosphonate, Giving Evidence that the Intercalation of Alkylamines into Cd(O3PR)·H2O Is Topotactic," *Inorganic Chemistry*, vol. 38, pp. 1831-1833, 2012/02/07 1999.
- [137] D. Kong, J. Zon, J. McBee, and A. Clearfield, "Rational Design and Synthesis of Porous Organic-Inorganic Hybrid Frameworks Constructed by 1,3,5-Benzenetriphosphonic Acid and Pyridine Synthons," *Inorganic Chemistry*, vol. 45, pp. 977-986, 2006.
- [138] C. Lei, J.-G. Mao, Y.-Q. Sun, H.-Y. Zeng, and A. Clearfield, "{Zn<sub>6</sub>[MeN(CH<sub>2</sub>CO<sub>2</sub>)(CH<sub>2</sub>PO<sub>3</sub>)]<sub>6</sub>(Zn)}<sub>4</sub>- Anion:The First Example of the Oxo-

Bridged Zn<sub>6</sub> Octahedron with a Centered Zn(II) Cation," *Inorganic Chemistry*, vol. 42, pp. 6157-6159, 2003.

- [139] K. J. Gagnon, H. P. Perry, and A. Clearfield, "Conventional and Unconventional Metal–Organic Frameworks Based on Phosphonate Ligands: MOFs and UMOFs," *Chemical Reviews*, vol. 112, pp. 1034-1054, 2012/02/08 2011.
- [140] A. Clearfield, "Chapter 1 The Early History and Growth of Metal Phosphonate Chemistry," in *Metal Phosphonate Chemistry: From Synthesis to Applications*, ed: The Royal Society of Chemistry, 2012.
- [141] W. Ouellette, G. Wang, H. Liu, G. T. Yee, C. J. O'Connor, and J. Zubieta, "The Hydrothermal and Structural Chemistry of Oxovanadium-Arylphosphonate Networks and Frameworks," *Inorganic Chemistry*, vol. 48, pp. 953-963, 2008.
- DeBurgomaster, K. Darling, S. Jones, and J. Zubieta, [142] P. "Metalorganodiphosphonates: Structural consequences of introducing aromatic tethering [Cu(phen){HO<sub>3</sub>P(C<sub>12</sub>H<sub>8</sub>)PO<sub>3</sub>H}], groups. The structures of  $[{Cu(phen)}_2{HO_3P(C_{12}H_8)PO_3H}]$  and  $[Cu(terpy){HO_3P(C_{12}H_8)PO_3H}]$  and of the bimetallic materials  $[{Cu(LL)}_2MoO_2{HO_3P(C_{12}H_8)PO_3H}_3]$  (LL = 2,2bipyridine, o-phenanthroline)," Inorganica Chimica Acta, vol. 364, pp. 150-156, 2010.
- [143] P. DeBurgomaster, W. Ouellette, H. Liu, C. J. O'Connor, and J. Zubieta, "Hydrothermal chemistry of vanadium oxides with aromatic di- and triphosphonates in the presence of secondary metal copper(II) cationic complex subunits," *CrystEngComm*, vol. 12, pp. 446-469, 2010.
- [144] N. G. Armatas, W. Ouellette, K. Whitenack, J. Pelcher, H. Liu, E. Romaine, C. J. O'Connor, and J. Zubieta, "Construction of Metal–Organic Oxides from Molybdophosphonate Clusters and Copper-Bipyrimidine Building Blocks," *Inorganic Chemistry*, vol. 48, pp. 8897-8910, 2009/09/21 2009.
- [145] G. Yucesan, J. E. Valeich, H. Liu, W. Ouellette, C. J. O'Connor, and J. Zubieta, "Solid state coordination chemistry of the oxovanadium-diphosphonate/copperbipyrimidine system: Crystal structures of [{Cu2(bpyr)}VO(H2O)(HO3PCH2PO3)2] and [{Cu2(bpyr)}{Cu2(bpyr)(H2O)2}(VO2)2(HO3PCH2PO3)2(HO3PCH2PO3H)2]," Inorganica Chimica Acta, vol. 362, pp. 1831-1839, 2009.
- [146] V. Chandrasekhar, T. Senapati, A. Dey, and S. Hossain, "Molecular transitionmetal phosphonates," *Dalton Transactions*, vol. 40, pp. 5394-5418, 2011.
- [147] L. Kürti and B. Czakó, *Strategic applications of named reactions in organic synthesis*. USA: Elsevier Academic Press, 2005.
- [148] S. R. Miller and P. A. Wright, "Nanoporous Metal Phosphonates," in *Encyclopedia* of *Inorganic Chemistry*, ed: John Wiley & Sons, Ltd, 2006, pp. 1-13.
- [149] G. M. Pearce, "Synthesis, adsorption and catalysis of large pore metal phosphonates," University of St Andrews, 2010, http://hdl.handle.net/10023/823
- [150] T. Zheng, J. M. Clemente-Juan, J. Ma, L. Dong, S.-S. Bao, J. Huang, E. Coronado, and L.-M. Zheng, "Breathing Effect in a Cobalt Phosphonate upon Dehydration/Rehydration: A Single-Crystal-to-Single-Crystal Study," *Chemistry – A European Journal*, vol. 19, pp. 16394-16402, 2013.
- [151] S.-F. Tang, J.-J. Cai, L.-J. Li, X.-X. Lv, C. Wang, and X.-B. Zhao, "A highly porous three-dimensional aluminum phosphonate with hexagonal channels: synthesis, structure and adsorption properties," *Dalton Transactions*, vol. 43, pp. 5970-5973, 2014.

- [152] K. D. Demadis and N. Stavgianoudaki, "Structural Diversity in Metal Phosphonate Frameworks: Impact on Applications," in *Metal Phosphonate Chemistry: From Synthesis to Applications*, ed: The Royal Society of Chemistry, 2012, pp. 438-492.
- [153] S. R. Miller, G. M. Pearce, P. A. Wright, F. Bonino, S. Chavan, S. Bordiga, I. Margiolaki, N. Guillou, G. Férey, S. Bourrelly, and P. L. Llewellyn, "Structural Transformations and Adsorption of Fuel-Related Gases of a Structurally Responsive Nickel Phosphonate Metal-Organic Framework, Ni-STA-12," *Journal of the American Chemical Society*, vol. 130, pp. 15967-15981, 2008.
- [154] M. T. Wharmby, J. P. S. Mowat, S. P. Thompson, and P. A. Wright, "Extending the Pore Size of Crystalline Metal Phosphonates toward the Mesoporous Regime by Isoreticular Synthesis," *Journal of the American Chemical Society*, vol. 133, pp. 1266-1269, 2011.
- [155] J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger, and G. K. H. Shimizu, "Enhancing Water Stability of Metal–Organic Frameworks via Phosphonate Monoester Linkers," *Journal of the American Chemical Society*, vol. 134, pp. 14338-14340, 2012/09/05 2012.
- [156] H. J. Choi, M. Dinca, A. Dailly, and J. R. Long, "Hydrogen storage in water-stable metal-organic frameworks incorporating 1,3- and 1,4-benzenedipyrazolate," *Energy & Environmental Science*, vol. 3, pp. 117-123, 2010.
- [157] J. Yang, A. Grzech, F. M. Mulder, and T. J. Dingemans, "Methyl modified MOF-5: a water stable hydrogen storage material," *Chemical Communications*, vol. 47, pp. 5244-5246, 2011.
- [158] A. M. B. Furtado, J. Liu, Y. Wang, and M. D. LeVan, "Mesoporous silica-metal organic composite: synthesis, characterization, and ammonia adsorption," *Journal of Materials Chemistry*, vol. 21, pp. 6698-6706, 2011.
- [159] J. A. Greathouse and M. D. Allendorf, "The Interaction of Water with MOF-5 Simulated by Molecular Dynamics," *Journal of the American Chemical Society*, vol. 128, pp. 10678-10679, 2006.
- [160] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> adsorption, selectivity and water tolerance of pillared-layer metal organic frameworks," *Microporous and Mesoporous Materials*, vol. 132, pp. 305-310, 2010.
- [161] Y. Li and R. T. Yang, "Gas Adsorption and Storage in Metal-Organic Framework MOF-177," *Langmuir*, vol. 23, pp. 12937-12944, 2007.
- [162] Y. Li and R. T. Yang, "Hydrogen storage in metal-organic and covalent-organic frameworks by spillover," *AIChE Journal*, vol. 54, pp. 269-279, 2008.
- [163] P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, and S. Kaskel, "Characterization of metal-organic frameworks by water adsorption," *Microporous and Mesoporous Materials*, vol. 120, pp. 325-330, 2009.
- [164] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, and O. M. Yaghi, "Exceptional chemical and thermal stability of zeolitic imidazolate frameworks," *Proceedings of the National Academy of Sciences*, vol. 103, pp. 10186-10191, July 5, 2006 2006.
- [165] Z. Liang, M. Marshall, C. H. Ng, and A. L. Chaffee, "Comparison of Conventional and HF-Free-Synthesized MIL-101 for CO<sub>2</sub> Adsorption Separation and Their Water Stabilities," *Energy & Fuels*, vol. 27, pp. 7612-7618, 2013/12/19 2013.
- [166] J. Yu and P. B. Balbuena, "Water Effects on Postcombustion CO<sub>2</sub> Capture in Mg-MOF-74," *The Journal of Physical Chemistry C*, vol. 117, pp. 3383-3388, 2013/02/21 2013.

- [167] A. C. Kizzie, A. G. Wong-Foy, and A. J. Matzger, "Effect of Humidity on the Performance of Microporous Coordination Polymers as Adsorbents for CO<sub>2</sub> Capture," *Langmuir*, vol. 27, pp. 6368-6373, 2011/05/17 2011.
- [168] J. Liu, A. I. Benin, A. M. B. Furtado, P. Jakubczak, R. R. Willis, and M. D. LeVan, "Stability Effects on CO<sub>2</sub> Adsorption for the DOBDC Series of Metal–Organic Frameworks," *Langmuir*, vol. 27, pp. 11451-11456, 2011/09/20 2011.
- [169] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, "Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants," *Sci. Rep.*, vol. 3, pp. 1-6, 2013.
- [170] E. Soubeyrand-Lenoir, C. Vagner, J. W. Yoon, P. Bazin, F. Ragon, Y. K. Hwang, C. Serre, J.-S. Chang, and P. L. Llewellyn, "How water fosters a remarkable 5-fold increase in low pressure CO<sub>2</sub> uptake within the mesoporous MIL-100(Fe)," *Journal* of the American Chemical Society, 2012/05/21 2012.
- [171] T. Wu, L. Shen, M. Luebbers, C. Hu, Q. Chen, Z. Ni, and R. I. Masel, "Enhancing the stability of metal-organic frameworks in humid air by incorporating water repellent functional groups," *Chemical Communications*, vol. 46, pp. 6120-6122, 2010.
- [172] J. G. Nguyen and S. M. Cohen, "Moisture-Resistant and Superhydrophobic Metal-Organic Frameworks Obtained via Postsynthetic Modification," *Journal of the American Chemical Society*, vol. 132, pp. 4560-4561, 2010.
- [173] L. Ding and A. Ö. Yazaydin, "How Well Do Metal–Organic Frameworks Tolerate Flue Gas Impurities?," *The Journal of Physical Chemistry C*, vol. 116, pp. 22987-22991, 2012/11/01 2012.
- [174] P. K. Allan, P. S. Wheatley, D. Aldous, M. I. Mohideen, C. Tang, J. A. Hriljac, I. L. Megson, K. W. Chapman, G. De Weireld, S. Vaesen, and R. E. Morris, "Metal-organic frameworks for the storage and delivery of biologically active hydrogen sulfide," *Dalton Transactions*, vol. 41, pp. 4060-4066, 2012.
- [175] S. Chavan, F. Bonino, L. Valenzano, B. Civalleri, C. Lamberti, N. Acerbi, J. H. Cavka, M. Leistner, and S. Bordiga, "Fundamental Aspects of H2S Adsorption on CPO-27-Ni," *The Journal of Physical Chemistry C*, vol. 117, pp. 15615-15622, 2013/08/01 2013.
- [176] J. Yu, Y. Ma, and P. B. Balbuena, "Evaluation of the Impact of H<sub>2</sub>O, O<sub>2</sub>, and SO<sub>2</sub> on Postcombustion CO<sub>2</sub> Capture in Metal–Organic Frameworks," *Langmuir*, vol. 28, pp. 8064-8071, 2012/05/29 2012.
- [177] B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas, and R. E. Morris, "High-Capacity Hydrogen and Nitric Oxide Adsorption and Storage in a Metal–Organic Framework," *Journal* of the American Chemical Society, vol. 129, pp. 1203-1209, 2007/02/01 2007.
- [178] L. Hamon, C. Serre, T. Devic, T. Loiseau, F. Millange, G. r. Férey, and G. D. Weireld, "Comparative Study of Hydrogen Sulfide Adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) Metal–Organic Frameworks at Room Temperature," *Journal of the American Chemical Society*, vol. 131, pp. 8775-8777, 2009.

# 2 Experimental details and characterisation techniques

This chapter aims to provide a more detailed description of the experimental details characterisation techniques.

# 2.1 Chemicals

Table 2.1 shows a list of chemicals and their purities used for synthesising the ligands and characterising the MOFs. The chemicals used for the synthesis of the MOFs are given in Chapters 3 to 6. Starting materials and solvents were purchased and used without further purification from commercial suppliers unless indicated otherwise.

Chemical name	Formula	Purity/Supplier
4,4'-bipiperidyl-dihydrochloride	$C_{10}H_{20}N_2 \cdot 2HCl$	99 %, Alfa Aesar
Sodium bicarbonate	NaHCO <sub>3</sub>	$\geq$ 99.7 %, Ajax Chemicals
Trimesic acid	$C_6H_3(CO_2H)_3$	95 %, Sigma Aldrich
Ethanol	C <sub>2</sub> H <sub>5</sub> OH	$\geq$ 99.7 %, Merck
Formaldehyde	CH <sub>2</sub> O	40 % w/v GR grade, Merck
Hydrobromic acid	HBr	Extra pure, Merck
Methanol	CH <sub>3</sub> OH	$\geq$ 99.8 %, Merck
Phosphorous acid	H <sub>3</sub> PO <sub>3</sub>	97 %, Alfa Aesar
Sulphuric acid	$H_2SO_4$	98 % AR grade, Merck
Deuterated chloroform	CDCl <sub>3</sub>	99.8 %, Merck
Argon	Ar	High purity, BOC and Air
		Liquide <sup>1</sup>
Carbon dioxide	CO <sub>2</sub>	Food grade, Coregas and
		Air Liquide <sup>1</sup>
Helium	He	High purity, Air Liquide
Liquid nitrogen	N <sub>2</sub>	Liquid nitrogen, School of
		Chemistry supply, BOC
		and Air Liquide
Nitrogen	N <sub>2</sub>	High purity, BOC and Air
		Liquide

Table 2.1: Chemicals for the synthesis of the ligands and gases used in this work.

<sup>1</sup>used after in-line purification by a zeolite 13X-based H<sub>2</sub>O trap

Table 2.1 (continued). Chemicals and gases used in this work.		
Chemical name	Formula	Purity/Supplier
$1 \pm 0.01$ % Nitric Oxide in Argon	NO	Air Liquide
$1 \pm 0.01$ % Nitrogen Dioxide in	NO <sub>2</sub>	Air Liquide
Argon		
$1 \pm 0.01$ % Sulfur Dioxide in	SO <sub>2</sub>	Air Liquide
Argon		

Table 2.1 (continued): Chemicals and gases used in this work.

#### 2.2 Synthesis and characterisation of ligands

#### 2.2.1 Synthesis and characterisation of trimethyl-1,3,5-benzenetricarboxylate

Trimethyl-1,3,5-benzenetricarboxylate was synthesised following the route published by Kathiresan et. al. [1].



Trimesic acid (10.01 g, 47.6 mmol) was suspended in 30 mL methanol and heated to reflux. 1.6 mL of conc. sulphuric acid was added and a clear solution was obtained, which was refluxed for 6 h. After 2 h a white solid precipitated from the solution. The mixture was cooled to room temperature, slowly neutralised with saturated sodium bicarbonate solution, filtered and washed with excess H<sub>2</sub>O. It was then dried at 105 °C to yield 9.75 g (81.1 % (Lit.: 95 %)) of a white solid. The product was characterised by melting point analysis, <sup>1</sup>H and <sup>13</sup>C-NMR and FTIR.

The melting point of trimethyl-1,3,5-benzenetricarboxylate was determined to be 144-145 °C, which is in good agreement with the range of 144-144.5 °C given in the literature.

The <sup>1</sup>H and <sup>13</sup>C-NMR spectra are shown in Figure 2.1 and 2.2. From both a good purity of trimethyl-1,3,5-benzenetricarboxylate can be concluded.



**Figure 2.1:** <sup>1</sup>H-NMR of trimethyl-1,3,5-benzenetricarboxylate in CDCl<sub>3</sub> recorded at 400.17 MHz.



**Figure 2.2:** <sup>13</sup>C-NMR of trimethyl-1,3,5-benzenetricarboxylate in CDCl<sub>3</sub> recorded at 100.62 MHz.



<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): *δ*=8.88 (s, 3 H, *H1*), 4.01 (s, 9 H, *H2*).

<sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>): *δ*=165.3 (3 C, *C1*), 134.5 (3 C, *C2*), 131.2 (3 C, *C3*), 52.7 (3 C, *C4*).

The FTIR spectrum (Figure 2.3) shows four characteristic bands of the aromatic ring at  $3098/3017 \text{ cm}^{-1}$  (aromatic (sp<sup>2</sup>) C-H stretch),  $1451/1432 \text{ cm}^{-1}$  (aromatic C=C stretch),  $999 \text{ cm}^{-1}$  (trisubstituted aromat) and  $738/721 \text{ cm}^{-1}$  (aromatic C-H bending). Two ester stretch vibrations can be found at  $1730 \text{ cm}^{-1}$  (C=O stretch) and  $1260/1247 \text{ cm}^{-1}$  (C-O stretch). The bands at  $2956/2849 \text{ cm}^{-1}$  and  $1342 \text{ cm}^{-1}$  are characteristic for the methyl (sp<sup>3</sup>) C-H stretch and for the methyl bending respectively.



Figure 2.3: FTIR spectra of trimethyl-1,3,5-benzenetricarboxylate.

# 2.2.2 Synthesis and characterisation of N,N'-4,4'-bipiperidinebis(methylenephosphonic acid) tetrahydrate (H<sub>4</sub>LL)

The synthesis of N,N'-4,4'-bipiperidinebis(methylene-phosphonic acid) tetrahydrate was described by Wharmby et al. using 4,4'-bipiperidine dihydrochloride, phosphorous acid, hydrobromic acid solution and formaldehyde in a Mannich reaction [2].



7.18 g (29.7 mmol) of 4,4'-bipiperidyl dihydrochloride and 6.41 g (78.1 mmol) phosphorous acid were dissolved in 30 mL H<sub>2</sub>O and 21 mL hydrobromic acid solution (47 wt.% aqueous solution) was added. Formaldehyde (13 mL) was added dropwise to the reaction over 30 minutes. The solution was then refluxed for 20 h at 120 °C. On cooling, the solvent volume was reduced and a white precipitate was formed. To ensure complete precipitation, the mixture was cooled to 5 °C overnight. The product was separated by filtration, washed with a cold ethanol-H<sub>2</sub>O solution (9:1, 3x10 mL) and dried at 40 °C to give 8.67 g (68 %) of N,N'-4,4'-bipiperidinebis(methylenephosphonic acid) tetrahydrate.

The results of the elemental analysis are shown in Table 2.2. The experiment was performed twice to determine the reproducibility of the results. The percentages obtained by elemental analysis are lower than those calculated for the crystallographic composition  $C_{12}H_{26}N_2O_6P_2$ ·4H<sub>2</sub>O, consistent with the presence of residual phosphorous acid. This result suggests that the ligand was not entirely in its pure form.

Table 2.2. Elemental chemical analysis of 114EE.				
	$\mathbf{H}_4$	LL	Calculated	
С	30.77%	30.91 %	33.65 %	
Н	5.94 %	6.16 %	8.0 %	
Ν	5.96 %	5.93 %	6.5 %	

Table 2.2: Elemental chemical analysis of H<sub>4</sub>LI

The <sup>13</sup>C and <sup>31</sup>P-NMR spectra are shown in Figure 2.4 and 2.5. In contrast to the literature N,N'-4,4'-bipiperidine(methylenephosphonic acid) tetrahydrate synthesised in this work was insoluble in D<sub>2</sub>O/NaOH. Therefore solid state <sup>13</sup>C and <sup>31</sup>P-NMR (<sup>1</sup>H decoupling) were performed. The <sup>31</sup>P-NMR in the literature is characterised by a triplet at 15.5 ppm, due to the acquisition with <sup>1</sup>H coupling [2]. The chemical shift at 13.89 ppm is indicative for the present phosphonate groups. The two smaller singlets at 10.21 and 8.23 ppm are

presumably due to the presence of some residual phosphorous acid, consistent with the results from the elemental analyses. The difference could be due to the lower resolution of solid state NMR or because of impurities of the ligand (e.g. polymerisation of product).



<sup>13</sup>C-NMR (400 MHz): δ=59.3 (2 C, *C1*), 52.7 (4 C, *C2*), 37.4 (2 C, *C3*), 28.1 (4 C, *C4*).

<sup>31</sup>P-NMR (400 MHz):  $\delta$ =13.89 (s), 10.21 (s), 8.23 (s).



Figure 2.4: <sup>13</sup>C-NMR of H<sub>4</sub>LL in solid state at 100.62 MHz.



Figure 2.5: <sup>31</sup>P-NMR of H<sub>4</sub>LL in the solid state recorded at 161.98 MHz.



<sup>13</sup>C-NMR (400 MHz): *δ*=59.3 (2 C, *C1*), 52.7 (4 C, *C2*), 37.4 (2 C, *C3*), 28.1 (4 C, *C4*).

<sup>31</sup>P-NMR (400 MHz):  $\delta$ =13.89 (s), 10.21 (s), 8.23 (s).

The IR spectrum of *N*,*N*'-4,4'-bipiperidinebis(methylenephosphonic acid) tetrahydrate is shown in Figure 2.6. The spectrum shows a broad band at 2944/2868 cm<sup>-1</sup> and 2743/2709 cm<sup>-1</sup> which are characteristic for methylene C-H stretch and P-O(H) stretch vibrations. The second P-O(H) stretch can be found at 877 cm<sup>-1</sup>. Three more characteristic bands of the phosphonate groups can be observed at 1339-1244 cm<sup>-1</sup> (P=O stretch), 1261/1244 cm<sup>-1</sup> (P-O-H bend) and 1023/975 cm<sup>-1</sup> (P-O stretch). The band at 1434 cm<sup>-1</sup> is characteristic for the CH<sub>2</sub> bend vibration. Between 1199 and 1135 cm<sup>-1</sup> the C-N stretch of

tertiary amines can be found. Two additional bands of the methyne groups can be observed at 1389 cm<sup>-1</sup> (methyne C-H bend) and 1300-700 cm<sup>-1</sup> (skeletal C-C vibration).



Figure 2.6: FTIR spectra of H<sub>4</sub>LL.

# 2.3 Synthesis of MOFs

Table 2.3 gives a brief summary of the MOFs produced for this thesis. More detailed preparation procedures are given in the chapters indicated in the table.

MOF	Refer to chapter	Brief summary of synthesis
MIL-53(Al)-NH <sub>2</sub>	4.2.2.2	Hydrothermal, 150 °C, 5 h
MIL-53(Al)-NH <sub>2</sub> -AM	4.2.2.3	PSM of MIL-53(Al)-NH <sub>2</sub>
MIL-100/MIL-110(Al)	3.2.2.2	Hydrothermal, 210 °C, 5 h
MIL-100(Fe)	3.3.3.2.2	Hydrothermal, 130 °C, 3 days
MIL-100(Fe)-ED-2.5	3.3.3.2.3	Grafting, overnight
MIL-100(Fe)-ED-3	3.3.3.2.3	Grafting, overnight
MIL-100(Fe)-PEI-3	3.3.3.2.3	Wet impregnation, overnight
MIL-100(Fe)-PEI-22	3.3.3.2.3	Wet impregnation, overnight
MIL-100(Fe)-PEI-25	3.3.3.2.3	Wet impregnation, overnight
MIL-101(Al)-NH <sub>2</sub>	3.5.3.2	Solvothermal, 110 °C, 19 h
MIL-101(Al)-NH <sub>2</sub> -PEI-48	3.5.3.3	Wet impregnation, overnight
MIL-101(Al)-NH <sub>2</sub> -PEI-96	3.5.3.3	Wet impregnation, overnight
MIL-101(Al)-NH <sub>2</sub> -DAB-AM-94	3.5.3.3	Wet impregnation, overnight
MIL-101(Al)-NH <sub>2</sub> -DETA-89	3.5.3.3	Wet impregnation, overnight

Table 2.3: Summary of MOFs prepared in this work.

MOF	Refer to chapter	Brief summary of synthesis
MIL-101(Cr)	5.2.3.1.2	Hydrothermal, 220 °C, 8 h
MIL-101(Cr)-NH <sub>2</sub>	3.4.3.2	Hydrothermal, 130 °C, 24 h
MIL-101(Cr)-NH <sub>2</sub> -PEI-68	3.4.3.3	Wet impregnation, overnight
MIL-101(Cr)-NH <sub>2</sub> -PEI-88	3.4.3.3	Wet impregnation, overnight
MIL-101(Cr)-NH <sub>2</sub> -PEI-130	3.4.3.3	Wet impregnation, overnight
MIL-101(Cr)-NH <sub>2</sub> -DETA-88	3.4.3.3	Wet impregnation, overnight
MIL-101(Cr)-NH <sub>2</sub> -DAB8-145	3.4.3.3	Wet impregnation, overnight
MIL-101(Cr)-NH <sub>2</sub> -ED-128	3.4.3.3	Grafting, overnight
STA-16(Co)	3.6.3.2	Hydrothermal, 220 °C, 3 days
CoMOF	6.2	Hydrothermal, 220 °C, 3 days

### 2.4 Characterisation techniques

### 2.4.1 Infrared spectroscopy

Infrared spectroscopy is a common technique for characterising a wide range of materials. The basic components of a FTIR spectrometer are shown in Figure 2.7. The source generates monochromatic light, which enters the interferometer. In most FTIR spectrometers a Michelson interferometer is used which consists of two perpendicular plane mirrors and a beamsplitter. The monochromatic light is sent to the beamsplitter, where part of the light is transmitted and travels toward the fixed mirror. The other part is reflected and travels towards the moving mirror. Both mirrors reflect the beams towards the beamsplitter, where both beams are recombined into a single beam, which then leaves the interferometer. The IR beam is passed through a sample and the transmission intensity is detected. The signal is then amplified and converted to a digital signal, which is send to a computer, in which the Fourier transformation is carried out. The principle of IR is based on the vibration of molecules, which can result in absorption of the IR radiation if a change in electric dipole moment occurs. The absorption/vibration is the result of a change in bond angle (bending) [3, 4].



Figure 2.7: Components of an FTIR spectrometer [5].

At the start of this project, Infrared spectra were recorded on potassium bromide pellets in a Perkin-Elmer Spectrum RXI Fourier-transformed infrared spectrometer in the spectral range of 4000 to 600/400 cm<sup>-1</sup>. Small amounts of sample were dispersed with potassium

bromide, ground and pressed into a pellet using a Specac brand press. The background correction, measured on a pure potassium bromide pellet, was performed automatically by the instrument control software.

In later stages of the project, infrared spectra were recorded on an Agilent Cary 630 Diamond ATR in the spectral range 4000 to 650 cm<sup>-1</sup>. Prior to each measurement the background was recorded. A small amount of sample was then placed on the diamond crystal, the pressure clamp was tightened and the spectrum was measured.

### 2.4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR experiments were conducted on the ligands synthesised in this work to elucidate their structure. Most modern spectrometers contain a high-resolution magnet based on superconducting solenoids. A coil of superconducting wire is immersed in a cryostat filled with liquid Helium at -269 °C. The magnetic field is generated by a current circulating in the coil. The Helium dewar is surrounded by layers of vacuum and liquid N<sub>2</sub> in order to prevent the loss of liquid Helium. The excitation of the NMR active nuclei is achieved by the application of a short intense pulse of radiofrequency radiation. After the pulse is switched off, the nuclei are releasing the energy they have acquired. The detector is recording the decrease in signal in the form of a free induction decay (FID). The pulse process is repeated and the sum of the FIDs is converted into the usual NMR spectra by Fourier transformation (FT). In solid state NMR, high-power decoupling is required in order to remove dipolar interactions, which can't be seen in liquid state. To avoid broadening due to chemicals shift anisotropies and residual <sup>1</sup>H-<sup>13</sup>C dipolar coupling, magic angle spinning (MAS) is applied in solid state NMR [4, 6, 7].

<sup>1</sup>H and <sup>13</sup>C-NMR spectra were recorded on a Bruker UltraShield 400 Plus spectrometer at 400.17 and 100.62 MHz, respectively. A solution of trimethyl-1,3,5-benzenetricarboxylate was prepared by dissolving 10 mg (<sup>1</sup>H) or 25 mg (<sup>13</sup>C) of sample in deuterated chloroform (CDCl<sub>3</sub>).

Due to the insolubility of N,N'-4,4'-bipiperidinebis(methylene-phosphonic acid) tetrahydrate in tested deuterated solvents,  $^{13}$ C-NMR (100.62 MHz) and  $^{31}$ P-NMR (161.98 MHz) were performed in the solid state on a Bruker Avance 400 (9.4 Tesla magnet) with a 4 mm multinuclear solid state probe at room temperature. The samples

were packed into 4 mm zirconium dioxide rotors with a Kel-F cap and the spectra were recorded using cp-mas (cross polarised magic angle spinning) technique.

The spectra were collected and processed using Brukers Topspin 2.1 program.

### 2.4.3 Melting point measurement

Melting point measurements were performed on the ligands synthesised in this work in order to determine their purity. A small amount of sample was placed in a capillary, which was then inserted into a melting point apparatus, SMP3 from Stuart Scientific. The required plateau temperature and heating rate were selected and the melting point was determined.

### 2.4.4 Elemental analysis

In order to determine, the carbon, hydrogen, nitrogen and phosphorous contents of the materials, elemental analysis was performed in the Campbell Microanalytical Laboratory at the University of Otago. The principle of elemental analysis is based on the high temperature oxidation of organic compounds and the conversion of the elements to gaseous molecules [4]. The experimental values were compared to the theoretical values, which were calculated from the empirical formulas.

### 2.4.5 Powder X-ray diffraction and Single crystal X-ray diffraction

X-rays are electromagnetic waves that are produced by the collision of high energy electrons with a metal anode inside a sealed vacuum tube. The loss of kinetic energy generates continuous X-rays of various wavelengths. X-rays of maximum energy are produced if a single collision results in a complete loss of energy. The generated X-rays exit the tube via beryllium windows and are scattered by the electrons around the nucleus of the atoms in the sample [8, 9].

W.H Bragg and W.L. Bragg described the diffraction of x-rays from a crystalline sample in form of mirror reflections of the incident beam from a series of parallel and equally spaced crystallographic planes. These planes are characterised by the same Miller indices *hkl*. In contrast to visible light, X-rays penetrate deep into the material and are therefore passing several planes of atoms in the lattice. The illustration of Bragg's law (Figure 2.8) shows that the angle of the incident beam is equal to the angle of the reflected beam. Depending on the position of the atoms, the X-rays travel different distances until they interact with the atoms of the sample. The path differences  $\Delta$  before and after the reflection of the electromagnetic waves can be determined by the distance  $d_{hkl}$  between the crystallographic planes (Eq. 2.3).

$$\Delta = \mathbf{d}_{hkl} \sin \theta \tag{2.3}$$

If the total path difference  $2\Delta$  is equal to an integer *n* of the wavelength  $\lambda$ , the waves are in phase (constructive interference) and reflection is observed. By applying this to Eq. 2.3, Bragg's law can be obtained (Eq. 2.4) [10-13].

$$n\lambda = 2d_{hkl}\sin\theta$$
 (2.4)

Although the principle of PXRD and single-crystal XRD are the same, the presentation of the data is different. In single-crystal XRD, the data is presented as a two-dimensional pattern of spots which correspond to the lattice planes, while in PXRD the data is plotted as one-dimensional diffraction patterns. Single-crystal XRD is commonly used to determine the structure of single crystals of sufficient size. In order to determine the phase purity and/or the size of the unit cell, PXRD can be performed [14].



Figure 2.8: Illustration of Bragg's law [12].

#### 2.4.5.1 Powder X-ray diffraction (PXRD)

Powder x-ray diffraction (PXRD) experiments were carried out on a Bruker D8 Focus Bragg-Brentano powder diffractometer containing a X-ray source with a copper anode, giving Cu K<sub>a</sub> radiation of a wavelength of 1.54059 Å (K<sub>a1</sub>) and 1.54443 Å (K<sub>a2</sub>) (Figure 2.9) The ratio of the K<sub>a1</sub> to K<sub>a2</sub> intensities is two to one. The range of scattering angles employed was 1 to 30 ° with a scan rate 0.1 to 0.5 ° min<sup>-1</sup>. Prior to the experiments, all samples were ground to give a fine powder, which was mounted on a silicon low background sample holder using ethanol. In some cases a second sample holder made of PMMA (polymethyl methacrylate) was used if sufficient sample was available. The grinding of the samples allows small crystallites to be oriented in every possible direction. The PXRD pattern were simulated using the module "Reflex Tools" in Materials Studio 6.0 [15].



**Figure 2.9:** General components of Bruker D8 Focus Bragg-Brentano powder diffractometer and sample holders used in this work.

# 2.4.5.2 Single crystal X-ray diffraction

Single crystal x-ray diffraction was performed on an OXFORD Gemini Ultra CCD diffractometer equipped with an Oxford Cryosystems 700 Cryostream. The basic components of the instrument are shown in Figure 2.10. The crystal was cooled to -150 °C, before collection the data using Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$ =1.5418 Å). The data was processed with CrysAlisPro software. The structure was solved by Direct Methods and refined using full matrix Least Squares with the SHELX-97 program suite [16]. A detailed description of the structure solution is given in the supplementary material of the communication in Chapter 6.2.



Figure 2.10: General components of the Oxford Gemini Ultra CCD diffractometer.

### 2.4.6 Helium pycnometry

The true densities of the materials were determined by helium pycnometry using an AccuPyc 1340 from Micromeritics. Helium was used as the measurement gas due to its small atom size and inert character, which allows the penetration into the smallest voids or pores. After calibrating the expansion and cell volume, the vacuum dried samples (0.1-0.4 g) were placed into a 1 cm<sup>3</sup> cell, before installing the cell into the analysis chamber. The cell chamber was then purged with helium until the purge fill pressure of approximately 1.3 bar was reached. After venting the chambers the helium density was calculated from the volume of helium displaced by a known mass of sample. In order to determine the reproducibility of the result, the helium densities were performed 20 times and the mean value was taken.

# 2.4.7 Textural property measurement

 $N_2$  physisorption at -196 °C was used to determine the specific surface area and the pore size distribution. At the start of this project a Coulter Omnisorp 360CX gas sorption analyser was used, which has a built-in degas station. During the project, a new TriStar II 3020 (Micromeritics) was purchased and used for the analyses. As the majority of samples were characterised utilising TriStar II 3020, the procedure of the measurement is described in the following paragraph. The  $N_2$  sorption experiments measured on the Coulter were performed in a similar manner.

All samples were pretreated under vacuum at temperatures between 90 °C and 220 °C (depending on the decomposition of the material, Table 2.4) for at least 12 h in the VacPrep 061 degasser (Micromeritics) in order to remove solvent molecules and adsorbed impurities inside the pores. Afterwards the sample tubes were backfilled with helium and installed in the TriStar II 3020. The samples were then evacuated and free space measurements using helium were performed, before the samples were brought to -196 °C. The gas was dosed into the manifold until a certain pressure was reached. The pressure and the temperature were recorded and the sample valve was opened. N<sub>2</sub> was adsorbed and the difference between expected and measured pressure was used to determine the nitrogen uptake. The pressure was increased in steps, and the measurement repeated at each step, up to a relative pressure of 1, after which analogous stepwise desorption measurements were taken.

In case of the non-porous CoMOF (Chapter 6) no reasonable data could be obtained on TriStar II 3020. Therefore, Ar physisorption was performed at -186 °C on ASAP 2020 (Micromeritics), which is equipped with a cryostat. The measurement principle is the same as described above.

MOF	Activation temperature / °C
MIL-100/MIL-110(Al)	220
MIL-100(Fe), MIL-101(Cr), MIL-53(Al)-NH <sub>2</sub> , STA-	150
16(Co), CoMOF	
MIL-101(Al)-NH <sub>2</sub> , MIL-101(Cr)-NH <sub>2</sub> and	110
PEI/DETA/DAB-8 modified MOFs	
ED modified MOFs	90

Table 2.4: Activation temperatures for MOFs.

The specific surface areas were calculated using the Brunauer-Emmet-Teller (BET) model over the relative pressure range of 0.01 to 0.2 [17]. The pore size distribution was determined via the Barrett-Joyner-Halenda (BJH) model using the desorption isotherm [18]. Both models are available in the data processing software of the TriStar II 3020.

### 2.4.8 Scanning electron microscopy (SEM)

A schematic of a SEM is shown in Figure 2.11. Firstly, electrons are generated in an electron gun and accelerated to an energy between 0.1 and 30 keV. The electron beam then passes two or more magnetic lenses, before hitting the sample. The magnetic condenser

lens enables the change of the electron probe diameter and the probe current. The magnetic objective lenses produce a focussed electron beam with a small spot size on the specimen surface, which is scanned across the specimen in two perpendicular directions (x, y) using deflection coils. The deflection coils are located above the objective lenses on either side of the optical axis [4, 19-21].



Figure 2.11: Basic components of the SEM [4].

After the electron beam enters the sample, the accelerated electrons are scattered elastically and in-elastically. Some electrons lose significant energy by inelastic collisions and leave the sample surface with a typical energy of 10 to 30 eV ( $E_{max}$ =50 eV). These secondary electrons are produced close to the sample surface (<50 nm) and are used for obtaining information about the morphology and topology of a sample. In case of elastic scattering, the electrons retain their kinetic energy and are reflected at random angles. These backscattered electrons can be obtained from depth up to 500 nm. The resolution of backscattered electron (BSE) images depends on the atomic number of the irradiated specimen area and the angle between the specimen and the electron beam/detector. BSE images can be useful to highlight compositional differences across a sample, due to the differences in atomic number of the elements and their distribution. Other possible mechanisms for the formation of secondary electrons include the interaction of the electron beam with the backscattered electrons or the collision of the backscattered electrons with the wall of the objective lens. A third type of signal can be used to quantitatively determine the composition of the sample. This technique is called energy dispersive x-ray spectroscopy (EDS) and uses the characteristic x-rays which are produced in a two-step process. In the first step the energy beam hits the sample and ionises an atom by removing

an electron from an inner valence shell. This vacancy is then filled by an outer shell valence electron and a photon is emitted [20, 22, 23].

In order to determine the particle shape and morphology of the MOFs, SEM images were obtained on a JEOL 7001F microscope, which is equipped with a Schottky-type field emission gun (FEG). The general setup of the microscope is shown in Figure 2.12.



**Figure 2.12:** Scanning electron microscope (JEOL 7001F), equipped with a Bruker X-flash EDX detector.

Before the characterisation of the samples with SEM, all samples were degassed under vacuum overnight in order to remove any moisture or solvents. A small amount of sample was mounted on a stub (diameter=12.5 mm) using double-sided carbon tape and loose powder was removed by  $N_2$  purge. To prevent the charging of the sample surface by electron beam interaction and/or by the low yield of secondary electrons during the imaging process, all materials were coated with platinum (2 mm thickness) for 0.5 minutes using a Cressington Sputter Coater.

The specimen exchange chamber is vented and the stub inserted. After evacuating the system the stub is transferred into the microscope. When the vacuum has reached  $5 \times 10^{-4}$  Pa or less, the electron gun is switched on and the alignment and astigmatism correction is performed before obtaining the images and/or EDS analysis.

### 2.4.9 Thermal stability measurement

In order to obtain information about the amount of volatile components and/or residual solvents as well as about the thermal stability of the materials, thermogravimetric analysis was performed using a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser

which features programmable mass flow controllers made by Bronkhorst, through which the gas (air and Ar) flows into the thermoanalyser. The total flow rate of 70 mL min<sup>-1</sup> was used for all experiments. Due to the fact that the gas stream was divided into two streams only 35 mL min<sup>-1</sup> were passed over the sample. The other half was directed over a reference hangdown, which automatically allows for buoyancy corrections during the experiment. A sample of 10-20 mg was used for thermal stability measurements. Blank runs were performed for each temperature program to account for any buoyancy effects present.



Figure 2.13: Temperature program for thermal stability measurements.

Two different temperature programs (Figure 2.13) were used in this work to investigate the decomposition of the materials. The difference between both profiles is the heating rate used. The aluminium and chromium MOFs were heated with a rate of 10 °C min<sup>-1</sup>, while a heating rate of 2 °C min<sup>-1</sup> was applied for the other MOFs (MIL-101(Fe)-NH<sub>2</sub>, STA-16(Co)).

In the first step, the sorbents are pre-treated at a temperature of 110 °C for 60 minutes to remove all volatile matter inside the pores. For the last 30 minutes of this period, the gas composition was changed from 100 vol% Ar to 50 vol% air and 50 vol% Ar. Afterwards the samples were heated to 900 °C to achieve a complete decomposition of the framework. After 15 minutes at 900 °C the air flow was switched off and the temperature was held for additional 15 minutes before the system was cooled down to 20 °C.

#### 2.5 Sorption measurements

#### 2.5.1 CO<sub>2</sub> sorption at low pressure

 $CO_2$  adsorption and desorption was measured by combined TGA and differential thermal analysis (DTA) using a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. The aim of these experiments is to assess the extent to which the sorbent is capable of adsorbing and releasing  $CO_2$  at one or more specific temperatures.



Figure 2.14: Gas and temperature program of adsorption/desorption measurement in  $Ar/CO_2$ .

After activating the MOFs under Ar at an elevated temperature (Table 2.4) for 1 h, the system was cooled down until the desired adsorption/desorption temperature was reached. The thermoanalyser was then allowed to equilibrate for 20 minutes before  $CO_2$  was switched on. The amount of  $CO_2$  was increased in five steps (2.1, 5.2, 14.7, 29.7 and 49.8 vol%  $CO_2$ ) and then reduced in five steps (29.7, 14.7, 5.2, 2.1 and 0 vol%  $CO_2$ ) by increasing the amount of Ar in the gas stream. This procedure of changing the gas feed composition is able to mimic a pressure swing adsorption process by varying the partial pressure of  $CO_2$ . After the last desorption step the temperature was kept constant for another 20 minutes. At the end of the experiment the MOFs were heated to their activation temperature in order to desorb the  $CO_2$  fully. The procedure is shown in Figure 2.14, the activation temperatures are given in Table 2.4. The timeframe of each experiment depended on the activation temperature as well as the adsorption/desorption temperature and on the length of each adsorption/desorption step. The measurements were repeated in
absence of the sample order to compensate for residual buoyancy effects present during the analyses. The limit of the TG resolution is  $\pm$  0.05 mg g<sup>-1</sup>. The heats of adsorption were calculated from the DTA data (see Chapter 3.3, 3.4 and 3.5) with an estimated standard error of  $\pm 2$  kJ mol<sup>-1</sup> [24].

#### 2.5.2 Gas sorption at high pressure

The sorption isotherms for CO<sub>2</sub> and N<sub>2</sub> were measured using a High Pressure Volumetric Analyser 200 (HPVA) from Micromeritics (Figure 2.15). Prior to transferring the samples into the sample tube, approximately 0.1 - 0.4 g of MOF were activated on the VacPrep 061 (Micromeritics) under vacuum overnight. The dried sample mass was determined and the sample tube installed onto the degas port, where the sample was degassed until the vacuum reached 0.04 mbar. After connecting the sample tube to the analysis port, the system was degassed and purged three times with helium before the valve on the sample tube was opened. Prior to the adsorption of the gases a free space measurement was performed at room temperature and at the analysis temperature. The analysis temperature was set using a thermostat bath (25-75 °C) or the oven (105 °C). A known amount of gas (adsorptive) was introduced into the sample chamber. When the sample reaches equilibrium with the adsorptive gas, the final equilibrium pressure is recorded and the quantity of gas adsorbed/desorbed is calculated. This process is repeated until the data at all preselected pressures have been acquired. Between measurements at different temperatures or with different adsorptives, the samples were evacuated at the degas port at the temperatures given in Table 2.4. Blank runs were performed for each temperature/adsorptive and subtracted from the sorption isotherms.

The H<sub>2</sub>O stability of the materials was determined by measuring sorption isotherms for  $CO_2$  and H<sub>2</sub>O vapour at 25 °C using a Intelligent Gravimetric Analyser (IGA-1 series, Hiden Analytical Ltd.), modified by the addition of a vapour generator. Prior to measuring the isotherms, the sample was outgassed overnight at elevated temperature (Table 2.4) under vacuum, before evacuating the sample 25 °C until no further weight loss was observed. Adsorption/desorption isotherms were acquired by progressively changing the absolute pressure of the adsorptive. A period of 15 to 30 minutes was allowed for the approach to equilibrium, except for H<sub>2</sub>O vapour for which up to 40 min at each pressure point were allowed. After recording a  $CO_2$  isotherm and measuring the H<sub>2</sub>O isotherm, a

second  $CO_2$  isotherm was measured, which was compared to the initial  $CO_2$  isotherm in order to determine the  $H_2O$  stability of the material.



Figure 2.15: System schematic of the HPVA-200 from Micromeritics.

The isosteric heat of adsorption  $\Delta H_{iso}$  was calculated by using the Clausius-Calpeyron equation (Eq. 2.5) using the CO<sub>2</sub> and N<sub>2</sub> isotherms at 25, 45, 75 and 105 °C [25].

$$\left(\frac{\Delta H_{iso}}{R}\right) = \left(\frac{\partial lnP}{\partial (1/T)}\right)_{\theta}$$
(2.5)

The Tóth isotherm model was fitted to the  $CO_2$  and  $N_2$  isotherm data in order to determine the isosteric heat as a function of loading. The Tóth isotherm equation (Eq. 2.6) was developed to describe the adsorption equilibrium on heterogeneous systems and multilayer adsorption. The three parameter equation presents an enhancement of the Langmuir equation (Eq. 2.6), in which the parameter *t* is related to the heterogeneity of the adsorbent-adsorbate system. The Tóth isotherm equation is reduced to the Langmuir isotherm equation if the parameter *t* is equal to 1 [26].

$$\theta = \frac{N}{N_{max}} = \frac{bP}{(1+(bP)^t)^{1/t}}$$
(2.6)

#### 2.5.3 CO<sub>2</sub> cycling experiments

The stability and regenerability of the MOFs were measured by thermogravimetric analysis using a Setaram TAG 24-16 simultaneaous symmetrical analyser which features programmable mass flow controllers made by Bronkhorst, through which Ar and  $CO_2$  were dosed into the thermoanalyser. A total flow rate of 70 mL min<sup>-1</sup> (e.g. 35 mL min<sup>-1</sup>)

sample gas and 35 mL min<sup>-1</sup> on the reference side of the balance) was used for all experiments. The samples were degassed under vacuum overnight prior to the cycling experiments. After activating 10-30 mg of MOF at elevated temperature (Table 2.4) under Ar for 1 h, the system was cooled to 25, 45, 75 or 105 °C depending on the kinetics observed in the adsorption experiments at low pressure. Ten cycles of adsorption/desorption were carried out by varying the  $CO_2$  partial pressure between 0.05 and 0.15 bar, allowing 20 minute equilibration time for each adsorption and desorption step. The temperature and gas program for the dry cycling procedure is shown in Figure 2.16.



**Figure 2.16:** Gas and temperature program of cycling experiments under dry conditions (Ar/CO<sub>2</sub>).

For the wet cycling experiments, the MOFs were saturated with 1 vol%  $H_2O$  vapour by exposing the samples to flowing wet Ar after the activation step, before treatment with wet CO<sub>2</sub>/Ar mixtures (1 %  $H_2O/CO_2/Ar$  70 mL min<sup>-1</sup>). The temperature and gas program for wet cycling procedure is shown in Figure 2.17.

After ten cycles, the CO<sub>2</sub>/Ar or H<sub>2</sub>O/CO<sub>2</sub>/Ar mixtures were replaced by pure Ar and the MOFs were heated to their activation temperature in order to remove the adsorbed gas fully (including H<sub>2</sub>O). The timeframe of each experiment depends on the activation temperature as well as the adsorption/desorption temperature and on the length of the H<sub>2</sub>O saturation step. The measurements were repeated without the sample present in order to

compensate residual buoyancy effects present during the analysis. The stabilities of the materials after the wet cycling experiments were further evaluated using PXRD (see Section 2.1.5.1).



Figure 2.17: Gas and temperature program of cycling experiments under wet conditions  $(Ar/CO_2/H_2O)$ .

#### 2.5.4 Sorption of flue gas contaminants

The sorption of flue gas contaminants was measured using a Setaram TAG 24-16 simultaneous symmetrical analyser. A detailed description of the gas and temperature programs is given in Chapter 5.2.

## 2.6 References

- [1] M. Kathiresan, L. Walder, F. Ye, and H. Reuter, "Viologen-based benzylic dendrimers: selective synthesis of 3,5-bis(hydroxymethyl)benzylbromide and conformational analysis of the corresponding viologen dendrimer subunit," *Tetrahedron Letters*, vol. 51, pp. 2188-2192, 2010.
- [2] M. T. Wharmby, J. P. S. Mowat, S. P. Thompson, and P. A. Wright, "Extending the Pore Size of Crystalline Metal Phosphonates toward the Mesoporous Regime by Isoreticular Synthesis," *Journal of the American Chemical Society*, vol. 133, pp. 1266-1269, 2011.
- [3] B. H. Stuart, "Introduction," in *Infrared Spectroscopy: Fundamentals and Applications*, ed: John Wiley & Sons, Ltd, 2005, pp. 1-13.
- [4] D. A. Skoog, F. J. Holler, and T. A. Nieman, *Principles of Instrumental Analysis*, 5th ed.: Saunders College Publishing, 1998.
- [5] B. H. Stuart, "Experimental Methods," in *Infrared Spectroscopy: Fundamentals and Applications*, ed: John Wiley & Sons, Ltd, 2005, pp. 15-44.

- [6] J. C. Lindon, "NMR Spectrometers," in *Encyclopedia of Spectroscopy and Spectrometry (Second Edition)*, J. C. Lindon, Ed., ed Oxford: Academic Press, 2010, pp. 1872-1880.
- [7] T. N. Mitchell and B. Costisella, "1D Experiments," in *NMR From Spectra to Structures*, ed: Springer Berlin Heidelberg, 2007, pp. 3-39.
- [8] V. K. Pecharsky and P. Y. Zavalij, "Properties, Sources, and Detection of Radiation," in *Fundamentals of Powder Diffraction and Structural Characterization of Materials*, ed: Springer US, 2009, pp. 107-132.
- [9] Y. Waseda, E. Matsubara, and K. Shinoda, "Fundamental Properties of X-rays," in *X-Ray Diffraction Crystallography*, ed: Springer Berlin Heidelberg, 2011, pp. 1-20.
- [10] R. E. Dinnebier and S. J. L. Billinge, "Chapter 1 Principles of Powder Diffraction," in *Powder Diffraction: Theory and Practice*, ed: The Royal Society of Chemistry, 2008, pp. 1-19.
- [11] V. K. Pecharsky and P. Y. Zavalij, "The Powder Diffraction Pattern," in *Fundamentals of Powder Diffraction and Structural Characterization of Materials*, ed: Springer US, 2009, pp. 151-202.
- [12] V. K. Pecharsky and P. Y. Zavalij, "Fundamentals of Diffraction," in Fundamentals of Powder Diffraction and Structural Characterization of Materials, ed: Springer US, 2009, pp. 133-149.
- [13] Y. Waseda, E. Matsubara, and K. Shinoda, "Scattering and Diffraction," in *X-Ray Diffraction Crystallography*, ed: Springer Berlin Heidelberg, 2011, pp. 67-106.
- [14] E. J. Munson, "Chapter 3 Analytical Techniques in Solid-state Characterization," in *Developing Solid Oral Dosage Forms*, Y. Qiu, Y. Chen, G. G. Z. Zhang, L. Liu, and W. R. Porter, Eds., ed San Diego: Academic Press, 2009, pp. 61-74.
- [15] ""Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.," "*Reflex Tools*" is a module in the Materials Studio Modeling software package from Accelrys Inc.
- [16] G. Sheldrick, "A short history of SHELX," *Acta Crystallogr. Sect. A*, vol. 64, pp. 112-122, 2008.
- [17] S. Brunauer, P. H. Emmett, and E. Teller, "Adsorption of Gases in Multimolecular Layers," *Journal of the American Chemical Society*, vol. 60, pp. 309-319, 2012/01/11 1938.
- [18] E. P. Barrett, L. G. Joyner, and P. P. Halenda, "The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms," *Journal of the American Chemical Society*, vol. 73, pp. 373-380, 2012/01/11 1951.
- [19] J. Goldstein, *Scanning Electron Microscopy and X-ray Microanalysis: Third Edition*: Springer US, 2003.
- [20] R. Egerton, "The Scanning Electron Microscope," in *Physical Principles of Electron Microscopy*, ed: Springer US, 2005, pp. 125-153.
- [21] S. Amelinckx, D. v. Dyck, J. v. Landuyt, and G. v. Tendeloo, "Scanning Beam Methods," in *Electron Microscopy*, ed: Wiley-VCH Verlag GmbH, 2007, pp. 305-497.
- [22] O. C. Wells, "Scanning Electron Microscopy," in *Encyclopedia of Materials: Science and Technology (Second Edition)*, K. H. J. B. Editors-in-Chief: , W. C. Robert, C. F. Merton, I. Bernard, J. K. Edward, M. Subhash, and V. Patrick, Eds., ed Oxford: Elsevier, 2001, pp. 8265-8269.
- [23] R. Mehta, "Interactions, Imaging and Spectra in SEM," in *Sanning Electron Microscopy*, D. V. Kazmiruk, Ed., ed.

http://http://www.intechopen.com/books/scanning-electronmicroscopy/interactions-imaging-spectra-in-sem: Intech, 2012.

- [24] G. P. Knowles, J. V. Graham, S. W. Delaney, and A. L. Chaffee, "Aminopropylfunctionalized mesoporous silicas as CO2 adsorbents," *Fuel Processing Technology*, vol. 86, pp. 1435-1448, 2005.
- [25] D. D. Do, "Adsorption Analysis:Equilibria and Kinetics," *Adsorption Analysis:Equilibria and Kinetics*, pp. Imperial College Press, UK, 1998.
- [26] J. Tóth, "Uniform interpretation of gas/solid adsorption," *Advances in Colloid and Interface Science*, vol. 55, pp. 1-239, 1995.

## **3** MOFs with coordinatively unsaturated sites for carbon capture

## 3.1 Chapter overview

This chapter describes a detailed investigation on the potential of MOFs with coordinatively unsaturated sites (CUS) for carbon capture.

MIL-100 and MIL-101 frameworks were chosen due to their environmentally benign and inexpensive building blocks and hydrothermal stability, which improve the usability on a technical scale. Furthermore the presence of CUS allows the grafting of amines. Jeremias et al. [1] evaluated the potential of MIL-100(Al, Fe) for thermally driven, sorption-based chilling or heat pump systems by conducting H<sub>2</sub>O adsorption and cycling experiments using humidified Ar. They found that these MOFs exhibited high H<sub>2</sub>O uptakes and good cycling stabilities, which suggest that these materials are possible candidates for post-combustion capture.

The first sub-chapter (3.2) reports the characterisation and  $CO_2$  sorption ability of a mixed MOF, which was found to contain approximately 60 % MIL-100(Al) and 40 % MIL-110(Al).

The following three papers in this chapter investigate the effect of PSM of MIL-100(Fe) (Chapter 3.3), MIL-101(Cr)-NH<sub>2</sub> (Chapter 3.4) and MIL-101(Al)-NH<sub>2</sub> (Chapter 3.5) on the CO<sub>2</sub> uptake at pressures up to 0.5 bar. The stability and regenerability of these materials were evaluated in dry and wet cycling experiments. Furthermore, CO<sub>2</sub> and N<sub>2</sub> isotherms on MIL-100(Fe), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> were measured in order to determine their potential for high pressure applications.

The fourth paper is a study on the low and high pressure  $CO_2$  adsorption on the phosphonate framework STA-16(Co) (Chapter 3.6). The  $CO_2/N_2$  selectivities were determined using the single component adsorption isotherms. Furthermore, the hydrothermal stability of the material was evaluated by measuring  $CO_2$  isotherms up to 5 bar before and after the treatment with H<sub>2</sub>O vapour at 30, 60 and 90 % RH.

# 3.2 Synthesis and characterisation of MIL-100/MIL-110(Al): an adsorption study

#### 3.2.1 Introduction

The framework of MIL-100(Al) is built up from trimers of octahedral aluminium oxide, which are arranged to form a supertetrahedral block (Figure 3.1a). Within this tetrahedral unit, each corner is occupied by a trimeric unit, connected to the other trimeric units through the trimesate ligands located on each face. The hybrid supertetrahedra further assemble into a zeotypic mesoporous MOF reminiscent of the MTN topology (related to the zeolite ZSM-39). The corresponding three-dimensional framework exhibits two types of cavity (Figure 3.1b). The first type is delimited by 12 pentagonal rings defining a dodecahedral cage with a window diameter of 5.2 Å, whereas the second type is delimited by 12 pentagonal rings and 4 hexagonal rings leading to a hexakaidodecahedron. The dodecahedral cages are connected together by shared 5-ring faces, forming infinite layers stacked in an ABC sequence. The second type of cage is generated at the intersection of these layers and they are connected to each other via hexagonal faces (window diameter of 8.8 Å) of diamond type [2, 3].



**Figure 3.1:** Crystal structure of MIL-100 (Al): (a) Hybrid supertetrahedra of MIL-100(Al). (b) One unit cell of MIL-100(Al) presenting both cages. Ball and stick view (Al octahedra: pink, C: grey, O: red, H: white).

In contrast to MIL-100(Al), the three-dimensional framework of MIL-110(Al) is built up from the connection of inorganic aluminium octamers through trimesate ligands delimiting large hexagonal channels (Figure 3.2). Each octamer SBU (secondary building unit) consists of two trimers of edge sharing octahedra and two edge-sharing "capping" octahedra. The formula of the caps can be written as  $AlO_3(OH)_3$  and the trimers are  $AlO_2(OH)_3(H_2O)$  or  $AlO_2(OH)_4$  depending upon the termination species present [4, 5].



**Figure 3.2:** Crystal Structure of MIL-110(Al): (a) View along the c axis showing the channels delimited by the discrete Al8 clusters and the trimesate group in MIL-110(Al). (b) View along the c axis showing the connection mode of the Al8 clusters in MIL-110(Al) with the trimesate species parallel to the walls of the channels. Ball and stick view (Al octahedra: pink (Al1) and orange (Al2), C: grey, O: red, H: white).

The complex nature of the synthesis was described by Volkringer et al, who reported the pH sensitivity for the formation of Aluminium MOFs containing trimesic acid as organic ligands. According to their finding MIL-100(Al) is formed at a pH between 0.5 and 0.7, while MIL-110 requires an even more acidic environment (pH=0 to 0.3) [2]. Despite several attempts to prepare a pure phase of MIL-100(Al) adjusting the pH to 0.57 at the start of the synthesis, a mixed material was obtained in all cases.

The following sub-chapters describe the synthesis and characterisation of a mixed MOF material, which contains MIL-100(Al) and MIL-110(Al) in a 50:50 mixture. The applicability for carbon capture has been assessed in terms of low pressure  $CO_2$  adsorption,  $CO_2/N_2$  selectivity and the H<sub>2</sub>O stability after treatment with up to 30 % H<sub>2</sub>O vapour. Additionally, ten cycle experiments of adsorption/desorption under dry and wet conditions were carried out by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar in order to determine the stability and regenerability of MIL-100(Al)/MIL-110(Al).

## 3.2.2 Experimental section

## 3.2.2.1 Chemicals

Aluminium nitrate nonahydrate (Extra pure, Merck), DMF (GR grade, Merck), methanol ( $\geq$  99.8 %, Merck), nitric acid (70 %, Ajax Chemicals), sodium bicarbonate ( $\geq$  99.7 %, Ajax Chemicals), sulphuric acid (98 % AR grade, Merck), trimesic acid (95 % Sigma Aldrich), argon (high purity, BOC and Air Liquide), carbon dioxide (Food grade, Coregas), helium (high purity, Air Liquide), liquid nitrogen (BOC and Air Liquide) and nitrogen (high purity, Air Liquide).

All reagents were commercially available and used without further purification.

#### 3.2.2.2 Synthesis of MIL-100/MIL-110(Al)

The synthesis and characterisation of trimethyl-1,3,5-benzenetricarboxylate (Me<sub>3</sub>BTC) is described in Section 2.1.1.1.

MIL-100(Al)/MIL-110(Al) was synthesized by heating a mixture of 2.31 g (6.16 mmol) of aluminium nitrate nonahydrate, 1.05 g (4.15 mmol) of trimethyl-1,3,5benzenetricarboxylate, 28 mL distilled H<sub>2</sub>O and 7.7 mL nitric acid (1 M) at 210 °C for 3.5 h. The yellow powder was collected by filtration, washed with H<sub>2</sub>O and dried at room temperature. 1 g of as-synthesized (*as*) sample was placed with 40 mL DMF into a Teflon® lined autoclave and heated at 150 °C for 4 h in order to remove the excess amount of Me<sub>3</sub>BTC. After filtration, the product was washed with distilled H<sub>2</sub>O for 12 h under reflux. The white powder was filtered and dried at room temperature.

#### 3.2.3 Results and discussion

#### 3.2.3.1 Characterisation of MIL-100/MIL-110(Al)

The elemental compositions of the *as* and activated MIL-100(Al)/MIL-110(Al) are shown in Table 3.1. The *as*- sample contains nitrate species trapped within the pore, which account for the presence of nitrogen. The differences in carbon and hydrogen contents before and after activation are due to unreacted trimesate entrapped within the pores. Although the samples were treated under vacuum at 220 °C prior to analysis, the amounts of hydrogen and nitrogen in the activated sample indicate that H<sub>2</sub>O treatment did not completely remove DMF. The carbon and hydrogen contents of MIL-100(Al) and MIL-110(Al) in the absence of the terminal H<sub>2</sub>O ligands and any solvent molecules entrapped within the pores were calculated from the empirical framework formula Al<sub>3</sub>O(OH)[C<sub>6</sub>H<sub>3</sub>(COO)<sub>3</sub>]<sub>2</sub> and Al<sub>8</sub>(OH)<sub>12</sub>{(OH)<sub>3</sub>}[C<sub>6</sub>H<sub>3</sub>(COO)<sub>3</sub>]<sub>3</sub>, respectively. The nitrogen content indicated the presence of one molecule of DMF after the activation of the mixed MOF material. Thus, the approximate ratio of MIL-100 to MIL-110 was determined to be 1.7 to 1.

The SEM images (Figure 3.3) confirm the formation of both MIL-100(Al) and MIL-110(Al) due to the presence of two different features. Whereas MIL-110 is known to form rod-shaped crystals (length of crystals: 0.5 to 7  $\mu$ m), MIL-100(Al) appears as octahedrally shaped crystals with sizes between 0.4 and 1.8  $\mu$ m.

MOF	C / %	H / %	N / %
MIL-100/MIL-110(Al) as	$25.77 \pm 0.14\%$	$3.40\pm0.38$	$1.38 \pm 0$
MIL-100/MIL-110(Al) activated	$37.31\pm0.33$	$2.34\pm0.1$	$0.87\pm0.07$
MIL-100(Al) empty pores calculated	40.93	1.34	0.00
MIL-110(Al) empty pores calculated	32.55	2.43	0.00

**Table 3.1:** Elementary chemical analysis of MIL-100(Al)/MIL-110(Al) as, MIL-100(Al)/MIL-110(Al) activated, MIL-100(Al) and MIL-110(Al) with empty pores.



**Figure 3.3:** SEM images of MIL-100(Al)/MIL-110(Al) showing the typical octahedral shape crystals of MIL-100(Al) and the rod shaped crystals of MIL-110(Al). On the right, a selected crystal of MIL-100(Al) is presented at higher magnification.

The powder X-ray diffraction (XRD) pattern of MIL-100(Al)/MIL-110(Al) (Figure 3.4a) matches the simulated XRD patterns for crystal structures of MIL-100(Al) [2] and MIL-110(Al) [4] reported in the literature. The comparison between the experimental and simulated patterns demonstrates the formation of two MOFs, MIL-100 and MIL-110, under the applied synthesis conditions. Although the synthetic conditions reported by Volkringer et al. [2] were used in this work, a mixed MOF material was obtained in all cases.

The IR spectrum (Figure 3.4b) of MIL-100(Al)/MIL-110(Al) *as* is consistent with the presence of excess Me<sub>3</sub>BTC. Bands assigned to C-O bonds of aluminium coordinated trimesate ligands are observed at 1686, 1670 and 1404 cm<sup>-1</sup>. The strong band assigned to OH vibrations indicates the presence of H<sub>2</sub>O molecules in the *as* and activated samples. The lack of a C=O band at 1720 cm<sup>-1</sup> and the intensity of the H<sub>2</sub>O band in the spectrum of the MIL-100(Al)/MIL-110(Al) *as* indicate that only a small amount of excess Me<sub>3</sub>BTC is entrapped within the pores. In the spectrum of the activated sample, bands of framework trimesate are present due to carboxylate C-O vibrations at 1686, 1669, 1464 and 1404 cm<sup>-1</sup>.



**Figure 3.4:** (a) XRD patterns of the samples of the MIL-100(Al)/MIL-110(Al) after activation compared to the simulated pattern for the crystal structures of MIL-100(Al) [2] and MIL-110(Al) [4]. (b) IR spectrum of MIL-100(Al)/MIL-110(Al) before and after activation with DMF and  $H_2O$ .

The thermal stability of MIL-100(Al)/MIL-110(Al) was evaluated by thermogravimetric analysis (TGA). The TGA curve (Figure 3.5a) is characterised by a two-step weight loss. The first weight loss is assigned to the loss of H<sub>2</sub>O molecules, while the second step corresponds to the removal of the trimesate ligand (from 370 °C) and the collapse of the three-dimensional framework. The final product at 650 °C is aluminium oxide with a remaining weight of 20.6 %. These results are in good agreement with those for pure phase MIL-100 and MIL-110(Al) available in the literature [2, 4]. The faster decompositions of MIL-100(Al) and MIL-110 reported in the literature are due to the use of pure O<sub>2</sub> [2, 4], but in this work an Ar/air mixture was applied resulting in a slower decomposition.

The N<sub>2</sub> adsorption/desorption isotherm at -196 °C (Figure 3.5b) measured on the evacuated MIL-100/MIL-110 is intermediate between type I and IV with a slight secondary uptake, and is indicative of the presence of both micro- and mesopores. Fitting the BET equation to the interval between  $p/p_0=0.01$  and 0.2 for the N<sub>2</sub> isotherm of the dehydrated sample gives a surface area of 1704 m<sup>2</sup> g<sup>-1</sup>. The surface area is lower than the literature value of 2152 m<sup>2</sup> g<sup>-1</sup> for pure phase MIL-100(Al) [2] due to the presence of MIL-110(Al) in the sample, which has a surface area of 1408 m<sup>2</sup> g<sup>-1</sup> [4]. This result is consistent with the calculated MIL-100 to MIL-110 ratio of 1.7:1 determined from the elemental analysis data.



**Figure 3.5:** (a) Decomposition of MIL-100(Al)/MIL-110(Al) compared to literature data [2] for MIL-100(Al). (b) Nitrogen adsorption/desorption isotherm at -196 °C for activated MIL-100(Al)/MIL-110(Al) after degassing at 210 °C overnight.

#### 3.2.3.2 Low pressure gas sorption measurements

The experimental details regarding the measurement of the low pressure  $CO_2$  adsorption/desorption data are given in Chapter 2.5.1.

Two sets of experiments were conducted at 25 °C in order to determine the effect of vacuum activation on the CO<sub>2</sub> adsorption capacity. In one set, a sample of MIL-100(Al)/MIL-110(Al) was activated under vacuum at 220 °C overnight before performing the sorption experiment. In the other set, the vacuum activation step was omitted. The comparison of both pseudo-isotherms<sup>a</sup> at 25 °C (Figure 3.6) before and after vacuum activation shows that higher CO<sub>2</sub> adsorption capacities were obtained after the vacuum activation of the material, due to the stronger interaction of CO<sub>2</sub> with the CUS. In contrast to this, chemisorbed H<sub>2</sub>O molecules, in the non-activated sample, shield the aluminium cations in the partially hydrated MIL-100(Al)/MIL-110(Al) sample such that CO<sub>2</sub> can only interact with organic groups in the framework. These bind the CO<sub>2</sub> more weakly than the coordinatively unsaturated Al<sup>3+</sup> sites, resulting in lower adsorption capacities. Furthermore, the adsorption of CO<sub>2</sub> at 25 °C in MIL-100/MIL-110(Al) was almost reversible after vacuum activation, while the non-activated sample showed a hysteresis in the pseudo-isotherm at the same temperature.

<sup>&</sup>lt;sup>a</sup> The adsorption/desorption isotherms obtained from the low pressure  $CO_2$  sorption measurements are referred to as pseudo-isotherms, because they refer to data collected with a fixed 20 min equilibration time. Equilibration is not always achieved within this timeframe A true adsorption/desorption isotherm would require adsorption/desorption equilibrium to be obtained.

The pseudo adsorption/desorption isotherms on the vacuum activated sample were measured at 25, 45, 75 and 105 °C and are shown in Figure 3.6a. Increasing the CO<sub>2</sub> concentration led to a rise in  $CO_2$  adsorption capacity, whereas an increase in temperature resulted in a decrease in adsorption capacity. The change with temperature can be explained by the exothermicity of the physisorption process, which would lead to a reduction in the equilibrium concentration of adsorbed species at higher temperatures. Because none of the pseudo-isotherms appear to have reached CO<sub>2</sub> saturation, MIL-100(Al)/MIL-110(Al) would have a much higher CO<sub>2</sub> adsorption capacity at higher pressures. A slight hysteresis was observed at all temperatures, which suggests strong interaction of CO<sub>2</sub> with the CUS, especially at higher temperatures. To verify this result the heats of adsorption were estimated from the DTA signals (not shown here) at both 25 and 105 °C. The values were determined after 10 min of CO<sub>2</sub> adsorption at 0.05 bar, as the majority of  $CO_2$  had been adsorbed within this time. The heat of adsorption was found to be slightly higher at 105 °C (66 kJ mol<sup>-1</sup>) than at 25 °C (60 kJ mol<sup>-1</sup>), which would be consistent with more irreversible  $CO_2$  adsorption at the higher temperature. These high values also confirm the strong interaction of CO<sub>2</sub> with the CUS.



**Figure 3.6:** (a) Low pressure  $CO_2$  pseudo-isotherms on MIL-100(Al)/MIL-110(Al) before (red) and after vacuum activation (black). (b) TGA profiles of the low pressure  $CO_2$  sorption on vacuum activated MIL-100/MIL-110(Al).

The CO<sub>2</sub> adsorption capacity of 3.70 wt% at approximately 0.5 bar and 25 °C is higher than those reported for IRMOF-1 (2.11 wt%), MOF-177 (2.36 wt%), IRMOF-3 (2.95 wt%) and ZIF-8 (2.76 wt%) [6]. However, it is much lower than those of HKUST-1 (10.12 wt%) [7], MOF-74(Ni) [8] (~27.50 wt%) and MOF-74(Mg) (~32.00 wt%) [8]. The working capacity at each temperature was calculated from the difference in CO<sub>2</sub>

adsorption capacity at 0.05 and 0.15 bar and correspond to 0.66, 0.45, 0.24 and 0.14 wt% at 25, 45, 75 and 105 °C, respectively. The decrease in working capacity with increasing temperature is consistent with the reduction in equilibrium concentration of adsorbed species at higher temperatures. In order to be competitive with existing MEA scrubbing systems, the working capacity of the adsorbents must be in the range of 13.2 wt% and 17.6 wt% [9]. The application of MIL-100(Al)/MIL-110(Al) in a post-combustion  $CO_2$  capture process is therefore seen to be limited.

The TGA profiles for the low pressure  $CO_2$  sorption on the activated material are shown in Figure 3.6b. The stepwise profile is indicative of good adsorption/desorption kinetics and confirms that the equilibration time of 20 min was sufficient to achieve equilibrium. The cycling experiments discussed in the following section were therefore conducted at 25 °C. A slight baseline drift was observed, but the DTG was with 0.04 mg g<sup>-1</sup> within the limits of TG resolution (see Chapter 2.5.1). Heating the samples to 220 °C in flowing Ar (t>200 min, not shown in Figure 3.6b) resulted in the complete desorption of CO<sub>2</sub>.

#### 3.2.3.3 Cycling experiments

The CO<sub>2</sub> working capacity and regenerability of MIL-100(Al)/MIL-110(Al) were evaluated by monitoring pseudo-equilibrium adsorption uptakes over ten adsorption/ desorption cycles at 25 °C under dry and wet conditions, using the methodology detailed in Chapters 2.5.3 and 2.5.4. Results from the multicycle stability tests are illustrated in Figure 3.7. The mixed MOF material was activated under vacuum prior to the cycling experiments.

Equilibrium was achieved during the allowed 20 min under both conditions, which is important when evaluating the potential of an adsorbent for a VSA or PSA process. Under dry conditions, the average working capacity of 0.67 wt% is comparable to the 0.66 wt% derived from the low pressure CO<sub>2</sub> pseudo-isotherm. A downwards shift of the base line is observed during the dry cycling process, which is due to baseline drift over the timescale of the experiment. H<sub>2</sub>O saturation was not achieved over the duration of the H<sub>2</sub>O/Ar treatment (400 min), which led to an upwards drift of the baseline, due to the progressive adsorption of H<sub>2</sub>O during the cycling process. The working capacity in the wet gas stream was reduced (~0.46 wt%).

