

SUPPORTING INFORMATION

Promoted Iron Nanocrystals Obtained via Ligand Exchange as Active and Selective Catalysts for Synthesis Gas Conversion

Marianna Casavola,^{||†} Jingxiu Xie,^{||†} Johannes D. Meeldijk,^{||} Nynke A. Krans,^{||} Andrey Goryachev,[‡] Jan P. Hofmann,[‡] A. Iulian Dugulan,[§] and Krijn P. de Jong^{||}*

^{||} Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, The Netherlands

[‡] Laboratory of Inorganic Materials Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Postbox 513, 5600 MB Eindhoven, The Netherlands

[§] Fundamental Aspects of Materials and Energy Group, Delft University of Technology, Mekelweg 15, 2629 JB Delft, The Netherlands.

Corresponding Author

* k.p.dejong@uu.nl

Contents: ICP-AES characterization; XPS characterization; TEM characterization; Catalyst performance at different pressures and promotion levels; in situ Mössbauer spectroscopy; Catalytic performance at 340 °C, 10 bar, H₂/CO/He = 60/30/10, GHSV = 3 600 h⁻¹.

ICP-AES CHARACTERIZATION

Table S1. ICP-AES measurements of different batches of catalysts synthesized using identical procedure as coded.

	Wt. loading (%) ^a			Atomic ratio		
	Fe	Na	S	Na/Fe	S/Fe	Na/S
blank CNT	0.0	0.09	<0.01			
blank CNT	<0.01	0.04	< dl			
blank CNT	0.1	0.06	< dl			
iFe	2.7	< dl	< dl			
iFe	2.7	0.05	< dl			
cFe	2.7	0.04	< dl			
cFe	3.1	0.07	< dl			
iFeP0.5	2.9	0.13	0.04	0.11	0.02	4
iFeP0.5	2.7	0.13	0.05	0.12	0.03	4
cFeP0.5-iwi	2.5	0.16	0.04	0.15	0.03	6
cFeP0.5-iwi	2.7	0.18	0.05	0.16	0.03	5
cFeP0.5	2.9	0.14	0.06	0.12	0.05	3
cFeP0.5	2.9	0.11	0.08	0.10	0.04	2
cFeP0.5	2.9	0.06	0.05	0.05	0.03	2
cFeP0.5	28	0.05	0.05	0.04	0.03	1

XPS CHARACTERIZATION

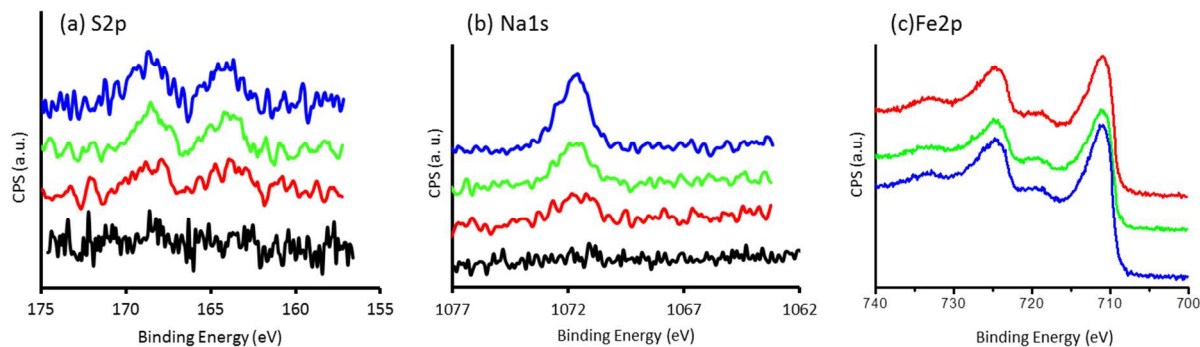


Figure S1. XPS spectra (a) S2p region, (b) Na1s region and (c) Fe2p region (cFe: black, cFeP0.25: red, cFeP0.5: green, cFeP1.0: blue).

