

Supporting Information

Cage-defining Ring: A Molecular Sieve Structural Indicator for Light Olefin  
Product Distribution from the Methanol-to-Olefins Reaction

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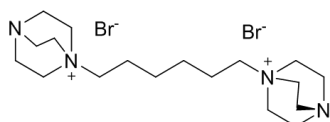
# Syntheses of Organic Structure-directing Agents (OSDAs)

## Materials

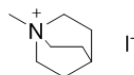
1,4-diazabicyclo[2.2.2]octane (DABCO, 99%, Sigma-Aldrich), 1,6-dibromohexane (98%, Sigma-Aldrich), quinuclidine (97%, Alfa Aesar), N-methylpiperidine (99%, Sigma-Aldrich), methyl iodide (99.5%, Cu-stabilized Sigma-Aldrich), 1,2,4,5-tetramethylimidazole (98%, TCI Chemical), 1,2-dimethylimidazole (98%, Sigma-Aldrich), 4-methylbenzyl chloride (98%, Sigma-Aldrich) were used as-received without further purification.

## Organic Syntheses

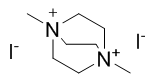
The quaternary ammonium OSDAs were firstly prepared as their halide forms by the  $S_N2$  reactions stated below.



1,1'-(hexane-1,6-diyl)bis(1,4-diazabicyclo[2.2.2]octanium) dibromide ( $C_6$ -diDABCO- $Br_2$ ) was prepared from the  $S_N2$  reaction of DABCO and 1,6-dibromohexane.<sup>1</sup> An excess amount of DABCO (67.3 g, 600 mmol) was dissolved in 200 ml of methanol in a 500 ml round-bottom flask, and heated up to 45 °C first. Separately, a dropping funnel was charged with 1,6-dibromohexane (24.4 g, 100 mmol) dissolved in 100 ml of methanol. The 1,6-dibromohexane methanol solution in the dropping funnel was slowly added to the DABCO methanol solution in the flask dropwise for 30 min while vigorously stirring to prevent the possible oligomerization at 45 °C. The reaction mixture was refluxed for 24 hours. Methanol was evaporated using a rotary evaporator, and the solid product was washed with a copious amount of diethyl ether (1 L) to remove excess DABCO. The product was dried in a vacuum at room temperature.  $^1H$  NMR (500 MHz,  $D_2O$ ):  $\delta$  3.34 (t, 12H), 3.21 (m, 4H), 3.12 (t, 12H), 1.73 (m, 4H), 1.37 (m, 4H).  $^{13}C$  NMR (125 MHz,  $D_2O$ ):  $\delta$  64.27, 52.05, 44.16, 25.12, 21.05.



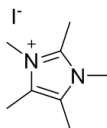
N-methylquinuclidinium iodide was prepared from the  $S_N2$  reaction of quinuclidine and methyl iodide.<sup>2</sup> Quinuclidine (10 g, 90 mmol) was dissolved in 150 ml of chloroform in a 500 ml round-bottom flask. Separately, a dropping funnel was charged with methyl iodide (25.5 g, 180 mmol). (*Caution: methyl iodide must be handled in a well-ventilated fume hood because it is very volatile (b.p., 42.4 °C), and it has a high biological acute toxicity if inhaled.*) Methyl iodide was added dropwise to the quinuclidine in chloroform solution slowly. The reaction mixture must be cooled down in a dry ice bath since the reaction proceeds very fast and is highly exothermic. After completion of addition of methyl iodide, the reaction mixture was stirred at room temperature for extra 72 hours. Solvent and excess methyl iodide were removed by a rotary evaporator (*Caution: toxic vapor containing methyl iodide is generated. Use appropriate personal protective equipment (PPE).*) The solid product was washed with a copious amount of diethyl ether and dried in a vacuum at room temperature.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  3.83 (t, 6H), 3.36 (s, 3H), 2.33 (septet, 1H), 2.10 (m, 6H).  $^{13}C$  NMR (125 MHz,  $D_2O$ ):  $\delta$  56.90, 51.83, 23.42, 18.57.



N,N'-dimethyl-1,4-diazabicyclo[2.2.2]octanium diiodide (DMDABCO<sup>2+</sup>(I)<sub>2</sub>) was prepared from the S<sub>N</sub>2 reaction of DABCO and methyl iodide.<sup>3</sup> DABCO (16.8 g, 150 mmol) was dissolved in 200 ml of chloroform in a 500 ml round-bottom flask. Separately, a dropping funnel was charged with methyl iodide (85.2 g, 600 mmol). (*Caution: methyl iodide must be handled in a well-ventilated fume hood because it is very volatile (b.p., 42.4 °C), and it has a high biological acute toxicity if inhaled.*) Methyl iodide was added dropwise to the DABCO in chloroform solution slowly. The reaction mixture must be cooled down in a dry ice bath since the reaction proceeds very fast and is highly exothermic. After completion of addition of methyl iodide, the reaction mixture was stirred at room temperature for extra 72 hours. Solvent and excess methyl iodide were removed by a rotary evaporator (*Caution: toxic vapor containing methyl iodide is generated. Use appropriate PPE.*) The solid product was washed with a copious amount of diethyl ether and dried in a vacuum at room temperature. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O): δ 4.68 (s, 6H), 3.44 (s, 12H). <sup>13</sup>C NMR (125 MHz, D<sub>2</sub>O): δ 53.45, 44.38.

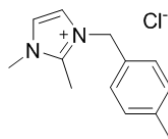


N,N'-dimethylpiperidine (DMP) was prepared from the S<sub>N</sub>2 reaction of N-methylpiperidine and methyl iodide.<sup>4</sup> N-methylpiperidine (9.2 g, 100 mmol) was dissolved in 200 ml of chloroform in a 500 ml round-bottom flask. Separately, a dropping funnel was charged with methyl iodide (42.6 g, 300 mmol). (*Caution: methyl iodide must be handled in a well-ventilated fume hood because it is very volatile (b.p., 42.4 °C), and it has a high biological acute toxicity if inhaled.*) Methyl iodide was added dropwise to the DABCO in chloroform solution slowly. The reaction mixture must be cooled down in a dry ice bath since the reaction proceeds very fast and is highly exothermic. After completion of addition of methyl iodide, the reaction mixture was stirred at room temperature for extra 72 hours. Solvent and excess methyl iodide were removed by a rotary evaporator (*Caution: toxic vapor containing methyl iodide is generated. Use appropriate PPE.*) The solid product was washed with a copious amount of diethyl ether and dried in a vacuum at room temperature. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD): δ 3.54 (t, 4H), 3.27 (s, 6H), 2.00 (m, 4H), 1.78 (qnt, 2H). <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>OD): δ 62.59, 51.25, 20.44, 19.96.



1,2,3,4,5-pentamethylimidazolium iodide (PMI<sup>+</sup>I<sup>-</sup>) was prepared from the S<sub>N</sub>2 reaction between 1,2,4,5-tetramethylimidazole and methyl iodide.<sup>5</sup> 1,2,4,5-tetramethylimidazole (18.7 g, 150 mmol) was dissolved in 200 ml of chloroform in a 500 ml round-bottom flask. Separately, a dropping funnel was charged with methyl iodide (63.9 g, 450 mmol). (*Caution: methyl iodide must be handled in a well-ventilated fume hood because it is very volatile (b.p., 42.4 °C), and it has a high biological acute toxicity if inhaled.*) Methyl iodide was added dropwise to the 1,2,4,5-tetramethylimidazole in chloroform solution slowly. The reaction mixture must be cooled down in a dry ice bath since the reaction proceeds very fast and is highly exothermic. After completion of addition of methyl iodide, the reaction mixture was stirred at room temperature for extra 72 hours. Solvent and excess methyl iodide were removed by a rotary evaporator (*Caution: toxic vapor containing methyl iodide is generated. Use appropriate PPE.*) The solid product was washed with a

copious amount of diethyl ether and dried in a vacuum at room temperature.  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  3.51 (s, 6H), 2.43 (s, 3H), 2.10 (s, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  142.06, 125.24, 31.26, 9.39, 7.68.



1,2-dimethyl-3-(4-methylbenzyl)imidazolium chloride (12DM34MBI $^+\text{Cl}^-$ ) was prepared from the  $\text{S}_{\text{N}}2$  reaction of 1,2-dimethylimidazolium and 4-methylbenzyl chloride.<sup>6</sup> 14.4 g of 1,2-dimethylimidazolium (150 mmol) was dissolved in 200 ml of toluene and the mixture was heated up to 45 °C while stirring. 21.1 g of 4-methylbenzyl chloride (150 mmol) was added dropwise. The reaction mixture was heated to 105 °C and the reaction proceeded for 24 hours. The desired product precipitated, since it is insoluble in toluene. The solid was separated by filtration, and washed with a copious amount of diethyl ether and dried in a vacuum at room temperature.  $^1\text{H}$  NMR (500 MHz,  $\text{D}_2\text{O}$ ):  $\delta$  7.18 (dd, 2H), 7.13 (d, 2H), 7.05 (d, 2H), 6.50 (s, 2H), 3.61 (s, 3H), 2.41 (s, 3H), 2.18 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz  $\text{D}_2\text{O}$ ):  $\delta$  144.14, 139.16, 130.64, 129.67, 127.68, 122.15, 120.89, 51.10, 34.49, 20.07, 8.93.