A comparison of the powder X-ray diffractogram of MIL-100(Al)/MIL-110(Al) after the wet cycling experiment with the simulated PXRD pattern of MIL-100(Al) and MIL-110(Al) is shown in Figure 3.10b. The diffraction pattern after the wet cycling experiment is consistent with the presence of both MIL-100(Al) and MIL-110(Al). The result suggests that the material exhibits a good hydrothermal stability under the cyclic conditions applied here.



**Figure 3.7:** TGA profiles for the dry (a) and wet (c) cycling experiments and the here from calculated adsorption and desorption capacities during dry (b) and wet (d) cycling experiments on MIL-100(Al)/MIL-110(Al).

## 3.2.3.4 High pressure gas sorption measurements

As  $CO_2$  saturation was not achieved at  $CO_2$  pressures of 0.5 bar, high pressure adsorption/desorption isotherms of  $CO_2$  were measured at 25, 45, 75 and 105 °C between 0

and 40 bar. The  $CO_2/N_2$  selectivity was also determined by measuring the sorption isotherm of N<sub>2</sub> (only at 25 °C and up to 40 bar).

Adsorption/desorption isotherms of  $CO_2$  measured at four different temperatures are shown in Figure 3.8. The reproducibility was confirmed by measuring a second  $CO_2$ isotherm at 25 °C, which is in good agreement with the first isotherm obtained at this temperature. At lower temperatures no hysteresis is observed in the studied pressure range. However, at 105 °C, hysteresis was observed together with an irreversible adsorbed component (~0.30 mol  $CO_2$  per mol CUS). This could be due to the strong interaction of  $CO_2$  with the CUS as suggested for the low pressure  $CO_2$  adsorption/desorption measurements.

Generally, the material displays good CO<sub>2</sub> adsorption capacity without saturation over the studied pressure and temperature range. The CO<sub>2</sub> adsorption capacity of 39.0 wt% at 25 °C and 15 bar is comparable to the ~42 wt% for MIL-101(Al)-NH<sub>2</sub> [10].The CO<sub>2</sub> adsorption capacity at 25 °C and 30 bar was found to be 51.4 wt%, which is higher than those reported for zeolite 13X (32.6 wt%) [11], zeolite NaX (34.3 wt%) [12], activated carbon NORIT R1 (44.0 wt%) and HKUST-1 (47.1 wt% at 40 bar) [12].

The sample mass of approximately 0.26 g was insufficient for obtaining reasonable  $N_2$  isotherms at higher temperatures. The comparison of the CO<sub>2</sub> and N<sub>2</sub> adsorption isotherm at 25 °C revealed, that N<sub>2</sub> saturation would be achieved at much higher pressures than CO<sub>2</sub> saturation, due to the almost linear increase in N<sub>2</sub> capacity over the studied pressure range. Clearly, the mixed MOF containing MIL-100(Al)/MIL-110(Al) shows a much greater affinity for CO<sub>2</sub> than for N<sub>2</sub> in the studied temperature and pressure range with "ideal" selectivities (ratio of single component adsorption capacities) ranging between 6 and 38 for CO<sub>2</sub> over N<sub>2</sub> in the studied pressure range. With increasing pressure the selectivity decreases and the highest selectivity of 38 is observed at a pressure of 0.9 bar.



**Figure 3.8:** High pressure (a) CO<sub>2</sub> isotherms at 25 ( $\blacksquare$ ), 45 ( $\blacklozenge$ ), 75 ( $\blacktriangle$ ) and 105 °C ( $\bullet$ ).and (b) N<sub>2</sub> isotherm at 25 °C. Closed symbols ( $\blacksquare$ ): adsorption, open symbols ( $\Box$ ): desorption.

#### 3.2.4 H<sub>2</sub>O stability of MIL-100(Al)/MIL-110(Al)

The low hydrothermal stability is a known problem for most MOFs, as discussed in Chapter 1.3.4. It is therefore necessary to study the  $H_2O$  stability of these materials in order to determine their practical usefulness as adsorbents. The procedure for the evaluation of the hydrothermal stability of MIL-100(Al)/MIL-110(Al) is described in Chapter 2.



**Figure 3.9:** (a) CO<sub>2</sub> adsorption/desorption isotherms at 25 °C before (black) and after (red) 30% H<sub>2</sub>O vapour adsorption/desorption. (b) H<sub>2</sub>O adsorption/desorption isotherm. Closed symbols ( $\blacksquare$ ): adsorption, open symbols ( $\square$ ): desorption.



**Figure 3.10:**Comparison of the PXRD pattern of MIL-100(Al)/MIL-110(Al) after (a) 30 %  $H_2O$  vapour adsorption (black) and (b) after wet cycling (black) with the simulated pattern for MIL-100(Al) [2] (red) and MIL-110(Al) [4] (blue).

After the high H<sub>2</sub>O uptake of 23 wt% at 25 °C and at 30 % RH, a decrease in CO<sub>2</sub> adsorption capacity from 19.2 wt% to 14.2 wt% at 5 bar was observed (Figure 3.9a). Hysteresis was observed in the H<sub>2</sub>O isotherm (Figure 3.9b), which is due to the strong interaction of the H<sub>2</sub>O molecules with the CUS. To understand the reason for the reduction in CO<sub>2</sub> adsorption capacity of 26%, PXRD was performed, which showed a decrease of the peak intensities at 20 values characteristic for MIL-110(Al). This result suggests that MIL-110(Al) was partially decomposed (Figure 3.10a), but MIL-100(Al) remained stable. It is therefore hypothesised, that a pure MIL-100(Al) sample might be obtainable after the treatment with H<sub>2</sub>O vapour at > 30 % RH and the subsequent purification of the MOF. However, this possibility was not investigated experimentally.

#### 3.2.5 Conclusion

A mixed MOF sample containing MIL-100(Al) and MIL-110(Al) in a 60:40 mixture was synthesised and characterised. MIL-100/MIL-110(Al) exhibited a good stability and regenerability during cycling processes under dry and wet conditions; however, the working capacities would need to be improved for it to be useful for industrial processes. The treatment with 1 % H<sub>2</sub>O vapour resulted in a 31 % decrease in working capacity, consistent with the progressive H<sub>2</sub>O adsorption during the cycling process. After the sorption of H<sub>2</sub>O at 30 % RH and the reactivation of the material, the CO<sub>2</sub> adsorption capacity was reduced by 26 % at 5 bar, which appears to be due to the partial decomposition of the MIL-110(Al) framework. Potential applications for MIL-100(Al) include high pressure CO<sub>2</sub> sorption and as an adsorbent for H<sub>2</sub>O vapour. Despite different

attempts to prepare pure MIL-100(Al), a mixture including MIL-110(Al) was obtained in all cases.

3.2.6 References

- [1] F. Jeremias, A. Khutia, S. K. Henninger, and C. Janiak, "MIL-100(Al, Fe) as water adsorbents for heat transformation purposes-a promising application," *Journal of Materials Chemistry*, 2012.
- [2] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.
- [3] T. K. Trung, N. A. Ramsahye, P. Trens, N. Tanchoux, C. Serre, F. Fajula, and G. Férey, "Adsorption of C5-C9 hydrocarbons in microporous MOFs MIL-100(Cr) and MIL-101(Cr): A manometric study," *Microporous and Mesoporous Materials*, vol. 134, pp. 134-140, 2010.
- [4] C. Volkringer, D. Popov, T. Loiseau, N. Guillou, G. Ferey, M. Haouas, F. Taulelle, C. Mellot-Draznieks, M. Burghammer, and C. Riekel, "A microdiffraction set-up for nanoporous metal-organic-framework-type solids," *Nat Mater*, vol. 6, pp. 760-764, 2007.
- [5] J. J. Low, A. I. Benin, P. Jakubczak, J. F. Abrahamian, S. A. Faheem, and R. R. Willis, "Virtual High Throughput Screening Confirmed Experimentally: Porous Coordination Polymer Hydration," *Journal of the American Chemical Society*, vol. 131, pp. 15834-15842, 2009.
- [6] A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, "Screening of Metal-Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach," *Journal of the American Chemical Society*, vol. 131, pp. 18198-18199, 2009.
- [7] P. Chowdhury, C. Bikkina, D. Meister, F. Dreisbach, and S. Gumma, "Comparison of adsorption isotherms on Cu-BTC metal organic frameworks synthesized from different routes," *Microporous and Mesoporous Materials*, vol. 117, pp. 406-413, 2009.
- [8] P. D. C. Dietzel, V. Besikiotis, and R. Blom, "Application of metal-organic frameworks with coordinatively unsaturated metal sites in storage and separation of methane and carbon dioxide," *Journal of Materials Chemistry*, vol. 19, pp. 7362-7370, 2009.
- [9] M. L. Gray, K. J. Champagne, D. Fauth, J. P. Baltrus, and H. Pennline, "Performance of immobilized tertiary amine solid sorbents for the capture of carbon dioxide," *International Journal of Greenhouse Gas Control*, vol. 2, pp. 3-8, 2008.
- [10] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, and F. Kapteijn, "Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties," *Chemistry of Materials*, vol. 23, pp. 2565-2572, 2011.
- [11] S. Cavenati, C. A. Grande, and A. E. Rodrigues, "Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures," *Journal of Chemical & Engineering Data*, vol. 49, pp. 1095-1101, 2004/07/01 2004.

G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. De Weireld,
A. Vimont, M. Daturi, and J.-S. Chang, "Why hybrid porous solids capture greenhouse gases?," *Chemical Society Reviews*, vol. 40, pp. 550-562, 2011.

## Declaration for Thesis Chapter

#### Postsynthetic modification of MIL-100(Fe): an adsorption study

#### Monash University

## **Declaration for Thesis Chapter 3.3**

#### **Declaration by candidate**

In the case of Chapter 3.3, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed samples; identified major	80 %
issues; developed interpretations; fully drafted paper and conclusion	

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co- authors only
Gregory P. Knowles	Aided method development (TGA), input to results analysis and manuscript revision	N/A
Alan L. Chaffee	Supervision, assisted interpretation of results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work\*.

Candidate's Signature

Main Supervisor's Signature

Date
30/10/2014

Date

30/10/2014

\*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

#### **3.3** Postsynthetic modification of MIL-100(Fe): an adsorption study

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author:

Fax:+61 3 990-54597

#### 3.3.1 Abstract

One approach for carbon capture is the use of adsorbents such as metal-organic frameworks (MOFs), which exhibit high surface areas, tuneable pore sizes and topologies. A series of ethylenediamine (ED) and polyethyleneimine (PEI) incorporated MIL-100(Fe) adsorbents with different loadings are reported for the first time in the present work. The samples were characterised by FTIR, PXRD, helium density, N<sub>2</sub> physisorption, elemental analysis and thermal decomposition. The effect of the amines was further evaluated by performing a series of low pressure (0 to 0.5 bar) CO<sub>2</sub> sorption at 25, 45 and 75 °C and ten cycle experiments under dry and wet conditions (1 vol% H<sub>2</sub>O) by varying the CO<sub>2</sub> partial pressure from 0.05 to 0.15 bar. The results showed that improvements of the CO<sub>2</sub> adsorption capacities were achieved in the low pressure CO<sub>2</sub> sorption experiments and that the majority of the tested materials exhibited good regenerability under dry cycling conditions. During the wet cycling process a decline in working capacity was found due to H<sub>2</sub>O uptakes of more than 6 wt%. This effect was smaller at higher cycling temperatures. PXRD studies after the wet cycling showed that the materials were hydrothermally stable. The potential of MIL-100(Fe) to selectively adsorb and separate CO<sub>2</sub> was confirmed by high pressure CO<sub>2</sub> and N<sub>2</sub> sorption measurements (T: 25-105 °C, p: 0-40 bar).

#### 3.3.2 Introduction

MOFs have recently emerged as a class of very promising organic-inorganic hybrid materials for diverse applications like gas storage, gas/vapour separation, catalysis and drug storage and delivery [1, 2]. The structures of these crystalline porous materials are based upon metal based nodes ( $AI^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ) coordinated to specific functional groups of organic linkers of various structure and size [3, 4]. Properties such as high pore volumes and surface areas, ordered and well characterised porous structure and

adjustable chemical functionality make MOFs excellent candidates for carbon dioxide capture [5].

The application of MOFs for post-combustion capture presents some challenges. Firstly, the majority of the MOFs reported to date exhibit low H<sub>2</sub>O stabilities. In these cases, the presence of H<sub>2</sub>O vapour in flue gas will result in phase transformations, collapse of the framework structures and reduced gas sorption capacities [6-8]. For industrial applications it would be beneficial to use hydrothermally stable MOFs, such as ZIF-8, MIL-100 and MIL-101, which are able to adsorb CO<sub>2</sub> in the presence of H<sub>2</sub>O and therefore help to reduce the capture costs [9-15]. In addition to the stability of the framework structures, H<sub>2</sub>O has shown to have a promoting effect on the CO<sub>2</sub> uptake in MIL-100(Fe) and MIL-101(Cr). Soubeyrand-Lenoir et al. reported a fivefold increase in the CO<sub>2</sub> capacity from 2.2 wt% to 10.5 wt% in MIL-100(Fe) at 40 % RH [16]. While the treatment of MIL-101(Cr) with 10 % RH caused an increase in CO<sub>2</sub> capacity from 2.16 wt% to 2.24 wt%, higher relative humidities resulted in reduced uptakes. This reduction was associated with the competitive adsorption of H<sub>2</sub>O and CO<sub>2</sub> [17]. Secondly, the CO<sub>2</sub> uptakes in most MOFs are limited at pressures relevant to post-combustion capture.

Higher CO<sub>2</sub> selectivities have been reported for MOFs containing coordinatively unsaturated sites (CUS), which induce strong local interactions with CO<sub>2</sub> due to its higher quadrupole moment and polarisibility compared to N<sub>2</sub> [18-21]. These Lewis acid sites allow the incorporation of amines such as ethylenediamine (ED), diethlyenediamine (DETA) and polyethyleneimine (PEI), which have been shown to further enhance the CO<sub>2</sub> capacities and the CO<sub>2</sub>/N<sub>2</sub> selectivities [5, 22, 23].



**Figure 3.11:** Schematic presentation of amine modification of the trimeric unit in MIL-100(Fe).

In this study, we report a series of ethylenediamine (ED) and polyethyleneimine (PEI) modified MIL-100(Fe) materials for  $CO_2$  capture. The supertetrahedral building blocks of

MIL-100(Fe) are built up from trimeric units of octahedral Fe(III) oxide which are connected by trimesate ligands. The corresponding three-dimensional framework contains mesocages (2.5 to 2.9 nm) which are accessible though microporous windows (0.5 to 0.9 nm) [24-26]. MIL-100(Fe) exhibits a high BET surface area (1754 m<sup>2</sup> g<sup>-1</sup>) [27], high porosity, good thermal and chemical stability, as well as good H<sub>2</sub>O stability and the presence of CUS. Furthermore, the framework contains environmental benign and inexpensive building blocks, which improve the prospect of usability on a technical scale [28].

The concept of the PSM of MIL-100(Fe) is shown in Figure 3.11. While in the assynthesised form the terminal molecules on two of the three metal octahedra are H<sub>2</sub>O molecules, the third is connected to an OH anion. The terminal H<sub>2</sub>O molecules can be removed by degassing the sample at 150 °C under vacuum, leading to Fe<sup>III</sup> CUS [29]. These Lewis acid sites can then be reacted with amines. In the present study, various loadings of ED and PEI were used and their impact on the performance in low pressure CO<sub>2</sub> adsorption/desorption (T: 25-75 °C, p: 0-0.5 bar) and in ten cycle experiments at 25 or 45 °C under dry and wet conditions (1 vol% H<sub>2</sub>O) was investigated. The CO<sub>2</sub> cycling simulated a vacuum swing adsorption (VSA) process by varying the CO<sub>2</sub> partial pressures between 0.05 and 0.15 bar. High pressure CO<sub>2</sub> and N<sub>2</sub> adsorption and desorption measurement were conducted at 25 to 105 °C to determine the potential application of MIL-100(Fe) in high pressure separation processes.

## 3.3.3 Experimental section

#### 3.3.3.1 Chemicals

Acetone (99 %, Merck), ethylenediamine (99 %, Aldrich), iron(III) chloride hexahydrate (99 %, Merck), methanol ( $\geq$  99.8 %, Merck), polyethyleneimine (423 g mol<sup>-1</sup>, Aldrich), sodium bicarbonate ( $\geq$  99.7 %, Ajax Chemicals), sulphuric acid (98 % AR grade, Merck), toluene (Merck), trimesic acid (95 %, Sigma Aldrich), argon (high purity, BOC and Air Liquide), carbon dioxide (Food grade, Coregas), helium (high purity, Air Liquide), liquid nitrogen (BOC and Air Liquide) and nitrogen (high purity, Air Liquide).

All reagents were used without further purification.

#### 3.3.3.2 Preparation of MOFs

#### 3.3.3.2.1 Synthesis of Me<sub>3</sub>BTC

Trimethyl-1,3,5-benzenetricarboxylate (Me<sub>3</sub>BTC) was synthesised by a method akin to that reported by Kathiresan et al. [30]. In a typical synthesis, a suspension of 10.01 g (47.6 mmol) of trimesic acid in 30 mL methanol was heated to reflux and 1.6 mL of concentrated sulphuric acid was added. After 6 h of refluxing, the mixture was cooled to room temperature, slowly neutralized with saturated sodium bicarbonate solution, filtered, washed with excess H<sub>2</sub>O and dried at 105 °C. The yield of the white powder was determined to be 9.75 g (81.1%).

#### 3.3.3.2.2 Synthesis of MIL-100(Fe)

MIL-100(Fe) was synthesized by the following method adapted from Canioni et al. [31]. A mixture of 1.63 g iron(III) hexahydrate (6.00 mmol) and 1.39 g trimethyl-1,3,5-benzenetricarboxylate (5.50 mmol) dispersed in 50 mL H<sub>2</sub>O was heated for 72 h at 130 °C in a Teflon® lined autoclave. The orange solid was recovered by filtration, washed with acetone and dried at room temperature under air.

#### 3.3.3.2.3 PSM of MIL-100(Fe)

MIL-100(Fe) was then modified by grafting ED and PEI onto unsaturated Fe(III) sites using two different approaches. The theoretical amine loadings and the amine loadings after the vacuum activation are listed in Table 1.

The first method applied for the modification of MIL-100(Fe) with ED was described by Hwang et al. on MIL-101(Cr) [32]. Prior to the PSM, MIL-100(Fe) was dehydrated at 150 °C overnight. In a typical synthesis, 20  $\mu$ L or 25  $\mu$ L of ED was added to a suspension of 0.50 g dehydrated MIL-100(Fe) in 30 mL anhydrous toluene. After refluxing for 12 h, the suspension was cooled to room temperature and the product was recovered by filtration. The PSM materials were washed with distilled H<sub>2</sub>O/ethanol and then dried at room temperature.

The PEI modifications of MIL-100(Fe) were prepared using the wet impregnation approach described by Lin et al. [23]. In a typical synthesis, PEI (423 g mol<sup>-1</sup>) was dissolved in 1 mL methanol and stirred for 10 min, before 0.2 g of activated MIL-100(Fe) was added. The mixture was purged with  $N_2$  overnight under room temperature. The PEI modified samples were then activated at 110 °C for 12 h under vacuum. The amine

loading, which is given at the end of each sample name, was calculated with the following equation:

$$Amine \ loading = \frac{mass_{amine}}{mass_{MIL-100(Fe)}} \times 100\%$$
(3.1)

The theoretical amine loadings and the amine loadings after the vacuum activation of all materials are listed in Table 3.2. The ED modified MIL-100(Fe) samples are denoted as MIL-100(Fe)-ED-2.5 and MIL-100(Fe)-ED-3. Four samples with different PEI loadings were prepared and were denoted as MIL-100(Fe)-PEI-3, MIL-100(Fe)-PEI-22, MIL-100(Fe)-PEI-25 and MIL-100(Fe)-PEI-50. However, CO<sub>2</sub> adsorption studies on the PEI-50 sample showed very low adsorption capacities and this sample was therefore not characterised further.

**Table 3.2:** An overview of the theoretical amine loadings, the loadings after vacuum activation (evac) and the corresponding molar loadings of the CUS.

Amine	Theoretical	Loading after	Loading after evac/
	loading / wt%	evac/ wt%	mol(amine)/mol(CUS)
ED	3.6	2.5	0.14
ED	4.5	3	0.16
PEI	5	3	0.02
PEI	25	22	0.17
PEI	30	25	0.19

#### 3.3.3.3 Characterisation of MIL-100(Fe) before and after PSM

MIL-100(Fe) samples were characterised before and after PSM with ED and PEI by elemental analysis,  $N_2$  adsorption/desorption at -196 °C, helium density, scanning electron microscopy (SEM), powder X-ray diffraction (PXRD), Fourier-transform infra-red spectrometry (FTIR) and thermal decomposition.

Elemental analysis was carried out in the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

The BET surface areas and pore volumes of MIL-100(Fe) before and after amine modification were determined by nitrogen adsorption/desorption at -196 °C using a TriStar II 3020 (Micromeritics) gas sorption analyser. Prior to the analysis, the samples were activated under vacuum in a Micromeritics VacPrep 061 degasser at 90 °C (ED-2.5, ED-3), 110 °C (PEI-3, PEI-22, PEI-25) and 150 °C (MIL-100(Fe)) for at least 12 h. The BET

surface areas and pore volumes were estimated at relative pressures between 0.01 to 0.2 and at  $p/p_0=0.99$ , respectively.

Helium densities of the activated samples were measured on the pycnometer AccuPyc 1340 (Micromeritics).

SEM images of MIL-100(Fe), MIL-100(Fe)-PEI-3 and MIL-100(Fe)-PEI-50 were recorded at an accelerating voltage of 15 kV using a JEOL 7001F field emission scanning electron microscope.

PXRD measurements were conducted on a Bruker D8 Focus powder diffractometer equipped with a copper anode ( $\lambda_{CuK\alpha}$  =1.5418 Å). The theoretical PXRD pattern of the crystal structure of MIL-100(Fe) [33] was simulated using the module "Reflex Tools" in Materials Studio 6.0 [34].

FTIR spectra were measured via an Agilent Cary 630 Diamond ATR in the spectral range of 650 to 4000 cm<sup>-1</sup>.

The thermal decomposition of the materials was measured using a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. The samples were heated to 110 °C under flowing Ar for 30 min. The gas flow was then changed to an Ar/air mixture and the temperature was maintained at 110 °C for further 30 min, before increasing the temperature to 900 °C with a heating ramp of 2 °C min<sup>-1</sup>. The Ar/air flow was maintained for 15 min at 900 °C, after which it was replaced by pure Ar. After 15 min at 900 under flowing Ar, the system was cooled to 20 °C.

## 3.3.3.4 Low pressure gas sorption experiments on MIL-100(Fe) before and after PSM

Low pressure CO<sub>2</sub> isotherms at 25, 45 and 75 °C were recorded on a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. After activating 10 to 30 mg of MOF at 90, 110 or 150 °C under Ar (70 mL min<sup>-1</sup>) for 1 h, the temperature was adjusted to the desired sorption temperature in an Ar atmosphere. The thermoanalyser was then allowed to equilibrate for 20 min before the gas flow was changed from pure Ar to an Ar/CO<sub>2</sub> mixture. The CO<sub>2</sub> sorption was measured by first increasing the CO<sub>2</sub> partial pressure in five steps (0.02, 0.05, 0.15, 0.30 and 0.50 bar), before decreasing the partial pressure in reverse order. At the end of the experiment the MOFs were reactivated at 90, 110 or 150 °C for 30 min under flowing Ar in order to desorb the CO<sub>2</sub> completely. Fresh samples

were used for each experiment. The measurements were repeated using approximately 30 mg of neat PEI. In contrast to the activation procedure applied for the MOFs, PEI was activated at 110 °C under Ar atmosphere for 2 h.

The heat flow (DTA) associated with the change in mass was also recorded and analysed.

#### 3.3.3.5 Cycling experiments on MIL-100(Fe) before and after PSM

Dry and wet cycling experiments were conducted using a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. All samples were activated under vacuum overnight (T=90, 110 or 150 °C) prior to the analysis. After activating 10 to 30 mg of MOF under Ar at 90, 110 or 150 °C for 1 h, the samples were cooled to 25 °C or 45 °C. The CO<sub>2</sub> partial pressure was varied between 0.05 and 0.15 bar over 10 cycles, allowing 20 min equilibration time for each adsorption and each desorption step. For the wet experiments, the MOFs were treated with wet Ar (1 vol% H<sub>2</sub>O) prior to the cycling of a wet CO<sub>2</sub>/Ar mixtures (1 vol% H<sub>2</sub>O/CO<sub>2</sub>/Ar). The time for the H<sub>2</sub>O saturation step varied between ~6 h (PSM materials) and 10 h (MIL-100(Fe)).

#### 3.3.3.6 High pressure gas sorption experiments on MIL-100(Fe)

 $CO_2$  and  $N_2$  isotherms at 25 to 105 °C up to 40 bar were measured via a High Pressure Volumetric Analyser 200 (HPVA) from Micromeritics. All isotherms were obtained on a single sample, which was reactivated at 150 °C under vacuum in between each isotherm.

#### 3.3.4 Results and discussion

#### 3.3.4.1 Characterisation of MIL-100(Fe) before and after PSM

A summary of the carbon, hydrogen and nitrogen content, BET surface areas, total pore volumes and helium densities is given in Table 3.3. The theoretical carbon (33.22 %) and hydrogen (1.70 %) contents of dehydrated MIL-100(Fe) were calculated from the empirical formula  $Fe_3O(OH)(H_2O)_2[C_6H_3(CO_2)_3]_2$ . The measured carbon and hydrogen contents correspond to the presence of approximately 18 lattice  $H_2O$  molecules. The PSM of MIL-100(Fe) led to an increase in the nitrogen content, consistent with the incorporation of the amines.

The N<sub>2</sub> sorption isotherms at -196 °C are shown in Figure 3.12a. At relative pressures below 0.01 the sharp rise with pressure indicates the supertetrahedra are being filled. With increasing pressure, N<sub>2</sub> was adsorbed into the medium cavities ( $p/p_0=0.09$ ) and then the larger cavities ( $p/p_0=0.16$ ) [35]. This stepwise profile was still apparent after the

incorporation of ED and 3 wt% PEI, due to the comparatively low amine loadings. At higher PEI loadings these low  $p/p_0$  steps are no longer visible in the adsorption isotherm, consistent with the filling of these cavities with amines. The BET surface area of MIL-100(Fe) was slightly lower than the 1754  $m^2 g^{-1}$  estimated by Shi and co-workers [27]. presumably due to differences in the methods of synthesis and purification. In contrast to the synthesis procedure applied here, MIL-100(Fe) was prepared at 95 °C under reflux and purified in hot H<sub>2</sub>O [27]. Despite the higher BET surface area (literature), their estimated pore volume of 0.80 g cm<sup>-3</sup> was lower [27]. A BET surface area of 1626 m<sup>2</sup> g<sup>-1</sup> and a pore volume of 0.79 g cm<sup>-3</sup> were reported by Huo et al. [36]. The total pore volume of MIL-100(Fe) determined in this work was in good agreement with the 0.88 cm<sup>3</sup> g<sup>-1</sup> reported by Canioni et al. [31]. The incorporation of ED and PEI was confirmed by the decrease in BET surface area and pore volume (Table 3.3). As expected, higher amine loadings resulted in lower surface areas and pore volumes. Interestingly MIL-100(Fe)-PEI-3 exhibited a higher surface area and pore volume than both ED modified materials at similar wt% loadings. This result can be understood in terms of the significantly lower molar PEI loading per CUS (Table 3.2) than in the case of ED. The molar PEI loading per CUS in MIL-100(Fe)-PEI-22 is comparable with the molar ED loading in MIL-100(Fe)-ED-3, but here the surface areas differ significantly. This result suggests that, at this higher loading, the PEI tended to block the pores, thus reducing the surface areas and pore volume more than ED, which was probably located entirely inside them. Such a location of the PEI molecules would likely make them a barrier to the diffusion of adsorbing molecules.

The theoretical maximum loadings were calculated by dividing the total pore volume of MIL-100(Fe) by the density of ED (0.899 g cm<sup>-3</sup>) [37] or PEI (1.07 g cm<sup>-3</sup>) [38]. On this basis, it can be calculated that loadings of 99 wt% ED and 83 wt% PEI would completely fill the pores. The ED loadings applied in this work were considerably lower than the theoretical maximum loading. At the beginning of this study, a sample containing 50 wt% PEI was prepared and the applicability for the adsorption of CO<sub>2</sub> adsorption was determined. However, low CO<sub>2</sub> adsorption capacities at 25-75 °C indicated that the pores were not accessible. A comparison of the SEM images of MIL-100(Fe), MIL-100(Fe)-PEI-3 and MIL-100(Fe)-PEI-50 showed that a loading of 50 wt% resulted in a complete coating of the exterior of the particles (Figure 3.17), suggesting there has been incomplete penetration. By comparison the incorporation of 3 wt% PEI had no obvious impact on the

morphology of the particles. For this reason, we focused on PEI loadings of less than 50 wt%.

MOF	%C	%H	%N	<b>BET surface</b>	Total pore	Helium
				area / $m^2 g^{-1}$	volume/	density/
					$cm^3 g^{-1}$	g cm <sup>-3</sup>
MIL-100(Fe)	21.63	3.95	-	1677	0.89	1.949
	$\pm 0.20$	$\pm 0.32$				$\pm 0.0099$
ED-2.5	26.28	3.78	0.93	863	0.50	1.8695
	$\pm 0.10$	$\pm 0.24$	$\pm 0.07$			$\pm 0.0055$
ED-3	31.25	1.09	2.92	832	0.46	1.8560
	$\pm 0.29$	$\pm 0.07$	$\pm 0.17$			$\pm 0.0070$
PEI-3	24.34	4.05	0.54	1078	0.60	1.8569
	$\pm 0.60$	$\pm 0.48$	$\pm 0.35$			$\pm 0.0044$
<b>PEI-22</b>	31.46	4.36	5.35	268	0.15	1.6881
	$\pm 0.14$	$\pm 0.37$	$\pm 0.21$			$\pm 0.0016$
PEI-25	32.70	4.63	7.63	259	0.13	1.6580
	$\pm 0.71$	$\pm 0.52$	$\pm 0.86$			$\pm 0.0016$

**Table 3.3:** Comparison of results obtained by Elemental analysis,  $N_2$  physisorption at -196 °C and helium density measurements.

The helium densities (Table 3.3) of the amine modified samples were lower than those of MIL-100(Fe), which also confirms the incorporation of ED and PEI into the framework. Increasing the amine loadings resulted in further reductions of the densities, as expected, due to the lower densities of neat ED and PEI in comparison with the helium density of MIL-100(Fe).

The stability of the MIL-100 framework after the modification with ED and PEI was investigated via PXRD. The powder diffractograms of MIL-100(Fe) and of the PSM materials are shown in Figure 3.12b. The phase purity of the synthesised MIL-100(Fe) was confirmed by comparing the experimental with the theoretical diffractogram [39] (Figure 3.18). Although the peak intensities decrease slightly in the presence of PEI in the framework, the diffraction pattern was still clearly observed. This result is consistent with previous reports that have shown a reduction in diffraction intensity due to the incorporation of amines [23, 40]. The particular low intensity of the MIL-100(Fe)-PEI-22 diffractogram relative to the other two PEI samples is thought to be due to the relatively

small amount of sample used for this particular analysis. The results of the PXRD studies confirm the structural integrity and the chemical stability of the MIL-100(Fe) structure upon amine treatment.



- MIL-100(Fe) – ED-2.5 - ED-3 - PEI-3 – PEI-22 – PEI-25

**Figure 3.12:** (a)  $N_2$  isotherms on MIL-100(Fe) before and after ED and PEI modification at -196 °C. (b) PXRD of MIL-100(Fe) before and after PSM.

The FTIR spectra of MIL-100(Fe) and the PSM samples are compared in Figure 3.20. Two bands at 1710 cm<sup>-1</sup> (asymmetric C=O stretch) [26] and 1356/1280 cm<sup>-1</sup> (C-O stretch) [31] indicate the presence of residual free trimesic acid, which decreased in intensity after the modification with amines. This suggests that free trimesic acid is probably hydrogen bonding with the amine (ED or PEI) and is just diluted by the added amine. The bands at 1620, 1561 and 1435 cm<sup>-1</sup> correspond to the adsorbed H<sub>2</sub>O, the C=C and the O-C-O stretching vibrations, respectively [17]. Despite the presence of ED in the structure no obvious changes in the FTIR pattern were observed at this low level of incorporation. It may be that the doublet (at approximately 3384 and 3507 cm<sup>-1</sup>) [41] expected from the amine moieties is overlapped by residual moisture in the sample, which can be seen as the broad band centred at 3300 cm<sup>-1</sup>. In contrast to this, the appearance of two new bands at 2929 cm<sup>-1</sup> (asymmetric CH<sub>2</sub> stretch) and 2801 cm<sup>-1</sup> (symmetric CH<sub>2</sub> stretch) [22], confirms the presence of PEI.

The thermal stability of the samples was determined by thermal decomposition measurements between 20 and 900 °C. MIL-100(Fe) showed an initial weight loss of approximately 30 % which corresponds to the loss of ~ 16 molecules of lattice H<sub>2</sub>O (Figure 3.19). At temperatures between 115 °C and 300 °C, the H<sub>2</sub>O molecules

coordinated to the iron trimers were removed (~ 5 to 6 %). This is in good agreement with the expected weight loss of 5.54 % calculated from the empirical formula  $Fe_3O(OH)(H_2O)_2$  [C<sub>6</sub>H<sub>3</sub>(CO<sub>2</sub>)<sub>3</sub>]<sub>2</sub>. The decomposition of the framework occurred above 300 °C. The decomposition profile is in reasonable good agreement with literature data (Figure 3.19) [31]. A slight difference in the decomposition profile was observed at low temperatures, consistent with the difference in the gas flow and heating rate programs employed. The literature used air flow over the entire temperature range, while the sample in this work was heated to 110 °C under flowing Ar. After the PSM with ED and PEI, the weight loss prior to the decomposition of the MIL-100(Fe) frameworks (300 °C), is consistent with the loss of ED and PEI. In contrast to MIL-100(Fe), the complete collapse of the framework was observed to occur more slowly and was not complete until above 500 °C [31].

## 3.3.4.2 Low pressure gas sorption experiments on MIL-100(Fe) before and after PSM

The effect of ED and PEI on the CO<sub>2</sub> adsorption and desorption of MIL-100(Fe) was investigated in the temperature range of 25 to 75 °C and in the pressure range of 0 to 0.5 bar. Additionally, the results after the PSM using PEI are compared to those of neat PEI in order to evaluate the efficiency of the modifications. The CO<sub>2</sub> adsorption and desorption pseudo-isotherms of neat ED were not measured as this was problematic, due to the higher volatility of the amine.

#### 3.3.4.2.1 MIL-100(Fe) before PSM

The CO<sub>2</sub> pseudo-isotherms of MIL-100(Fe) at 25, 45 and 75 °C are shown in Figure 3.13. A decrease in CO<sub>2</sub> adsorption capacity with increasing temperature was observed, consistent with the reduction in equilibrium concentration of adsorbed species due to the higher kinetic energies at higher temperatures. Because CO<sub>2</sub> saturation was not achieved in the studied pressure and temperature range, MIL-100(Fe) would have a much higher CO<sub>2</sub> adsorption capacity at higher pressures. Equilibrium adsorption was almost achieved at all temperatures, which implies that the MOF exhibits good adsorption/desorption kinetics. This is important for the performance in a cycling process. Nevertheless a slow and slight increase in CO<sub>2</sub> adsorption continued to develop during the 20 min equilibration at each step. Hysteresis of the pseudo-isotherms indicated some irreversibility of the CO<sub>2</sub> adsorption in MIL-100(Fe), especially at 45 and 75 °C, which may be due to

chemisorption. Similar hysteresis has also been reported for HKUST-1, and is thought to be due to strong interactions of the  $CO_2$  with the CUS [42].

The CO<sub>2</sub> adsorption capacity in MIL-100(Fe) of 3.10 wt% (0.23 mol(CO<sub>2</sub>)/mol(CUS)) is higher than those of IRMOF-1 (2.11 wt%) and MOF-177 (2.36 wt%) [43] at 25 °C and 0.5 bar. In comparison with NaX (17.7 wt%) [16], MOF-74(Ni) (22 wt%) [44] and HKUST-1 (4 wt%) [45], the  $CO_2$ adsorption capacity of 1.25 wt% (0.09 mol(CO<sub>2</sub>)/mol(CUS)) is significantly lower under the same conditions (25 °C, 0.2 bar). The differences in the CO<sub>2</sub> adsorption capacities are presumably due to different adsorption energies. The comparison of the CO<sub>2</sub> adsorption capacities in the different MOFs suggests that further improvements of the adsorption capacities in MIL-100(Fe) are required. Improvement of the adsorption capacities of MIL-100(Fe) were therefore sought via PSM using ED and PEI.

#### 3.3.4.2.2 Effect of ED loading

The CO<sub>2</sub> pseudo-isotherms of MIL-100(Fe) before and after the modification with ED at 25, 45 and 75 °C are compared in Figure 3.13. In the studied pressure range no CO<sub>2</sub> saturation was observed in PSM materials, consistent with the results obtained for the neat MOF. The rise in CO<sub>2</sub> adsorption capacity (Figure 3.13, left) is also gradual instead of steep after the PSM with ED, consistent with the low amine content. Irreversible adsorption was also observed, which implies strong interactions between CO<sub>2</sub> and the free CUS and/or the amine groups. In contrast to this, Demessence et al. reported a steep increase in CO<sub>2</sub> adsorption capacities in ED (59 wt%) modified H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>] [46], due to the chemisorption of CO<sub>2</sub> on the amine groups [5]. This suggests that an increase in ED loading in MIL-100(Fe) will presumably result in a change of the pseudo-isotherm shape.

The CO<sub>2</sub> adsorption capacity decreased with increasing temperature, consistent with the expected behaviour for classical adsorption where a reduction in the equilibrium concentration of adsorbed species is caused by the higher kinetic energies at higher temperature. PSM of MIL-100(Fe) with 2.5 wt% ED resulted in improved CO<sub>2</sub> adsorption capacity at 25 °C over the entire pressure range studied. At 25 °C and 0.5 bar a rise in CO<sub>2</sub> adsorption capacity of 0.19 wt% was observed in MIL-100(Fe)-ED-2.5, which corresponds to 0.21 mmol of CO<sub>2</sub> per mmol of ED. In contrast to this, MIL-100(Fe)-ED-3 exhibited comparable CO<sub>2</sub> adsorption capacities up to 0.15 bar and reduced adsorption capacities at

pressures above 0.15 bar. At 45 and 75 °C on the other hand, the  $CO_2$  adsorption capacities in the MIL-100(Fe)-ED-3 were improved at least up to 0.3 bar, but the adsorption capacities in MIL-100(Fe)-ED-2.5 were similar or lower than those of MIL-100(Fe). These results suggest that the limited amount of amine sites is limiting the improvement in  $CO_2$ adsorption capacities.

The TGA profiles show that the equilibration time of 20 min was sufficient to reach stable uptakes during the adsorption and desorption steps. Therefore, the adsorption kinetics of the ED modified materials make these MOFs applicable for cycling processes at all studied temperatures. The cycling temperature for these PSM materials was therefore selected to be 25 °C, due to good adsorption kinetics and high adsorption capacities.

The heats of adsorption were calculated from the DTA signals (Figure 3.21) at 25 °C and 0.02 bar. The values stated here were determined after 10 min of adsorption, as the majority of CO<sub>2</sub> had been adsorbed within this time for all samples, whether before or after PSM. The heats of adsorption decreased in the order MIL-100(Fe)-ED-3 (42 kJ mol<sup>-1</sup>) > MIL-100(Fe) (39 kJ mol<sup>-1</sup>) > MIL-100(Fe)-ED-2.5 (37 kJ mol<sup>-1</sup>). These values indicate a moderate interaction between CO<sub>2</sub> and the CUS in MIL-100(Fe). Heats of adsorption are likely co-occurring in MIL-100(Fe)-ED-2.5 and MIL-100(Fe)-ED-3 involving both CUS and amine sites. Similarly low heats of adsorption have been reported and such a mixed adsorption mechanism has been suggested for MOF-74(Ni) before (41.5 kJ mol<sup>-1</sup> at 0.01 bar) and after PSM (40.5 kJ mol<sup>-1</sup> at 0.033 mbar) with piperazine [47, 48].



**Figure 3.13:** CO<sub>2</sub> pseudo-isotherms of MIL-100(Fe) before and after ED modification (left) at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ) and 75 °C ( $\blacktriangle$ ). TGA profiles of the low pressure CO<sub>2</sub> sorption (right). Closed symbols ( $\blacksquare$ ): adsorption and open symbols ( $\Box$ ): desorption.
## 3.3.4.2.3 Effect of PEI loading

The comparison of the low pressure pseudo-isotherms and the TGA profiles of MIL-100(Fe), its PEI modifications and neat PEI are shown in Figure 3.14.

The pseudo-isotherms of neat PEI show an increase of the CO<sub>2</sub> adsorption capacity with increasing temperature. This is consistent with the improved mobility of PEI and the better CO<sub>2</sub> diffusivity at higher temperatures. CO<sub>2</sub> saturation was almost achieved in the studied pressure range, which suggests that the neat amine is not applicable for high pressure separation processes. The pseudo-isotherms exhibit strong hysteresis at all temperatures, due to the chemisorption of  $CO_2$ . It is notable that an increase in  $CO_2$  adsorption capacity is actually observed upon lowering the CO<sub>2</sub> partial pressure at all temperatures. This indicates that the sorption kinetics of neat PEI are too slow to achieve equilibrium adsorption on the timescale of the experiment. The progressive adsorption during each equilibration step is shown in the TGA profiles at the different temperatures. Partial desorption of CO<sub>2</sub> was only observed at 75 °C as the pressures was reduced below 0.02 bar. The irreversible adsorption of CO<sub>2</sub> on PEI confirms the chemisorption of the adsorbate. Extending the equilibration time will eventually result in an equilibration of the amount adsorbed, but this extension is likely to be disadvantageous for industrial applications. These results suggest that neat PEI would not applicable for cycling processes (at least on the timescale examined here).

In contrast to neat PEI, the PEI modified materials behaved more regularly. The decrease in adsorption capacity observed with increasing temperature is consistent with the results observed for MIL-100(Fe) before and after PSM with ED. However, at 25 and 45 °C the adsorption of  $CO_2$  exhibited some irreversibility. This suggests that  $CO_2$  is strongly interacting with either the free CUS and/or the free amine sites.

The increase in PEI loading from 3 wt% to 22 wt% resulted in a decrease in adsorption kinetics at 25 °C, as a result of poorer diffusion with the increase in PEI loading (Figure 3.14, right). However, the PEI modified materials all exhibited better adsorption kinetics than the neat amine at all temperatures studied. This result suggests that the PSM materials could be applicable in a vacuum swing adsorption (VSA) process.





**Figure 3.14:** CO<sub>2</sub> pseudo-isotherms (left) and TGA profiles (right) of MIL-100(Fe), its PEI modification and neat PEI at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ) and 75 °C ( $\blacktriangle$ ).Closed ( $\blacksquare$ ) and open ( $\Box$ ) symbols represent adsorption and desorption, respectively.

MIL-100(Fe)-PEI-3 was the only PEI modified MIL-100(Fe) that showed a slight increase in CO<sub>2</sub> adsorption capacity, relative to the parent MOF, over the entire pressure range at 25 °C. Small improvements were observed at low pressures in the PEI-22 modified sample at 25 °C and 45 °C. In the case of MIL-100(Fe)-PEI-25 no increased adsorption capacities were apparent. At higher temperatures, the incorporation of amines led to reductions in CO2 adsorption capacities compared to MIL-100(Fe). Assuming the adsorption of one PEI molecule per CUS, it can be calculated that a maximum of 20 % of all CUS would be occupied by PEI at the highest loading. Hence, most of the CUS sites could, in principle, be available for  $CO_2$  adsorption. The decrease in  $CO_2$  adsorption capacity at higher temperatures then suggests that the PEI acts as a diffusion barrier for access to the preferential adsorption sites. Furthermore, neat PEI outperformed the PEI modified materials at 75 °C with an adsorption capacity of 3.50 wt% at 0.5 bar. It can therefore be concluded, that the small extent of improvement in the CO<sub>2</sub> adsorption capacities in MIL-100(Fe)-PEI-3 and the reduction in CO<sub>2</sub> adsorption capacities after the PSM with 22 and 25 wt% PEI were possibly due to the low pore volumes after the PSM and the low amine loading in case of MIL-100(Fe)-PEI-3.

The theoretical maximum PEI loading (see Section 3.3.4.1) implied that the PEI loadings higher than those reported here might have been achieved. However, testing a sample loaded with 50 wt% PEI resulted in even lower adsorption capacities (Figure 3.22, details are not reported). The SEM evidence (Figure 3.17) clearly shows that PEI coats the surface. While it is likely that the PEI is also present within the pores, it is only the surface PEI that would be available for  $CO_2$  adsorption. This surface PEI probably blocks access to the PEI below the surface and within the substrate, at least on the time scale of the experiments reported here. This would explain why such low  $CO_2$  adsorption was obtained for a high PEI loading.

The DTA profiles at 25 °C are shown in the supplementary material (Figure 3.21). The heat of adsorption for MIL-100(Fe)-PEI-3 was calculated at 0.02 bar and after 10 min of adsorption. The so determined value of 55 kJ mol<sup>-1</sup> is higher than the values for MIL-100(Fe) and the ED modified materials determined at the same conditions. This result suggests that  $CO_2$  is chemisorbed onto accessible amine sites of the PEI. Because of the low magnitude of  $CO_2$  adsorption in MIL-100(Fe)-PEI-22 and MIL-100(Fe)-PEI-25, the heats of adsorption could not be determined.

#### 3.3.4.3 Cycling experiments on MIL-100(Fe) before and after PSM

The CO<sub>2</sub> adsorption capacity and regenerability of the MOFs were evaluated by monitoring pseudo-equilibrium adsorption uptakes over ten adsorption/desorption cycles under dry and wet conditions (1 vol% H<sub>2</sub>O). The majority of the cycling experiments were performed at 25 °C, due to the adsorption kinetics determined from the TGA profiles of the low pressure sorption experiments. Due to the noisy TGA profiles of MIL-100(Fe)-PEI-22 and MIL-100(Fe)-PEI-25, the cycling temperature was set to 45 °C. However, the effect of temperature on the cycling ability was also determined by repeating the cycling on the PEI-22 sample at 25 °C. It should be noted that the timescale shown for the dry cycling profiles (Figure 3.15c) correspond to the initial activation of the samples (between -155 and approximately -55 min, Ar atmosphere), the cooling (between -55 and -20 min, Ar atmosphere) and the equilibration step (between -20 and 0 min, Ar atmosphere) prior to the ten cycles of adsorption and desorption (t=0-420 min, Ar/CO<sub>2</sub>), the subsequent equilibration step (t=420-460 min, Ar atmosphere) at 25 or 45 °C and the regeneration step (t>460 min, Ar atmosphere).

The  $CO_2$  working capacities under dry conditions are presented in Figure 3.15a. It can be seen, that the working capacities vary slightly from cycle to cycle, which can be attributed to the 'noise' because of the small weight changes considered here being at the limits of TG resolution. The working capacity of MIL-100(Fe) (0.61)wt%, 0.05 mol(CO<sub>2</sub>)/mol(CUS)) was comparable to the theoretical value of 0.59 wt%  $(0.05 \text{ mol}(\text{CO}_2)/\text{mol}(\text{CUS}))$  determined from the low pressure CO<sub>2</sub> pseudo-isotherms. This was also the case for all other samples cycled at 25 °C (except: MIL-100(Fe)-PEI-22). The graph shows that the working capacities measured under dry conditions were similar for MIL-100(Fe), MIL-100(Fe)-ED-2.5, MIL-100(Fe)-ED-3 and MIL-100(Fe)-PEI-3. The relatively constant working capacities determined in these materials over successive cycles indicates good regenerability during the simulated vacuum swing process. The relative large spread in the working capacities, from 0.38 wt% to 0.69 wt%, in MIL-100(Fe)-PEI-22 at 25 °C is a consequence of the slower adsorption kinetics, leading to greater variability in the data. This was also apparent in the upwards drift of the baseline in the TGA profile (Figure 3.15c) over the course of the ten cycles, due to the progressively increasing CO<sub>2</sub> adsorption. Increasing the cycling temperature to 45 °C resulted in a decrease in working capacities over the ten cycles. Higher PEI loadings led to poorer

regenerability, which is evident as a gradual decline of the working capacities through successive cycles.

The TGA profiles of the wet cycling experiments are shown in Figure 3.15d. The H<sub>2</sub>O treatment at 25 °C of MIL-100(Fe) for ~10 h and of ED-3, PEI-3 and PEI-22 modified samples for ~7 h did not result in saturation. Saturation of the framework with 1 vol% H<sub>2</sub>O was achieved by increasing the cycling temperature to 45 °C or by increasing the ED loading to 3 wt%. The H<sub>2</sub>O uptake was found to decrease in the order MIL-100(Fe)  $(15.59 \text{ wt\%}, 2.82 \text{ mol}(H_2\text{O})/\text{mol}(\text{CUS})) > \text{PEI-3} (12.22 \text{ wt\%}) > \text{PEI-22/25 °C} (10.02 \text{ wt\%})$ > ED-3 (8.57 wt%) > ED-2.5 (6.85 wt%) > PEI-25 (5.90 wt%) > PEI-22/45 °C (4.11 wt%). The high H<sub>2</sub>O uptake led to lower working capacities in each cycle in comparison with those obtained under dry conditions (Figure 3.15b). The progressively increasing H<sub>2</sub>O adsorption also caused a decrease in the working capacities over subsequent cycles in several cases. Despite the results reported by Soubeyrand-Lenoir [16], no improvements in the CO<sub>2</sub> capacities in MIL-100(Fe) were observed in the presence of H<sub>2</sub>O vapour. A possible explanation for this difference is the lower amount of H<sub>2</sub>O vapour (1 vol%) used in this work. The working capacities of MIL-100(Fe)-ED-2.5, MIL-100(Fe)-ED-3, MIL-100(Fe)-PEI-3 and MIL-100(Fe)-PEI-22 (25 °C ) were higher under wet conditions than those of MIL-100(Fe).

PXRD studies after the wet cycling experiments (Figure 3.23) confirmed the  $H_2O$  stability of MIL-100(Fe), the ED modified materials and MIL-100(Fe)-PEI-22. In the case of the PEI-3 and PEI-25 samples a significant reduction in peak intensity was observed, which could be due to the low sample amount available for the analyses.

In conclusion due to the low working capacities and the high impact of  $H_2O$  vapour, the application of these materials in post-combustion capture is seen to be limited. The high  $H_2O$  uptake and stability might make MIL-100(Fe) worth considering as an adsorbent for the removal of  $H_2O$ . Indeed, Jeremias et al. evaluated the potential of MIL-100(Al, Fe) for thermally driven, sorption-based chilling or heat pump systems by conducting  $H_2O$  adsorption and cycling experiments using humidified argon, which confirmed the cyclic stability [28].



**Figure 3.15:** Working capacities (=difference between CO<sub>2</sub> uptake at 0.05 and 0.15 bar) during (a) dry and (b) wet (1 vol% H<sub>2</sub>O) cycling. TGA profiles of the dry (c) and the wet (d) cycling experiments at 25 ( $\blacksquare$ ) and 45 °C ( $\blacklozenge$ ).

## 3.3.4.4 High pressure gas sorption experiments on MIL-100(Fe)

The potential applicability of MIL-100(Fe) for use in high pressure separation was examined via high pressure sorption experiments at 25, 45, 75 and 105 °C over the pressure range of 0 to 40 bar. Adsorption/desorption isotherms of  $CO_2$  and  $N_2$  measured at four different temperatures are shown in Figure 3.16a, b and c and  $CO_2/N_2$  selectivities (Figure 3.16d) were determined.

In the studied pressure range, no saturation was observed for either of the adsorbates, but the shape of the  $CO_2$  isotherms suggests that saturation would be achieved at much lower pressures than for N<sub>2</sub>. The adsorption of CO<sub>2</sub> and N<sub>2</sub> was mostly reversible at all temperatures, consistent with the predominance of physisorption of the adsorbates under these conditions. However, at pressures below 0.5 bar (at 25 and 45 °C) some CO<sub>2</sub> was retained in the structure upon desorption (Figure 3.16b), which is consistent with the results for the low pressure CO<sub>2</sub> sorption experiments.

At 40 bar and 25 °C, the CO<sub>2</sub> adsorption capacity of 36.4 wt% (2.69 mol(CO<sub>2</sub>)/mol(CUS)) was lower than the adsorption capacity of approximately 72 wt% reported for MIL-100(Cr) (30 °C, 40 bar) [49]. On the other hand, the CO<sub>2</sub> adsorption capacities were higher than those of MIL-53(Al) (29.95 wt%, 25 °C, 25 bar) [50], MIL-53(Al)-NH<sub>2</sub> (29.49 wt%, 30 °C, 13 bar) [51], zeolite 13X (32.6 wt%, 32 bar, 25 °C) [52] and zeolite NaX (34.3 wt%, 30 bar, 30 °C) [53].



**Figure 3.16:** High pressure (a, b)  $CO_2$  and (c)  $N_2$  isotherms of MIL-100(Fe) at 25 (**n**), 45 (**•**), 75 (**•**) and 105 °C (**•**). (d)  $CO_2/N_2$  selectivities as a function of pressure at 25 (black), 45 (red), 75 (blue) and 105 °C (green). Closed (**n**) and open ( $\Box$ ) symbols represent adsorption and desorption, respectively.

MIL-100(Fe) exhibited a much greater affinity for CO<sub>2</sub> than for N<sub>2</sub> in the studied temperature and pressure range. The selectivities (Figure 3.16d) represent the ratios of the single component adsorption capacities and vary between 7 and 24 for CO<sub>2</sub> over N<sub>2</sub> at 25 °C. The selectivities were found to decrease with increasing pressure, but above 1 bar the CO<sub>2</sub>/N<sub>2</sub> ratios at the different temperatures were comparable. At pressures relevant to a VSA process (0.05 to 0.15 bar), the CO<sub>2</sub>/N<sub>2</sub> selectivities ranged from 20 to 24 at 25 °C and from 9 to 14 at 105 °C. However, these values were calculated, according to convention, for an equimolar gas mixture, which is not the real case in post-combustion CO<sub>2</sub> capture. Thus, future work should include a determination of the CO<sub>2</sub>/N<sub>2</sub> selectivities under realistic to post-combustion capture conditions.

The results suggest that MIL-100(Fe) can potentially be applied in high pressure separation processes such as pre-combustion capture or natural gas separation. Future studies should therefore focus on the evaluation of the  $CO_2/H_2$  and  $CO_2/CH_4$  selectivities.

## 3.3.5 Conclusion

A series of PSM MIL-100(Fe) frameworks were prepared and characterised. At low ED loading (2.5 and 3 wt%), minor improvements in the CO<sub>2</sub> adsorption capacities were observed. In contrast to this, PEI modified samples containing 22 and 25 wt% amine were found to be ineffective for the enhancement of the CO<sub>2</sub> adsorption capacities. This contrasts with other studies, which have shown that PEI can result in significant improvements.[23] The results of the N<sub>2</sub> adsorption/desorption at -196 °C suggest that PEI has considerably reduced the pore volume. It may therefore be acting as a diffusion barrier, especially at higher loadings, which will then hinder CO<sub>2</sub> from being adsorbed on the CUS of the MIL-100(Fe). Cycling studies under dry conditions confirmed the reversibility of the adsorption for the majority of the materials, but also indicated that the materials are not applicable for post-combustion capture due to their comparatively low working capacities between 0.05 and 0.15 bar. During the wet cycling experiments, high H<sub>2</sub>O adsorption capacities were observed, which resulted in lower CO<sub>2</sub> working capacities than those found under dry conditions. Interestingly, when using 1 vol% H<sub>2</sub>O in the feed gas stream,  $H_2O$  adsorption did not saturate the materials over the duration of the experiments at 25 °C (except for MIL-100(Fe)-ED-3). The ED modified materials and MIL-100(Fe)-PEI-3 exhibited higher working capacities than MIL-100(Fe) under wet conditions at 25 °C, but still lower than under dry conditions. It is hypothesised that a further increase in ED loading might result in further improvements of the  $CO_2$  adsorption and working capacities. The MIL-100(Fe) framework was found to selectively adsorb  $CO_2$  over N<sub>2</sub> over the entire pressure and temperature range. The sorption results indicate that while the material is not useful for post-combustion capture, it is a potential candidate for the separation of H<sub>2</sub>O at low pressures or  $CO_2$  at high pressures.

## 3.3.6 Acknowledgements

Financial support was provided by the Australian Government through the CRC Program to support this CO2CRC Project. The authors acknowledge use of facilities within the Monash Centre for Electron Microscopy. This research used equipment was supported under the Australian Research Council's *Centres of Excellence* funding scheme (COE for Design in Light Metals). Dr. Xi-ya Fang (SEM) and Dr. Martin Duriska (PXRD) are acknowledged for their technical advice and training on various instruments which have been used for this work.

## 3.3.7 References

- [1] R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, and H. C. Zhou, "Potential applications of metalorganic frameworks," *Coordination Chemistry Reviews*, vol. 253, pp. 3042-3066, 2009.
- [2] W. Xuan, C. Zhu, Y. Liu, and Y. Cui, "Mesoporous metal-organic framework materials," *Chemical Society Reviews*, vol. 41, pp. 1677-1695, 2012.
- [3] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, pp. 1791-1823, 2011.
- [4] H.-L. Jiang and Q. Xu, "Porous metal-organic frameworks as platforms for functional applications," *Chemical Communications*, vol. 47, pp. 3351-3370, 2011.
- [5] A. Demessence, D. M. D'Alessandro, M. L. Foo, and J. R. Long, "Strong CO<sub>2</sub> Binding in a Water-Stable, Triazolate-Bridged Metal-Organic Framework Functionalized with Ethylenediamine," *Journal of the American Chemical Society*, vol. 131, pp. 8784-8786, 2009.
- [6] H. J. Choi, M. Dinca, A. Dailly, and J. R. Long, "Hydrogen storage in water-stable metal-organic frameworks incorporating 1,3- and 1,4-benzenedipyrazolate," *Energy & Environmental Science*, vol. 3, pp. 117-123, 2010.
- [7] J. Yang, A. Grzech, F. M. Mulder, and T. J. Dingemans, "Methyl modified MOF-5: a water stable hydrogen storage material," *Chemical Communications*, vol. 47, pp. 5244-5246, 2011.
- [8] A. M. B. Furtado, J. Liu, Y. Wang, and M. D. LeVan, "Mesoporous silica-metal organic composite: synthesis, characterization, and ammonia adsorption," *Journal of Materials Chemistry*, vol. 21, pp. 6698-6706, 2011.

- [9] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X)," *Energy & Fuels*, vol. 23, pp. 2785-2789, 2009.
- [10] J. A. Greathouse and M. D. Allendorf, "The Interaction of Water with MOF-5 Simulated by Molecular Dynamics," *Journal of the American Chemical Society*, vol. 128, pp. 10678-10679, 2006.
- [11] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> adsorption, selectivity and water tolerance of pillared-layer metal organic frameworks," *Microporous and Mesoporous Materials*, vol. 132, pp. 305-310, 2010.
- [12] Y. Li and R. T. Yang, "Gas Adsorption and Storage in Metal-Organic Framework MOF-177," *Langmuir*, vol. 23, pp. 12937-12944, 2007.
- [13] Y. Li and R. T. Yang, "Hydrogen storage in metal-organic and covalent-organic frameworks by spillover," *AIChE Journal*, vol. 54, pp. 269-279, 2008.
- [14] P. Küsgens, M. Rose, I. Senkovska, H. Fröde, A. Henschel, S. Siegle, and S. Kaskel, "Characterization of metal-organic frameworks by water adsorption," *Microporous and Mesoporous Materials*, vol. 120, pp. 325-330, 2009.
- [15] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, and O. M. Yaghi, "Exceptional chemical and thermal stability of zeolitic imidazolate frameworks," *Proceedings of the National Academy of Sciences*, vol. 103, pp. 10186-10191, July 5, 2006 2006.
- [16] E. Soubeyrand-Lenoir, C. Vagner, J. W. Yoon, P. Bazin, F. Ragon, Y. K. Hwang, C. Serre, J.-S. Chang, and P. L. Llewellyn, "How water fosters a remarkable 5-fold increase in low pressure CO<sub>2</sub> uptake within the mesoporous MIL-100(Fe)," *Journal* of the American Chemical Society, 2012/05/21 2012.
- [17] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, "Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants," *Sci. Rep.*, vol. 3, pp. 1-6, 2013.
- [18] G.-P. Hao, W.-C. Li, and A.-H. Lu, "Novel porous solids for carbon dioxide capture," *Journal of Materials Chemistry*, vol. 21, pp. 6447-6451, 2011.
- [19] Y.-S. Bae, O. K. Farha, J. T. Hupp, and R. Q. Snurr, "Enhancement of CO<sub>2</sub>/N<sub>2</sub> selectivity in a metal-organic framework by cavity modification," *Journal of Materials Chemistry*, vol. 19, pp. 2131-2134, 2009.
- [20] A. Ö. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis, and R. Q. Snurr, "Enhanced CO<sub>2</sub> Adsorption in Metal-Organic Frameworks via Occupation of Open-Metal Sites by Coordinated Water Molecules," *Chemistry of Materials*, vol. 21, pp. 1425-1430, 2009.
- [21] D. Britt, H. Furukawa, B. Wang, T. G. Glover, and O. M. Yaghi, "Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites," *Proceedings of the National Academy of Sciences*, vol. 106, pp. 20637-20640, December 8, 2009 2009.
- [22] S.-N. Kim, S.-T. Yang, J. Kim, J.-E. Park, and W.-S. Ahn, "Post-synthesis functionalization of MIL-101 using diethylenetriamine: a study on adsorption and catalysis," *CrystEngComm*, vol. 14, pp. 4142-4147, 2012.
- [23] Y. Lin, Q. Yan, C. Kong, and L. Chen, "Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO<sub>2</sub> Capture," *Sci. Rep.*, vol. 3, pp. 1-7, 2013.
- [24] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.

- [25] T. K. Trung, N. A. Ramsahye, P. Trens, N. Tanchoux, C. Serre, F. Fajula, and G. Férey, "Adsorption of C5-C9 hydrocarbons in microporous MOFs MIL-100(Cr) and MIL-101(Cr): A manometric study," *Microporous and Mesoporous Materials*, vol. 134, pp. 134-140, 2010.
- [26] Y.-K. Seo, J. W. Yoon, J. S. Lee, U. H. Lee, Y. K. Hwang, C.-H. Jun, P. Horcajada, C. Serre, and J.-S. Chang, "Large scale fluorine-free synthesis of hierarchically porous iron(III) trimesate MIL-100(Fe) with a zeolite MTN topology," *Microporous and Mesoporous Materials*, vol. 157, pp. 137-145, 2012.
- [27] J. Shi, S. Hei, and H. Liu, "Synthesis of MIL-100(Fe) at Low Temperature and Atmospheric Pressure," *Journal of Chemistry*, vol. vol. 2013, pp. Article ID 792827, 4 pages, 2013.
- [28] F. Jeremias, A. Khutia, S. K. Henninger, and C. Janiak, "MIL-100(Al, Fe) as water adsorbents for heat transformation purposes-a promising application," *Journal of Materials Chemistry*, 2012.
- [29] J. W. Yoon, Y.-K. Seo, Y. K. Hwang, J.-S. Chang, H. Leclerc, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, E. Bloch, P. L. Llewellyn, C. Serre, P. Horcajada, J.-M. Grenèche, A. E. Rodrigues, and G. Férey, "Controlled Reducibility of a Metal– Organic Framework with Coordinatively Unsaturated Sites for Preferential Gas Sorption," *Angewandte Chemie International Edition*, vol. 49, pp. 5949-5952, 2010.
- [30] M. Kathiresan, L. Walder, F. Ye, and H. Reuter, "Viologen-based benzylic dendrimers: selective synthesis of 3,5-bis(hydroxymethyl)benzylbromide and conformational analysis of the corresponding viologen dendrimer subunit," *Tetrahedron Letters*, vol. 51, pp. 2188-2192, 2010.
- [31] R. Canioni, C. Roch-Marchal, F. Secheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Ferey, J.-M. Greneche, F. Lefebvre, J.-S. Chang, Y.-K. Hwang, O. Lebedev, S. Turner, and G. Van Tendeloo, "Stable polyoxometalate insertion within the mesoporous metal organic framework MIL-100(Fe)," *Journal of Materials Chemistry*, vol. 21, pp. 1226-1233, 2011.
- [32] Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, and G. Férey, "Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation," *Angewandte Chemie International Edition*, vol. 47, pp. 4144-4148, 2008.
- [33] J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard, and O. M. Yaghi, "Gas Adsorption Sites in a Large-Pore Metal-Organic Framework," *Science*, vol. 309, pp. 1350-1354, August 26, 2005 2005.
- [34] ""Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.," "*Reflex Tools*" is a module in the Materials Studio Modeling software package from Accelrys Inc.
- [35] G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, and I. Margiolaki, "A Hybrid Solid with Giant Pores Prepared by a Combination of Targeted Chemistry, Simulation, and Powder Diffraction," *Angewandte Chemie International Edition*, vol. 43, pp. 6296-6301, 2004.
- [36] S.-H. Huo and X.-P. Yan, "Metal-organic framework MIL-100(Fe) for the adsorption of malachite green from aqueous solution," *Journal of Materials Chemistry*, vol. 22, pp. 7449-7455, 2012.
- [37] <u>http://www.sigmaaldrich.com/catalog/product/sial/e26266?lang=en&region=AU</u>, (accessed 10/08/2014).

- [38] <u>http://www.sigmaaldrich.com/catalog/product/aldrich/468533?lang=en&region=AU</u>, (accessed 10/08/2014).
- [39] P. Horcajada, S. Surble, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Greneche, I. Margiolaki, and G. Ferey, "Synthesis and catalytic properties of MIL-100(Fe), an iron(iii) carboxylate with large pores," *Chemical Communications*, pp. 2820-2822, 2007.
- [40] Y. Kuwahara, D.-Y. Kang, J. R. Copeland, N. A. Brunelli, S. A. Didas, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita, and C. W. Jones, "Dramatic Enhancement of CO<sub>2</sub> Uptake by Poly(ethyleneimine) Using Zirconosilicate Supports," *Journal of the American Chemical Society*, vol. 134, pp. 10757-10760, 2012/07/04 2012.
- [41] M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, and K. P. Lillerud, "Synthesis and Stability of Tagged UiO-66 Zr-MOFs," *Chemistry of Materials*, vol. 22, pp. 6632-6640, 2010/12/28 2010.
- [42] S. Ye, X. Jiang, L.-W. Ruan, B. Liu, Y.-M. Wang, J.-F. Zhu, and L.-G. Qiu, "Postcombustion CO<sub>2</sub> capture with the HKUST-1 and MIL-101(Cr) metal–organic frameworks: Adsorption, separation and regeneration investigations," *Microporous and Mesoporous Materials*, vol. 179, pp. 191-197, 2013.
- [43] A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, "Screening of Metal-Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach," *Journal of the American Chemical Society*, vol. 131, pp. 18198-18199, 2009.
- [44] P. D. C. Dietzel, V. Besikiotis, and R. Blom, "Application of metal-organic frameworks with coordinatively unsaturated metal sites in storage and separation of methane and carbon dioxide," *Journal of Materials Chemistry*, vol. 19, pp. 7362-7370, 2009.
- [45] P. Chowdhury, C. Bikkina, D. Meister, F. Dreisbach, and S. Gumma, "Comparison of adsorption isotherms on Cu-BTC metal organic frameworks synthesized from different routes," *Microporous and Mesoporous Materials*, vol. 117, pp. 406-413, 2009.
- [46] S. Choi, T. Watanabe, T.-H. Bae, D. S. Sholl, and C. W. Jones, "Modification of the Mg/DOBDC MOF with Amines to Enhance CO<sub>2</sub> Adsorption from Ultradilute Gases," *The Journal of Physical Chemistry Letters*, vol. 3, pp. 1136-1141, 2012/05/25 2012.
- [47] P. D. C. Dietzel, R. E. Johnsen, H. Fjellvag, S. Bordiga, E. Groppo, S. Chavan, and R. Blom, "Adsorption properties and structure of CO<sub>2</sub> adsorbed on open coordination sites of metal-organic framework Ni2(dhtp) from gas adsorption, IR spectroscopy and X-ray diffraction," *Chemical Communications*, pp. 5125-5127, 2008.
- [48] A. Das, P. D. Southon, M. Zhao, C. J. Kepert, A. T. Harris, and D. M. D'Alessandro, "Carbon dioxide adsorption by physisorption and chemisorption interactions in piperazine-grafted Ni2(dobdc) (dobdc = 1,4-dioxido-2,5-benzenedicarboxylate)," *Dalton Transactions*, vol. 41, pp. 11739-11744, 2012.
- [49] P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jhung, and G. Férey, "High Uptakes of CO<sub>2</sub> and CH<sub>4</sub> in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101," *Langmuir*, vol. 24, pp. 7245-7250, 2008.

- [50] B. Arstad, H. Fjellvåg, K. Kongshaug, O. Swang, and R. Blom, "Amine functionalised metal organic frameworks (MOFs) as adsorbents for carbon dioxide," *Adsorption*, vol. 14, pp. 755-762, 2008.
- [51] S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, and F. Kapteijn, "An Amine-Functionalized MIL-53 Metal-Organic Framework with Large Separation Power for CO<sub>2</sub> and CH<sub>4</sub>," *Journal of the American Chemical Society*, vol. 131, pp. 6326-6327, 2009.
- [52] S. Cavenati, C. A. Grande, and A. E. Rodrigues, "Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures," *Journal of Chemical & Engineering Data*, vol. 49, pp. 1095-1101, 2004/07/01 2004.
- [53] G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi, and J.-S. Chang, "Why hybrid porous solids capture greenhouse gases?," *Chemical Society Reviews*, vol. 40, pp. 550-562, 2011.

# Supplementary material

# Postsynthetic modification of MIL-100(Fe): an adsorption study

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author:



# 3.3.8 SEM images



Figure 3.17: SEM images of (a) MIL-100(Fe), (b) MIL-100(Fe)-PEI-3 and (c) MIL-100(Fe)-PEI-50.

# 3.3.9 Experimental and theoretical PXRD



Figure 3.18: Comparison of simulated [1] and experimental XRD pattern of MIL-100(Fe).



## **3.3.10** Thermal decomposition





# 3.3.11 FTIR spectra

- MIL-100(Fe) – ED-2.5 - ED-3 - PEI-3 – PEI-22 – PEI-25 Figure 3.20: FTIR spectra of MIL-100(Fe) before and after PSM.



## 3.3.12 DTA profiles



3.3.13 CO<sub>2</sub> adsorption in MIL-100(Fe)-PEI-50



**Figure 3.22:** (a) CO<sub>2</sub> pseudo-isotherms of MIL-100(Fe)-PEI-50 at 25 ( $\blacksquare$ ), 45 ( $\blacklozenge$ ) and 75 °C ( $\blacktriangle$ ). (b) TGA profiles of the low pressure CO<sub>2</sub> sorption at 25 (black), 45 (red) and 75 °C (blue). Closed ( $\blacksquare$ ) and open ( $\square$ ) symbols represent adsorption and desorption, respectively.



3.3.14 Impact of H<sub>2</sub>O – PXRD after wet cycling

**Figure 3.23:** PXRD of MIL-100(Fe) and its amine modifications before (black) and after (blue) the sorption of  $H_2O$ .

## 3.3.15 References supplementary information

- [1] P. Horcajada, S. Surble, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Greneche, I. Margiolaki, and G. Ferey, "Synthesis and catalytic properties of MIL-100(Fe), an iron(iii) carboxylate with large pores," *Chemical Communications*, pp. 2820-2822, 2007.
- [2] R. Canioni, C. Roch-Marchal, F. Secheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Ferey, J.-M. Greneche, F. Lefebvre, J.-S. Chang, Y.-K. Hwang, O. Lebedev, S. Turner, and G. Van Tendeloo, "Stable polyoxometalate insertion within the mesoporous metal organic framework MIL-100(Fe)," *Journal of Materials Chemistry*, vol. 21, pp. 1226-1233, 2011.

# **Declaration for Thesis Chapter**

## CO2 adsorption in postsynthetic modified MIL-101(Cr)-NH2

#### Monash University

## **Declaration for Thesis Chapter 3.4**

#### **Declaration by candidate**

In the case of Chapter 3.4, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed samples; identified major	80 %
issues; developed interpretations; fully drafted paper and conclusion	

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co- authors only
Gregory P. Knowles	Aided method development (TGA), input to results analysis and manuscript revision	N/A
Alan L. Chaffee	Supervision, assisted interpretation of results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work\*.

Candidate's Signature	Date 30/10/2014
Main	Date
Supervisor's Signature	30/10/14

\*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

## 3.4 CO<sub>2</sub> adsorption in postsynthetic modified MIL-101(Cr)-NH<sub>2</sub>

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author:

Fax:+61 3 990-54597

## 3.4.1 Abstract

A series of polyethyleneimine (PEI), diethylenetriamine (DETA) and polypropyleneimine octamine dendrimer (DAB-AM-8) modified MIL-101(Cr)-NH<sub>2</sub> frameworks were prepared and characterised via PXRD, ATR, N<sub>2</sub> adsorption/desorption at -196 °C, helium density, SEM and elemental analysis. The impact of the postsynthetic modification (PSM) of MIL-101(Cr)-NH<sub>2</sub> on the CO<sub>2</sub> adsorption and working capacities was investigated by conducting low pressure CO<sub>2</sub> sorption measurements (T=25-105 °C, p=0-0.05 bar) and ten cycle experiments under dry and humid (1 vol% H<sub>2</sub>O) conditions. A rise in sorption temperature was beneficial for reversible CO<sub>2</sub> sorption (0-0.5 bar) with reasonable sorption rates and adsorption capacities in DAB-AM-8 and PEI modified frameworks. PSM with DETA was found to be ineffective due to significantly lower adsorption capacities than in the neat DETA. The most promising material was MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145, which exhibited the highest working capacities of 0.97 wt% and 0.98 wt% under dry and humid cycling conditions at 105 °C, respectively. The potential of MIL-10(Cr)-NH<sub>2</sub> high pressure separation applications was confirmed via high pressure CO<sub>2</sub> and N<sub>2</sub> sorption experiments (T=25-105 °C, p=0-40 bar).