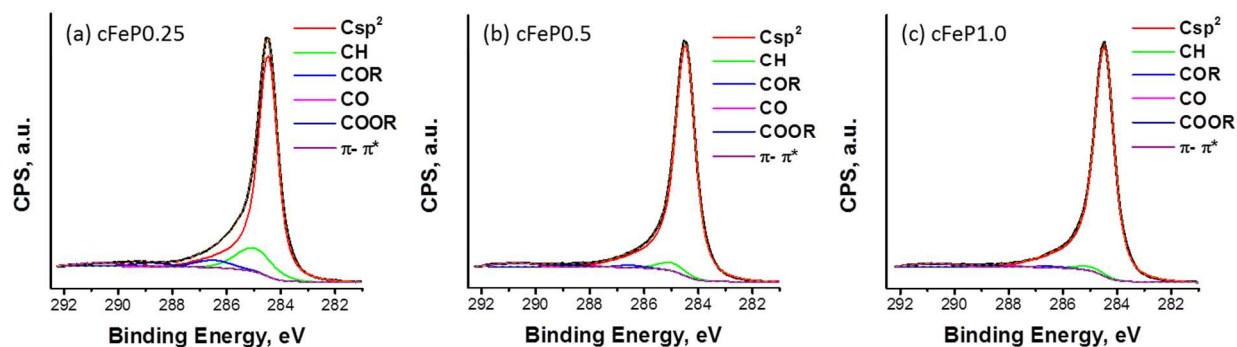


Figure S2. XPS spectra C1s region of (a) cFeP0.25, (b) cFeP0.5 and (c) cFeP1.0.

Intensity of CH (C sp³) decreases from cFeP0.25 > cFeP0.5 > cFeP1.0

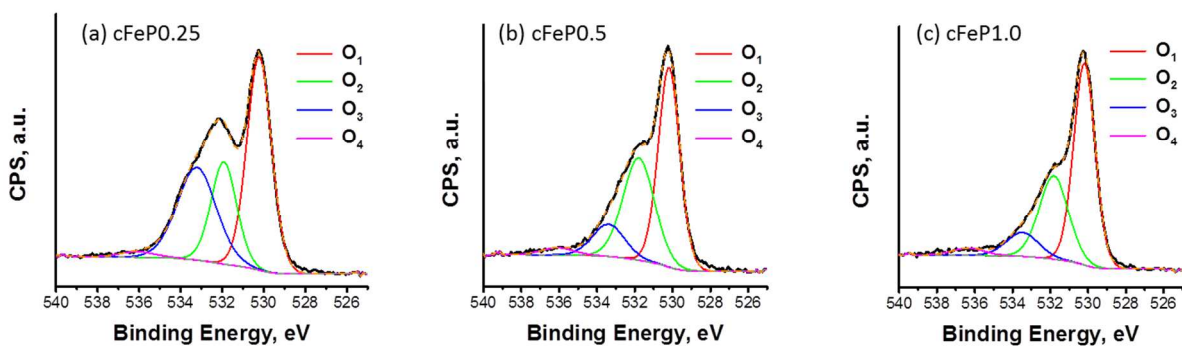


Figure S3. XPS spectra O1s region of (a) cFeP0.25, (b) cFeP0.5 and (c) cFeP1.0

O₁ is specific for Fe-oxide; O₂ is specific for Fe-hydroxide; O₃ may be due to organics present in the sample; O₄ is due to H₂O adsorbed.

TEM CHARACTERIZATION

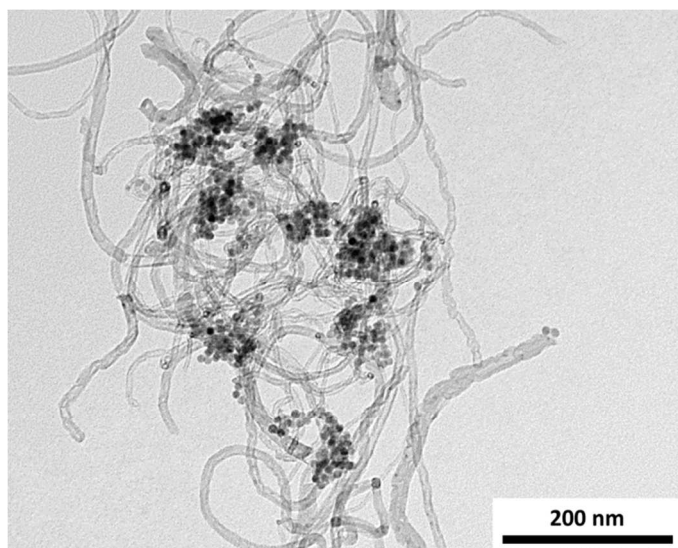


Figure S4. TEM image showing aggregation of Fe NC after prolonged Na_2S mixing.