### Ion-exchange and Titration

The quaternary ammonium halides described above were exchanged into their hydroxide forms, if required. The organic salts were dissolved in distilled water and mixed with DOWEX<sup>TM</sup> Monosphere<sup>TM</sup> 550A hydroxide ion-exchange resin (Dow Chemical). 600 ml of distilled water and 300 ml volume of ion-exchange resin per 100 mmol of OSDA halide were used. The mixture was stirred for 24 hours at room temperature. The used resin was separated by filtration. The solution phase was collected in a round-bottom flask and concentrated using a rotary evaporator. The quantification of the concentration of OSDA hydroxide was performed using a Mettler Toledo DL22 Potentiometric pH meter.

# Syntheses of Molecular Sieves

## Materials

All materials for synthesizing small-pore molecular sieve materials were used as-received without further purifications from the stated vendors. The moisture contents of the solid sources were determined by temperature gravimetric analysis (TGA). Aluminum sources used were aluminum hydroxide hydrogel (Barcroft 250, SPI Pharma, 30.6 wt. % of moisture), pseudoboehmite alumina (Catapal B, VISTA, 23.2 wt. % of moisture), hydrated alumina (Reheis F2000, 33.8 wt. % of moisture), sodium aluminate (37.9 wt. %  $\text{Na}_2\text{O}$ , 51.1 wt. % of  $\text{Al}_2\text{O}_3$ , Alfa Aesar) and aluminum isopropoxide (98%, Sigma-Aldrich). For some syntheses, zeolite Y was employed as the silicon and aluminum sources. Zeolyst CBV500 (Si/Al ratio = 2.6, 14.3 wt. % of moisture), CBV712 (Si/Al = 6, 15.1 wt. % of moisture), and CBV720 (Si/Al = 15, 8.8 wt. % of moisture) were used as-received. The source of phosphorus for  $\text{AlPO}_4$ -based material syntheses, was concentrated phosphoric acid (85 wt. % in water, Macron). Silica sources were colloidal silica (Ludox AS-series, Sigma-Aldrich), fumed silica (Cab-O-Sil, ACROS), sodium silicate (PQ Corporation Waterglass N, 8.9 wt. %  $\text{Na}_2\text{O}$ , 28.7 wt. %  $\text{SiO}_2$  in  $\text{H}_2\text{O}$ ), and tetraethyl orthosilicate (TEOS, 99.9%, Alfa Aesar). For cobalt sources, cobalt (II) sulfate hydrate (Sigma-Aldrich) and cobalt (II) acetate tetrahydrate (98%, Sigma-Aldrich) were used. The source of magnesium was magnesium acetate tetrahydrate (98%, Sigma-Aldrich). For alkali hydroxide mineralizing agents, sodium hydroxide (pellets, EMD milipore), potassium hydroxide (45% in  $\text{H}_2\text{O}$ , Sigma-Aldrich) and cesium hydroxide (50 wt. % in  $\text{H}_2\text{O}$ , Sigma-Aldrich) were used. Sodium nitrate (99.9%, Sigma-Aldrich) and potassium nitrate (99.9%, Sigma-Aldrich) were also used if required by the recipes.

The following OSDAs were used as-received from the stated vendors: tetraethylammonium hydroxide (TEAOH, 35 wt. % in  $\text{H}_2\text{O}$ , Sigma-Aldrich), tetramethylammonium hydroxide (TMAOH, 25 wt. % in  $\text{H}_2\text{O}$ , Sigma-Aldrich), diethylamine (DEA, Sigma-Aldrich), morpholine (Sigma-Aldrich), cyclohexylamine (Sigma-Aldrich), diisopropylethylamine (DIPEA, Sigma-Aldrich), 1,1,3,5-tetramethylpiperidinium hydroxide (TMPOH, 0.788 mmol  $\text{g}^{-1}$  in  $\text{H}_2\text{O}$ , Sachem), N,N,N',N'-tetramethylhexane-1,6-diamine (TMHD, 99%, Sigma-Aldrich), trimethylamine (TMA, 33 wt. % in ethanol, Fluka), tetra-n-butylammonium hydroxide (TBAOH, 55 wt. % in  $\text{H}_2\text{O}$ , Alfa Aesar), hexamethyleneimine (99%, Sigma-Aldrich), 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6 ether, 99%, Sigma-Aldrich), 1,4,8,11-tetraazacyclotetradecane (Cyclam, 98%, Sigma-Aldrich), 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (Kryptofix® 222 or just K222, 98%, Sigma-Aldrich), and cetyltrimethylammonium bromide (CTAB, Sigma-Aldrich).

The following OSDAs were synthesized according to the procedures provided in the previous section: 1,1'-(hexane-1,6-diyl)bis(1,4-diazabicyclo[2.2.2]octanium) dibromide ( $\text{C}_6\text{-diDABCO-Br}_2$ ), N-methylquinuclidinium hydroxide ( $\text{MQuin}^+\text{OH}^-$ ), N,N'-dimethyl-1,4-diazabicyclo[2.2.2]octanium dihydroxide ( $\text{DMDABCO}^{2+}(\text{OH}^-)_2$ ), N,N-dimethylpiperidinium hydroxide ( $\text{DMP}^+\text{OH}^-$ ), 1,2,3,4,5-pentamethylimidazolium hydroxide ( $\text{PMI}^+\text{OH}^-$ ), 1,2-dimethyl-3-(4-methylbenzyl)imidazolium hydroxide ( $\text{12DM34MBI}^+\text{OH}^-$ ).

## General Procedures

All zeolites were prepared as outlined here, unless otherwise stated. First, alkali aluminate gels were prepared. Aluminum sources were dissolved in basic aqueous solutions of alkali hydroxide and OSDA hydroxide. The mixtures were stirred until they became translucent. Finally, silicon sources were added, and the mixture stirred for 24 hours at room temperature.

All  $\text{AlPO}_4$ -based materials were prepared as outlined here, unless stated otherwise. First, aluminum sources (e.g., alumina, pseudoboehmite, aluminum hydroxide, etc.) were mixed with twice the weight of distilled

water. The mixtures were stirred at room temperature for 2 hours to fully hydrate. Next, the desired amounts of concentrated phosphoric acid were mixed with the same weight of distilled water and added dropwise. Then, the mixtures were stirred for an extra 3 hours. The desired amounts of silica-sources (*e.g.*, Ludox colloidal silica, fumed silica, etc.) or other metal-sources were added to the gels. The water contents were adjusted to meet the desired gel compositions by adding extra water or by evaporating desired amounts of water using flowing air, then the gels were stirred for extra 30 min at room temperature. Finally, the desired amount of OSDAs (*i.e.*, amines or quaternary ammonium hydroxide solutions) were added to the gels. The mixtures were stirred for 24 hours at room temperature.

23 ml PTFE (polytetrafluoroethylene) liners for Parr steel autoclaves were charged with the gels for zeolites or  $\text{AlPO}_4$ -materials prepared as stated above, and the crystallizations were performed at the conditions stated in the next section. The collected product molecular sieves were washed with distilled water and acetone consecutively using a centrifuge (3,000 rpm, 3×2 min). The isolated solid samples were dried in a convection oven at 100 °C overnight. Confirmation that the desired materials were obtained from the synthesis was based on the powder X-ray diffractometry and the scanning electron microscopy.

## Synthesis Conditions (Zeolites)

The organic materials used to crystallize zeolites are schematically illustrated in Figure S1.

SSZ-39 was prepared by converting commercial Y zeolite using a one-to-one-ratio *cis/trans* mixture of N,N,3,5-tetramethylpiperidinium hydroxide (TMPOH) as the OSDA. The synthesis was performed without use of sodium hydroxide, modified from ref <sup>7</sup>. Desired amounts of fumed silica, OSDA solution, and distilled water were mixed in a PTFE liner and homogenized by stirring. After that, a desired amount of Zeolyst CBV500 was dispersed in the mixture. Further aging steps at room temperature did not influence the results. The final gel composition was 1  $\text{SiO}_2$  : 0.067 Al : 0.706 TMPOH : 20.38  $\text{H}_2\text{O}$ . The crystallization was performed in a 140 °C rotating oven for 28 days.

The LEV zeolites used in this work were synthesized using two methods with the following OSDAs: MQuinOH<sup>2</sup> and DMDABCO(OH)<sub>2</sub>.<sup>3</sup> The LEV zeolite synthesized using MQuinOH as the OSDA is known as Nu-3 (or SSZ-17), and has high silica elemental compositions ( $\text{Si/Al} > 10$ ). Desired amounts of MQuinOH solution, sodium hydroxide and distilled water were mixed. A desired amount of Reheis F2000 hydrated alumina was dispersed in the mixture and stirred for 1 hour. Then, colloidal silica Ludox AS-40 was added dropwise. The gel composition was 1  $\text{SiO}_2$  : 0.024  $\text{Al}_2\text{O}_3$  : 0.199 MQuinOH : 0.187 NaOH : 40.11  $\text{H}_2\text{O}$ . The mixture was stirred for 24 hours before starting the crystallization. The crystallization was performed in a 175 °C rotating oven for 6 days.