## 3.4.2 Introduction

The escalating level of atmospheric  $CO_2$  is one of the most pressing environmental concerns of our age and plays a major role in global warming and climate change [1-3]. Since the late 19<sup>th</sup> century the  $CO_2$  concentration has increased by 30 % and is expected to double over the next two decades [4]. Strategies to reduce  $CO_2$  emissions are urgently required, especially given that fossil fuel combustion is projected to increase in the near future in order to meet the rise in energy demand [5].

Carbon capture and storage (CCS) from large point sources such as power plants is one approach for reducing the anthropogenic  $CO_2$  emission. The main disadvantage to date is the cost for  $CO_2$  capture and concentration, which is purported to account for 75 % of the overall cost of the CCS. Therefore, cutting the capture cost appears to be the most important challenge to make the CCS process economically feasible within the energy industry [6-9]. The state of the art technologies for capturing  $CO_2$  include absorption by aqueous amines (e.g. monoethanolamine, diethanolamine, etc.). The high energy requirement for regenerating the absorbents, the loss of effectiveness over time due to the low thermal stability, the loss due to evaporation and the tendency to induce corrosion, leads to a poor overall efficiency [10-14]. Therefore, other applications, such as membranes or adsorption on suitable solids, merit consideration.

One promising group of porous adsorbent materials for gas capture are metal-organic frameworks (MOFs), which have attracted tremendous attention over the past decade due to their porosity, high surface area, high pore volume, tuneable pore sizes and topologies [15-17]. In order to be applicable to realistic flue streams,  $CO_2$  adsorbents should fulfill the following requirements:

- high CO<sub>2</sub> capture capacity,
- high selectivity for CO<sub>2</sub> over other components in flue gas, syngas and natural gas,
- high thermal and hydrothermal stability,
- good regenerability.

To effectively remove CO<sub>2</sub>, industrial processes will typically use pressure swing or vacuum swing adsorption (PSA/VSA) techniques, where CO<sub>2</sub> is adsorbed at modestly elevated pressures and is the released to a storage tank at lower pressures [18]. While PSA systems typically adsorb at inlet pressures near 6 bar and desorb at 1 bar, VSA uses an inlet pressure of ~1 bar and evacuates to ~0.05 bar for desorption [18, 19]. In order to increase the overall capture/separation efficiency, swing adsorption processes are often implemented in multiple stages [18].

The main disadvantage of most MOFs is their low hydrothermal stability due to the weak M-O-coordination, which allows the attack of  $H_2O$  molecules. Phase transformations, decomposition of the frameworks, poor reproducibility and decreases in gas sorption capacities are often observed. Common reactions of  $H_2O$  with the metal oxide cluster in

MOFs can involve ligand displacement and/or hydrolysis. During the ligand displacement a H<sub>2</sub>O molecule is inserted into a metal-ligand bond as shown in Eq. 3.2:

$$M-L + H_2O \to M-(OH_2)\cdots L$$
(3.2)

As soon as the metal-ligand bond is broken,  $H_2O$  dissociates into a hydroxide anion and proton. The hydroxide anion then binds to the metal, and the proton binds to the displaced ligand (Eq.3.3) [20-22].

$$M-L + H_2O \rightarrow M-(OH) + LH$$
(3.3)

One hydrothermally stable framework is MIL-101(Cr), which is built from trimers of Cr(III) oxide octahedra. Two of the three chromium octahedra are each coordinated to a terminal H<sub>2</sub>O molecule, while the third is coordinated to an OH<sup>-</sup> anion [23]. Upon heating the framework to 150 °C the terminal H<sub>2</sub>O molecules can be removed, providing coordinatively unsaturated sites (CUS), which allow the postsynthetic modification (PSM) of the framework [24]. The arrangement of the metal octahedra results in the formation of a supertetrahedral building block [25, 26]. Each corner of the tetrahedral unit is occupied by the trimeric units which are connected to each other through terephthalic acid ligands located on each face [27]. The assembly of the hybrid supertetrahedra further results in the formation of a zeotypic mesoporous MOF reminiscent of the MTN topology (related to the zeolite ZSM-39) [25, 26, 28]. The corresponding three-dimensional framework exhibits two types of cavity, a dodecahedral and a hexakaidododecahedral cage. The first type is delimited by 12 pentagonal rings with a window diameter of 1.2 nm, while the second type is delimited by 12 pentagonal rings and 4 hexagonal rings [25, 27, 29]. The dodecahedral cages are connected together by sharing 5-ring faces in order to form infinite layers stacked in an ABC sequence. The second cage is generated at the intersection of the rods via hexagonal faces (window diameter 1.6 nm) with a diamond type [27].

The effect of DETA and PEI grafted onto the unsaturated metal centres of MIL-101(Cr) were studied by Kim et al. [30], Anbia et al. [31] and Lin et al. [32]. While the modification of the framework with DETA resulted in a higher CO<sub>2</sub> adsorption capacity at pressures below 0.15 bar, the capacity decreased from 7.9 wt% to 3.1 wt% at 25 °C and 1 bar due to the significant decreases in surface area after the modification [30]. Anbia et al. reported an increase of the CO<sub>2</sub> adsorption capacity from 9.15 wt% to 11.75 wt% (25 °C, 34 bar) after the modification of MIL-101(Cr) with pentaethylenehexamine [31]. Lin et al. reported the use of linear PEI with an average molecular weight of 300 g mol<sup>-1</sup>, which afforded a high performance sorbent for post-combustion capture [32]. However, to

date no impregnation of amines into MIL-101(Cr)-NH<sub>2</sub> have been reported, despite the high  $CO_2/N_2$  selectivity (119:1) and high  $CO_2$  adsorption capacity of 15.9 wt% at 20 °C and 1 bar reported by Khutia and co-worker [33].

Two different strategies for the synthesis of MIL-101(Cr)-NH<sub>2</sub> have been reported. The first strategy involves the "prefunctionalisation" approach and was first reported by Lin and co-worker [34]. The hydroxide assisted hydrothermal synthesis using chromium nitrate, 2-aminoterephthalic acid and sodium hydroxide was conducted at 150 °C for 12 h [34]. A second synthetic procedure using the "prefunctionalisation" approach was described by Jiang et al. [35], in which MIL-101(Cr)-NH<sub>2</sub> was hydrothermally synthesised at 130 °C for 24 h without the addition of sodium hydroxide. Bernt and co-workers reported the PSM of MIL-101(Cr) via nitration and subsequent reduction of the nitro groups to amino groups [36].

In this study, MIL-101(Cr)-NH<sub>2</sub> (synthesised according to the procedure reported by Jiang et al. [35]) was used as a starting material for PSM with ED, DAB-AM-8, DETA and PEI. The effect of different PEI loadings (75, 100, 150 wt%) was determined and the most efficient loading on a wt% basis was selected for PSM with ED, DAB-AM-8 and DETA. The applicability for CO<sub>2</sub> capture was assessed in terms of low pressure CO<sub>2</sub> adsorption/desorption (0-0.5 bar) and ten cycle experiments of adsorption/desorption under dry and wet conditions (1 vol% H<sub>2</sub>O), which were carried out by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar. Furthermore, high pressure CO<sub>2</sub> and N<sub>2</sub> sorption measurements on MIL-101(Cr)-NH<sub>2</sub> were conducted between 0 and 40 bar in the temperature range of 25 to 105 °C to investigate its potential for high pressure separation processes.

## 3.4.3 Experimental section

## 3.4.3.1 Chemicals

2-aminoterephthalic acid (99 %, Sigma Aldrich), chromium nitrate nonahydrate (99 %, Aldrich), ethylenediamine (99 %, Sigma Aldrich), DAB-AM-8 (Sigma Aldrich), diethylenetriamine (99 %, Sigma Aldrich), DMF (GR grade, Merck), ethanol ( $\geq$  99.7 %, Merck), methanol ( $\geq$  99.8 %, Merck), PEI (423 g mol<sup>-1</sup>, mixture of branched and linear PEI, Aldrich), argon (high purity, BOC and Air Liquide), carbon dioxide (Food grade, Coregas), helium (high purity, Air Liquide), liquid nitrogen (BOC and Air Liquide) and nitrogen (high purity, Air Liquide).

All reagents were used without further purification.

## 3.4.3.2 Synthesis of MIL-101(Cr)-NH<sub>2</sub>

MIL-101(Cr)-NH<sub>2</sub> was synthesised by a procedure akin to that reported by Jiang et al. [35]. In a typical synthesis, 2.50 g (6.25 mmol) of  $Cr(NO_3)_3$ ·9H<sub>2</sub>O and 1.15 g (6.35 mmol) of 2-aminoterephthalic acid were dispersed in 35 mL H<sub>2</sub>O, before stirring it for 3 h at room temperature. The mixture was heated for 24 h at 130 °C in a Teflon® lined autoclave. After cooling the autoclave to room temperature, the product was collected by centrifugation (10 min, 6000 rpm) and washed five times with ethanol before drying under flowing N<sub>2</sub> at room temperature.

## 3.4.3.3 PSM of MIL-101(Cr)-NH<sub>2</sub>

The wet impregnation of MIL-101(Cr)-NH<sub>2</sub> with DAB-AM-8, DETA and PEI was conducted by the following method adapted from Lin and co-workers [32]. Prior to the modification, MIL-101(Cr)-NH<sub>2</sub> was activated under vacuum at 110 °C overnight. The desired amount of DAB-AM-8, DETA or PEI was dissolved in approximately 1 mL of methanol under stirring for 10 min. 0.2 g of dehydrated MOF were added to the solution, which was then stirred for another 10 min. The mixture was then purged with N<sub>2</sub> overnight at room temperature. Finally, the modified samples were activated under vacuum at 110 °C overnight.

PSM of MIL-101(Cr)-NH<sub>2</sub> with ED was conducted in accord with the method reported by Hwang et al. [24]. A suspension of 0.2 g of MOF, 0.3 g of ED and 30 mL toluene was stirred under reflux overnight. The product was recovered by centrifugation and washed with H<sub>2</sub>O and ethanol, before drying it at room temperature. The sample was activated under vacuum at 90 °C overnight.

Three MIL-101(Cr)-NH<sub>2</sub>-PEI samples with different PEI loadings were prepared (75, 100 and 150 wt%). The loading of the MOF with ED and DAB-AM-8 was chosen to be 150 wt%, as MIL-101(Cr)-NH<sub>2</sub>-PEI-130 exhibited the most promising CO<sub>2</sub> adsorption capacities during the low pressure CO<sub>2</sub> adsorption/desorption measurements. MIL-101(Cr)-NH<sub>2</sub> modified with 150 wt% DETA was prepared, but N<sub>2</sub> adsorption/desorption at -196 °C showed a blockage of the pores resulting in negligible CO<sub>2</sub> capacities at all temperatures. Therefore, a second sample was prepared using 100 wt% of DETA. The following equation was used to obtain the theoretical loading of the materials:

$$Amine \ loading = \frac{mass_{amine}}{mass_{MIL-101(Cr)-NH_2}} \times 100 \tag{3.4}$$

An overview of the theoretical loading (wt%) and the loading after vacuum activation (wt% and mol(amine) per mol(CUS)) is given in Table 3.4. In the following sections the samples are denoted as MIL-101(Cr)-NH<sub>2</sub>-PEI-68, MIL-101(Cr)-NH<sub>2</sub>-PEI-88, MIL-101(Cr)-NH<sub>2</sub>-PEI-130, MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145, MIL-101(Cr)-NH<sub>2</sub>-DETA-88 and MIL-101(Cr)-NH<sub>2</sub>-ED-128.

Amine	Theoretical loading	Loading after evac /	Loading after evac /	
	/ wt%	wt%	mol(amine) per mol(CUS)	
PEI	75	68	0.60	
PEI	100	88	0.78	
PEI	150	130	1.14	
DAB-AM-8	150	145	0.70	
DETA	100	88	3.18	
ED	150	128	7.96	

**Table 3.4:** Overview of the theoretical amine loadings (wt%), the amine loadings after vacuum activation (evac) and the corresponding molar loadings of the CUS.

## 3.4.3.4 Characterisation of MIL-101(Cr)-NH<sub>2</sub> before and after PSM

The characterisation of postsynthetically modified MIL- $101(Cr)-NH_2$  samples was conducted after vacuum activation, while MIL- $101(Cr)-NH_2$  was characterised in its assynthesised form (corresponds to sample dried under flowing N<sub>2</sub> at room temperature), unless stated otherwise.

Nitrogen adsorption/desorption was conducted at -196 °C on a Micromeritics TriStar II 3020 gas sorption analyser to evaluate the surface area and total pore volume of each sample. The samples were activated under vacuum at 90 or 110 °C overnight. The Brunauer-Emmett Teller (BET) surface areas were calculated from the data in the relative pressure range of 0.01-0.2 on the adsorption isotherm and the pore volumes were estimated at  $p/p_0=0.99$ .

Carbon, hydrogen and nitrogen contents were determined by elemental analysis in the Campbell Microanalytical Laboratory at the University at Otago, New Zealand. The measurements were conducted twice and the standard deviation was calculated. Helium densities were recorded using an AccuPyc 1340 (Micromeritics). Prior to the analysis, the samples were activated under vacuum. Approximately 0.1 to 0.2 g of MOF was placed into a  $1 \text{ cm}^3$  cell and the measurement was performed

The thermal decomposition was measured via thermal gravimetric analysis (TGA) using a Setaram TAG24-16 simultaneous symmetrical thermoanalyser. The sorbents were heated to 110 °C under Ar flow for 1 h to remove residual moisture inside the pores. After 30 min, the gas composition was changed from 100 vol% Ar to 50 vol% air and 50 vol% Ar. The sample was then heated to 900 °C with a heating ramp of 10 °C min<sup>-1</sup>. 15 min after reaching 900 °C the gas flow was changed from an Ar/air mixture to 100 vol% Ar and the temperature was held for an additional 15 min before the system was cooled under Ar.

Scanning electron microscopy (SEM) images were recorded on selected MOFs using a JEOL 7001F field emission scanning electron microscope. The accelerating voltage was set to 15 kV.

Powder x-ray diffraction (PXRD) experiments were conducted on a Bruker D8 Focus powder diffractometer with CuK $\alpha$  radiation ( $\lambda$ =1.5418 Å) at ambient laboratory conditions. The diffractograms were measured before and after amine modification as well as after the wet cycling. The PXRD pattern of MIL-101(Cr) was simulated using the module "Reflex Tools" in Materials Studio 6.0 [37].

Fourier transform infrared (FTIR) spectra were recorded on an Agilent Cary 630 FTIR in the spectral range 4000 to 650 cm<sup>-1</sup> at ambient laboratory conditions. Prior to each measurement the background was measured. A small amount of sample was then placed on the diamond attenuated total reflectance (ATR) crystal and the spectrum was recorded.

# 3.4.3.5 Low pressure gas sorption measurements on MIL-101(Cr)-NH<sub>2</sub> before and after PSM

A Setaram TAG24-16 simultaneous symmetrical thermoanalyser was used to measure the change in mass of samples (TGA) and the associated heat flow (DTA) as they were subjected to CO<sub>2</sub>. Isotherms on MIL-101(Cr)-NH<sub>2</sub> and neat PEI were obtained at 25, 45, 75 and 105 °C, but the maximum adsorption temperature for the PSM materials varied between 75 and 105 °C depending on the adsorption kinetics. CO<sub>2</sub> isotherms on neat DAB-AM-8 were measured at 75 and 105 °C, due to the slow kinetics and low adsorption

capacities at lower temperatures.  $CO_2$  isotherms in neat DETA were obtained in the temperature range of 25 to 75 °C.

Prior to the experiments, the samples (except neat PEI, DAB-AM-8 and DETA) were activated under vacuum at 90 or 110 °C. Approximately 10 to 20 mg of sample were used for each experiment. The first step of the TGA program was the pre-treatment at 110 °C under Ar (70 mL min<sup>-1</sup>) for 1 h in order to remove residual moisture. The pre-treatment of neat PEI, DAB-AM-8 and DETA was extended to 2 h. The system was then cooled to the desired adsorption temperature and the thermoanalyser was allowed to equilibrate for 20 min. The gas flow was then changed from 100 vol% Ar to an Ar/CO<sub>2</sub> mixture. The CO<sub>2</sub> partial pressure was increased in five steps (0.2, 0.5, 0.15, 0.30, 0.50 bar), before the amount of CO<sub>2</sub> in the gas stream was decreased for desorption at the same step points (and then finally to 0 bar). Changes in gas feed composition mimic a pressure swing adsorption process by varying the partial pressure of CO<sub>2</sub>. The temperature remained constant for another 20 min after the last desorption step, before the MOFs were heated at 110 °C under Ar for 30 min in order to desorb the CO<sub>2</sub> completely.

#### 3.4.3.6 Cycling experiments on MIL-101(Cr)-NH<sub>2</sub> before and after PSM

Cycling experiments were conducted on a Setaram TAG24-16 simultaneous symmetrical thermoanalyser by measuring the change in mass. The total flow rate was 70 mL min<sup>-1</sup> (e.g., 35 mL min<sup>-1</sup> sample gas and 35 mL min<sup>-1</sup> on the reference side of the balance). Prior to the experiments, all samples were activated under vacuum at 90 or 110 °C, before 10 to 20 mg of MOF were heated in-situ under Ar for 1 h. The system was then cooled until the desired cycling temperature was reached. While the cycling on MIL-101(Cr)-NH<sub>2</sub> was performed at 25 °C, higher temperatures (45, 75 or 105 °C) were used for the amine modified samples. Ten cycles of adsorption/desorption were carried out by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar. The equilibration time of each adsorption/desorption step was set to 20 min. For the wet cycling experiments, the MOFs were first treated with 1 vol% H<sub>2</sub>O vapour for ~7 h by exposing the samples to flowing wet Ar after the activation step, before treatment with wet CO<sub>2</sub>/Ar mixtures (1 vol% H<sub>2</sub>O/CO<sub>2</sub>/Ar, 70 mL min<sup>-1</sup>).

#### 3.4.3.7 High pressure gas sorption on MIL-101(Cr)-NH<sub>2</sub>

 $CO_2$  and  $N_2$  adsorption and desorption were measured using a Micromeritics High Pressure Volumetric Analyser (HPVA). Prior to measuring the isotherms, MIL-101(Cr)-

 $NH_2$  was activated at 110 °C under vacuum overnight. The sample was then transferred from the degas to the analysis port and gas sorption was measured at 25, 45, 75 and 105 °C up to 40 bar. The sample was re-activated after each isotherm.

#### 3.4.4 Results and discussion

#### 3.4.4.1 Characterisation of MIL-101(Cr)-NH<sub>2</sub> before and after PSM

MIL-101(Cr)-NH<sub>2</sub> and its modification products were characterised by  $N_2$  adsorption/desorption at -196 °C, elemental analysis, helium desorption, TGA, SEM, PXRD and FTIR. The results are discussed below.

The N<sub>2</sub> sorption isotherms at -196 °C are shown in Figure 3.24. The type IV isotherm of MIL-101(Cr)-NH<sub>2</sub> exhibited the characteristic two step profile for MIL-101 frameworks. At a relative pressure of 0.1, a significant amount of N<sub>2</sub> was adsorbed onto the surface of the porous cavities. A further increase in relative pressure resulted in the filling of the pores ( $p/p_0$ ~0.4) [38]. At high relative pressure, the isotherm features a type H2 hysteresis loop, consistent with the agglomeration of the nanoparticles [35]. This was also observed for nanoparticles of MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub> [35, 39]. After the PSM the hysteresis was still present, but the type varied from H2 (MIL-101(Cr)-NH<sub>2</sub>-PEI-68/88/130, MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145) to H3 (MIL-101(Cr)-NH<sub>2</sub>-ED-128, MIL-101(Cr)-NH<sub>2</sub>-DETA-88). The isotherms remained type IV after the modification; however, the characteristic step profile was attenuated due to the filling of the cavities with the amines.

BET surface areas and pore volumes are compared in Table 3.5. MIL-101(Cr)-NH<sub>2</sub> gave a surface area of 2269 m<sup>2</sup> g<sup>-1</sup>, which was slightly higher than the reported 2070 m<sup>2</sup> g<sup>-1</sup> [35]. This discrepancy could be due to the vacuum activation overnight applied in this work compared to the 4 h stated by Jiang et al.[35] Furthermore, there may be a difference in the relative pressure range over which the BET surface area was estimated, since this was not specified in the prior work. From the determined total pore volume of MIL-101(Cr)-NH<sub>2</sub> and the densities of ED (0.90 g cm<sup>-3</sup>), DAB-AM-8 (0.99 g cm<sup>-3</sup>), DETA (0.96 g cm<sup>-3</sup>) and PEI (1.07 g cm<sup>-3</sup>), the loadings that would fully occupy the pore volume were estimated to be 200 wt%, 182 wt%, 188 wt% and 168 wt%, respectively. Therefore, the highest loading to be employed was chosen as 150 wt% for each of the amines, so as to avoid complete pore filling. Nevertheless, complete pore filling was observed in the modification with 150 wt% DETA, so that the maximum applied loading for this amine was reduced to

100 wt%. Upon impregnation with amines, a significant decrease in BET surface area and total pore volume was observed, which implies the successful grafting onto the CUS in the framework structure.



**Figure 3.24:**  $N_2$  isotherms measured at -196 °C on MIL-101(Cr)-NH<sub>2</sub> before and after PSM. The right graph shows the isotherms of the amine modified materials on an enlarged scale for better comparison.

The elemental compositions of MIL-101(Cr)-NH<sub>2</sub> before and after modification materials are shown in Table 3.5. The theoretical elemental composition of MIL-101(Cr)-NH<sub>2</sub> was calculated from the empirical formula  $Cr_3O(OH)(H_2O)_2[BDC-NH_2]_3$  to yield 37.81% C, 2.64 % H and 5.51 % N. The comparison of theoretical and experimental composition indicates the presence of approximately one lattice H<sub>2</sub>O molecule. An increase in carbon, hydrogen and nitrogen content confirmed the incorporation of the amines into the structure. As expected an increase in amine loading resulted in a rise in nitrogen content.

The helium densities before and after PSM (except for MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145) are listed in Table 3.5. The PSM of MIL-101(Cr)-NH<sub>2</sub> resulted in a decline in helium densities, which was more pronounced at higher loadings. The densities of the PSM materials increased in the order PEI<DETA<ED, consistent with the densities of the neat amines.

MOF	%C	%H	%N	<b>BET surface</b>	Total pore	Helium
				area / m <sup>2</sup> g <sup>-1</sup>	volume/	density/
					cm <sup>3</sup> g <sup>-1</sup>	g cm <sup>-3</sup>
MIL-101(Cr)-NH <sub>2</sub>	37.06	2.93	5.33	2269	1.80	1.6906
	±0.87	±0.53	±0.42			±0.0019
<b>PEI-68</b>	39.71	5.89	15.53	238	0.51	1.3979
	±0.45	$\pm 0.28$	±0.39			$\pm 0.0018$
<b>PEI-88</b>	39.30	6.09	16.80	71	0.26	_*
	±0.17	±0.10	±0.07			
PEI-130	41.08	6.31	18.27	23	0.13	1.3415
	±0.10	±0.32	±0.17			$\pm 0.0022$
ED-128	35.91	4.88	12.98	77	0.43	1.6409
	±0.12	±0.22	±0.25			±0.0034
DAB-AM-8-145	45.76	7.57	14.31	121	0.34	_*
	±0.60	±0.60	±0.19			
DETA-88	39.70	5.36	16.05	46	0.40	1.4729
	±0.31	±0.25	±0.20			±0.0022

**Table 3.5:** Elemental composition, BET surface area, total pore volume and helium density of MIL-101(Cr)-NH<sub>2</sub> and its modifications.

<sup>\*</sup>insufficient sample amount for analyses

The TGA decomposition profiles of the MOFs are shown in the supplementary materials (Figure 3.34a). Between 40 and 110 °C MIL-101(Cr)-NH<sub>2</sub> showed an initial weight loss of approximately 30 molecules of lattice H<sub>2</sub>O per formula unit. The higher amount of lattice H<sub>2</sub>O molecules determined via TGA compared to the results from the elemental analysis is consistent with loss of H<sub>2</sub>O during the vacuum activation of MIL-101(Cr)-NH<sub>2</sub> prior to the elemental analysis. At temperatures between 110 and 360 °C, the H<sub>2</sub>O molecules coordinated to the chromium trimers were removed (~ 4 to 5 wt%). This result is in good agreement with the expected weight loss of 4.73 wt% calculated from the empirical formula Cr<sub>3</sub>O(OH)(H<sub>2</sub>O)<sub>2</sub>[BDC-NH<sub>2</sub>]<sub>3</sub>. The first weight loss was substantially reduced after the PSM of MIL-101(Cr)-NH<sub>2</sub>, presumably due to the reduced pore volumes and the vacuum activation of the modified materials during their preparation. The incorporation of amines appears to have caused a reduction in the thermal stability since, starting at approximately 200 to 240 °C (depending on the amine incorporated), a gradual weight loss developed for all PSM materials, consistent with the loss of the amines. However, the

temperatures corresponding to the complete decomposition of the framework increased somewhat, in the order MIL-101(Cr)-NH<sub>2</sub> < ED-128 < DAB-AM-8-145 < DETA-88 < PEI-68 < PEI-88 < PEI-130.



**Figure 3.25:** SEM images of (a) MIL-101(Cr)-NH<sub>2</sub>, (b) MIL-101(Cr)-NH<sub>2</sub>-DETA-88, (c) MIL-101(Cr)-NH<sub>2</sub>-PEI-68 and (d) MIL-101(Cr)-NH<sub>2</sub>-PEI-88.

SEM images were obtained for MIL-101(Cr)-NH<sub>2</sub> and after loading with 88 wt% DETA, 68 wt% PEI and 88 wt% PEI. The agglomeration of the nanoparticles of MIL-101(Cr)-NH<sub>2</sub> was clearly visible in Figure 3.25a and was still present after the modification with 68 wt% PEI. However, higher loadings of DETA and PEI led to a reduction of agglomeration and a more uniform surface morphology. Ferreira et al. also observed that, the higher amounts of 2-aminoterephthalic acid in MIL-101(Cr) tended to reduce the particle size and crystallinity, resulting in less defined morphologies [40], consistent with the reduction in morphology definition observed here.

The IR spectra of MIL-101(Cr)-NH<sub>2</sub> before and after PSM are compared with the spectra of the neat amines in Figure 3.26. The incorporation of amines into MIL-101(Cr)-NH<sub>2</sub> resulted in a shift in the position of IR absorption bands corresponding to the asymmetric

(3480 cm<sup>-1</sup>) and symmetric (3372 cm<sup>-1</sup>) stretch [36] of the amine moieties towards the asymmetric (~3335 cm<sup>-1</sup>) and symmetric (~3260 cm<sup>-1</sup>) stretch of the neat amines, which is consistent with the high amine loadings used in this work. The successful modification was further confirmed by the presence of asymmetric (~2930 cm<sup>-1</sup>) and symmetric (~2800 cm<sup>-1</sup>) CH<sub>2</sub> stretch vibrations [30].



**Figure 3.26:** FTIR spectra of MIL-101(Cr)-NH<sub>2</sub> before and after the PSM with (a) PEI, (b) DAB-AM-8, (c) ED and (d) DETA. The spectra are compared to the spectra of the neat amines.

The results of the PXRD experiments are shown in Figure 3.34b. The broadness of the Bragg peaks of MIL-101(Cr)-NH<sub>2</sub> is in good agreement with the data published by Jiang et al. [35] and is consistent with the small particle size. The incorporation of amines resulted in an apparent reduction of crystallinity (broader and less intense peaks), and was also

found to be dependent on the loading and the type of amine. At a PEI loading of 68 wt%, the intensity of the peak at  $2\theta$ =9.2° was higher than for the 88 wt% and 130 wt% cases. MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 showed an overall stronger diffraction pattern than MIL-101(Cr)-NH<sub>2</sub>-PEI. In fact, the peaks at 3.2° and 5.1° were visible in the diffraction pattern of MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145. The incorporation of ED and DETA resulted in the lowering of the apparent crystallinity. These changes are attributed to the pore filling of MIL-101(Cr)-NH<sub>2</sub>. Likewise, diminished intensities were also reported after the modification of MIL-101(Cr) and SBA-15 with PEI [32, 41].

# 3.4.4.2 Low pressure gas sorption measurements on MIL-101(Cr)-NH<sub>2</sub> before and after PSM

Low pressure (0-0.5 bar)  $CO_2$  adsorption and desorption pseudo-isotherms at 25, 45, 75 and 105 °C were measured to investigate the impact of different PEI loadings and different amines on the  $CO_2$  uptakes and sorption kinetics. The results of the low gas sorption experiments are discussed in the following five sections.

## 3.4.4.2.1 Effect of PEI loading

In Figure 3.27a to d, the CO<sub>2</sub> adsorption/desorption pseudo-isotherms of MIL-101(Cr)-NH<sub>2</sub> before and after PSM with PEI are compared. In the studied pressure range, no CO<sub>2</sub> saturation was observed in MIL-101(Cr)-NH<sub>2</sub>, but after the PSM with PEI the CO<sub>2</sub> adsorption capacities were found to increase only slightly at pressures above ~0.15 bar. This result suggests that the PEI modified materials are not applicable for high pressure separations as CO<sub>2</sub> saturation is achieved at low pressures. With increasing temperature, the CO<sub>2</sub> adsorption capacities of MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Cr)-NH<sub>2</sub>-PEI-68 and MIL-101(Cr)-NH<sub>2</sub>-PEI-88 were all found to decrease. This is consistent with the expected behaviour for classical adsorption where the higher kinetic energies at higher temperatures lead to a reduction in the equilibrium concentration of adsorbed species. However, the CO<sub>2</sub> adsorption behaviour on MIL-101(Cr)-NH2-PEI-130 was different. In this case, the amount of CO<sub>2</sub> adsorbed was comparable at 25 and 45 °C and was found to increase with temperature up to 75 °C. Since the internal porosity of MIL-101(Cr)-NH<sub>2</sub>-PEI-130 is essentially fully occupied by the PEI, CO<sub>2</sub> penetration into the sample at the temperatures is very slow and incomplete on the timescale of the experiment. Equilibrium adsorption is never achieved. At the higher temperature, 105 °C, the mobility of PEI is enhanced such that  $CO_2$  can penetrate more quickly and effectively but, at the same time, the higher temperature causes a reduction in the equilibrium concentration of the adsorbed species. The hysteresis between adsorption and desorption in the neat MIL-101(Cr)-NH<sub>2</sub> is consistent with the strong interactions of the CO<sub>2</sub> with the CUS in the framework structure. These findings are in good agreement with studies on HKUST-1, for which it was shown that vacuum was insufficient for the regeneration of the material, while a completely reversible adsorption was easily achieved by increasing the temperature under a N<sub>2</sub> purge [42]. The hysteresis between adsorption and desorption in the PSM materials at lower temperatures indicates an apparent irreversibility in the CO<sub>2</sub> adsorption, due to the timescale of the experiment (20 min equilibration time). This result suggests that the diffusion of CO<sub>2</sub> into the pores was limited at lower temperatures.

At 25 °C the CO<sub>2</sub> adsorption capacities for PEI modified MIL-101(Cr)-NH<sub>2</sub> increased in the order MIL-101(Cr)-NH<sub>2</sub>-PEI-130 < MIL-101(Cr)-NH<sub>2</sub>-PEI-68 < MIL-101(Cr)-NH<sub>2</sub>-PEI-88. The lower CO<sub>2</sub> capacity of MIL-101(Cr)-NH<sub>2</sub>-PEI-68 can be explained by the smaller amount of amine groups present. Despite having the smallest CO<sub>2</sub> adsorption capacity at low temperature, MIL-101(Cr)-NH<sub>2</sub>-PEI-130 showed the highest adsorption capacity in comparison with the lower PEI loadings at 75 °C. This is attributed to the mobility of PEI at this temperature; because of this pores that were not accessible at lower temperature become accessible allowing CO<sub>2</sub> to diffuse into the pores.

In order to determine the nature of the adsorption mechanism before and after PEI modification, the heats of adsorption were calculated from the DTA signals at 25 °C (Figure 3.34c). The values stated here were determined at 0.2 bar and after 10 min of adsorption. This duration was chosen for MIL-101(Cr)-NH<sub>2</sub> and all PEI modified materials, as the majority of CO<sub>2</sub> was adsorbed into the materials. The heats of adsorption decreased from MIL-101(Cr)-NH<sub>2</sub>-PEI-68 (68 kJ mol<sup>-1</sup>) > MIL-101(Cr)-NH<sub>2</sub>-PEI-130 (63 kJ mol<sup>-1</sup>) ~ MIL-101(Cr)-NH<sub>2</sub>-PEI-88 (62 kJ mol<sup>-1</sup>) > MIL-101(Cr)-NH<sub>2</sub> (37 kJ mol<sup>-1</sup>). While CO<sub>2</sub> was physisorbed into MIL-101(Cr)-NH<sub>2</sub>, the heats of adsorption of the PSM materials indicate that the adsorption of CO<sub>2</sub> is essentially via chemisorption rather than physisorption. This would also explain the hysteresis in the sorption pseudo-isotherms of the PEI materials and the change in pseudo-isotherm shape. Similar findings were reported after the PSM of H<sub>3</sub>(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub> (H<sub>3</sub>BTTri= 1,3,5-tri(1*H*-1,2,3-triazol-4-yl)benzene with N,N'-dimethylendiamine and MOF-74(Ni) with piperazine [43, 44].



**Figure 3.27:** CO<sub>2</sub> adsorption ( $\blacksquare$ )/desorption ( $\square$ ) pseudo-isotherms for MIL-101(Cr)-NH<sub>2</sub> before and after PEI modification at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\bullet$ ).

## 3.4.4.2.2 Effect of different amines on the CO<sub>2</sub> uptakes

The CO<sub>2</sub> pseudo-isotherms of MIL-101(Cr)-NH<sub>2</sub> before and after PSM with DAB-AM-8, DETA and ED are presented in Figure 3.28. Due to the low CO<sub>2</sub> uptakes of MIL-101(Cr)-NH<sub>2</sub>-ED-150 and the higher volatility of ED, the sorption pseudo-isotherms for this sample were measured only up to 75 °C.

Figure 3.28 shows that increasing the  $CO_2$  pressure resulted in a rise in  $CO_2$  adsorption capacities and that the  $CO_2$  capacities for the PSM materials decrease in the order DAB-AM-8 > PEI > DETA > ED. This can be correlated with the number of amine sites available for adsorption across this set of samples, which follows the same order. A change in the pseudo-isotherm shape after the PSM with DAB-AM-8, DETA and ED was

observed, similar to that obtained after the PSM with PEI. This, again, implies a change in adsorption mechanism from physisorption, prior to PSM, to chemisorption after PSM.

In the studied pressure and temperature range no CO<sub>2</sub> saturation in MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 was observed, although it is obvious from the shape of the pseudoisotherms that the amine modified samples would reach saturation at much lower CO<sub>2</sub> pressures than MIL-101(Cr)-NH<sub>2</sub>. In contrast to MIL-101(Cr)-NH<sub>2</sub>-PEI-130, the CO<sub>2</sub> adsorption capacity was found to decrease with increasing temperature, in all cases, consistent with the expected behaviour for classical adsorption where the higher kinetic energies at higher temperatures lead to a reduction in the equilibrium concentration of adsorbed species. The adsorption and desorption pseudo-isotherms exhibited very significant hysteresis after the PSM with DAB-AM-8, which was less pronounced at higher temperatures as a result of the more facile approach to equilibrium. A comparison of the CO<sub>2</sub> pseudo-isotherms of MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 revealed that enhanced CO<sub>2</sub> adsorption capacities, over the entire pressure and temperature range, were obtained after the PSM with this amine, especially at low pressures and/or high temperatures. For instance, the DAB-AM-8 modified framework exhibited a CO<sub>2</sub> adsorption capacity of 4.20 wt% at 0.5 bar and 105 °C, which was significantly higher than the CO<sub>2</sub> adsorption capacity 0.39 wt% in MIL-101(Cr)-NH<sub>2</sub> under the same conditions.

MIL-101(Cr)-NH<sub>2</sub>-DETA-88 and MIL-101(Cr)-NH<sub>2</sub>-ED-128 were nearly saturated with  $CO_2$  and only small improvements of the  $CO_2$  adsorption capacities were observed (especially at 75 °C), which were negligible in comparison with the results after the PSM with DAB-AM-8 and PEI. As discussed for the DAB-AM-8-145 and PEI modified materials, the adsorption/desorption pseudo-isotherms exhibited a hysteresis after the PSM with DETA and ED, consistent with the chemisorption of  $CO_2$  onto the primary and/or secondary amines.

The measured heats of adsorption again indicate that  $CO_2$  was chemisorbed in MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 (138 kJ mol<sup>-1</sup>) and in MIL-101(Cr)-NH<sub>2</sub>-DETA-88 (118 kJ mol<sup>-1</sup>). The heat of adsorption of the ED modified framework was found to be 30 kJ mol<sup>-1</sup>, more consistent with the physisorption of  $CO_2$ . While the heats determined here provide a good indication, in some case an under- or overestimation of values is possible due to a baseline drift in the DTA profile (Figure 3.34c) and the comparatively


low CO<sub>2</sub> adsorption capacities considered here, especially for the DETA and ED modified samples.

**Figure 3.28:** CO<sub>2</sub> adsorption ( $\blacksquare$ )/desorption ( $\square$ ) pseudo-isotherms for MIL-101(Cr)-NH<sub>2</sub> before and after amine modification at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\blacklozenge$ ).

#### 3.4.4.2.3 Effect of different amines on the sorption kinetics

Figure 3.29 shows the effect of temperature on the adsorption/desorption rates before and after amine modification. At 25 and 45 °C, the CO<sub>2</sub> adsorbed on the DAB-AM-8-145, PEI-68 and PEI-88 modified samples increased rapidly with each pressure step. PEI-130 on the other hand showed a slow continuous uptake of CO<sub>2</sub> at low temperatures. The adsorption/desorption clearly did not reach equilibrium in the 20 min allowed for each adsorption/desorption step at these temperatures, due to the restricted diffusivity of CO<sub>2</sub> within most amines at low temperatures. While the adsorption/desorption in ED and DETA modified MIL-101(Cr)-NH<sub>2</sub> reached equilibrium in 20 min at 25 °C, PEI and DAB-

AM-8 modified samples required 75 °C or 105 °C for this to occur. This shift upwards in the "optimal" operating temperature may be beneficial for a VSA process aiming to separate  $CO_2$  from flue gas, since there would be a reduced need to cool the flue gas, which potentially lowers the cost required for the capture process.



- MIL-101(Cr)-NH<sub>2</sub> - PEI-68 - PEI-88 - PEI-130 - DAB-AM-8-145 - ED-128 - DETA-88

**Figure 3.29:** TGA profiles of MIL-101(Cr)-NH<sub>2</sub> before and after amine modification at (a) 25 °C, (b) 45 °C, (c) 75 °C and (d) 105 °C.

With higher PEI loadings the adsorption/desorption rate decreased at lower temperatures in the order MIL-101(Cr)-NH<sub>2</sub>-PEI-68 < MIL-101(Cr)-NH<sub>2</sub>-PEI-88 < MIL-101(Cr)-NH<sub>2</sub>-PEI-130 and equilibrium was reached within the timescale of the experiment at the higher temperatures. Increasing the temperature resulted in an increase of the mobility of PEI at higher temperatures allowing the diffusion of CO<sub>2</sub> into pores that were not accessible at lower temperatures.

#### 3.4.4.2.4 Comparison to neat DAB-AM-8, DETA and PEI

Where possible the low pressure  $CO_2$  sorption experiments were repeated using the neat amines in order to get a better understanding of the performance of the amine modified materials. However, due to its relatively high volatility, the sorption pseudo-isotherms of ED could not be measured.

Figure 3.30a shows the sorption pseudo-isotherms of DAB-AM-8, DETA and PEI at different temperatures. In most cases, the CO<sub>2</sub> adsorption capacities increased with increasing temperature. DETA exhibited the highest sorption capacities between 25 and 75 °C, reaching a maximum of 16.2 wt% at 75 °C and 0.5 bar. Furthermore, CO<sub>2</sub> saturation for most amines was achieved at pressures below 0.2 bar. One exception was the sorption of CO<sub>2</sub> on PEI at 105 °C, which did not reach a saturated uptake in the studied pressure range. The maximum adsorption capacity in PEI was 4.29 wt% at 0.5 bar and 105 °C.

The TGA profiles for the neat amines given in Figure 3.30b to d were recorded in an identical manner to those of the composite materials in Figure 3.29. The profiles show that after an initial rapid uptake of  $CO_2$  at pressures below 0.2 bar, the sorption process becomes slower at higher pressures. Two exceptions to this are the adsorption of  $CO_2$  in DAB-AM-8 and PEI at 105 °C, which show a slow uptake at low pressures. Furthermore, all amines still absorbed CO<sub>2</sub> during the 20 min of equilibration after each pressure increase. Due to the comparatively low CO<sub>2</sub> adsorption capacities and the slow diffusivities, neat DAB-AM-8 and PEI have relatively poor CO<sub>2</sub> capture performance. This result also indicates that with increasing number of amine groups, the CO<sub>2</sub> sorption kinetic becomes slower. It is hypothesised that longer equilibration times will lead to an increase in CO<sub>2</sub> adsorption capacity. Very little desorption was observed upon lowering the pressure, which suggests that CO<sub>2</sub> was strongly chemisorbed in the amines. Upon final heating the amines to 90 or 110 °C the amount desorbed was increased, but since more CO<sub>2</sub> was adsorbed at higher temperatures, this does not imply a reduction in the retention of CO<sub>2</sub> after the final re-activation step. In fact more CO<sub>2</sub> was retained. An example is the sorption of  $CO_2$  in DETA, which is completely reversible upon heating after adsorption/desorption at 25 °C, while 7.69 wt% CO<sub>2</sub> remained chemisorbed after adsorption/desorption at 75 °C and subsequent heating. One possible explanation is the



lower  $CO_2$  adsorption capacity at lower temperatures, which could enable complete desorption upon heating.

**Figure 3.30:** (a)  $CO_2$  adsorption (**n**) pseudo-isotherms for DAB-AM-8 (red), DETA (black) and PEI (green) at 25 °C (**n**), 45 °C (**4**), 75 °C (**A**) and 105 °C (**•**). TGA profiles of DAB-AM-8 (b), DETA (c) and PEI (d) at 25 °C (black), 45 °C (red), 75 °C (blue) and 105 °C (green). Between t=220 min and t~250 min the amines were heated to 90 °C (DETA) or 110 °C (PEI, DAB-AM-8) and then cooled under flowing Ar.

Figure 3.31 shows the comparison of the adsorption pseudo-isotherms of the PSM materials with those of the neat amines. In comparison with the amine modified MOFs, only MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 showed a higher CO<sub>2</sub> adsorption capacity than the neat amine over the entire pressure and temperature range. Although the sorption pseudo-isotherms at 25 and 45 °C were not measured on neat DAB-AM-8 due to very slow adsorption/desorption rates at these temperatures, it can be expected that the adsorption capacity is lower than the 0.60 wt% at 75 °C. The results show that the CO<sub>2</sub> adsorption capacities in MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 were indeed improved

beyond those observed in MIL-101(Cr)-NH<sub>2</sub> and in neat DAB-AM-8. The PEI modified frameworks exhibited significantly higher CO<sub>2</sub> adsorption capacities at 25 and 45 °C over the entire pressure range, but at 75 °C only MIL-101(Cr)-NH<sub>2</sub>-PEI-130 had a higher adsorption capacity up to 0.15 bar. A further increase in temperature resulted in a lower CO<sub>2</sub> adsorption capacity compared to the 4.39 wt% in neat PEI. In contrast to these results, the neat DETA outperformed the amine modified material at all temperatures and over the entire studied pressure range. One explanation could be the low accessibility of the amine groups in MIL-101(Cr)-NH<sub>2</sub>-DETA-88. Despite the lower CO<sub>2</sub> adsorption capacities in some cases, the incorporation of these amines led to an improvement of the sorption kinetics especially at higher temperatures and therefore allowed CO<sub>2</sub> to be desorbed upon lowering the pressure. This is necessary for a good performance under cyclic conditions.



- Neat amines – PEI-68 – PEI-88 – PEI-130 – DAB-AM-8-145 – DETA-88 Figure 3.31: Comparison of CO<sub>2</sub> adsorption pseudo-isotherms for MIL-101(Cr) modified frameworks with neat DAB-AM-8, DETA and PEI at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\blacklozenge$ ).

#### 3.4.4.3 Cycling experiments on MIL-101(Cr)-NH<sub>2</sub> before and after PSM

For industrial applications, adsorbents are required that exhibit a good stability and regenerability over many cycles preferably in the presence of  $H_2O$  vapour. The stability and regenerability before and after PSM were assessed by performing cycling experiments under dry and wet conditions (1 vol%  $H_2O$ ).

Table 3.6 summarizes the cycling conditions, the  $H_2O$  uptake and the average working capacities during the dry and wet cycling experiments. As discussed above, the cycling experiments of the PSM materials needed to be performed at higher temperatures in order to obtain faster adsorption kinetics and therefore to reach equilibration of the uptake during the 20 min allowed for each cycle. The average of the working capacities over the ten cycles was determined for a better comparison of these materials. The working capacity estimated from the low pressure pseudo-isotherms was observed in the first cycle in each PSM material, but from cycle two onwards, working capacities were smaller due to the chemisorption of  $CO_2$ .

MOF	Cycling temperature / °C	H <sub>2</sub> O uptake / wt%	Average CO <sub>2</sub> working capacity dry/ wt%	Average CO <sub>2</sub> working capacity wet/ wt%
MIL-101(Cr)-NH <sub>2</sub>	25	8.55	0.81	0.85
MIL-101(Cr)-NH <sub>2</sub> -PEI- 68	75	1.61	0.38	0.35
MIL-101(Cr)-NH <sub>2</sub> -PEI- 88	75	-	0.47	0.41
MIL-101(Cr)-NH <sub>2</sub> -PEI- 130	105	-	0.16	0.23
MIL-101(Cr)-NH <sub>2</sub> -ED- 128	45	5.18	0.27	0.15
MIL-101(Cr)-NH <sub>2</sub> -DAB- AM-8-145	105	0.74	0.97	0.98
MIL-101(Cr)-NH <sub>2</sub> - DETA-88	45	1.76	0.25	0.28

**Table 3.6:** Summary of cycling conditions and results.

The comparison of the average working capacities under dry and wet conditions revealed, that most of these MOFs show a good regenerability and stability even in the presence of H<sub>2</sub>O vapour. Although some of these PSM materials exhibited higher CO<sub>2</sub> adsorption capacities at 0.05 bar during the low pressure experiments, the working capacities in the cycling experiments are lower than those of MIL-101(Cr)-NH<sub>2</sub> (except for MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145). At this point it should be mentioned that if these results would be compared with CO<sub>2</sub> uptakes of MIL-101(Cr)-NH<sub>2</sub> at temperatures of 45 °C and above, most of these modifications would improve the performance during cycling. While the working capacities are smaller than those reported for MCF modified with linear PEI (M<sub>w</sub>=2500), which range from approximately 3.8 wt% to 2.5 wt%, the results for MCF modified with branched PEI (M<sub>w</sub>=1200) are similar to those observed in MIL-101(Cr)-NH<sub>2</sub>-PEI-88 under dry conditions [45].

MIL-101(Cr)-NH<sub>2</sub> exhibited a H<sub>2</sub>O uptake of 8.55 wt%, which makes the material an attractive H<sub>2</sub>O adsorbent. The PSM of the framework resulted in diminished H<sub>2</sub>O uptakes consistent with the smaller pore volumes (Table 3.5). However, despite similar pore volumes in MIL-101(Cr)-NH<sub>2</sub>-DETA-88 and MIL-101(Cr)-NH<sub>2</sub>-ED-128, the ED modified framework exhibited a significantly higher H<sub>2</sub>O uptake than after PSM with DETA, consistent with the loss of ED during the experiment. The PSM materials containing DAB-AM-8, DETA and PEI exhibited similar or slightly higher CO<sub>2</sub> working capacities under humid conditions, which confirm the regenerability of these materials under cycling conditions. In contrast to this, the MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 exhibited a working capacity that was 0.16 wt% higher under dry conditions. This result suggests that H<sub>2</sub>O is slightly improving the CO<sub>2</sub> uptake in this framework.

The TGA profiles of the dry and wet cycling experiments are shown in Figure 3.32a and b. Equilibrium adsorption under dry conditions was achieved in most materials during the allowed equilibration time of 20 min. One exception to this was MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145, which exhibited continuously increasing adsorption during these 20 min under both conditions. This result suggests that the adsorption kinetics for this sample are still too slow to achieve equilibrium adsorption. The additional mass loss of MIL-101(Cr)-NH<sub>2</sub> at the end of the dry experiment at t=500 min compared to the mass change at t=-55 min could have been due to the incomplete removal of moisture during the initial activation step at 110 °C for 1 h and was therefore lost during the final heating after the cycling experiments. During the initial H<sub>2</sub>O pre-treatment step (t=0 to 400 min), no saturation was

obtained in MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Cr)-NH<sub>2</sub>-ED-128, which resulted in a progressive increase in H<sub>2</sub>O adsorption during the cycles and therefore equilibrium adsorption was not achieved, especially in MIL-101(Cr)-NH<sub>2</sub>. MIL-101(Cr)-NH<sub>2</sub>-PEI-130 showed a small weight loss during the initial H<sub>2</sub>O saturation step (Figure 3.32b), which implies that some of the PEI was volatilised in the presence of steam prior to the cycling process. This volatilisation could result in a slight increase in pore volume of the PEI-130 sample, hence increasing the working capacity. An additional weight loss after the final heating period (t=890 min) in the PEI-88 and PEI-130 samples was observed, which could be due to some volatilisation of PEI that is not strongly bound to the CUS, because of its high concentration. In the case of the DAB-AM-8 modified framework, no H<sub>2</sub>O uptake was observed during the first 200 min, after which H<sub>2</sub>O was adsorbed into the framework. At the end of the wet cycling, the samples were heated at 90 to 110 °C in order to desorb the H<sub>2</sub>O fully. While the PEI modified materials did return to their original weight after this treatment, the other PSM materials remained heavier than before the experiments, though the nature of the retained material was not ascertained.



- MIL-101(Cr)-NH<sub>2</sub> - PEI-68 - PEI-88 - PEI-130 - DAB-AM-8-145 - ED-128 - DETA-88

**Figure 3.32:** TGA profiles of MIL-101(Cr)-NH<sub>2</sub> before and after amine modification under (a) dry and (b) wet (1 vol%  $H_2O$ ) conditions.

The stabilities of the samples during the wet cycling experiments were evaluated by PXRD. The comparison of the diffraction patterns before and after the exposure to  $H_2O$  vapour is shown in the supplementary material (Figure 3.35 and Figure 3.36). The hydrothermal stability of MIL-101(Cr)-NH<sub>2</sub> was confirmed, with no changes in the diffraction pattern being observed. The PSM with PEI and DAB-AM-8 resulted in

reduction in peak intensities and hence the apparent crystallinities. To determine the cause of this loss, the cycling studies should be extended in order to get a better insight into the long term stability of the materials. The PXRD studies indicate that the MOFs with high amounts of amines are more susceptible to a loss in crystallinity and therefore a partial decomposition of the framework during wet cycling processes. However, it should be mentioned that the crystallinity of the materials is relatively poor to start with and it might be better to compare the 'before and after' structures by determining the BET surface area and pore volume.

#### 3.4.4.4 High pressure gas sorption on MIL-101(Cr)-NH<sub>2</sub>

The CO<sub>2</sub> and N<sub>2</sub> isotherms of MIL-101(Cr)-NH<sub>2</sub> were measured in the temperature range between 25 to 105 °C and at pressures up to 40 bar to investigate the potential of the framework for high pressure separation processes and to determine the  $CO_2/N_2$  selectivities.

The adsorption and desorption isotherms of CO<sub>2</sub> and N<sub>2</sub> are shown in Figure 3.33a and b, respectively. The adsorption capacities decreased with increasing temperatures, which was due to the physisorption of the adsorbates and is consistent with the results from the low pressure CO<sub>2</sub> experiments. Therefore, MIL-101(Cr)-NH<sub>2</sub> could potentially be used in a PSA or temperature swing adsorption (TSA) processes. The CO<sub>2</sub> adsorption at 25 °C and 15 bar was found to be 46.0 wt%, which is lower than the 73.94 wt% for MIL-101(Cr) [46]. The lower capacity is presumably due to the presence of the amine groups which results in a reduction of the pore volume. However, in comparison with other amine modified MOFs like MIL-53(Al)-NH<sub>2</sub> (26 wt%, 30 °C) and MIL-101(Al)-NH<sub>2</sub> (42 wt%), the adsorption capacity was higher. Recently Khutia et al. studied the CO<sub>2</sub> adsorption in MIL-101(Cr)-NH<sub>2</sub>, which was prepared via postsynthetic modification of MIL-101(Cr) [33]. The material exhibited a CO<sub>2</sub> adsorption capacity of 15.9 wt% at 1 bar and 20 °C, which was nearly twice as high as the adsorption capacity of 7.9 wt% at 1.2 bar and 25 °C in the pre-functionalized MOF studied here. This difference could presumably be due to structural differences between the two MOFs as a result of the different synthesis strategies. At temperatures up to 75 °C, no saturation of the MOF with either CO<sub>2</sub> and N<sub>2</sub> was observed in the studied pressure range.

The  $CO_2/N_2$  selectivities at 25 to 105 °C as a function of pressure are shown in Figure 3.33c, as determined from the single component isotherms. With increasing pressure the

framework became less selective towards  $CO_2$ . In contrast to this, a temperature rise caused an increase in selectivity. At pressures above 5 to 10 bar, depending on the temperature, the  $CO_2/N_2$  selectivities remained constant. Furthermore, the selectivities were found to be ~9 at 25 °C, ~11 at 45 °C and ~ 15 at 105 °C. The value at 25 °C is slightly higher than the selectivity of ~8 reported MIL-101(Cr) synthesised in the presence of HF [46]. The relative scatter of the selectivities at lower pressures can be attributed to the higher inaccuracy of the measured adsorption capacities. The higher selectivities at lower pressure could be beneficial for post-combustion capture. However, future studies should focus on measuring binary gas adsorption using a gas mixture relevant to flue gas in order to get results that are more meaningful in an industrial context.



**Figure 3.33:** (a) High pressure  $CO_2$  and (b) high pressure  $N_2$  adsorption isotherms on MIL-101(Cr)-NH<sub>2</sub>. (c)  $CO_2/N_2$  selectivities calculated from the single component isotherms at 25 °C. (**n**), 45 °C (**4**), 75 °C (**A**) and 105 °C (**o**). (d) Isosteric heat of adsorption determined by fitting the Tóth isotherm model to the  $CO_2$  isotherms.

Figure 3.33d shows the isosteric heat of adsorption as a function of loading. The enthalpies were calculated using the Clausius Clapeyron equation. The Tóth isotherm model was fitted to the CO<sub>2</sub> isotherms at 25, 45, 75 and 105 °C. At zero coverage the isosteric heat of adsorption was estimated to be  $24\pm3$  kJ mol<sup>-1</sup>, which was much lower than 37 kJ mol<sup>-1</sup> determined from the DTA data. Furthermore, the isosteric heat of adsorption was also lower than the value of 43 kJ mol<sup>-1</sup> reported for MIL-101(Cr)-NH<sub>2</sub>, which was synthesised via PSM of MIL-101(Cr) [33]. A difference in heat of adsorption was expected due to the lower CO<sub>2</sub> adsorption capacity.

#### 3.4.5 Conclusion

In the present study, MIL-101(Cr)-NH<sub>2</sub> was postsynthetically modified with a series of amines at various loadings. All materials were evaluated for their potential suitability for post-combustion capture using ten cycle experiments with and without 1 vol%  $H_2O$  vapour.

The incorporation of the amines was confirmed by elemental analysis, FTIR, helium density and  $N_2$  adsorption/desorption at -196 °C. Significant decreases in BET surface areas, pore volumes and crystallinities were observed as a result of the PSM of MIL-101(Cr)-NH<sub>2</sub>.

The improvement in  $CO_2$  adsorption capacity was strongly depending on the type of amine, the loading, the temperature and the pressure. With increasing PEI loading the optimum adsorption temperature was found to occur at higher temperatures due to faster kinetics at elevated temperatures. The most promising PSM material was MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145, which showed higher adsorption capacities over the studied pressure and temperature range as well as comparable or slightly higher working capacities during the cycling experiments. On the other hand, ED and DETA modifications only resulted in small improvements in the adsorption capacities. To get a better understanding of the stability under wet cycling conditions additional characterisation techniques should be applied in the future (e.g. N<sub>2</sub> adsorption/desorption at -196 °C after exposure to 1 vol% H<sub>2</sub>O). However, while the increase in cycling temperature might be beneficial for post-combustion capture due to the potential decrease in gas handling costs, the incorporation of amines resulted in increased heats of adsorptions, which is disadvantageous. Furthermore, despite the improvements in CO<sub>2</sub> adsorption capacities, the uptakes are still lower than in other adsorbent materials like MCF modified with linear PEI.

Due to the fact that the PSM materials almost reached saturation with  $CO_2$  at low pressures, only MIL-101(Cr)-NH<sub>2</sub> was evaluated for high pressure  $CO_2$  capture. The  $CO_2$  adsorption capacities measured in this work were compared with data reported for MIL-101(Cr)-NH<sub>2</sub>. The results showed that higher adsorption capacities can be obtained in MIL-101(Cr)-NH<sub>2</sub> obtained via PSM of MIL-101(Cr). Therefore improvements in the synthesis procedure of prefunctionalised MIL-101(Cr)-NH<sub>2</sub> are necessary.

Although these materials might not be attractive for post-combustion capture due to the relative low  $CO_2$  uptake during cyclic tests, improvements of the  $CO_2$  adsorption under certain conditions and improvements in the cycling temperature were achieved.

#### 3.4.6 Acknowledgements

The financial support was provided by the Australian Government through the CRC Program to support this CO2CRC project. The authors acknowledge the use of facilities within the Monash Centre for Electron Microscopy. This research used equipment whose purchase was supported under the Australian Research Council's *Centres of Excellence* funding scheme (COE for Design in Light Metals).

#### 3.4.7 References

- [1] N. Stern, ""The Economics of Climate Change The Stern Review"," Cambridge2007.
- [2] R. K. Pachauri and A. Reisinger, "IPCC Fourth Assessment Report," *Intergovernmental Panel on Climate Change*, 2007.
- [3] R. Garnaut, ""The Garnaut Review 2011 Australia in the Global Response to Climate Change"," Cambridge2011.
- [4] R. Babarao and J. Jiang, "Molecular Screening of Metal-Organic Frameworks for CO<sub>2</sub> Storage," *Langmuir*, vol. 24, pp. 6270-6278, 2008.
- [5] IEA, "CO<sub>2</sub> Emissions from Fuel Combustion, Highlights," Available: <u>http://www.iea.org/co2highlights/co2highlights.pdf</u> (accessed: 27/07/2014)2012.
- [6] D. M. D'Alessandro, B. Smit, and J. R. Long, "Carbon Dioxide Capture: Prospects for New Materials," *Angewandte Chemie International Edition*, vol. 49, pp. 6058-6082, 2010.
- [7] H. Yang, Z. Xu, M. Fan, R. Gupta, R. B. Slimane, A. E. Bland, and I. Wright, "Progress in carbon dioxide separation and capture: A review," *Journal of Environmental Sciences*, vol. 20, pp. 14-27, 2008.
- [8] S. I. Plasynski, J. T. Litynski, H. G. McIlvried, and R. D. Srivastava, "Progress and New Developments in Carbon Capture and Storage," *Critical Reviews in Plant Sciences*, vol. 28, pp. 123-138, 2009.
- [9] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, and R. D. Srivastava, "Advances in CO<sub>2</sub> capture technology--The U.S. Department of Energy's Carbon Sequestration Program," *International Journal of Greenhouse Gas Control*, vol. 2, pp. 9-20, 2008.

- [10] A. Torrisi, R. G. Bell, and C. Mellot-Draznieks, "Functionalized MOFs for Enhanced CO<sub>2</sub> Capture," *Crystal Growth & Design*, vol. 10, pp. 2839-2841, 2010.
- [11] R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi, and T. K. Woo, "Direct Observation and Quantification of CO<sub>2</sub> Binding Within an Amine-Functionalized Nanoporous Solid," *Science*, vol. 330, pp. 650-653, October 29, 2010 2010.
- [12] C. Lastoskie, "Caging Carbon Dioxide," *Science*, vol. 330, pp. 595-596, October 29, 2010 2010.
- [13] M. Mikkelsen, M. Jorgensen, and F. C. Krebs, "The teraton challenge. A review of fixation and transformation of carbon dioxide," *Energy & Environmental Science*, vol. 3, pp. 43-81, 2010.
- Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X)," *Energy & Fuels*, vol. 23, pp. 2785-2789, 2009.
- [15] Q. Wang, J. Luo, Z. Zhong, and A. Borgna, "CO<sub>2</sub> capture by solid adsorbents and their applications: current status and new trends," *Energy & Environmental Science*, vol. 4, pp. 42-55, 2011.
- [16] C. Janiak and J. K. Vieth, "MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs)," *New Journal of Chemistry*, vol. 34, pp. 2366-2388, 2010.
- [17] A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, "Screening of Metal-Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach," *Journal of the American Chemical Society*, vol. 131, pp. 18198-18199, 2009.
- [18] J. M. Simmons, H. Wu, W. Zhou, and T. Yildirim, "Carbon capture in metalorganic frameworks-a comparative study," *Energy & Environmental Science*, vol. 4, pp. 2177-2185, 2011.
- [19] M. T. Ho, G. W. Allinson, and D. E. Wiley, "Reducing the Cost of CO<sub>2</sub> Capture from Flue Gases Using Pressure Swing Adsorption," *Industrial & Engineering Chemistry Research*, vol. 47, pp. 4883-4890, 2008/07/01 2008.
- [20] H. J. Choi, M. Dinca, A. Dailly, and J. R. Long, "Hydrogen storage in water-stable metal-organic frameworks incorporating 1,3- and 1,4-benzenedipyrazolate," *Energy & Environmental Science*, vol. 3, pp. 117-123, 2010.
- [21] J. Yang, A. Grzech, F. M. Mulder, and T. J. Dingemans, "Methyl modified MOF-5: a water stable hydrogen storage material," *Chemical Communications*, vol. 47, pp. 5244-5246, 2011.
- [22] A. M. B. Furtado, J. Liu, Y. Wang, and M. D. LeVan, "Mesoporous silica-metal organic composite: synthesis, characterization, and ammonia adsorption," *Journal of Materials Chemistry*, vol. 21, pp. 6698-6706, 2011.
- [23] J. W. Yoon, Y.-K. Seo, Y. K. Hwang, J.-S. Chang, H. Leclerc, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, E. Bloch, P. L. Llewellyn, C. Serre, P. Horcajada, J.-M. Grenèche, A. E. Rodrigues, and G. Férey, "Controlled Reducibility of a Metal– Organic Framework with Coordinatively Unsaturated Sites for Preferential Gas Sorption," *Angewandte Chemie International Edition*, vol. 49, pp. 5949-5952, 2010.
- [24] Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, and G. Férey, "Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal

Encapsulation," *Angewandte Chemie International Edition*, vol. 47, pp. 4144-4148, 2008.

- [25] P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jhung, and G. Férey, "High Uptakes of CO<sub>2</sub> and CH<sub>4</sub> in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101," *Langmuir*, vol. 24, pp. 7245-7250, 2008.
- [26] T. K. Trung, N. A. Ramsahye, P. Trens, N. Tanchoux, C. Serre, F. Fajula, and G. Férey, "Adsorption of C5-C9 hydrocarbons in microporous MOFs MIL-100(Cr) and MIL-101(Cr): A manometric study," *Microporous and Mesoporous Materials*, vol. 134, pp. 134-140, 2010.
- [27] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.
- [28] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, and F. Kapteijn, "Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties," *Chemistry of Materials*, vol. 23, pp. 2565-2572, 2011.
- [29] M. Hartmann and M. Fischer, "Amino-functionalized basic catalysts with MIL-101 structure," *Microporous and Mesoporous Materials*, vol. 164, pp. 38-43, 2012.
- [30] S.-N. Kim, S.-T. Yang, J. Kim, J.-E. Park, and W.-S. Ahn, "Post-synthesis functionalization of MIL-101 using diethylenetriamine: a study on adsorption and catalysis," *CrystEngComm*, vol. 14, pp. 4142-4147, 2012.
- [31] M. Anbia and V. Hoseini, "Enhancement of CO<sub>2</sub> adsorption on nanoporous chromium terephthalate (MIL-101) by amine modification," *Journal of Natural Gas Chemistry*, vol. 21, pp. 339-343, 2012.
- [32] Y. Lin, Q. Yan, C. Kong, and L. Chen, "Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO<sub>2</sub> Capture," *Sci. Rep.*, vol. 3, pp. 1-7, 2013.
- [33] A. Khutia and C. Janiak, "Programming MIL-101Cr for selective and enhanced CO<sub>2</sub> adsorption at low pressure by postsynthetic amine functionalization," *Dalton Transactions*, vol. 43, pp. 1338-1347, 2014.
- [34] Y. Lin, C. Kong, and L. Chen, "Direct synthesis of amine-functionalized MIL-101(Cr) nanoparticles and application for CO<sub>2</sub> capture," *RSC Advances*, vol. 2, pp. 6417-6419, 2012.
- [35] D. Jiang, L. L. Keenan, A. D. Burrows, and K. J. Edler, "Synthesis and postsynthetic modification of MIL-101(Cr)-NH2via a tandem diazotisation process," *Chemical Communications*, vol. 48, pp. 12053-12055, 2012.
- [36] S. Bernt, V. Guillerm, C. Serre, and N. Stock, "Direct covalent post-synthetic chemical modification of Cr-MIL-101 using nitrating acid," *Chemical Communications*, vol. 47, pp. 2838-2840, 2011.
- [37] ""Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.," "*Reflex Tools*" is a module in the Materials Studio Modeling software package from Accelrys Inc.
- [38] D.-Y. Hong, Y. K. Hwang, C. Serre, G. Férey, and J.-S. Chang, "Porous Chromium Terephthalate MIL-101 with Coordinatively Unsaturated Sites: Surface Functionalization, Encapsulation, Sorption and Catalysis," *Advanced Functional Materials*, vol. 19, pp. 1537-1552, 2009.
- [39] D. Jiang, A. D. Burrows, and K. J. Edler, "Size-controlled synthesis of MIL-101(Cr) nanoparticles with enhanced selectivity for CO<sub>2</sub> over N<sub>2</sub>," *CrystEngComm*, vol. 13, pp. 6916-6919, 2011.

- [40] R. B. Ferreira, P. M. Scheetz, and A. L. B. Formiga, "Synthesis of amine-tagged metal-organic frameworks isostructural to MIL-101(Cr)," *RSC Advances*, vol. 3, pp. 10181-10184, 2013.
- [41] Y. Kuwahara, D.-Y. Kang, J. R. Copeland, N. A. Brunelli, S. A. Didas, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita, and C. W. Jones, "Dramatic Enhancement of CO<sub>2</sub> Uptake by Poly(ethyleneimine) Using Zirconosilicate Supports," *Journal of the American Chemical Society*, vol. 134, pp. 10757-10760, 2012/07/04 2012.
- [42] S. Ye, X. Jiang, L.-W. Ruan, B. Liu, Y.-M. Wang, J.-F. Zhu, and L.-G. Qiu, "Postcombustion CO<sub>2</sub> capture with the HKUST-1 and MIL-101(Cr) metal–organic frameworks: Adsorption, separation and regeneration investigations," *Microporous and Mesoporous Materials*, vol. 179, pp. 191-197, 2013.
- [43] T. M. McDonald, D. M. D'Alessandro, R. Krishna, and J. R. Long, "Enhanced carbon dioxide capture upon incorporation of N,N'-dimethylethylenediamine in the metal-organic framework CuBTTri," *Chemical Science*, vol. 2, pp. 2022-2028, 2011.
- [44] A. Das, M. Choucair, P. D. Southon, J. A. Mason, M. Zhao, C. J. Kepert, A. T. Harris, and D. M. D'Alessandro, "Application of the piperazine-grafted CuBTTri metal-organic framework in postcombustion carbon dioxide capture," *Microporous and Mesoporous Materials*, vol. 174, pp. 74-80, 2013.
- [45] D. J. N. Subagyono, M. Marshall, G. P. Knowles, and A. L. Chaffee, "CO<sub>2</sub> adsorption by amine modified siliceous mesostructured cellular foam (MCF) in humidified gas," *Microporous and Mesoporous Materials*, vol. 186, pp. 84-93, 2014.
- [46] Z. Liang, M. Marshall, C. H. Ng, and A. L. Chaffee, "Comparison of Conventional and HF-Free-Synthesized MIL-101 for CO<sub>2</sub> Adsorption Separation and Their Water Stabilities," *Energy & Fuels*, vol. 27, pp. 7612-7618, 2013/12/19 2013.

## Supplementary material

## CO<sub>2</sub> adsorption in postsynthetic modified MIL-101(Cr)-NH<sub>2</sub>

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia



Fax:+61 3 990-54597





**- DETA-88** 

**Figure 3.34:** (a) TGA decomposition profiles on MIL-10(Cr)-NH<sub>2</sub> before and after PSM. (b) PXRD on MIL-101(Cr)-NH<sub>2</sub> before and after PSM. For a better clarity of the results obtained, the intensities of the diffraction patterns of the amine modified materials were multiplied by 5. (c) DTA profiles of MIL-101(Cr)-NH<sub>2</sub> before and after amine modification at 25 °C.



3.4.9 Comparison of PXRD results before and after wet cycling

**Figure 3.35:** PXRD of MIL-101(Cr)-NH<sub>2</sub> and its PEI and DAB-AM-8 modifications before (black) and after (blue) the wet cycling experiments.



**Figure 3.36:** PXRD of DETA and ED modified MIL-101(Cr)-NH<sub>2</sub> before (black) and after (blue) the wet cycling experiments.

### **Declaration for Thesis Chapter**

Postsynthetic modification of MIL-101(AI)-NH $_{\rm 2}$  with amines and their effect on the CO $_{\rm 2}$  sorption

#### Monash University

### **Declaration for Thesis Chapter 3.5**

#### Declaration by candidate

In the case of Chapter 3.5, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed samples; identified major	70 %
issues; developed interpretations; fully drafted paper and conclusion	

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co- authors only
Gregory P. Knowles	Aided method development (TGA), input to results analysis and manuscript revision	N/A .
Marc Marshall	Conducted high pressure sorption experiments on IGA, input to result analysis	N/A
Alan L. Chaffee	Supervision, assisted interpretation of results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work\*.

Candidate's Signature

Date
30/10/2014

Main Supervisor's Signature

Date
30/10/14

\*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

# 3.5 Postsynthetic modification of MIL-101(Al)-NH<sub>2</sub> with amines and their effect on the CO<sub>2</sub> sorption

Christin Patzschke,<sup>*a,b*</sup> Marc Marshall,<sup>*b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author:

#### 3.5.1 Abstract

A series of polyethyleneimine (PEI), diethylenetriamine (DETA) and polypropyleneimine octamine dendrimer (DAB-AM-8) modified MIL-101(Al)-NH<sub>2</sub> frameworks were synthesised and characterised via elemental analysis, N2 adsorption/desorption at -196 °C, helium density, PXRD, FTIR, SEM and thermal decomposition. The effect of the amines on the capture of CO<sub>2</sub> was evaluated by performing low pressure CO<sub>2</sub> (0-0.5 bar, 25-105 °C) and ten cycle experiments (0.05-0.15 bar). While the postsynthetic modification (PSM) of MIL-101(Al)-NH<sub>2</sub> with 96 wt% PEI resulted in an improvement of the CO<sub>2</sub> adsorption capacities during the low pressure CO<sub>2</sub> adsorption, the PSM with 94 wt% of DAB-AM-8 or with 89 wt% DETA did not. A rise in adsorption temperature was found to be beneficial for achieving reasonable adsorption/desorption rates after the PSM. The working capacities during the dry and wet cycling experiments were decreased in the presence of DAB-AM-8, DETA and PEI compared to neat MIL-101(Al)-NH<sub>2</sub>. While all materials exhibited good regenerability under dry conditions, the presence of 1 vol% H<sub>2</sub>O vapour resulted in a decline in working capacities in the majority of the PSM materials. Due to the CO<sub>2</sub> saturation of the PSM materials at low pressures, high pressure adsorption isotherms were only measured on MIL-101(Al)-NH<sub>2</sub>. The CO<sub>2</sub> and N<sub>2</sub> adsorption capacities were determined to be 58.37 wt% and 7.99 wt% at 25 °C and 40 bar, respectively. Despite the high hydrothermal stability of MIL-101(Cr), the sorption of 30 % relative humidity (RH) resulted in a decrease in CO<sub>2</sub> adsorption capacity, which suggested a low H<sub>2</sub>O stability.

#### 3.5.2 Introduction

Postsynthetic modification (PSM) of metal-organic frameworks (MOFs) has shown to be a powerful tool for the improvement of the CO<sub>2</sub> adsorption capacities at low pressures and

the  $CO_2/N_2$  selectivities [1-5]. The increase in the  $CO_2$  capacities at pressures relevant to post-combustion capture is necessary in order to make MOFs more competitive to other adsorbents such as amine modified siliceous materials or zeolites [6-10]. A number of studies are available that have focused on the grafting of amine groups onto coordinatively unsaturated sites (CUS).

Demessence et al. reported the PSM of the Cu<sup>II</sup> sites of H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>] (H<sub>3</sub>BTTri= 1,3,5-tris(1*H*-1,2,3-triazol-5-yl)benzene) using ethylenediamine (ED). While a steep rise in CO<sub>2</sub> adsorption capacity was observed at low pressure, the pore size of the parent material was found to be too small to permit complete access to the terminal alkylamines. Therefore, the grafting of ED led to higher CO<sub>2</sub> adsorption capacities at pressures up to 0.06 bar, but at 1 bar a decrease in the adsorption capacities from 14.3 wt% to 5.5 wt% was observed. In contrast to this, the CO<sub>2</sub>/N<sub>2</sub> selectivities of the PSM material were improved over the entire pressure range [1].