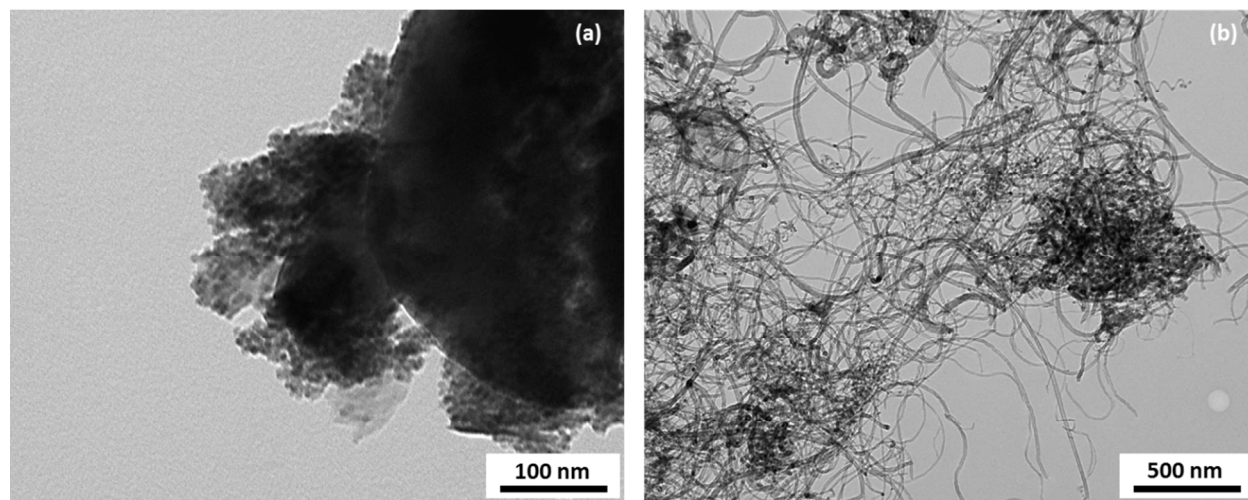


Figure S5. TEM micrographs of iron oxide NCs after ligand exchange with Na_2S and successive reaction with CNT supports. The NCs form aggregates rather than assembling on the CNTs surface.