A lower-silica LEV zeolite was prepared using DMDABCO(OH)<sub>2</sub> as the OSDA. Desired amounts of 20% sodium hydroxide solution, sodium silicate, DMDABCO(OH)<sub>2</sub> solution, and distilled water were mixed in a PTFE liner and homogenized by stirring. Next, a desired amount of Zeolyst CBV720 was dispersed in the mixture. The mixture was stirred for 1 day. A desired portion of water was evaporated using flowing air. The final gel composition was 1  $\text{SiO}_2$  : 0.0147 Al : 0.178 DMDABCO(OH)<sub>2</sub> : 0.580 NaOH : 9.43  $\text{H}_2\text{O}$ . The crystallization was performed in a 150 °C rotating oven for 3 days.

SSZ-98 was prepared by converting commercial Y zeolite using N,N-dimethylpiperidinium hydroxide (DMPOH) as the OSDA.<sup>4</sup> Desired amounts of DMPOH solution, potassium hydroxide solution and water was mixed in a PTFE liner and stirred. Next, a desired amount of Zeolyst CBV720 was dispersed in the mixture. The mixture was sealed and transferred to a 150 °C static oven. The final gel composition was 1

SiO<sub>2</sub> : 0.033 Al<sub>2</sub>O<sub>3</sub> : 0.267 DMPOH : 0.497 KOH : 38.840 H<sub>2</sub>O. The crystallization was performed for 3 days.

Zeolite RTH was prepared using PMIOH as the OSDA.<sup>5</sup> Desired amounts of TEOS and aluminum isopropoxide were hydrolyzed in a mixture of PMIOH solution by stirring at room temperature for 24 hours. Next, excess amounts of water and alcohol species formed as the results of hydrolysis were evaporated under flowing air. Desired amount of hydrogen fluoride (HF, 45 wt. % in H<sub>2</sub>O, Sigma-Aldrich) was added dropwise to the gel. (*Caution: Hydrogen fluoride is a dangerous substance that can cause fatal burns and irreversible damages to human skin, tissue, and bone. It must be handled with appropriate PPE including a lab coat, a respirator, a full-face shield, an acid-apron, a pair of long-sleeve nitrile gloves, etc. with a proper ventilation in a fume hood.*) The viscous transparent gel became powdery as a result of the addition of HF. The resultant fluoride gel was further dried in a fume hood for 1–2 days. A desired amount of distilled water was added to achieve the desired gel composition. The final gel composition was 0.95 SiO<sub>2</sub> : 0.05 Al : 0.5 PMIOH : 0.50 HF : 7.0 H<sub>2</sub>O. The crystallization was performed in a 160 °C rotating oven for 2 weeks. Decreasing aluminum contents in gels (below Si/Al = 50) resulted in the formation of high-silica STW impurities.

High-silica LTA zeolite was prepared using 12DM34MBI<sup>+</sup>OH<sup>-</sup> and TMAOH as the co-OSDAs in fluoride media.<sup>6</sup> Desired amounts of TEOS and aluminum isopropoxide were hydrolyzed in a mixture of 12DM34MBI<sup>+</sup>OH<sup>-</sup> and TMAOH solution by stirring at room temperature for 24 hours. Next, excess amounts of water and alcohol species formed as the results of hydrolysis were evaporated under flowing air. Desired amount of hydrogen fluoride (HF, 45 wt. % in H<sub>2</sub>O, Sigma-Aldrich) was added dropwise to the gel. (*Caution: Hydrogen fluoride is a dangerous substance that can cause fatal burns and irreversible damages to human skin, tissue, and bone. It must be handled with appropriate PPE including a lab coat, a respirator, a full-face shield, an acid-apron, a pair of long-sleeve nitrile gloves, etc. with a proper ventilation in a fume hood.*) The viscous transparent gel became powdery as a result of the addition of HF. The resultant fluoride gel was further dried in a fume hood for 1–2 days. A desired amount of distilled water was added to achieve the desired gel composition. Pure-silica LTA was added as the seed lastly. The final gel composition was 0.95–0.99 SiO<sub>2</sub> : 0.013–0.048 Al : 0.45 12DM34MBI<sup>+</sup>OH<sup>-</sup> : 0.05 TMAOH : 0.50 HF : 5.0 H<sub>2</sub>O. The crystallization was performed in a 125 °C static oven for 1–3 weeks. Increasing aluminum contents in gels required longer crystallization times.

Zeolite Rho was synthesized using 18-crown-6 ether as the OSDA as Chatelain et al. have described.<sup>8</sup> Ludox HS-40 and sodium aluminate were used as the silica and alumina sources, respectively. The gel composition was 1 SiO<sub>2</sub> : 0.1 Al<sub>2</sub>O<sub>3</sub> : 0.130 Na<sub>2</sub>O : 0.030 Cs<sub>2</sub>O : 0.050 18-crown-6 : 10.0 H<sub>2</sub>O. The crystallization was performed in a 110 °C static oven for 2–8 days.

Zeolite KFI was synthesized without OSDAs.<sup>9</sup> Zeolyst CBV712 was used as the sole silica and alumina source. Desired amounts of sodium hydroxide, sodium nitrate, and potassium nitrate were dissolved in distilled water. After that, a desired amount zeolite Y was dispersed in the solution. The final gel composition was 1 SiO<sub>2</sub> : 0.0833 Al<sub>2</sub>O<sub>3</sub> : 3.3 Na<sup>+</sup> : 7.0 K<sup>+</sup> : 0.56 OH<sup>-</sup> : 9.74 NO<sub>3</sub><sup>-</sup> : 117 H<sub>2</sub>O. The crystallization was performed in a 140 °C static oven for 3 days. The same procedure was repeated for 3 times by wet-seeding the next batches with a portion of the previous batch used to enhance the crystallinity.

UZM-5 zeolite was prepared based on the charge density mismatch (CDM) synthesis strategy.<sup>10</sup> Colloidal silica AS-40 and aluminum isopropoxide were used as the silica and alumina sources, respectively. The final gel composition was 1 SiO<sub>2</sub> : 0.063 Al<sub>2</sub>O<sub>3</sub> : 1.0 TEOH : 0.125 TMAOH : 29.438 H<sub>2</sub>O. The crystallization was performed in a 150 °C rotating oven for 10 days.



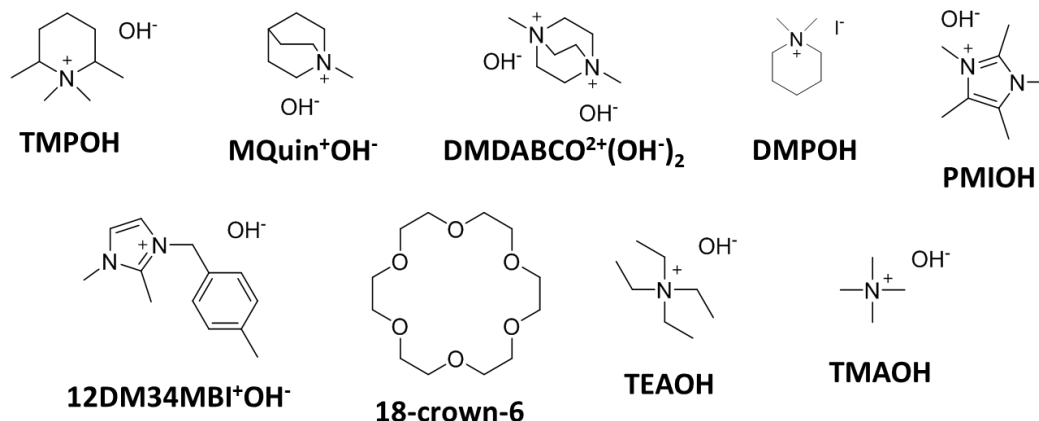


Figure S1. Schematic illustrations of the organic materials used to synthesize zeolites in this work.

### Synthesis Conditions (AlPO<sub>4</sub>-based Materials)

The organic materials used to crystallize AlPO<sub>4</sub>-based molecular sieve are schematically illustrated in Figure S2.

SAPO-34 was prepared from TEOH.<sup>11</sup> The molar composition of the gel was 1 Al<sub>2</sub>O<sub>3</sub> : 1 P<sub>2</sub>O<sub>5</sub> : 0.075 SiO<sub>2</sub> : 3 TEOH : 50 H<sub>2</sub>O. Catapal B alumina and Ludox HS-40 silica sol were used as the aluminum and silicon sources, respectively. The crystallization was performed at 200 °C in a static oven for 24 hours.

CoAPO-34 and MgAPO-34 were synthesized by using morpholine as the OSDA.<sup>12-13</sup> The gel composition was x Al<sub>2</sub>O<sub>3</sub> : 1 P<sub>2</sub>O<sub>5</sub> : y MO (M = Co, Mg) : 2.7 Morpholine : 60 H<sub>2</sub>O. For (x,y), (0.8, 0.4) and (0.7, 0.6) were tried. The aluminum, cobalt, and magnesium sources used here were Catapal B alumina, cobalt (II) sulfate hydrate, and magnesium acetate tetrahydrate, respectively. The crystallization was performed at 185 °C in a rotating oven for 72 hours.

SAPO-56 was synthesized using TMHA as the OSDA.<sup>14</sup> The gel composition was 0.8 Al<sub>2</sub>O<sub>3</sub> : 1.0 P<sub>2</sub>O<sub>5</sub> : 0.3–0.6 SiO<sub>2</sub> : 2 TMHA : 40 H<sub>2</sub>O. Catapal B alumina and Cab-O-Sil fumed silica were used as the aluminum and silicon sources, respectively. The crystallization was performed at 200 °C in a static oven for 96 hours.