The highest binding strength for  $CO_2$  (-96 kJ mol<sup>-1</sup> at zero coverage) to date was reported for H<sub>3</sub>[(Cu<sub>4</sub>Cl)<sub>3</sub>(BTTri)<sub>8</sub>] functionalised with *N*,*N*'-dimethylethylenediamine. The cycling capacity under dry conditions (~7 wt%) was higher than the working capacity of 5.5 wt% in 30 % MEA solution [11].

Increased CO<sub>2</sub> adsorption capacities (1.51 vs 1.35 mmol g<sup>-1</sup> at room temperature and 400 ppm CO<sub>2</sub>), improved stability and regenerability of CPO-27(Mg) containing ED have been reported by Choi et al. [5]. On the other hand, the incorporation of piperazine onto the Ni<sup>II</sup> sites in CPO-27(Ni) caused a decrease in adsorption capacity from 25.5 wt% to 14.1 wt% at 1 bar and 25 °C. However, the material exhibited an improved CO<sub>2</sub>/N<sub>2</sub> selectivity from 30 to 51 as well as a good stability and regenerability in a temperature swing process [12].

The PSM of MIL-101(Cr) with a variety of amines has been studied extensively [2-4, 13, 14]. An increase in  $CO_2$  adsorption capacity at pressures below 0.15 bar was observed after the modification with diethylenetriamine (DETA). However, the decrease in pore volume resulted in a decrease in uptake from 7.9 wt% to 3.1 wt% at 1 bar and 25 °C [3]. In contrast to this, the modification with pentaethylenehexamine (PEHA) increased the adsorption capacity from 3.74 to 5.72 wt% at 10 bar [4]. A high-performance sorbent for post-combustion capture was obtained by grafting PEI onto the Cr<sup>III</sup> sites. PEI loadings of

50 to 160 wt% resulted in increases in  $CO_2$  capacities in the studied pressure range of 0 to 1.8 bar [15].

In this work, MIL-101(Al)-NH<sub>2</sub> was synthesised, characterised and postsynthetically modified. The framework consists of trimeric Al(III) octahedra which are connected by 2-aminoterephthalic acid ligands to form a supertetrahedral building unit [16]. The supertetrahedra further assemble into a zeotypic MOF with two types of cages, a dodecahedral and a hexakadodecahedral cage, which are assessable through micorporous windows of 1.2 and 1.6 nm [16-19]. Within the supertetrahedral building unit two of the three Al(III) octahedra contain a terminal H<sub>2</sub>O molecule, which can be removed upon heating at 110 °C to give CUS.

Serra Crespo et al. reported the applicability of MIL-101(Al)-NH<sub>2</sub> for natural gas and biogas upgrading [16]. Although, MIL-101(Al)-NH<sub>2</sub> was found to selectively adsorb CO<sub>2</sub>, no studies are available that focus on the utilisation of the MOF in post-combustion capture. Furthermore, the presence of CUS in the framework is attractive for PSM to improve the CO<sub>2</sub> capacities and CO<sub>2</sub>/N<sub>2</sub> selectivities especially at pressures relevant to post-combustion carbon capture ( $\leq 0.15$  bar). Enhanced CO<sub>2</sub> adsorption and working capacities were sought by PSM with DAB-AM-8, DETA and PEI. Two different loadings of PEI were studied and the most effective theoretical loading was determined to be 100 wt%. The applicability for post-combustion capture was evaluated by low pressure CO<sub>2</sub> sorption (0-0.5 bar, 25-105 °C) as well as dry and wet cycling experiments. Ten cycles of adsorption and desorption were conducted by varying the CO<sub>2</sub> partial pressures between 0.05 and 0.15 bar, allowing 20 min for the equilibration of each adsorption and desorption step. Furthermore, the CO<sub>2</sub>/N<sub>2</sub> selectivity and H<sub>2</sub>O stability of MIL-101(Al)-NH<sub>2</sub> were determined by high pressure CO<sub>2</sub>, N<sub>2</sub> (0-40 bar) and H<sub>2</sub>O sorption.

#### **3.5.3** Experimental section

#### 3.5.3.1 Chemicals

AlCl<sub>3</sub>·6H<sub>2</sub>O (99 % Sigma Aldrich), 2-aminoterephthalic acid (99 %, Sigma Aldrich), DAB-AM-8 (Sigma Aldrich), diethylenetriamine (99 %, Sigma Aldrich), DMF (GR grade, Merck), ethanol ( $\geq$  99.7 %, Merck), methanol ( $\geq$  99.8 %, Merck), PEI (423 g mol<sup>-1</sup>, mixture of branched and linear PEI, Aldrich), argon (high purity, BOC and Air Liquide), carbon dioxide (Food grade, Coregas), helium (high purity, Air Liquide), liquid nitrogen (BOC and Air Liquide) and nitrogen (high purity, Air Liquide). All reagents were used without further purification.

#### 3.5.3.2 Synthesis of MIL-101(Al)-NH<sub>2</sub>

MIL-101(Al)-NH<sub>2</sub> was synthesised by the following method adapted from Hartmann and Fischer [17]. In a typical synthesis, a solution of 0.27 g (1.50 mmol) of 2-aminoterephthalic acid and 60 mL DMF was heated to 110 °C under stirring, after which 0.72 g (3.00 mmol) of AlCl<sub>3</sub>·6H<sub>2</sub>O were added in seven equal portions allowing 15 min between each addition. After the last addition of the metal salt, the mixture was stirred for 3 h, before the stirrer was switched off and the temperature was kept at 110 °C for another 16 h. The yellow powder was filtered and washed with DMF and ethanol. The product was further activated by Soxhlet extraction with ethanol, before being dried at 90 °C for 24 h.

#### 3.5.3.3 Amine modification of MIL-101(Al)-NH<sub>2</sub>

The PSM of MIL-101(Al)-NH<sub>2</sub> with DAB-AM-8, DETA and PEI was performed via wet impregnation. The method applied in this work was akin to that reported for the modification of MIL-101(Cr) with PEI [2]. Before the PSM, MIL-101(Al)-NH<sub>2</sub> was heated at 110 °C under vacuum overnight, removing the residual solvent and the coordinated H<sub>2</sub>O molecules. In a first step the amine was dispersed in 1 mL methanol and stirred for approximately 10 min under N<sub>2</sub> atmosphere. 0.2 g of activated MOF was then added and the mixture was purged with N<sub>2</sub> overnight. The amine modified materials were heated under vacuum at 110 °C. The loading of the sample was calculated using the following equation:

$$Amine\ loading = \frac{mass_{amine}}{mass_{MIL-101(Al)-NH_2}} \times 100 \tag{3.5}$$

Amine	Theoretical loading /	Loading after evac /	Loading after evac /
	wt%	wt%	mol(amine)/mol(CUS)
PEI	50	48	0.40
PEI	100	96	0.80
DAB-AM-8	100	94	0.43
DETA	100	89	3.05

Table 3.7: Overview of the targeted loading and the actual loading after vacuum activation.

An overview of the targeted loadings (in wt%) and the actual loadings after vacuum activation (in wt% and mol(amine)/mol(CUS)) is given in Table 3.7. Each sample is

denoted by three expressions connected by dashes in the following way. The first gives the MOF, which was always MIL-101(Al)-NH<sub>2</sub>, the second the amine loaded (PEI, DAB-AM-8 or DETA) and the third the actual loading of amine after activation as wt% of the MOF weight before PSM, e.g. MIL-101(Al)-NH<sub>2</sub>-PEI-48.

#### 3.5.3.4 Characterisation of MIL-101(Al)-NH<sub>2</sub> before and after PSM

All samples were activated at 110 °C in a Micromeritics VacPrep 061 degasser overnight prior to the characterisation by  $N_2$  adsorption/desorption, helium density and SEM.

The N<sub>2</sub> adsorption and desorption experiments were carried out on a TriStar II 3020 gas sorption analyser from Micromeritics at -196 °C. The sample tubes containing 0.1 to 0.2 g of activated MOF were backfilled with helium and installed in the TriStar. The relative pressure range of 0.01 to 0.2 was used to estimate the BET surface areas of the materials. The total pore volume was determined at  $p/p_0=0.99$ .

Helium densities were obtained on the reactivated samples previously used for the  $N_2$  adsorption/desorption measurements at -196 °C. The data was collected on an AccuPyc 1340 from Micromeritics.

SEM images before and after the PSM were recorded on a JEOL 7001F microscope using a magnification of 5 or 15kV.

The following characterisation techniques were conducted on the as-synthesised materials. However, it should be noted that the synthesis procedure of the PSM materials included the activation under vacuum.

The elemental composition of the materials was determined at the Campbell Microanalytical Laboratory at the University of Otago.

Powder X-ray diffraction (PXRD) measurements before and after PSM as well as after the wet cycling experiments were conducted on a Bruker D8 Focus Bragg-Brentano powder X-ray diffractometer using Cu  $K_{\alpha}$  radiation. The samples were mounted on a silicon low background sample holder using ethanol and the powder X-ray diffractograms were recorded in a 2 $\theta$ -range of 1 to 30 °.

Fourier transform infra-red (FTIR) spectroscopy was conducted on an Agilent Cary 630 Diamond ATR in the spectral range of 4000 to 650 cm<sup>-1</sup>.

Thermal decomposition of the materials was measured via thermogravimetric analysis (TGA) using a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. The samples were first heated to 110 °C under Ar atmosphere in order to remove any residual

moisture. After 30 min at 110 °C, the gas flow was changed from 100 vol% Ar to a 50 vol% Ar and 50 vol% air mixture and the temperature was maintained for further 30 min. The samples were then heated to 900 °C with a heating ramp of 10 °C min<sup>-1</sup>. After 15 min at 900 °C the gas flow was changed from an Ar/air mixture to pure Ar. The temperature was then maintained for another 15 min, before the samples were cooled to 20 °C.

## 3.5.3.5 Low pressure gas sorption measurements on MIL-101(Al)-NH<sub>2</sub> before and after PSM

Low pressure  $CO_2$  adsorption/desorption was measured on a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. Prior to the experiment all samples were activated under vacuum at 110 °C overnight. Approximately 20 mg of sample was used for each experiment. The samples were first heated to 110 °C under flowing Ar for 1 h. The samples were then cooled until the desired sorption temperature (25, 45, 75 and 105 °C) was reached. After approximately 35 min at the sorption temperature, the gas composition was changed from 100 vol% Ar to an Ar/CO<sub>2</sub> mixture. The CO<sub>2</sub> partial pressure was increased in five steps (0.02, 0.05, 0.15, 0.3, 0.5 bar), before CO<sub>2</sub> was desorbed by reducing the pressure in reverse order to 0 bar. The equilibration time for each adsorption and desorption step was set to 20 min. The adsorption and desorption points determined during this sequence were compiled to provide a "pseudo-isotherm". After the last desorption step the samples were reactivated under Ar at 110 °C for 30 min. The recorded DTA signals were analysed and where possible the heats of adsorption calculated.

#### **3.5.3.6** Cycling experiments on MIL-101(Al)-NH<sub>2</sub> before and after PSM

The dry and wet cycling experiments were performed on the vacuum activated samples (110 °C, overnight) using a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. After the in-situ activation of the samples (1 h at 110 °C under flowing Ar), they were cooled to 25 °C (MIL-101(Al)-NH<sub>2</sub>) or 105 °C (PSM materials) under Ar atmosphere. Under dry cycling conditions, the Ar gas stream was replaced by an Ar/CO<sub>2</sub> mixture approximately 40 min after reaching the sorption temperature. In contrast to this, the materials were treated with 1 vol% H<sub>2</sub>O vapour using an Ar/H<sub>2</sub>O mixture for approximately 7 h in the wet cycling experiments. After saturation with H<sub>2</sub>O vapour was reached, the gas mixture was changed to Ar/CO<sub>2</sub>/H<sub>2</sub>O. The CO<sub>2</sub> partial pressure was then varied between 0.05 and 0.15 bar until 10 cycles of adsorption and desorption were

conducted. An equilibration time of 20 min was allowed for each adsorption and desorption step. After the 10 cycles were performed, the gas flow was set to pure Ar and the samples were reactivated at 110 °C for 30 min.

#### 3.5.3.7 High pressure gas sorption on MIL-101(Al)-NH<sub>2</sub>

Two sets of high pressure adsorption/desorption measurements were conducted on MIL-101(Al)-NH<sub>2</sub>.

The first set of experiments were carried out using a HPVA 200 (Micromeritics) Approximately 0.3 g of MOF were activated under vacuum at 110 °C overnight. The sorption experiments using either  $CO_2$  or  $N_2$  were conducted in the pressure range of 0 to 40 bar. In the case of  $CO_2$ , the isotherms were measured at 25, 45, 75 and 105 °C. The heat of adsorption was calculated by using the Clausius-Clapeyron equation. The Tóth isotherm model was fitted to the adsorption isotherm at 25, 45 and 105 °C to determine the heat of adsorption as a function of loading [20]. N<sub>2</sub> isotherms were only measured at 25 and 105 °C. All isotherms were obtained on a single sample. Between each isotherm, the sample was activated under vacuum at 110 °C.

The hydrothermal stability of the framework was determined by measuring CO<sub>2</sub> isotherms before and after the treatment of the sample with 30 % relative humidity (RH) using an Intelligent Gravimetric Analyser (IGA-1 series, Hiden Analytical Ltd.). Prior to the analysis, the sample was activated under vacuum at 110 °C overnight in the VacPrep 061 (Micromeritics). Approximately 0.03 g of MOF were installed into the IGA. The sample was treated under vacuum at 25 °C until no further weight changes were observed. The CO<sub>2</sub> isotherms were measured at 25 °C up to 5 bar and the isotherms before and after H<sub>2</sub>O adsorption/desorption (30 % relative humidity (RH)) were compared to determine the H<sub>2</sub>O stability of the material. The equilibration time for each adsorption/desorption step ranged from 15 to 30 min for CO<sub>2</sub> and from 10 to 40 min for H<sub>2</sub>O. The sample was re-evacuated after each run at 25 °C until the initial sample weight was reached.

#### 3.5.4 Results and discussion

#### 3.5.4.1 Characterisation of MIL-101(Al)-NH<sub>2</sub> before and after PSM

MIL-101(Al)-NH<sub>2</sub> and its modifications were characterised via  $N_2$  adsorption/desorption at -196 °C, elemental analysis, helium density, PXRD, FTIR, SEM and TGA in order to

validate the structure of the framework and to determine the impact of DAB-AM-8, DETA and PEI.

The N<sub>2</sub> physisorption isotherms at -196 °C are shown in Figure 3.37. The well-known characteristic steps in the isotherm, typical for MIL-100 and MIL-101 frameworks, were observed [16, 17, 19, 21-23]. Before N<sub>2</sub> was adsorbed into the larger cavities at a relative pressure higher than 0.2, the supertetrahedra and later the medium cavities were filled [21]. In contrast to the isotherm data reported by Serra-Crespo et al. [16], a hysteresis loop was observed in this work. One possible explanation for this is a smaller particle size of MIL-101(Al)-NH<sub>2</sub> prepared in this work, such that hysteresis results from pore space within agglomerates of the smaller particles. Similar results have been reported for nanoparticles of MIL-101(Cr)-NH<sub>2</sub> [24]. Upon DETA and PEI modification the isotherm shape changed from an H4 isotherm to type II, which is characteristic for non-porous materials. This result is consistent with pore filling by the incorporated amines. The N<sub>2</sub> isotherm of the DAB-AM-8 modified MOF showed a type III isotherm due to the weak adsorbent-adsorbate interactions.



- MIL-101(Al)-NH<sub>2</sub> - PEI-48 - PEI-96 - DAB-AM-8-94 - DETA-89

**Figure 3.37:**  $N_2$  isotherms measured at -196 °C on MIL-101(Al)-NH<sub>2</sub> before and after PSM. The right graph expands the isotherms of the amine modified materials for a better comparison.

A comparison of the BET surface areas and total pore volumes of MIL-101(Al)-NH<sub>2</sub> before and after PSM is given in Table 3.8. The calculated BET surface area for MIL-101(Al)-NH<sub>2</sub> was higher than the value of 2100 m<sup>2</sup> g<sup>-1</sup> reported by Serra-Crespo et al. [16], but lower than the 3090 m<sup>2</sup> g<sup>-1</sup> determined by Hartmann and co-worker [17]. Differences

in BET surface areas can be a result of lower/higher crystallinities, different purities and different relative pressure ranges used for their estimation. For instance Serra Crespo et al. calculated the BET surface area at relative pressures between 0.05 and 0.15, but Hartmann et al. did not state the relative pressure range in which the surface area was estimated. This is a common problem and suggests the need of a standardised protocol to provide a better comparison between different publications. The incorporation of DAB-AM-8, DETA and PEI resulted in a reduction of the BET surface areas and pore volumes due to the increased space demand of the amines. The maximum possible amine loadings of DAB-AM-8 (156 wt%), DETA (161 wt%) and PEI (145 wt%) were calculated by dividing the total pore volume of MIL-101(Al)-NH<sub>2</sub> with the densities from DAB-AM-8 (0.99 g cm<sup>-3</sup>) [25], DETA (0.96 g cm<sup>-3</sup>) [26] and PEI (1.07 g cm<sup>-3</sup>) [27]. These loadings were expected to result in a complete pore filling, hence pore blockage. Therefore, the maximum amine loading applied in this work was reduced to 100 wt%. Even so, the significant reductions in BET surface areas and pore volumes after the incorporation of DAB-AM-8, DETA and PEI indicate that the pores were almost completely filled.

101(AI)-INH <sub>2</sub> and its modifications.							
MOF	%C	%Н	%N	%Cl	BET surface area / m <sup>2</sup> g <sup>-1</sup>	Total pore volume/ cm <sup>3</sup> g <sup>-1</sup>	He density / g cm <sup>-3</sup>
MIL-101(Al)-	32.31	3.93	4.48	3.51	2649	1.55	1.5804
NH <sub>2</sub>	±0.27	±0.25	±0.16	±0.28			±0.0029
<b>PEI-48</b>	40.21	6.05	13.56	2.25	33	0.19	*
	±0.34	±0.26	±0.39	±0.36			
PEI-96	40.92	6.73	15.58	1.74	34	0.16	1.3234
	±0.30	±0.28	±0.20	±0.26			±0.0027
DAB-AM-8-94	39.04	7.37	11.23	-	1.5	0.003	1.3187
	$\pm 1.07$	±0.17	±0.16				±0.0016
DETA-89	37.22	6.44	14.42	-	1.2	0.02	1.4474
	±0.35	±0.24	±0.16				±0.0025

**Table 3.8:** Elemental composition, BET surface area and total pore volume of MIL-101(Al)-NH<sub>2</sub> and its modifications.

*insufficient sample amount for analyses* 

The theoretical elemental composition of MIL-101(Al)-NH<sub>2</sub> was calculated from the empirical formula Al<sub>3</sub>OCl(H<sub>2</sub>O)<sub>2</sub>[BDC-NH<sub>2</sub>]<sub>3</sub> to yield 40.84% C, 2.71 % H, 5.95 % N and 5.02 % Cl. The comparison with the experimental data indicates the presence of

approximately 11 lattice  $H_2O$  molecules in the framework structure. The PSM of MIL-101(Al)-NH<sub>2</sub> resulted in higher carbon, hydrogen and nitrogen contents, consistent with the incorporation of the amines. As expected an increase in PEI loading caused an increase of the nitrogen content.

The helium densities were reduced after the PSM, which was expected due to the lower densities of the neat amines, and confirm the successful PSM of MIL-101(Al)-NH<sub>2</sub>.

The comparison of the FTIR spectra before and after the PSM of MIL-101(Al)-NH<sub>2</sub> is shown in Figure 3.38a. The incorporation of the amines was confirmed by the increase in the bands at 3469 cm<sup>-1</sup> and 3361 cm<sup>-1</sup> corresponding to the asymmetric and the symmetric stretch of the amine moieties, respectively [16]. Furthermore, a shift of these absorption modes towards lower wavenumbers was observed, consistent with those of the neat amines (not shown here). This observation was also reported after the PSM of MIL-101(Cr)-NH<sub>2</sub> [28]. The presence of methylene groups in the neat amines, resulted in the presence of an additional doublet at 2940 cm<sup>-1</sup> (asymmetric CH<sub>2</sub> stretch) and 2835 cm<sup>-1</sup> (symmetric CH<sub>2</sub> stretch) [3]. Additionally, a change in the absorption for the symmetric (1576 cm<sup>-1</sup>) and asymmetric (1442 cm<sup>-1</sup>) C-O stretch [29] as well as the O-C-O stretch (1393 cm<sup>-1</sup>) [30], which were all shifted after PSM. These changes in frequencies are presumably due to the coordination of the amines onto the CUS in MIL-101(Al)-NH<sub>2</sub>.



- MIL-101(Al)-NH<sub>2</sub> – PEI-48– PEI-96 – DAB-AM-8-94 – DETA-89 Figure 3.38: (a) FTIR spectra and (b) PXRD of MIL-101(Al)-NH<sub>2</sub> before and after PSM. The structural integrity of MIL-101(Al)-NH<sub>2</sub> before and after the PSM was determined by PXRD (Figure 3.38b). The formation of the MIL-101 framework was confirmed by the

comparison with the theoretical diffractogram of MIL-101(Cr) [31], which was calculated from the crystal structure using Materials Studio [32] (Figure 3.47). Significant decreases in crystallinity were observed after the PSM with DAB-AM-8, DETA and PEI. However, we hypothesize that the framework structure was still intact and that the apparent loss in intensity is an effect of pore filling by the amines. The deterioration of the intensities after PEI modification was also reported for MIL-101(Cr) and SBA-15 [2, 33].

The thermal decomposition profile of MIL-101(Al)-NH<sub>2</sub> is shown in the supplementary information (Figure 3.48a). After the loss of physisorbed H<sub>2</sub>O up to 110 °C, the weight decreased at a constant rate up to 380 °C and then the rate of weight loss increased. Earlier work has taken the temperature at which the rate of weight loss increased as the decomposition temperature and the temperature of 380 °C deduced from Figure 3.48 is consistent with the decomposition temperature of 377 °C reported by Serra-Crespo et al. [16]. The weight became constant at 785 °C, implying total decomposition of the framework at this temperature. Serra-Crespo et al. found that the weight became constant at the much lower temperature of ~525 °C, suggesting that decomposition of the framework occurred at a lower temperature than that found in this work [16]. The reason for this difference is probably due to differences in the gas composition used for the combustion. The use of the Ar/air mixture in this work has probably resulted in a slower combustion of the material than would occur with the application of pure air. The combustion of the PSM materials was conducted in the same manner as for MIL-101(Al)-NH<sub>2</sub>. Between 70 and 110 °C, the PSM materials exhibited a weight loss of 1 wt% (MIL-101(Al)-NH<sub>2</sub>-PEI-96) to 6 wt% (MIL-101(Al)-NH<sub>2</sub>-PEI-48), consistent with the loss of physisorbed H<sub>2</sub>O. A second weight loss was observed between approximately 190 and 260 °C for the PEI and DAB-AM-8 modified samples and between approximately 160 and 300 °C for MIL-101(Al)-NH<sub>2</sub>-DETA-89. This weight loss is presumably due to the loss of the amines. The TGA profiles show that the decomposition progressed at relatively low temperatures for the DAB-AM-8 (T=260-720 °C) and PEI modified materials (T=260-670 °C), while for MIL-101(Al)-NH<sub>2</sub>-DETA-89 the decomposition progressed more slowly (T=300-800 °C).



**Figure 3.39:** SEM images of (a) MIL-101(Al)-NH<sub>2</sub>, (b) MIL-101(Al)-NH<sub>2</sub>-PEI-48, (c) MIL-101(Al)-NH<sub>2</sub>-PEI-96, (d) MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 and (e) MIL-101(Al)-NH<sub>2</sub>-DETA-89.

SEM images (Figure 3.39) of MIL-101(Al)-NH<sub>2</sub> and its modifications were recorded to determine the impact of the incorporated amines on the morphology. The smallest particles of MIL-101(Al)-NH<sub>2</sub> are approximately 200 nm in diameter with multiple faces. This is consistent with SEM images of MIL-101(Al)-NH<sub>2</sub> reported in the literature [34]. The expected octahedral morphology of MIL-101 [2, 35, 36] was not observed, perhaps due to the small particle size of the material that was recovered or perhaps due to the 2-aminoterephthalic acid. This observation was also reported for MIL-101(Cr)-NH<sub>2</sub>, in which the incorporation of varying amounts of the amine modified ligand resulted in

changes in crystallinities and morphologies [36]. Férey's group also observed that, the higher amounts of 2-aminoterephthalic acid in MIL-101(Cr) tended to lower the crystallinity resulting in less defined morphologies [23]. In order to test this hypothesis, it would be interesting to prepare MIL-101(Al) using a mixture of 2-aminoterephthalic acid and terephthalic acid. However, this could be challenging as the synthesis of MIL-101(Al) has not yet been reported. The PSM with DAB-AM-8 and DETA resulted in the coating of the MOF, which was more pronounced in MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94. These results are consistent with the very low total pore volumes of the DAB-AM-8 and DETA modified samples. In contrast to this, the PSM with PEI and the different PEI loadings had no obvious impact on the morphology.

## 3.5.4.2 Low pressure gas sorption measurements on MIL-101(Al)-NH<sub>2</sub> before and after PSM

Low pressure  $CO_2$  adsorption and desorption pseudo-isotherms (determined as described in Section 3.5.3.5) were measured at 25, 45, 75 and 105 °C in the pressure range of 0 to 0.5 bar. Prior to the sorption experiments, the samples were activated under vacuum at 110 °C overnight in order to remove any residual moisture. From these experiments, the effect of (a) PEI loading and (b) the nature of the amines on the  $CO_2$  adsorption capacity and the adsorption/desorption kinetics were investigated.

#### 3.5.4.2.1 MIL-101(Al)-NH<sub>2</sub> before PSM

The CO<sub>2</sub> pseudo-isotherms of MIL-101(Al)-NH<sub>2</sub> at 25, 45, 75 and 105 °C are shown in Figure 3.40. Increasing the temperature resulted in a decrease in CO<sub>2</sub> adsorption capacity consistent with the expected behaviour for classical adsorption, where the higher kinetic energy at higher temperatures leads to a reduction in the equilibrium concentration of adsorbed species. The CO<sub>2</sub> adsorption capacity of 1.66 wt% (0.13 mol(CO<sub>2</sub>)/mol(CUS)) at 25 °C and 0.15 bar is higher than those reported for MOF-5 (0.75 wt%) [37], MOF-177 (~0.70 wt%) [38] and MIL-101(Cr) (1.41 wt%) [2], but lower than those of MOF-74(Mg) (25.83 wt%) [38], NaX (13.38 wt%)[39] and CuBTTri (3.08 wt%) [1]. The working capacity (=difference in CO<sub>2</sub> adsorption capacity between 0.05 and 0.15 bar) was determined to be 0.89 wt% at 25 °C. CO<sub>2</sub> saturation was not achieved in the studied pressure range at all temperatures, which suggests that the material can be applied for high pressure CO<sub>2</sub> adsorption/desorption. At 25 and 45 °C the adsorption of CO<sub>2</sub> was completely reversible, but at 75 and 105 °C a slight hysteresis in the pseudo-isotherms was

observed. The presence of the hysteresis is regarded as an artefact due to imperfect baseline correction, especially at 75 °C. The apparent zero uptakes up to 0.15 bar at 105 °C are potentially due to the low weight changes, which are at the limits of the TG resolution.

The heat of adsorption was calculated from the DTA signal (Figure 3.48b) at 25 °C (CO<sub>2</sub> partial pressure=0.2 bar; t=10 min after increasing the CO<sub>2</sub> partial pressure). This time was chosen as the majority of CO<sub>2</sub> was adsorbed in MIL-101(Al)-NH<sub>2</sub>. The heat of adsorption was determined to be 43 kJ mol<sup>-1</sup>, which indicates a moderate initial interaction between CO<sub>2</sub> and the CUS [12]. The adsorption enthalpy is higher than the 22 kJ mol<sup>-1</sup> (determined from the high pressure (0-30 bar) CO<sub>2</sub> isotherms via single site Langmuir isotherm fit) by Serra Crespo et al. [16], which suggests the physisorption of CO<sub>2</sub> rather than chemisorption. However, the heat of adsorption determined here is comparable to the heat of adsorption of 43 kJ mol<sup>-1</sup> at zero coverage reported for MIL-101(Cr)-NH<sub>2</sub> [40].

#### 3.5.4.2.2 Effect of PEI loading

A comparison of the  $CO_2$  adsorption/desorption pseudo-isotherms of MIL-101(Al)-NH<sub>2</sub>, neat PEI and the modified PEI frameworks is shown in Figure 3.40.

Neat PEI exhibited almost no  $CO_2$  adsorption (0.35 wt% at 0.5 bar) at 25 °C. As temperature rises, the  $CO_2$  adsorption in the neat PEI increases, consistent with the higher mobility and  $CO_2$  diffusivity at higher temperatures. The adsorption of  $CO_2$  appears irreversible over the timescale of the experiments at all temperatures, due to the strong chemisorption of  $CO_2$  on the amine sites of neat PEI. Upon lowering the partial pressure an apparent increase in  $CO_2$  adsorption capacity is still observed. This can be explained as being due to slow sorption kinetics over the timescale of the experiment (discussed below in Section 3.5.4.2.4). While at 25 and 45 °C, no  $CO_2$  was desorbed, increasing the temperature resulted in a partial desorption of  $CO_2$  at low partial pressures (<0.05 bar). This is consistent with the increase in sorption kinetics due to the higher mobility of neat PEI at higher temperatures.

The adsorption capacities of MIL-101(Al)-NH<sub>2</sub>-PEI-48 were decreasing with increasing temperature, consistent with the expected behaviour for classical adsorption as discussed for MIL-101(Al)-NH<sub>2</sub>. One exception to this was the CO<sub>2</sub> adsorption capacity at 45 °C, which exhibited comparable adsorption capacities to those observed at 25 °C. This result is consistent with the slower adsorption kinetics at low temperatures. Improved CO<sub>2</sub>

adsorption capacities compared to neat PEI and MIL-101(Al)-NH<sub>2</sub> were obtained at 25 °C up to approximately 0.25 bar and over the entire studied pressure range at 45 °C. However, the neat PEI exhibited higher CO<sub>2</sub> adsorption capacities at 75 and 105 °C. This is consistent with the higher volumetric density of amine sites in neat PEI and the higher mobility of the amine at elevated temperatures. The CO<sub>2</sub> adsorption was irreversible at all temperatures, which suggests that CO<sub>2</sub> is chemisorbed in MIL-101(Al)-NH<sub>2</sub>-PEI-48. In contrast to neat PEI, no progressive adsorption of CO<sub>2</sub> was observed upon lowering the partial CO<sub>2</sub> pressure. This result suggests that the kinetics are faster than for neat PEI. Over the entire studied pressure range CO<sub>2</sub> was partially desorbed at low CO<sub>2</sub> partial pressures (<0.05 bar), which supports the hypothesis that CO<sub>2</sub> is chemisorbed.



- MIL-101(Al)-NH<sub>2</sub> - PEI-48- PEI-96 - PEI

**Figure 3.40:** Comparison of CO<sub>2</sub> pseudo-isotherms of MIL-101(Al)-NH<sub>2</sub> and its PEI modifications with neat PEI at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\bullet$ ).Closed symbols ( $\blacksquare$ ) and open symbols ( $\Box$ ) represent the adsorption and desorption of CO<sub>2</sub>, respectively.

Increasing the PEI loading from 48 to 96 wt% resulted in an increase in CO<sub>2</sub> adsorption capacity. Furthermore, the comparison with the pseudo-isotherms of neat PEI and MIL-101(Al)-NH<sub>2</sub> reveal that an improvement in CO<sub>2</sub> adsorption capacity was achieved over the entire pressure and temperature range. In contrast to MIL-101(Al)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub>-PEI-48, the amount of CO<sub>2</sub> adsorbed increased with temperature up to 75 °C. At these temperatures equilibrium adsorption is never achieved. This result is consistent with the very slow and incomplete penetration of CO<sub>2</sub> on the timescale of the experiment. At 105 °C a reduction in equilibrium concentration of adsorbed species was observed, but at the same time CO<sub>2</sub> can penetrate more quickly and effectively due to the increase in the mobility of PEI. Lowering the CO<sub>2</sub> partial pressure to 0.3 bar at 25 °C led to a progressive adsorption as was observed for neat PEI, but at higher temperatures this was not the case. This is consistent with the increase in adsorption/desorption kinetics with the rise in temperature. The hysteresis in the pseudo-isotherms and the partial desorption of CO<sub>2</sub> suggest that the adsorption of CO<sub>2</sub> is occurring via chemisorption rather than physisorption.

In order to verify the change in adsorption mechanism, the DTA signals of the adsorption at 25 °C were analysed (Figure 3.48b). The heats of adsorption were determined to be 71 kJ mol<sup>-1</sup> and 67 kJ mol<sup>-1</sup> for MIL-101(Al)-NH<sub>2</sub>-PEI-48 and MIL-101(Al)-NH<sub>2</sub>-PEI-96, respectively. These values are much higher than the 43 kJ mol<sup>-1</sup> calculated for MIL-101(Al)-NH<sub>2</sub> and suggest that CO<sub>2</sub> was chemisorbed. This is in good agreement with the observations from the pseudo-adsorption isotherms. Although, the DTA results give a good indication of the adsorption mechanism, the comparatively low adsorption capacities represent a challenge for obtaining accurate results. Drifts in the baseline and the interference of background noise may result in an under-and/or overestimation of the enthalpies.

#### 3.5.4.2.3 Effect of DAB-AM-8 and DETA

Due to the better performance of MIL-101(Al)-NH<sub>2</sub>-PEI-96 over the entire pressure and temperature range, the theoretical loading of DAB-AM-8 and DETA was chosen to be 100 wt%. The low pressure  $CO_2$  pseudo-isotherms of MIL-101(Al)-NH<sub>2</sub> before and after modification with DAB-AM-8 and DETA as well as of neat DAB-AM-8 and DEAT are shown in Figure 3.41.

The pseudo-isotherms of neat DAB-AM-8 were only measured at 75 and 105 °C, due to the low CO<sub>2</sub> adsorption capacities at 75 °C (0.60 wt% at 0.5 bar). Increasing the temperature to 105 °C led to a rise in CO<sub>2</sub> adsorption capacity (2.32 wt% at 0.5 bar), consistent with the higher mobility of DAB-AM-8 and the better CO<sub>2</sub> diffusivity at higher temperatures. At both temperatures, a progressive adsorption of CO<sub>2</sub> was observed upon lowering the partial pressure to 0.05 bar, followed by a partial desorption. This result is consistent with the strong chemisorption of CO<sub>2</sub> as explained for neat PEI.

Impregnating MIL-101(Al)-NH<sub>2</sub> with DAB-AM-8 resulted in a decrease in CO<sub>2</sub> adsorption capacities relative to MIL-101(Al)-NH<sub>2</sub> at 25, 45 and 75 °C, but at 105 °C the CO<sub>2</sub> adsorption capacities were higher than for the neat MOF. However, neat DAB-AM-8 exhibited higher CO<sub>2</sub> adsorption capacities than the modified MOF since the neat amine contains more amine sites that can bind CO<sub>2</sub>. A rise in temperature from 25 to 105 °C resulted in an increase in CO<sub>2</sub> adsorption capacities. This result is consistent with the faster penetration of CO<sub>2</sub> due to the higher mobility of DAB-AM-8. The irreversible adsorption of CO<sub>2</sub> over the entire studied temperature range suggests that CO<sub>2</sub> was chemisorbed. The CO<sub>2</sub> adsorption capacities of MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 are lower than those observed for MIL-101(Al)-NH<sub>2</sub>-PEI-48 and MIL-101(Al)-NH<sub>2</sub>-PEI-94. These results together with the low pore volume (Table 3.8) suggest that a decrease in DAB-AM-8 loading might be required to achieve an improvement in the low pressure CO<sub>2</sub> adsorption.

The pseudo-isotherms of neat DETA were measured at 25, 45 and 75 °C. In contrast to neat PEI and neat DAB-AM-8, the neat amine exhibits high  $CO_2$  uptakes over the entire temperature range studied. An increase in  $CO_2$  adsorption capacity with increasing temperature was observed, consistent with the higher mobility of DETA and the higher  $CO_2$  diffusivity at higher temperatures. Progressive adsorption upon lowering the pressure was observed at all three temperatures, but a partial desorption was only observed at 75 °C. This is consistent with the improvement in sorption kinetics at higher temperatures (see Section 3.5.4.2.4).

MIL-101(Al)-NH<sub>2</sub>-DETA-89 exhibited comparable  $CO_2$  adsorption capacities over the entire temperature and pressure range studied. The  $CO_2$  adsorption was irreversible at all temperatures, but the amount desorbed increased with a rise in temperature. This result suggests that  $CO_2$  is chemisorbed and that the adsorption/desorption kinetics are faster at higher temperatures. The comparison of the pseudo-isotherms of MIL-101(Al)-NH<sub>2</sub>-
DETA-89 with those of MIL-101(Al)-NH<sub>2</sub> reveal that improved CO<sub>2</sub> adsorption capacities were only achieved at 105 °C. However, neat DETA performed much better at 25 to 75 °C. Although the CO<sub>2</sub> pseudo-isotherm of neat DETA was not measured at 105 °C, it is expected that the equilibrium CO<sub>2</sub> adsorption would be higher than 16.24 wt% (75 °C, 0.5 bar) seeing that there was an increase in CO<sub>2</sub> adsorption capacity during the desorption of CO<sub>2</sub> at 75 °C. These results suggest that, improvements of the CO<sub>2</sub> adsorption capacities via DETA modification are limited.



- MIL-101(Al)-NH<sub>2</sub> – DAB-AM-8-94 – DETA-89 – DAB-AM-8 – DETA Figure 3.41: CO<sub>2</sub> pseudo-isotherms on MIL-101(Al)-NH<sub>2</sub> before and after modification with DAB-AM-8 and DETA in comparison with the neat amines at 25 °C ( $\blacksquare$ ), 45 °C ( $\blacklozenge$ ), 75 °C ( $\blacktriangle$ ) and 105 °C ( $\blacklozenge$ ).Closed symbols ( $\blacksquare$ ) and open symbols ( $\square$ ) represent the adsorption and desorption of CO<sub>2</sub>, respectively.

The DTA profiles at 25 °C are shown in the supplementary information (Figure 3.48b). However, due to the low adsorption capacities of the DAB-AM-8 and DETA modified frameworks, the heats of adsorption could not be reliably determined.

The PEI modified frameworks exhibited higher  $CO_2$  adsorption capacities than MIL-101(Al)-NH<sub>2</sub>-DETA-89, over the entire pressure and temperature range. The  $CO_2$  adsorption capacities of MIL-101(Al)-NH<sub>2</sub>-DETA-89 are comparable to those of MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 at 25 to 75 °C, but are lower at 105 °C.

#### 3.5.4.2.4 Effect of different amines on the sorption kinetics

The TGA profiles of MIL-101(Al)-NH<sub>2</sub> before and after PSM are compared to the profiles of the neat amines (Figure 3.42 and Figure 3.43). A clearly defined stepwise profile is indicative for good adsorption/desorption kinetics. That would enable the material to adsorb and desorb  $CO_2$  in a cycling process.

The results show that MIL-101(Al)-NH<sub>2</sub> exhibited fast kinetics over the entire studied temperature range. For this reason the cycling experiments discussed in the following section were conducted at 25  $^{\circ}$ C.

At pressures below 0.2 bar, the neat amines exhibited an initial rapid uptake of CO<sub>2</sub>, after which the CO<sub>2</sub> sorption becomes slower. However, the TGA profiles of DAB-AM-8 and PEI show a slower uptake of CO<sub>2</sub> at 105 °C than at 75 °C. Additionally, equilibrium adsorption/desorption was not observed during the 20 min after each pressure increase or decrease. These results indicate that the CO<sub>2</sub> adsorption/desorption kinetics decrease with increasing number of amine groups. Equilibrium adsorption and desorption after each pressure increase or decrease might be achieved if the equilibration times are extended. As discussed for the pseudo-isotherms of the neat amines, very little desorption of CO<sub>2</sub> was observed upon lowering the pressure. Heating the neat amines to 90 °C (DETA) or 110 °C (DAB-AM-8, DETA) under flowing Ar resulted in an increase of the amount of CO<sub>2</sub> desorbed. For instance, the sorption of CO<sub>2</sub> at 25°C and the subsequent heating in flowing Ar resulted in a complete desorption of CO<sub>2</sub> from DETA and PEI. In contrast to this, some CO<sub>2</sub> was retained after the sorption at higher temperatures (45, 75 or 105) and the subsequent heating under Ar atmosphere. It was found, that the higher the sorption temperature and therefore the CO<sub>2</sub> uptake, the more CO<sub>2</sub> was retained. Extending the time



of the final heating step will potentially result in a complete desorption even at the higher sorption temperatures.

**Figure 3.42:** CO<sub>2</sub> sorption TGA profiles of MIL-101(Al)-NH<sub>2</sub>, its PEI modifications and neat PEI at 25 °C (black), 45 °C (red), 75 °C (blue) and 105 °C (green).



**Figure 3.43:** CO<sub>2</sub> sorption TGA profiles of MIL-101(Al)-NH<sub>2</sub>-DETA-89, MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94, DETA and DAB-AM-8 at 25 °C (black), 45 °C (red), 75 °C (blue) and 105 °C (green).

The incorporation of DAB-AM-8, DETA and PEI in MIL-101(Al)-NH<sub>2</sub> led to a decrease in the kinetics at temperatures between 25 °C to 75 °C compared to the neat MOF, which was observed in the progressive adsorption of CO<sub>2</sub> during the 20 min allowed after each CO<sub>2</sub> pressure increase/decrease, hence equilibrium adsorption was not achieved. This result suggests that these materials will not perform well in a cycling process at low temperatures. While an extension of the equilibration times (> 20 min) is projected to result in a more stepwise profile, the increase in time is disadvantageous for industrial applications. For this reason the cycling experiments on the amine modified materials were performed at 105 °C. The noise in the TGA profiles of MIL-101(Al)-NH<sub>2</sub>-DETA-89 and MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 at 25 °C are due to the low CO<sub>2</sub> adsorption capacities and the imperfect baseline correction. Even at higher temperatures these materials did not completely reach equilibrium during the adsorption steps.

### 3.5.4.3 Cycling experiments on MIL-101(Al)-NH<sub>2</sub> before and after PSM

Cycling experiments under dry and wet (1 vol%  $H_2O$ ) conditions were conducted to investigate the effect of DAB-AM-8, DETA and PEI on the CO<sub>2</sub> working capacity, regenerability and H<sub>2</sub>O stability of MIL-101(Al)-NH<sub>2</sub>. The cycling experiments were conducted at 25 °C (MIL-101(Al)-NH<sub>2</sub>) or at 105 °C (PSM materials). The results of the cycling experiments are show in Figure 3.44. The timescale shown for the dry cycling profiles includes the initial activation of the samples (between -155 and approximately -55 min, Ar atmosphere), the cooling step (between -55 and -20 min, Ar atmosphere) and the equilibration step (between -20 and 0 min, Ar atmosphere) prior to the ten cycles of adsorption and desorption (t=0-420 min, Ar/CO<sub>2</sub>), the subsequent equilibration step (t=420-460 min, Ar atmosphere) at 25 or 105 °C and the regeneration step (t>460 min, Ar atmosphere).

Figure 3.44a shows that under dry conditions, equilibrium was achieved in MIL-101(Al)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub>-DETA-89. In all other cases, a progressive increase in the mass during the adsorption steps was observed. Furthermore the modification with DAB-AM-8 resulted in a progressive adsorption over the timescale of the cycling experiment so that equilibrium adsorption was not achieved, as a result of the relatively slow adsorption/desorption kinetics discussed above. The additional mass loss after the final heating period (t=500 min) in MIL-101(Al)-NH<sub>2</sub> is believed to be due to the loss of additional moisture as a result of the insufficient activation time at the start of the experiment.

A comparison of the working capacities under dry conditions is shown in Figure 3.44c. The PSM of MIL-101(Al)-NH<sub>2</sub> clearly resulted in a decrease in working capacities in the order MIL-101(Al)-NH<sub>2</sub> (0.94 wt%, 25 °C) > MIL-101(Al)-NH<sub>2</sub>-PEI-96 (0.49 wt%) > MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 (0.36 wt%) > MIL-101(Al)-NH<sub>2</sub>-PEI-48 (0.26 wt%) > MIL-101(Al)-NH<sub>2</sub>-DETA-89 (0.11 wt%). Thus, despite the higher CO<sub>2</sub> adsorption capacities of the PEI-96 sample during the low pressure sorption experiments over the entire pressure range (0-0.5 bar), the working capacities during the cycling were much lower. However, as the CO<sub>2</sub> pseudo-isotherms indicated that CO<sub>2</sub> saturation was almost achieved at 0.15 bar for the PSM materials, these materials would probably perform better

at pressures below 0.05 bar and might then have a higher working capacity than MIL-101(Al)-NH<sub>2</sub>. Another reason that the working capacities of MIL-101(Al)-NH<sub>2</sub> at 105 °C are expected to be lower than those found for the amine modifications is the fact that the unmodified material showed significantly lower CO<sub>2</sub> adsorption at higher temperatures than the PSM materials (see Figure 3.40 and Figure 3.41). All materials exhibited good regenerabilities under dry conditions and stable working capacities from cycle to cycle.



- MIL-101(Al)-NH<sub>2</sub> – PEI-48– PEI-96 – DAB-AM-8-94 – DETA-89 Figure 3.44: TGA profiles of MIL-101(Al)-NH<sub>2</sub> before and after amine modifications

Figure 3.44: TGA profiles of MIL-101(AI)-NH<sub>2</sub> before and after amine modifications under dry (a) and wet (b) conditions. Working capacities during the 10 cycles under dry (c) and wet (d) conditions. The line and marker colours correspond to the MOF and the symbols to the cycling temperature (25 °C ( $\blacksquare$ ) and 105 °C ( $\bullet$ )).

The TGA profiles of the wet cycling experiments are shown in Figure 3.44b. The saturation of MIL-101(Al)-NH<sub>2</sub> with 1 vol% H<sub>2</sub>O vapour was achieved after 330 min and corresponds to an uptake of 15.54 wt% (3.04 mol H<sub>2</sub>O per mol CUS). After the PSM with

PEI, DAB-AM-8 and DETA, a mass loss is observed, which suggests that some of these amine molecules are replaced by  $H_2O$  molecules. Equilibrium  $CO_2$  adsorption was achieved in MIL-101(Al)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub>-PEI-48 and MIL-101(Al)-NH<sub>2</sub>-PEI-96. No clear defined cycling profile is observed for MIL-101(Al)-NH<sub>2</sub>-DETA-89. An increase in mass in MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 was observed during the cycling of the Ar/H<sub>2</sub>O/CO<sub>2</sub> mixture (t>400 min), which suggests that H<sub>2</sub>O and/or CO<sub>2</sub> are progressively adsorbed during the cycling process.

Under wet conditions (Figure 3.44d), the working capacities decreased in the order MIL-101(Al)-NH<sub>2</sub> (0.91 wt%) > MIL-101(Al)-NH<sub>2</sub>-PEI-96 (0.69 wt%) > MIL-101(Al)-NH<sub>2</sub>-DAB-AM-8-94 (0.27 wt%) > MIL-101(Al)-NH<sub>2</sub>-PEI-48 (0.23 wt%) > MIL-101(Al)-NH<sub>2</sub>-DETA-89 (0.10), which is in good agreement with the results from the dry cycling experiments. The regenerability and stability of the working capacities from cycle to cycle of MIL-101(Al)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub>-DETA-89 were comparable to those obtained under dry cycling conditions, but in the case of PEI and DAB-AM-8 modified frameworks a significant reduction in regenerability and stability were observed. This reduction in working capacities could be due to the competitive adsorption of H<sub>2</sub>O and CO<sub>2</sub>, such that H<sub>2</sub>O molecules are occupying preferential adsorption sites of CO<sub>2</sub>.

The H<sub>2</sub>O stabilities of the materials were evaluated by PXRD (Figure 3.50). All samples showed a decrease in crystallinity, which is indicative for a partial/complete collapse of the frameworks. In the case of MIL-101(Al)-NH<sub>2</sub>, the diffraction at  $2\theta \sim 9^{\circ}$  was still present. It is hypothesised that the partial collapse of MIL-101(Al)-NH<sub>2</sub> occurs during the final heating stage (t=460 min) as the working capacities of the material remained stable during the cycling process. All diffraction patterns were measured using less than 10 mg of sample. This could potentially account for the diminished crystallinities, especially for the amine modified samples. It would therefore be helpful to measure the BET surface after the treatment with H<sub>2</sub>O vapour to validate the stability of the PSM materials.

## 3.5.4.4 High pressure gas sorption on MIL-101(Al)-NH<sub>2</sub>

High pressure adsorption and desorption (0-40 bar) on MIL-101(Al)-NH<sub>2</sub> was conducted to determine the  $CO_2/N_2$  selectivity and to investigate the applicability in high pressure separation processes. Furthermore, by measuring  $CO_2$  isotherms (0-5 bar) before and after the adsorption and desorption of H<sub>2</sub>O (30 % RH), the hydrothermal stability of the framework was evaluated.

#### 3.5.4.4.1 High pressure CO<sub>2</sub> and N<sub>2</sub> sorption

Figure 3.45a and b show the CO<sub>2</sub> and N<sub>2</sub> isotherms measured on the HPVA. MIL-101(Al)-NH<sub>2</sub> displayed a reasonably high CO<sub>2</sub> uptake of 58.4 wt% (4.68 mol(CO<sub>2</sub>)/mol(CUS)) at 25 °C and 40 bar. The impact of the amine group on the adsorption capacity cannot be determined, because the preparation of MIL-101(Al) has been unsuccessful to date. The CO<sub>2</sub> adsorption capacity at 25 °C and 40 bar was lower than those reported for MIL-101(Cr) (154.03 wt%) and MOF-177 (147.43 wt%) [18, 41]. The comparison with literature data for MIL-101(Al)-NH<sub>2</sub> revealed that the adsorption capacities obtained in this work were slightly lower [16]. For instance at 25 °C and 30 bar, the CO<sub>2</sub> adsorption capacity reported in the literature was about 5.70 wt% higher. On the other hand, the performance at high pressure was better than those reported for MIL-53(Al)-NH<sub>2</sub> (29.49 wt%, 30 °C, 13bar), zeolite NaX (32.6 wt%, 25 °C, 32 bar) and zeolite 13X (34.3 wt%, 30 °C, 30bar) [18, 41, 42]. Despite the lower N<sub>2</sub> adsorption capacities, the saturation of MIL-101(Al)-NH<sub>2</sub> with N<sub>2</sub> will be achieved at higher pressures than in the case of CO<sub>2</sub>. The CO<sub>2</sub> isotherms indicate that CO<sub>2</sub> saturation was almost achieved. The adsorption of both adsorbates was found to be reversible and suggest that no chemisorption of  $CO_2$  on the amine sites was present.

The CO<sub>2</sub>/N<sub>2</sub> selectivities (Figure 3.49a) calculated from the single component adsorption capacities ranged from 7 to 12 and 5 to 22 at 25 °C and 105 °C, respectively. The CO<sub>2</sub>/N<sub>2</sub> selectivities of 5 to 9 (25 °C, 0-25 bar) reported by Serra-Crespo and co-worker are slightly smaller than those determined in this work.[16] The selectivities were found to decrease with increasing pressure until they were almost constant. At pressures below 1.5 bar the CO<sub>2</sub>/N<sub>2</sub> selectivities were much higher at 105 °C, than at 25 °C. Although this method gives a good indication of the selectivity, the adsorption of binary gas mixtures with a composition relevant to flue gas should be performed in order to get more accurate results.

The isosteric heat of adsorption (Figure 3.49b) was calculated by fitting the Tóth isotherm model to the CO<sub>2</sub> adsorption isotherms at 25, 45 and 105 °C. The enthalpy was determined to be  $24\pm1$  kJ mol<sup>-1</sup> at zero loading (Figure 3.49b) and confirms the physisorption of the CO<sub>2</sub>. The value was in good agreement with the literature value of 22 kJ mol<sup>-1</sup> [16], but the isosteric heat was lower than the heat of adsorption determined from the DTA data (see Section 3.5.4.2.1). The isosteric heat of adsorption was lower than those reported for MIL-

101(Cr) (44 kJ mol<sup>-1</sup>) [18], MIL-101(Cr)-NH<sub>2</sub> (43 kJ mol<sup>-1</sup>), HKUST-1 (30 kJ mol<sup>-1</sup>)[43] and zeolite 13X (49 kJ mol<sup>-1</sup>) [44]. The comparatively low enthalpy is beneficial for industrial applications, due to the reduction in energy consumption.



**Figure 3.45:** High pressure (a)  $CO_2$  isotherms at 25 °C (**■**), 45 °C (**♦**), 75 °C (**▲**) and 105 °C (**●**) and (b)  $N_2$  isotherms at 25 °C (**■**) and 105 °C (**●**) on MIL-101(Al)-NH<sub>2</sub> recorded on the HPVA in the pressure range of 0 to 40 bar . Closed symbols (**■**) and open symbols (**□**) represent the adsorption and desorption of the adsorbates, respectively.

## 3.5.4.4.2 Hydrothermal stability

Figure 3.46a and b present the results obtained from the IGA experiments. The initial CO<sub>2</sub> adsorption capacities were slightly lower than those obtained using the HPVA. This difference is consistent with the differences in the sample mass of ~0.03 g (IGA) vs. 0.31 g (HPVA) used during the experiments and the different activation procedures. In both instruments the samples were activated under vacuum, but the activation temperature varied between 25 °C (IGA) and 110 °C (HPVA). The red CO<sub>2</sub> isotherm was measured after the sorption of H<sub>2</sub>O at 30 % RH and showed a reduction in CO<sub>2</sub> adsorption capacity. With increasing pressure this difference became more pronounced. This is interesting since MIL-100 and MIL-101 frameworks are typically hydrothermally stability [45, 46]. The MOF exhibited a high H<sub>2</sub>O uptake of 22.30 wt% (4.37 mol H<sub>2</sub>O per mol CUS) at 0.01 bar, which led to high H<sub>2</sub>O/CO<sub>2</sub> selectivities. The CO<sub>2</sub> adsorption capacity at 0.1 bar was found to be approximately 131 times smaller than the H<sub>2</sub>O uptake. The hysteresis in the H<sub>2</sub>O isotherm is presumably a result of the strong interaction of the H<sub>2</sub>O molecules with the CUS.

The comparison of the PXRD diffractograms of MIL-101(Al)-NH<sub>2</sub> before and after the IGA measurements is shown in the supplementary information (Figure 3.50). The decrease

in CO<sub>2</sub> uptake after the treatment with H<sub>2</sub>O at 30 % RH is probably due to the decomposition of the framework, consistent with the severe decrease in diffraction intensity. The low hydrothermal stability of the framework might potentially be a result of the presence of amine groups. However, in order to confirm this hypothesis, the impact of RH  $\geq$  30 % on a series of different MIL-101-NH<sub>2</sub> frameworks should be evaluated.



**Figure 3.46:** (a) CO<sub>2</sub> isotherms before (black) and after (red) H<sub>2</sub>O adsorption/desorption at 25 °C (b) H<sub>2</sub>O isotherm at 30 % RH and 25 °C. The measurements were conducted on the IGA. Closed symbols ( $\blacksquare$ ) and open symbols ( $\Box$ ) represent the adsorption and desorption of the adsorbates, respectively.

# 3.5.5 Conclusion

This study showed that the PSM of MIL-101(Al)-NH<sub>2</sub> was successfully achieved. The best performing PSM material was MIL-101(Al)-NH<sub>2</sub>-PEI-96, which exhibited higher adsorption capacities in the low pressure CO<sub>2</sub> experiments. However, a blockage of the pores was observed in the case of MIL-101(Al)-NH<sub>2</sub> loaded with 94 wt% DAB-AM-8 and 89 wt% DETA. A decrease in the DAB-AM-8 loading, such that some porosity remains, might improve the CO<sub>2</sub> adsorption capacities. However, potential improvements in the CO<sub>2</sub> uptake in DETA modified MIL-101(Al)-NH<sub>2</sub> relative to neat DETA are seen to be limited due to the high adsorption capacity of the neat amine.

While MIL-101(Al)-NH<sub>2</sub> exhibited fast adsorption/desorption kinetics at 25 °C, the incorporation of amines resulted in slow kinetics at low temperatures and faster kinetics at 105 °C. As a result the cycling temperature was set to 105 °C for the PSM materials, which is potentially beneficial for post-combustion carbon capture. However, the working capacities during cycling of the DAB-AM-8, DETA and PEI modified materials were

lower than those obtained for MIL-101(Al)-NH<sub>2</sub>. Furthermore, the incorporation of amines resulted in an increase in the heat of adsorption, which can make heat management within a fixed bed adsorber more difficult.

PXRD studies of MIL-101(Al)-NH<sub>2</sub> after the wet cycling experiment and after the treatment with H<sub>2</sub>O vapour at 30 % RH indicated a decomposition of the framework, leading to a reduction in the CO<sub>2</sub> adsorption, particularly during the higher pressure adsorption/desorption measurements. The stable working capacities in MIL-101(Al)-NH<sub>2</sub> under wet cyclic conditions suggests that the collapse of the framework might have occurred during the final heating stage of the experiment. Although the H<sub>2</sub>O adsorption capacity was 22.30 wt%, the low stability renders the material inapplicable as an adsorbent for the removal of H<sub>2</sub>O. It is expected that the MIL-101(Al)-NH<sub>2</sub> framework is more promising for the capture of CO<sub>2</sub> at higher pressures.

## 3.5.6 Acknowledgements

The financial support was provided by the Australian Government through the CRC Program to support this CO2CRC project. The authors acknowledge the use of facilities within the Monash Centre for Electron Microscopy. This research used equipment whose purchase was supported under the Australian Research Council's *Centres of Excellence* funding scheme (COE for Design in Light Metals).

## 3.5.7 References

- [1] A. Demessence, D. M. D'Alessandro, M. L. Foo, and J. R. Long, "Strong CO<sub>2</sub> Binding in a Water-Stable, Triazolate-Bridged Metal-Organic Framework Functionalized with Ethylenediamine," *Journal of the American Chemical Society*, vol. 131, pp. 8784-8786, 2009.
- Y. Lin, Q. Yan, C. Kong, and L. Chen, "Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO<sub>2</sub> Capture," *Sci. Rep.*, vol. 3, pp. 1-7, 2013.
- [3] S.-N. Kim, S.-T. Yang, J. Kim, J.-E. Park, and W.-S. Ahn, "Post-synthesis functionalization of MIL-101 using diethylenetriamine: a study on adsorption and catalysis," *CrystEngComm*, vol. 14, pp. 4142-4147, 2012.
- [4] M. Anbia and V. Hoseini, "Enhancement of CO<sub>2</sub> adsorption on nanoporous chromium terephthalate (MIL-101) by amine modification," *Journal of Natural Gas Chemistry*, vol. 21, pp. 339-343, 2012.
- [5] S. Choi, T. Watanabe, T.-H. Bae, D. S. Sholl, and C. W. Jones, "Modification of the Mg/DOBDC MOF with Amines to Enhance CO<sub>2</sub> Adsorption from Ultradilute Gases," *The Journal of Physical Chemistry Letters*, vol. 3, pp. 1136-1141, 2012/05/25 2012.
- [6] D. J. N. Subagyono, M. Marshall, G. P. Knowles, and A. L. Chaffee, "CO<sub>2</sub> adsorption by amine modified siliceous mesostructured cellular foam (MCF) in

humidified gas," *Microporous and Mesoporous Materials*, vol. 186, pp. 84-93, 2014.

- [7] A. Sayari, Y. Belmabkhout, and R. Serna-Guerrero, "Flue gas treatment via CO<sub>2</sub> adsorption," *Chemical Engineering Journal*, vol. 171, pp. 760-774, 2011.
- [8] S. Keskin, T. M. van Heest, and D. S. Sholl, "Can Metal–Organic Framework Materials Play a Useful Role in Large-Scale Carbon Dioxide Separations?," *ChemSusChem*, vol. 3, pp. 879-891, 2010.
- [9] T.-H. Bae, M. R. Hudson, J. A. Mason, W. L. Queen, J. J. Dutton, K. Sumida, K. J. Micklash, S. S. Kaye, C. M. Brown, and J. R. Long, "Evaluation of cation-exchanged zeolite adsorbents for post-combustion carbon dioxide capture," *Energy & Environmental Science*, vol. 6, pp. 128-138, 2013.
- [10] Z. n. Bacsik, N. Ahlsten, A. Ziadi, G. Zhao, A. E. Garcia-Bennett, B. n. Martín-Matute, and N. Hedin, "Mechanisms and Kinetics for Sorption of CO<sub>2</sub> on Bicontinuous Mesoporous Silica Modified with n-Propylamine," *Langmuir*, vol. 27, pp. 11118-11128, 2011/09/06 2011.
- [11] T. M. McDonald, D. M. D'Alessandro, R. Krishna, and J. R. Long, "Enhanced carbon dioxide capture upon incorporation of N,N'-dimethylethylenediamine in the metal-organic framework CuBTTri," *Chemical Science*, vol. 2, pp. 2022-2028, 2011.
- [12] A. Das, P. D. Southon, M. Zhao, C. J. Kepert, A. T. Harris, and D. M. D'Alessandro, "Carbon dioxide adsorption by physisorption and chemisorption interactions in piperazine-grafted Ni2(dobdc) (dobdc = 1,4-dioxido-2,5-benzenedicarboxylate)," *Dalton Transactions*, vol. 41, pp. 11739-11744, 2012.
- [13] S. Bernt, V. Guillerm, C. Serre, and N. Stock, "Direct covalent post-synthetic chemical modification of Cr-MIL-101 using nitrating acid," *Chemical Communications*, vol. 47, pp. 2838-2840, 2011.
- [14] Y. K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jhung, Y.-K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre, and G. Férey, "Amine Grafting on Coordinatively Unsaturated Metal Centers of MOFs: Consequences for Catalysis and Metal Encapsulation," *Angewandte Chemie International Edition*, vol. 47, pp. 4144-4148, 2008.
- [15] Y. Lin, C. Kong, and L. Chen, "Direct synthesis of amine-functionalized MIL-101(Cr) nanoparticles and application for CO<sub>2</sub> capture," *RSC Advances*, vol. 2, pp. 6417-6419, 2012.
- [16] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, and F. Kapteijn, "Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties," *Chemistry of Materials*, vol. 23, pp. 2565-2572, 2011.
- [17] M. Hartmann and M. Fischer, "Amino-functionalized basic catalysts with MIL-101 structure," *Microporous and Mesoporous Materials*, vol. 164, pp. 38-43, 2012.
- P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jhung, and G. Férey, "High Uptakes of CO<sub>2</sub> and CH<sub>4</sub> in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101," *Langmuir*, vol. 24, pp. 7245-7250, 2008.
- [19] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.
- [20] J. Tóth, "Uniform interpretation of gas/solid adsorption," *Advances in Colloid and Interface Science*, vol. 55, pp. 1-239, 1995.

- [21] D.-Y. Hong, Y. K. Hwang, C. Serre, G. Férey, and J.-S. Chang, "Porous Chromium Terephthalate MIL-101 with Coordinatively Unsaturated Sites: Surface Functionalization, Encapsulation, Sorption and Catalysis," *Advanced Functional Materials*, vol. 19, pp. 1537-1552, 2009.
- [22] D. Jiang, A. D. Burrows, and K. J. Edler, "Size-controlled synthesis of MIL-101(Cr) nanoparticles with enhanced selectivity for CO<sub>2</sub> over N<sub>2</sub>," *CrystEngComm*, vol. 13, pp. 6916-6919, 2011.
- [23] P. Horcajada, S. Surble, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Greneche, I. Margiolaki, and G. Ferey, "Synthesis and catalytic properties of MIL-100(Fe), an iron(iii) carboxylate with large pores," *Chemical Communications*, pp. 2820-2822, 2007.
- [24] D. Jiang, L. L. Keenan, A. D. Burrows, and K. J. Edler, "Synthesis and postsynthetic modification of MIL-101(Cr)-NH2via a tandem diazotisation process," *Chemical Communications*, vol. 48, pp. 12053-12055, 2012.
- [25] <u>http://www.sigmaaldrich.com/catalog/product/aldrich/460729?lang=en&region=AU</u>, (accessed 10/08/2014).
- [26] <u>http://www.sigmaaldrich.com/catalog/product/sial/d93856?lang=en&region=AU</u>, (accessed 10/08/2014).
- [27] <u>http://www.sigmaaldrich.com/catalog/product/aldrich/468533?lang=en&region=AU</u>, (accessed 10/08/2014).
- [28] C. Patzschke, G. P. Knowles, and A. L. Chaffee, "CO<sub>2</sub> Adsorption in Post-Synthetic Modified MIL-101(Cr)-NH<sub>2</sub>," *Thesis Chapter 3.4*, 2014.
- [29] B. Wu, X. Lin, L. Ge, L. Wu, and T. Xu, "A novel route for preparing highly proton conductive membrane materials with metal-organic frameworks," *Chemical Communications*, vol. 49, pp. 143-145, 2013.
- [30] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, "Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants," *Sci. Rep.*, vol. 3, pp. 1-6, 2013.
- [31] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, and I. Margiolaki, "A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area," *Science*, vol. 309, pp. 2040-2042, September 23, 2005 2005.
- [32] ""Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.," "*Reflex Tools*" is a module in the Materials Studio Modeling software package from Accelrys Inc.
- [33] Y. Kuwahara, D.-Y. Kang, J. R. Copeland, N. A. Brunelli, S. A. Didas, P. Bollini, C. Sievers, T. Kamegawa, H. Yamashita, and C. W. Jones, "Dramatic Enhancement of CO<sub>2</sub> Uptake by Poly(ethyleneimine) Using Zirconosilicate Supports," *Journal of the American Chemical Society*, vol. 134, pp. 10757-10760, 2012/07/04 2012.
- [34] T. Toyao, M. Fujiwaki, Y. Horiuchi, and M. Matsuoka, "Application of an aminofunctionalised metal-organic framework: an approach to a one-pot acid-base reaction," *RSC Advances*, vol. 3, pp. 21582-21587, 2013.
- [35] O. I. Lebedev, F. Millange, C. Serre, G. Van Tendeloo, and G. Férey, "First Direct Imaging of Giant Pores of the Metal–Organic Framework MIL-101," *Chemistry of Materials*, vol. 17, pp. 6525-6527, 2005/12/01 2005.
- [36] R. B. Ferreira, P. M. Scheetz, and A. L. B. Formiga, "Synthesis of amine-tagged metal-organic frameworks isostructural to MIL-101(Cr)," *RSC Advances*, vol. 3, pp. 10181-10184, 2013.

- [37] J.-S. Choi, W.-J. Son, J. Kim, and W.-S. Ahn, "Metal–organic framework MOF-5 prepared by microwave heating: Factors to be considered," *Microporous and Mesoporous Materials*, vol. 116, pp. 727-731, 2008.
- [38] J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna, and J. R. Long, "Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption," *Energy & Environmental Science*, vol. 4, pp. 3030-3040, 2011.
- [39] J.-S. Lee, J.-H. Kim, J.-T. Kim, J.-K. Suh, J.-M. Lee, and C.-H. Lee, "Adsorption Equilibria of CO<sub>2</sub> on Zeolite 13X and Zeolite X/Activated Carbon Composite," *Journal of Chemical & Engineering Data*, vol. 47, pp. 1237-1242, 2002/09/01 2002.
- [40] A. Khutia and C. Janiak, "Programming MIL-101Cr for selective and enhanced CO<sub>2</sub> adsorption at low pressure by postsynthetic amine functionalization," *Dalton Transactions*, vol. 43, pp. 1338-1347, 2014.
- [41] G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi, and J.-S. Chang, "Why hybrid porous solids capture greenhouse gases?," *Chemical Society Reviews*, vol. 40, pp. 550-562, 2011.
- [42] S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, and F. Kapteijn, "An Amine-Functionalized MIL-53 Metal-Organic Framework with Large Separation Power for CO<sub>2</sub> and CH<sub>4</sub>," *Journal of the American Chemical Society*, vol. 131, p. 6326, 2009.
- [43] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X)," *Energy & Fuels*, vol. 23, pp. 2785-2789, 2009.
- [44] J. A. Dunne, M. Rao, S. Sircar, R. J. Gorte, and A. L. Myers, "Calorimetric Heats of Adsorption and Adsorption Isotherms. 2. O<sub>2</sub>, N<sub>2</sub>, Ar, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, and SF6 on NaX, H-ZSM-5, and Na-ZSM-5 Zeolites," *Langmuir*, vol. 12, pp. 5896-5904, 1996/01/01 1996.
- [45] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> adsorption, selectivity and water tolerance of pillared-layer metal organic frameworks," *Microporous and Mesoporous Materials*, vol. 132, pp. 305-310, 2010.
- [46] Z. Liang, M. Marshall, C. H. Ng, and A. L. Chaffee, "Comparison of Conventional and HF-Free-Synthesized MIL-101 for CO<sub>2</sub> Adsorption Separation and Their Water Stabilities," *Energy & Fuels*, vol. 27, pp. 7612-7618, 2013/12/19 2013.

# Supplementary material

# Postsynthetic modification of MIL-101(Al)-NH<sub>2</sub> with Amines and their effect on the CO<sub>2</sub> sorption

Christin Patzschke,<sup>*a,b*</sup> Marc Marshall,<sup>*b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author:

, Fax:+61 3 990-54597

# 3.5.8 Theoretical and experimental PXRD of MIL-101(Al)-NH<sub>2</sub>



**Figure 3.47:** Comparison of the theoretical PXRD calculated from the crystal structure of MIL-101(Cr) [1](red) and the PXRD of MIL-101(Al)-NH<sub>2</sub> (black).



# 3.5.9 Thermal decomposition and DTA profiles



**Figure 3.48:** (a) Thermal decomposition of MIL-101(Al)-NH<sub>2</sub> before and after amine modification. (b) DTA profiles of MIL-101(Al)-NH<sub>2</sub> before and after amine modification at 25 °C.





**Figure 3.49:** (a)  $CO_2/N_2$  selectivities at 25 (black) and 105 °C (red). (b) Isosteric heat of adsorption determined by fitting the Tóth isotherm model to the  $CO_2$  isotherms.



3.5.11 Impact of H<sub>2</sub>O – PXRD

Figure 3.50: PXRD of MIL-101(Al)-NH<sub>2</sub> and its amine modifications before (black) and after (blue) the sorption of  $H_2O$ .

# 3.5.12 References supplementary information

[1] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, and I. Margiolaki, "A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area," *Science*, vol. 309, pp. 2040-2042, September 23, 2005 2005.

# **Declaration for Thesis Chapter**

### An adsorption study on STA-16(Co)

### Monash University

# **Declaration for Thesis Chapter 3.6**

#### **Declaration by candidate**

In the case of Chapter 3.6, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed samples; identified major	80 %
issues; developed interpretations; fully drafted paper and conclusion	

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co- authors only
Marc Marshall	Conducted high pressure sorption experiments on IGA, input to results analysis and manuscript revision	N/A
Alan L. Chaffee	Supervision, assisted interpretation of results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work\*.

 
 Candidate's Signature
 Date 30/10/2014

 Main Supervisor's Signature
 Date 30/10 (14

\*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

#### **3.6** An adsorption study on STA-16(Co)

Christin Patzschke,<sup>*a,b*</sup> Marc Marshall<sup>*b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup> <sup>*a*</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), b School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia



#### 3.6.1 Abstract

Adsorption is considered a promising method for carbon capture. CO<sub>2</sub> adsorbents take a variety of forms, but one approach is the use of metal-organic frameworks (MOFs). STA-16(Co) was prepared and characterised. The potential of STA-16(Co) to selectively adsorb and separate CO<sub>2</sub> is considered. Isotherms for CO<sub>2</sub> and N<sub>2</sub> were measured from 0 to 40 bar at temperatures between 25 and 105 °C to evaluate the potential application in high pressure separation processes. Low pressure CO<sub>2</sub> pseudo-isotherms were measured from 0 to 0.5 bar at temperatures between 25 and 105 °C and dry and wet cycling experiments were conducted to determine the applicability of STA-16(Co) in a vacuum swing adsorption (VSA) process. The presence of 1 % H<sub>2</sub>O vapour during ten cycle experiments to the majority of MOFs, STA-16(Co) exhibited a good H<sub>2</sub>O stability and maintained its CO<sub>2</sub> adsorption capacity after adsorption/desorption of H<sub>2</sub>O vapour at 30 and 60 % RH at 25 °C. However the treatment at 90 % RH resulted in a small decrease in CO<sub>2</sub> adsorption

#### 3.6.2 Introduction

One of the major challenges in the  $21^{st}$  century is the increase in CO<sub>2</sub> emissions due to the combustion of coal, oil and natural gas [1-3]. In order to meet the high energy demand, fossil fuels will remain the backbone of worldwide electricity production and therefore methods for the reduction of our CO<sub>2</sub> emissions are urgently required [4]. Carbon capture and storage (CCS) has been proposed as a promising strategy to reduce anthropogenic greenhouse gas emissions and thereby halt climate change and global warming. Traditional technologies capture CO<sub>2</sub> by using aqueous amines (e.g. MEA, DEA), which have been shown to have a high selectivity towards CO<sub>2</sub>. The main disadvantages of aqueous alkanolamines include a high energy requirement for the regeneration of the absorbents, loss of effectiveness over time due to their low thermal stability, loss due to evaporation,

the tendency to induce corrosion and the formation of heat stable salts, which decrease the efficiency of  $CO_2$  capture [5-10].

The evaluation of adsorption as an alternative to amine-based absorption/stripping processes has received much attention during the past decade. The application of pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) processes in carbon capture is attractive due to the low energy requirement, which could result in a reduction of the capture costs [11]. Adsorbents are required that show a high thermal and hydrothermal stability, high CO<sub>2</sub> capacity, high selectivity towards CO<sub>2</sub> and a good long term stability [4, 12, 13]. Zeolite 13X has shown great potential for post-combustion capture, with a CO<sub>2</sub> uptake of 20.7 wt% at 25 °C and 1 bar [14]. However, its low hydrothermal stability, energy intensive regeneration, due to the large heat of adsorptions, and their low selectivity are the major drawbacks of these materials [3, 15, 16].