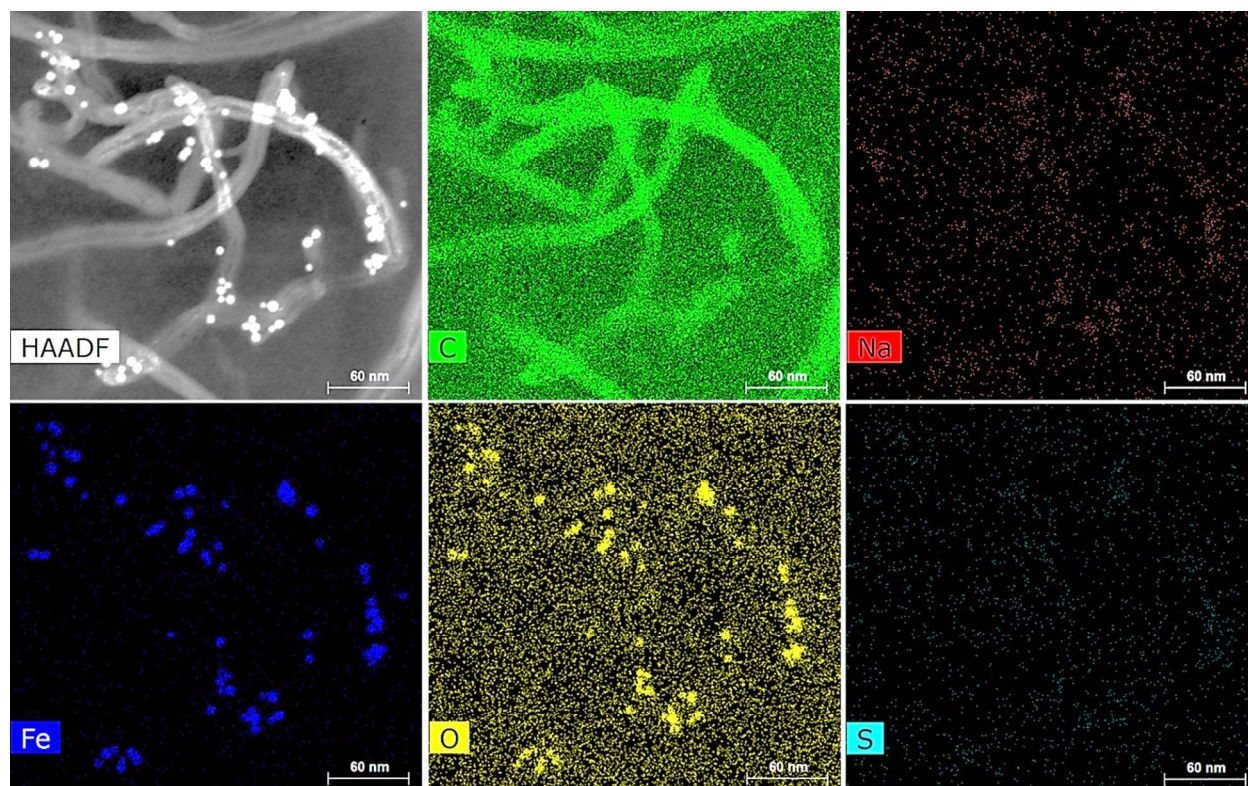


Figure S6. Qualitative STEM-EDX elemental mapping of cFeP0.5 model catalyst (Fe NC size of 7 nm and iron loading of 3 wt%) treated with Na_2S .

CATALYTIC PERFORMANCE AT DIFFERENT PRESSURES AND PROMOTION LEVELS

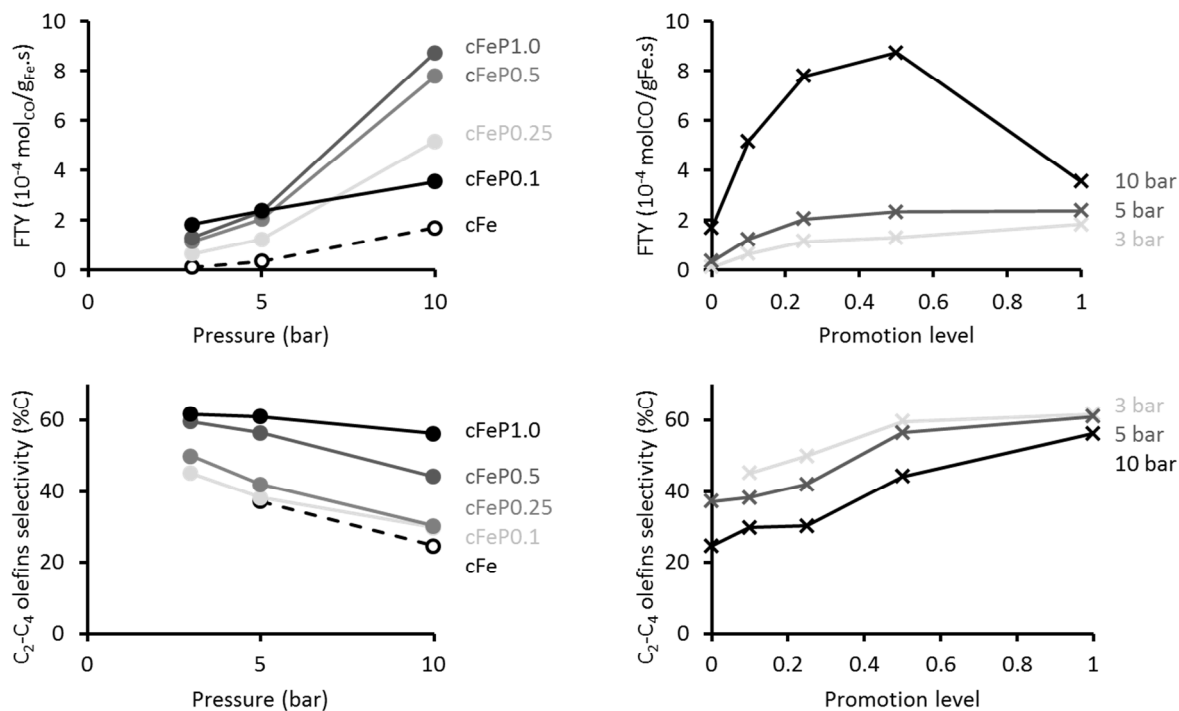


Figure S7. Effect of (a) pressure and (b) promotion level on activity (FTY); and (c) pressure and (d) promotion level on C₂-C₄ olefins selectivity.