STA-18 was synthesized using C<sub>6</sub>-diDABCO-Br<sub>2</sub> and TMA as the co-OSDAs.<sup>1</sup> The gel composition was 1.0 Al(OH)<sub>3</sub> : 0.7 H<sub>3</sub>PO<sub>4</sub> : 0.3 SiO<sub>2</sub> : 0.08–0.10 C<sub>6</sub>-diDABCO-Br<sub>2</sub> : 0.13 TMA : 0.28 TBAOH : 40 H<sub>2</sub>O. Aluminum hydroxide hydrogel and Cab-O-Sil fumed silica were used as the aluminum and silicon sources, respectively. The crystallization was performed at 190 °C in a rotating oven for 7 days.

SAPO-35 was synthesized using hexamethyleneimine as the OSDA. 1.0 Al<sub>2</sub>O<sub>3</sub> : 1.0 P<sub>2</sub>O<sub>5</sub> : 0.3–0.6 SiO<sub>2</sub> : 1.5 hexamethyleneimine : 55 H<sub>2</sub>O.<sup>15</sup> Catapal B alumina and Cab-O-Sil fumed silica were used as the aluminum and silicon sources, respectively. The crystallization was performed at 200 °C in a static oven for 24 hours. SAPO-16 (AST) was observed as the major impurity phase, but it could be separated from SAPO-35 by repeated steps of fractional centrifugation at 500 rpm.

SAPO-18 was prepared from TMPOH.<sup>16</sup> The gel composition was 1 Al<sub>2</sub>O<sub>3</sub> : 0.8 P<sub>2</sub>O<sub>5</sub> : 0.172 SiO<sub>2</sub> : 1 TMPOH : 19.2 H<sub>2</sub>O. The aluminum and silicon sources were Catapal B (VISTA) alumina and Ludox AS-40 silica sol (Sigma-Aldrich). The crystallization was performed at 190 °C in a rotating oven for 2 days.

CoAPO-18 and MgAPO-18 were prepared from the same diisopropylethylamine (DIPEA) OSDA with a gel composition of 1  $\text{Al}_2\text{O}_3$  : 1  $\text{P}_2\text{O}_5$  : 0.08 MO (M = Co, Mg) : 1.7 DIPEA : 50  $\text{H}_2\text{O}$ .<sup>17</sup> The crystallization was performed at 160 °C in a rotating oven for 8–11 days.

STA-7 was synthesized using Cyclam as the OSDA.<sup>18</sup> The gel composition was 1.0  $\text{Al}(\text{OH})_3$  : 0.6–0.8  $\text{H}_3\text{PO}_4$  : 0.2–0.4  $\text{SiO}_2$  : 0.108 Cyclam : 40  $\text{H}_2\text{O}$ . The aluminum and silicon sources were aluminum hydroxide dry-gel (Barcroft 250, SPI Pharma) and fumed silica. The crystallization was performed at 190 °C in a rotating oven for 72 hours. In some cases, white fluffy impurity was observed, and required extra purification steps. The desired STA-7 product was slightly yellowish and denser than the white impurity phase. The purification was performed using the fractional centrifugation at 500 rpm in distilled water. The top white phase was removed from the mixture by repeated centrifugation.

DNL-6 was synthesized using DEA and CTAB.<sup>19</sup> The gel composition was 1.0  $\text{Al}(\text{OH})_3$  : 0.8  $\text{H}_3\text{PO}_4$  : 0.2  $\text{SiO}_2$  : 1 DEA : 0.10–0.15 CTAB : 50  $\text{H}_2\text{O}$ . The aluminum and silicon sources were aluminum isopropoxide and TEOS. The hydrolysis alcohol products (i.e., ethanol and isopropanol) were removed by heating the gels at 80 °C. The crystallization was performed at 160 °C in a rotating oven for 48 hours.

SAPO-42 and STA-14 were synthesized using K222 and TBAOH as the OSDAs.<sup>18</sup> The gel composition was 1.0  $\text{Al}(\text{OH})_3$  : 0.8  $\text{H}_3\text{PO}_4$  : 0.2  $\text{SiO}_2$  : 0.108 K222 : 0.108x TBAOH : 40  $\text{H}_2\text{O}$  where x = 0–6. When x < 2, SAPO-42 was obtained, and when x > 5, STA-14 was obtained. This implies that  $\text{TEA}^+$  cations can structure-direct the *pau* small cages in this system. The crystallization was performed at 190 °C in a rotating oven for 48 hours.

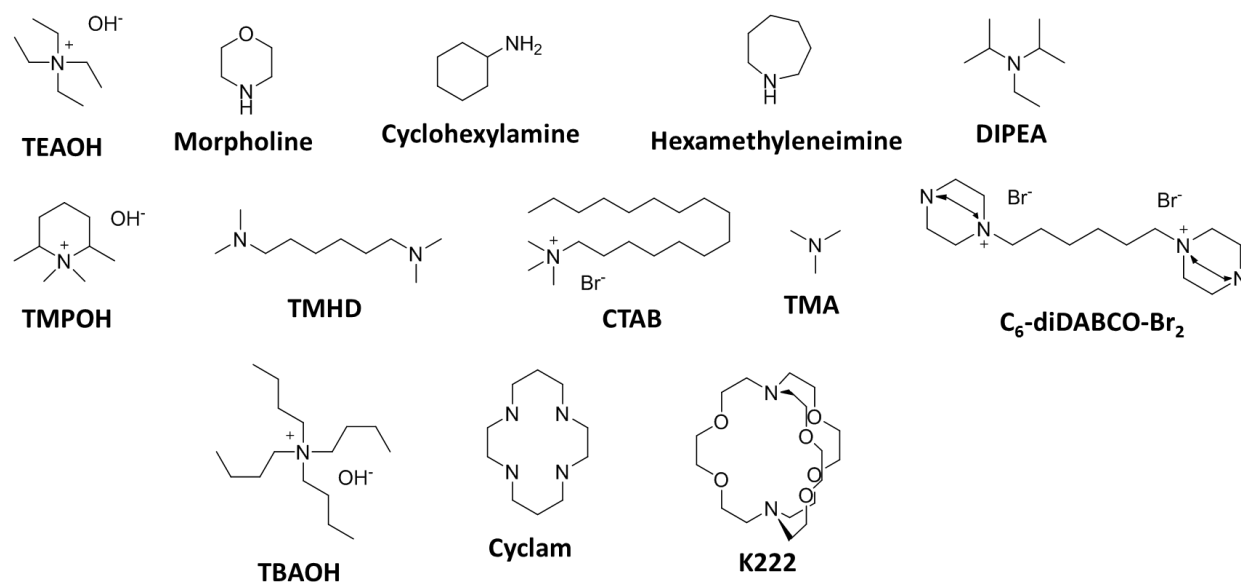


Figure S2. Schematic illustrations of the organic materials used to synthesize small-pore,  $\text{AlPO}_4$ -based molecular sieves in this work.

# Characterization of Materials

## Sample Information

Table S1. Materials information and reaction results from the molecular sieves investigated in this work.

Topological Information			Sample/Reaction Results					
Material	Framework	Channel dimensionality	Si/Al ratio (M/T ratio) <sup>[a][b]</sup>	Olefin Selectivity <sup>[c]</sup> (%)			Time to 85% MeOH conversion <sup>[d]</sup> [min]	Time to 1% DME formation <sup>[d]</sup> [min]
				Ethylene	Propylene	Butylenes		
SAPO-34 <sup>[e]</sup>	CHA	3	(0.123)	33.1	41.9	9.9	259	154
CoAPO-34			(0.022)	44.2	40.3	6.9	127	158
MgAPO-34			(0.015)	41.5	40.0	7.7	53	71
SAPO-56	AFX	3	(0.137)	31.3	32.7	9.6	295	250
STA-18	SFW	3	(0.176)	24.2	26.9	12.6	85	67
DMDABCO-LEV zeolite	LEV	2	8.3	34.4	30.0	7.8	34	28
Nu-3			17.7	35.2	26.5	6.8	259	154
SAPO-35			(0.120)	27.6	34.7	5.1	41	26
SSZ-98	ERI	3	6.0	29.3	20.1	7.8	141	108
SSZ-39	AEI	3	10.0	14.3	38.5	14.1	215	221
SAPO-18			(0.063)	23.8	47.0	12.8	514	327
CoAPO-18			(0.073)	19.8	42.3	14.2	260	146
MgAPO-18			(0.031)	17.1	40.0	14.6	216	105
Zeolite RTH	RTH	2	13.2	8.9	27.9	13.5	93	94
STA-7(1)	SAV	3	(0.133)	18.8	32.5	15.5	101	79
STA-7(2)			(0.185)	19.3	32.9	16.0	106	93
Zeolite LTA	LTA	3	28.8	21.0	19.1	17.5	148	111
SAPO-42			(0.150)	18.4	28.6	14.2	104	47
Zeolite RHO	RHO	3	5.4	20.1	10.4	15.2	90	76
DNL-6			(0.140)	23.4	23.0	18.4	128	112
Zeolite KFI	KFI	3	4.0	21.8	13.8	11.8	48	43
STA-14			(0.113)	20.5	30.4	12.5	69	44
UZM-5	UFI	2	6.2	19.0	21.7	14.6	37	24

[a] Characterized using EDS. [b] M=Si, Co, or Mg in  $\text{AlPO}_4$ -frameworks; T=M+Al+P, i.e., all tetrahedral atoms forming frameworks. [c] Evaluated at high methanol conversion level (98–100%) [d] Evaluated by intrapolation. [e] Synthesized using TEOH as the OSDA.