Metal-organic frameworks (MOFs) are promising candidates for carbon capture due to their very high porosity and surface area, ordered and well characterized porous structure, and adjustable chemical functionality [17-19]. Coordinatively unsaturated sites (CUS) can induce strong local interactions with  $CO_2$  resulting in lower binding energies, lower enthalpies of adsorption and a high selectivity towards  $CO_2$  [12, 20-22].

The majority of  $CO_2$  adsorption studies to date involve MOFs containing carboxylate, pyridine and polyazolate linker molecules. Very limited data is available on phosphonate MOFs [23-27]. One reason for this is the strong affinity and chelation of phosphonate groups to metal ions, which results in the formation of dense layered structures [28]. Phosphonate groups can bind to a variety of metal cations through one, two or three of the oxygen atoms [29]. Due to the small pore size (<0.6 nm) of most metal phosphonates, the reported  $CO_2$  adsorption capacities are low. To be applicable for post-combustion capture, stability in the presence of H<sub>2</sub>O vapour is important. While the majority of the carboxylate MOFs decompose or undergo a phase change under high H<sub>2</sub>O vapour pressure, MOFs containing phosphonate monoesters as organic linker molecules are generally hydrothermally stable [30].

The organic linker N,N'-4,4'-bipiperidinebis-(methylenephosphonic acid) tetrahydrate (H<sub>4</sub>LL) contains two phosphonic acids, which are each capable of three states of protonation, as well as two amino nitrogen atoms capable of two protonation states. The reaction of H<sub>4</sub>LL and Co(OAc)<sub>2</sub> results in the formation of a phosphonate MOF with a

pore diameter of 1.8 nm, which is known as STA-16(Co). The coordination of the Co(II) cations to four phosphonate oxygen atoms, one piperazinyl nitrogen atom and one oxygen atom of a H<sub>2</sub>O molecule results in a distorted CoO<sub>5</sub>N octahedron. A metal phosphonate spiral, which is built up by edge-sharing CoO<sub>5</sub>N octahedra, is connected to three others in order to give a hexagonal array of channels (Figure 3.51). One P=O bond from each phosphonate group projects into the hexagonal channels and can hydrogen-bond with lattice and coordinated H<sub>2</sub>O molecules. The terminal H<sub>2</sub>O ligands of the CoO<sub>5</sub>N octahedra can be removed upon vacuum activation at 150 °C to give CUS [31, 32].



**Figure 3.51:** The hexagonal array of channels in STA-16(Co) (Phosphonate tetrahedral: green, Co(II) octahedra: blue, C: grey, N: dark blue, O: red). The lattice  $H_2O$  molecules and the hydrogen atoms have been omitted [31].

Here we report the adsorption properties and hydrothermal stability of STA-16(Co). The applicability as an adsorbent has been assessed in terms of low pressure  $CO_2$  adsorption, single component adsorption of  $CO_2$  and  $N_2$  up to 40 bar and the hydrothermal stability. The stability and regenerability of the material was determined by performing ten cycle adsorption/desorption experiments under dry and wet conditions. The  $CO_2/N_2$  selectivities and the applicability of STA-16(Co) were determined by performing high pressure  $CO_2$  and  $N_2$  adsorption/desorption measurements. In order to evaluate the hydrothermal stability,  $H_2O$  sorption isotherms were measured to different relative humidities.

# 3.6.3 Experimental section

# 3.6.3.1 Chemicals

4,4'-bipiperidine dihydrochloride (99 %, Alfa Aesar), Cobalt(II) acetate tetrahydrate ( $\geq$  98 %, Sigma Aldrich), formaldehyde (40 % w/v GR grade, Merck), hydrobromic acid (Merck), phosphorous acid (97 % Alfa Aesar) and potassium hydroxide (GR grade, Merck).

# 3.6.3.2 Synthesis of STA-16(Co)

The syntheses of  $H_4LL$  and STA-16(Co) were performed following the procedure described by Wharmby et al. [31, 32].

In a typical synthesis H<sub>4</sub>LL, was prepared using 4,4'-bipiperidine dihydrochloride, phosphorous acid, hydrobromic acid solution and formaldehyde in a Mannich reaction. 0.99 g of H<sub>4</sub>LL were placed in a 100 mL Teflon lined autoclave and 44.7 mL of distilled H<sub>2</sub>O were added. After the further addition of 5.7 mL of potassium hydroxide solution (1 M), the mixture was stirred until the majority of the ligand had dissolved. 1.36 g of cobalt(II) acetate tetrahydrate were added and the mixture was aged for 30 minutes at room temperature, then heated at 220 °C in a Teflon lined autoclave for 65 hours. The purple powder was filtered and washed with distilled H<sub>2</sub>O.

# 3.6.3.3 Characterisation of STA-16(Co)

Powder x-ray diffractograms (PXRD) were measured on a Bruker D8 Focus powder diffractometer using  $CuK_{\alpha}$  radiation ( $\lambda$ =1.5418 Å). The module "Reflex Tools" in Materials Studio 6.0 was used to calculate the theoretical diffractogram [33].

SEM images and EDS analysis were performed on a JEOL 7001F field emission scanning electron microscope using an accelerating voltage of 15 kV.

A Perkin-Elmer Spectrum RXI Fourier-transform infrared spectrometer was used to obtain the IR spectrum on a KBr pellet in the spectral range 4000 to 400 cm<sup>-1</sup>.

Elemental analysis was performed in the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

The thermal decomposition was measured using the Setaram TAG 24 symmetrical thermoanalyser. The first step was the removal of volatile matter inside the pores at  $110 \,^{\circ}$ C for 1 h. During the last 30 min of this period, the gas composition was changed from

100 vol% Ar to 50 vol% air and 50 vol% Ar. The sample was then heated to 900 °C with a heating ramp of 10 °C min<sup>-1</sup> in the Ar/air mixture. After 15 min at 900 °C the air flow was switched off and after another 15 min the system was cooled to 20 °C.

## 3.6.3.4 Low pressure gas sorption

Low pressure CO<sub>2</sub> isotherms at 25, 45, 75 and 105 °C were measured using the Setaram TAG 24 symmetrical thermoanalyser. Prior to the experiment, the sample was activated under vacuum at 150 °C overnight. Approximately 20 mg of sample were used for each experiment. The first step of the TGA program was the pre-treatment at 150 °C under Ar (70 mL min<sup>-1</sup>) for 1 h in order to remove moisture. The system was then cooled down under Ar until the adsorption temperature was reached. The thermoanalyser was allowed to equilibrate for 20 minutes before CO<sub>2</sub> flow was begun. The amount of CO<sub>2</sub> was increased in five steps (2.1, 5.2, 14.7, 29.7 and 49.8 vol%), then the desorption was started by decreasing the amount of CO<sub>2</sub> in the gas stream. The change in gas feed composition is able to mimic a vacuum swing adsorption process by varying the partial pressure of CO<sub>2</sub>. After the last desorption step, the temperature was held constant for another 20 min. At the end of the experiment the MOF was heated to 150 °C in order to desorb the CO<sub>2</sub> completely. Fresh samples were used for each experiment.

## 3.6.3.5 Cycling experiments

The stability and regenerability of STA-16 was measured by thermogravimetric analysis using the Setaram TAG 24 symmetrical thermoanalyser. The sample was degassed under vacuum at 150 °C for 12 h prior to the cycling experiment. After activating approximately 20 mg at 150 °C under Ar in order to remove any residual moisture, the temperature was adjusted to 25 °C. Ten cycles of adsorption/desorption were carried out by varying the  $CO_2$  partial pressure between 0.05 and 0.15 bar. The equilibration time for each adsorption and desorption step was set to 20 min. For the wet experiments, the MOF was saturated with 1 vol.% H<sub>2</sub>O vapour by exposing the samples to flowing wet Ar after the activation step, before treatment with wet  $CO_2/Ar$  mixtures (1 % H<sub>2</sub>O/CO<sub>2</sub>/Ar, 70 mL min<sup>-1</sup>).

#### **3.6.3.6** High pressure gas sorption

The sorption isotherms for  $CO_2$  and  $N_2$  were measured using a HPVA instrument (Micromeritics). Prior to measuring the isotherms, the sample was activated at 150 °C under high vacuum overnight. The sample (0.36 g) was then transferred from the degas to

the analysis port and the gas sorption was measured at 25/30, 45, 75 and 105 °C up to 40 bar. The sample was re-activated after each isotherm. The isosteric heat of adsorption  $\Delta H_{iso}$  as a function of CO<sub>2</sub> loading was determined by fitting the Tóth isotherm model to the CO<sub>2</sub> isotherms obtained at 25, 45, 75 and 105 °C [34]. From this data the heat of adsorption was also calculated using the Clausius-Clapeyron equation.

The hydrothermal stability of STA-16(Co) was determined by measuring CO<sub>2</sub> and H<sub>2</sub>O vapour sorption isotherms using an Intelligent Gravimetric Analyzer (IGA-1 series, Hiden Analytical Ltd.). Before and after each H<sub>2</sub>O sorption, CO<sub>2</sub> isotherms (0-5 bar) were measured in order to evaluate the stability of the framework. The MOF was activated at 150 °C in the VacPrep 061 (Micromeritics) and approximately 30 mg were used for the measurements. The sample was installed in the instrument and outgassed at room temperature until the sample weight remained constant. The minimum and maximum times per data point were set to 15 to 30 min for CO<sub>2</sub> and 10 to 40 min for H<sub>2</sub>O. If the mass gain reached within 1 % of the calculated equilibrium value the pressure was changed immediately to the next value, even if the maximum time had not elapsed. The sample was activated under vacuum in between in each isotherm. After the adsorption of H<sub>2</sub>O at 90 % relative humidity (RH), the activation using vacuum at room temperature was insufficient and the temperature needed to be increased to 95 to 100 °C to remove the adsorbed H<sub>2</sub>O completely.

## 3.6.4 Results and discussion

## 3.6.4.1 Characterisation of STA-16(Co)

The experimental and theoretical elemental compositions of STA-16(Co) are compared in Table 3.9. The results are in reasonable agreement with the calculated values for carbon, hydrogen and nitrogen. The theoretical composition of STA-16(Co) was calculated from the empirical framework formula  $Co_2(H_2O)_2C_{12}H_{22}N_2P_2O_6$ ·11H<sub>2</sub>O.

Tuble 5.7. Elementary enemiear anarysis of 5177 10(CO).					
MOF	%C	%H	%N		
STA-16(Co)	$18.54\pm0.41$	$6.72 \pm 0.33$	$3.51\pm0.16$		
STA-16(Co) calculated	20.50	6.87	3.98		

**Table 3.9:** Elementary chemical analysis of STA-16(Co).

The SEM image shows the formation of elongated crystals of various sizes from 0.2  $\mu$ m to 1.6  $\mu$ m (Figure 3.52). Energy dispersive X-ray analysis indicated Co:P and Co:N mole ratios of 1.06:1 and 1.09:1, respectively. These results are in good agreement with the



theoretical ratios of 1:1 calculated from the empirical formula  $Co_2(H_2O)_2C_{12}H_{22}N_2P_2O_6$ .

Figure 3.52: SEM images of STA-16(Co) at a magnification of 10000 (a) and 20000 (b).

The comparison of the measured powder X-ray diffraction (XRD) pattern of STA-16(Co) and the calculated XRD pattern for the crystal structure shown in Figure 3.53a confirms the purity of the bulk sample. The calculated XRD pattern of STA-16(Co) was calculated from the crystal structure reported by Wharmby et al., which was measured at -173 °C using synchrotron radiation [31].

The IR spectrum of STA-16(Co) (Figure 3.53b) shows a band at 2950 cm<sup>-1</sup> which is characteristic for methylene C-H vibrations. The strong bands at 3432 cm<sup>-1</sup> (O-H) stretch and 1654/1637 cm<sup>-1</sup> (O-H bend) are due to hydrogen-bonded adsorbed H<sub>2</sub>O molecules. The C-C stretch and the C-N stretch are observed at 1454 and 1378 cm<sup>-1</sup>, respectively. Two P-O(H) stretch vibrations are visible at 2865 cm<sup>-1</sup> and in the region of 1167 to 966 cm<sup>-1</sup>. The bands at 1351 to 1224 cm<sup>-1</sup> are characteristic for the P=O stretch.

The thermal stability of STA-16(Co) was evaluated by thermogravimetric analysis (TGA). The TGA profile (Figure 3.53c) showed a weight loss of 26.1 wt% (16-96 °C), assigned to the loss of physisorbed H<sub>2</sub>O, immediately followed by a second loss of 5.8 wt% (expected value: 5.2 wt%), assigned to the loss of one H<sub>2</sub>O molecule per Co<sup>2+</sup>. The discrepancy can be explained by the loss of some residual physisorbed H<sub>2</sub>O in the second event. This H<sub>2</sub>O loss was followed by a plateau until 230 °C, after which the framework decomposed. The decomposition temperature is in good agreement with the 230 °C reported by Wharmby et al. [31].



**Figure 3.53:** (a) Comparison of experimental (black, 25  $^{\circ}$ C) and the calculated diffractogram of STA-16(Co) (red, -173  $^{\circ}$ C). (b) IR spectrum of STA-16(Co). (c) Thermal decomposition of STA-16(Co) compared to literature data [31].

# 3.6.4.2 Low pressure gas sorption

Prior to the sorption experiments, STA-16(Co) was activated at 150 °C overnight. A comparison of the pseudo-isotherms at 25, 45 and 75 °C is shown in Figure 3.54a. The MOF did not show any measurable CO<sub>2</sub> adsorption capacity at 105 °C in the pressure range studied. Increasing the CO<sub>2</sub> concentration led to a rise in CO<sub>2</sub> adsorption capacity, whereas an increase in temperature resulted in a decrease in CO<sub>2</sub> adsorption capacity. The change with temperature is due to the greater kinetic energy of the molecules at higher temperature, which allows weakly bound molecules to leave the surface of the adsorbent more readily. The CO<sub>2</sub> adsorption capacity of 3.43 wt% at 25 °C and 0.5 bar is higher than those reported for IRMOF-1 (2.11 wt%), MOF-177 (2.36 wt%), IRMOF-3 (2.95 wt%) and

ZIF-8 (2.76 wt%) [19]. However, it is much lower than those of HKUST-1 (~10.12 wt%) [35], MOF-74(Ni) (~27.50 wt%) [36] and MOF-74(Mg) (~32.00 wt%) [36].

The material showed good adsorption/desorption kinetics at low temperatures, as can be seen in the stepwise profile in Figure 3.54b. The adsorption was completely reversible upon decreasing the pressure of  $CO_2$  at 25 and 75 °C. Hysteresis of the pseudo-isotherms at 45 °C indicated some irreversibility of the  $CO_2$  adsorption. To verify the irreversibility at 45 °C the TGA measurements were repeated at all temperatures and identical result were obtained (25 and 75 °C not shown here). A possible explanation for this phenomenon is the occurrence of some change in structure at 45 °C, which is slow and therefore results in irreversible adsorption upon lowering the  $CO_2$  pressure. At higher temperatures this structural change becomes more rapid and almost reversible adsorption can be achieved. The nature of this potential structural change is however unknown.



**Figure 3.54:** Low pressure  $CO_2$  pseudo-isotherms (a) and TGA profiles (b) on STA-16(Co). The closed symbols ( $\blacksquare$ ) represent the adsorption of  $CO_2$  and the open symbols ( $\Box$ ) represent the desorption.

## 3.6.4.3 Cycling experiments

The CO<sub>2</sub> working capacities and the practical regenerability of STA-16(Co) were evaluated by monitoring pseudo-equilibrium adsorption uptakes over ten cycles of adsorption and desorption at 25 °C under dry and wet (1 vol% H<sub>2</sub>O) conditions using a standard procedure applied in our laboratory [37]. The TGA profiles and the corresponding working capacities are illustrated in Figure 3.55.

The dry cycling profile is shown in Figure 3.55a. The figure shows the weight loss during the activation at 150 °C under flowing Ar (t=-100 to -50 min), the cooling to 25 °C under flowing Ar (t=-50 to -20 min) and the equilibration of the mass at 25 °C under Ar atmosphere (t=-20 to 0 min). After approximately 420 min the Ar/CO<sub>2</sub> mixture was replaced by pure Ar and the temperature was held for another 40 min. The weight gain during the cooling step is regarded as an artefact due to the change in temperature. The sample was then heated to 150 °C under flowing Ar (t>460 min). The TGA profile indicates a gradual increase of CO<sub>2</sub> adsorption from cycle to cycle, implying incomplete equilibration of the adsorbed  $CO_2$  during the 20 min allowed for each adsorption step. This result suggests that the adsorption kinetics were relatively slow, compared to other materials we have studied, and therefore equilibrium adsorption was not quite achieved. Irreversibility of the adsorption process was also observed, in that the amount of CO<sub>2</sub> desorbed was in most cases a little smaller than the amount adsorbed in the previous step. This could be consistent with the interaction of  $CO_2$  (slow adsorption and slower desorption) with the CUS of STA-16(Co). However, regenerating the sample at 150 °C under flowing Ar resulted in complete desorption of CO<sub>2</sub>. The net result of this interaction with the CUS was a decrease in working capacity (Figure 3.55c) over the 10 cycles of approximately 45 %. The average working capacity calculated from the adsorption capacities in cycle two to ten was approximately 0.8 wt% (0.05 mol(CO<sub>2</sub>)/mol(CUS)), which is higher than the 0.7 wt% (0.04 mol(CO<sub>2</sub>)/mol(CUS)) expected from the low pressure CO<sub>2</sub> data.

In contrast to what was observed for the dry cycling experiments equilibration in 20 min was achieved under wet conditions (Figure 3.55b). It took 400 min of treatment with 1 vol% H<sub>2</sub>O vapour to reach equilibrium H<sub>2</sub>O uptake, corresponding to 14.9 wt% (2.09 mol(H<sub>2</sub>O)/mol(CUS)). The high H<sub>2</sub>O uptake and the time required for saturating the material shows that STA-16(Co) is highly hydrophilic, with a high selectivity for H<sub>2</sub>O relative to CO<sub>2</sub>. The high H<sub>2</sub>O uptake reduced the pore volume by at least a fifth and since H<sub>2</sub>O will occupy the sites for preferential CO<sub>2</sub> adsorption the decrease in CO<sub>2</sub> working capacities (~0.23 wt%; 0.01 mol(CO<sub>2</sub>)/mol(CUS)) were much smaller than under dry conditions. However, the overall loss of working capacity from cycle one to cycle ten was only 23 % compared to 45 % under dry conditions. Most of the H<sub>2</sub>O was removed by heating STA-16(Co) at 150 °C for 30 min in a flow of Ar, with only 0.7 wt%

 $(0.10 \text{ mol}(\text{H}_2\text{O})/\text{mol}(\text{CUS}))$  remaining inside the pores. This result suggests that the recovery time of 30 min at 150 °C under flowing Ar was insufficient to remove the chemisorbed H<sub>2</sub>O molecules completely, but it is expected that an extension in the final activation step will eventually result in the complete desorption of these H<sub>2</sub>O molecules. Thus, while the material remained stable in the presence of H<sub>2</sub>O, its application in post-combustion CO<sub>2</sub> capture from wet atmospheres is limited.



**Figure 3.55:** TGA profiles of dry (a) and wet (b) cycling experiments at 25  $^{\circ}$ C and CO<sub>2</sub> working capacities in 10 cycles under dry (c) and wet (d) conditions.

## 3.6.4.4 High pressure CO<sub>2</sub> and N<sub>2</sub> sorption

The CO<sub>2</sub> and N<sub>2</sub> sorption isotherms of STA-16(Co) were determined over a temperature range of 25-105 °C (CO<sub>2</sub>) and 25-75 °C (N<sub>2</sub>) and a pressure range of 0-40 bar in order to determine the CO<sub>2</sub>/N<sub>2</sub> selectivities and to evaluate the potential of STA-16(Co) for high pressure separation processes.

The sorption isotherms are shown in Figure 3.56. The size of the sample used was too small to obtain accurate results for  $N_2$  adsorption capacity at 105 °C, which is low, so that a 105 °C  $N_2$  isotherm could not be obtained. At lower temperatures a slight hysteresis in the sorption isotherms of both  $CO_2$  and  $N_2$  are observed which can be explained by the strong interaction of the adsorbates with the coordinatively unsaturated sites. Similar hysteresis has been reported for HKUST-1 [38]. While increasing the pressure resulted in an increase in capacity, an increase in temperature had the opposite effect. For both adsorbates, no saturation was observed in the studied temperature and pressure range, but the  $N_2$  sorption isotherms showed a more linear shape than those observed for  $CO_2$ . The shape of the  $CO_2$  isotherms suggest that saturation is likely to occur at approximately 40 bar, whereas the saturation for  $N_2$  will only occur at much higher pressure.

The CO<sub>2</sub> adsorption capacity of STA-16(Co) was 21.1 wt% (1.21 mol(CO<sub>2</sub>)/mol(CUS)) at 30 °C and 15 bar, which is higher than the CO<sub>2</sub> adsorption capacity reported for STA-12(Ni) (15.4 wt%) [39]. This is consistent with the higher pore volume in STA-16(Co) (0.68 cm<sup>3</sup> g<sup>-1</sup>) [31] than in STA-12(Ni) (0.20 cm<sup>3</sup> g<sup>-1</sup>) [40]. In comparison with carboxylate MOFs like HKUST-1 (~55.9 wt%) [9], MIL-53(Al)-NH<sub>2</sub> (~26.0 wt%) [41] and MIL-101(Cr) (~74.8 wt%) [42] the adsorption capacity was lower under similar conditions. This result is consistent with the total pore volume available within the pores and the electron density distribution throughout the pore system. In contrast to this, Choi et al. reported a similar adsorption capacity for zeolite 13X (22.8 wt%) [43]. The comparatively low CO<sub>2</sub> adsorption capacities over the studied pressure and temperature range suggest that STA-16(Co) might not be an attractive adsorbent for natural gas or pre-combustion processes.

Comparison of Figure 3.56a and b shows that STA-16(Co) has a higher affinity for CO<sub>2</sub> than for N<sub>2</sub>, which is advantageous for a post-combustion capture process. The CO<sub>2</sub>/N<sub>2</sub> selectivity was determined by dividing the CO<sub>2</sub> adsorption capacity by the N<sub>2</sub> capacity at each pressure point. Figure 3.56c shows the CO<sub>2</sub>/N<sub>2</sub> selectivity at 25 °C as a function of pressure. Increasing the pressure resulted in a gradual reduction in the selectivity. At low pressure (1.2 bar) a maximum in selectivity is observed. The selectivity was higher than those reported for MOF-5 (~3) [44] and ZIF-8 (~4) [45], but much lower than that of MOF-74(Zn) (35) [45]. The CO<sub>2</sub>/N<sub>2</sub> selectivity range of 8 to approximately 11 is comparable to values reported for HKUST-1 (~5-10) [45]. The next step should be to evaluate the selectivities for specific applications such post-combustion, pre-combustion



and natural gas separation by conducting adsorption/desorption experiments using binary/ternary/multi component gas mixtures.

**Figure 3.56:** (a) High pressure  $CO_2(\bullet)$  and (b) high pressure  $N_2$  sorption isotherms ( $\blacksquare$ ) on STA-16(Co). The closed symbols ( $\bullet$ ,  $\blacksquare$ ) represent the adsorption of the adsorbates and the open symbols ( $\circ$ ,  $\Box$ ) represent the desorption. (c)  $CO_2/N_2$  selectivity at 25/30 °C. (d) Isosteric heat of adsorption for  $CO_2$  on STA-16(Co).

The isosteric heat of adsorption as a function of loading is shown in Figure 3.56d. At zero coverage the isosteric heat of adsorption was estimated to be 37 kJ mol<sup>-1</sup> using the Tóth isotherm equation. But at practical loadings for a pressure swing adsorption (PSA) process the isosteric heat would correspond to ~30 kJ mol<sup>-1</sup>. The isosteric heat of adsorption at zero coverage is comparable to those reported for STA-12(Ni) (36 kJ mol<sup>-1</sup>) [40], MIL-101(Cr) (34 kJ mol<sup>-1</sup>) [46], MOF-74(Mg) (42 kJ mol<sup>-1</sup>) [47] and zeolite 13X (37 kJ mol<sup>-1</sup>) [48]. The value is higher than the adsorption enthalpies at zero coverage of HKUST-1

(28.1 kJ mol<sup>-1</sup>), MOF-5 (15 kJ mol<sup>-1</sup>) and ZIF-8 (17 kJ mol<sup>-1</sup>) [45]. The isosteric heat of adsorption decreases with increasing loading to approximately 1 mmol g<sup>-1</sup>, above which it increases slightly. At low loadings the heat of adsorption is high due to the occupation of high-energy adsorption sites. After these adsorption sites are occupied, the less energetic sites will be filled, hence the heat of adsorption declines.

## 3.6.4.5 Hydrothermal stability of STA-16(Co)

The hydrothermal stability is an important factor in determining the practical usefulness of adsorbents. In this study, the stability of STA-16(Co) was assessed by measuring CO<sub>2</sub> sorption isotherms before and after the sorption of H<sub>2</sub>O vapour and by PXRD. The H<sub>2</sub>O vapour sorption isotherms of STA-16(Co) to different relative humidities are compared in Figure 3.57a and b. The H<sub>2</sub>O adsorption capacities increased with increasing relative humidity. Due to the presence of coordinatively unsaturated sites in the framework structure, high H<sub>2</sub>O uptakes were observed even at low pressures. The steep increase at 0-0.015 bar is a result of the hydrophilic pore surface. Furthermore, hysteresis was present at low pressure, implying a strong interaction of H<sub>2</sub>O with the Co(II) sites. While vacuum activation at ambient temperature was sufficient after the treatment at 30 % RH and 60 % RH, the sample needed to be activated at 95 to 100 °C after H<sub>2</sub>O sorption at 90 % RH.

The CO<sub>2</sub> isotherms before and after the H<sub>2</sub>O vapour sorption are shown in Figure 3.57c. No changes in CO<sub>2</sub> adsorption capacities were observed after the adsorption of H<sub>2</sub>O up to 30 % RH or 60 % RH, confirming the stability of STA-16(Co). However, after the H<sub>2</sub>O sorption at 90 % RH a slight decrease in CO<sub>2</sub> adsorption capacity was observed from 13.2 wt% to 12.5 wt% at 25 °C and 5 bar. In comparison to this, HKUST-1 and  $M_2(BDC)_2(DABCO)$  (M=Ni,Zn) were found to be unstable at 30 % RH and 60 % RH, respectively [49].

PXRD studies revealed that the H<sub>2</sub>O sorption at up to 60 % RH did not result in a loss in crystallinity (Figure 3.57d). However, comparison with the as-synthesised STA-16 framework revealed that the intensities of some peaks above  $2\theta$ =14 ° had increased. For instance, after H<sub>2</sub>O sorption the peak at  $2\theta$ =25.6 ° became the most intense peak in the diffraction pattern and shifted slightly to 25.2 °. These results suggest that the small decrease in CO<sub>2</sub> adsorption capacity on adsorption of H<sub>2</sub>O up to 90 % RH is occurring together with a change in crystal structure.



**Figure 3.57:** (a) H<sub>2</sub>O isotherms of 30 %RH (black), 60 % RH (red) and 90 %RH (green) at 25 °C. (b) H<sub>2</sub>O isotherms of 30 %RH (black), 60 % RH (red) and 90 %RH (green) at 25 °C on an enlarged scale. (c) CO<sub>2</sub> isotherms before (black) and after adsorption of 30 % RH (red), 60 % RH (green) and 90 % RH (blue) at 25 °C and 0 to 5 bar. Closed ( $\blacksquare$ ) and open ( $\Box$ ) symbols denote adsorption and desorption respectively. (d) PXRD before (black) and after 90 % RH treatment (blue).

# 3.6.5 Conclusion

STA-16(Co) was prepared and its potential application in a VSA or PSA process was evaluated by measuring low pressure  $CO_2$  isotherms, high pressure  $CO_2$  and  $N_2$  isotherms and by performing cycling experiments with and without  $H_2O$  vapour. The uptake at low and high pressure was found to be significantly lower than those reported for carboxylate MOFs such as MOF-74 and HKUST-1. The strong interaction of  $CO_2$  with the coordinatively unsaturated sites of the framework results in a progressive decrease of the  $CO_2$  cyclic working capacity by 45 % from its value for the first cycle under dry

conditions. The presence of  $H_2O$  vapour reduced the capacity loss to 23 %, but the high  $H_2O$  capacity also led to a significant decrease in the absolute amount of  $CO_2$  captured. The applicability of STA-16(Co) for capturing  $CO_2$  in post-combustion, pre-combustion and natural gas separation is seen to be limited, due to the relatively low uptakes at both low and high pressure. However, STA-16(Co) could be used as a pre-layer in post-combustion processes to remove  $H_2O$  vapour. The material was found to be stable up to 60 % RH, though above this RH structural change in the framework occurred. The material could be regenerated after exposure to wet atmospheres by heating at 150 °C under Ar flow. Although regeneration under vacuum at room temperature was possible, the time required was too long for industrial processes (days to weeks).

# 3.6.6 Acknowledgements

Financial support was provided by the Australian Government through the CRC Program to support this CO2CRC Project. The authors acknowledge use of facilities within the Monash Centre for Electron Microscopy. This research used equipment whose purchase was supported under the Australian Research Council's *Centres of Excellence* funding scheme (COE for Design in Light Metals). Dr. Gregory O. Knowles (TGA), Dr. Xi-ya Fang (SEM) and Dr. Martin Duriska/Craig Forsyth (PXRD) are acknowledged for their technical advice and training on various instruments which have been used for this work.

# 3.6.7 References

- [1] K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, and J. R. Long, "Carbon Dioxide Capture in Metal–Organic Frameworks," *Chemical Reviews*, vol. 112, pp. 724-781, 2012/02/08 2011.
- [2] R. K. Pachauri and A. Reisinger, "IPCC Fourth Assessment Report," *Intergovernmental Panel on Climate Change*, 2007.
- [3] N. Hedin, L. Andersson, L. Bergström, and J. Yan, "Adsorbents for the postcombustion capture of CO<sub>2</sub> using rapid temperature swing or vacuum swing adsorption," *Applied Energy*, vol. 104, pp. 418-433, 2013.
- [4] H. Wu, R. S. Reali, D. A. Smith, M. C. Trachtenberg, and J. Li, "Highly Selective CO<sub>2</sub> Capture by a Flexible Microporous Metal–Organic Framework (MMOF) Material," *Chemistry – A European Journal*, vol. 16, pp. 13951-13954, 2010.
- [5] M. Mikkelsen, M. Jorgensen, and F. C. Krebs, "The teraton challenge. A review of fixation and transformation of carbon dioxide," *Energy & Environmental Science*, vol. 3, pp. 43-81, 2010.
- [6] A. Torrisi, R. G. Bell, and C. Mellot-Draznieks, "Functionalized MOFs for Enhanced CO<sub>2</sub> Capture," *Crystal Growth & Design*, vol. 10, pp. 2839-2841, 2010.
- [7] R. Vaidhyanathan, S. S. Iremonger, G. K. H. Shimizu, P. G. Boyd, S. Alavi, and T. K. Woo, "Direct Observation and Quantification of CO<sub>2</sub> Binding Within an Amine-

Functionalized Nanoporous Solid," *Science*, vol. 330, pp. 650-653, October 29, 2010 2010.

- [8] C. Lastoskie, "Caging Carbon Dioxide," *Science*, vol. 330, pp. 595-596, October 29, 2010 2010.
- Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X)," *Energy & Fuels*, vol. 23, pp. 2785-2789, 2009.
- [10] K. A. Mumford, K. H. Smith, C. J. Anderson, S. Shen, W. Tao, Y. A. Suryaputradinata, A. Qader, B. Hooper, R. A. Innocenzi, S. E. Kentish, and G. W. Stevens, "Post-combustion Capture of CO<sub>2</sub>: Results from the Solvent Absorption Capture Plant at Hazelwood Power Station Using Potassium Carbonate Solvent," *Energy & Fuels*, vol. 26, pp. 138-146, 2012/01/19 2011.
- [11] <u>http://www.co2crc.com.au/aboutccs/cap\_adsorption.html</u>, (accessed 20.09.2013).
- [12] Y.-S. Bae, O. K. Farha, J. T. Hupp, and R. Q. Snurr, "Enhancement of CO<sub>2</sub>/N<sub>2</sub> selectivity in a metal-organic framework by cavity modification," *Journal of Materials Chemistry*, vol. 19, pp. 2131-2134, 2009.
- [13] Y.-S. Bae, K. L. Mulfort, H. Frost, P. Ryan, S. Punnathanam, L. J. Broadbelt, J. T. Hupp, and R. Q. Snurr, "Separation of CO<sub>2</sub> from CH<sub>4</sub> Using Mixed-Ligand Metal-Organic Frameworks," *Langmuir*, vol. 24, pp. 8592-8598, 2008.
- [14] S. Keskin, T. M. van Heest, and D. S. Sholl, "Can Metal–Organic Framework Materials Play a Useful Role in Large-Scale Carbon Dioxide Separations?," *ChemSusChem*, vol. 3, pp. 879-891, 2010.
- [15] S. D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A. G. Russell, Q. Wei, and M. Fan, "Review of recent advances in carbon dioxide separation and capture," *RSC Advances*, 2013.
- [16] J. Wilcox, "Adsorption," in *Carbon Capture*, ed: Springer New York, 2012, pp. 115-175.
- [17] Q. Wang, J. Luo, Z. Zhong, and A. Borgna, "CO<sub>2</sub> capture by solid adsorbents and their applications: current status and new trends," *Energy & Environmental Science*, vol. 4, pp. 42-55, 2011.
- [18] C. Janiak and J. K. Vieth, "MOFs, MILs and more: concepts, properties and applications for porous coordination networks (PCNs)," *New Journal of Chemistry*, vol. 34, pp. 2366-2388, 2010.
- [19] A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, "Screening of Metal-Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach," *Journal of the American Chemical Society*, vol. 131, pp. 18198-18199, 2009.
- [20] G.-P. Hao, W.-C. Li, and A.-H. Lu, "Novel porous solids for carbon dioxide capture," *Journal of Materials Chemistry*, vol. 21, pp. 6447-6451, 2011.
- [21] A. Ö. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis, and R. Q. Snurr, "Enhanced CO<sub>2</sub> Adsorption in Metal-Organic Frameworks via Occupation of Open-Metal Sites by Coordinated Water Molecules," *Chemistry of Materials*, vol. 21, pp. 1425-1430, 2009.
- [22] D. Britt, H. Furukawa, B. Wang, T. G. Glover, and O. M. Yaghi, "Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites," *Proceedings of the National Academy of Sciences*, vol. 106, pp. 20637-20640, December 8, 2009 2009.
- [23] J. A. Groves, S. R. Miller, S. J. Warrender, C. Mellot-Draznieks, P. Lightfoot, and P. A. Wright, "The first route to large pore metal phosphonates," *Chemical Communications*, pp. 3305-3307, 2006.
- [24] S. S. Iremonger, J. Liang, R. Vaidhyanathan, and G. K. H. Shimizu, "A permanently porous van der Waals solid by using phosphonate monoester linkers in a metal organic framework," *Chemical Communications*, vol. 47, pp. 4430-4432, 2011.
- [25] K. Maeda, J. Akimoto, Y. Kiyozumi, and F. Mizukami, "Structure of aluminium methylphosphonate, AIMepO-[small beta], with unidimensional channels formed from ladder-like organic-inorganic polymer chains," *Journal of the Chemical Society, Chemical Communications*, pp. 1033-1034, 1995.
- [26] K. Maeda, J. Akimoto, Y. Kiyozumi, and F. Mizukami, "AlMepO-α: A Novel Open-Framework Aluminum Methylphosphonate with Organo-Lined Unidimensional Channels," *Angewandte Chemie International Edition in English*, vol. 34, pp. 1199-1201, 1995.
- [27] K. Maeda, Y. Kiyozumi, and F. Mizukami, "Synthesis of the First Microporous Aluminum Phosphonate with Organic Groups Covalently Bonded to the Skeleton," *Angewandte Chemie International Edition in English*, vol. 33, pp. 2335-2337, 1994.
- [28] G. K. H. Shimizu, R. Vaidhyanathan, and J. M. Taylor, "Phosphonate and sulfonate metal organic frameworks," *Chemical Society Reviews*, vol. 38, pp. 1430-1449, 2009.
- [29] S. R. Miller and P. A. Wright, "Nanoporous Metal Phosphonates," in *Encyclopedia* of *Inorganic Chemistry*, ed: John Wiley & Sons, Ltd, 2006, pp. 1-13.
- [30] J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger, and G. K. H. Shimizu, "Enhancing Water Stability of Metal–Organic Frameworks via Phosphonate Monoester Linkers," *Journal of the American Chemical Society*, vol. 134, pp. 14338-14340, 2012/09/05 2012.
- [31] M. T. Wharmby, J. P. S. Mowat, S. P. Thompson, and P. A. Wright, "Extending the Pore Size of Crystalline Metal Phosphonates toward the Mesoporous Regime by Isoreticular Synthesis," *Journal of the American Chemical Society*, vol. 133, pp. 1266-1269, 2011.
- [32] P. A. Wright, M. T. Wharmby, and J. P. S. Mowat, Novel Large Pore Metal Organic Frameworks, Pub. number: US 2013/0296162, 07.11.2013. (http://worldwide.espacenet.com/publicationDetails/originalDocument?FT=D&dat e=20131107&DB=&locale=en\_EP&CC=US&NR=2013296162A1&KC=A1&ND =1).
- [33] ""Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.," "*Reflex Tools*" is a module in the Materials Studio Modeling software package from Accelrys Inc.
- [34] J. Tóth, "Uniform interpretation of gas/solid adsorption," *Advances in Colloid and Interface Science*, vol. 55, pp. 1-239, 1995.
- [35] P. Chowdhury, C. Bikkina, D. Meister, F. Dreisbach, and S. Gumma, "Comparison of adsorption isotherms on Cu-BTC metal organic frameworks synthesized from different routes," *Microporous and Mesoporous Materials*, vol. 117, pp. 406-413, 2009.
- [36] P. D. C. Dietzel, V. Besikiotis, and R. Blom, "Application of metal-organic frameworks with coordinatively unsaturated metal sites in storage and separation of

methane and carbon dioxide," Journal of Materials Chemistry, vol. 19, pp. 7362-7370, 2009.

- [37] D. J. N. Subagyono, M. Marshall, G. P. Knowles, and A. L. Chaffee, "CO<sub>2</sub> adsorption by amine modified siliceous mesostructured cellular foam (MCF) in humidified gas," *Microporous and Mesoporous Materials*, vol. 186, pp. 84-93, 2014.
- [38] S. Ye, X. Jiang, L.-W. Ruan, B. Liu, Y.-M. Wang, J.-F. Zhu, and L.-G. Qiu, "Postcombustion CO<sub>2</sub> capture with the HKUST-1 and MIL-101(Cr) metal–organic frameworks: Adsorption, separation and regeneration investigations," *Microporous and Mesoporous Materials*, vol. 179, pp. 191-197, 2013.
- [39] G. M. Pearce, "Synthesis, adsorption and catalysis of large pore metal phosphonates," University of St Andrews, 2010, http://hdl.handle.net/10023/823
- [40] S. R. Miller, G. M. Pearce, P. A. Wright, F. Bonino, S. Chavan, S. Bordiga, I. Margiolaki, N. Guillou, G. Férey, S. Bourrelly, and P. L. Llewellyn, "Structural Transformations and Adsorption of Fuel-Related Gases of a Structurally Responsive Nickel Phosphonate Metal-Organic Framework, Ni-STA-12," *Journal of the American Chemical Society*, vol. 130, pp. 15967-15981, 2008.
- [41] S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, and F. Kapteijn, "An Amine-Functionalized MIL-53 Metal-Organic Framework with Large Separation Power for CO<sub>2</sub> and CH<sub>4</sub>," *Journal of the American Chemical Society*, vol. 131, pp. 6326-6327, 2009.
- P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jhung, and G. Férey, "High Uptakes of CO<sub>2</sub> and CH<sub>4</sub> in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101," *Langmuir*, vol. 24, pp. 7245-7250, 2008.
- [43] S. Choi, J. H. Drese, and C. W. Jones, "Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources," *ChemSusChem*, vol. 2, pp. 796-854, 2009.
- [44] B. Liu and B. Smit, "Comparative Molecular Simulation Study of CO<sub>2</sub>/N<sub>2</sub> and CH4/N2 Separation in Zeolites and Metal–Organic Frameworks," *Langmuir*, vol. 25, pp. 5918-5926, 2009/05/19 2009.
- [45] J. M. Simmons, H. Wu, W. Zhou, and T. Yildirim, "Carbon capture in metalorganic frameworks-a comparative study," *Energy & Environmental Science*, vol. 4, pp. 2177-2185, 2011.
- [46] Z. Liang, M. Marshall, C. H. Ng, and A. L. Chaffee, "Comparison of Conventional and HF-Free-Synthesized MIL-101 for CO<sub>2</sub> Adsorption Separation and Their Water Stabilities," *Energy & Fuels*, vol. 27, pp. 7612-7618, 2013/12/19 2013.
- [47] J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna, and J. R. Long, "Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption," *Energy & Environmental Science*, vol. 4, pp. 3030-3040, 2011.
- [48] S. Cavenati, C. A. Grande, and A. E. Rodrigues, "Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures," *Journal of Chemical & Engineering Data*, vol. 49, pp. 1095-1101, 2004/07/01 2004.
- [49] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> adsorption, selectivity and water tolerance of pillared-layer metal organic frameworks," *Microporous and Mesoporous Materials*, vol. 132, pp. 305-310, 2010.

# 4 Flexible MOFs for carbon capture

# 4.1 Chapter overview

In the previous chapter, a series of MOFs containing CUS were evaluated for their potential for carbon capture. Another class of MOFs are flexible materials that can change their pore volume depending on the adsorbate, pressure and temperature. These materials are promising for carbon capture due to their high selectivities (see Chapter 1).

This chapter focuses on the flexible framework MIL-53(Al)-NH<sub>2</sub>. The potential for postcombustion capture was evaluated by performing a series of low pressure adsorption/desorption and cycling experiments. Due to the lack in performance under wet conditions, the material was modified with benzoic anhydride in an attempt to improve the capture ability under wet conditions. The impact of this PSM on the  $CO_2$  adsorption capacities and working capacities was determined.

# 4.2 MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM for carbon capture

## 4.2.1 Introduction

The selective capture of  $CO_2$  from flue gas, syngas or natural gas still remains one of the biggest challenges when evaluating the potential of MOFs for carbon capture [1, 2]. One approach to overcome this problem is the use of flexible MOFs, whose pores can open or close depending on the gas type and pressure [3, 4]. Various flexible MOFs have been studied for their ability to adsorb  $CO_2$ .

Choi et al. prepared two flexible MOFs, SNU-M10 and SNU-M11 using square-planar Ni(II) macrocylic complexes as linear linkers and 1,1'-biphenyl-3,3',5,5'-tetracarboxylate as a square planar organic building block. Both materials showed a high thermal stability up to 300 °C, good air and H<sub>2</sub>O stability and a high selectivity of CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub> and CO<sub>2</sub>/H<sub>2</sub>. The performance of SNU-M10 for post-combustion capture was confirmed by cycling experiments at 25 °C using 15 % CO<sub>2</sub> in N<sub>2</sub>, which showed a reversible uptake of 0.77 wt%. In contrast to this, SNU-M11 is not applicable for post-combustion carbon capture due to the lack of uptake at 25 °C and pressures up to 20 bar [5].

The gate opening of  $Cu(bpp)_2(BF4)_2$  and the effect of different activation temperatures were studied by Kotani and co-workers. Vacuum activation at 120 and 140 °C was found to result in a two-step CO<sub>2</sub> isotherm at 0 °C, with the gate opening taking place at p/p<sub>0</sub> of 0.012. The CO<sub>2</sub> uptakes at 1 atm were 8.2 wt% and 9.5 wt% for the pre-treatment at 120 and 140 °C, respectively [6].

The flexible MOF containing 4,4'-bipyridine, tetrakis[4-(carboxyphenyl)oxamethyl]methane and zinc metal centres was prepared by Thallapally et al. At 25 °C and 1 bar, the CO<sub>2</sub> uptake reached 5 wt% and a further increase in the pressure to 10 bar resulted in the breathing of the framework. N<sub>2</sub> (up to 1 bar) and H<sub>2</sub> (up to 20 bar) showed no detectable uptake, indicating a high selectivity of CO<sub>2</sub> over these gases [7].

MIL-53 and its functionalised derivatives are examples of breathing materials. The framework is built up by the interconnection of infinite trans chains of corner-sharing (via OH groups) AlO<sub>4</sub>(OH)<sub>2</sub> octahedra by 2-aminoterephthalte ligands. The two carboxylate functions are linked to two distinct adjacent aluminium cations. In this way a crystalline material with 1-D channels with different pore sizes depending on the nature of the inserted molecules [8, 9]. A schematic representation of the breathing effect in MIL-53(Al)-NH<sub>2</sub> upon CO<sub>2</sub> adsorption is shown in Figure 4.1. The very narrow pore form (*vnp*) is present at CO<sub>2</sub> pressures between 0 to 3 bar. This phase is a result of the hydrogen bonding between the amine groups and the bridging OH-groups and is not observed in the case of MIL-53(Al). At CO<sub>2</sub> pressures of 3 to 12 bar, the cell volume increases from 937.5 to 987.2 Å<sup>3</sup> and the corresponding structure is denoted as MIL-53(Al)-NH<sub>2</sub> *np*. From 3.5 bar, small amounts of MIL-53(Al)-NH<sub>2</sub>-*lp* are observed, which increases with increasing pressure. This large pore form exhibits a cell volume of 1451.4 Å<sup>3</sup>. The desorption can be achieved by purging helium over the sample for at least 15 min, mild thermal treatment or by reducing the pressure [10].

Lescouet et al. [11] prepared MIL-53(Al)-NH<sub>2</sub> containing different amounts of amine and measured the CO<sub>2</sub> adsorption/desorption isotherms at 30 °C between 0.02 and 32 bar. All isotherms exhibited two distinct adsorption steps, characteristic for the breathing of the MIL-53 framework. During the first adsorption step, with a CO<sub>2</sub> adsorption capacity of 8.80 wt%, MIL-53(Al)-NH<sub>2</sub> exists in the *np* form. This CO<sub>2</sub> adsorption capacity was observed for all samples, irrespective of the amine content. At higher pressures the phase transformation from the *np* to the *lp* form was observed in all samples, which exhibited varying CO<sub>2</sub> adsorption capacities. The gate opening pressure was found to increase with increasing amine content. At pressures below 1 bar a linear relationship between the amine

content and the Henry constant was found due to the formation of hydrogen bonds with the amino groups and the bridging hydroxide groups resulting in higher isosteric heats [11].

DRIFT measurements and DFT calculations were conducted by Stavitski et al. Closer observations of the amine region in the DRIFT spectra of MIL-53(Al)-NH<sub>2</sub> exposed to various pressures of  $CO_2$  did not indicate the formation of a chemical bond between the amine groups and the  $CO_2$  (see also Chapter 1.3.2.1) [12].



**Figure 4.1:** Schematic view of the breathing phenomenon of MIL-53(Al)-NH<sub>2</sub> upon adsorption/desorption of CO<sub>2</sub>. Ball and stick view (Al octahedra: pink, C: grey, O: red, N: blue) [10].

The effect of different synthesis times of MIL-53(Al)-NH<sub>2</sub> on the CO<sub>2</sub> uptake was reported by Kim and co-workers. The extension of the synthesis time up to 5 days resulted in an increase in pore volume, BET surface area and CO<sub>2</sub> adsorption capacity. The surface areas varied between 526 m<sup>2</sup> g<sup>-1</sup> (2 days) and 937 m<sup>2</sup> g<sup>-1</sup> (5 days). After 5 days a maximum in CO<sub>2</sub> adsorption capacity of 8 wt% was reached at 25 °C and 1 bar. However, in comparison with MIL-53(Al) (11.2 wt%), the CO<sub>2</sub> capacities are lower due to the smaller BET surface area and pore volume. The suitability of MIL-53(Al)-NH<sub>2</sub> for a PSA process was evaluated by performing six cycle experiments between 5 and 20 bar at 25 and 50 °C. The CO<sub>2</sub> adsorption capacity at 20 bar was found to be 29.1 and 23.0 wt%, respectively. The cycling experiments indicated good stability and regenerability in a PSA process [13].

Due to the high chemical stability of the framework structure, a variety of postsynthetic modifications of MIL-53(Al)-NH<sub>2</sub> using diphosgene, thiophosgene, formic acid and

chloromethylene have been reported [9, 14, 15]. The effect of different alkyl anhydrides (acetamide, butyramide, hexanoamide) used for the modification of MIL-53(Al)-NH<sub>2</sub> was reported by Ngyuen et al. Although the conversion of the amine group decreased with longer alkyl chains in the anhydride, contact angle measurements indicated the superhydrophobic character of the butyramide and hexanoamide modified samples [16].

# 4.2.2 Experimental section

## 4.2.2.1 Chemicals

Acetonitrile ( $\geq$  99.9%, Merck), aluminium chloride hexahydrate (99%, Sigma Aldrich), 2aminoterephthalic acid (99%, Sigma Aldrich), benzoic anhydride ( $\geq$  95%, Sigma Aldrich), chloroform (99%, Merck), DMF (GR grade, Merck), argon (high purity, BOC and Air Liquide), carbon dioxide (Food grade, Coregas), helium (high purity, Air Liquide) and liquid nitrogen (BOC and Air Liquide).

All reagents were commercially available and used without further purification.

# 4.2.2.2 Synthesis of MIL-53(Al)-NH<sub>2</sub>

MIL-53(Al)-NH<sub>2</sub> was synthesised and activated as described previously by Ahnfeldt et al. [9].

A mixture of 4.44 g (18.39 mmol) aluminium chloride hexahydrate, 3.39 g (18.71 mmol) 2-aminoterephthalic acid and 45 mL H<sub>2</sub>O was placed into a Teflon® lined autoclave and heated at 150 °C for 5 h. The product was filtered and washed with H<sub>2</sub>O. To remove the excess amount of 2-aminoterphtalic acid, MIL-53(Al)-NH<sub>2</sub> was treated with 100 mL DMF at 150 °C for 16 h. The yellow coloured product was filtered and dried at room temperature.

# 4.2.2.3 PSM of MIL-53(Al)-NH<sub>2</sub>

The postsynthetic modification of MIL-53(Al)-NH<sub>2</sub> with benzoic anhydride was performed using a procedure described by Nguyen et al. [16].



0.48 g of MIL-53(Al)-NH<sub>2</sub> were transferred into a vial and heated at 150  $^{\circ}$ C for 20 h. After quickly capping the vial and cooling to room temperature, MIL-53(Al)-NH<sub>2</sub> was

transferred with 40 mL acetonitrile into a Teflon® lined autoclave and 1.88 g (8.31 mmol) of benzoic anhydride was added. The mixture was heated at 80 °C for 24 h. The reaction was cooled to room temperature and centrifuged (4000 rpm, 10 minutes) and the reaction solution was decanted. The solid was washed by suspending the solid in chloroform (10 mL), centrifuged, and the solvent was decanted four times. MIL-53(Al)-AM was then dried at 50 °C for 1 h.

#### 4.2.3 Results and discussion

#### 4.2.3.1 Characterisation of MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM

The FTIR spectra of MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM are shown in Figure 4.2. The doublet at 3500 and 3387 cm<sup>-1</sup> corresponds to the asymmetrical and symmetrical stretching of the primary amine moieties and/or amide groups. These absorptions seem to be formed by the contribution of two different bands, pointing at two amine species in the framework [17]. Three other characteristic bands of the amino group can be observed at 1620 cm<sup>-1</sup> (N-H bending vibration) and 1340/1257 cm<sup>-1</sup> (C-N stretching absorption distinctive of aromatic amines) [18]. The bands at 1570 cm<sup>-1</sup> and 1499 cm<sup>-1</sup> correspond to the symmetric C=O and the aromatic C=C stretching vibrations, respectively [8, 19]. The characteristic band for the hydroxide groups of the *trans* corner-sharing to octahedral AlO<sub>4</sub>(OH)<sub>2</sub> chains can be found at 3651 cm<sup>-1</sup> [17]. The formation of MIL-53(Al)-NH<sub>2</sub> *lt* upon thermal treatment is confirmed by the absence of bands characteristic for CH<sub>3</sub> (~3060 and 2924 cm<sup>-1</sup>) and C=O (~ 1670 cm<sup>-1</sup>) groups of DMF molecules [9, 20]. After the reaction with benzoic anhydride, a new band can be observed at 1750 cm<sup>-1</sup>, which is indicative for the C=O stretch of the amide [21].



Figure 4.2: IR spectra of MIL-53(Al)-NH $_2$  before and after modification with benzoic anhydride.

The composition of MIL-53(Al)-NH<sub>2</sub> was calculated from the empirical framework formula Al(OH)[C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub>(COO)<sub>2</sub>] $\cdot$ 0.9H<sub>2</sub>O. The composition for the anhydride modified sample was calculated assuming a 100 % transformation of the amine group into an amide using the empirical framework formula Al(OH)[C<sub>6</sub>H<sub>3</sub>(COO)<sub>2</sub>NHCOC<sub>6</sub>H<sub>5</sub>] $\cdot$ 0.9H<sub>2</sub>O. However, while the values for MIL-53(Al)-NH<sub>2</sub> are in good agreement with the theoretical carbon, hydrogen and nitrogen contents, the results for MIL-53(Al)-AM suggest that only 20 % of the amine groups were converted into amide groups, which is in good agreement with the results obtained from IR and thermal decomposition.

	MIL-53(Al)-	MIL-53(Al)-NH <sub>2</sub> np	MIL-53(Al)-AM	MIL-53(Al)-
	$\mathbf{NH}_2$	calculated		AM calculated
C / %	$40.01 \pm 0$	40.15	$42.17\pm0.26$	52.46
Η/%	$3.27\pm0$	3.29	$2.67\pm0.01$	3.46
N / %	$5.82 \pm 0$	5.85	$5.11\pm0.12$	4.08

**Table 4.1:** Elemental analysis of MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM.

The PXRD diffractogram of MIL-53(Al)-NH<sub>2</sub> before and after modification with benzoic anhydride and the simulated pattern for the np and lp form of MIL-53(Al)-NH<sub>2</sub> are shown in Figure 4.3. The good agreement of the experimental and theoretical diffractogram of the narrow pore phase, confirms the formation of MIL-53(Al)-NH<sub>2</sub> with a high phase purity. The broadness of the peaks is related to the small crystallite size. The modification of the amine groups with benzoic anhydride results in a shift of the 2 $\theta$  peaks above 10° to smaller angles. This shift could be due to the formation of an intermediate phase between the npand lp phases after the PSM.



**Figure 4.3:** Comparison of the PXRD pattern of MIL-53(Al)-NH<sub>2</sub>, MIL-53(Al)-AM and the simulated diffraction patterns [10] for MIL-53(Al)-NH<sub>2</sub> np and MIL-53(Al)-NH<sub>2</sub> lp.

SEM pictures were taken in order to compare the morphology of MIL-53(Al)-NH<sub>2</sub> before and after the modification with benzoic anhydride. The SEM pictures of MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM are shown in Figure 4.4. MIL-53(Al)-NH<sub>2</sub> forms elongated crystals of 0.2 to 1  $\mu$ m. In contrast to this Kim et al. reported crystal sizes varying from 1 to 12  $\mu$ m depending on the duration of the synthesis [13]. The extended reaction times in their work resulted in further crystal growth, hence bigger crystals. No changes in morphology or crystal size were observed after the PSM with benzoic anhydride.



Figure 4.4: SEM images of MIL-53(Al)-NH<sub>2</sub> (left) and MIL-53(Al)-AM (right).

The thermal decomposition of MIL-53(Al)-NH<sub>2</sub> (Figure 4.5a) is characterised by a twostep weight loss. The first step corresponds to the release of approximately 0.75 H<sub>2</sub>O molecules within the pores, and the second weight loss is due to the decomposition of the framework. The framework structure is stable up to 410 °C, which is in good agreement with the literature data [9]. In this work, an Ar/air mixture was used for the combustion experiment. This resulted in a faster decomposition of the framework and in a higher weight loss relative to the literature profile which was measured under N<sub>2</sub>. MIL-53(Al)-AM is characterized by a three-step weight loss. The first step corresponds to the release of H<sub>2</sub>O molecules within the pores, and the third weight loss is due to the decomposition of the framework. The second weight loss of 9.6 wt% between 150 °C and 410 °C correspond to the loss of the amide group. The result is in good agreement with the elemental analysis data and confirms the conversion of 20 % of the amine groups into amides.

The  $N_2$  isotherm of MIL-53(Al)-AM at -196 °C is shown in Figure 4.5b. Despite several attempts to measure the  $N_2$  isotherm of MIL-53(Al)-NH<sub>2</sub> using Tristar II 3020, the isotherm could not be completed within 48 h due the high microporosity of the material.<sup>a</sup> In contrast to this, Kim et al. measured the  $N_2$  adsorption/desorption isotherms on MIL-

<sup>&</sup>lt;sup>a</sup> Possible reasons for this include: (1) the setpoints (e.g. gas dosage) were not optimal and (2) the temperature could not be maintained at -196  $^{\circ}$ C beyond 48 h.

53(Al)-NH<sub>2</sub> at -196 °C using a Micromeritics ASAP-2020 gas sorption analyser, which allows a more precise analysis of microporous materials [13]. For this reason, the results of the benzoic anhydride modified material are compared with literature data. Fitting the BET equation between relative pressures of 0.01 and 0.2 to the resulting N<sub>2</sub> isotherm gives an estimated surface area of 21 m<sup>2</sup> g<sup>-1</sup> for MIL-53(Al)-AM. This value is significantly lower than the 937 m<sup>2</sup> g<sup>-1</sup> reported for MIL-53(Al)-NH<sub>2</sub> [13]. Furthermore, the pore volume is reduced from 0.53 to 0.06 cm<sup>3</sup> g<sup>-1</sup> for MIL-53(Al)-AM. This result indicates that the PSM with benzoic anhydride is limited and suggests that the conversion of 20 % might be the maximal achievable modification. The isotherm shape of MIL-53(Al)-NH<sub>2</sub> can be characterised as type I before (based on the literature isotherm) [22] and as type II after the modification with benzoic anhydride. At higher partial pressures a hysteresis is observed in the N<sub>2</sub> isotherm of MIL-53(Al)-NH<sub>2</sub>, which is not present after the modification with the anhydride [9, 13]. These results are consistent with the almost complete pore filling after the PSM such that the pores are not accessible to N<sub>2</sub>.



**Figure 4.5:** (a) Comparison of the thermal decomposition of MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM with literature data [9]. (b)  $N_2$  isotherm on MIL-53(Al)-AM at -196 °C.

#### 4.2.3.2 Low pressure gas sorption measurements

 $CO_2$  adsorption/desorption pseudo-isotherms of MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM at different temperatures are presented in Figure 4.6. The low pressure  $CO_2$  sorption measurements were conducted following the procedure described in Chapter 2.5.1.

Increasing the  $CO_2$  pressure led to a rise in  $CO_2$  adsorption, whereas an increase in temperature resulted in a decrease in adsorption. The latter is consistent with the exothermic nature of the physisorption process, which causes a reduction in equilibrium

concentration of adsorbed species at higher temperatures. The  $CO_2$  adsorption in MIL-53(Al)-NH<sub>2</sub> was completely reversible, which suggests that  $CO_2$  was physisorbed rather than chemisorbed. As expected no phase transition from the *vnp* into the *lp* form was observed due to the  $CO_2$  partial pressure being well below 3 bar (see Chapter 4.2.1). After the PSM of MIL-53(Al)-NH<sub>2</sub> the  $CO_2$  adsorption remained reversible, hence no change in the  $CO_2$  adsorption mechanism.



**Figure 4.6:** CO<sub>2</sub> adsorption ( $\blacksquare$ )/desorption ( $\square$ ) isotherms on (a) MIL-53(Al)-NH<sub>2</sub> and (b) MIL-53(Al)-AM. CO<sub>2</sub> adsorption/desorption profile of (c) MIL-53(Al)-NH<sub>2</sub> and (d) MIL-53(Al)-AM.

The PSM of MIL-53(Al)-NH<sub>2</sub> resulted in a significant reduction in CO<sub>2</sub> adsorption capacity from 7.96 wt% to 1.40 wt% at 0.5 bar and 25 °C. The CO<sub>2</sub> adsorption capacity of MIL-53(Al)-NH<sub>2</sub> at 0.5 bar and 25 °C is higher than those reported for MOF-177 (2.36 wt%), IRMOF-3 (2.95 wt%) and ZIF-8 (2.76 wt%) [23]. MIL-53(Al)-NH<sub>2</sub> prepared

by Kim et al. (Chapter 4.2.1), with a reaction time of 5 days at 130 °C, exhibited an uptake of 8 wt% at 1 bar (25 °C). This suggests that the CO<sub>2</sub> capacity of MIL-53(Al)-NH<sub>2</sub> synthesised here (reaction time of 5 h at 150 °C) is potentially higher at 1 bar, than the reported 8 wt% [13]. The comparison with the PXRD of Kim et al. [13] suggests a better crystallinity for the MIL-53(Al)-NH<sub>2</sub> synthesised here, which may explain the higher CO<sub>2</sub> adsorption capacity.

The TGA profiles (Figure 4.6c and d) of both samples indicate good adsorption kinetics over the entire temperature and pressure range, consistent with the observed equilibrium adsorption. Due to the higher  $CO_2$  adsorption capacities at lower temperatures the cycling experiments were performed at 25 °C.

## 4.2.3.3 Material stability during cycling processes under dry and wet conditions

The CO<sub>2</sub> working capacity and regenerability of MIL-53(Al)-NH<sub>2</sub> before and after modification with benzoic anhydride were evaluated by monitoring pseudo-equilibrium adsorption uptakes over ten adsorption/desorption cycles under dry conditions and after the saturation with 1 vol% H<sub>2</sub>O vapour. The temperature and gas flow programs are shown in Chapter 2.5.3. To ensure the presence of MIL-53(Al)-NH<sub>2</sub>-*vnp*, the samples were activated under vacuum prior to the cycling experiments.

The working capacities from the dry multicycle stability test are shown in Figure 4.7 as a function of cycle number. Under dry conditions MIL-53(Al)-NH<sub>2</sub> shows good stability and regenerability, showing relative stable  $CO_2$  working capacities of 2.84 wt% to 3.03 wt%. The partial transformation of the amine groups of the organic linker molecules in MIL-53(Al)-NH<sub>2</sub> into amide groups, resulted in a severe decrease in working capacity (0.36 wt% to 0.45 wt%). This can be explained by the smaller pore volume available after the modification. Close examination of the TGA profiles showed that the equilibrium was achieved under the equilibration conditions (20 min) used in this work.

The TGA profiles of the wet cycling experiment (Figure 4.8) show that the introduction of amide groups into the structure of MIL-53(Al)-NH<sub>2</sub> results in a reduction of the H<sub>2</sub>O uptake from 7.87 wt% to 2.62 wt%. The TGA profile of MIL-53(Al)-AM (Figure 4.8d) exhibits an extra step during the H<sub>2</sub>O pre-treatment (t=0-200 min). Although the sample appears to have reached saturation after approximately 100 min, a second adsorption step can be seen after 120 min. This result suggests that a phase transformation might have





**Figure 4.7:**  $CO_2$  working capacity at 25 °C and TGA profiles of MIL-53(Al)-NH<sub>2</sub> and of MIL-53(Al)-AM under dry conditions.

After the saturation with 1 vol% H<sub>2</sub>O vapour, MIL-53(Al)-NH<sub>2</sub> nearly lost the ability to capture CO<sub>2</sub> with working capacities varying between 0.00 and 0.12 wt%. In cycles four, six and nine no uptake was observed, but this is potentially due to the resolution of the instrument. The severe decrease in CO<sub>2</sub> working capacity is a result of H<sub>2</sub>O molecules occupying adsorption sites that are available for CO<sub>2</sub> under dry conditions. The higher hydrophobicity of the modified organic linker molecule in MIL-53(Al)-AM led to more stable CO<sub>2</sub> working capacities uptake over the 10 cycles between 0.05 and 0.10 wt%. However, in comparison with the results obtained under dry cycling conditions, the CO<sub>2</sub> uptake was further decreased.



**Figure 4.8:** CO<sub>2</sub> working capacity at 25 °C and TGA profiles of MIL-53(Al)-NH<sub>2</sub> and of MIL-53(Al)-AM under wet conditions.

The material stability after the wet cycling process was confirmed by PXRD. A comparison of the diffractogram before and after wet cycling on MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM is shown in Figure 4.9. Due to the small amount of sample used in the cycling experiment, the PXRD were measured using the low silicon sample holder by mounting the samples with ethanol. This results in a decrease in the intensities of the peaks. Thus, the intensities of MIL-53(Al)-AM after the wet cycling experiments were multiplied by 50 for a better comparison. It can be seen that the diffraction patterns obtained after wet cycling are in good agreement with the initial diffractograms, indicating good hydrothermal stability of the framework.



**Figure 4.9:** PXRD pattern of (a) MIL-53(Al)-NH<sub>2</sub> and (b) MIL-53(Al)-AM before (black) and after (blue) the wet cycling experiments.

## 4.2.4 Conclusion

MIL-53(Al)-NH<sub>2</sub> is a potential adsorbent for post-combustion carbon capture, due to good stability and regenerability under dry cycling conditions. However, due to the presence of H<sub>2</sub>O in flue gas, a pre-treatment step would be required to remove the H<sub>2</sub>O prior to the capture process. Despite the MIL-53(Al)-NH<sub>2</sub> framework being in the *vnp* form during the sorption and cycling studies, much higher adsorption (7.96 wt% at 0.5 bar and 25 °C) and working capacities (~3 wt% at 25 °C) were obtained under dry conditions compared to those ( $\leq 1$  wt% at 25 °C) obtained for the MOFs containing CUS (MIL-100(Fe), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub> and STA-16(Co)) discussed in Chapter 3. The PSM with benzoic anhydride was successfully achieved and resulted in an improvement of the working capacities during the wet cycling experiment compared to those observed for MIL-53(Al)-NH<sub>2</sub>. However, decreases in CO<sub>2</sub> adsorption capacity and working capacity under dry cycling conditions were also observed due to the smaller pore volume in comparison with MIL-53(Al)-NH<sub>2</sub>.

#### 4.2.5 References

- Y. Lin, Q. Yan, C. Kong, and L. Chen, "Polyethyleneimine Incorporated Metal-Organic Frameworks Adsorbent for Highly Selective CO<sub>2</sub> Capture," *Sci. Rep.*, vol. 3, pp. 1-7, 2013.
- [2] K. S. Walton, A. R. Millward, D. Dubbeldam, H. Frost, J. J. Low, O. M. Yaghi, and R. Q. Snurr, "Understanding Inflections and Steps in Carbon Dioxide Adsorption Isotherms in Metal-Organic Frameworks," *Journal of the American Chemical Society*, vol. 130, pp. 406-407, 2007.

- [3] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, pp. 1791-1823, 2011.
- [4] J. Wang, J. Luo, J. Zhao, D.-S. Li, G. Li, Q. Huo, and Y. Liu, "Assembly of Two Flexible Metal–Organic Frameworks with Stepwise Gas Adsorption and Highly Selective CO2 Adsorption," *Crystal Growth & Design*, vol. 14, pp. 2375-2380, 2014/05/07 2014.
- [5] H.-S. Choi and M. P. Suh, "Highly Selective CO<sub>2</sub> Capture in Flexible 3D Coordination Polymer Networks," *Angewandte Chemie International Edition*, vol. 48, pp. 6865-6869, 2009.
- [6] R. Kotani, A. Kondo, and K. Maeda, "Gate adsorption of CO<sub>2</sub> on a flexible onedimensional copper-based coordination polymer crystal," *Chemical Communications*, vol. 48, pp. 11316-11318, 2012.
- [7] P. K. Thallapally, J. Tian, M. Radha Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, and J. L. Atwood, "Flexible (Breathing) Interpenetrated Metal-Organic Frameworks for CO<sub>2</sub> Separation Applications," *Journal of the American Chemical Society*, vol. 130, pp. 16842-16843, 2008.
- [8] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, and G. Férey, "A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration," *Chemistry – A European Journal*, vol. 10, pp. 1373-1382, 2004.
- [9] T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey, and N. Stock, "Synthesis and Modification of a Functionalized 3D Open-Framework Structure with MIL-53 Topology," *Inorganic Chemistry*, vol. 48, pp. 3057-3064, 2009.
- [10] S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. Serra-Crespo, J. Juan-Alcañiz, A. Martinez Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V. Baron, and J. F. M. Denayer, "Adsorption and Separation of Light Gases on an Amino-Functionalized Metal–Organic Framework: An Adsorption and In-Situ XRD Study," *ChemSusChem*, vol. 5, pp. 740-750, 2012.
- [11] T. Lescouet, E. Kockrick, G. Bergeret, M. Pera-Titus, and D. Farrusseng, "Engineering MIL-53(Al) flexibility by controlling amino tags," *Dalton Transactions*, vol. 40, pp. 11359-11361, 2011.
- [12] E. Stavitski, E. A. Pidko, S. Couck, T. Remy, E. J. M. Hensen, B. M. Weckhuysen, J. Denayer, J. Gascon, and F. Kapteijn, "Complexity behind CO<sub>2</sub> Capture on NH<sub>2</sub>-MIL-53(Al)," *Langmuir*, vol. 27, pp. 3970-3976, 2011.
- [13] J. Kim, W. Y. Kim, and W.-S. Ahn, "Amine-functionalized MIL-53(Al) for CO2/N2 separation: Effect of textural properties," *Fuel*, vol. 102, pp. 574-579, 2012.
- [14] C. Volkringer and S. M. Cohen, "Generating Reactive MILs: Isocyanate- and Isothiocyanate-Bearing MILs through Postsynthetic Modification," *Angewandte Chemie International Edition*, vol. 49, pp. 4644-4648, 2010.
- [15] M. G. Goesten, K. B. Sai Sankar Gupta, E. V. Ramos-Fernandez, H. Khajavi, J. Gascon, and F. Kapteijn, "Chloromethylation as a functionalisation pathway for metal-organic frameworks," *CrystEngComm*, vol. 14, pp. 4109-4111, 2012.
- [16] J. G. Nguyen and S. M. Cohen, "Moisture-Resistant and Superhydrophobic Metal-Organic Frameworks Obtained via Postsynthetic Modification," *Journal of the American Chemical Society*, vol. 132, pp. 4560-4561, 2010.

- [17] S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, and F. Kapteijn, "An Amine-Functionalized MIL-53 Metal-Organic Framework with Large Separation Power for CO<sub>2</sub> and CH<sub>4</sub>," *Journal of the American Chemical Society*, vol. 131, pp. 6326-6327, 2009.
- [18] M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, and K. P. Lillerud, "Synthesis and Stability of Tagged UiO-66 Zr-MOFs," *Chemistry of Materials*, vol. 22, pp. 6632-6640, 2010/12/28 2010.
- [19] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, "Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants," *Sci. Rep.*, vol. 3, pp. 1-6, 2013.
- [20] R. Łyszczek, "Synthesis, structure, thermal and luminescent behaviors of lanthanide—Pyridine-3,5-dicarboxylate frameworks series," *Thermochimica Acta*, vol. 509, pp. 120-127, 2010.
- [21] M. Kandiah, S. Usseglio, S. Svelle, U. Olsbye, K. P. Lillerud, and M. Tilset, "Postsynthetic modification of the metal-organic framework compound UiO-66," *Journal of Materials Chemistry*, vol. 20, pp. 9848-9851, 2010.
- [22] K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, and T. Siemieniewska, "Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity," *Pure & Appl. Chem.*, vol. 57, pp. 603-619, 1985.
- [23] A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, "Screening of Metal-Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach," *Journal of the American Chemical Society*, vol. 131, pp. 18198-18199, 2009.

## 5 Effect of flue gas contaminants

## 5.1 Chapter overview

In previous chapters, a series of MOFs were evaluated for the potential for carbon capture, based on their  $CO_2$  uptakes and their regenerability in dry and wet cycling experiments. However, in real flue gas impurities are present that might have an impact on the sorbent stability and the  $CO_2$  capacity.

This chapter contains two papers including supplementary information that investigate the effect of the flue gas contaminants NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability and CO<sub>2</sub> sorption ability. A series of screening and cycling tests were performed to determine the impact of these contaminants on the CO<sub>2</sub> uptakes. Furthermore, insights in the framework stability and the sorption mechanism were sought by PXRD and FTIR studies.

The first paper studies the effect of metal cations and amine groups on the stability and performance in the presence of the flue gas contaminants. The MOFs chosen for this paper include MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub>. The presence of Cr(III) centres and the absence of amine groups was found to provide better chemical stability. All frameworks were partially decomposed and the  $CO_2$  capacities were diminished in the presence of contaminants, due to their progressive accumulation.

For the second paper, MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) were selected in order to determine the effects of CUS, the flexibility and the nature of the ligands (carboxylate vs. phosphonate) on the sorption of NO, NO<sub>2</sub> and SO<sub>2</sub>. PXRD studies revealed a decrease in intensity, due to a loss in long-range crystallographic ordering or due the collapse of the MOF structures. The flexibility of MIL-53(Al)-NH<sub>2</sub> was found to be beneficial for the complete desorption of 5000 ppm NO<sub>2</sub> upon heating at 110 °C in flowing Ar. In contrast to this, the rigid MOFs containing CUS were found to chemisorb NO<sub>2</sub> resulting in an irreversible adsorption of the contaminant especially at higher contaminant concentrations. Deteriorated CO<sub>2</sub> capacities and crystallinities were observed in the presence of NO, NO<sub>2</sub> and SO<sub>2</sub>, which suggests that the removal of these contaminants prior to the capture process will be required.

# **Declaration for Thesis Chapter**

Effect of flue gas contaminants on the stability and the post-combustion  $CO_2$  capture in MIL-101 frameworks

Monash University

# **Declaration for Thesis Chapter 5.2**

#### **Declaration by candidate**

In the case of Chapter 5.2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed samples; identified major	80 %
issues; developed interpretations; fully drafted paper and conclusion	

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co- authors only
Gregory P. Knowles	Aided method development (TGA), input to results analysis and manuscript revision	N/A
Alan L. Chaffee	Supervision, assisted interpretation of results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work\*.