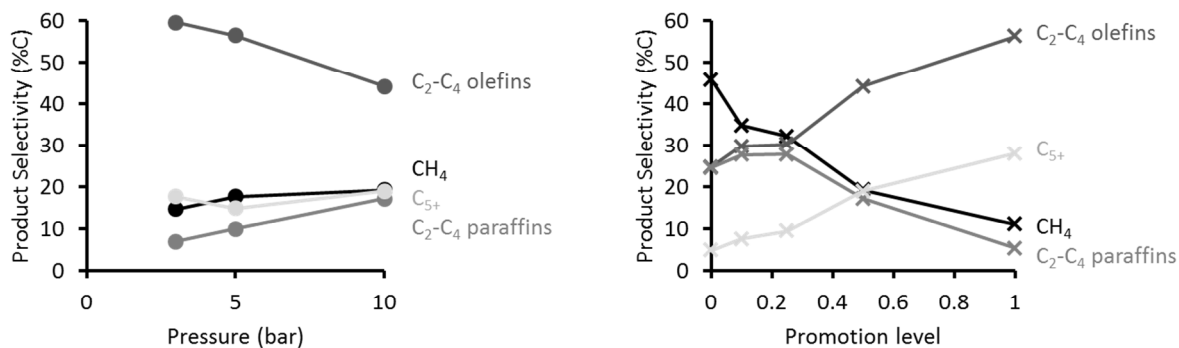


Figure S8. Effect of (a) pressure on product selectivity (catalyst cFeP0.5) and (b) promotion level on product selectivities (at 10 bar).

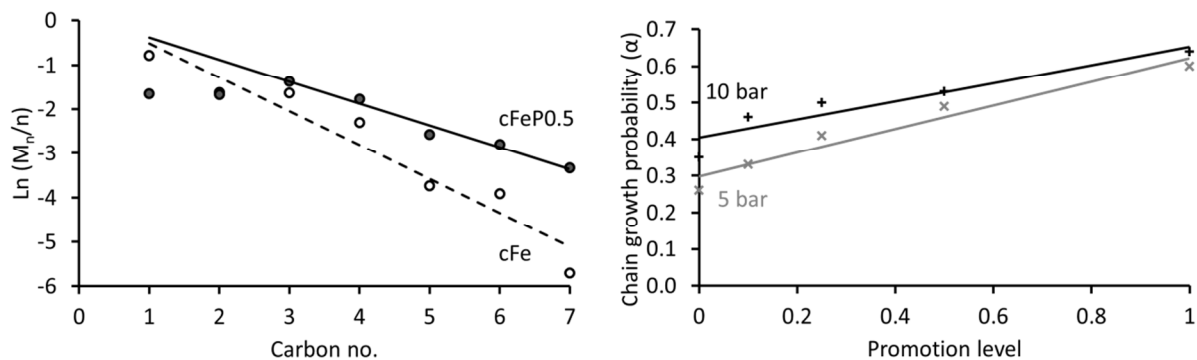


Figure S9. (a) Derivation of C_1 content from ASF prediction which determines α values and (b) effect of promotion level and pressure on α values.