## Powder X-ray Diffraction (PXRD) Profiles

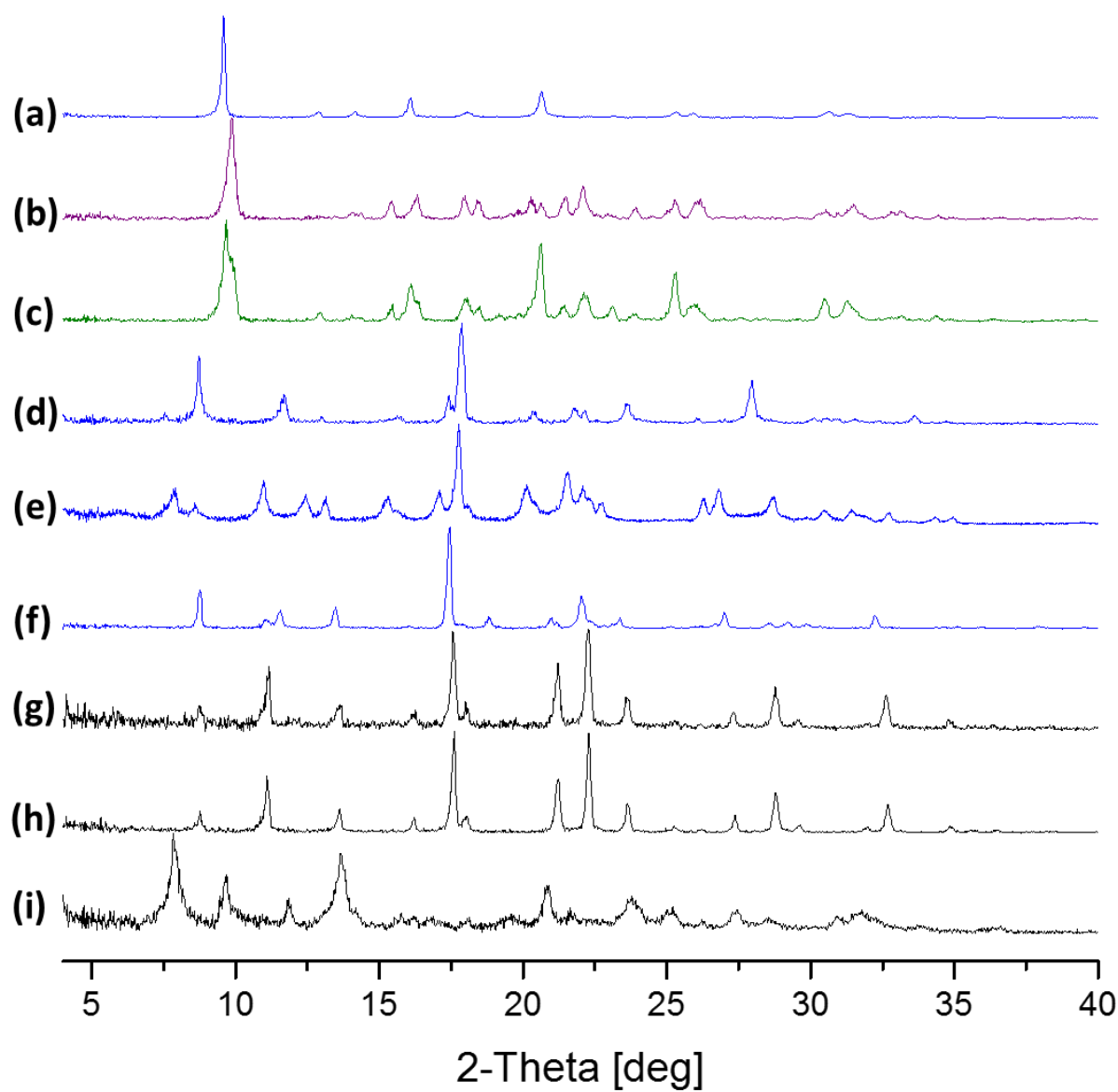


Figure S3. PXRD profiles of Category I and II materials: (a) TEAOH SAPO-34, (b) CoAPO-34, (c) MgAPO-34, (d) SAPO-56, (e) STA-18, (f) SAPO-35, (g) DMDABCO-LEV zeolite, (h) Nu-3 LEV, and (i) SSZ-98 ERI

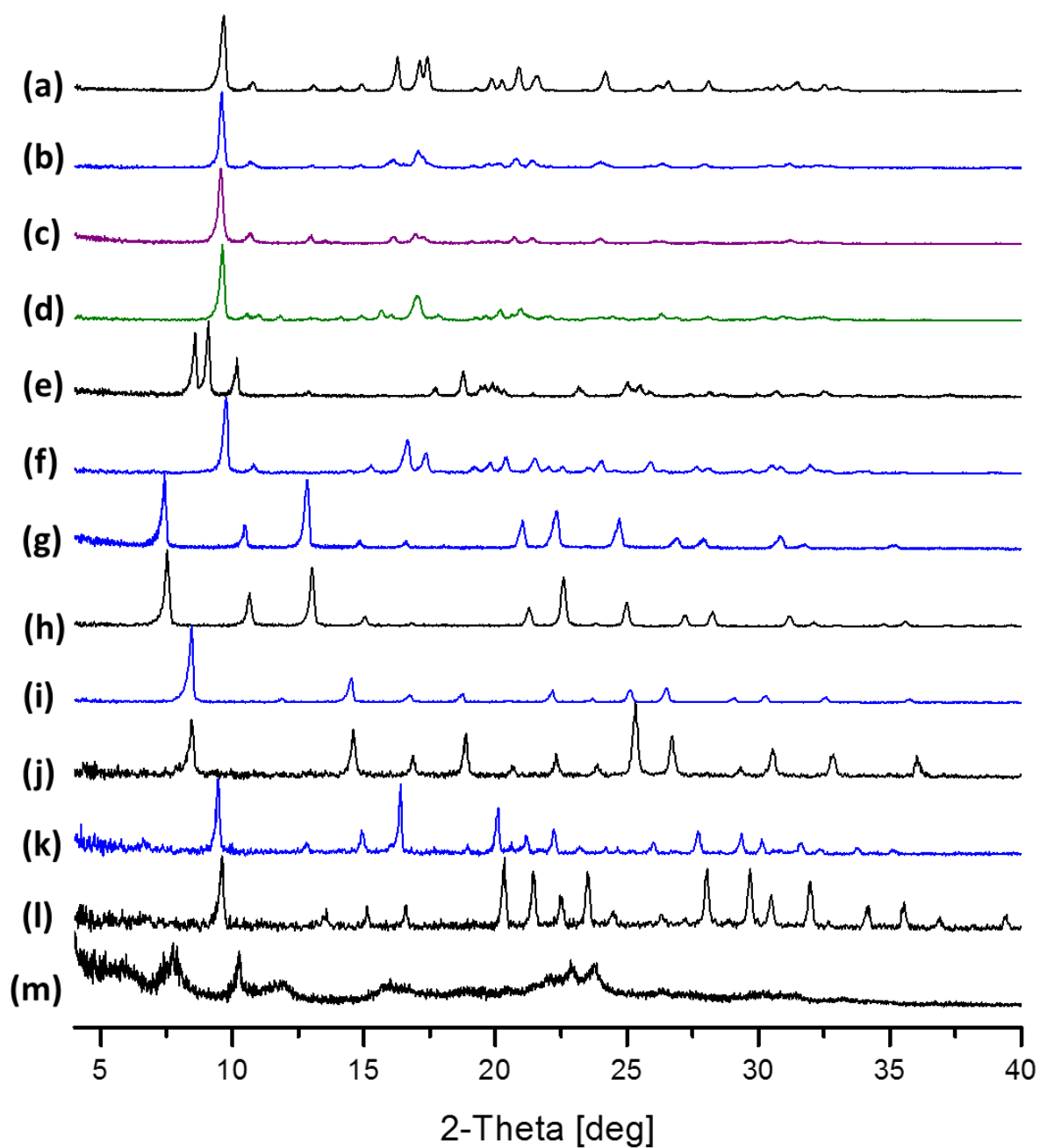


Figure S4. PXRD profiles of Category III and IV materials: (a) SSZ-39, (b) SAPO-18, (c) CoAPO-18, (d) MgAPO-18, (e) zeolite RTH, (f) STA-7(1), (g) SAPO-42, (h) zeolite LTA, (i) DNL-6, (j) zeolite RHO, (k) STA-14, (l) zeolite KFI, and (m) UZM-5.