 
 Candidate's Signature
 Date 30/10/2014

 Main Supervisor's Signature
 Date 30/10/14

\*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

# 5.2 Effect of flue gas contaminants on the stability and the post-combustion CO<sub>2</sub> capture in MIL-101 frameworks

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author: Phone:+ Fax:+61 3 990-54597

## 5.2.1 Abstract

The effect of the flue gas contaminants NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability of MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> and their potential to facilitate CO<sub>2</sub> capture by adsorption were investigated. PXRD and FTIR studies of the samples after each had been individually exposed to 10000 ppm of contaminant, at both room and elevated temperatures (50 °C or 80 °C), were conducted in order to determine possible adsorption sites and the impact on the stability of the frameworks. By separately heating the MOFs from 20 to 110 °C under an Ar/contaminant (5000 ppm) mixture, the temperature range in which NO, NO<sub>2</sub> and SO<sub>2</sub> are adsorbed was determined to be 50 to 75 °C for NO and SO<sub>2</sub> and 80 °C for NO<sub>2</sub>. The effect of different concentrations (500 ppm (NO, NO<sub>2</sub>), 2000 ppm (SO<sub>2</sub>) and 5000 ppm (NO, NO<sub>2</sub>, SO<sub>2</sub>) was investigated by individually varying the partial pressure of the contaminants between 0 and 500 or 2000 or 5000 ppm at 25 °C in five cycle experiments. The impact of 500 ppm NO/NO<sub>2</sub> and 2000 ppm SO<sub>2</sub> on the CO<sub>2</sub> capture ability was evaluated by conducting five cycle experiments under an  $Ar/CO_2$  contaminant atmosphere, then comparing the results to the CO<sub>2</sub> working capacities obtained by varying the CO<sub>2</sub> partial pressure between 0.05 to 0.15 bar. The loss in longrange crystallographic ordering or the partial/complete collapse of the frameworks as well as the diminished CO<sub>2</sub> capacities due to the accumulation of the contaminants makes the removal of NO, NO<sub>2</sub> and CO<sub>2</sub> a necessity if these sorbents are considered for postcombustion capture.

#### 5.2.2 Introduction

Anthropogenic greenhouse gas emissions have been reported to be the main contributor to global warming and climate change [1-3]. Of these,  $CO_2$  which is produced by the combustion of coal (43 %), oil (36 %) and natural gas (20 %) comprises the vast majority

[4]. Strategies to reduce anthropogenic greenhouse gas emissions, and in particular  $CO_2$  emissions, are thus being considered, especially given that power generation via fossil fuel combustion is only projected to increase in the near future [5]. One possible strategy is carbon capture and storage (CCS) using metal organic frameworks (MOFs), which are nanoporous materials consisting of metal ions or clusters coordinated by organic bridging ligands [6, 7]. MOFs have attracted tremendous attention during the past decade and are attractive for the capture of  $CO_2$  due to their tuneable pore sizes and topologies [8-13]. MOFs containing coordinatively unsaturated sites (CUS) are of particular interest for carbon capture as these Lewis acid sites can selectively adsorb  $CO_2$  from  $CO_2/N_2$  and  $CO_2/CH_4$  mixtures [14-18].

One of the most extensively studied MOFs containing CUS is HKUST-1  $[Cu_3(C_6H_3(CO_2)_3)_2(H_2O)_3]$  [19]. The paddle-wheel moiety of HKUST-1 is built up by dimeric copper octahedra, each of which are coordinated to four carboxylate functionalities, one from each of four ligated 1,3,5-benzenetricarboxylate moieties, leaving one CUS on each copper atom [20]. The framework preferentially adsorbs CO<sub>2</sub> into the smaller of the two interconnected cages [21] and exhibits a CO<sub>2</sub> adsorption capacity of 55.89 wt% at 25 °C and 15 bar [22]. In a pressure swing adsorption process (PSA), the working capacity in the hydrated form of HKUST-1 was determined to be 35.65 wt%, which is almost four times higher than in zeolite 13X (9.68 wt%) [22].

While numerous studies have focused on the sorption of  $CO_2$  and  $N_2$  in MOFs [17, 23-27], little is known about the effect of flue gas contaminants on their structures and their  $CO_2$ capacities. The flue gas contaminants  $SO_x$  and  $NO_x$  are of special interest, when evaluating adsorbents for post-combustion  $CO_2$  capture. Flue gas from Australian brown coal power plants, which do not utilise independent removal processes for  $SO_x$  and  $NO_x$ , contains approximately 1800 ppm  $SO_x$  and 500 ppm  $NO_x$  [28]. These contaminant concentrations are higher than those in flue gas from power stations in the USA and in most power stations in Europe, because in USA and Europe the concentrations of these contaminants is lowered by desulphurisation (FGD) and  $NO_x$  removal. The emission of these contaminants is responsible for the formation of acid rain and it is therefore necessary to capture these during the post-combustion process [29]. Reduced adsorbent lifetime and increased capture costs are a result of the irreversible adsorption of the flue gas contaminants in most sorbents such as zeolite NaX [30], APTS-SBA-15 (APTS:  $\gamma$ -(aminopropyl)- triethoxysilane) [31], MCM-41-PEI-50 ("molecular basket") [32] and calcium oxide [33, 34].

Recent computational studies on the effect of flue gas impurities include GCMC simulations and molecular modelling on MOFs containing CUS [21, 35]. Ding et al. performed GCMC simulations on HKUST-1 and MOF-74, which indicated no change in CO<sub>2</sub> capacity with increasing NO and NO<sub>2</sub> concentrations, while a decrease was observed with increasing SO<sub>2</sub> concentration due to the higher selectivity towards SO<sub>2</sub> than CO<sub>2</sub> [21]. MOF-74 is characterised by a honeycomb structure with one-dimensional channels [36], in which SO<sub>2</sub> is occupying preferential adsorption sites of CO<sub>2</sub> and therefore reducing the CO<sub>2</sub> capacity significantly [21]. In contrast to this, SO<sub>2</sub> is adsorbed into the smaller cages of HKUST-1, while CO<sub>2</sub> that is not adsorbed in the small cage can be adsorbed on the CUS in the larger cage [21]. The presence of CUS has been shown to be beneficial for the storage of NO in HKUST-1. From the 9 wt% of NO adsorbed at 25 °C and 1 bar only 2.4 wt% were desorbed by lowering the pressure to almost 0 bar [37].



**Figure 5.1:** Crystal structure of MIL-101(Cr). Hybrid supertetrahedra (left) and one unit cell of MIL-101(Cr) presenting both cages (right). Ball and stick view (Cr octahedra: green, C: grey and O: red, H: omitted) [38].

The MOFs MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> similarly provide CUS and so are also of interest for CO<sub>2</sub> capture. Furthermore, MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> also incorporate amine groups which are well known to facilitate CO<sub>2</sub> sorption [39-41]. The framework structure of MIL-101 (Figure 5.1) is built from trimers of metal(III) oxide octahedra which are arranged to form a supertetrahedral building block [42]. Within this supertetrahedral unit, each corner is occupied by the trimeric unit

connected to each other by terephthalic acid or 2-aminoterephthalic acid ligands, which are located on each face [43]. The hybrid supertetrahedra further assembles into a zeotypic mesoporous MOF reminiscent of the MTN topology (related to zeolite ZSM-39) [42, 44]. The corresponding three-dimensional framework exhibits two types of cavity. The medium cavity is delimited by 12 pentagonal rings defining a dodecahedral cage, while the large cavity is delimited by 12 pentagonal rings and 4 hexagonal rings leading to a hexakaidodecahedron [42, 43, 45]. These two cages are assessable through microporous windows of 1.2 and 1.6 nm.[42, 44] The BET surface areas decrease in the order MIL-101(Cr) (2944 [46]/4230 m<sup>2</sup> g<sup>-1</sup> [47])> MIL-101(Al)-NH<sub>2</sub> (2649 m<sup>2</sup> g<sup>-1</sup>) [41] > MIL-101(Cr)-NH<sub>2</sub> (2269 m<sup>2</sup>g<sup>-1</sup>) [48]. Depending on the synthetic conditions, the total pore volumes vary from 2.15 [47] and 2.57 cm<sup>3</sup> g<sup>-1</sup> [46] for MIL-101(Cr), from 1.80 [48] to 2.26 cm<sup>3</sup> g<sup>-1</sup> [49] for MIL-101(Cr)-NH<sub>2</sub> and from 0.75 [44] to 1.58 cm<sup>3</sup> g<sup>-1</sup> [41] for MIL-101(Al)-NH<sub>2</sub>.

CO<sub>2</sub> adsorption has been investigated in MIL-101(Cr), which contains coordinatively unsaturated  $Cr^{3+}$  sites resulting in high CO<sub>2</sub> adsorption capacities (73.94 wt%, 25 °C, 15 bar) and a CO<sub>2</sub>/N<sub>2</sub> selectivity of approximately 9 [23]. Experimental studies on MIL-101(Cr) by Liu et al. showed a gradual decrease in CO<sub>2</sub> capacity with increasing the NO concentration from 0 to 2000 ppm, which can be explained with the strong interaction of the NO with the coordinatively unsaturated sites (CUS). The adsorption of SO<sub>2</sub> was found to have a small impact on the  $CO_2$  adsorption due to the lack of ligation to the CUS [50]. The potential of MIL-101(Cr)-NH<sub>2</sub> for post-combustion carbon capture was investigated by Khutia and co-worker. The high CO<sub>2</sub>/N<sub>2</sub> selectivity of 100/1 at 25 °C and high adsorption capacities of 6.4 wt% at 25 °C and 0.2 bar make the material a suitable candidate for capture applications [51]. Serra-Crespo et al. suggested that MIL-101(Al)-NH<sub>2</sub> could be a potential candidate for natural gas and biogas upgrading due to a high CO<sub>2</sub>/CH<sub>4</sub> selectivity between 3 to 5 and an acceptable CO<sub>2</sub> adsorption capacity of 61.61 wt% at 25 °C and 30 bar [44]. While these studies focus on the selective adsorption of CO<sub>2</sub>, the impact of flue gas contaminants on the CO<sub>2</sub> capacities and framework stabilities have not been investigated.

In this study, the MOFs MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> were synthesised as previously discussed [46, 48] and the effect of NO, NO<sub>2</sub> and SO<sub>2</sub> on the framework stability and CO<sub>2</sub> capture ability was investigated. The adsorption of concentrated flue gas contaminants (10000 ppm) at different temperatures and the

following powder X-ray diffraction (PXRD) and Fourier transform infra-red spectrometry (FTIR) measurements allowed the evaluation of the framework stabilities and possible adsorption mechanisms. The range of temperatures over which these flue gas contaminants were adsorbed, was determined by heating the samples in the presence of contaminant (5000 ppm) from 20 to 110 °C. Five cycles of adsorption and desorption using 5000 ppm and the concentrations relevant to flue gas (NO, NO<sub>2</sub>: 500 ppm and SO<sub>2</sub>: 2000 ppm) were conducted at 25 °C to study the effect of different concentrations. The impact of these contaminants on the CO<sub>2</sub> adsorption/desorption was investigated by the comparison of CO<sub>2</sub> and CO<sub>2</sub>/contaminant cycling data, in which the CO<sub>2</sub> partial pressure was varied between 0.05 and 0.15 bar and the contaminant between 0 and 500 ppm for NO and NO<sub>2</sub> and between 0 and 2000 ppm for SO<sub>2</sub>.

#### 5.2.3 Experimental section

#### 5.2.3.1 Synthesis of MOFs

## 5.2.3.1.1 Chemicals

AlCl<sub>3</sub>·6H<sub>2</sub>O (99 %, Sigma Aldrich), 2-aminoterephthalic acid (99 %, Sigma Aldrich), Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99 %, Sigma Aldrich), DMF (GR grade, Merck), ethanol ( $\geq$  99.7 %, Merck), terephthalic acid (98%, Sigma Aldrich), argon (high purity, Air Liquide), carbon dioxide (Food grade, Coregas), 1 % nitric oxide in argon (Air Liquide), 1% nitrogen dioxide in argon (Air Liquide) and 1 % sulphur dioxide in argon (Air Liquide).

All reagents were used without further purification.

## 5.2.3.1.2 Synthesis of MIL-101(Cr)

Bulk MIL-101(Cr) was synthesized by a procedure akin to that reported by Jiang et al. [46].

9.6 mL H<sub>2</sub>O was added to 0.80 g (2.00 mmol)  $Cr(NO_3)_3$ ·9H<sub>2</sub>O and 0.33 g (1.99 mmol) terephthalic acid. After stirring for 10 min at room temperature, the suspension was heated in a Teflon® lined autoclave at 220 °C for 8 h. The autoclave was allowed to cool, before the recrystallized terephthalic acid was removed by filtration. The mixture was then centrifuged at 6000 rpm for 5 min. The green powder was isolated and washed three times with ethanol. The product was treated with hot ethanol at 80 °C for 4 h followed by treatment with hot 30mM NH<sub>4</sub>F at 60 °C for 5 h. MIL-101(Cr) was washed with hot H<sub>2</sub>O in order to remove residual NH<sub>4</sub>F.

# 5.2.3.1.3 Synthesis of MIL-101(Cr)-NH<sub>2</sub>

MIL-101(Cr)-NH<sub>2</sub> was synthesised by the method described elsewhere [48], which was adapted from that reported by Jiang et al. [49] The solvothermal synthesis was conducted in a Teflon lined autoclave at 130 °C for 24 h.

# 5.2.3.1.4 Synthesis of MIL-101(Al)-NH<sub>2</sub>

The synthesis of MIL-101(Al)-NH<sub>2</sub> was reported previously [41] and is in accord with the method reported by Hartmann et al. [45] In a typical synthesis, a solution of 2-aminoterephthalic acid in DMF was heated to 110 °C and AlCl<sub>3</sub>·6H<sub>2</sub>O was added in seven equal portions. After the last addition the mixture was stirred for 3 h, before the stirrer was switched off and the temperature was kept at 110 °C for another 16 h. MIL-101(Al)-NH<sub>2</sub> was purified via Soxhlet extraction in ethanol.

# 5.2.3.2 Characterisation of the MOFs

The validation of the framework structures, MIL-101(Cr)-NH<sub>2</sub> [48] and MIL-101(Al)-NH<sub>2</sub> [41], via elemental analysis, helium density, N<sub>2</sub> adsorption and desorption measurements at -196 °C, FTIR, PXRD and TGA were reported previously. The formation of MIL-101(Cr) was confirmed by PXRD, augmented by N<sub>2</sub> adsorption and desorption measurements at -196 °C, which are presented in the supplementary material.

# 5.2.3.3 Exposure to concentrated flue gas contaminants

# 5.2.3.3.1 Flue gas contaminant screening test

A Setaram TAG 24-16 simultaneous symmetrical thermoanalyser was used to measure the change in mass (TGA) of the samples as they were subjected to impurities over a heat ramp.

Samples were first activated in-situ by heating them in Ar to 110 °C, then maintaining them at 110 °C for 1 h, before they were then cooled to 20 °C. The thermoanalyser was then allowed to equilibrate, still in flowing Ar, for approximately 30 min before the Ar/impurity mixtures were switched on. A heating rate of 2 °C min<sup>-1</sup> was then applied to slowly heat the samples to 110 °C in the presence of dilute (5000 ppm) NO, NO<sub>2</sub> or SO<sub>2</sub> in Ar mixtures. After 30 min at 110°C, the Ar/impurity mixture was replaced by pure Ar. The temperature program is shown in Figure 5.2.



Figure 5.2: Thermo-gravimetric analysis process conditions for the flue gas contaminant screening tests.

#### 5.2.3.3.2 PXRD and FTIR studies after the exposure to 10000 ppm of contaminant

A VacPrep 061 degasser from Micromeritics was used to expose the samples to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub>. The gases used in the following experiment were purged through a gas delivery tube over the samples in a partially sealed vial. Prior to the adsorption process, all samples were degassed at 110 °C under vacuum and the initial sample mass was recorded. Approximately 100 to 200 mg of sample was heated under flowing Ar to 110 °C in order to remove any residual moisture. After holding the temperature for 1 h, the samples were cooled down to room temperature, before the Ar was replaced by the Ar/impurity mixture (1 % impurity in Ar). The flow rate was set to 25 mL min<sup>-1</sup> for the first 20 min, after which it was reduced to 5 mL min<sup>-1</sup>. The samples were treated with the impurity for 1 h, before the vial was capped and the sample mass was recorded. A small part of each sample was transferred into a separate vial for further characterisation by FTIR and PXRD. In a second set of experiments, the remaining sample was heated at 50 °C (NO, SO<sub>2</sub>) or 80 °C (NO<sub>2</sub>) in the presence of the Ar/impurity mixture.

Powder X-ray diffraction was measured via a Bruker D8 Focus powder diffractometer using  $CuK_{\alpha}$  radiation ( $\lambda$ =1.5418 Å). PXRD experiments were carried out on the samples at ambient laboratory conditions before and after the sorption of the impurities. The 2 $\theta$  range was set to 1 to 30° with a scan speed of 0.5 ° min<sup>-1</sup>.

Fourier transform infra-red (FTIR) spectrometry was conducted via an Agilent Cary 630 Diamond ATR in the spectral range of 4000 to 700 cm<sup>-1</sup> at ambient laboratory conditions.

## 5.2.3.4 Sorption of flue gas contaminants

A Setaram TAG 24-16 simultaneous symmetrical thermoanalyser was used to measure the change in mass (TGA) of the samples as they were subjected (a) to impurities by varying the partial pressures between 0 and 5000/2000/500 ppm in five cycle experiments (Section 5.2.3.4.1) and (b) to impurities and CO<sub>2</sub> by varying the partial pressure between 0 and 500/2000 ppm (impurities) and between 0.05 and 0.15 bar (CO<sub>2</sub>) during five cycle experiments (Section 5.2.3.4.2). Additionally, the samples were exposed to CO<sub>2</sub> by varying the partial pressure between 0.05 and 0.15 bar during ten cycle experiments (Section 5.2.3.4.2). Additionally, the samples were exposed to CO<sub>2</sub> by varying the partial pressure between 0.05 and 0.15 bar during ten cycle experiments (Section 5.2.3.4.2). A total flow rate of 70 mL min<sup>-1</sup> (e.g. 35 mL min<sup>-1</sup> sample gas and 35 mL min<sup>-1</sup> on the reference side of the balance) was applied to all experiments. Detailed descriptions of the gas and temperature programs are given as follows.

## 5.2.3.4.1 Flue gas contaminant cycling experiments

The temperature and gas program for the flue gas contaminant cycling is shown in Figure 5.3a. 10-20 mg of each MOF was first activated under Ar at 110 °C for 1 h, before they were cooled to 25 °C. The thermoanalyser was then allowed to equilibrate for approximately 40 min after which five cycles of adsorption/desorption were carried out by varying the concentration of the impurities between 0 and 500 ppm and between 0 and 5000 ppm for NO and NO<sub>2</sub>. Due to the higher concentration of SO<sub>2</sub> in flue gas, the concentration was varied between 0 and 2000 ppm and between 0 and 5000 ppm. The equilibration time for each adsorption and desorption step was set to 20 min. After the last cycle, the temperature was maintained for 40 min under Ar, before the samples were heated to 110 °C in Ar atmosphere in order to desorb the impurities.

## 5.2.3.4.2 Flue gas contaminant cycling in the presence of $CO_2$

The temperature and gas program for the cycling experiments in the presence of the impurities is presented in Figure 5.3b. The samples were activated akin to the procedure described for the flue gas contaminant cycling experiment. Five cycles of adsorption/desorption were carried out by varying the  $CO_2$  partial pressure between 0.05 and 0.15 bar and by varying the impurity concentration from 0 to 500 ppm for NO and NO<sub>2</sub> or from 0 to 2000 ppm for SO<sub>2</sub>, allowing 20 min equilibration time for each adsorption and desorption step. The temperature of 25 °C was maintained for 40 min in Ar atmosphere, after which the samples were heated to 110 °C.

 $CO_2$  cycling experiments were performed in a similar manner as described above. After activating and cooling the samples in Ar, five cycles of adsorption and desorption were carried out by varying the partial pressure of  $CO_2$  between 0.05 and 0.15 bar.



**Figure 5.3:** Thermo-gravimetric analysis process conditions used for the (a) Flue gas contaminant cycling experiments, and the (b) Flue gas contaminant cycling in the presence of  $CO_2$  experiments.

## 5.2.4 Results and discussion

#### 5.2.4.1 Exposure to concentrated flue gas contaminants

Thermogravimetric analysis of MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> was first conducted to determine the range of temperatures in which a mass change occurred upon exposure to 5000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub> individually. In separate experiments, each MOF was treated with 10000 ppm of NO, NO<sub>2</sub> or SO<sub>2</sub> at different temperatures (room temperature and 50 or 80 °C) in order to obtain a better understanding of the adsorption mechanism and the effect of flue gas contaminants on the framework stability. The changes in structure were then recorded by FTIR and PXRD. The concentration of 10000 ppm was expected to give rise to stronger bands in the FTIR spectra and also more significant changes in the diffractograms compared to typical concentrations of NO, NO<sub>2</sub> (500 ppm) and SO<sub>2</sub> (1800 ppm). The results of the PXRD and FTIR studies are discussed in the next two sections.

#### 5.2.4.1.1 Flue gas contaminant screening tests

Figure 5.4 shows the mass variations observed as each of the samples were separately heated with a heating rate of 2  $^{\circ}$ C min<sup>-1</sup> from 20 to 110  $^{\circ}$ C under an Ar/contaminant

atmosphere and then held at 110 °C for 80 min. After 30 min at 110 °C, the Ar/contaminant mixture was replaced by pure Ar.

The results of the screening tests using NO (Figure 5.4a) show that each sorbent initially gained mass and then subsequently lost all of the mass gain along the heat ramp.<sup>a</sup> This is consistent with the adsorption of NO and its subsequent desorption from each of the MOFs. The mass uptake maxima decreased in the order MIL-101(Cr) (0.18 mol NO per mol CUS) > MIL-101(Cr)-NH<sub>2</sub> (0.15 mol NO per mol CUS) > MIL-101(Al)-NH<sub>2</sub> (0.11 mol NO per mol CUS) occurring at 55, 75 and 50 °C, respectively. The difference in temperature required for maximum mass uptake was presumably due to slight differences in adsorption energy between the MOFs examined. The temperature for the exposure to 10000 ppm NO (Section 5.2.4.1.2 and Section 5.2.4.1.3) was therefore selected to be 50 °C, as at this temperature, each sorbent exhibited a near maximum weight gain. The near-quantitative desorption of the NO for each MOF, just a little further along the heat ramp suggests that the adsorption/desorption can be classified as a physisorption rather than a chemisorption process.

The results of the screening tests using NO<sub>2</sub> (Figure 5.4b) show that each sorbent initially gained mass up to 80 °C, which correspond to 0.31, 0.21 and 0.17 mol NO<sub>2</sub> per mol CUS for MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub>, respectively. For this reason the subsequent exposure to 10000 ppm of NO<sub>2</sub>, discussed in the next section, was conducted at 80 °C. This gain in mass is consistent with the adsorption of NO<sub>2</sub>. Beyond 80 °C MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> exhibited mass loss further along the heat ramp consistent with the partial desorption of NO<sub>2</sub>; however, MIL-101(Cr) did not. These results suggest that in each case some of the NO<sub>2</sub> becomes chemisorbed into the structure. At temperatures above 80 °C, MIL-101(Cr) exhibited constant mass over the remainder of the heat ramp as well as for the subsequent isothermal portion of the experiment, suggesting that 0.86 mmol g<sup>-1</sup> is the amount of NO<sub>2</sub> that can be chemisorbed within this framework. The results of the screening tests with NO<sub>2</sub> imply that the interaction with MIL-101(Cr) was stronger than for the amine modified frameworks, due to the lack of any desorption.

<sup>&</sup>lt;sup>a</sup> The small net mass loss for MIL-101(Al)-NH<sub>2</sub> is potentially due to the collapse of the framework as will be discussed in Section 5.2.4.1.3. The inopportune TG noise in the TGA profile of the NO screening at 117 °C (t>52 min) suggests that the blank measurement should be repeated. The apparent mass gain of MIL-101(Cr) at 117 °C (t>52 min) could potentially be due to electronic noise or due to the occurrence of a second adsorption step.



**Figure 5.4:**TGA of exposure of MIL-101(Cr) (red), MIL-101(Cr)-NH<sub>2</sub> (green) and MIL-101(Al)-NH<sub>2</sub> (blue) to atmospheres comprising 5000 ppm of (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub> over a heat ramp from 20 to 110 °C with a heating rate of 2 °C min<sup>-1</sup>.

The results of the screening tests using SO<sub>2</sub> (Figure 5.4c) show that each sorbent initially gained mass consistent with the adsorption of SO<sub>2</sub>. The maximum in mass gain (0.21 mol SO<sub>2</sub> per mol CUS) was observed at 50 °C in MIL-101(Cr), which was followed by the complete loss of all mass gained over the remainder of the heat ramp and constant mass after the isothermal period was reached. MIL-101(Al)-NH<sub>2</sub> behaved similarly and exhibited a maximum mass gain of 0.08 mol SO<sub>2</sub> per mol CUS.<sup>a</sup> The complete desorption of SO<sub>2</sub> in MIL-101(Cr) and MIL-101(Al)-NH<sub>2</sub> suggests that adsorption proceeded via a physisorption rather than a chemisorption process, as observed for NO. However, the SO<sub>2</sub> screening test on MIL-101(Cr)-NH<sub>2</sub> showed an initial gain of 0.21 mmol g<sup>-1</sup> (0.08 mol SO<sub>2</sub> per mol CUS) up to 50 °C, followed by a mass loss of 0.06 mmol g<sup>-1</sup> up to 90 °C and then

a further mass uptake that extended beyond the heat ramp throughout the duration of the isothermal period under the Ar/SO<sub>2</sub> atmosphere. After the change to pure Ar (t = 65 to 125 min, not shown here) a slow mass loss of approximately 0.08 mmol g<sup>-1</sup> was observed during the remaining duration of the isothermal period. This result indicates a possible change in adsorption mechanism from physisorption (T  $\leq$  50 °C) to chemisorption (T  $\geq$  90 °C) of SO<sub>2</sub> in MIL-101(Cr)-NH<sub>2</sub>.

It can therefore be concluded that the adsorption mechanism is strongly dependent on the contaminant and, in the case of  $SO_2$  adsorption in MIL-101(Cr)-NH<sub>2</sub>, also on the temperature. In most cases, NO and  $SO_2$  were physisorbed into all sorbents, while NO<sub>2</sub> was chemisorbed. Furthermore, the gain in mass was dependent on the pore volumes of the MOFs with the highest mass change being observed in MIL-101(Cr) after the screening tests with NO, NO<sub>2</sub> and SO<sub>2</sub>.

#### 5.2.4.1.2 FTIR studies

The IR spectra obtained for the frameworks before and after separate exposure to 10000 ppm NO, NO<sub>2</sub> and SO<sub>2</sub> at both ambient and elevated temperatures are shown in Figure 5.5 in the range of 1700 to 700 cm<sup>-1</sup>. The FTIR spectra after each screening test are presented in the supplementary information.

Characteristic absorption bands for MIL-101(Cr) (Figure 5.5a) include: (1) the C=O stretch [52] at 1631 cm<sup>-1</sup>, (2) the aromatic C=C stretch [50] 1510 cm<sup>-1</sup>, (3) the O-C-O stretch [50] at 1398 cm<sup>-1</sup> and (4) the C-H deformation stretch [50] at 1167, 1017, 884 and 742 cm<sup>-1</sup>. The exposure to NO and SO<sub>2</sub> had no obvious impact on these absorption modes at both room temperature and 50 °C. Furthermore, the absence of any additional bands indicates the physisorption of these contaminants rather than chemisorption, which is consistent with the results obtained of the screening tests. The exposure to NO<sub>2</sub> induced a loss of the mode of IR absorbance at 1631 cm<sup>-1</sup> (especially at 80 °C), which corresponds to the C=O stretch. This result suggests that NO<sub>2</sub> is interacting with the framework structure. This was further confirmed by the appearance of two new bands at 1571 and 1217 cm<sup>-1</sup>, which were more pronounced after exposure to NO<sub>2</sub> at 80 °C and are characteristic for chelating bidentate nitrate species [53]. Additionally, two new bands developed at 988 and 792 cm<sup>-1</sup>, which can be assigned to symmetric stretching [54] and bending [55] of NO<sub>2</sub> molecules. Thus, the FTIR results are in good agreement with suggestions from the screening tests that NO<sub>2</sub> is chemisorbed onto MIL-101(Cr).



**Figure 5.5:** FTIR spectra of (a) MIL-101(Cr), (b) MIL-101(Cr)-NH<sub>2</sub> and (c) MIL-101(Al)-NH<sub>2</sub> before and after treatment with 10000 ppm of contaminant at room (RT) and more elevated temperature. (d) Comparison of FTIR spectra before and after NO<sub>2</sub> treatment on MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> with BDC-NH<sub>2</sub>.

Figure 5.5b shows the IR spectra of MIL-101(Cr)-NH<sub>2</sub> before and after exposure to each contaminant. The characteristic absorption bands in MIL-101(Cr)-NH<sub>2</sub> are: (1) the asymmetrical and symmetrical stretch of NH<sub>2</sub> at 3495 and 3376 cm<sup>-1</sup> (2) the N-H bend [56] at 1617 cm<sup>-1</sup>, (3) the symmetric C=O stretch [52] at 1587 cm<sup>-1</sup>, (4) the aromatic C=C stretch [50] 1502 cm<sup>-1</sup>, (5) the O-C-O stretch [50] at 1387 cm<sup>-1</sup> and (6) the C-N stretch [56] at 1338 cm<sup>-1</sup> and (7) the C-H deformation stretching vibrations [50] at 1163, 1025, 883 and 764 cm<sup>-1</sup>. The exposure to NO induced a change in absorbance modes at 1587 cm<sup>-1</sup> and 1387 cm<sup>-1</sup>, which were more pronounced after treatment at 50 °C. However, no additional bands were observed, which is consistent with physisorption rather than chemisorption of

NO onto the CUS at both room temperature and 50 °C and is also consistent with the results of the screening experiments. The exposure to NO<sub>2</sub> resulted in changes in the IR absorbance modes at 1587 cm<sup>-1</sup>and 1338 cm<sup>-1</sup>. The change in the IR absorption corresponding to the C=O stretch was more pronounced than after exposure to NO, which is consistent with the higher mass uptake of NO<sub>2</sub> (0.55 mmol g<sup>-1</sup> at 80 °C) compared to NO (0.41 mmol g<sup>-1</sup> at 75 °C). Additionally two new bands appeared at 1571 and 1217 cm<sup>-1</sup> which indicate the formation of chelating bidentate nitrate species [53] and therefore the chemisorption of NO<sub>2</sub> onto the CUS. In the case of SO<sub>2</sub>, a change in the absorption mode at 1587 cm<sup>-1</sup> was observed, which was less pronounced than for NO and NO<sub>2</sub>. This is consistent with the lower mass uptake observed during the screening experiments and indicates the physisorption of SO<sub>2</sub>. No new peaks suggestive of chemisorption were observed after the exposure to SO<sub>2</sub> at room temperature or at 50 °C. However, since the results in the screening tests suggest some retention of SO<sub>2</sub> at 117 °C, the exposure experiment should be conducted again at higher temperature to verify if chemisorption takes place.

The IR spectrum of MIL-101(Al)-NH<sub>2</sub> (Figure 5.5c) exhibited the following characteristic bands: (1) the asymmetrical and symmetrical stretch of  $NH_2$  [45] at 3450 and 3354 cm<sup>-1</sup> (2) the N-H bend [56] at 1621 cm<sup>-1</sup> (3) the symmetric C=O stretch [52] at 1576 cm<sup>-1</sup>, (4) the O-C-O stretch [50] at 1387 cm<sup>-1</sup> and (5) the C-N stretch [56] at 1337 cm<sup>-1</sup>. The changes in FTIR absorption observed for MIL-101(Al)-NH<sub>2</sub> following exposure to NO and NO<sub>2</sub> (especially at 50 or 80 °C) exhibited different behaviour from MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub>. There was an apparent reduction in the intensity of the absorption centred at 1576 cm<sup>-1</sup> accompanied by broadening of the band. These results suggest that a change in structure is taking places, which is more pronounced in the presence of  $NO_2$  and is consistent with the higher mass change during the screening tests. A change in absorption mode at 1253 cm<sup>-1</sup> as well as the appearance of two new bands at 1547 and 1213 cm<sup>-1</sup>, observed upon exposure to  $NO_2$ , can, again, be assigned to the chemisorption of  $NO_2$  as a chelating bidentate nitrate species [53]. The comparison of both spectra, after NO<sub>2</sub> exposure, with the FTIR spectrum of 2-aminoterephthalic acid (Figure 5.5d) revealed similar features and therefore the decomposition of the framework structure, especially at 80 °C). This would also explain the colour change from yellow to ochre, which was not observed upon separate exposure to NO and SO<sub>2</sub>. The exposure to 10000 ppm of SO<sub>2</sub> did not result in any obvious changes in the IR spectra at both room temperature and 50 °C.

This was also observed for MIL-101(Cr) and is consistent with the physisorption of this contaminant at these temperatures.

In contrast to the results discussed above, no obvious changes were observed in the FTIR spectra after the individual screening tests (supplementary information). The smaller contaminant concentration of 5000 ppm used during the screening tests as well as the complete or partial desorption of each contaminant (obtained during Ar/contaminant flow and/or during the final Ar purge at 117 °C) could account for the lack of changes in the absorption modes. The remainder of NO<sub>2</sub> (in all frameworks) and SO<sub>2</sub> (in MIL-101(Cr)-NH<sub>2</sub>) might be too small to be detected.

#### 5.2.4.1.3 PXRD studies

Intensity data obtained for each of the MOFs after the exposure to the contaminants were multiplied by 5 to facilitate comparison with the more intense data obtained for the fresh materials. As discussed above, a colour change was only obtained after subjecting MIL-101(Al)-NH<sub>2</sub> to NO<sub>2</sub>. In all other cases, the colour remained unchanged. PXRD data for the samples after each individual screening test are shown in the supplementary information.

The powder X-ray diffractograms of MIL-101(Cr) before and after separate exposure to the contaminants are shown in Figure 5.6a. A decrease in intensities was observed after the adsorption of all contaminants. These results suggest that either a loss in long-range crystallographic ordering or a progressive loss of the framework structure has occurred. This was also observed in the powder X-ray diffractograms of MIL-101(Cr) after the subsequent screening tests with 5000 ppm NO, NO<sub>2</sub> or SO<sub>2</sub> (supplementary information). Furthermore, subjecting the framework to NO and NO<sub>2</sub> at more elevated temperatures increased the loss in crystallinity. In the case of NO<sub>2</sub> this could be associated with chemisorption onto the CUS. In contrast to this, the intensities after the adsorption of SO<sub>2</sub> at room temperature remained almost unchanged upon heating the sample to 50 °C.

Figure 5.6b presents a comparison of the powder X-ray diffractograms of MIL-101(Cr)- $NH_2$  before and after exposure to concentrated contaminants. The diffraction pattern observed for the fresh MOF is similar, but has broader diffraction peaks than MIL-101(Cr), akin to those previously reported by Khutia et al. [51]. The broader peaks are attributed to the presence of the amine groups limiting the extent of order that is observed

for MIL-101(Cr). The subsequent exposure of MIL-101(Cr)-NH<sub>2</sub> to 10000 ppm NO, NO<sub>2</sub> or SO<sub>2</sub> resulted in a decrease in intensities, which is consistent with a loss in long-range crystallographic ordering or a progressive loss of the framework structure. This decrease was found to occur irrespective of the adsorption temperature of the contaminants. In a separate set of NO, NO<sub>2</sub> and SO<sub>2</sub> screening experiments, the decrease was more pronounced, which suggests that further loss in long-range crystallographic ordering or the collapse of the framework occur upon desorption of the contaminants.



**Figure 5.6:** PXRD of (a) MIL-101(Cr), (b) MIL-101(Cr)-NH<sub>2</sub> and (c) MIL-101(Al)-NH<sub>2</sub> before and after the treatment with 10000 ppm at room (RT) and more elevated temperature.

The powder X-ray diffractograms of MIL-101(Al)- $NH_2$  and the exposed samples are shown in Figure 5.6c. A decrease in crystallinity was observed after subjecting the

framework to NO and SO<sub>2</sub> which suggests that either a loss in long-range crystallographic ordering or a partial decomposition of the structure was taking place. In contrast to this, the PXRD measurements of MIL-101(Al)-NH<sub>2</sub> after each individual screening test (supplementary information) showed a complete loss of long-range crystallographic ordering or a complete decomposition of the framework. It can therefore be assumed that the complete loss in crystallographic ordering or the collapse is a result of the desorption of the contaminants during the screening tests. The collapse of the framework could account for some of the net mass loss observed in the TGA profiles (Figure 4a and c). The diffraction pattern of MIL-101(Al)-NH<sub>2</sub> changed significantly in the presence of NO<sub>2</sub>, which resulted in a broadening of the peaks and was more pronounced after the exposure at 80 °C than at room temperature. This result suggests the complete decomposition of the framework and is consistent with the observations during the FTIR studies and powder X-ray diffractogram after the screening test (supplementary information).

It can therefore be concluded that the Cr(III) frameworks exhibit a higher chemical stability towards the flue gas contaminants than MIL-101(Al)-NH<sub>2</sub>. However, the decrease in crystallinity after the exposure with NO, NO<sub>2</sub> and SO<sub>2</sub> in all materials implies that a loss in long-range crystallographic ordering or a partial in collapse of all frameworks took place. Furthermore, a complete collapse of the framework was observed after each screening test (supplementary material) and is considered to be due to the complete or partial desorption of all contaminants (obtained during Ar/contaminant flow and/or during the final Ar purge at 117 °C). Although contaminant concentrations of 10000 ppm are not relevant for post-combustion capture, these experiments have provided good insight into the framework stability in the presence of contaminants. In order to confirm the collapse, N<sub>2</sub> adsorption at -196 °C could be conducted, but this was not possible with the limited amount of sample available.

#### 5.2.4.2 Sorption of flue gas contaminants

#### 5.2.4.2.1 Flue gas contaminant cycling experiments

Figure 5.7-5.9 show the results of the five cycle experiments carried out at 25 °C. The contaminant concentration was varied between 0 ppm and 500 ppm (NO or NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>) and 5000 ppm (NO or NO<sub>2</sub> or SO<sub>2</sub>) to determine the effect of different flue gas contaminants on the framework stability and the sorption behaviour. Although the maximum uptakes in the screening test were found at 50 to 80 °C, the cycling experiments
were performed at 25 °C due to the higher  $CO_2$  capacities at lower temperatures. The mass uptakes were calculated on a molar basis by subtracting the mass change at 500 or 2000 or 5000 ppm by the mass change at 0 ppm. The time scale shown in the TGA profiles (Figures 7 to 9, left) include the Ar pre-treatment at 110 °C (t<0 min) and the final Ar treatment at 110 °C under Ar at t>220 min.<sup>b</sup> The PXRD and FTIR results after the contaminant cycling are shown in the supplementary material. No changes were observed in the FTIR spectra unless stated otherwise.

The cycling of MIL-101(Cr) with each individual contaminant (Figure 5.7) resulted in a higher mass change in the presence of 5000 ppm NO, NO<sub>2</sub> and SO<sub>2</sub> compared to 500 ppm NO and NO<sub>2</sub> or 2000 ppm SO<sub>2</sub>. The progressive increase in mass during the course of the cycling experiments suggests the accumulation of all contaminants, especially at 5000 ppm. This was also observed in the progressively reduction in mass uptake from cycle to cycle. For instance in the case of 5000 ppm NO<sub>2</sub>, the mass uptake in cycle five was almost 64 % lower than in cycle two, while at 500 ppm this difference was approximately 53 %. The molar mass uptakes also indicate that NO and NO<sub>2</sub> at 5000 ppm were adsorbed to a higher extent than in the case of SO<sub>2</sub>. At concentrations relevant to flue gas, the mass uptakes of NO<sub>2</sub> and SO<sub>2</sub> were comparable in cycles four and five, while the mass uptake of NO was smaller.

A partial desorption of the NO (5000 ppm), NO<sub>2</sub> (5000 ppm) and SO<sub>2</sub> (2000 and 5000 ppm) upon lowering the pressure to 0 ppm was observed in most cycles, especially in the case of SO<sub>2</sub> (2000 and 5000 ppm). The apparent mass gain observed during the first desorption step, in the case of cycling with 5000 ppm NO and in all five desorption steps with 500 ppm NO and NO<sub>2</sub> is considered to be an artefact due to non-ideal gas flow in the gas feed system. This is due to incomplete clearance of the contaminant gas from the feed gas stream over the 20 min desorption steps. This resulted in continued adsorption especially at the lower concentrations of NO and NO<sub>2</sub>. Complete desorption was achieved during the heat ramp from 25 to 110 °C under Ar in the case of 500 ppm NO, 2000 and 5000 ppm SO<sub>2</sub>. This is consistent with the physisorption of these contaminants. Heating MIL-101(Cr) in Ar at 110 °C resulted in an incomplete desorption of NO<sub>2</sub> (especially at 5000 ppm), probably due to the chemisorption of the contaminant onto the CUS as

<sup>&</sup>lt;sup>b</sup> The apparent mass gain in the TGA profiles (Figure 7-9, left) after the temperature reduction from 110 to 25 °C (between t= -48.5 to 0 min) and from 110 to 20 °C (t>258 min) is regarded as an artefact due to the change in temperature.

observed during the FTIR studies after the exposure to 10000 ppm  $NO_2$ . FTIR spectra of MIL-101(Cr) after the sorption of 500 and 5000 ppm  $NO_2$  also revealed a broadening of the bands, probably due to the strong interaction of the contaminant with the CUS.



**Figure 5.7:** TGA profile (left) and mass uptakes (right) of different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-101(Cr) during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm.

The TGA profiles and mass uptakes of the contaminant cycling on MIL-101(Cr)-NH<sub>2</sub> are shown in Figure 5.8. A rise in contaminant concentration resulted in higher mass gains for all contaminants studied here. As in the case of MIL-101(Cr), the accumulation of the contaminants and therefore the slowing adsorption kinetics resulted in reducing mass uptakes from one cycle to the next. The molar mass uptakes of the contaminant concentrations relevant to flue gas were comparable and constituted less than 0.10 mmol g<sup>-1</sup>. The reduction in mass uptakes, progressing from cycle one to cycle five, were found to be less than in the case of MIL-101(Cr), consistent with lower mass changes overall. The maximum loss in mass uptake from cycle one to cycle five was observed for 5000 ppm NO and was calculated to be 60 %.

No mass loss was obtained during the desorption steps in the cycling experiments with 5000 ppm NO, 5000 ppm NO<sub>2</sub> and 500 ppm NO<sub>2</sub> with the mass remaining constant. This might also be expected to be the case for cycling with 500 ppm NO. The reason for the apparent ongoing mass gain is probably the incomplete clearance of the contaminant gas as was discussed for MIL-101(Cr).<sup>b</sup> Partial desorption upon lowering the pressure to 0 ppm was only observed in the case of SO<sub>2</sub> (2000 and 5000 ppm). The more ready desorption of SO<sub>2</sub> suggests that its interaction with the framework is much weaker than for NO and NO<sub>2</sub>.

Heating MIL-101(Cr)-NH<sub>2</sub> to 110 °C under Ar atmosphere resulted in complete desorption of 2000 ppm and 5000 ppm SO<sub>2</sub>, 500 ppm NO and 500 ppm NO<sub>2</sub>. In contrast to this, 5000 ppm NO and 5000 ppm NO<sub>2</sub> were only partially desorbed upon heating. These results would suggest that the high concentrations of NO and NO<sub>2</sub> were chemisorbed rather than physisorbed. However, from the FTIR studies conducted after the exposure to 10000 ppm chemisorption was only clearly indicated in the case of NO<sub>2</sub>. It is therefore expected, that the adsorption of 5000 ppm NO proceeded via physisorption rather than chemisorption and that extending the final regeneration time at 110 °C would result in the complete desorption of NO. The reason for the apparent negative mass change in the cases of 500 ppm NO, 2000 ppm and 5000 ppm SO<sub>2</sub> is thought to be the collapse of the framework structure, consistent with PXRD measurements of the samples (supplementary information).



**Figure 5.8:** TGA profile (left) and mass uptakes on a molar basis (right) of different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-101(Cr)-NH<sub>2</sub> during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm.

The mass changes and uptakes of the contaminant cycling experiments on MIL-101(Al)-NH<sub>2</sub> are shown in Figure 5.9. As expected, the rise in contaminant concentration resulted in an increase in mass change. The decrease in mass change (wt%) in the order 5000 ppm  $NO_2 > 5000$  ppm NO > 5000 ppm  $SO_2$  is in good agreement with the results of the screening tests. As discussed for MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub>, the accumulation of the contaminants led to a reducing mass uptake from cycle to cycle. The highest change in mass uptake from cycle one to cycle five was observed for 5000 ppm NO (65 %), which is consistent with the results for the Cr(III) frameworks. For the contaminant concentrations relevant to flue gas, the mass uptakes were also lower than 0.10 mmol  $g^{-1}$ , perhaps in part due to the lower pore volume of MIL-101(Al)-NH<sub>2</sub> relative to MIL-101(Cr).

The partial desorption of 2000 ppm and 5000 ppm SO<sub>2</sub> upon lowering the partial pressure to 0 ppm is consistent with the results for MIL-101(Cr) and MIL-101(Cr)-NH<sub>2</sub>. The relatively constant mass uptake observed for succeeding cycles with 5000 ppm NO, 5000 ppm and 500 ppm NO<sub>2</sub> is consistent with the stronger interactions of these contaminants with the framework structure occur than for SO<sub>2</sub>. The reason for the apparent rise in mass during the desorption part of the cycling of 500 ppm NO and 500 ppm NO<sub>2</sub> is probably the incomplete clearance of the contaminant gas as was discussed for MIL-101(Cr).<sup>b</sup> Complete desorption of 500 and 5000 ppm NO, 500 ppm NO<sub>2</sub>, 2000 and 5000 ppm SO<sub>2</sub> was achieved by heating the samples at 110 °C under Ar. The negative mass change is believed to be due to the collapse of the framework as determined via PXRD (supplementary information). In the case of 5000 ppm NO<sub>2</sub>, the desorption was incomplete during the heating due to irreversible adsorption of the contaminant. Furthermore, a loss of crystallinity was observed, probably indicating partial collapse of the framework, thus accounting for the mass loss.



**Figure 5.9:** TGA profile (left) and mass uptakes on a molar basis (right) of different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-101(Al)-NH<sub>2</sub> during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm.

It can be concluded that in most cases only  $SO_2$  was partially desorbed during the cycling process due to the lower interaction with the framework structure. Accumulation of the contaminants occurred in all cases and is expected to have a considerable impact on the

 $CO_2$  capture ability. MIL-101(Cr) exhibited a higher chemical stability than the amine modified frameworks, whose crystallinity, as revealed by PXRD (supplementary information), had been destroyed during the contaminant cycling experiments.

#### 5.2.4.2.2 Flue gas contaminant cycling in the presence of CO<sub>2</sub>

Figure 5.10 to 5.12 show the results of the  $CO_2$ /contaminant cycling experiments carried out at 25 °C. The  $CO_2$  and contaminant partial pressures were varied between 0.05 and 0.15 bar and between 0 and 500 (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>), respectively, to demonstrate the likely impact of the flue gas contaminants on the  $CO_2$  capacity. The results from the  $CO_2$ /contaminant cycling were then compared to the first five cycles of the  $CO_2$  cycling. The mass loss was calculated by subtracting the mass reading after the exposure to 0.15 bar by the mass reading at 0.05 bar. The weight change during the pretreatment step under Ar has been omitted from the figures for better clarity of the results obtained. The results of the FTIR and PXRD results are shown in the supplementary materials. No further discussion on the FTIR results is provided in this section due to the absence of any obvious changes in IR absorption, which is consistent with the FTIR data from the screening tests.

The TGA profiles and the amounts desorbed in each cycle during the CO<sub>2</sub>/contaminant and CO<sub>2</sub> cycling in MIL-101(Cr) are shown in Figure 5.10. MIL-101(Cr) exhibited a reversible CO<sub>2</sub> uptake of 0.16 mmol g<sup>-1</sup> (0.06 mol of CO<sub>2</sub> per mol of CUS) in the absence of contaminants. In comparison with the mass uptakes of the contaminants (see Section 5.2.4.2.1) at concentrations relevant to flue gas, only the NO uptakes were found to be smaller over the duration of the cycling process. In the case of NO<sub>2</sub> and SO<sub>2</sub>, the uptakes were higher than the CO<sub>2</sub> uptakes in the first two cycles.

Equilibrium was achieved during the cycling with  $CO_2$  and in part for the  $CO_2/NO$  cycling within the 20 min for each adsorption and desorption step. The mass records showed additional adsorption in the presence of  $NO_2$  and  $SO_2$  beyond that observed for  $CO_2$  alone, consistent with the accumulation of these contaminants as previously noted in the contaminant cycling experiments. Based on the lack of desorption of NO and  $NO_2$  upon lowering the partial pressure, as noted in the contaminant cycling section, the following assumptions were made to estimate the amount of  $CO_2$  adsorbed during the  $CO_2/contaminant$  cycling: (1) all mass loss during the cycling was due to the desorption of  $CO_2$  and (2) the amount of  $CO_2$  desorbed equals the amount of  $CO_2$  adsorbed. Under these

assumptions, the cyclic CO<sub>2</sub> capacities were determined to be ~0.10 mmol  $g^{-1}$  and ~0.11 mmol g<sup>-1</sup> in the presence of NO and NO<sub>2</sub>, respectively. The diminished CO<sub>2</sub> capacities were consistent with the accumulation of these contaminants. However, these assumptions are not valid for the  $CO_2/SO_2$  cycling, due to the partial desorption of  $SO_2$ , as observed in the contaminant cycling experiments. The following assumptions were made to estimate the  $CO_2$  capacity during the  $CO_2/SO_2$  experiments: (1) the initial steep increase in mass, as the CO<sub>2</sub> partial pressure was increased from 0.05 to 0.15 bar, was due to the adsorption of  $CO_2$  and (2) the subsequent slower adsorption accounted for  $SO_2$ . Thus, the estimated CO<sub>2</sub> and SO<sub>2</sub> capacities were 0.35 mmol  $g^{-1}$  and 0.28 mmol  $g^{-1}$  in the first cycle, respectively, and diminished to. 0.24 mmol  $g^{-1}$  CO<sub>2</sub> and 0.07 mmol  $g^{-1}$  SO<sub>2</sub> in cycle five. Under the assumptions made, the calculated CO<sub>2</sub> capacities were much higher in the presence of SO<sub>2</sub> than those observed during the CO<sub>2</sub> cycling without the contaminant. While this result implies that  $SO_2$  resulted in an improvement in  $CO_2$  capacity, this might not necessarily be the case, if the assumptions are not completely valid. Further experiments are required to verify this result (e.g. binary gas adsorption, breakthrough PXRD measurements experiments). (supplementary information) after the CO<sub>2</sub>/contaminant cycling revealed a decrease in crystallinity, which is consistent with the results after the exposure to 10000 ppm of contaminant.



**Figure 5.10:** TGA profile (left) and the calculated mass loss (right) of  $CO_2$  with and without NO, SO<sub>2</sub> and NO<sub>2</sub> on MIL-101(Cr) at 25 °C. Cycling experiments were conducted by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar and the contaminant partial pressure between 0 ppm and 500 (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>).

The results for the  $CO_2$ /contaminant and  $CO_2$  cycling experiments in MIL-101(Cr)-NH<sub>2</sub> are shown in Figure 5.11. MIL-101(Cr)-NH<sub>2</sub> exhibited a higher  $CO_2$  uptake of

0.18 mmol g<sup>-1</sup> (0.07 mol of CO<sub>2</sub> per mol of CUS) than MIL-101(Cr), due to the presence of the amine group. The comparison with the mass uptakes of 500 ppm NO, 500 ppm NO<sub>2</sub> and 2000 ppm SO<sub>2</sub>, obtained from the contaminant cycling experiments, revealed that CO<sub>2</sub> is adsorbed more selectively into the framework, as the contaminant uptakes were less than 0.1 mmol g<sup>-1</sup>.



**Figure 5.11:** TGA profile (left) and the calculated mass loss (right) of  $CO_2$  with and without NO,  $SO_2$  and  $NO_2$  on MIL-101(Cr)-NH<sub>2</sub> at 25 °C. Cycling experiments were conducted by varying the  $CO_2$  partial pressure between 0.05 and 0.15 bar and the contaminant partial pressure between 0 ppm and 500 (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>).

The CO<sub>2</sub> cycling profile shows that equilibration of the mass was achieved in each adsorption and desorption step, while this was not the case for CO<sub>2</sub>/NO, CO<sub>2</sub>/NO<sub>2</sub> and CO<sub>2</sub>/SO<sub>2</sub>. This is consistent with the slower adsorption kinetics of the contaminants than for CO<sub>2</sub>. Additional mass changes, beyond that of CO<sub>2</sub>, alone were observed in the presence of the contaminants, consistent with their accumulation. The CO<sub>2</sub> capacities during the CO<sub>2</sub>/contaminant cycling experiments were estimated using the assumptions stated above for MIL-101(Cr). In both CO<sub>2</sub>/NO and CO<sub>2</sub>/NO<sub>2</sub> cycling, the CO<sub>2</sub> capacities were diminished to 0.15 mmol g<sup>-1</sup>, as a result of the accumulations of NO and NO<sub>2</sub>. The CO<sub>2</sub> capacities during the CO<sub>2</sub>/SO<sub>2</sub> cycling were estimated to be 0.18 mmol g<sup>-1</sup> in all five cycles, which were comparable to the CO<sub>2</sub> uptake of 0.18 mmol g<sup>-1</sup> obtained during the CO<sub>2</sub> cycling without contaminants. However, it is expected that the accumulation of SO<sub>2</sub> will slightly diminish the CO<sub>2</sub> capacities. PXRD studies (supplementary information) revealed the loss in long range crystallographic ordering or the collapse of MIL-101(Cr)-NH<sub>2</sub> after the contaminant cycling experiments without CO<sub>2</sub>.

The TGA profiles and calculated mass losses in each cycle of MIL-101(Al)-NH<sub>2</sub> are shown in Figure 5.12. Further enhancement of the CO<sub>2</sub> uptakes in MIL-101 frameworks was achieved by replacing the Cr(III) with Al(III) cations, which accounted for uptakes of 0.23 mmol g<sup>-1</sup> (0.08 mol of CO<sub>2</sub> per mol of CUS). The comparison of the CO<sub>2</sub> mass uptake (CO<sub>2</sub> cycling) with the contaminant mass uptakes (contaminant cycling) revealed that CO<sub>2</sub> is adsorbed more selectively into MIL-101(Al)-NH<sub>2</sub>, due to the comparatively low contaminant uptakes of less than 0.1 mmol g<sup>-1</sup>.

While equilibrium was achieved within the 20 min for each adsorption and desorption step during the  $CO_2$  cycling experiment, a mass gain and/or loss was observed during the equilibration time during the  $CO_2$ /contaminant cycling, consistent with the slower adsorption kinetics of the contaminants compared to  $CO_2$ . Furthermore, the accumulation of the contaminants resulted in diminished  $CO_2$  capacities of 0.19, 0.15 and 0.17 mmol g<sup>-1</sup> in the presence of NO, NO<sub>2</sub> and SO<sub>2</sub>, respectively, estimated using the same assumptions explained for MIL-101(Cr). PXRD measurements of MIL-101(Al)-NH<sub>2</sub> after the  $CO_2$ /contaminant cycling experiments (supplementary material) revealed the collapse of the framework, which is in good agreement with the results obtained after the screening tests.



**Figure 5.12:** TGA profile (left) and mass loss (right) of  $CO_2$  with and without NO,  $SO_2$  and NO<sub>2</sub> on MIL-101(Al)-NH<sub>2</sub> at 25 °C. Cycling experiments were conducted by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar and the contaminant partial pressure between 0 ppm and 500 (NO, NO<sub>2</sub>)/2000 ppm (SO<sub>2</sub>).

Thus, in all three MOFs, diminished  $CO_2$  capacities in the presence of NO, NO<sub>2</sub> and SO<sub>2</sub> were observed in most cases and suggest that the removal of these contaminants prior to a post-combustion capture process is necessary. It would be beneficial to conduct single

component and binary gas adsorption/desorption measurements as well as breakthrough experiments in order to more accurately determine the  $CO_2$  uptakes and the  $CO_2$ /contaminant selectivites in the presence of the contaminants.

#### 5.2.5 Conclusion

The effect of NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability of MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub> and their potential to facilitate CO<sub>2</sub> capture was evaluated by conducting a series of FTIR and PXRD studies, screening tests and cycling experiments.

FTIR studies before and after the treatment with 10000 ppm of contaminants indicated that  $NO_2$  interacted strongly with the CUS by forming a chelating bidentate nitrate species in MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub> and MIL-101(Al)-NH<sub>2</sub>. This interaction was found to be stronger in the presence of chromium cations and in the absence of amine groups. NO and SO<sub>2</sub> on the other hand appeared to be physisorbed in all frameworks.

The PXRD screening study revealed a significant decrease in the crystallinities of all MOFs after the separate exposure to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub> consistent with the loss in long-range crystallographic ordering or the partial collapse of the frameworks. For MIL-101(Al)-NH<sub>2</sub> after the adsorption of NO<sub>2</sub>, complete collapse of the framework was observed. PXRD measurements conducted after the screening and cycling experiments also revealed a complete loss of crystallinity of both amine modified frameworks under all conditions which accompanied the removal of the contaminants during the regeneration step at 110 °C under Ar.

Screening tests confirmed the physisorption of NO as well as  $SO_2$  and the chemisorption of  $NO_2$  in most cases.  $CO_2$ /contaminant cycling studies revealed that the  $CO_2$  uptake depreciated in the presence of the contaminants, which suggests that these contaminants need to be removed prior to the capture process.

Further studies, including contaminant cycling in the presence of  $H_2O$  vapour (which is also a component of flue gas) and longer cycling experiments would be beneficial to help determine if NO, NO<sub>2</sub> and SO<sub>2</sub> all need to be removed prior to the capture process or if the removal of only one or two of these contaminants is sufficient. Additionally in order to confirm the collapse of the MOFs it would be beneficial to measure  $N_2$  adsorption and desorption isotherms at -196 °C in order to estimate the surface areas.

# 5.2.6 Acknowledgements

Financial support was provided by the Australian Government trough the CRC Program to support this CO2CRC project.

# 5.2.7 References

- [1] N. Stern, ""The Economics of Climate Change The Stern Review"," Cambridge2007.
- [2] R. K. Pachauri and A. Reisinger, "IPCC Fourth Assessment Report," *Intergovernmental Panel on Climate Change*, 2007.
- [3] R. Garnaut, ""The Garnaut Review 2011 Australia in the Global Response to Climate Change"," Cambridge2011.
- [4] IEA, "CO<sub>2</sub> Emissions from Fuel Combustion, Highlights," Available: <u>http://www.iea.org/co2highlights/co2highlights.pdf</u> (accessed: 27/07/2014)2012.
- [5] H. Wu, R. S. Reali, D. A. Smith, M. C. Trachtenberg, and J. Li, "Highly Selective CO<sub>2</sub> Capture by a Flexible Microporous Metal–Organic Framework (MMOF) Material," *Chemistry – A European Journal*, vol. 16, pp. 13951-13954, 2010.
- [6] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, pp. 1791-1823, 2011.
- [7] H.-L. Jiang and Q. Xu, "Porous metal-organic frameworks as platforms for functional applications," *Chemical Communications*, vol. 47, pp. 3351-3370, 2011.
- [8] G. Férey, "Hybrid porous solids: past, present, future," *Chemical Society Reviews*, vol. 37, pp. 191-214, 2008.
- [9] O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi, and J. Kim, "Reticular synthesis and the design of new materials," *Nature*, vol. 423, pp. 705-714, 2003.
- [10] S. Kitagawa, R. Kitaura, and S.-i. Noro, "Functional Porous Coordination Polymers," *Angewandte Chemie International Edition*, vol. 43, pp. 2334-2375, 2004.
- [11] S. R. Batten, S. M. Neville, and D. R. Turner, *Coordination Polymers: Design, Analysis and Application*: RSC Publishing, 2009.
- [12] W. Xuan, C. Zhu, Y. Liu, and Y. Cui, "Mesoporous metal-organic framework materials," *Chemical Society Reviews*, vol. 41, pp. 1677-1695, 2012.
- [13] R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, and H. C. Zhou, "Potential applications of metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 253, pp. 3042-3066, 2009.
- [14] D. M. D'Alessandro, B. Smit, and J. R. Long, "Carbon Dioxide Capture: Prospects for New Materials," *Angewandte Chemie International Edition*, vol. 49, pp. 6058-6082, 2010.
- [15] A. Ö. Yazaydin, A. I. Benin, S. A. Faheem, P. Jakubczak, J. J. Low, R. R. Willis, and R. Q. Snurr, "Enhanced CO<sub>2</sub> Adsorption in Metal-Organic Frameworks via Occupation of Open-Metal Sites by Coordinated Water Molecules," *Chemistry of Materials*, vol. 21, pp. 1425-1430, 2009.
- [16] G.-P. Hao, W.-C. Li, and A.-H. Lu, "Novel porous solids for carbon dioxide capture," *Journal of Materials Chemistry*, vol. 21, pp. 6447-6451, 2011.

- [17] Y.-S. Bae, O. K. Farha, J. T. Hupp, and R. Q. Snurr, "Enhancement of CO<sub>2</sub>/N<sub>2</sub> selectivity in a metal-organic framework by cavity modification," *Journal of Materials Chemistry*, vol. 19, pp. 2131-2134, 2009.
- [18] D. Britt, H. Furukawa, B. Wang, T. G. Glover, and O. M. Yaghi, "Highly efficient separation of carbon dioxide by a metal-organic framework replete with open metal sites," *Proceedings of the National Academy of Sciences*, vol. 106, pp. 20637-20640, December 8, 2009 2009.
- [19] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, "A Chemically Functionalizable Nanoporous Material [Cu3(TMA)2(H2O)3]n," *Science*, vol. 283, pp. 1148-1150, February 19, 1999 1999.
- [20] S. Marx, W. Kleist, and A. Baiker, "Synthesis, structural properties, and catalytic behavior of Cu-BTC and mixed-linker Cu-BTC-PyDC in the oxidation of benzene derivatives," *Journal of Catalysis*, vol. 281, pp. 76-87, 2011.
- [21] L. Ding and A. Ö. Yazaydin, "How Well Do Metal–Organic Frameworks Tolerate Flue Gas Impurities?," *The Journal of Physical Chemistry C*, vol. 116, pp. 22987-22991, 2012/11/01 2012.
- [22] Z. Liang, M. Marshall, and A. L. Chaffee, "CO<sub>2</sub> Adsorption-Based Separation by Metal Organic Framework (Cu-BTC) versus Zeolite (13X)," *Energy & Fuels*, vol. 23, pp. 2785-2789, 2009.
- [23] Z. Liang, M. Marshall, C. H. Ng, and A. L. Chaffee, "Comparison of Conventional and HF-Free-Synthesized MIL-101 for CO<sub>2</sub> Adsorption Separation and Their Water Stabilities," *Energy & Fuels*, vol. 27, pp. 7612-7618, 2013/12/19 2013.
- [24] D. Wu, Q. Xu, D. Liu, and C. Zhong, "Exceptional CO<sub>2</sub> Capture Capability and Molecular-Level Segregation in a Li-Modified Metal-Organic Framework," *The Journal of Physical Chemistry C*, vol. 114, pp. 16611-16617, 2010.
- [25] J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna, and J. R. Long, "Evaluating metal-organic frameworks for post-combustion carbon dioxide capture via temperature swing adsorption," *Energy & Environmental Science*, vol. 4, pp. 3030-3040, 2011.
- [26] P. D. C. Dietzel, V. Besikiotis, and R. Blom, "Application of metal-organic frameworks with coordinatively unsaturated metal sites in storage and separation of methane and carbon dioxide," *Journal of Materials Chemistry*, vol. 19, pp. 7362-7370, 2009.
- [27] A. Ö. Yazaydin, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low, and R. R. Willis, "Screening of Metal-Organic Frameworks for Carbon Dioxide Capture from Flue Gas Using a Combined Experimental and Modeling Approach," *Journal of the American Chemical Society*, vol. 131, pp. 18198-18199, 2009.
- [28] T. C. Drage, C. E. Snape, L. A. Stevens, J. Wood, J. Wang, A. I. Cooper, R. Dawson, X. Guo, C. Satterley, and R. Irons, "Materials challenges for the development of solid sorbents for post-combustion carbon capture," *Journal of Materials Chemistry*, vol. 22, pp. 2815-2823, 2012.
- [29] J. B. DeCoste and G. W. Peterson, "Metal–Organic Frameworks for Air Purification of Toxic Chemicals," *Chemical Reviews*, 2014.
- [30] H. Deng, H. Yi, X. Tang, H. Liu, and X. Zhou, "Interactive Effect for Simultaneous Removal of SO<sub>2</sub>, NO, and CO<sub>2</sub> in Flue Gas on Ion Exchanged Zeolites," *Industrial* & Engineering Chemistry Research, vol. 52, pp. 6778-6784, 2013/05/22 2013.
- [31] R. A. Khatri, S. S. C. Chuang, Y. Soong, and M. Gray, "Thermal and Chemical Stability of Regenerable Solid Amine Sorbent for CO<sub>2</sub> Capture," *Energy & Fuels*, vol. 20, pp. 1514-1520, 2006/07/01 2006.

- [32] X. Xu, C. Song, B. G. Miller, and A. W. Scaroni, "Adsorption separation of carbon dioxide from flue gas of natural gas-fired boiler by a novel nanoporous "molecular basket" adsorbent," *Fuel Processing Technology*, vol. 86, pp. 1457-1472, 2005.
- [33] F. N. Ridha, V. Manovic, A. Macchi, and E. J. Anthony, "The effect of SO<sub>2</sub> on CO<sub>2</sub> capture by CaO-based pellets prepared with a kaolin derived Al(OH)<sub>3</sub> binder," *Applied Energy*, vol. 92, pp. 415-420, 2012.
- [34] H. Lu and P. G. Smirniotis, "Calcium Oxide Doped Sorbents for CO<sub>2</sub> Uptake in the Presence of SO<sub>2</sub> at High Temperatures," *Industrial & Engineering Chemistry Research*, vol. 48, pp. 5454-5459, 2009/06/03 2009.
- [35] J. Yu, Y. Ma, and P. B. Balbuena, "Evaluation of the Impact of H<sub>2</sub>O, O<sub>2</sub>, and SO<sub>2</sub> on Postcombustion CO<sub>2</sub> Capture in Metal–Organic Frameworks," *Langmuir*, vol. 28, pp. 8064-8071, 2012/05/29 2012.
- [36] A. Das, P. D. Southon, M. Zhao, C. J. Kepert, A. T. Harris, and D. M. D'Alessandro, "Carbon dioxide adsorption by physisorption and chemisorption interactions in piperazine-grafted Ni2(dobdc) (dobdc = 1,4-dioxido-2,5-benzenedicarboxylate)," *Dalton Transactions*, vol. 41, pp. 11739-11744, 2012.
- [37] B. Xiao, P. S. Wheatley, X. Zhao, A. J. Fletcher, S. Fox, A. G. Rossi, I. L. Megson, S. Bordiga, L. Regli, K. M. Thomas, and R. E. Morris, "High-Capacity Hydrogen and Nitric Oxide Adsorption and Storage in a Metal–Organic Framework," *Journal* of the American Chemical Society, vol. 129, pp. 1203-1209, 2007/02/01 2007.
- [38] O. I. Lebedev, F. Millange, C. Serre, G. Van Tendeloo, and G. Férey, "First Direct Imaging of Giant Pores of the Metal–Organic Framework MIL-101," *Chemistry of Materials*, vol. 17, pp. 6525-6527, 2005/12/01 2005.
- [39] A. Torrisi, R. G. Bell, and C. Mellot-Draznieks, "Predicting the impact of functionalized ligands on CO<sub>2</sub> adsorption in MOFs: A combined DFT and Grand Canonical Monte Carlo study," *Microporous and Mesoporous Materials*, vol. 168, pp. 225-238, 2013.
- [40] Z. Zhang, Y. Zhao, Q. Gong, Z. Li, and J. Li, "MOFs for CO<sub>2</sub> capture and separation from flue gas mixtures: the effect of multifunctional sites on their adsorption capacity and selectivity," *Chemical Communications*, vol. 49, pp. 653-661, 2013.
- [41] C. Patzschke, G. P. Knowles, M. Marshall, and A. L. Chaffee, "Post-Synthetic Modification of MIL-101(Al)-NH<sub>2</sub> with Amines and their Effect on the CO<sub>2</sub> Sorption," *Thesis Chapter 3.5*, 2014.
- P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jhung, and G. Férey, "High Uptakes of CO<sub>2</sub> and CH<sub>4</sub> in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101," *Langmuir*, vol. 24, pp. 7245-7250, 2008.
- [43] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.
- [44] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, and F. Kapteijn, "Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties," *Chemistry of Materials*, vol. 23, pp. 2565-2572, 2011.
- [45] M. Hartmann and M. Fischer, "Amino-functionalized basic catalysts with MIL-101 structure," *Microporous and Mesoporous Materials*, vol. 164, pp. 38-43, 2012.
- [46] D. Jiang, A. D. Burrows, and K. J. Edler, "Size-controlled synthesis of MIL-101(Cr) nanoparticles with enhanced selectivity for CO<sub>2</sub> over N<sub>2</sub>," *CrystEngComm*, vol. 13, pp. 6916-6919, 2011.

- [47] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, and I. Margiolaki, "A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area," *Science*, vol. 309, pp. 2040-2042, September 23, 2005 2005.
- [48] C. Patzschke, G. P. Knowles, and A. L. Chaffee, "CO<sub>2</sub> Adsorption in Post-Synthetic Modified MIL-101(Cr)-NH2," *Thesis Chapter 3.4*, 2014.
- [49] D. Jiang, L. L. Keenan, A. D. Burrows, and K. J. Edler, "Synthesis and postsynthetic modification of MIL-101(Cr)-NH<sub>2</sub> via a tandem diazotisation process," *Chemical Communications*, vol. 48, pp. 12053-12055, 2012.
- [50] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, "Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants," *Sci. Rep.*, vol. 3, pp. 1-6, 2013.
- [51] A. Khutia and C. Janiak, "Programming MIL-101Cr for selective and enhanced CO<sub>2</sub> adsorption at low pressure by postsynthetic amine functionalization," *Dalton Transactions*, vol. 43, pp. 1338-1347, 2014.
- [52] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, and G. Férey, "A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration," *Chemistry – A European Journal*, vol. 10, pp. 1373-1382, 2004.
- [53] C. Sedlmair, K. Seshan, A. Jentys, and J. A. Lercher, "Elementary steps of NOx adsorption and surface reaction on a commercial storage–reduction catalyst," *Journal of Catalysis*, vol. 214, pp. 308-316, 2003.
- [54] S. P. Sinha, "Investigation on the Rare Earth Terpyridyl System IV. Terpyridyl Complexes of Higher Lanthanides," *Z. Naturforschg.*, vol. 20 a, pp. 1661-1664, 1965.
- [55] H. Beckers, X. Zeng, and H. Willner, "Intermediates Involved in the Oxidation of Nitrogen Monoxide: Photochemistry of the cis-N<sub>2</sub>O<sub>2</sub>·O<sub>2</sub> complex and of sym-N2O4 in Solid Ne Matrices," *Chemistry – A European Journal*, vol. 16, pp. 1506-1520, 2010.
- [56] M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, and K. P. Lillerud, "Synthesis and Stability of Tagged UiO-66 Zr-MOFs," *Chemistry of Materials*, vol. 22, pp. 6632-6640, 2010/12/28 2010.

# Supplementary material

# Effect of flue gas contaminants on the stability and the post-combustion CO<sub>2</sub> capture in MIL-101 frameworks

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author:

Fax:+61 3 990-54597

## 5.2.8 Characterisation of MIL-101(Cr)

 $N_2$  adsorption and desorption from MIL-101(Cr) was conducted at -196 °C. The sample was activated under vacuum at 150 °C overnight in a Micromeritics VacPrep 061 degasser. After cooling the sample to room temperature, the sample tube was backfilled with helium and installed in a Micromeritics Tristar II gas sorption analyser. The BET surface area was calculated over the relative pressure range of 0.01 and 0.2 on the adsorption isotherms. It should be noted that in this pressure range, adsorption of  $N_2$  still occurs. The pore volume was estimated at  $p/p_0=0.99$ . The comparison of the measured and the calculated XRD pattern of MIL-101(Cr) confirms the purity of the bulk sample.



**Figure 5.13:** (a)  $N_2$  adsorption/desorption isotherm at -196 °C for activated MIL-101(Cr). (b) Comparison of experimental (black) and the calculated diffractogram (red) of MIL-101(Cr) [1].



5.2.9 FTIR of MIL-101(Cr) after contaminant sorption – TGA

**Figure 5.14:** FTIR spectra of MIL-101(Cr) before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.2.10 FTIR of MIL-101(Cr)-NH<sub>2</sub> after contaminant sorption – TGA

**Figure 5.15:** FTIR spectra of MIL-101(Cr)-NH<sub>2</sub> before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.2.11 FTIR of MIL-101(Al)-NH2 after contaminant sorption – TGA

**Figure 5.16:** FTIR spectra of MIL-101(Al)-NH<sub>2</sub> before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.2.12 PXRD of MIL-101(Cr) after contaminant sorption- TGA

**Figure 5.17:** PXRD of MIL-101(Cr) before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.2.13 PXRD of MIL-101(Cr)-NH<sub>2</sub> after contaminant sorption – TGA

**Figure 5.18:** PXRD of MIL-101(Cr)-NH<sub>2</sub> before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.2.14 PXRD of MIL-101(Al)-NH<sub>2</sub> after contaminant sorption – TGA

**Figure 5.19:** PXRD of MIL-101(Al)-NH<sub>2</sub> before and after screening tests, contaminant and  $CO_2$ /contaminant experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.

# 5.2.15 References

[1] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, and I. Margiolaki, "A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area," *Science*, vol. 309, pp. 2040-2042, September 23, 2005 2005.