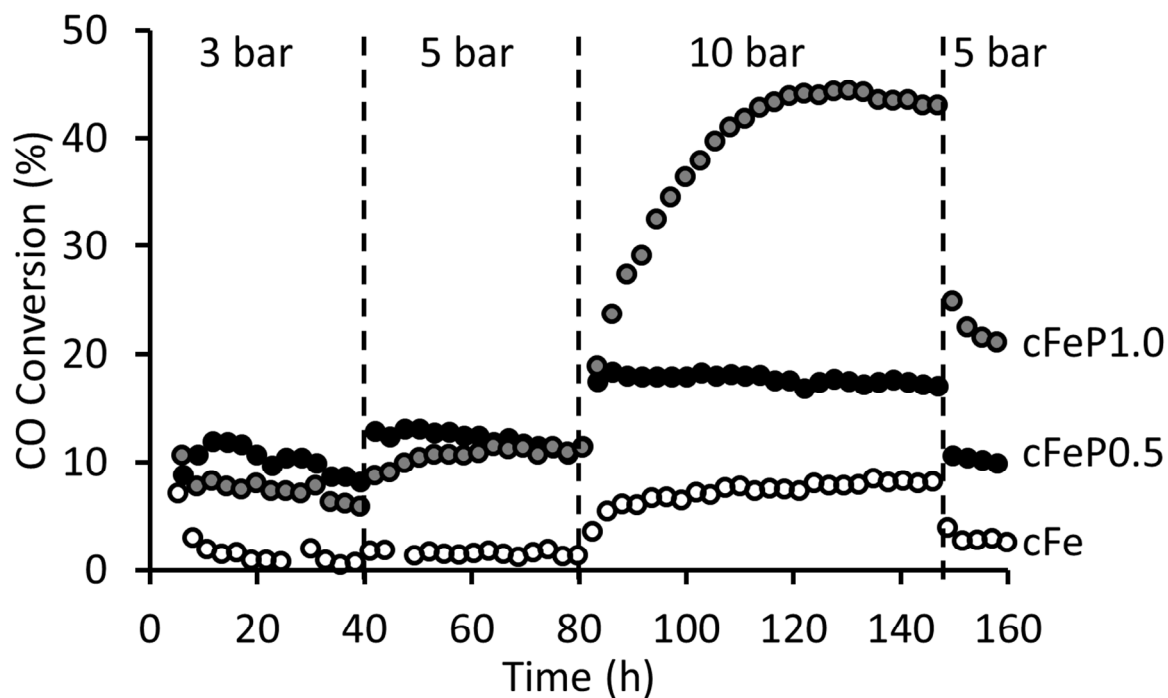


Figure S10. Catalytic activity over time (340 °C, 3 - 10 bar, $H_2/CO/He = 60/30/10$, $GHSV = 3\,600\ h^{-1}$).

Table S2. Catalytic Performance of CNT-Supported Fe Catalysts under FTO Conditions (340 °C, 3 bar, H₂/CO/He = 60/30/10, GHSV = 3 600 h⁻¹, TOS = 40 h at 3 bar).

	CO conv. (%)	FTY (10 ⁻⁴ mol _{CO} /g _{Fe} · s)	α	CO ₂ sel. (%)	Product Selectivity (% C _{at} , hydrocarbons only)			
					CH ₄	C ₂ -C ₄ olefins	C ₂ -C ₄ para.	C ₅ +
cFe	1	0.1	-	-	-	-	-	-
cFeP0.1	3	0.6	0.29	35	34	38	21	7
cFeP0.25	5	1.1	0.29	40	30	42	18	9
cFeP0.5	6	1.3	0.48	45	18	57	10	15
cFeP1.0	9	1.8	0.58	51	11	61	4	23

Table S3. Catalytic Performance of CNT-Supported Fe Catalysts under FTO Conditions (340 °C, 5 bar, H₂/CO/He = 60/30/10, GHSV = 3 600 h⁻¹, TOS = 40 h at 5 bar).

	CO conv. (%)	FTY (10 ⁻⁴ mol _{CO} /g _{Fe} · s)	α	CO ₂ sel. (%)	Product Selectivity (% C _{at} , hydrocarbons only)			
					CH ₄	C ₂ -C ₄ olefins	C ₂ -C ₄ para.	C ₅ +
cFe	2	0.3	0.26	-	47	37	12	4
cFeP0.1	6	1.2	0.33	32	34	38	21	7
cFeP0.25	9	2.0	0.41	37	30	42	18	9
cFeP0.5	12	2.3	0.49	43	18	57	10	15
cFeP1.0	12	2.4	0.60	46	11	61	4	23

Table S4. Catalytic Performance of CNT-Supported Fe Catalysts under FTO Conditions (340 °C, 10 bar, H₂/CO/He = 60/30/10, GHSV = 3 600 h⁻¹, TOS = 40 h at 10 bar).