## Scanning Electron Micrograph (SEM) Images

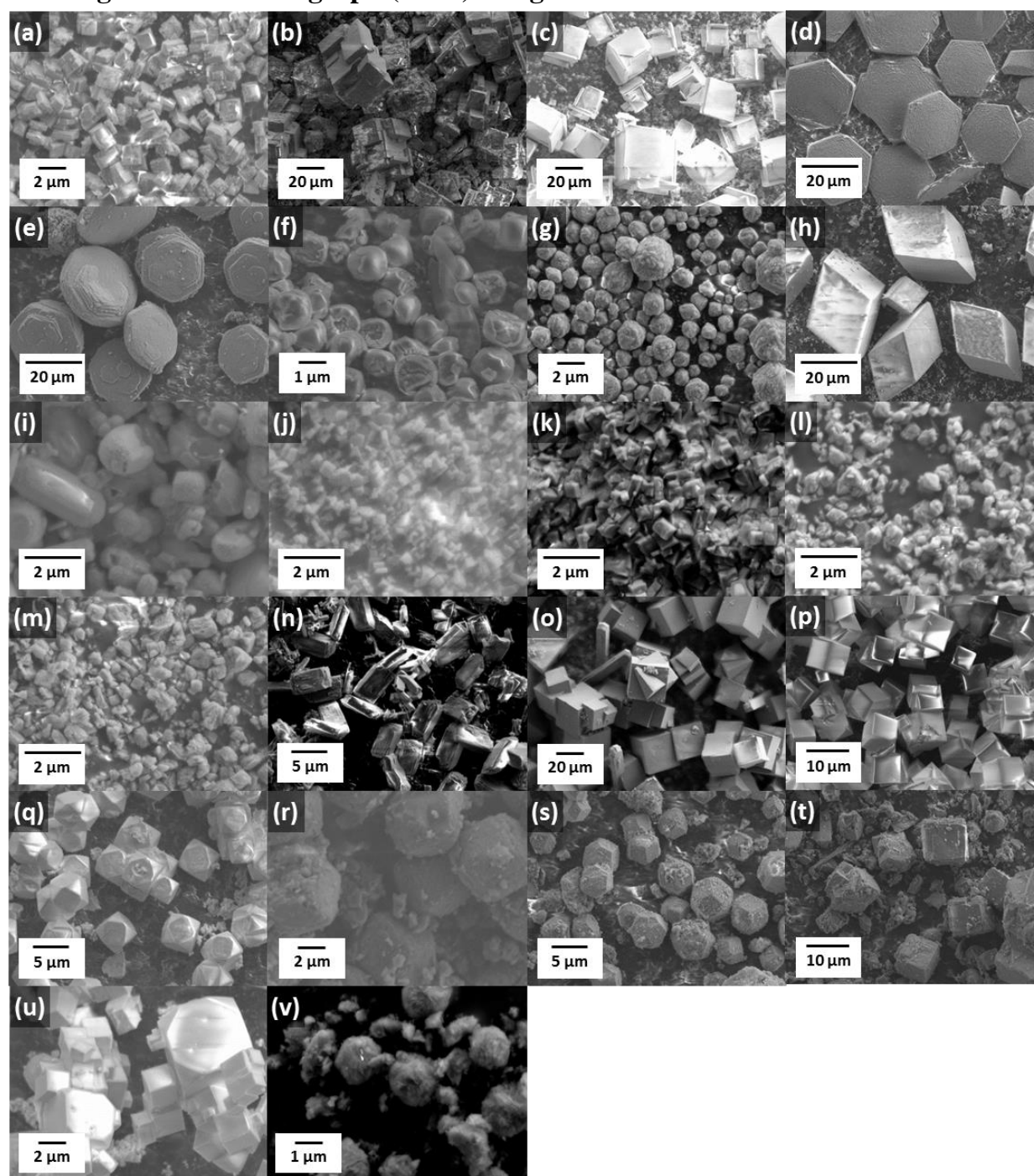


Figure S5. Scanning Electron Micrographs of the catalysts shown in this work: (a) SAPO-34, (b) CoAPO-34, (c) MgAPO-34, (d) SAPO-56, (e) STA-18, (f) DMDABCO-LEV zeolite, (g) Nu-3, (h) SAPO-35, (i) SSZ-98, (j) SSZ-39, (k) SAPO-18, (l) CoAPO-18, (m) MgAPO-18, (n) zeolite RTH, (o) STA-7(1), (p) zeolite LTA, (q) SAPO-42, (r) zeolite RHO, (s) DNL-6, (t) zeolite KFI, (u) STA-14, and (v) UZM-5.

## Visualization of Cage Structures and Their Cage-defining Rings

Crystallographic data for each framework was imported from the International Zeolite Association-Structure Committee (IZA-SC) Database. The visualizations were based on the hard-sphere model, where the van der Waals radii of tetrahedral (silicon) and oxygen atoms are 1.35 Å. The radius of the “probe molecule” used here is 1.80 Å, and is essentially the same as the kinetic diameter of a methanol molecule.

From the imported crystallographic data, the following scalar field was generated.<sup>20</sup>

$$d(x, y, z) = \min \sqrt{(X_i - x)^2 + (Y_i - y)^2 + (Z_i - z)^2} - r_{\text{framework}} - r_{\text{probe}}$$

where  $(X_i, Y_i, Z_i)$  is the Cartesian position of the  $i$ -th framework atom. ( $r_{\text{framework}} = 1.35$  Å,  $r_{\text{probe}} = 1.80$  Å, as mentioned above.)  $d(x, y, z)$  is the distance between the surface of the hard-sphere probe molecule at  $(x, y, z)$  and that of the hard-sphere framework atom closest to the probe molecule. Where  $d(x, y, z) = 0$ , the probe molecule hard sphere contacts the framework. Therefore, the visualization of the parametric surface  $d(x, y, z) = 0$  will show the ‘real’ shape of accessible volume for the probe molecule (here, represents methanol). The maximum radius of a sphere that can be included within a cage can be also found using the same equation by finding the maximum value of  $d(x, y, z)$  when  $r_{\text{probe}} = 0$ .

The surface visualizations were generated using Wolfram Mathematica 10.1 Student Edition Package equipped with the Crystallica application developed by Bianca Eifert at Justus Liebig University Giessen, Germany, and the VESTA platform by Fujio Izumi at Quantum Beam Center, National Institute for Materials Science, Japan.<sup>21</sup>

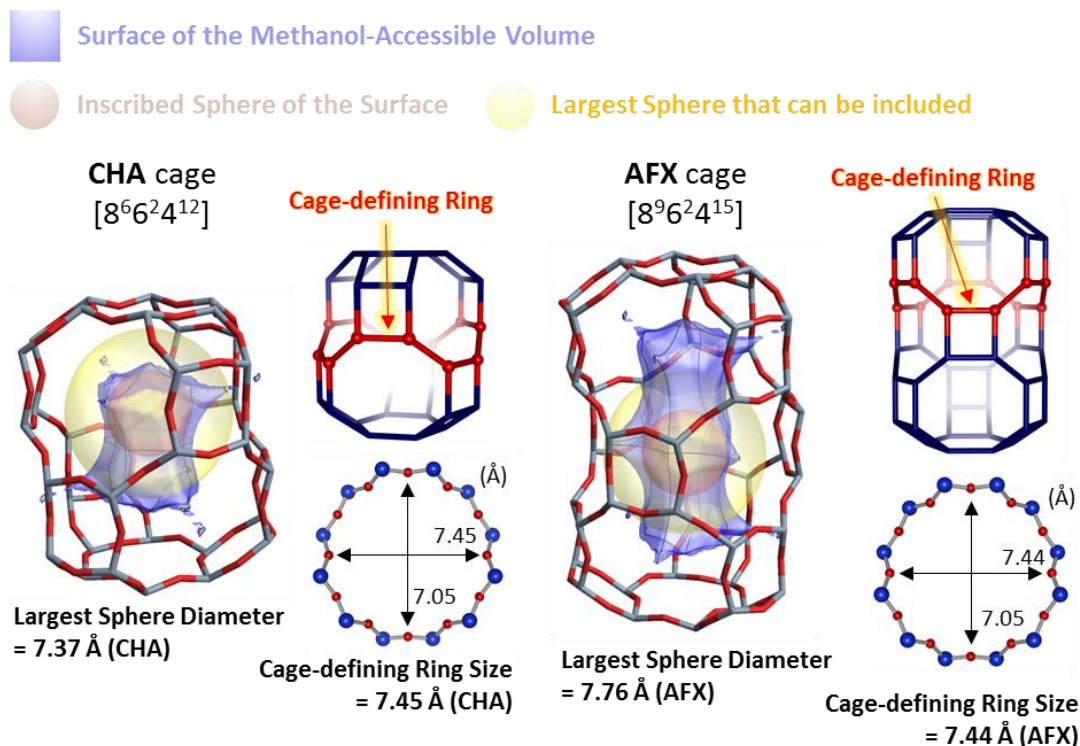


Figure S6. The cage visualizations, selection of the cage-defining rings, and their sizes for CHA and AFX.