# **Declaration for Thesis Chapter**

Adsorption of flue gas contaminants in MIL-100(Fe), MIL-53(AI)-NH<sub>2</sub> and STA-16(Co) and their effect on the framework stabilities and  $CO_2$  uptakes

**Monash University** 

# **Declaration for Thesis Chapter 5.3**

#### Declaration by candidate

In the case of Chapter 5.3, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed samples; identified major	80 %
issues; developed interpretations; fully drafted paper and conclusion	

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co- authors only
Gregory P. Knowles	Aided method development (TGA), input to results analysis and manuscript revision	N/A .
Alan L. Chaffee	Supervision, assisted interpretation of results, editorial assistance	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work\*.

 
 Candidate's Signature
 Date 30/10/2014

 Main Supervisor's Signature
 Date 30/10/(4

\*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

# 5.3 Adsorption of flue gas contaminants in MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16 and their effect on the framework stabilities and CO<sub>2</sub> uptakes

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author: Fax:+61 3 990-54597

#### 5.3.1 Abstract

The effect of the flue gas contaminants NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability of MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) and on their potential to facilitate CO<sub>2</sub> capture was studied. The samples were individually treated with 10000 ppm of contaminant and their structural stability and their potential adsorption modes were investigated by PXRD and FTIR. Screening tests were conducted by heating the samples from 20 to 110 °C under an Ar/contaminant atmosphere (5000 ppm NO, NO<sub>2</sub>, SO<sub>2</sub>). The impact of different contaminant concentrations was determined by varying the partial pressure between 0 and 500 or 2000 or 5000 ppm in five cycles at 25 °C. The effect of the contaminant cycling experiments at 25 °C. Loss of long-range crystallographic ordering or partial or complete decomposition of all frameworks and diminished CO<sub>2</sub> uptakes in the presence of NO, NO<sub>2</sub> and SO<sub>2</sub> suggest that these flue gas contaminants would have to be removed prior to a post-combustion CO<sub>2</sub> separation process. While NO<sub>2</sub> was irreversibly adsorbed on the CUS in MIL-100(Fe) and STA-16(Co), the flexibility of MIL-53(Al)-NH<sub>2</sub> resulted in a reversible adsorption.

#### 5.3.2 Introduction

Metal-organic frameworks (MOFs) have attracted tremendous attention over the past decade and have been studied for their application in catalysis, adsorption, luminescence, fluorescence and drug delivery and storage [1, 2]. Their crystalline framework consists of metal ions and organic linker molecules that are connected to each other via specific functional groups [3, 4]. MOFs have shown great promise for the air purification of toxic

gases, due to their tuneable pore sizes and topologies, high surface areas and adjustable functionality [5].

NO and NO<sub>2</sub> are free radicals that can interact strongly with coordinatively unsaturated sites (CUS) [5]. This interaction results in a strong hysteresis in the NO and NO<sub>2</sub> sorption isotherms with HKUST-1, MOF-74(Ni) and MIL-88(Fe) [6-8]. The metal centre and the presence of moisture were found to play an important role in the adsorption of NO,  $NO_2$ and SO<sub>2</sub>. For example, while MOF-74(Ni) exhibited a NO uptake of 18.31 wt% (1.07 mol NO per mol CUS, p≤10 mbar), DFT calculations showed a negligible uptake for MOF-74(Mg). This result can be explained by the absence of d-electrons in Mg(II) resulting in a lack of  $\pi$ -back-bonding from the metal centre to NO and hence only weak interactions between NO and the metal centre [7, 9]. Glover et al. studied the effect of CUS and presence of moisture on the SO<sub>2</sub> capacities of MOF-74 by performing breakthrough experiments with 380 ppm SO<sub>2</sub> at 20 °C. In contrast to the results described for NO, the presence of Mg(II) resulted in a much higher SO<sub>2</sub> adsorption capacity than in the case of MOF-74(Ni). This difference between MOF-74(Mg) and MOF-74(Ni) was even more pronounced under humid conditions, in which an actual decrease in the SO<sub>2</sub> uptake was observed for MOF-74(Ni), resulting in negligible SO<sub>2</sub> uptake [10]. These results are in good agreement with the DFT and GCMC calculations reported by Ding et al., which indicated that MOF-74(Ni) is suitable for capturing CO<sub>2</sub> in the presence of SO<sub>2</sub>, while the Mg analogue will remove SO<sub>2</sub> preferentially [11]. The adsorption of NO<sub>2</sub> on HKUST-1 resulted in the formation of a nitrate species coordinated to the metal sites. A decrease in capacity from 6.63 wt% to 3.39 wt% was observed in the presence of moisture due to the competitive adsorption and coordination of H<sub>2</sub>O molecules [12-14].

Although research has focused on the evaluation of MOFs for the removal of toxic gases [5, 15-17], only limited studies are available that focus on the impact of flue gas contaminants on the potential to facilitate  $CO_2$  capture. This knowledge is crucial for the process design due to the fact that flue gas contains approximately 500 ppm  $NO_x$  and 1800 ppm  $SO_x$ , which can result in a decrease in adsorbent lifetime, therefore increasing the capture costs [18, 19]. A current research focus is minimization of the capture costs in a CCS process. Hence, it would be beneficial if  $CO_2$  could be captured in the presence of these contaminants and therefore avoiding the need of a separate removal step.

MOFs containing coordinatively unsaturated sites (CUS) and flexible frameworks are of particular interest for capturing CO<sub>2</sub> due to the high surface areas, high pore volumes and selective adsorption of CO<sub>2</sub> [20-24]. Two MOFs containing CUS include MIL-100(Fe) and STA-16(Co), which exhibit a strong interaction of CO<sub>2</sub> with the CUS due to the stronger quadrupole moment compared to N<sub>2</sub>. Furthermore, the high hydrothermal stability of these frameworks is beneficial for capturing CO<sub>2</sub> from gas stream containing H<sub>2</sub>O vapour [25, 26]. Additionally, the presence of 40 % relative humidity was found to foster a fivefold increase in CO<sub>2</sub> capacity from 2.2 to 10.5 wt% at 25 °C and 0.2 bar [27]. An overview of these two structures is given in the following paragraphs.



**Figure 5.20:** Crystal structures of MIL-100(Fe) and STA-16(Co). (a) One unit cell of MIL-100(Fe) presenting both cages [28]. (b) The hexagonal channels in STA-16(Co) [29]. Ball and stick view (Fe octahedra: orange, Co octahedra: blue, phosphonate tetrahedra: green, C; grey, O: red, N: dark blue, H: white).

The structure of MIL-100(Fe) is shown in Figure 5.20a. The supertetrahedral building block is built from trimers of Fe(III) oxide octhedra, in which each corner is occupied by the trimeric unit [30]. These units are connected to each other through the tricarboxylate ligands located on each face [31]. The assembly of the supertetrahedra results into a zeotypic MOF with two sets of mesoporous cages which are assessable through two microporous windows [31, 32]. The three-dimensional framework consists of two types of cavity. The first cavity has a window diameter of 0.5 nm and is delimited by 12 pentagonal rings [30, 33]. The second type is delimited by 12 pentagonal rings and 4 hexagonal rings defining a hexakaidodecahedron with a window diameter of 0.86 nm [30, 33]. The CUS can be obtained by vacuum activating the MOF at 150  $^{\circ}$ C [32].

The phosphonate MOF (Figure 5.20b), STA-16(Co), has a pore diameter of 1.8 nm and contains CUS. The MOF contains one crystallographically distinct Co(II) centre, which is coordinated to four phosphonate oxygen atoms, one piperazinyl N atom and one oxygen atom of a  $H_2O$  molecule. Metal spirals are formed by edge sharing distorted ocathedra.

The connection of one spiral to three others results in hexagonal channels, in which one P=O bond from each phosphonate group is hydrogen bonded to lattice  $H_2O$  molecules. These  $H_2O$  molecules also exhibit hydrogen bonds to the coordinated  $H_2O$  [29].



**Figure 5.21:** Schematic view of the breathing effect of MIL-53(Al) upon adsorption of H<sub>2</sub>O. Ball and stick view (Al octahedra: pink, C: grey, O: red, H: white) [34].

MIL-53(Al) and its amine functionalized derivative are examples for flexible materials. Notably MIL-53(Al)-NH<sub>2</sub> was found to be a promising material for post-combustion capture due to a high CO<sub>2</sub>/N<sub>2</sub> selectvity of 20 to 1 and high CO<sub>2</sub> capacity of 7.8 wt% at 25 °C and 1 bar [35]. The interconnection of infinite trans chains of corner-sharing AlO<sub>4</sub>(OH)<sub>2</sub> octahedra by 2-aminoterephthalic acid leads to the formation of a 3D framework with 1-D shaped tunnels [35, 36]. Depending on the nature of the adsorbed molecules and the pressure, the 1-D channels exhibit different pore sizes. At CO<sub>2</sub> pressures below 3 bar, MIL-53(Al)-NH<sub>2</sub> is in the very narrow pore (*vnp*) form which exhibits a pore volume of 937.5 Å<sup>3</sup>. The narrow pore (*np*) is characterised by a pore volume of 987.2 Å<sup>3</sup> and is present up to 12 bar. At pressures higher than 3.5 bar the *np* form coexists with the large pore (*lp*) form (1451.4 Å<sup>3</sup>) [37]. The breathing effect of MIL-53(Al) upon H<sub>2</sub>O adsorption and desorption is shown in Figure 5.21. In the presence of H<sub>2</sub>O molecules, the MIL-53(Al) framework exists in the *np* form with channel dimension of 2.6x13.6 Å<sup>2</sup>, which can be transformed into the *lp* form (8.5x8.5 Å<sup>2</sup>) by evacuating the sample above 100 °C [34, 38].

The effect of the flue gas contaminants NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability and ability to capture CO<sub>2</sub> was evaluated by conducting a series of Fourier transform infra-red (FTIR), powder X-ray diffraction (PXRD), screening tests and cycling experiments on MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co). The exposure of the samples with 10000 ppm of contaminant at different temperatures (room temperature and 50 or 80 °C) and the

following FTIR and PXRD analyses allowed the evaluation of the structural integrity and possible adsorption mechanisms of the contaminants. The range of temperatures over which NO, NO<sub>2</sub> and SO<sub>2</sub> were adsorbed was determined by subjecting the samples to an Ar/ contaminant (5000 ppm) mixture under a heating ramp from 20 to 110 °C (heating rate of 2 °C min<sup>-1</sup>). Contaminant cycling experiments were conducted by varying the partial pressures between 0 and 500 ppm (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>) or 5000 ppm (NO, NO<sub>2</sub>, SO<sub>2</sub>) at 25 °C until five cycles of adsorption and desorption were performed to investigate the impact of different contaminant concentrations. The effect of the flue gas contaminants on the CO<sub>2</sub> capture ability was evaluated by conducting CO<sub>2</sub>/contaminant and CO<sub>2</sub> cycling experiments by varying the CO<sub>2</sub> partial pressures between 0.05 and 0.15 bar and the contaminant partial pressures between 0 and 500 or 2000 ppm at 25 °C.

#### 5.3.3 Experimental section

#### 5.3.3.1 Synthesis of MOFs

#### 5.3.3.1.1 Chemicals

Aluminium chloride hexahydrate (99 %, Sigma Aldrich), 2-aminoterephthalic acid (99 %, Sigma Aldrich), 4,4'-bipiperidine dihydrochloride (99 %, Alfa Aesar), cobalt(II) acetate tetrahydrate ( $\geq$  98 %, Sigma Aldrich), DMF (GR grade, Merck), ethanol ( $\geq$  99.7 %, Merck), formaldehyde (40 % w/v GR grade, Merck), hydrobromic acid (Merck), iron(II) chloride hexahydrate (99 %, Merck), methanol ( $\geq$  99.8 %, Merck), phosphorous acid (97 %, Alfa Aesar), potassium hydroxide (GR grade, Merck), sodium bicarbonate ( $\geq$ 99.7 %, Ajax Chemicals), sulphuric acid (98 % AR grade, Merck), trimesic acid (95 %, Sigma Aldrich). argon (high purity, Air Liquide), carbon dioxide (Food grade, Coregas), 1 % nitric oxide in argon (Air Liquide), 1 % nitrogen dioxide in argon (Air Liquide) and 1 % sulphur dioxide in argon (Air Liquide).

All reagents were used without further purification.

#### 5.3.3.1.2 Synthesis of MIL-100(Fe)

The synthesis of trimethyl-1,3,5-benzenetricarboxylate (Me<sub>3</sub>BTC) and MIL-100(Fe) was reported previously [39] and followed the procedures akin to that reported by Kathiresan et al. [40] and Canioni et al. [33]. MIL-100(Fe) was solvothermally synthesised in a Teflon® lined autoclave at 130 °C for 72 h. The product was activated at 150 °C under vacuum.

## 5.3.3.1.3 Synthesis of MIL-53(Al)-NH<sub>2</sub>

The synthesis of MIL-53(Al)-NH<sub>2</sub> was conducted following the procedure akin to that reported by Ahnfeldt et al. [36]. 4.44 g (18.4 mmol) of AlCl<sub>3</sub>·6H<sub>2</sub>O and 3.39 g (18.7 mmol) of 2-aminoterephthalic acid were dissolved in 45 mL H<sub>2</sub>O and heated in a Teflon® lined autoclave ate 150 °C for 5 h. The yellow powder was recovered by filtration and washed with H<sub>2</sub>O. The excess amount of 2-aminoterephthalic acid was removed by treating the as-synthesised MIL-53(Al)-NH<sub>2</sub> with 100 mL DMF at 150 °C for 16 h. The product was filtered, dried at room temperature and activated under vacuum at 150 °C overnight.

#### 5.3.3.1.4 Synthesis of STA-16(Co)

Synthetic details for STA-16(Co) were reported elsewhere [26] and are in accord with the procedure described by Wharmby et al. [29, 41]. The solvothermal synthesis of STA-16(Co) was conducted in a Teflon® lined autoclave at 220 °C for 65 h. The product was activated under vacuum at 150 °C overnight.

#### 5.3.3.2 Characterisation of the MOFs

The formation of MIL-100(Fe) and STA-16(Co) was validated by conducting elemental analysis, FTIR, PXRD and thermal gravimetric analysis (TGA). The results of these analyses can be found elsewhere [26, 39]. The structure of MIL-53(Al)-NH<sub>2</sub> was confirmed by elemental analysis and PXRD (supplementary information).

#### 5.3.3.3 Exposure to concentrated flue gas contaminants

# 5.3.3.3.1 Screening tests of flue gas contaminants

The change in mass (TGA) of the samples as they were exposed to the contaminants over a heat ramp was measured using a Setaram TAG 24-16 simultaneous symmetrical thermoanalyser. A more detailed description of the screening test was given previously [42].

In a typical screening test, the in-situ activated (110 °C, 1 h, Ar atmosphere) samples were subjected to an Ar/contaminant (5000 ppm) atmosphere over a heat ramp from 20 to 110 °C with a heating rate of 2 ° min<sup>-1</sup>. After 30 min at 110 °C the gas flow was changed from an Ar/contaminant mixture to flowing Ar, which was purged over the sample for 1 h while maintaining the temperature, before the system was cooled down.

# 5.3.3.3.2 PXRD and FTIR studies after the exposure to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub>

Approximately 100 to 200 mg of MOF were separately subjected to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub> using a Micromeritics VacPrep 061 degasser. Prior to the experiment the vacuum activated samples (150 °C, overnight) were heated to 110 °C under flowing Ar and the temperature was maintained for 1 h to ensure the complete removal of adsorbed moisture. The gas was purged through a gas delivery tube over the sample in a partially sealed vial. After cooling the samples to room temperature under flowing Ar, the gas flow was replaced by the Ar/contaminant mixture (1 % contaminant in Ar). The samples were then treated with the contaminants at room temperature for 1 h (flow rates: 25 mL min<sup>-1</sup> for 20 min and 5 mL min<sup>-1</sup> for 40 min). Approximately 50 to 100 mg of each sample were then characterised by PXRD and FTIR. The other 50 to 100 mg of MOF were heated at 50 °C (NO, SO<sub>2</sub>) or 80 °C (NO<sub>2</sub>) under flowing Ar/contaminant mixture (1 % contaminant at mosphere.

PXRD was measured via a Bruker D8 Focus Bragg-Brentano powder diffractometer using Cu K<sub> $\alpha$ </sub> radiation at ambient laboratory conditions. The samples (before and after exposure to 10000 ppm of contaminant) were mounted on a silicon sample holder with ethanol. The scan rate and the 2 $\theta$ -range were set to 0.5 ° min<sup>-1</sup> and 1 to 30°, respectively.

FTIR spectra were measured using an Agilent Cary 630 Diamond ATR in the spectral range of 4000 to 650 cm<sup>-1</sup> at ambient laboratory conditions.

#### 5.3.3.4 Sorption of flue gas contaminants and CO<sub>2</sub>

A Setaram TAG 24-16 simultaneous symmetrical thermoanalyser was used to measure the change in mass (TGA) of the samples as they were exposed to the contaminants (a) in five cycle experiments at 25 °C (Section 5.3.3.4.1) and (b) in five cycle experiments in the presence of CO<sub>2</sub> at 25 °C (Section 5.3.3.4.2). Additionally, the samples were subjected to CO<sub>2</sub> in ten cycle experiments at 25 °C. A short description of the different procedures is given as follows. A more detailed outline of the TGA and gas programs is given in a previous publication [42].

#### 5.3.3.4.1 Flue gas contaminant cycling experiments

Two cycling experiments were conducted for each contaminant using different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub>. Prior to the cycling with NO, NO<sub>2</sub> and SO<sub>2</sub>, the samples were activated at 110 °C for 1 h under an Ar atmosphere. After cooling the samples to 25 °C and maintaining the temperature for 30 min, the Ar/contaminant mixtures were cycled by varying the partial pressure either between 0 and 500 ppm or 0 and 5000 ppm for NO and NO<sub>2</sub> and between 0 and 2000 ppm or 0 and 5000 ppm for SO<sub>2</sub>. Five cycles of adsorption and desorption were performed, allowing 20 min equilibration for each step. Afterwards the samples were re-activated at 110 °C under flowing Ar for 30 min.

#### 5.3.3.4.2 Flue gas contaminant cycling experiments in the presence of CO<sub>2</sub>

The individual flue gas contaminant concentrations used on this part were 500 ppm NO, 500 ppm NO<sub>2</sub> and 2000 ppm for SO<sub>2</sub>. The procedure used for the CO<sub>2</sub>/contaminant cycling was similar to the procedure described above. After the in-situ activation (110 °C under flowing Ar, 1 h) and the equilibration step (25 °C under flowing Ar, 30 min), the five cycles of adsorption and desorption were conducted by varying the CO<sub>2</sub> partial pressure between 0.05 bar and 0.15 bar and the contaminant partial pressure between 0 and 500 (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>), allowing 20 min equilibration time for each adsorption and desorption step.

 $CO_2$  cycling experiments were conducted at 25 °C by varying the  $CO_2$  partial pressure between 0.05 and 0.15 bar on the in-situ activated (150 °C under flowing Ar, 1 h) samples. The equilibration time for each adsorption and desorption step was set to 20 min. After the tenth cycle the  $CO_2/Ar$  mixture was replaced by Ar and the samples were re-activated (150 °C under flowing Ar, 30 min).

#### 5.3.4 Results and discussion

#### 5.3.4.1 Exposure to concentrated flue gas contaminants

Thermogravimetric analysis of MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) was first conducted to evaluate the range of temperatures in which a mass gain or loss occurred upon exposure to 5000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub> individually. Each MOF was separately subjected to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub> at 25 °C (NO, NO<sub>2</sub>, SO<sub>2</sub>) and 50 °C (NO, SO<sub>2</sub>) or 80 °C (NO<sub>2</sub>) to determine the impact on the framework stabilities and possible

adsorption mechanisms. The changes in structure were then determined via PXRD and FTIR. The contaminant concentration of 10000 ppm was expected to give rise to stronger IR absorptions and also more significant changes in the diffractograms than the concentrations typical of flue gas (NO, NO<sub>2</sub>: 500 ppm and SO<sub>2</sub>: 2000 ppm).

#### 5.3.4.1.1 Screening test of flue gas contaminants

Figure 5.22 shows the mass variations observed as MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) were separately subjected to 5000 ppm of contaminant over a heat ramp from 20 to 110 °C with a heating rate of 2 °C min<sup>-1</sup>. The time of 65 min corresponds to the duration of exposure to an Ar/contaminant mixture. After 65 min, the flowing Ar/contaminant mixture was replaced by flowing Ar and the temperature remained at 110 °C for 1 h (omitted in the graphs). Mixed coloured samples of STA-16(Co) (pinkish purple and dark purple) were obtained after the NO<sub>2</sub> and SO<sub>2</sub> screening tests.

Figure 5.22a shows the results of the screening tests using NO. An initial mass gain and then subsequent mass loss were observed along the heat ramp and the isothermal period, consistent with the adsorption of NO and its subsequent desorption from each of the MOFs.<sup>a</sup> The mass uptake maximum in MIL-53(Al)-NH<sub>2</sub> (0.19 mmol g<sup>-1</sup>, 0.04 mol NO per mol NH<sub>2</sub>) occurred at 55 °C, but the maxima in the rigid frameworks, MIL-100(Fe) (0.15 mmol g<sup>-1</sup>; 0.05 mol NO per mol CUS) and STA-16(Co) (0.30 mmol g<sup>-1</sup>; 0.08 mol NO per mol CUS) were observed at 65 °C and 75 °C, respectively. The difference in temperature required to reach maximum mass uptake can be attributed to slightly different adsorption energies between the MOFs examined. The exposure experiments, discussed in the next section, were therefore conducted at 50 °C as each of the MOFs, just a little further along the heat ramp and during the isothermal period suggests that the adsorption and desorption of NO can be classified as a physisorption process.

The results of the screening tests using NO<sub>2</sub> (Figure 5.22b) show that MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub> initially gained 0.28 mmol  $g^{-1}$  (0.09 mol NO<sub>2</sub> per mol CUS) and 0.83 mmol  $g^{-1}$  (0.20 mol NO<sub>2</sub> per mol NH<sub>2</sub>), respectively, along the heat ramp up to 80 °C.

<sup>&</sup>lt;sup>a</sup> The small net mass loss for all MOFs during the NO screening and for MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub> during the SO<sub>2</sub> screening at 117 °C are regarded as artefacts due to an imperfect blank correction rather than mass loss due the decomposition (ligand replacement) of the frameworks. The feature in the TGA profiles of the NO screening experiments (t>52 min) are regarded as artefacts due to electronic noise. To correct these artefacts the blank experiments should be repeated.

This mass gain is consistent with the adsorption of NO<sub>2</sub>. A little further along the heat ramp, a decline in mass was observed, consistent with the partial desorption of NO<sub>2</sub> from MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub>. Further desorption of NO<sub>2</sub> was observed from MIL-100(Fe) under the isothermal period, but no further mass changes occurred in MIL-53(Al)-NH<sub>2</sub>. After 65 min (not shown here) the Ar/NO<sub>2</sub> mixture was replaced by pure Ar, which was purged over the sample for 1 h at 110 °C, before the samples were cooled to 20 °C. This final Ar treatment of MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub> resulted in the desorption of 0.11 mmol g<sup>-1</sup> and 0.07 mmol g<sup>-1</sup> of NO<sub>2</sub>, respectively. However, STA-16(Co) adsorbed 1.28 mmol g<sup>-1</sup> (0.33 mol NO<sub>2</sub> per mol CUS) of NO<sub>2</sub> along the heat ramp and under the isothermal period, but no desorption of NO<sub>2</sub> was observed during the 65 min period of the Ar/NO<sub>2</sub> flow. The final Ar treatment at t>65 min (not shown here) resulted in the desorption of 0.21 mmol g<sup>-1</sup> of NO<sub>2</sub>. The slow and partial desorption of NO<sub>2</sub> from each of the MOFs suggests that some of the NO<sub>2</sub> becomes chemisorbed into the structures. The subsequent exposure of the MOFs to 10000 ppm of NO<sub>2</sub> was conducted at 80 °C, as the screening experiments showed that the maximum mass gain occurred at this temperature.

The results of the screening tests using  $SO_2$  (Figure 5.22c) show an initial mass gain in each of the MOFs consistent with the adsorption of SO<sub>2</sub>. The maximum mass uptake declined in the order STA-16(Co) (0.47 mmol  $g^{-1}$ ; 0.12 mol SO<sub>2</sub> per mol CUS) > MIL-53(Al)-NH<sub>2</sub> (0.24 mmol g<sup>-1</sup>, 0.06 mol SO<sub>2</sub> per mol NH<sub>2</sub>) > MIL-100(Fe) (0.14 mmol g<sup>-1</sup>; 0.04 mol SO<sub>2</sub> per mol CUS) and occurred at 70, 50 and 45 °C, respectively. As discussed for the NO screening tests, this difference in temperature is presumably due to the different adsorption energies of the MOFs examined. The subsequent exposure to 10000 ppm SO<sub>2</sub> (next section) was conducted at 50 °C, as, at this temperature, each sorbent exhibited a near maximum weight gain. MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub> exhibited a quantitative mass loss a little further along the heat ramp, consistent with the desorption of SO<sub>2</sub>; however, STA-16(Co) did not.<sup>a</sup> SO<sub>2</sub> was only partially desorbed from STA-16(Co) beyond 70 °C and during the isothermal period. After 65 min (not shown here) the Ar/SO<sub>2</sub> mixuture was replaced by flowing Ar for 1 h, which resulted in a further desorption of SO<sub>2</sub> from STA-16(Co) with 0.06 mmol g<sup>-1</sup> of SO<sub>2</sub> being retained after the isothermal period. The slow desorption from STA-16(Co) suggests that an increase in the duration of the final Ar purge will presumably result in a complete desorption of SO<sub>2</sub>. It is therefore assumed that the adsorption of SO<sub>2</sub> occurred via a physisorption process for each of the MOFs examined.



**Figure 5.22:** TGA of exposure of MIL-100(Fe) (black), MIL-53(Al)-NH<sub>2</sub> (yellow) and STA-16(Co) (purple) to atmospheres comprising 5000 ppm of (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub> over a heat ramp from 20 to 110 °C with a heating rat of 2 °C min<sup>-1</sup>.

The results of the screening tests suggest that the adsorption mechanism is strongly dependent on the MOF. The adsorption of NO and  $SO_2$  in each of the MOFs occurred via a physisorption process, but some of the NO<sub>2</sub> was apparently chemisorbed into the frameworks. Furthermore, higher mass changes were observed for the phosphonate MOF, STA-16(Co), during the screening tests of all three contaminants.

#### 5.3.4.1.2 PXRD studies after the exposure to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub>

The results of the PXRD studies for the frameworks before and after separate exposure to 10000 ppm NO, NO<sub>2</sub> and SO<sub>2</sub> at ambient and elevated temperatures are shown in Figure 5.23. The intensities of MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub> were multiplied by 5 to facilitate comparison with the more intense data for the fresh materials. No changes in

colour were observed for MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub>. A mixed coloured (pinkish purple and dark purple) sample of STA-16(Co) was obtained after the exposure to NO (50 °C) and SO<sub>2</sub> (room temperature, 50 °C). The PXRD results of the samples before and after the screening tests are shown in the supplementary information.

Figure 3.23a shows the intensity data obtained for fresh and spent MIL-100(Fe). The intensity of the pattern was diminished after the separate exposure to NO, NO<sub>2</sub> and SO<sub>2</sub> consistent with the loss of crystallinity. This loss of crystallinity might be due to the loss of long-range crystallographic ordering or due to the partial collapse of the framework. Increasing the temperature from room temperature to 50 °C (NO, SO<sub>2</sub>) or 80 °C (NO<sub>2</sub>) did not have any considerable impact on the intensities of the diffraction pattern. This is consistent with the powder X-ray diffractograms after the screening tests (supplementary information), which showed a progressive decline in intensities of MIL-100(Fe).

The powder X-ray diffractograms of MIL-53(Al)-NH<sub>2</sub> before and after separate exposure to the contaminants are shown in Figure 5.23b. Subjecting the MOF to either NO, NO<sub>2</sub> or SO<sub>2</sub> again resulted in a progressive decrease in intensity, which suggests either a loss in long-range crystallographic ordering or a partial decomposition of the framework. The powder patterns of MIL-53(Al)-NH<sub>2</sub> after the adsorption of NO and SO<sub>2</sub> did not show any additional peaks, which implies that the remainder of the framework existed in its *np* form. In contrast to this, the exposure of MIL-53(Al)-NH<sub>2</sub> to NO<sub>2</sub> at 25 °C resulted in partial phase change from the *np* into the *lp* form, which was completed at 80 °C (Figure 5.23d). Evacuating the NO<sub>2</sub> treated sample at room temperature resulted in a transformation back into the *np* form consistent with the reversibility of the breathing effect. The intensity data after the 5000 ppm NO<sub>2</sub> screening test (supplementary information) also showed a decrease in intensity, which is consistent with the results discussed above. Furthermore, a splitting of the peak at 20~12° was observed, which suggests that MIL-53(Al)-NH<sub>2</sub> existed in both *lp* and *np* form.



**Figure 5.23:** PXRD of (a) MIL-100(Fe), (b) MIL-53(Al)-NH<sub>2</sub> and (c) STA-16(Co) before and after contaminant treatment (10000 ppm) at room temperature (RT) and at 50 or 80 °C. (d) Comparison of MIL-53(Al) lp with the samples exposed to NO<sub>2</sub> and CoMOF with STA-16(Co) exposed to SO<sub>2</sub>. MIL-53(Al) lp [38] and CoMOF [43] were simulated using Materials Studio [44].

The powder X-ray diffraction patterns of fresh and exposed STA-16(Co) are shown in Figure 5.23c. The adsorption of each contaminant was found to result in the decline in the intensities consistent with the loss of long-range crystallographic ordering or the partial collapse of the framework in most cases. The exposure to NO<sub>2</sub> at 80 °C led to a complete loss of the long-range crystallographic ordering or a complete loss of the structure. Additional peaks after the exposure to NO at 50 °C and SO<sub>2</sub> at room temperature and 50 °C were observed, which indicated the partial transformation of STA-16(Co) into the non-porous polymorph CoMOF (PXRD pattern compared in Figure 5.23d), whose

structure was reported recently (see also Chapter 6) [43]. This result is consistent with the observed colour change. The partial transformation of STA-16(Co) into the CoMOF was also observed after the screening tests (see Section 5.3.4.1.1) with NO<sub>2</sub> and SO<sub>2</sub> (supplementary information). In contrast to the intensity data of STA-16(Co) measured after the exposure to 10000 ppm NO<sub>2</sub> discussed above, the powder diffractogram after the screening test with 5000 ppm NO<sub>2</sub> did not show a complete loss in intensity. This suggests that complete loss in long-range crystallographic ordering or decomposition of the framework only occurs at NO<sub>2</sub> concentration above 5000 ppm. In the case of the NO screening test (supplementary information), no additional peaks corresponding to the CoMOF were observed, which is also sought to be due to the lower contaminant concentration of 5000 ppm used in the screening test.

It can be concluded, that the flue gas contaminants NO, NO<sub>2</sub> and SO<sub>2</sub> have a significant impact on the stability of MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) at 10000 ppm. It is therefore required to remove these contaminants prior to the post-combustion capture of CO<sub>2</sub>. Further analyses, e.g. N<sub>2</sub> adsorption and desorption at -196 °C, should be conducted on the MOFs after the exposure to the contaminants to determine the loss of pore volume.

#### 5.3.4.1.3 FTIR studies after the exposure to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub>

The results of the FTIR measurements of MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) before and after separate exposure to 10000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub> at both ambient and elevated temperatures are shown in Figure 5.24. The spectra of MIL-100(Fe) and STA-16(Co) are shown in the spectral range of 1700 to 700 cm<sup>-1</sup>. For MIL-53(Al)-NH<sub>2</sub> the spectral range was extended to 2300 to 700 cm<sup>-1</sup>. At higher wavenumbers no changes in the spectra were observed. This region is therefore omitted. The FTIR spectra of the MOFs after the screening tests are presented in the supplementary material and exhibited no changes unless stated otherwise.

The IR spectra of MIL-100(Fe) before and after the separate exposure to the contaminants are shown in Figure 5.24a. Characteristic IR bands of fresh MIL-100(Fe) include (1) the band at 1620 cm<sup>-1</sup> corresponding to adsorbed H<sub>2</sub>O, (2) the C=C stretch at 1569 cm<sup>-1</sup>, (3) the O-C-O stretch at 1435 cm<sup>-1</sup> and (4) the C-H deformation at 1107, 924 and 756 cm<sup>-1</sup> [45]. After the exposure to NO<sub>2</sub> one new mode of absorption was observed at 1524 cm<sup>-1</sup>, consistent with the formation of a monodentate nitrate species [46]. This result suggest that
$NO_2$  was chemisorbed onto the uncoordinated Fe(III) sites and is in good agreement with the results obtained from the screening test. Subjecting MIL-100(Fe) to NO and SO<sub>2</sub> did not result in any obvious perturbations of the framework structure, which implies that these contaminants are physisorbed rather than chemisorbed. This is consistent with the results from the screening tests.



-MOF -NO RT -NO 50 °C -NO<sub>2</sub> RT -NO<sub>2</sub> 80 °C - SO<sub>2</sub> RT - SO<sub>2</sub> 50 °C Figure 5.24: FTIR spectra of (a) MIL-100(Fe), (b) MIL-53(Al)-NH<sub>2</sub> and (c) STA-16(Co) before and after exposure to the contaminants (10000 ppm) at room temperature (RT), 50 °C (NO, SO<sub>2</sub>) and 80 °C (NO<sub>2</sub>).

The IR spectra of MIL-53(Al)-NH<sub>2</sub> before and after individual exposure to 10000 ppm NO, NO<sub>2</sub> and SO<sub>2</sub> are shown in Figure 5.24b. MIL-53(Al)-NH<sub>2</sub> exhibited the following characteristic IR absorptions: (1) the asymmetrical and symmetrical stretching of primary amine groups [21] at 3500 and 3387 cm<sup>-1</sup>, respectively, (2) the N-H bending [47] at 1620 cm<sup>-1</sup>, (3) the symmetric C=O stretch[38] at 1555 cm<sup>-1</sup>, (4) the aromatic C=C stretch

[45] at 1493 cm<sup>-1</sup>, (5) the C-N stretch distinctive of aromatic amines [47] at 1340 cm<sup>-1</sup>, (5) the symmetric O-C-O stretch [38, 45] at 1439 and 1379 cm<sup>-1</sup> and (6) the C-H deformation [47] at 1160 and 772 cm<sup>-1</sup>. Subjecting MIL-53(Al)-NH<sub>2</sub> to NO resulted in no obvious changes in the structure, but additional absorption modes were observed after the exposure to NO<sub>2</sub> and SO<sub>2</sub>. The appearance of the band at 2254 cm<sup>-1</sup> after the adsorption of NO<sub>2</sub> is due to hydrogen bonded NO<sup>+</sup> species, which is formed via a disproportionation reaction of  $N_2O_4$  [48]. Two new IR absorptions were observed at 1512 and 1031 cm<sup>-1</sup> consistent with the asymmetric and symmetric stretching vibration of NO<sub>3</sub><sup>-</sup> species, a by-product of NO<sup>+</sup>, respectively [48]. Further perturbations of the framework structure include changes in the absorption modes of (1) the C-O stretching vibration centred at 1439 cm<sup>-1</sup> (especially at 80 °C), (2) the C-H deformation centred at 1160 cm<sup>-1</sup> and (3) the N-H bend centred at  $1620 \text{ cm}^{-1}$ . These results suggest that NO<sub>2</sub> is physisorbed rather than chemisorbed into the framework as was indicated in the 5000 ppm NO<sub>2</sub> screening experiments discussed above. This difference in adsorption mechanism could potentially be due to the exposure of MIL-53(Al)-NH<sub>2</sub> to NO<sub>2</sub> up to a temperature of 117 °C during the screening experiments. Further experiments, such as in-situ PXRD and in-situ FTIR, could be conducted in order to get a better understanding of the different adsorption behaviours under the different conditions. After exposing MIL-53(Al)-NH<sub>2</sub> to SO<sub>2</sub> a new IR absorption mode was present at 1144 cm<sup>-1</sup>, which can be assigned to the symmetric S=O stretch [49]. This result suggests that SO<sub>2</sub> was adsorbed via physisorption rather than chemisorption.

Figure 5.24c shows the IR spectra of fresh and exposed STA-16(Co). Characteristic modes of absorption in STA-16(Co) include: (1) the H-O-H stretch [50] and bend at 3432 cm<sup>-1</sup> and 1654/1637 cm<sup>-1</sup>, respectively, (2) the methylene C-H [50] stretch at 2950 cm<sup>-1</sup>, (3) the P-O(H) stretch [50] at 2865 and in the region of 1167 to 966 cm<sup>-1</sup>, (4) the C-C stretch [51] at 1454 cm<sup>-1</sup>, (5) the C-N-stretch at 1378 cm<sup>-1</sup> and (6) the P=O stretch [43] at 1351 to 1224 cm<sup>-1</sup>. The disappearance of the band at 1573 cm<sup>-1</sup> in the spectra of the contaminant exposed STA-16(Co) samples was due to the removal of hydrogen bonded H<sub>2</sub>O molecules during the vacuum pre-treatment. Some moisture was re-adsorbed during the storage of STA-16(Co), which is apparent in the NO spectra. Heating STA-16(Co) at 50 °C in the presence of NO resulted in new bands at 1624 cm<sup>-1</sup> assigned to adsorbed NO, consistent with the physisorption of this contaminant [52]. A new mode of absorption appeared at 1470 cm<sup>-1</sup> after the exposure to NO<sub>2</sub>, consistent with the formation of the monodentate nitrate species.[46] This result suggests that NO<sub>2</sub> was chemisorbed onto the CUS, which is

in good agreement with the result from the screening test. Further perturbations of the framework were observed in a broadening of the bands upon NO<sub>2</sub> exposure, which can be attributed to the interaction of the contaminant with the CUS. Exposure of STA-16(Co) to  $SO_2$  did not result in any changes of the present absorption modes and suggests that the contaminant was physisorbed into the framework.

In conclusion, the presence of CUS in MIL-100(Fe) and STA-16(Co) resulted in the chemisorption of NO<sub>2</sub> via the formation of a monodentate nitrate species. NO and SO<sub>2</sub> were found to be physisorbed into MIL-100(Fe) and STA-16(Co), due to the lack of ligation to the uncoordinated Fe(III) and Co(II) sites. Although structural changes were observed in MIL-53(Al)-NH<sub>2</sub>, especially upon NO<sub>2</sub> exposure, each of the contaminants was physisorbed into the framework.

#### 5.3.4.2 Sorption of flue gas contaminants and CO<sub>2</sub>

#### 5.3.4.2.1 Flue gas contaminant cycling experiments

Figure 5.25 to 5.27 show the mass changes of the five cycle experiments carried out at 25 °C corresponding mass uptakes in each and the cycle. The partial pressures/concentrations of the contaminants were varied between 0 and 500 ppm (NO or NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>) or 5000 ppm (NO or NO<sub>2</sub> or SO<sub>2</sub>) to determine the impact of different flue gas contaminant concentrations on the framework stability and the sorption behaviour. The temperature was set to 25 °C due to higher CO<sub>2</sub> uptakes of these materials at lower temperatures. The time scale shown in the TGA profiles include the pre-treatment at 110 °C under Ar at t<0 min and the final treatment at 110 °C under Ar at t>220 min.<sup>b</sup> The mass gained during the adsorption step in each cycle (Figure 5.25-5.27, right) was calculated by subtracting the mass change at 500, 2000 or 5000 ppm by the mass change at 0 ppm. The samples were analysed via PXRD and FTIR after each contaminant cycling experiment (supplementary materials). No changes in the diffractogram or FTIR spectra were observed unless stated otherwise.

The individual contaminant cycling profiles of MIL-100(Fe) (Figure 5.25) show higher mass changes in the presence of 5000 ppm of NO, NO<sub>2</sub> and SO<sub>2</sub> than for the cycling of 500 ppm NO or NO<sub>2</sub> and 2000 ppm SO<sub>2</sub>. A progressive mass gain was observed in each cycling experiment, consistent with the accumulation of the contaminants and the slow

<sup>&</sup>lt;sup>b</sup> The mass gains during the cooling steps in the TGA profiles of MIL-100(Fe) and STA-16(Co) are regarded as artefacts due to the change in temperature.

adsorption/desorption kinetics. The accumulation of NO, NO<sub>2</sub> and SO<sub>2</sub> further resulted in a progressive decline in mass gained from cycle one to five. The greatest reduction in mass uptake was observed in the cycling experiment using 5000 ppm NO, for which the uptake in cycle five was just 20 % of cycle one. This result suggests that the NO saturation at the higher contaminant concentration was almost achieved. The mass uptakes of MIL-100(Fe) during the cycling with the contaminant concentrations relevant to flue gas revealed that NO and NO<sub>2</sub> were adsorbed to a similar extent. The higher concentration of SO<sub>2</sub> in flue gas resulted in a higher mass gain than in the case of NO and NO<sub>2</sub>.

During the cycling process a partial desorption of NO<sub>2</sub> (5000 ppm) and SO<sub>2</sub> (2000 and 5000 ppm) upon lowering the partial pressure to 0 ppm was observed in most cycles. The TGA profiles of the cycling experiments using 5000 or 500 ppm NO and 500 ppm NO<sub>2</sub> showed an apparent mass increase during the desorption steps.<sup>c</sup> Heating the samples to 110 °C for 30 min under flowing Ar resulted in the quantitative desorption of NO (500 and 5000 ppm) and SO<sub>2</sub> (2000 and 5000 ppm), consistent with the physisorption of these contaminants. These results are in good agreement with those form the FTIR studies of MIL-100(Fe) after the separate exposure to 10000 ppm of NO and SO<sub>2</sub>. Almost quantitative desorption upon heating was also observed during the cycling with 500 ppm NO<sub>2</sub>, but not with 5000 ppm NO<sub>2</sub>. These results suggest that NO<sub>2</sub> was chemisorbed at both 500 and 5000 ppm, consistent with the observations from the screening tests and the formation of a monodentate nitrate species in the FTIR spectra of MIL-100(Fe) after the exposure to 10000 ppm NO<sub>2</sub>. Furthermore, the almost quantitative desorption of 500 ppm NO<sub>2</sub> upon heating is considered to be a result of the lower overall mass change (0.30 mmol g<sup>-1</sup>) than in the case of 5000 ppm NO<sub>2</sub>.

PXRD measurements of MIL-100(Fe) after the contaminant cycling revealed a decline in intensities corresponding to the loss in long-range crystallographic ordering or the partial decomposition of the framework, consistent with those previously noted after the exposure to 10000 ppm of contaminants.

The TGA profiles of the contaminant cycling on MIL-53(Al)-NH<sub>2</sub> and the mass changes in the adsorption part of each cycle are shown in Figure 5.26. An increase in contaminant

<sup>&</sup>lt;sup>c</sup> The mass increase occurs due to non-ideal gas flow in the TGA feed gas arrangement such that there is incomplete clearance of the contaminant gas from the feed gas stream over the time scale of the desorption step of these experiments (20 min). The residual contaminant gas in the feed gas together with the high affinity of the adsorbent for the NO/NO<sub>2</sub> leads to the continuous adsorption of these contaminants.

concentration resulted in higher mass changes for all contaminants examined. The accumulation of the contaminants was in most cases more pronounced for MIL-53(Al)-NH<sub>2</sub> than for MIL-100(Fe), which is in good agreement with the mass changes observed during the screening tests. No further mass uptake was observed in cycle five of the 5000 ppm NO cycling experiment, consistent with the accumulation of 0.50 mmol  $g^{-1}$  of NO (0.12 mmol NO per mol NH<sub>2</sub>). This result suggests that NO saturation was achieved at the higher concentration.



**Figure 5.25:** TGA profile (left) and the mass gain (right) of different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-100(Fe) during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm.

Lowering the partial pressure to 0 ppm resulted in a partial mass loss during the cycling experiments using 2000 or 5000 ppm SO<sub>2</sub>, but no desorption was observed during the cycling with NO<sub>2</sub> and NO at both concentrations. While the TGA profiles of NO<sub>2</sub> at 5000 and 500 ppm show a constant mass upon lowering the partial pressure, an apparent rise in mass was observed for 500 and 5000 ppm NO.<sup>°</sup> These results suggest that the interaction between the framework and SO<sub>2</sub> was weaker than for NO and NO<sub>2</sub>. The quantitative desorption was obtained upon heating the samples to 110 °C under Ar for 30 min after all cycling processes, consistent with the physisorption of all contaminants examined.

PXRD diffractograms (supplementary information) revealed that the flexibility of the framework was reversible under heating at 110 °C under Ar atmosphere for 30 min. This is contradictory with the results obtained after the screening test in which both lp and np phase of MIL-53(Al)-NH<sub>2</sub> were present. This implies that the flexibility becomes irreversible at higher adsorption temperatures.



**Figure 5.26:** TGA profile (left) and the mass gain (right) of different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-53(Al)-NH<sub>2</sub> and during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm.

The mass changes observed during the contaminant cycling experiments on STA-16(Co) (Figure 5.27) revealed that increasing the contaminant concentration/partial pressure resulted in higher mass changes, consistent with the results obtained during the cycling on MIL-100(Fe) and MIL-53(Al)-NH<sub>2</sub>. The progressive reduction in mass uptake from cycle to cycle was due to the accumulation of the contaminants.

A partial desorption upon lowering the partial pressures during the  $SO_2$  cycling and constant mass during the NO<sub>2</sub> cycling were observed. The TGA profiles of STA-16(Co) using 5000 and 500 ppm NO show an apparent increase in mass during the desorption part of the cycling.<sup>c</sup> Similar to the results discussed for MIL-100(Fe), complete desorption was achieved in most cases upon heating at 110 °C under flowing Ar for 30 min. One exception to this was the cycling with 5000 and 500 ppm NO<sub>2</sub>, consistent with the chemisorption of the contaminant. This lack in complete desorption was more pronounced for the cycling at 5000 ppm NO<sub>2</sub>, which showed only a loss of 0.40 mmol g<sup>-1</sup>. This result suggests that desorption was more readily achieved at lower concentrations due to the lower overall mass change. The quantitative desorption of NO and SO<sub>2</sub> is consistent with the physisorption of these contaminants.

Powder diffractograms of STA-16(Co) after the contaminant cycling revealed a loss in crystallinity, consistent with a loss in long-range crystallographic ordering or a partial decomposition of the structure. A partial transformation into the non-porous CoMOF was only observed after the cycling using 2000 ppm SO<sub>2</sub>, which is in good agreement with

PXRD data after exposure to 10000 ppm  $SO_2$ . The absence of peaks corresponding to CoMOF after the cycling with 5000 ppm  $SO_2$  is considered to be due to the very small sample amount used for the PXRD measurement, which might have not been representative for the bulk of the sample.



**Figure 5.27:** TGA profile (left) and the mass gain (right) of different concentrations of NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) during the contaminant cycling at 25 °C. The partial pressures of the contaminant were varied between 0 and 500 or 2000 or 5000 ppm.

The results of the contaminant cycling experiments showed that the chemisorption of  $NO_2$  onto CUS in MIL-100(Fe) and STA-16(Co) resulted in the irreversible adsorption of the contaminant, especially at 5000 ppm. At this concentration of  $NO_2$ , the mass change in MIL-53(Al)-NH<sub>2</sub> was found to be completely reversible, which can be attributed to the flexibility of the framework as discussed previously (Sections 5.3.4.1.3 and 5.3.4.1.3). The accumulations of the contaminants in MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) will presumably have a significant impact on the CO<sub>2</sub> capture during post-combustion.

#### 5.3.4.2.2 Flue gas contaminant cycling experiments in the presence of $CO_2$

Figure 5.28 to 5.30 show the mass variations as each of the samples were separately subjected to the contaminants in the presence of  $CO_2$  during the five cycle experiments at 25 °C to demonstrate the likely impact of the flue gas contaminants on the  $CO_2$  capacity. The partial pressures of  $CO_2$  were varied between 0.05 and 0.15 bar, but the contaminant partial pressures were varied between 0 and 500 ppm for NO and NO<sub>2</sub> and between 0 and 2000 ppm for SO<sub>2</sub>. The results were then compared to the first five cycles of the  $CO_2$  cycling experiments. The mass loss in each cycle is defined as the difference in mass

change between 0.15 and 0.05 bar. FTIR spectra and powder diffractograms after the  $CO_2$ /contaminant cycling are shown in the supplementary information and did not show any changes unless stated otherwise.

Figure 5.28 shows the mass changes and losses during the  $CO_2$ /contaminant and  $CO_2$  cycling processes in MIL-100(Fe). The average mass uptake during the  $CO_2$  cycling in the absence of contaminants was determined to be 0.15 mmol g<sup>-1</sup>. A comparison of the average  $CO_2$  uptake and the mass uptakes of NO, NO<sub>2</sub> and SO<sub>2</sub> at concentrations typical of flue gas suggests that  $CO_2$  was presumably adsorbed selectively into the framework during the  $CO_2$ /contaminant experiments.

The TGA profile of the  $CO_2$  cycling shows that equilibrium was achieved during the 20 min allowed in each adsorption and desorption step, consistent with the good adsorption and desorption kinetics. Equilibrium was not achieved during the CO<sub>2</sub>/NO (cycles one to four),  $CO_2/NO_2$  and  $CO_2/SO_2$  as a result of the slower adsorption kinetics. Furthermore, the accumulation of the flue gas contaminants observed during the contaminant cycling experiments in the absence of CO<sub>2</sub> resulted in additional mass changes beyond those observed for CO<sub>2</sub> alone. The CO<sub>2</sub> capacities during the CO<sub>2</sub>/NO and  $CO_2/NO_2$  cycling process were estimated using the following assumptions: (1) the mass loss observed during the CO2/NO and CO2/NO2 cycling experiments was due to the desorption of CO<sub>2</sub>, as NO and NO<sub>2</sub> was not desorbed during the contaminant cycling experiments in the absence of  $CO_2$ , and (2) the amount of  $CO_2$  desorbed was consistent with the amount of  $CO_2$  adsorbed. Under these assumptions, the  $CO_2$  capacities were found to be diminished to 0.08 mmol  $g^{-1}$  in each cycle for both NO and NO<sub>2</sub>. This result is consistent with the comparable mass uptakes in each cycle during the contaminant cycling in the absence of  $CO_2$ . A different assumption needs to be applied in the case of  $CO_2/SO_2$ cycling due to the partial desorption of 2000 ppm SO<sub>2</sub> during the contaminant cycling. We assigned the steep mass gain at the beginning of each adsorption step to the adsorption of  $CO_2$  and the following rise in mass to the adsorption of  $SO_2$ . The calculated  $CO_2$  and  $SO_2$ uptakes were approximately 0.11 mmol  $g^{-1}$  and 0.05 mmol  $g^{-1}$ . The value for SO<sub>2</sub> is in good agreement with the mass gain in the last cycle of the contaminant cycling experiment. The reduction in  $CO_2$  uptake in each cycle from 0.15 mmol g<sup>-1</sup> in the absence of the contaminant to 0.11 mmol  $g^{-1}$  in the presence of SO<sub>2</sub> is a result of the accumulation and competitive adsorption of SO<sub>2</sub>.



**Figure 5.28:** TGA profile (left) and mass loss (right) of  $CO_2$  with and without NO,  $NO_2$  and  $SO_2$  on MIL-100(Fe) at 25 °C. Cycling experiments were conducted by varying the  $CO_2$  partial pressure between 0.05 and 0.15 bar and the contaminant partial pressure between 0 ppm and 500 ppm (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>).

After the CO<sub>2</sub>/contaminant cycling experiments the crystallinities were diminished (supplementary information), which is consistent with the loss in long-range crystallographic ordering or the partial collapse of the framework. This result is in good agreement with those previously noted after the screening tests, individual exposure to 10000 ppm of contaminant and contaminant cycling.

The mass variations after subjecting MIL-53(Al)-NH<sub>2</sub> to the CO<sub>2</sub>/contaminant mixtures or to CO<sub>2</sub> alone during the cycle experiments are shown in Figure 5.29. The comparison of the average CO<sub>2</sub> uptake (0.66 mmol g<sup>-1</sup>) with the average mass gain in each cycle during the contaminant cycling with 500 ppn NO (0.04 mmol g<sup>-1</sup>) or NO<sub>2</sub> (0.08 mmol g<sup>-1</sup>) and 2000 ppm SO<sub>2</sub> (0.11 mmol g<sup>-1</sup>) revealed that CO<sub>2</sub> should be adsorbed more selectively than the contaminants.

During the CO<sub>2</sub> cycling with and without NO equilibration in mass was observed in each adsorption step. The additional mass gain during the equilibration time of 20 min in the TGA profiles of CO<sub>2</sub>/NO<sub>2</sub> and CO<sub>2</sub>/SO<sub>2</sub> is consistent with the slow adsorption kinetics of NO<sub>2</sub> and SO<sub>2</sub>. The mass changes prior to the first cycle (Feature A in Figure 10 left) corresponding to the adsorption of CO<sub>2</sub> at 0.05 bar vary from experiment to experiment.<sup>d</sup>

<sup>&</sup>lt;sup>d</sup> Feature A was a result of a default of the flow meter, which resulted in a small flow of  $CO_2$  during the initial pre-treatment of the sample, especially during the equilibriation (40 min at 25 °C in flowing Ar) prior to the contaminant/CO<sub>2</sub> cycling process. As a result the mass change during the contaminant/CO<sub>2</sub> cycling is lower than during the  $CO_2$  cycling experiment.

The increase in mass at 0.05 bar from one cycle to the next during the CO<sub>2</sub>/contaminant cycling experiments is consistent with the accumulation of the contaminants. The calculation of the CO<sub>2</sub> capacities during the CO<sub>2</sub>/contaminant experiments was conducted by using the assumptions made for MIL-100(Fe). The calculated CO<sub>2</sub> uptakes were determined to be 0.52, 0.41 and 0.32 mmol g<sup>-1</sup> for NO, NO<sub>2</sub> and SO<sub>2</sub>, respectively. The degree to which the CO<sub>2</sub> capacities were diminished is consistent with the higher mass gain in each cycle in the 2000 ppm SO<sub>2</sub> cycling experiments in the absence of CO<sub>2</sub>, than in the 500 ppm NO and 500 ppm NO<sub>2</sub> cycling experiments in the absence of CO<sub>2</sub>.



**Figure 5.29:** TGA profile (left) and mass loss (right) of  $CO_2$  with and without NO, NO<sub>2</sub> and SO<sub>2</sub> on MIL-53(Al)-NH<sub>2</sub> at 25 °C. Cycling experiments were conducted by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar and the contaminant partial pressure between 0 ppm and 500 ppm (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>).

After the CO<sub>2</sub>/contaminant cycling experiments the crystallinities were diminished (supplementary information), which is consistent with the loss in long-range crystallographic ordering or the partial collapse of the framework. No additional peaks corresponding to the lp form of MIL-53(Al)-NH<sub>2</sub> were observed after the CO<sub>2</sub>/NO<sub>2</sub> cycling experiment, which suggests that the flexibility of the MOF is reversible upon heating to 110 °C under flowing Ar for 30 min.

The changes in mass after subjecting STA-16(Co) to the CO<sub>2</sub>/contaminant mixtures or to  $CO_2$  alone are shown in Figure 5.30. The comparison of the average  $CO_2$  uptake (0.21 mmol g<sup>-1</sup>) with the contaminant uptakes from the contaminant cycling experiments suggests that  $CO_2$  should be selectively adsorbed in the presence of NO and NO<sub>2</sub>, but a more competitive adsorption is projected to occur in the presence of SO<sub>2</sub>.

The equilibration time of 20 min for each adsorption and each desorption step was insufficient in most cases. The progressing mass increase during the  $CO_2$  cycling experiment suggests that strong interactions of the  $CO_2$  with the CUS occur, which result in slow adsorption kinetics (see Chapter 3.6). The accumulation of the contaminants was especially observed during the  $CO_2/SO_2$  cycling experiment, which showed mass changes beyond those observed for  $CO_2$  alone. In contrast to this, the overall mass changes in the  $CO_2/NO_2$  TGA profiles were lower than those observed for  $CO_2$  alone.



**Figure 5.30:** TGA profile (left) and mass loss (right) of CO<sub>2</sub> with and without NO, NO<sub>2</sub> and SO<sub>2</sub> on STA-16(Co) at 25 °C. Cycling experiments were conducted by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar and the contaminant partial pressure between 0 ppm and 500 ppm (NO, NO<sub>2</sub>) or 2000 ppm (SO<sub>2</sub>).

The estimation of the  $CO_2$  capacities was conducted using the assumptions stated above for MIL-100(Fe). The  $CO_2$  uptakes were diminished to approximately 0.11, 0.09 and 0.14 mmol g<sup>-1</sup> for NO, NO<sub>2</sub> and SO<sub>2</sub>, respectively.

The PXRD measurements after the  $CO_2$ /contaminant cycling experiments revealed a decrease in crystallinity, consistent with the loss in long-range crystallographic ordering or the partial decomposition of the framework. In contrast to the contaminant cycling experiments in the absence of  $CO_2$ , no additional peaks corresponding to the partial transformation into the CoMOF were present. This suggests that  $CO_2$  presumably prevents the transformation.

The presence of the contaminants resulted in a deterioration of the  $CO_2$  capacities during cycling processes, which suggests that the removal of these contaminants is required prior to the post-combustion capture of  $CO_2$ . However, further analyses should be conducted to

determine the  $CO_2$ /contaminant selectivities and the accurate  $CO_2$  uptakes. Furthermore, the presence of  $H_2O$  in flue gas is likely to impact the adsorption of the contaminants and needs to be evaluated.

#### 5.3.5 Conclusion

The effects of NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability and capture ability of MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) were studied by conducting a series of screening tests, FTIR studies, PXRD studies and CO<sub>2</sub> cycling experiments with and without the contaminants.

FTIR studies before and after the exposure of the materials to 10000 ppm of contaminants indicated that  $NO_2$  interacted strongly with the CUS of MIL-100(Fe) and STA-16(Co) by forming a monodentate nitrate species. The spectra of each of the MOFs after the exposure to NO and SO<sub>2</sub> indicated that these contaminants were physisorbed. Furthermore, the adsorption of NO<sub>2</sub> in MIL-53(Al)-NH<sub>2</sub> was found to proceed via physisorption rather than chemisorption.

PXRD studies revealed the deterioration of the crystallinities in all MOFs examined, consistent with the loss in long-range crystallographic ordering or the partial decompositions of the frameworks. STA-16(Co) was partially transformed into the CoMOF, a non-porous polymorph, and in the case of NO<sub>2</sub> adsorption at 80 °C the framework was completely decomposed. The adsorption of 10000 ppm of NO<sub>2</sub> into the flexible framework of MIL-53(Al)-NH<sub>2</sub> resulted in a phase change from the *np* into the *lp* form. The flexibility of the framework was found to be reversible upon vacuum activation at room temperature or upon heating to 110 °C under flowing Ar for 30 min.

The flexibility of MIL-53(Al)-NH<sub>2</sub> was found to be beneficial for the complete recovery of the material after the TGA experiment with 5000 ppm of NO<sub>2</sub>. MIL-100(Fe) and STA-16(Co) exhibited an irreversible adsorption of 5000 ppm NO<sub>2</sub>, which was due to the strong interaction of the contaminant with the CUS, consistent with the chemisorption of the contaminant. In the case of the contaminant concentrations typical of flue gas, no desorption of NO and NO<sub>2</sub> was observed upon lowering the partial pressure. SO<sub>2</sub> on the hand was partially desorbed from all materials examined.

The presence of contaminants was found to have a significant impact on the  $CO_2$  capture ability of all three MOFs, which was confirmed by the diminished  $CO_2$  capacities. This result together with the deteriorated crystallinities suggests that the removal of NO, NO<sub>2</sub> and SO<sub>2</sub> would be required if these materials were to be considered for post-combustion CO<sub>2</sub> capture. However, further studies, including the CO<sub>2</sub>/contaminant cycling in the presence of H<sub>2</sub>O, breakthrough experiments and N<sub>2</sub> adsorption/desorption measurements at -196 °C should be conducted in order to determine the impact of H<sub>2</sub>O on the contaminant sorption, the CO<sub>2</sub>/contaminant selectivity and the extent of the decomposition of the MOFs.

#### 5.3.6 Acknowledgement

The authors acknowledge the financial support by the Australian Government through the CRC Program to support this CO2CRC project.

#### 5.3.7 References

- [1] R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, and H. C. Zhou, "Potential applications of metalorganic frameworks," *Coordination Chemistry Reviews*, vol. 253, pp. 3042-3066, 2009.
- [2] W. Xuan, C. Zhu, Y. Liu, and Y. Cui, "Mesoporous metal-organic framework materials," *Chemical Society Reviews*, vol. 41, pp. 1677-1695, 2012.
- [3] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, and H.-C. Zhou, "Carbon dioxide capture-related gas adsorption and separation in metal-organic frameworks," *Coordination Chemistry Reviews*, vol. 255, pp. 1791-1823, 2011.
- [4] H.-L. Jiang and Q. Xu, "Porous metal-organic frameworks as platforms for functional applications," *Chemical Communications*, vol. 47, pp. 3351-3370, 2011.
- [5] J. B. DeCoste and G. W. Peterson, "Metal–Organic Frameworks for Air Purification of Toxic Chemicals," *Chemical Reviews*, vol. 114, pp. 5695-5727, 2014/06/11 2014.
- [6] S. Bordiga, L. Regli, F. Bonino, E. Groppo, C. Lamberti, B. Xiao, P. S. Wheatley, R. E. Morris, and A. Zecchina, "Adsorption properties of HKUST-1 toward hydrogen and other small molecules monitored by IR," *Physical Chemistry Chemical Physics*, vol. 9, pp. 2676-2685, 2007.
- [7] F. Bonino, S. Chavan, J. G. Vitillo, E. Groppo, G. Agostini, C. Lamberti, P. D. C. Dietzel, C. Prestipino, and S. Bordiga, "Local Structure of CPO-27-Ni Metallorganic Framework upon Dehydration and Coordination of NO," *Chemistry of Materials*, vol. 20, pp. 4957-4968, 2008/08/01 2008.
- [8] A. C. McKinlay, J. F. Eubank, S. Wuttke, B. Xiao, P. S. Wheatley, P. Bazin, J. C. Lavalley, M. Daturi, A. Vimont, G. De Weireld, P. Horcajada, C. Serre, and R. E. Morris, "Nitric Oxide Adsorption and Delivery in Flexible MIL-88(Fe) Metal-Organic Frameworks," *Chemistry of Materials*, vol. 25, pp. 1592-1599, 2013/05/14 2013.
- [9] K. Yu, K. Kiesling, and J. R. Schmidt, "Trace Flue Gas Contaminants Poison Coordinatively Unsaturated Metal–Organic Frameworks: Implications for CO<sub>2</sub> Adsorption and Separation," *J. Phys. Chem. C*, vol. 116, p. 20480, 2012.
- [10] T. G. Glover, G. W. Peterson, B. J. Schindler, D. Britt, and O. Yaghi, *Chemical Engineering Science*, vol. 66, p. 163, 2011.

- [11] L. Ding and A. Ö. Yazaydin, "How Well Do Metal–Organic Frameworks Tolerate Flue Gas Impurities?," *The Journal of Physical Chemistry C*, vol. 116, pp. 22987-22991, 2012/11/01 2012.
- [12] C. Petit, S. Wrabetz, and T. J. Bandosz, *Journal of Materials Chemistry*, vol. 22, p. 21443, 2012.
- [13] C. Petit, B. Levasseur, B. Mendoza, and T. J. Bandosz, *Microporous and Mesoporous Materials*, vol. 154, p. 107, 2012.
- [14] B. Levasseur, C. Petit, and T. J. Bandosz, *ACS Appl. Mater. Interfaces*, vol. 2, p. 3606, 2010.
- [15] A. Roy, A. K. Srivastava, B. Singh, T. H. Mahato, D. Shah, and A. K. Halve, "Degradation of sulfur mustard and 2-chloroethyl ethyl sulfide on Cu–BTC metal organic framework," *Microporous and Mesoporous Materials*, vol. 162, pp. 207-212, 2012.
- [16] D. Britt, D. Tranchemontagne, and O. M. Yaghi, "Metal-organic frameworks with high capacity and selectivity for harmful gases," *Proceedings of the National Academy of Sciences*, vol. 105, pp. 11623-11627, August 19, 2008 2008.
- [17] L. Hamon, C. Serre, T. Devic, T. Loiseau, F. Millange, G. r. Férey, and G. D. Weireld, "Comparative Study of Hydrogen Sulfide Adsorption in the MIL-53(Al, Cr, Fe), MIL-47(V), MIL-100(Cr), and MIL-101(Cr) Metal–Organic Frameworks at Room Temperature," *Journal of the American Chemical Society*, vol. 131, pp. 8775-8777, 2009.
- [18] T. C. Drage, C. E. Snape, L. A. Stevens, J. Wood, J. Wang, A. I. Cooper, R. Dawson, X. Guo, C. Satterley, and R. Irons, "Materials challenges for the development of solid sorbents for post-combustion carbon capture," *Journal of Materials Chemistry*, vol. 22, pp. 2815-2823, 2012.
- [19] F. Rezaei and C. W. Jones, "Stability of Supported Amine Adsorbents to SO<sub>2</sub> and NOx in Postcombustion CO<sub>2</sub> Capture. 2. Multicomponent Adsorption," *Industrial* & Engineering Chemistry Research, vol. 53, pp. 12103-12110, 2014/07/30 2014.
- [20] D. M. D'Alessandro, B. Smit, and J. R. Long, "Carbon Dioxide Capture: Prospects for New Materials," *Angewandte Chemie International Edition*, vol. 49, pp. 6058-6082, 2010.
- [21] S. Couck, J. F. M. Denayer, G. V. Baron, T. Rémy, J. Gascon, and F. Kapteijn, "An Amine-Functionalized MIL-53 Metal-Organic Framework with Large Separation Power for CO<sub>2</sub> and CH<sub>4</sub>," *Journal of the American Chemical Society*, vol. 131, pp. 6326-6327, 2009.
- [22] J. Seo, R. Matsuda, H. Sakamoto, C. Bonneau, and S. Kitagawa, "A Pillared-Layer Coordination Polymer with a Rotatable Pillar Acting as a Molecular Gate for Guest Molecules," *Journal of the American Chemical Society*, vol. 131, pp. 12792-12800, 2009/09/09 2009.
- [23] S. Bourrelly, P. L. Llewellyn, C. Serre, F. Millange, T. Loiseau, and G. Férey, "Different Adsorption Behaviors of Methane and Carbon Dioxide in the Isotypic Nanoporous Metal Terephthalates MIL-53 and MIL-47," *Journal of the American Chemical Society*, vol. 127, pp. 13519-13521, 2005.
- [24] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, and F. Kapteijn, "Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties," *Chemistry of Materials*, vol. 23, pp. 2565-2572, 2011.
- [25] F. Jeremias, A. Khutia, S. K. Henninger, and C. Janiak, "MIL-100(Al, Fe) as water adsorbents for heat transformation purposes-a promising application," *Journal of Materials Chemistry*, 2012.

- [26] C. Patzschke, M. Marshall, and A. L. Chaffee, "An Adsorption Study on STA-16(Co)," *Thesis Chapter 3.6*, 2014.
- [27] E. Soubeyrand-Lenoir, C. Vagner, J. W. Yoon, P. Bazin, F. Ragon, Y. K. Hwang, C. Serre, J.-S. Chang, and P. L. Llewellyn, "How water fosters a remarkable 5-fold increase in low pressure CO<sub>2</sub> uptake within the mesoporous MIL-100(Fe)," *Journal* of the American Chemical Society, 2012/05/21 2012.
- [28] P. Horcajada, S. Surble, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Greneche, I. Margiolaki, and G. Ferey, "Synthesis and catalytic properties of MIL-100(Fe), an iron(iii) carboxylate with large pores," *Chemical Communications*, pp. 2820-2822, 2007.
- [29] M. T. Wharmby, J. P. S. Mowat, S. P. Thompson, and P. A. Wright, "Extending the Pore Size of Crystalline Metal Phosphonates toward the Mesoporous Regime by Isoreticular Synthesis," *Journal of the American Chemical Society*, vol. 133, pp. 1266-1269, 2011.
- [30] P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J.-S. Chang, D.-Y. Hong, Y. Kyu Hwang, S. Hwa Jhung, and G. Férey, "High Uptakes of CO<sub>2</sub> and CH<sub>4</sub> in Mesoporous Metal-Organic Frameworks MIL-100 and MIL-101," *Langmuir*, vol. 24, pp. 7245-7250, 2008.
- [31] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.
- [32] J. W. Yoon, Y.-K. Seo, Y. K. Hwang, J.-S. Chang, H. Leclerc, S. Wuttke, P. Bazin, A. Vimont, M. Daturi, E. Bloch, P. L. Llewellyn, C. Serre, P. Horcajada, J.-M. Grenèche, A. E. Rodrigues, and G. Férey, "Controlled Reducibility of a Metal– Organic Framework with Coordinatively Unsaturated Sites for Preferential Gas Sorption," *Angewandte Chemie International Edition*, vol. 49, pp. 5949-5952, 2010.
- [33] R. Canioni, C. Roch-Marchal, F. Secheresse, P. Horcajada, C. Serre, M. Hardi-Dan, G. Ferey, J.-M. Greneche, F. Lefebvre, J.-S. Chang, Y.-K. Hwang, O. Lebedev, S. Turner, and G. Van Tendeloo, "Stable polyoxometalate insertion within the mesoporous metal organic framework MIL-100(Fe)," *Journal of Materials Chemistry*, vol. 21, pp. 1226-1233, 2011.
- [34] T. K. Trung, P. Trens, N. Tanchoux, S. Bourrelly, P. L. Llewellyn, S. Loera-Serna, C. Serre, T. Loiseau, F. o. Fajula, and G. r. Ferey, "Hydrocarbon Adsorption in the Flexible Metal Organic Frameworks MIL-53(Al, Cr)," *Journal of the American Chemical Society*, vol. 130, pp. 16926-16932, 2012/02/01 2008.
- [35] J. Kim, W. Y. Kim, and W.-S. Ahn, "Amine-functionalized MIL-53(Al) for CO2/N2 separation: Effect of textural properties," *Fuel*, vol. 102, pp. 574-579, 2012.
- [36] T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey, and N. Stock, "Synthesis and Modification of a Functionalized 3D Open-Framework Structure with MIL-53 Topology," *Inorganic Chemistry*, vol. 48, pp. 3057-3064, 2009.
- [37] S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. Serra-Crespo, J. Juan-Alcañiz, A. Martinez Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V. Baron, and J. F. M. Denayer, "Adsorption and Separation of Light Gases on an Amino-Functionalized Metal–Organic Framework: An Adsorption and In-Situ XRD Study," *ChemSusChem*, vol. 5, pp. 740-750, 2012.

- [38] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, and G. Férey, "A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration," *Chemistry – A European Journal*, vol. 10, pp. 1373-1382, 2004.
- [39] C. Patzschke, G. P. Knowles, and A. L. Chaffee, "Post-Synthetic Modification of MIL-100(Fe): An Adsorption Study," *Thesis Chapter 3.3*, 2014.
- [40] M. Kathiresan, L. Walder, F. Ye, and H. Reuter, "Viologen-based benzylic dendrimers: selective synthesis of 3,5-bis(hydroxymethyl)benzylbromide and conformational analysis of the corresponding viologen dendrimer subunit," *Tetrahedron Letters*, vol. 51, pp. 2188-2192, 2010.
- [41] P. A. Wright, M. T. Wharmby, and J. P. S. Mowat, Novel Large Pore Metal Organic Frameworks, Pub. number: US 2013/0296162, 07.11.2013. (http://worldwide.espacenet.com/publicationDetails/originalDocument?FT=D&dat e=20131107&DB=&locale=en\_EP&CC=US&NR=2013296162A1&KC=A1&ND =1).
- [42] C. Patzschke, "Effect of Flue Gas Contaminants on the Stability and the Post-Combustion CO<sub>2</sub> Capture in MIL-101 frameworks," *Thesis Chapter 6.1*, 2014.
- [43] C. Patzschke, C. M. Forsyth, S. R. Batten, and A. L. Chaffee, "Formation of a nonporous cobalt-phosphonate framework by small pH change in the preparation of the microporous STA-16(Co)," *CrystEngComm*, vol. 16, pp. 6296-6299, 2014.
- [44] ""Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.," "*Reflex Tools*" is a module in the Materials Studio Modeling software package from Accelrys Inc.
- [45] Q. Liu, L. Ning, S. Zheng, M. Tao, Y. Shi, and Y. He, "Adsorption of Carbon Dioxide by MIL-101(Cr): Regeneration Conditions and Influence of Flue Gas Contaminants," *Sci. Rep.*, vol. 3, pp. 1-6, 2013.
- [46] C. Sedlmair, K. Seshan, A. Jentys, and J. A. Lercher, "Elementary steps of NO<sub>x</sub> adsorption and surface reaction on a commercial storage–reduction catalyst," *Journal of Catalysis*, vol. 214, pp. 308-316, 2003.
- [47] M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, and K. P. Lillerud, "Synthesis and Stability of Tagged UiO-66 Zr-MOFs," *Chemistry of Materials*, vol. 22, pp. 6632-6640, 2010/12/28 2010.
- [48] K. I. Hadjiivanov, "Identification of Neutral and Charged N x O y Surface Species by IR Spectroscopy," *Catalysis Reviews*, vol. 42, pp. 71-144, 2000/05/15 2000.
- [49] K. Tan, P. Canepa, Q. Gong, J. Liu, D. H. Johnson, A. Dyevoich, P. K. Thallapally, T. Thonhauser, J. Li, and Y. J. Chabal, "Mechanism of Preferential Adsorption of SO2 into Two Microporous Paddle Wheel Frameworks M(bdc)(ted)0.5," *Chemistry of Materials*, vol. 25, pp. 4653-4662, 2013/12/10 2013.
- [50] K.-R. Ma, C.-L. Wei, Y. Zhang, Y.-H. Kan, M.-H. Cong, and X.-J. Yang, "Structures and Spectroscopy Studies of Two M(II)-Phosphonate Coordination Polymers Based on Alkaline Earth Metals (M = Ba, Mg)," *Journal of Spectroscopy*, vol. 2013, p. 9, 2013.
- [51] S. R. Miller, G. M. Pearce, P. A. Wright, F. Bonino, S. Chavan, S. Bordiga, I. Margiolaki, N. Guillou, G. Férey, S. Bourrelly, and P. L. Llewellyn, "Structural Transformations and Adsorption of Fuel-Related Gases of a Structurally Responsive Nickel Phosphonate Metal-Organic Framework, Ni-STA-12," *Journal of the American Chemical Society*, vol. 130, pp. 15967-15981, 2008.