	CO conv. (%)	FTY (10 ⁻⁴ mol _{CO} /g _{Fe} · s)	α	CO ₂ sel. (%)	Product Selectivity (% C _{at} , hydrocarbons only)			
					CH ₄	C ₂ -C ₄ olefins	C ₂ -C ₄ para.	C ₅ +
cFe	8	1.7	0.35	24	46	25	25	5
cFeP0.1	26	5.2	0.46	36	35	30	28	8
cFeP0.25	34	7.8	0.50	38	32	30	28	9
cFeP0.5	44	8.7	0.53	44	19	44	17	19
cFeP1.0	17	3.5	0.64	44	11	56	5	28

IN-SITU MOSSBAUER SPECTROSCOPY

Table S5. The Mössbauer fitted parameters of UFe and 0.6PFe samples, obtained at 4.2 K.

<i>Sample/ Treatment</i>	<i>IS (mm·s⁻¹)</i>	<i>QS (mm·s⁻¹)</i>	<i>Hyperfine field (T)</i>	<i>Γ (mm·s⁻¹)</i>	<i>Phase</i>	<i>Spectral contribution (%)</i>
cFe	0.24	-	21.2*	1.25	Fe _x C	24
Ar/H ₂ =2	0.39	0.15	52.8	0.89	Fe ³⁺	4
340 °C,	1.17	-0.10	36.9	1.69	Fe ²⁺	36
3 bar, 2 h	1.49	-1.84	38.4	1.69	Fe ²⁺	36
cFe	0.24	-	27.4	0.79	χ-Fe ₅ C ₂ (I)	11
H ₂ /CO=2	0.20	-	22.4	0.79	χ-Fe ₅ C ₂ (II)	10
340 °C,	0.22	-	12.6	0.79	χ-Fe ₅ C ₂ (III)	6
3 bar, 40 h	0.39	-0.03	51.5	0.89	Fe ³⁺	10
+	1.02	-0.05	36.6	1.04	Fe ²⁺	29
5 bar, 40 h	1.45	-1.32	39.9	1.26	Fe ²⁺	30
	0.96	2.14	-	0.38	Fe ²⁺	4
cFe	0.24	-	24.7	0.67	χ-Fe ₅ C ₂ (I)	15
H ₂ /CO=2	0.20	-	20.3	0.67	χ-Fe ₅ C ₂ (II)	10
340 °C,	0.22	-	13.0	0.67	χ-Fe ₅ C ₂ (III)	5
10 bar, 40 h	0.45	-0.21	52.5	0.75	Fe ³⁺	5
	1.13	-0.27	36.4	0.81	Fe ²⁺	37
	1.49	-1.37	39.9	0.81	Fe ²⁺	24
	1.09	2.04	-	0.32	Fe ²⁺	4
cFeP0.5	0.00	-	34.6	0.41	Fe ⁰	34
Ar/H ₂ =2	0.32	0.20	45.4	1.80	Fe ³⁺	18
340 °C,	1.25	0.19	34.4	1.15	Fe ²⁺	25
3 bar, 2 h	1.23	-0.85	38.3	1.15	Fe ²⁺	18
	1.02	2.20	-	0.62	Fe ²⁺	5
cFeP0.5	0.27	-	18.3	0.49	ε'-Fe _{2.2} C	46
H ₂ /CO=2	0.29	-	25.6	0.32	χ-Fe ₅ C ₂ (I)	8
340 °C,	0.17	-	20.7	0.32	χ-Fe ₅ C ₂ (II)	7
3 bar, 40 h	0.19	-	10.2	0.32	χ-Fe ₅ C ₂ (III)	6
+	1.17	0.49	35.5	0.84	Fe ²⁺	14
5 bar, 40 h	1.16	-0.93	37.1	0.84	Fe ²⁺	19
cFeP0.5	0.26	-	18.2	0.45	ε'-Fe _{2.2} C	57
H ₂ /CO=2	0.27	-	25.8	0.38	χ-Fe ₅ C ₂ (I)	12
340 °C,	0.14	-	20.7	0.38	χ-Fe ₅ C ₂ (II)	11
10 bar, 40 h	0.18	-	10.2	0.38	χ-Fe ₅ C ₂ (III)	9
	1.17	-0.35	34.0	0.85	Fe ²⁺	11

Experimental uncertainties: Isomer shift: I.S. ± 0.02 mm s⁻¹; Quadrupole splitting: Q.S. ± 0.02 mm s⁻¹; Line width: Γ ± 0.03 mm s⁻¹; Hyperfine field: ± 0.1 T; Spectral contribution: ± 3%. *Mean magnetic hyperfine field.