Surface of the Methanol-Accessible Volume

Inscribed Sphere of the Surface

Largest Sphere that can be included

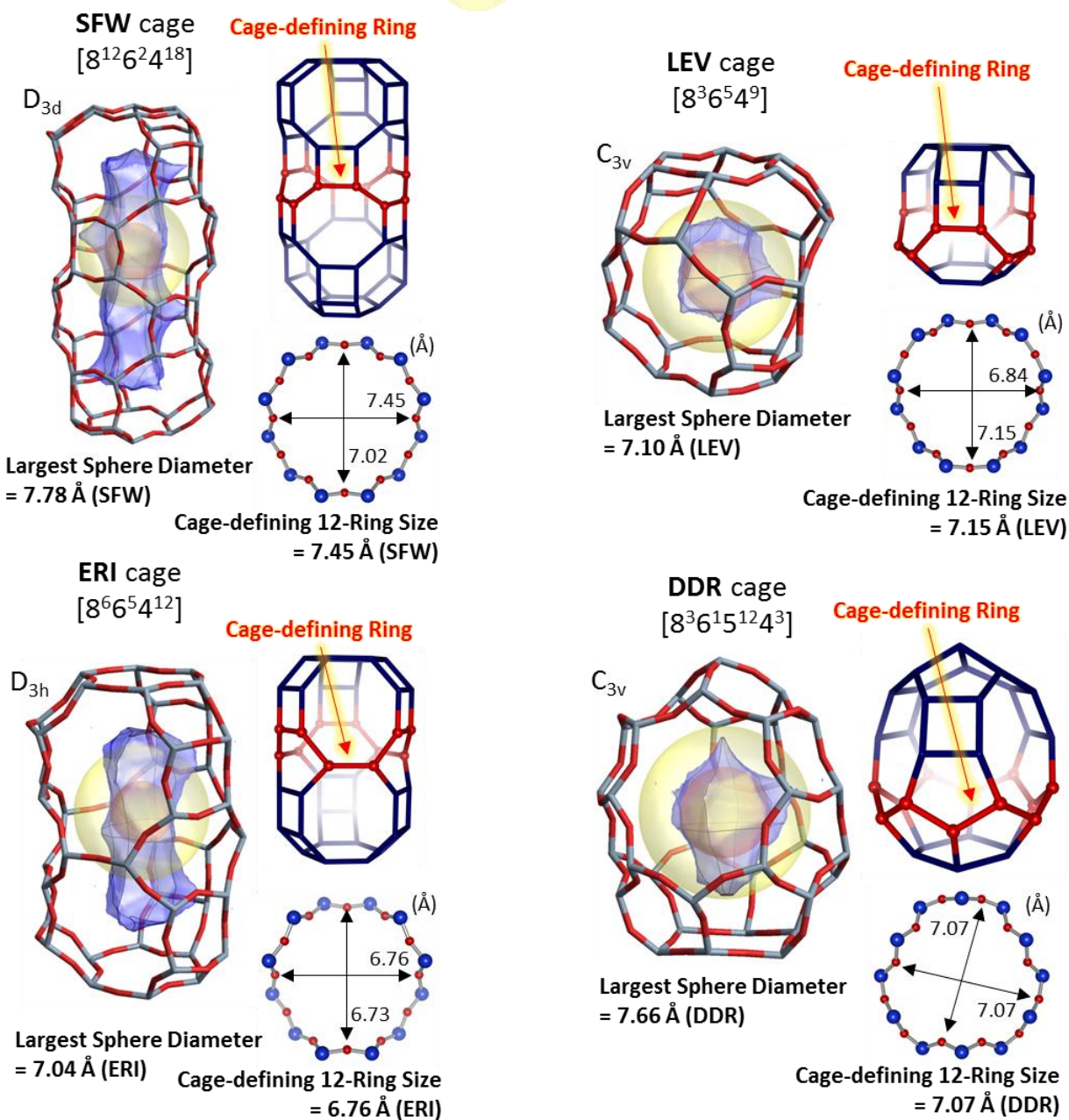


Figure S7. The cage visualizations, selection of the cage-defining rings, and their sizes for SFW, LEV, ERI, and DDR.



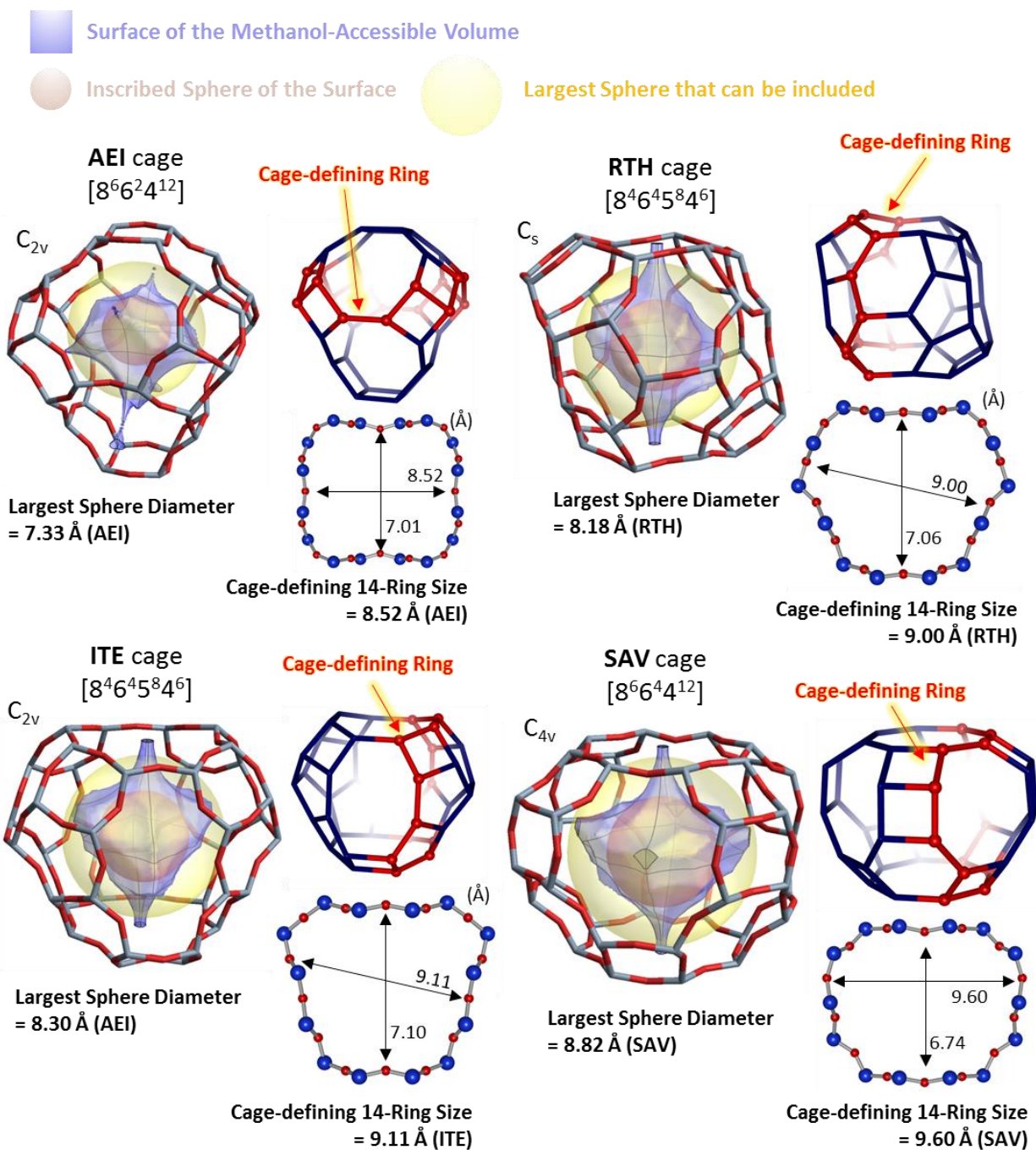


Figure S8. The cage visualizations, selection of the cage-defining rings, and their sizes for AEI, RTH, ITE, and SAV.