[52] webbook.nist.gov/cgi/cbook.cgi?ID=C10102439&Mask=80, (accessed 16.08.2014).

# Supplementary material

## Adsorption of flue gas contaminants in carboxylate and phosphonate MOFs and their effect on the framework stability and CO<sub>2</sub> uptake

Christin Patzschke,<sup>*a,b*</sup> Gregory P. Knowles<sup>*a,b*</sup> and Alan L. Chaffee<sup>*a,b*\*</sup>

<sup>a</sup> Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC),

<sup>b</sup> School of Chemistry, Monash University, P.O. Box 23, VIC 3800, Australia

\* corresponding author:

Fax:+61 3 990-54597

#### 5.3.8 Structure validation of MIL-53(Al)-NH<sub>2</sub>

Elemental analysis was conducted by the Campbell Microanalytical Laboratory at the University of Otago, New Zealand. The theoretical composition of MIL-53(Al)-NH<sub>2</sub> was calculated from the empirical framework formula  $Al(OH)[C_6H_3(COO)_2NHCOC_6H_5]$ ·0.9H<sub>2</sub>O. The experimental C, H and N contents were in good agreement with the theoretical values and confirm the formation of MIL-53(Al)-NH<sub>2</sub>.

**Table 5.1:** Comparison of experimental and theoretical C, H and N contents of MIL- $53(Al)-NH_2 np$ .

	C / %	H / %	N / %
MIL-53(Al)-NH <sub>2</sub>	40.01	3.27	5.82
MIL-53(Al)-NH <sub>2</sub> np calculated	40.15	3.29	5.85

The phase purity of MIL-53(Al)- $NH_2$  was confirmed via PXRD. The experimental data was in good agreement with the calculated diffractogram.



**Figure 5.31:** Powder X-ray diffractogram of MIL-53(Al)-NH<sub>2</sub> (black) in comparison with the calculated diffraction pattern for MIL-53(Al)-NH<sub>2</sub> *np* (red) [1].



5.3.9 FTIR of MIL-100(Fe) after contaminant sorption – TGA

**Figure 5.32:** FTIR spectra of MIL-100(Fe) before and after the screening tests, the contaminant cycling (25 °C) and the CO<sub>2</sub>/contaminant cycling (25 °C) experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.3.10 FTIR of MIL-53(Al)-NH2 after contaminant sorption – TGA

**Figure 5.33:** FTIR spectra of MIL-53(Al)-NH<sub>2</sub> before and after the screening tests, the contaminant cycling (25 °C) and the CO<sub>2</sub>/contaminant cycling (25 °C) experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.3.11 FTIR of STA-16(Co) after contaminant sorption – TGA

**Figure 5.34:** FTIR spectra of STA-16(Co) before and after the screening tests, the contaminant cycling (25 °C) and the CO<sub>2</sub>/contaminant cycling (25 °C) experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.3.12 PXRD of MIL-100(Fe) after contaminant sorption – TGA

**Figure 5.35:** PXRD of MIL-100(Fe) before and after the screening tests, the contaminant cycling (25 °C) and the CO<sub>2</sub>/contaminant cycling (25 °C) experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



#### 5.3.13 PXRD of MIL-53(Al)-NH2 after contaminant sorption – TGA

**Figure 5.36:** PXRD of MIL-53(Al)-NH<sub>2</sub> before and after the screening tests, the contaminant cycling (25 °C) and the CO<sub>2</sub>/contaminant cycling (25 °C) experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.



5.3.14 PXRD of STA-16(Co) after contaminant sorption – TGA

**Figure 5.37:** PXRD of STA-16(Co) before and after the screening tests, the contaminant cycling (25 °C) and the CO<sub>2</sub>/contaminant cycling (25 °C) experiments with (a) NO, (b) NO<sub>2</sub> and (c) SO<sub>2</sub>.

#### 5.3.15 References supplementary information

[1] S. Couck, E. Gobechiya, C. E. A. Kirschhock, P. Serra-Crespo, J. Juan-Alcañiz, A. Martinez Joaristi, E. Stavitski, J. Gascon, F. Kapteijn, G. V. Baron, and J. F. M. Denayer, "Adsorption and Separation of Light Gases on an Amino-Functionalized Metal–Organic Framework: An Adsorption and In-Situ XRD Study," *ChemSusChem*, vol. 5, pp. 740-750, 2012.

## 6 Non-porous MOF

## 6.1 Chapter overview

Phosphonate MOFs are hypothesised to offer an alternative to the well known MOFs containing carboxylate ligands. However, the formation of porous phosphonate MOFs is challenging, as described in Chapter 1.3.3. During the course of this study problems were encountered during the synthesis of STA-16(Co) and this led to an investigation into the modification of reaction conditions.

The communication presented in this chapter shows that the pH has a significant effect on the formation of porous phosphonate MOFs. The change of the initial pH during the synthesis of the microporous STA-16(Co) resulted in the formation of a non-porous framework structure, which was further characterised by single-crystal XRD, PXRD, FTIR, elemental analysis, SEM/EDS and argon physisorption. The CoMOF was found to be a polymorph of STA-16 with distinct structural differences. Despite the challenge in growing single crystals of phosphonate MOFs, large crystals were readily obtained .during the preparation of the MOF.

Page 314-322: Reproduced by permission of The Royal Society of Chemistry, 2014.

Full citation: http://dx.doi.org/ 10.1039/C4CE00509K

C. Patzschke, C. M. Forsyth, S. R. Batten, and A. L. Chaffee, "Formation of a non-porous cobalt-phosphonate framework by small pH change in the preparation of the microporous STA-16(Co)," *CrystEngComm*, vol. 16, pp. 6296-6299, 2014.

## **Declaration for Thesis Chapter**

Formation of a non-porous cobalt-phosphonate framework by small pH change in the preparation of the microporous STA-16(Co)

Monash University

#### **Declaration for Thesis Chapter 6.2**

#### **Declaration by candidate**

In the case of Chapter 6.2, the nature and extent of my contribution to the work was the following:

Nature of contribution	Extent of contribution (%)
Proposed original idea; prepared and analysed sample (except single-	60 %
crystal XRD); drafted paper	

The following co-authors contributed to the work. If co-authors are students at Monash University, the extent of their contribution in percentage terms must be stated:

Name	Nature of contribution	Extent of contribution (%) for student co- authors only
Craig M. Forsyth	Performed single-crystal XRD and solved structure, input to experimental section	N/A
Stuart R. Batten	Supervision, input to structure description, editorial assistance	N/A
Alan L. Chaffee	Supervision, editorial assistance.	N/A

The undersigned hereby certify that the above declaration correctly reflects the nature and extent of the candidate's and co-authors' contributions to this work\*.

Candidate's Signature	Date 30/10/2014
Main Supervisor's Sìgnature	<b>Date</b> 30/10/14

\*Note: Where the responsible author is not the candidate's main supervisor, the main supervisor should consult with the responsible author to agree on the respective contributions of the authors.

# 6.2 Formation of a non-porous cobalt-phosphonate framework by small pH change in the preparation of the microporous STA-16(Co)

# CrystEngComm

#### COMMUNICATION

# ROYAL SOCIETY OF CHEMISTRY

## Formation of a non-porous cobalt-phosphonate framework by small pH change in the preparation of the microporous STA-16(Co)<sup>†</sup>

Cite this: CrystEngComm, 2014, 16, 6296 Received 11th March 2014,

Christin Patzschke,<sup>ab</sup> Craig M. Forsyth,<sup>a</sup> Stuart R. Batten<sup>ac</sup> and Alan L. Chaffee\*<sup>ab</sup>

Accepted 15th May 2014 DOI: 10.1039/c4ce00509k

www.rsc.org/crystengcomm

The initial pH in the preparation of STA-16(Co) was found to have a great impact on the assembly of the MOF and the resulting porosity. The formation of a non-porous Co(n)-phosphonate pillared layer-structure was observed after changing the initial pH from 6.2 to 7.2 with distinct differences in the coordination environment of the cobalt centres.

Metal–organic frameworks (MOFs) have recently emerged as a class of very promising organic–inorganic hybrid materials for diverse applications like gas storage, gas/vapour separation, catalysis, luminescence, fluorescence and drug storage and delivery.<sup>1,2</sup>

The vast majority of MOFs contain carboxylate or nitrogen donors (pyridines, polyazolates). There are fewer examples of phosphonate and sulfonate based systems, even though metal phosphonates were among the first microporous inorganic hybrid adsorbents to be investigated.<sup>3-7</sup> Reasons for this include:

• the predisposition of simple metal phosphonates to form dense layered motifs due to the strong affinity and chelation of phosphonate groups to metal ions, which makes forming high surface area materials a challenge;

the growth of single crystals is generally more difficult as they often precipitate rapidly as less ordered, insoluble phases;
the coordination chemistry of phosphonates is less pre-

dictable owing to more possible ligation modes and three possible states of protonation.<sup>8,9</sup>

<sup>c</sup> Department of Chemistry, Faculty of Science, King Abdulaziz University,

However, many research groups, notably those of Clearfield<sup>10-17</sup> and Zubieta,<sup>18-22</sup> have pioneered the use of phosphonate ligands in transition-metal chemistry involving solvothermal synthetic procedures. Metal phosphonates find wide range of applications in cation exchange, sorption, catalysis, catalyst supports, sensors as well as non-linear optics.<sup>23</sup>

The solubility of divalent metal phosphonates is high enough to obtain single crystals by hydrothermal/solvothermal techniques. In contrast to this, trivalent and tetravalent metal phosphonates are highly insoluble and tend to precipitate as poorly ordered layered materials, which are rarely crystalline.<sup>16</sup>

Most metal phosphonates don't possess pores larger than 0.6 nm resulting in a low uptake of adsorbates. However, porous structures can be obtained by incorporation of co-ligands/templates or a direct reaction of metal salts with phosphonic acids.<sup>24,25</sup> For example the formation of porous structures using N,N'-4,4'-bipiperidinebis(methylenephosphonic acid) tetra-hydrate (H4LL) was successfully accomplished.26 The organic linker contains two phosphonic acids, both capable of three total states of protonation, as well as two amino nitrogen atoms capable of two protonation states. Wharmby et al. were the first to report the preparation and characterization of a phosphonate MOF containing a hexagonal array of channels parallel to the c-axis with a free diameter of 1.8 nm, which is known as STA-16(Co). The framework structure, determined by Rietveld analysis of powder diffraction data, contains one crystallographically distinct cobalt center, which is coordinated in a distorted octahedral fashion to four phosphonate oxygens, one piperazinyl nitrogen and one oxygen atom of a water molecule. Hydrogen bonding of the lattice and coordinated water molecules with the P=O bond projecting into the channels is present. The framework crystallizes in the trigonal space group R3 and can be described with the empirical formula  $Co_2(H_2O)_2[LL] \cdot 11H_2O (LL = C_{12}H_{22}N_2P_2O_6).^{21}$ 

In this communication we describe the synthesis and characterisation of a related non-porous cobalt-phosphonate

This journal is © The Royal Society of Chemistry 2014

<sup>&</sup>lt;sup>a</sup> School of Chemistry, Monash University, Victoria 3800, Australia. E-mail: alan.chaffee@monash.edu

<sup>&</sup>lt;sup>b</sup> Cooperative Research Centre for Greenhouse Gas Technology (CO2CRC), School of Chemistry, Monash University, Victoria 3800, Australia

Jeddah, Saudi Arabia

<sup>†</sup> Electronic supplementary information (ESI) available: Experimental procedures, single-crystal structure X-ray diffraction data. CCDC 986602. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00509k

#### CrystEngComm

framework (CoMOF), which can be obtained by changing the initial pH during the synthesis of the microporous STA-16 framework from 6.2 to 7.2. The effect of different pH values between 6.2 and 7.9 on the formation of the porous vs. non-porous framework was studied.

The synthesis was performed under hydrothermal conditions giving purple needle like crystals.<sup>‡</sup> The procedure for the synthesis of STA-16(Co) was repeated and in contrast to the pH of 8 stated by Wright *et al.*,<sup>28</sup> we measured the pH to be 6.2. Increases in the pH to 6.8 resulted in the formation of both STA-16(Co) and CoMOF, while alkaline conditions (pH 7.2, 7.6 and 7.9) were found to form only the non-porous CoMOF.

Structural characterization by single crystal X-ray crystallography showed the empirical formula of the product to be  $Co_2(H_2O)_2[LL]$  (LL =  $C_{12}H_{22}N_2P_2O_6)$ .§ While both CoMOF and STA-16(Co) contain two coordinated water molecules, no lattice water is present in the non-porous framework structure.

CoMOF crystallizes in the monoclinic space group  $P2_1/c$ and features a 3D framework structure. The asymmetric unit contains one LL ligand, two cobalt atoms (Co(1) and Co(2)) and two water molecules coordinated to Co(1). Each ligand LL coordinates to seven metal atoms, three at one end (one Co(1) and two Co(2)) and four at the other end (two Co(1) and two Co(2)). All oxygen and nitrogen atoms of the ligand coordinate (Fig. 1, left).

The two crystallographically distinct cobalt atoms display different coordination environments (Fig. 1, right). The Co(1) center is coordinated in a distorted octahedral geometry by three oxygen atoms of the phosphonate group, one piperazinyl nitrogen atom (N(1)) and two oxygen atoms of water molecules. The Co(1)–N(1) distance is 2.228(2) Å, the Co(1)–O(water) distances are 2.147(2) and 2.162(2) Å and the Co(1)–O(phosphonate) distances range from 1.978(2) to 2.099(2) Å. The coordination environment of Co(2) also shows a distorted octahedral geometry, and is built up by the coordination of five oxygen atoms and one piperazinyl nitrogen atom (N(2)) (Co(2)–O(phosphonate): 2.040(2) to 2.542(2) Å, Co(2)–N(2): 2.332(2) Å). At the N(2) end of the



Fig. 1 The local coordination geometries of the ligand LL and the cobalt atoms. Carbon atoms are shown as green, nitrogen blue, oxygen red, phosphorous grey, Co(1) orange, and Co(2) purple.

This journal is © The Royal Society of Chemistry 2014

#### Communication

ligand two of the oxygens chelate to a Co(2), while the third bridges a Co(1) and a Co(2) in  $\mu_2$ -fashion. One P=O bond from each phosphonate group forms hydrogen bonds to a water molecule coordinating to the Co(1) centre. The H-bonding distances between the oxygen atoms are 2.758(3) and 3.064(4) Å.

The two  $\mu_2$ -oxygen atoms of the ligands bridge one of each metal type into dinuclear pairs, as shown in Fig. 1(right). These pairs are then bridged by the remaining phosphonate oxygen atoms to adjacent pairs, forming a 2D sheet (Fig. 2, top). While the sheet appears superficially to have (6,3) topology, closer inspection reveals a more complicated connectivity, with one phosphonate bridging two dinuclear clusters, while the other connects three. The sheets are then connected by the organic backbones of the LL ligands, to give an overall 3D pillared-layer type network (Fig. 2, bottom).

The comparison of the measured powder X-ray diffractogram with the theoretical diffractograms of CoMOF and STA-16 (Fig. 3) confirms the purity of the bulk sample with no STA-16 detected. The theoretical diffractograms were calculated from the crystal structures using the module "Reflex Tools" in Materials Studio 6.0.<sup>29</sup> Fig. S1† shows the diffractograms obtained from the samples synthesized at different pH values. The results indicate that STA-16(Co) is formed under slightly acidic conditions, while the formation of a phase pure CoMOF requires slightly basic conditions. Increasing the pH towards 7 results in the formation of a mixed phase material, containing STA-16 and CoMOF.

The SEM image (Fig. 4) shows the formation of elongated crystals of various sizes between 1 to 350  $\mu$ m. Energy



Fig. 2 A 2D layer formed by the bridging of  $Co_2$  dinuclear species by the phosphonate groups of the ligand LL (top). The overall 3D pillared layer structure (bottom).

CrystEngComm, 2014, 16, 6296-6299 | 6297





Fig. 3 Comparison of experimental (black, 25 °C) and the predicted diffractograms of CoMOF (red, -150 °C) and STA-16(Co) (blue, -173 °C).

dispersive X-ray analysis indicated a Co:P ratio of 1.2:1, which is in good agreement with the expected ratio of 1:1 based on the empirical formula  $\rm Co_2C_{12}H_{26}N_2O_8P_2$ .

Thermogravimetric analysis of CoMOF shows a plateau until 230 °C, after which thermal decomposition of the framework occurs. The decomposition temperature of 230 °C was also reported for STA-16(Co).<sup>27</sup>

Argon sorption data measured at -186 °C using a ASAP 2020 porosimeter indicate a total pore volume of 0.004 cm<sup>3</sup> g<sup>-1</sup> and a BET surface area of about 3 m<sup>2</sup> g<sup>-1</sup>, confirming the lack of porosity. In contrast to this, the pore volume of STA-16(Co) was reported to be 0.68 cm<sup>3</sup> g<sup>-1</sup> (at  $p/p_0 = 0.4$ ), which is 170 times higher.<sup>27</sup>

The IR spectrum (Fig. S4<sup>†</sup>) of CoMOF shows strong bands at 3427 cm<sup>-1</sup> (O–H stretch) and 1652/1612 cm<sup>-1</sup> (O–H bend), which are due to the water molecule coordinating to the Co(1) center. The bands at 2907 to 3003 cm<sup>-1</sup> and 2838/2874 cm<sup>-1</sup> are characteristic for methylene C–H stretch and P–O(H) stretch vibrations. The second P–O(H) stretch can be found at 869 cm<sup>-1</sup>. C–C stretches were observed between 1444 and 1389 cm<sup>-1</sup>. Three characteristic bands of the phosphonate groups are observed at 1346 to 1292 cm<sup>-1</sup> (P=O stretch),



Fig. 4 SEM image of the CoMOF taken at 15 kV.

6298 | CrystEngComm, 2014, 16, 6296-6299

CrystEngComm

1271/1256  $\rm cm^{-1}$  (P–O–H bend) and 1005/988  $\rm cm^{-1}$  (P–O stretch). The alkyl C–N stretch can be found at 1271 and 1256  $\rm cm^{-1}.$ 

In summary, we have shown that the pH has a significant effect on the chelation of the phosphonate groups to the cobalt cations during the synthesis of STA-16(Co). Adjusting the pH to 7.2 results in the formation of a non-porous cobaltphosphonate framework with a 3D pillared-layer structure, instead of a porous MOF. In both materials the cobalt atoms are coordinated in a distorted octahedral geometry, however the metal phosphonate interactions form a 2D substructure in CoMOF and 1D chains in STA-16(Co). This is the crucial difference between forming porous and non-porous motifs, and suggests that careful control of pH in the synthesis of other non-porous pillared-layer phosphonate systems may lead to new porous phases.

#### Acknowledgements

Financial support was provided by the Australian Government through the CRC Program to support this CO2CRC project. The authors acknowledge use of facilities within the Monash Centre for Electron Microscopy. This research used equipment whose purchase was supported under the Australian Research Council's *Centres of Excellence* funding scheme (COE for Design in Light Metals).

#### Notes and references

‡ All reagents were commercially available and used without further purification except for N,N'4,4'-bipiperidinebis(methylene-phosphonic acid) tetrahydrate (H<sub>4</sub>LL) whose synthesis has been described in the literature.<sup>27</sup> The hydrothermal synthesis of the CoMOF was performed by suspending 499 mg of cobalt(in) acetate tetrahydrate and 428 mg H<sub>4</sub>LL in 16.2 mL water and adjusting the pH to 7.2 by adding potassium hydroxide. After aging the suspension for 30 minutes at room temperature, the mixture was heated to 220 °C for 72 h. The resulting purple needle like crystals were washed with water and dried at room temperature. Yield: 256 mg (51%). Anal. Caled. for Co<sub>2</sub>C<sub>12</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>: C 28.5, H 5.2, N 5.5, P 12.2%. Found: C 27.6, H 5.16, N 5.5, P 12.1%.

§ Selected crystal data for CoMOF:  $Co_2C_{12}H_{26}N_2O_8P_2$ , FW = 506.15, monoclinic,  $P2_1/c$ , a = 15.0954(6), b = 11.5689(4), c = 10.6232(4),  $\beta$  = 110.192(4), V = 1741.19(11), Z = 4, 3699 observed reflections  $[R_{int} = 0.0333]$ ,  $R_1$   $(I > 2\sigma) = 0.0356$ ,  $wR_2$  (all data) = 0.0892.

- 1 R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang and H. C. Zhou, *Coord. Chem. Rev.*, 2009, 253, 3042–3066.
- 2 W. Xuan, C. Zhu, Y. Liu and Y. Cui, Chem. Soc. Rev., 2012, 41, 1677–1695.
- 3 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, Angew. Chem., Int. Ed. Engl., 1995, 34, 1199-1201.
- 4 J. A. Groves, S. R. Miller, S. J. Warrender, C. Mellot-Draznieks, P. Lightfoot and P. A. Wright, *Chem. Commun.*, 2006, 3305–3307.
- 5 S. S. Iremonger, J. Liang, R. Vaidhyanathan and G. K. H. Shimizu, *Chem. Commun.*, 2011, 47, 4430–4432.
- 6 K. Maeda, J. Akimoto, Y. Kiyozumi and F. Mizukami, J. Chem. Soc., Chem. Commun., 1995, 1033-1034.

This journal is © The Royal Society of Chemistry 2014

Communication

#### CrystEngComm

- 7 K. Maeda, Y. Kiyozumi and F. Mizukami, Angew. Chem., Int. Ed. Engl., 1994, 33, 2335–2337.
- 8 G. K. H. Shimizu, R. Vaidhyanathan and J. M. Taylor, *Chem. Soc. Rev.*, 2009, 38, 1430–1449.
- 9 F. Zhai, Q. Zheng, Z. Chen, Y. Ling, X. Liu, L. Weng and Y. Zhou, CrystEngComm, 2013, 15, 2040–2043.
- 10 J. D. Wang, A. Clearfield and P. Guang-Zhi, Mater. Chem. Phys., 1993, 35, 208-216.
- 11 B. Zhang and A. Clearfield, J. Am. Chem. Soc., 1997, 119, 2751-2752.
- 12 C. V. K. Sharma, A. Clearfield, A. Cabeza, M. A. G. Aranda and S. Bruque, J. Am. Chem. Soc., 2001, 123, 2885–2886.
- 13 F. Fredoueil, D. Massiot, P. Janvier, F. Gingl, M. Bujoli-Doeuff, M. Evain, A. Clearfield and B. Bujoli, *Inorg. Chem.*, 1999, 38, 1831–1833.
- 14 D. Kong, J. Zon, J. McBee and A. Clearfield, Inorg. Chem., 2006, 45, 977–986.
- 15 C. Lei, J.-G. Mao, Y.-Q. Sun, H.-Y. Zeng and A. Clearfield, Inorg. Chem., 2003, 42, 6157–6159.
- 16 K. J. Gagnon, H. P. Perry and A. Clearfield, Chem. Rev., 2011, 112, 1034-1054.
- 17 A. Clearfield, Metal Phosphonate Chemistry, John Wiley & Sons, New York, 1998, vol. 47, p. 371.
- 18 W. Ouellette, G. Wang, H. Liu, G. T. Yee, C. J. O'Connor and J. Zubieta, *Inorg. Chem.*, 2008, 48, 953–963.
- 19 P. DeBurgomaster, K. Darling, S. Jones and J. Zubieta, Inorg. Chim. Acta, 2010, 364, 150–156.

- 20 P. DeBurgomaster, W. Ouellette, H. Liu, C. J. O'Connor and J. Zubieta, CrystEngComm, 2010, 12, 446–469.
- 21 N. G. Armatas, W. Ouellette, K. Whitenack, J. Pelcher, H. Liu, E. Romaine, C. J. O'Connor and J. Zubieta, *Inorg. Chem.*, 2009, 48, 8897–8910.
- 22 G. Yucesan, J. E. Valeich, H. Liu, W. Ouellette, C. J. O'Connor and J. Zubieta, *Inorg. Chim. Acta*, 2009, 362, 1831–1839.
- 23 V. Chandrasekhar, T. Senapati, A. Dey and S. Hossain, Dalton Trans., 2011, 40, 5394-5418.
- 24 T. Zheng, J. M. Clemente-Juan, J. Ma, L. Dong, S.-S. Bao, J. Huang, E. Coronado and L.-M. Zheng, *Chem. – Eur. J.*, 2013, 19, 16394–16402.
- 25 S.-F. Tang, J.-J. Cai, L.-J. Li, X.-X. Lv, C. Wang and X.-B. Zhao, Dalton Trans., 2014, 43, 5970–5973.
- 26 K. D. Demadis and N. Stavgianoudaki, in *Metal Phosphonate Chemistry: From Synthesis to Applications*, The Royal Society of Chemistry, 2012, pp. 438–492.
- 27 M. T. Wharmby, J. P. S. Mowat, S. P. Thompson and P. A. Wright, J. Am. Chem. Soc., 2011, 133, 1266–1269.
- 28 P. A. Wright, M. T. Wharmby and J. P. S. Mowat, Novel Large Pore Metal Organic Frameworks, US 0296162, 2013, 07.11.2013. (http:// worldwide.espacenet.com/publicationDetails/originalDocument? FT=D&date=20131107&DB=&locale=en\_EP&CC=US&NR= 2013296162A1&KC=A1&ND=1).
- 29 "Reflex Tools" is a module in the Materials Studio Modeling software package from Accelrys Inc.

This journal is © The Royal Society of Chemistry 2014

CrystEngComm, 2014, 16, 6296–6299 | 6299

## **Supporting information**

#### Formation of a Non-Porous Cobalt-Phosphonate Framework by small pH Change in the Preparation of the Microporous STA-16(Co)

Christin Patzschke, Craig M. Forsyth, Stuart R. Batten and Alan L. Chaffee\*

School of Chemistry, Monash University, Victoria 3800, Australia;

E-mail:

#### 6.2.1 Instrumentation

A purple crystal of CoMOF was mounted on an OXFORD Gemini Ultra CCD diffractometer equipped with an Oxford Cryosystems 700 Cryostream and cooled to -150 °C. The data were collected with Cu K<sub>a</sub> radiation ( $\lambda$ =1.5418 Å). The structure was solved by Direct Methods and refined using full matrix Least Squares with the SHELX-97 program suite.[1] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon were placed in calculated positions using a riding model with d(C-H) = 0.99 Å and  $U_{iso}(H)=1.2\times U_{eq}(C)$ . Hydrogen atoms attached to oxygen were refined with the O-H distance restrained to 0.84(1) Å and the H-O-H angle approximately 109 degrees. The data was treated as a pseudo-merohedral twin (twin law:-1 0 -1 0 -1 0 0 0 1, corresponding to a 180 degree rotation about *a*, BASF 0.03) which reduced *R*1 by approximately 2%. However, there remained an electron density maxima of 3.3 e.Å<sup>-3</sup> in the final difference Fourier map, located *ca* 1.95 Å from O(8) and is presumed to be a consequence of further unaccounted for twinning. Attempts to model the electron density peak as a disordered water molecule were unstable and were not pursued further.

The phase purities of the bulk samples were identified by X-ray powder diffraction on a Bruker D8 Focus powder diffractometer using Cu K $\alpha$  radiation. The PXRD pattern was simulated using the module "Reflex Tools" in Materials Studio 6.0.

The C, H, N and P contents were determined by elemental analysis in the Campbell Microanalytical Laboratory at the University of Otago, New Zealand.

SEM images and EDX were obtained using a JEOL 7001F Field Emission Scanning Electron Microscope. The accelerating voltage was set to 15 kV.

The FTIR spectra were recorded on KBr pellets in a Perkin-Elmer Spectrum RXI Fourier-transform infrared spectrometer in the spectral range 4000 to 400 cm<sup>-1</sup>.

Thermogravimetric analysis was performed using a Setaram TAG 24 symmetrical thermoanalyzer from room temperature to 900  $^{\circ}$ C at a ramp of 2  $^{\circ}$ C min<sup>-1</sup> under an air and argon mixture.

Argon physisorption at -186  $^{\circ}$ C was measured on a ASAP 2020 porosimeter. Prior to analysis the MOF was degassed at 150  $^{\circ}$ C.

#### 6.2.2 Single-crystal X-ray structure determination and refinement details

Compound	CoMOF
Empirical formula	$Co_2C_{12}H_{26}N_2O_8P_2$
Formula weight/ g mol <sup>-1</sup>	506.15
Crystal system	Monoclinic
Space group	P 21/c
a / Å	15.0954(6)
b / Å	11.5689(4)
c / Å	10.6232(4)
β / °	110.192(4)
$V / Å^3$	1741.19(11)
Ζ	4
$D_{calcd} / g cm^{-3}$	1.931
$\mu / \text{mm}^{-1}$	2.135
F(000)	1040
Measured reflection/unique	18166/3992
Observed reflection	3699
R <sub>int</sub>	0.0333
Goodness-of fit on $F^2$	1.037
$R_1$ , $wR_2$ (obs. data)	0.0356, 0.0853
$R_1$ , $wR_2$ (all data)	0.0405, 0.0892

Table S1: Details for structural analysis of CoMOF.

#### 6.2.3 PXRD





## 6.2.4 Thermal decomposition



Figure S2: Thermal decomposition of CoMOF.



6.2.5 Argon physisorption and pore size distribution

**Figure S3.1:** Adsorption ( $\blacksquare$ ) and desorption ( $\Box$ ) isotherms of Ar uptake on CoMOF at -186 °C.



Figure S3.2: Nonlinear DFT-calculated pore size distribution, assuming cylindrical pores.

## 6.2.6 FTIR spectrum



Figure S4: FTIR spectrum of CoMOF.

## 6.2.7 References supplementary information

[1] G. Sheldrick, "A short history of SHELX," *Acta Crystallogr. Sect. A*, vol. 64, pp. 112-122, 2008.
#### 7 Conclusion and future work

#### 7.1 Conclusion

A variety of MOFs, including the rigid framework types containing CUS (MIL-100(Fe), MIL-101(Al)-NH<sub>2</sub>, MIL-101(Cr)-NH<sub>2</sub>, STA-16(Co)) and a flexible framework (MIL-53(Al)-NH<sub>2</sub>) were synthesised and characterised via FTIR, PXRD, helium density, N<sub>2</sub> adsorption/desorption, SEM and elemental analysis. The applicability of these materials for post-combustion capture was evaluated via low pressure CO<sub>2</sub> sorption experiments ( $\leq 0.5$  bar), by varying the CO<sub>2</sub> partial pressure between 0.05 and 0.15 bar until ten cycles of adsorption and desorption were carried out under both dry and wet (1 vol% H<sub>2</sub>O) conditions. The effect of the flue gas contaminants NO, NO<sub>2</sub> and SO<sub>2</sub> on the CO<sub>2</sub> capture abilities and MOF stabilities was also studied.

The most promising MOF under dry cycling conditions was the flexible MIL-53(Al)-NH<sub>2</sub>, which exhibited a working capacity of 2.88 wt% at 25 °C. In contrast to this, the working capacities of the rigid frameworks, MIL-100/MIL-110(Al), MIL-100(Fe), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub> and STA-16(Co), were all found to be less than 1 wt%. While the presence of 1 vol% H<sub>2</sub>O almost completely disabled the CO<sub>2</sub> adsorption and desorption in MIL-53(Al)-NH<sub>2</sub>, the rigid frameworks were still able to adsorb and desorb CO<sub>2</sub>. The majority of the MOFs investigated in this work exhibited high H<sub>2</sub>O uptake as well as a good H<sub>2</sub>O stability and are potentially applicable as selective H<sub>2</sub>O adsorbents.

An improvement of the cycling ability in MIL-53(Al)-NH<sub>2</sub> was sought by PSM with benzoic anhydride (MIL-53(Al)-AM). The presence of the bulky anhydride resulted in a severe decrease of the working capacities from 2.88 wt% before PSM to 0.37 wt% after PSM under dry cycling conditions. Further reduction in the working capacity was observed under humid conditions. Despite the diminished working capacities, PXRD of both MIL-53(Al)-NH<sub>2</sub> and MIL-53(Al)-AM confirmed the stability of the frameworks during the wet cycling. However, the removal H<sub>2</sub>O from the flue gas prior to the capture process will be necessary if MIL-53(Al)-NH<sub>2</sub> was to be considered as an adsorbent for post-combustion capture.

Improved working capacities in MIL-100(Fe), MIL-101(Al)-NH<sub>2</sub> and MIL-101(Cr)-NH<sub>2</sub> were sought by grafting amine groups onto the CUS. The following amine modifications were conducted:

- PSM of MIL-100(Fe) using 5, 25 and 30 wt% PEI, 3.6 and 4.5 wt% ED,
- PSM of MIL-101(Cr)-NH<sub>2</sub> using 75, 100 and 150 wt% PEI, 100 wt% DETA, 150 wt% DAB-AM-8 and 150 wt% ED,
- PSM of MIL-101(Al)-NH<sub>2</sub> using 50 and 100 wt% PEI, 100 wt% DETA and 100 wt% DAB-AM-8.

PSM of the MOFs was successfully achieved, as confirmed by a variety of characterisation methods (FTIR, elemental analysis, helium density, N<sub>2</sub> adsorption/desorption at -196 °C). The effect of the amines on the CO<sub>2</sub> adsorption was evaluated by conducting low pressure CO<sub>2</sub> adsorption/desorption and cycling experiments. It was found that the extent of CO<sub>2</sub> adsorption was affected by various factors, including CUS type/metal centre, pore volume, amine type, amine loading and temperature. General conclusions from this study are:

- ➤ An increase in CO<sub>2</sub> partial pressure (0-0.5 bar) always led to a rise in CO<sub>2</sub> adsorption capacity.
- CO<sub>2</sub> saturation was almost achieved in PSM materials in the partial pressure range of 0-0.5 bar, which suggests that these PSM materials are only applicable for low pressure separation processes.
- > Improved CO<sub>2</sub> adsorption capacities were obtained in most PSM materials, especially at partial pressures  $\leq 0.15$  bar.
- The CO<sub>2</sub> adsorption/desorption rates of the neat amines and most PSM materials improved with increasing temperature, especially in the case of DAB-AM-8 and PEI modified frameworks, due to the higher mobility of the amines and the better diffusivity of CO<sub>2</sub>. Therefore, cycling experiments were mostly conducted at 75 or 105 °C.
- The heats of adsorption of some PSM materials indicated a change of adsorption mode from physisorption to chemisorption, especially in amine modified MIL-101(Al)-NH<sub>2</sub> and MIL-101(Cr)-NH<sub>2</sub>.
- ED and DETA modifications were found to have a lower impact on the CO<sub>2</sub> adsorption capacities than DAB-AM-8 and PEI, due to the lower amine densities. Moreover, higher loadings of DAB-AM-8 and PEI resulted in an increase in CO<sub>2</sub> adsorption capacity with increasing temperatures.
- > All DETA modified materials were outperformed by neat DETA.

- The properties of the MOFs play an important role in determining their capability to be modified with "bulky" amines and high amine loadings. PSM of MIL-100(Fe) with ED and PEI resulted in only small improvements, due to the low loadings achieved in the case of ED and the coating of the surface at PEI loadings of 50 wt%.
- The most promising materials were MIL-101(Al)-NH<sub>2</sub>-PEI-96 and MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145, which exhibited higher CO<sub>2</sub> adsorption capacities than the neat amines and the parent MOFs over the entire pressure and temperature range studied (low pressure CO<sub>2</sub> experiments).
- Only MIL-101(Cr)-NH<sub>2</sub>-DAB-AM-8-145 outperformed its parent MOF with CO<sub>2</sub> working capacities of 0.97 wt% vs. 0.81wt% and 0.98 wt% vs. 0.85 wt% under dry and wet cycling conditions, respectively.
- The PSM of the MOFs reduced the H<sub>2</sub>O uptake, especially at higher loadings and higher temperatures, due to the pore filling with the amines.
- Due to the decline in crystallinity upon PSM, especially in MIL-101(Al)-NH<sub>2</sub> and MIL-101(Cr)-NH<sub>2</sub>, the evaluation of their H<sub>2</sub>O stability via PXRD was not possible.

The effects of NO, NO<sub>2</sub> and SO<sub>2</sub> on the stability and capture ability of MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub>, MIL-100(Fe), MIL-53(Al)-NH<sub>2</sub> and STA-16(Co) were determined via a series of screening tests, cycling experiments as well as PXRD and FTIR studies. General conclusions from this study are:

- PXRD studies revealed a decrease in crystallinity in all MOFs, which suggests the the loss in long-range crystallographic ordering or the partial decomposition of all MOFs examined. A phase transformation of STA-16(Co) into the non-porous CoMOF was observed upon NO and SO<sub>2</sub> exposure, but complete loss of crystallographic long-range ordering or the complete collapse of the framework occurred upon NO<sub>2</sub> exposure. If the MOFs decompose in the presence of the flue gas contaminants, then these contaminants need to be removed prior to the capture process, if these materials were to be considered for industrial applications.
- MIL-53(Al)-NH<sub>2</sub> was found to be flexible upon NO<sub>2</sub> adsorption. This phenomenon was reversible upon vacuum activation at room temperature or upon heating the MOF at 110 °C under flowing Ar for 30 min. The flexibility of MIL-53(Al)-NH<sub>2</sub> was found to be beneficial for the complete desorption of 5000 ppm NO<sub>2</sub>.

- NO<sub>2</sub> interacted strongly with those MOFs containing CUS resulting in irreversible adsorption (5000 ppm NO<sub>2</sub>) upon heating under Ar atmosphere. This result was confirmed by FTIR studies, which showed the formation of a monodentate nitrate species (MIL-100(Fe), STA-16(Co)) or chelating bidentate species (MIL-101(Cr), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub>).
- During the contaminant cycling experiments at contaminant concentrations typical of flue gas, contaminant desorption upon lowering the contaminant partial pressure was only achieved in the case of 2000 ppm SO<sub>2</sub>. No subsequent desorption of 500 ppm NO and 500 ppm NO<sub>2</sub> was observed upon lowering the partial pressure.
- The progressive accumulation of NO, NO<sub>2</sub> and SO<sub>2</sub> resulted in diminished CO<sub>2</sub> capacities, which also suggested that the removal of these contaminants from flue gas would be required if these materials were to be considered for post-combustion CO<sub>2</sub> capture.

The hydrothermal stabilities of MIL-100/MIL-110(Al), MIL-101(Al)-NH<sub>2</sub> and STA-16(Co) were evaluated by measuring CO<sub>2</sub> adsorption isotherms (0-5 bar) before and after the adsorption/desorption of H<sub>2</sub>O at 25 °C. The exposure to 30 % RH resulted in a collapse of MIL-110(Al) and MIL-101(Al)-NH<sub>2</sub>, while MIL-100(Al) and STA-16(Co) remained stable. The phosphonate MOF, STA-16(Co), was further subjected to 60 and 90 % RH. While the framework remained stable at 60 % RH, a phase transformation occurred after the adsorption/desorption of 90 % RH.

The suitability of MIL-100/MIL-110(Al), MIL-100(Fe), MIL-101(Cr)-NH<sub>2</sub>, MIL-101(Al)-NH<sub>2</sub> and STA-16(Co) for high pressure separation processes was confirmed by conducting high pressure (0-40 bar) CO<sub>2</sub> and N<sub>2</sub> sorption experiments. While these materials might not be suitable for post-combustion capture, they do exhibit reasonable CO<sub>2</sub> adsorption capacities at 40 bar and they also selectively adsorb CO<sub>2</sub> over N<sub>2</sub>. The CO<sub>2</sub> capacity was found to decline in the order MIL-101(Cr)-NH<sub>2</sub> (75.2 wt%) > MIL-101(Al)-NH<sub>2</sub> (56.8 wt%) ~ MIL-100/MIL-110(Al) (53.6 wt%) > MIL-100(Fe) (46.4 wt%) > STA-16(Co) (33.1 wt%) at 25 °C and 40 bar. In most cases, the CO<sub>2</sub> adsorption capacities were much higher than those reported for the benchmark system zeolite 13X (~32.6 wt% at 25 °C and 40 bar) [1].

#### 7.2 Future work

A number of problems were encountered in this project regarding the syntheses of MIL-100(AI) and STA-16(Co). Although the synthetic procedures reported in the literature were repeated, mixed MOF materials were obtained in both cases. Changes in the pH were unsuccessful in providing a phase pure MOF. Future studies should focus on the improvement of the synthesis conditions in order to achieve a reproducible preparation of these MOFs. Due to the presence of CUS in both framework structures, it is anticipated that their PSM could result in higher CO<sub>2</sub> adsorption capacities.

While the regenerability of most MOFs was confirmed by  $CO_2$  cycling experiments, longer cycling studies and the performance in the presence of higher relative humidities need to be considered. The H<sub>2</sub>O content in flue gas is higher than the 1 vol% H<sub>2</sub>O vapour used in this work and therefore could have a big impact on the CO<sub>2</sub> working capacities and the H<sub>2</sub>O stability of the materials. Due to the use of the adsorbents over many cycles, an increase in the number of test cycles would give better insight into the long term stability of the MOFs. Furthermore, in order to get a better understanding of the H<sub>2</sub>O stability of MOFs during the wet cycling experiments, especially of PSM materials, N<sub>2</sub> adsorption and desorption at -196 °C should be conducted after the exposure of a sample large enough for N<sub>2</sub> adsorption/desorption (~200 mg) to 1 vol%H<sub>2</sub>O.

Furthermore, in industry adsorbents are commonly used in the form of pellets. The effect of pelletisation on the  $CO_2$  uptake as well as on the stability of the framework structures need to be studied. A number of considerations need to be made:

- How stable are the pellets? Will the adsorption of H<sub>2</sub>O vapour result in degradation of the pellet?
- Will the pressure used to press the pellets destroy the framework structure? If so, how can the stability of the MOF be improved?
- ➢ How and when should the pelletised material be activated? Does this have an impact on the CO₂ adsorption capacity and working capacity?
- ➤ How should the flexible MOFs be handled?

Due to the low  $CO_2$  content in the flue gas, the competitive adsorption in binary ( $CO_2/N_2$ ) and ternary ( $CO_2/N_2/H_2O$ ) gas mixtures needs to be carefully evaluated prior to industrial application. The MOFs studied in this work are strongly selective for  $H_2O$  and it needs to be determined how these materials would perform under more realistic flue gas conditions.

Flue gas contaminants have a big impact on the  $CO_2$  capture ability and the stability of the studied MOFs. Future studies should focus on cycling experiments using  $CO_2$ /impurity/H<sub>2</sub>O mixtures. Studies in the literature have shown that H<sub>2</sub>O can prevent the decrease in  $CO_2$  capacity in the presence of the contaminants. Furthermore, N<sub>2</sub> adsorption and desorption at -196 °C should be conducted after the exposure to the flue gas contaminant to help determine if the MOFs are decomposing (pore collapse).

#### 7.3 References

[1] S. Cavenati, C. A. Grande, and A. E. Rodrigues, "Adsorption Equilibrium of Methane, Carbon Dioxide, and Nitrogen on Zeolite 13X at High Pressures," *Journal of Chemical & Engineering Data*, vol. 49, pp. 1095-1101, 2004/07/01 2004.

# **Appendix 1: MOF structures**

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
Ca-MOF	Ca <sup>2+</sup>		Ca[C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub> (COO) <sub>2</sub> ][DMF]	[1]
MIL-47	$V^{4+}$	COOH R=H, NH <sub>2</sub> , NO <sub>2</sub> , Br	$M(O)[C_6H_3H(COO)_2]$	[2]
MIL-53	Al <sup>3+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup>		$\frac{\text{MIL-53 as}}{M(\text{OH})[C_{6}\text{H}_{3}\text{R}(\text{COO})_{2}]} \cdot \\ [C_{6}\text{H}_{4}(\text{COOH})_{2}]_{0.7} \\ \underline{\text{MIL-53 } np} \\ M(\text{OH})[C_{6}\text{H}_{3}\text{R}(\text{COO})_{2}] \\ \underline{\text{MIL-53 } lp} \\ M(\text{OH})[C_{6}\text{H}_{3}\text{R}(\text{COO})_{2} \cdot \text{H}_{2}\text{O}}$	[3-7]
MIL-68	$\begin{array}{c} Al^{3+}, \\ Fe^{3+}, \\ Ga^{3+}, \\ In^{3+}, \\ Sc^{3+}, V^{3+} \end{array}$		M(OH)[C <sub>6</sub> H <sub>3</sub> R(COO) <sub>2</sub> ]·(solv) <sub>x</sub>	[8-11]
MIL-101	$\begin{array}{c c} Al^{3+}, \\ Cr^{3+}, \\ Fe^{3+}, \\ Fe^{3+}, \end{array}$		M <sub>3</sub> X(H <sub>2</sub> O) <sub>2</sub> O[C <sub>6</sub> H <sub>3</sub> R(CO <sub>2</sub> ) <sub>2</sub> ] <sub>3</sub> (X=F, OH)	[12-18]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
MOF-5 (IRMOF-1, R=H) IRMOF-3 (R=NH <sub>2</sub> ), Banasorb <sup>TM</sup> -22 (R=OCF <sub>3</sub> )	Zn <sup>2+</sup>	соон	$Zn_4O[C_6H_3R(COO)_2]_3$	[19-21]
MOF-235	Al <sup>3+</sup> , Fe <sup>3+</sup>		$[Fe_{3}O(C_{6}H_{3}R(COO)_{2})_{3}(DMF)_{3}]$ $[FeCl] (DMF)_{3}$	[22]
MOF-LIC-1	$\mathrm{Gd}^{3+}$		$[Gd_{2}(N-C_{6}H_{3}NH_{2}(CO_{2})_{2})_{3}$ $(C_{3}H_{7}NO)_{4}]_{n}$	[23]
UiO-66	$Zr^{2+}$	COOH R=H, NH <sub>2</sub> , NO <sub>2</sub> , Br	$ZrO[C_6H_3R(COO)_2]$	[24-27]
HKUST-1 (Cu-BTC), UHM-30 (R=NH <sub>2</sub> )	Cu <sup>2+</sup>	COOH	$Cu_3[C_6H_2R(COO)_3]_2$	[28, 29]
MIL-100 (R=H)	Al <sup>3+</sup> , Cr <sup>3+</sup> , Fe <sup>3+</sup> , Mn <sup>3+</sup>	HOOC R=H, NH <sub>2</sub> COOH	M <sub>3</sub> O(OH)[C <sub>6</sub> H <sub>3</sub> (COO) <sub>3</sub> ] <sub>2</sub>	[30-33]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
AzM-BP (modification of IRMOF-9)	Zn <sup>2+</sup>		$Zn_4O(C_{14}H_{10}O_4N_6)_3$	[20, 34]
Bio-MOF-11	Co <sup>2+</sup>	NH2 N N N N N N	Co <sub>2</sub> [C <sub>5</sub> N <sub>5</sub> H <sub>5</sub> ] <sub>2</sub> [CO <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> ·2DMF ·0.5H <sub>2</sub> O	[35]
Cu(bpp) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>	Cu <sup>2+</sup>		$CuC_{26}H_{28}B_2F_8N_4$	[36]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
CALF-25	Ba <sup>2+</sup>	C <sub>2</sub> H <sub>5</sub> O <sub>3</sub> P PO <sub>3</sub> C <sub>2</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> O <sub>3</sub> P PO <sub>3</sub> C <sub>2</sub> H <sub>5</sub>	$BaC_{24}H_{28}P_4O_{12}$	[37]
CPO-27 (MOF-74, M- DOBDC)	Co <sup>2+</sup> , Mg <sup>2+</sup> , Ni <sup>2+</sup> , Zn <sup>2+</sup>	но соон он соон	M <sub>2</sub> [C <sub>6</sub> H <sub>2</sub> (OH) <sub>2</sub> (COO) <sub>2</sub> ][H <sub>2</sub> O] <sub>2</sub> ·8H <sub>2</sub> O	[38-42]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
Cu(bpy) <sub>2</sub> (BF <sub>4</sub> ) <sub>2</sub>	Cu <sup>2+</sup>		$CuC_{20}H_{20}N_4B_2F_8O_2$	[43]
H <sub>3</sub> [(Cu <sub>4</sub> Cl) <sub>3</sub> (BTTri) <sub>8</sub> ]	Cu <sup>2+</sup>		$Cu_{12}C_{72}H_{96}C_{13}N_{72}O_{12}$	[44]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
DMOF-1 (M(BDC-NH <sub>2</sub> )(TED) <sub>0.5</sub> , USO-2(Ni))	Zn <sup>2+</sup> Cu <sup>2+</sup> Ni <sup>2+</sup>		[M(C <sub>6</sub> H <sub>3</sub> R(CO <sub>2</sub> ) <sub>2</sub> )(C <sub>6</sub> H <sub>12</sub> N <sub>2</sub> )]	[45-47]
{(In <sub>3</sub> O(OH)(ADC) <sub>2</sub> (NH <sub>2</sub> IN) <sub>2</sub> }·2.67 H <sub>2</sub> O	In <sup>3+</sup>		[(In <sub>3</sub> O)(OH)(ADC) <sub>2</sub> (NH <sub>2</sub> IN) <sub>2</sub> ] ·2.67H <sub>2</sub> O	[48]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
MOF-177	Zn <sup>2+</sup>	соон	Zn <sub>4</sub> O[C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> COO) <sub>2</sub> ]·15DEF ·3H <sub>2</sub> O	[49]
PCN-100	Zn <sup>2+</sup>		Zn <sub>4</sub> O[C <sub>3</sub> N <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> NHCOO) <sub>3</sub> ] <sub>2</sub> ·17 DEF·3 H <sub>2</sub> O	[50]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
PCN-101	Zn <sup>2+</sup>		Zn <sub>4</sub> O[C <sub>6</sub> H <sub>3</sub> (C <sub>6</sub> H <sub>4</sub> NHCOO) <sub>3</sub> ] <sub>2</sub> ·16 DEF·5 H <sub>2</sub> O	[50]
SNU-M10	N: <sup>2+</sup>	ноос	NiC <sub>18</sub> H <sub>27</sub> N <sub>5</sub> O <sub>4</sub>	[51]
SNU-M11	1N1	ноос	NiC <sub>19</sub> H <sub>29</sub> N <sub>5</sub> O <sub>4</sub>	[31]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
STA-12	$Co^{2+}, Fe^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Ni^{2+}, Ni^{2+}$	H <sub>2</sub> O <sub>3</sub> P N PO <sub>3</sub> H <sub>2</sub>	M₂[C₄H <sub>8</sub> N₂CH₂P₂O <sub>6</sub> ]∙nH₂O	[52, 53]
STA-16	Co <sup>2+</sup> , Ni <sup>2+</sup>	H <sub>2</sub> O <sub>3</sub> P	$M_2(H_2O)_2[C_{12}H_{22}N_2P_2O_6]\cdot nH_2O$	[54]
СоМОГ	Co <sup>2+</sup>	PO <sub>3</sub> H <sub>2</sub>	$Co_2(H_2O)_2[C_{12}H_{22}N_2P_2O_6]$	[55]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
UMCM-1	Zn <sup>2+</sup>	COOH COOH R=H, NH2	$\frac{\text{Zn}_{4}\text{O}[(\text{C}_{6}\text{H}_{3}\text{R}(\text{CO}_{2})_{2})}{(\text{C}_{24}\text{H}_{15}(\text{CO}_{2})_{3})_{4/3}]}$	[56]
YO-MOF	Zn <sup>2+</sup>		Zn <sub>2</sub> [C <sub>30</sub> H <sub>18</sub> (COO) <sub>4</sub> ][C <sub>24</sub> H <sub>12</sub> N <sub>4</sub> O <sub>4</sub> ]	[57]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
ZIF-8	Zn <sup>2+</sup>	HN N	$Zn[C_4H_6N_2]_2$	[58]
Zn <sub>2</sub> (Atz) <sub>2</sub> (ox)	Zn <sup>2+</sup>	$N$ $N$ $N$ $N$ $N$ $N$ $N$ $N$ $C_2O_4H_2$	$Zn_2[C_2H_4N_4]_2[C_2O_4H_2]$	[59]
Zn(ad)(ain)·DMF	Zn <sup>2+</sup>	NH2 COOH	$Zn(C_5H_4N_5)(C_6H_5N_2O_2)\cdot(C_3H_7NO)$	[60]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
Zn <sub>4</sub> O(H <sub>2</sub> 2) <sub>3</sub>	Zn <sup>2+</sup>	H <sub>2</sub> N CO <sub>2</sub> CH <sub>3</sub> CO <sub>2</sub> CH <sub>3</sub>	$Zn_4C_{42}H_{27}N_3O_{13}$	[61]
Zn5(trencba)2(OH)2Cl2·4H2O	Zn <sup>2+</sup>		$Zn_5(C_{30}H_{33}N_4O_6)_2(OH)_2Cl_2\cdot 4H_2O$	[62]

MOF	Metal centre (M)	Ligand	Empirical Formula	Reference
Flexible ZnMOF (Chapter 4)	Zn <sup>2+</sup>		$Zn_4C_{94}H_{81.5}N_7O_{30}$	[63]

#### References

- [1] P.-C. Liang, H.-K. Liu, C.-T. Yeh, C.-H. Lin, and V. t. z. Zima, "Supramolecular Assembly of Calcium Metal–Organic Frameworks with Structural Transformations," *Crystal Growth & Design*, vol. 11, pp. 699-708, 2011/03/02 2011.
- [2] K. Barthelet, J. Marrot, D. Riou, and G. Férey, "A Breathing Hybrid Organic– Inorganic Solid with Very Large Pores and High Magnetic Characteristics," *Angewandte Chemie International Edition*, vol. 41, pp. 281-284, 2002.
- [3] T. Loiseau, C. Serre, C. Huguenard, G. Fink, F. Taulelle, M. Henry, T. Bataille, and G. Férey, "A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration," *Chemistry – A European Journal*, vol. 10, pp. 1373-1382, 2004.
- [4] T. Ahnfeldt, D. Gunzelmann, T. Loiseau, D. Hirsemann, J. Senker, G. Férey, and N. Stock, "Synthesis and Modification of a Functionalized 3D Open-Framework Structure with MIL-53 Topology," *Inorganic Chemistry*, vol. 48, pp. 3057-3064, 2009.
- [5] C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër, and G. Férey, "Very Large Breathing Effect in the First Nanoporous Chromium(III)-Based Solids: MIL-53 or CrIII(OH) {O2C-C6H4-CO2} {HO2C-C6H4-CO2H}x·H2Oy," *Journal of the American Chemical Society*, vol. 124, pp. 13519-13526, 2002/11/01 2002.
- [6] F. Millange, N. Guillou, R. I. Walton, J.-M. Greneche, I. Margiolaki, and G. Ferey, "Effect of the nature of the metal on the breathing steps in MOFs with dynamic frameworks," *Chemical Communications*, pp. 4732-4734, 2008.
- [7] F. Millange, C. Serre, and G. Ferey, "Synthesis, structure determination and properties of MIL-53as and MIL-53ht: the first Criii hybrid inorganic-organic microporous solids: Criii(OH)[middle dot]{O2C-C6H4-CO2}[middle dot]{HO2C-C6H4-CO2H}x," *Chemical Communications*, pp. 822-823, 2002.
- [8] K. Barthelet, J. Marrot, G. Ferey, and D. Riou, "VIII(OH){O2C-C6H4-CO2}.(HO2C-C6H4-CO2H)x(DMF)y(H2O)z (or MIL-68), a new vanadocarboxylate with a large pore hybrid topology : reticular synthesis with infinite inorganic building blocks?," *Chemical Communications*, pp. 520-521, 2004.
- [9] C. Volkringer, M. Meddouri, T. Loiseau, N. Guillou, J. Marrot, G. Férey, M. Haouas, F. Taulelle, N. Audebrand, and M. Latroche, "The Kagomé Topology of the Gallium and Indium Metal-Organic Framework Types with a MIL-68 Structure: Synthesis, XRD, Solid-State NMR Characterizations, and Hydrogen Adsorption," *Inorganic Chemistry*, vol. 47, pp. 11892-11901, 2008/12/15 2008.
- [10] L. Mitchell, B. Gonzalez-Santiago, J. P. S. Mowat, M. E. Gunn, P. Williamson, N. Acerbi, M. L. Clarke, and P. A. Wright, "Remarkable Lewis acid catalytic performance of the scandium trimesate metal organic framework MIL-100(Sc) for C-C and C[double bond, length as m-dash]N bond-forming reactions," *Catalysis Science & Technology*, vol. 3, pp. 606-617, 2013.
- [11] A. Fateeva, P. Horcajada, T. Devic, C. Serre, J. Marrot, J.-M. Grenèche, M. Morcrette, J.-M. Tarascon, G. Maurin, and G. Férey, "Synthesis, Structure, Characterization, and Redox Properties of the Porous MIL-68(Fe) Solid," *European Journal of Inorganic Chemistry*, vol. 2010, pp. 3789-3794, 2010.
- [12] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon, and F. Kapteijn, "Synthesis and Characterization of an Amino Functionalized MIL-101(Al): Separation and Catalytic Properties," *Chemistry of Materials*, vol. 23, pp. 2565-2572, 2011.

- [13] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, and I. Margiolaki, "A Chromium Terephthalate-Based Solid with Unusually Large Pore Volumes and Surface Area," *Science*, vol. 309, pp. 2040-2042, September 23, 2005 2005.
- [14] S. Bauer, C. Serre, T. Devic, P. Horcajada, J. Marrot, G. Férey, and N. Stock, "High-Throughput Assisted Rationalization of the Formation of Metal Organic Frameworks in the Iron(III) Aminoterephthalate Solvothermal System," *Inorganic Chemistry*, vol. 47, pp. 7568-7576, 2008.
- [15] K. M. L. Taylor-Pashow, J. D. Rocca, Z. Xie, S. Tran, and W. Lin, "Postsynthetic Modifications of Iron-Carboxylate Nanoscale Metal–Organic Frameworks for Imaging and Drug Delivery," *Journal of the American Chemical Society*, vol. 131, pp. 14261-14263, 2009/10/14 2009.
- [16] S. Bernt, V. Guillerm, C. Serre, and N. Stock, "Direct covalent post-synthetic chemical modification of Cr-MIL-101 using nitrating acid," *Chemical Communications*, vol. 47, pp. 2838-2840, 2011.
- [17] R. B. Ferreira, P. M. Scheetz, and A. L. B. Formiga, "Synthesis of amine-tagged metal-organic frameworks isostructural to MIL-101(Cr)," *RSC Advances*, vol. 3, pp. 10181-10184, 2013.
- [18] Y. Lin, C. Kong, and L. Chen, "Direct synthesis of amine-functionalized MIL-101(Cr) nanoparticles and application for CO2 capture," *RSC Advances*, vol. 2, pp. 6417-6419, 2012.
- [19] H. Li, M. Eddaoudi, M. O'Keeffe, and O. M. Yaghi, "Design and synthesis of an exceptionally stable and highly porous metal-organic framework," *Nature*, vol. 402, pp. 276-279, 1999.
- [20] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, and O. M. Yaghi, "Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage," *Science*, vol. 295, pp. 469-472, January 18, 2002 2002.
- [21] T. Wu, L. Shen, M. Luebbers, C. Hu, Q. Chen, Z. Ni, and R. I. Masel, "Enhancing the stability of metal-organic frameworks in humid air by incorporating water repellent functional groups," *Chemical Communications*, vol. 46, pp. 6120-6122, 2010.
- [22] A. C. Sudik, A. P. Côté, and O. M. Yaghi, "Metal-Organic Frameworks Based on Trigonal Prismatic Building Blocks and the New "acs" Topology," *Inorganic Chemistry*, vol. 44, pp. 2998-3000, 2005/05/01 2005.
- [23] J. S. Costa, P. Gamez, C. A. Black, O. Roubeau, S. J. Teat, and J. Reedijk, "Chemical Modification of a Bridging Ligand Inside a Metal–Organic Framework while Maintaining the 3D Structure," *European Journal of Inorganic Chemistry*, vol. 2008, pp. 1551-1554, 2008.
- [24] J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, and K. P. Lillerud, "A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability," *Journal of the American Chemical Society*, vol. 130, pp. 13850-13851, 2008/10/22 2008.
- [25] S. J. Garibay and S. M. Cohen, "Isoreticular synthesis and modification of frameworks with the UiO-66 topology," *Chemical Communications*, vol. 46, pp. 7700-7702, 2010.
- [26] M. Kandiah, M. H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E. A. Quadrelli, F. Bonino, and K. P. Lillerud, "Synthesis and Stability of Tagged UiO-66 Zr-MOFs," *Chemistry of Materials*, vol. 22, pp. 6632-6640, 2010/12/28 2010.

- [27] Y. Huang, W. Qin, Z. Li, and Y. Li, "Enhanced stability and CO2 affinity of a UiO-66 type metal-organic framework decorated with dimethyl groups," *Dalton Transactions*, vol. 41, pp. 9283-9285, 2012.
- [28] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, and I. D. Williams, "A Chemically Functionalizable Nanoporous Material [Cu3(TMA)2(H2O)3]n," *Science*, vol. 283, pp. 1148-1150, February 19, 1999 1999.
- [29] K. Peikert, F. Hoffmann, and M. Froba, "Amino substituted Cu<sub>3</sub>(btc)<sub>2</sub>: a new metalorganic framework with a versatile functionality," *Chemical Communications*, vol. 48, pp. 11196-11198, 2012.
- [30] C. Volkringer, D. Popov, T. Loiseau, G. Férey, M. Burghammer, C. Riekel, M. Haouas, and F. Taulelle, "Synthesis, Single-Crystal X-ray Microdiffraction, and NMR Characterizations of the Giant Pore Metal-Organic Framework Aluminum Trimesate MIL-100," *Chemistry of Materials*, vol. 21, pp. 5695-5697, 2009.
- [31] G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, and I. Margiolaki, "A Hybrid Solid with Giant Pores Prepared by a Combination of Targeted Chemistry, Simulation, and Powder Diffraction," *Angewandte Chemie International Edition*, vol. 43, pp. 6296-6301, 2004.
- [32] P. Horcajada, S. Surble, C. Serre, D.-Y. Hong, Y.-K. Seo, J.-S. Chang, J.-M. Greneche, I. Margiolaki, and G. Ferey, "Synthesis and catalytic properties of MIL-100(Fe), an iron(iii) carboxylate with large pores," *Chemical Communications*, pp. 2820-2822, 2007.
- [33] H. Reinsch and N. Stock, "Formation and characterisation of Mn-MIL-100," *CrystEngComm*, vol. 15, pp. 544-550, 2013.
- [34] S. Nagata, H. Sato, K. Sugikawa, K. Kokado, and K. Sada, "Conversion of azide to primary amine via Staudinger reaction in metal-organic frameworks," *CrystEngComm*, vol. 14, pp. 4137-4141, 2012.
- [35] J. An, S. J. Geib, and N. L. Rosi, "Cation-Triggered Drug Release from a Porous Zinc-Adeninate Metal-Organic Framework," *Journal of the American Chemical Society*, vol. 131, pp. 8376-8377, 2009/06/24 2009.
- [36] R. Kotani, A. Kondo, and K. Maeda, "Gate adsorption of CO2 on a flexible onedimensional copper-based coordination polymer crystal," *Chemical Communications*, vol. 48, pp. 11316-11318, 2012.
- [37] J. M. Taylor, R. Vaidhyanathan, S. S. Iremonger, and G. K. H. Shimizu, "Enhancing Water Stability of Metal–Organic Frameworks via Phosphonate Monoester Linkers," *Journal of the American Chemical Society*, vol. 134, pp. 14338-14340, 2012/09/05 2012.
- [38] N. L. Rosi, J. Kim, M. Eddaoudi, B. Chen, M. O'Keeffe, and O. M. Yaghi, "Rod Packings and Metal–Organic Frameworks Constructed from Rod-Shaped Secondary Building Units," *Journal of the American Chemical Society*, vol. 127, pp. 1504-1518, 2005/02/01 2005.
- [39] P. D. C. Dietzel, R. E. Johnsen, R. Blom, and H. Fjellvåg, "Structural Changes and Coordinatively Unsaturated Metal Atoms on Dehydration of Honeycomb Analogous Microporous Metal–Organic Frameworks," *Chemistry – A European Journal*, vol. 14, pp. 2389-2397, 2008.
- [40] P. D. C. Dietzel, Y. Morita, R. Blom, and H. Fjellvåg, "An In Situ High-Temperature Single-Crystal Investigation of a Dehydrated Metal–Organic Framework Compound and Field-Induced Magnetization of One-Dimensional Metal–Oxygen Chains," *Angewandte Chemie International Edition*, vol. 44, pp. 6354-6358, 2005.

- [41] P. D. C. Dietzel, B. Panella, M. Hirscher, R. Blom, and H. Fjellvag, "Hydrogen adsorption in a nickel based coordination polymer with open metal sites in the cylindrical cavities of the desolvated framework," *Chemical Communications*, pp. 959-961, 2006.
- [42] S. R. Caskey, A. G. Wong-Foy, and A. J. Matzger, "Dramatic Tuning of Carbon Dioxide Uptake via Metal Substitution in a Coordination Polymer with Cylindrical Pores," *Journal of the American Chemical Society*, vol. 130, pp. 10870-10871, 2008/08/01 2008.
- [43] D. Li and K. Kaneko, "Hydrogen bond-regulated microporous nature of copper complex-assembled microcrystals," *Chemical Physics Letters*, vol. 335, pp. 50-56, 2001.
- [44] A. Demessence, D. M. D'Alessandro, M. L. Foo, and J. R. Long, "Strong CO<sub>2</sub> Binding in a Water-Stable, Triazolate-Bridged Metal-Organic Framework Functionalized with Ethylenediamine," *Journal of the American Chemical Society*, vol. 131, pp. 8784-8786, 2009.
- [45] D. N. Dybtsev, H. Chun, and K. Kim, "Rigid and Flexible: A Highly Porous Metal– Organic Framework with Unusual Guest-Dependent Dynamic Behavior," *Angewandte Chemie International Edition*, vol. 43, pp. 5033-5036, 2004.
- [46] J. Y. Lee, D. H. Olson, L. Pan, T. J. Emge, and J. Li, "Microporous Metal–Organic Frameworks with High Gas Sorption and Separation Capacity," *Advanced Functional Materials*, vol. 17, pp. 1255-1262, 2007.
- [47] B. Arstad, H. Fjellvåg, K. Kongshaug, O. Swang, and R. Blom, "Amine functionalised metal organic frameworks (MOFs) as adsorbents for carbon dioxide," *Adsorption*, vol. 14, pp. 755-762, 2008.
- [48] X. Gu, Z.-H. Lu, and Q. Xu, "High-connected mesoporous metal-organic framework," *Chemical Communications*, vol. 46, pp. 7400-7402, 2010.
- [49] H. K. Chae, D. Y. Siberio-Perez, J. Kim, Y. Go, M. Eddaoudi, A. J. Matzger, M. O'Keeffe, and O. M. Yaghi, "A route to high surface area, porosity and inclusion of large molecules in crystals," *Nature*, vol. 427, pp. 523-527, 2004.
- [50] Q.-R. Fang, D.-Q. Yuan, J. Sculley, J.-R. Li, Z.-B. Han, and H.-C. Zhou, "Functional Mesoporous Metal-Organic Frameworks for the Capture of Heavy Metal Ions and Size-Selective Catalysis," *Inorganic Chemistry*, vol. 49, pp. 11637-11642, 2010.
- [51] H.-S. Choi and M. P. Suh, "Highly Selective CO<sub>2</sub> Capture in Flexible 3D Coordination Polymer Networks," *Angewandte Chemie International Edition*, vol. 48, pp. 6865-6869, 2009.
- [52] M. T. Wharmby, G. M. Pearce, J. P. S. Mowat, J. M. Griffin, S. E. Ashbrook, P. A. Wright, L.-H. Schilling, A. Lieb, N. Stock, S. Chavan, S. Bordiga, E. Garcia, G. D. Pirngruber, M. Vreeke, and L. Gora, "Synthesis and crystal chemistry of the STA-12 family of metal N,N'-piperazinebis(methylenephosphonate)s and applications of STA-12(Ni) in the separation of gases," *Microporous and Mesoporous Materials*, vol. 157, pp. 3-17, 2012.
- [53] J. A. Groves, S. R. Miller, S. J. Warrender, C. Mellot-Draznieks, P. Lightfoot, and P. A. Wright, "The first route to large pore metal phosphonates," *Chemical Communications*, pp. 3305-3307, 2006.
- [54] M. T. Wharmby, J. P. S. Mowat, S. P. Thompson, and P. A. Wright, "Extending the Pore Size of Crystalline Metal Phosphonates toward the Mesoporous Regime by Isoreticular Synthesis," *Journal of the American Chemical Society*, vol. 133, pp. 1266-1269, 2011.

- [55] C. Patzschke, C. M. Forsyth, S. R. Batten, and A. L. Chaffee, "Formation of a nonporous cobalt-phosphonate framework by small pH change in the preparation of the microporous STA-16(Co)," *CrystEngComm*, vol. 16, pp. 6296-6299, 2014.
- [56] K. Koh, A. G. Wong-Foy, and A. J. Matzger, "A Crystalline Mesoporous Coordination Copolymer with High Microporosity," *Angewandte Chemie International Edition*, vol. 47, pp. 677-680, 2008.
- [57] K. L. Mulfort, O. K. Farha, C. D. Malliakas, M. G. Kanatzidis, and J. T. Hupp, "An Interpenetrated Framework Material with Hysteretic CO<sub>2</sub> Uptake," *Chemistry A European Journal*, vol. 16, pp. 276-281, 2010.
- [58] K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe, and O. M. Yaghi, "Exceptional chemical and thermal stability of zeolitic imidazolate frameworks," *Proceedings of the National Academy of Sciences*, vol. 103, pp. 10186-10191, July 5, 2006 2006.
- [59] R. Vaidhyanathan, S. S. Iremonger, K. W. Dawson, and G. K. H. Shimizu, "An amine-functionalized metal organic framework for preferential CO<sub>2</sub> adsorption at low pressures," *Chemical Communications*, pp. 5230-5232, 2009.
- [60] E. Yang, H.-Y. Li, F. Wang, H. Yang, and J. Zhang, "Enhancing CO2 adsorption enthalpy and selectivity via amino functionalization of a tetrahedral framework material," *CrystEngComm*, vol. 15, pp. 658-661, 2013.
- [61] R. K. Deshpande, J. L. Minnaar, and S. G. Telfer, "Thermolabile Groups in Metal-Organic Frameworks: Suppression of Network Interpenetration, Post-Synthetic Cavity Expansion, and Protection of Reactive Functional Groups," *Angewandte Chemie International Edition*, vol. 49, pp. 4598-4602, 2010.
- [62] L. Wen, D. e. Wang, C. Wang, F. Wang, D. Li, and K. Deng, "A 3D porous zinc MOF constructed from a flexible tripodal ligand: Synthesis, structure, and photoluminescence property," *Journal of Solid State Chemistry*, vol. 182, pp. 574-579, 2009.
- [63] P. K. Thallapally, J. Tian, M. Radha Kishan, C. A. Fernandez, S. J. Dalgarno, P. B. McGrail, J. E. Warren, and J. L. Atwood, "Flexible (Breathing) Interpenetrated Metal-Organic Frameworks for CO<sub>2</sub> Separation Applications," *Journal of the American Chemical Society*, vol. 130, pp. 16842-16843, 2008.

348

# **Appendix 2: About the author**

# **Education**

## **PhD** Candidate

School of Chemistry, Monash University, Clayton, VIC, Australia

- Research project "Amine modified metal-organic frameworks for carbon capture"
- Financial support by the Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC) and Monash University's Faculty of Science Dean's International Postgraduate Research scholarship.

### Master of Science, Chemistry

University of Leipzig, Germany

- Course work (10/2008 02/2010) and research component (03/2010 08/2010)
- Research project "Purification of natural gas using Basolite<sup>TM</sup> A100 via adsorption"

## **Bachelor of Science, Chemistry**

University of Leipzig, Germany

- Course work (10/2005 09/2008) and research project (1 month)
- Research project "Determination of surface acidic centres on sulfated zirconia using pyridine and benzonitrile via DRIFT spectroscopy"

# **Employment**

## **Chemistry Laboratory Demonstrator**

March 2012 – Present

- Assisting and supervising students attending the laboratory classes "Chemistry" (1<sup>st</sup> year chemistry), "Chemistry II" (1st year chemistry), "Chemistry in Context II", "Foundation Chemistry" (1<sup>st</sup> year engineering), "Food Chemistry" (2<sup>nd</sup> year chemistry), "Synthetic Chemistry" (2<sup>nd</sup> year chemistry)
- Marking of weekly student laboratory reports

March 2011 – November 2014

October 2008 - August 2010

October 2005 – September 2008

#### **Research Assistant**

November 2010 – February 2011

August 2010 – September 2010

School of Chemistry, Monash University, Clayton, VIC, Australia

• Research project "Approaches to the solubilisation of brown coal in ionic liquids"

#### **Research Assistant**

Institute of Non-Classical Chemistry (INC), Leipzig, Germany

• Research project "Hydrogen storage using activated carbons and MOFs"

## Volunteer Work

## Volunteer

December 2013 – Present

RSPCA, Burwood, VIC, Australia

Cleaning kennels and walking dogs on a weekly basis (December 2013 – May 2014) and on a fortnightly basis since June 2014.

# Journal publications

J. Mollmer, M. Lange, A. Moller, C. Patzschke, K. Stein, D. Lassig, J. Lincke, R. Glaser, H. Krautscheid and R. Staudt, "Pure and mixed gas adsorption of  $CH_4$  and  $N_2$  on the metal-organic framework Basolite<sup>TM</sup> A100 and a novel copper-based 1,2,4-triazolyl isophthalate MOF", *Journal of Materials Chemistry*, vol. 22, pp. 10274-10286, 2012.

M. Bastos-Neto, C. Patzschke, M. Lange, J. Mollmer, A. Moller, S. Fichtner, C. Schrage, D. Lassig, J. Lincke, R. Staudt, H. Krautscheid and R. Glaser, "Assessment of hydrogen storage by physisorption in porous materials", *Energy & Environmental Sciences*, vol. 5, pp. 8294-8303,2012.

C. Patzschke, C.M. Forsyth, S.R. Batten and A.L. Chaffee, "Formation of a non-porous cobalt-phosphonate framework by small pH change in the preparation of the microporous STA-16(Co)", *CrystEngComm*, vol.16, pp. 6296-6299, 2014.