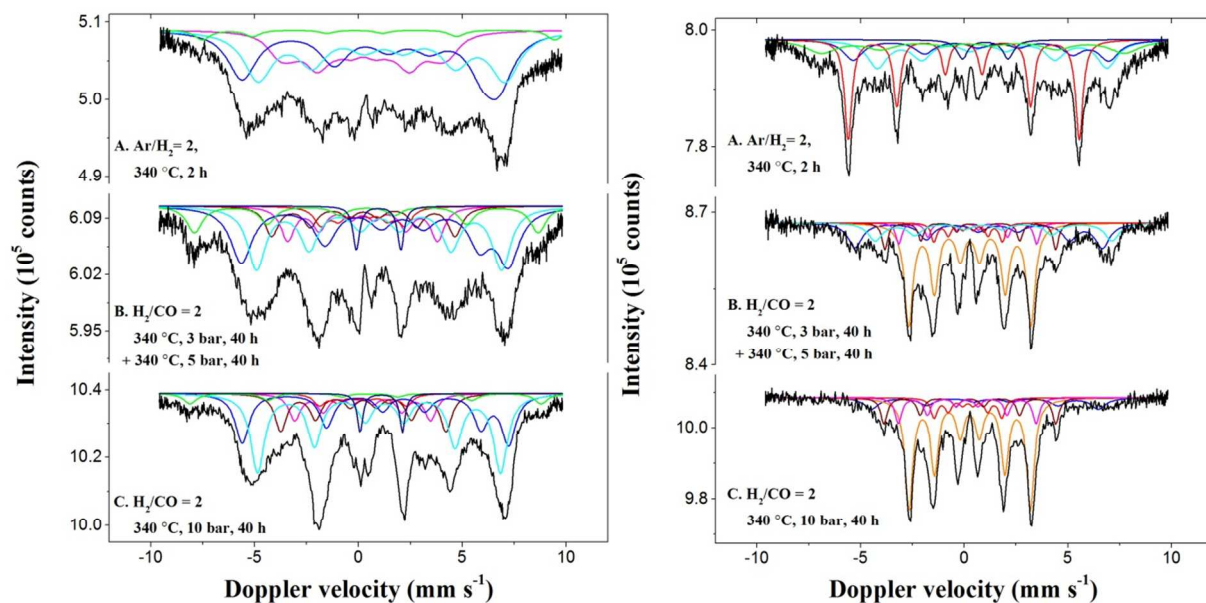


Figure S11. In situ Mossbauer spectra of (a) cFe after reduction, (b) cFe at 340 °C and 5 bar, (c) cFe at 340 °C and 10 bar, (d) cFeP0.5 after reduction, (e) cFeP0.5 at 340 °C and 5 bar, and (f) cFeP0.5 at 340 °C and 10 bar.

CATALYTIC PERFORMANCE AT 340 °C, 10 BAR, $\text{H}_2/\text{CO}/\text{He} = 60/30/10$, GHSV = 3 600 h^{-1}

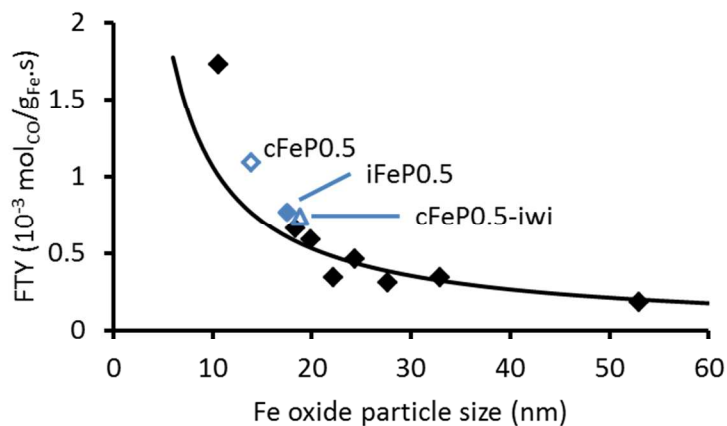


Figure S12. Catalytic activity as a function of average iron particle size of spent promoted catalysts (black symbols were reproduced from earlier research⁵⁷, and blue symbols were results from current study).