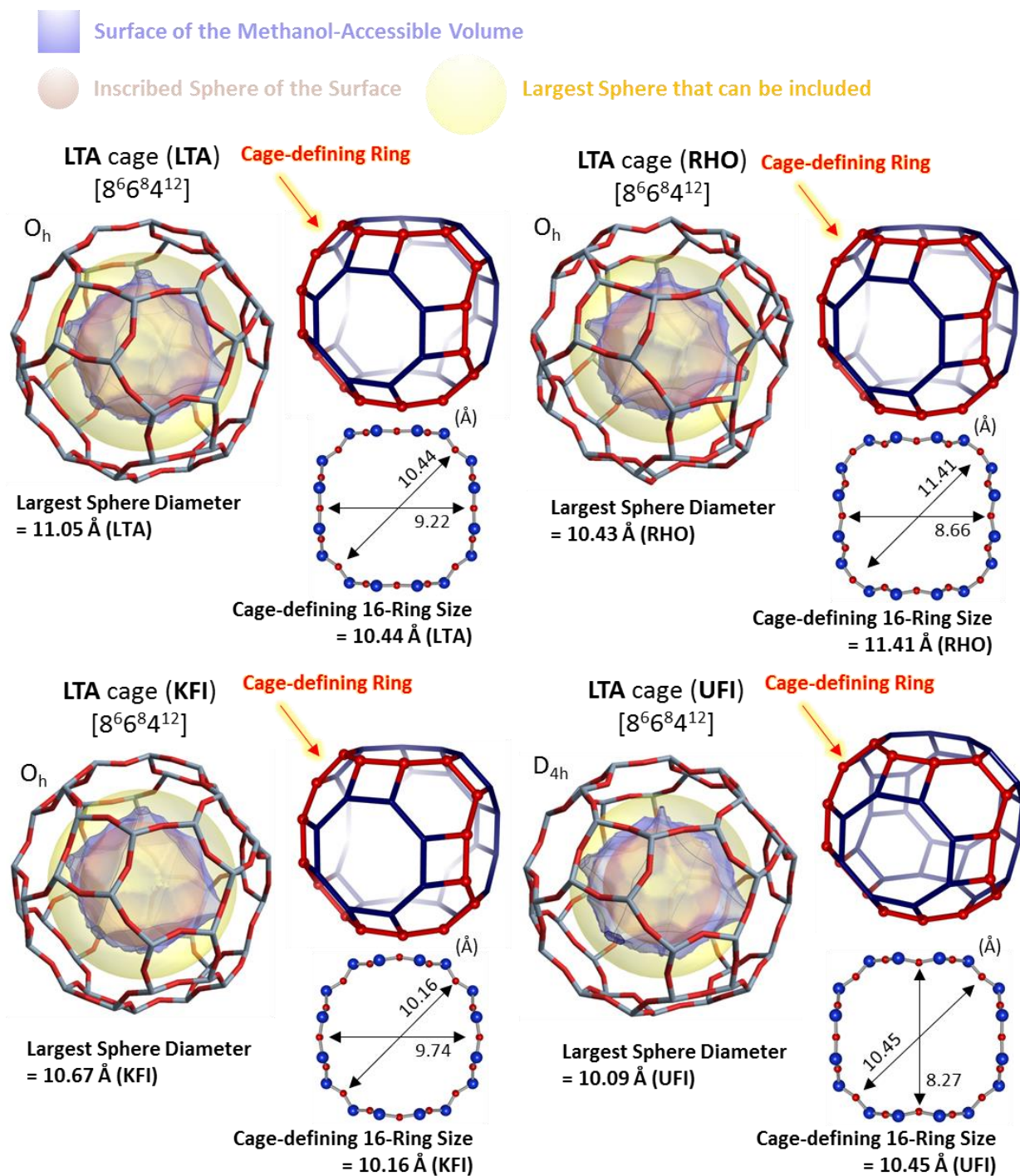


Figure S9. The cage visualizations, selection of the cage-defining rings, and their sizes for LTA, RHO, KFI, and UFI.

# MTO Time-of-stream Selectivity Profiles

## Category I

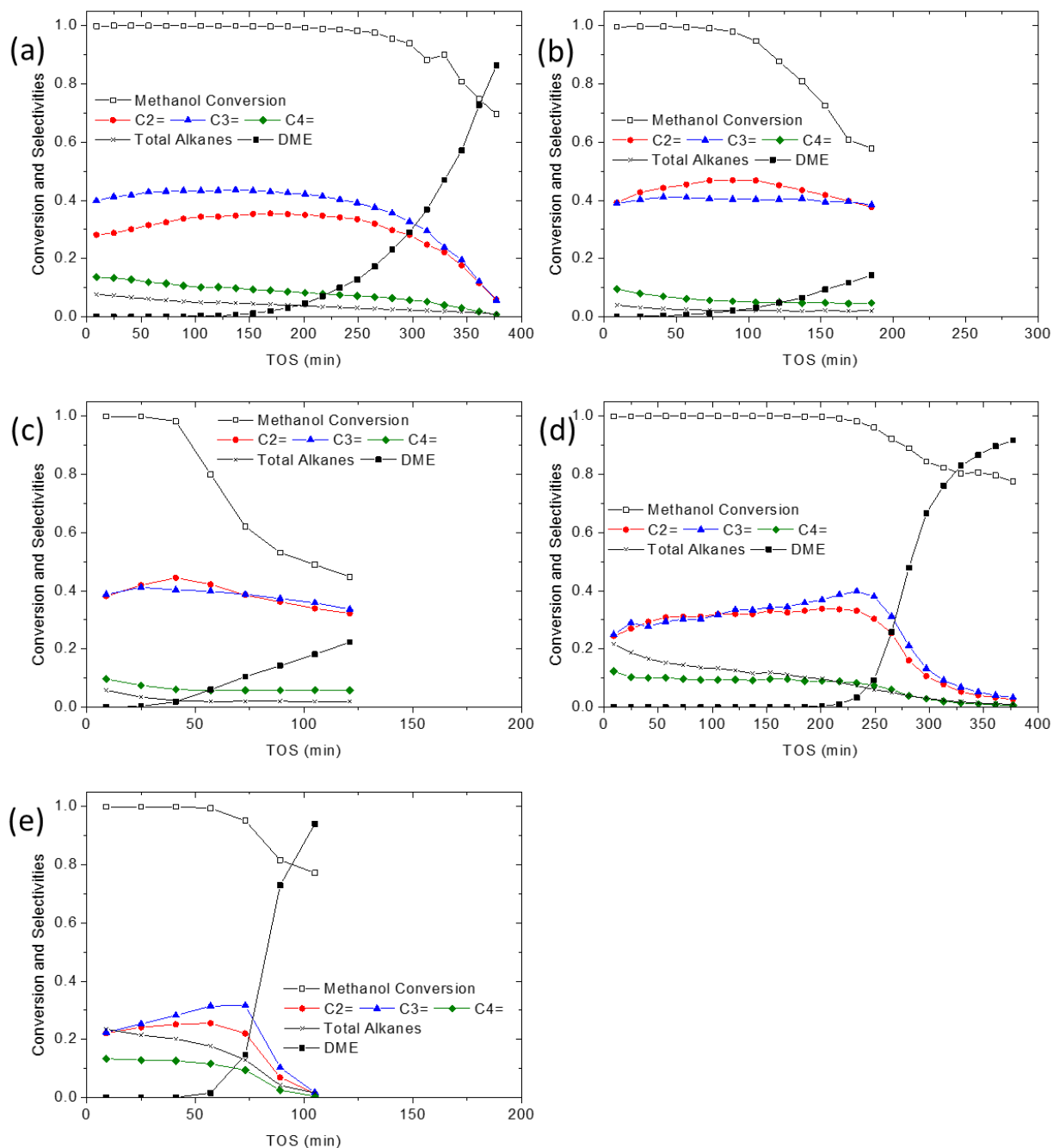


Figure S10. MTO-reaction time-on-stream profiles of: (a) SAPO-34, (b) CoAPO-34, (c) MgAPO-34, (d) SAPO-56, and (e) STA-18

## Category II

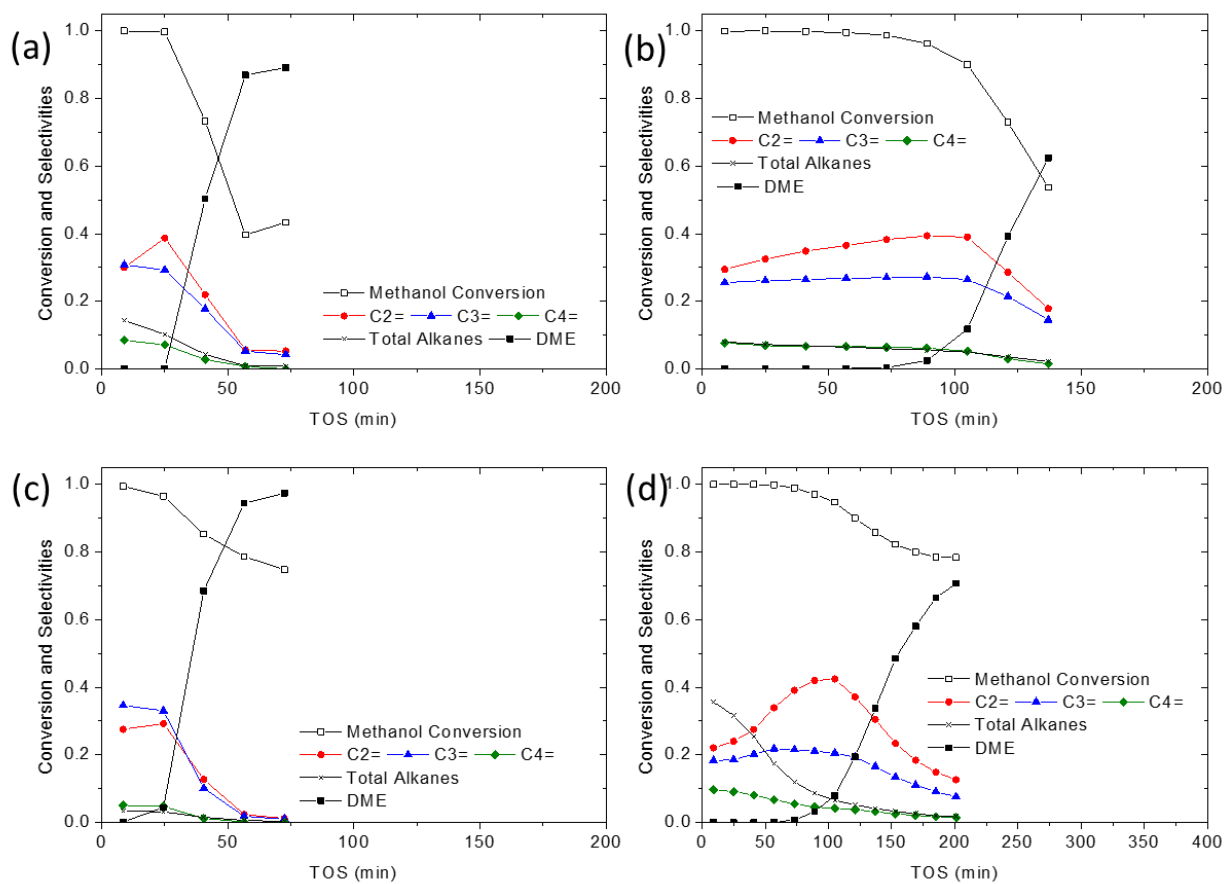


Figure S11. MTO-reaction time-on-stream profiles of: (a) dimethyl-DABCO LEV zeolite, (b) SSZ-17, (c) SAPO-35, and (d) SSZ-98.

### Category III

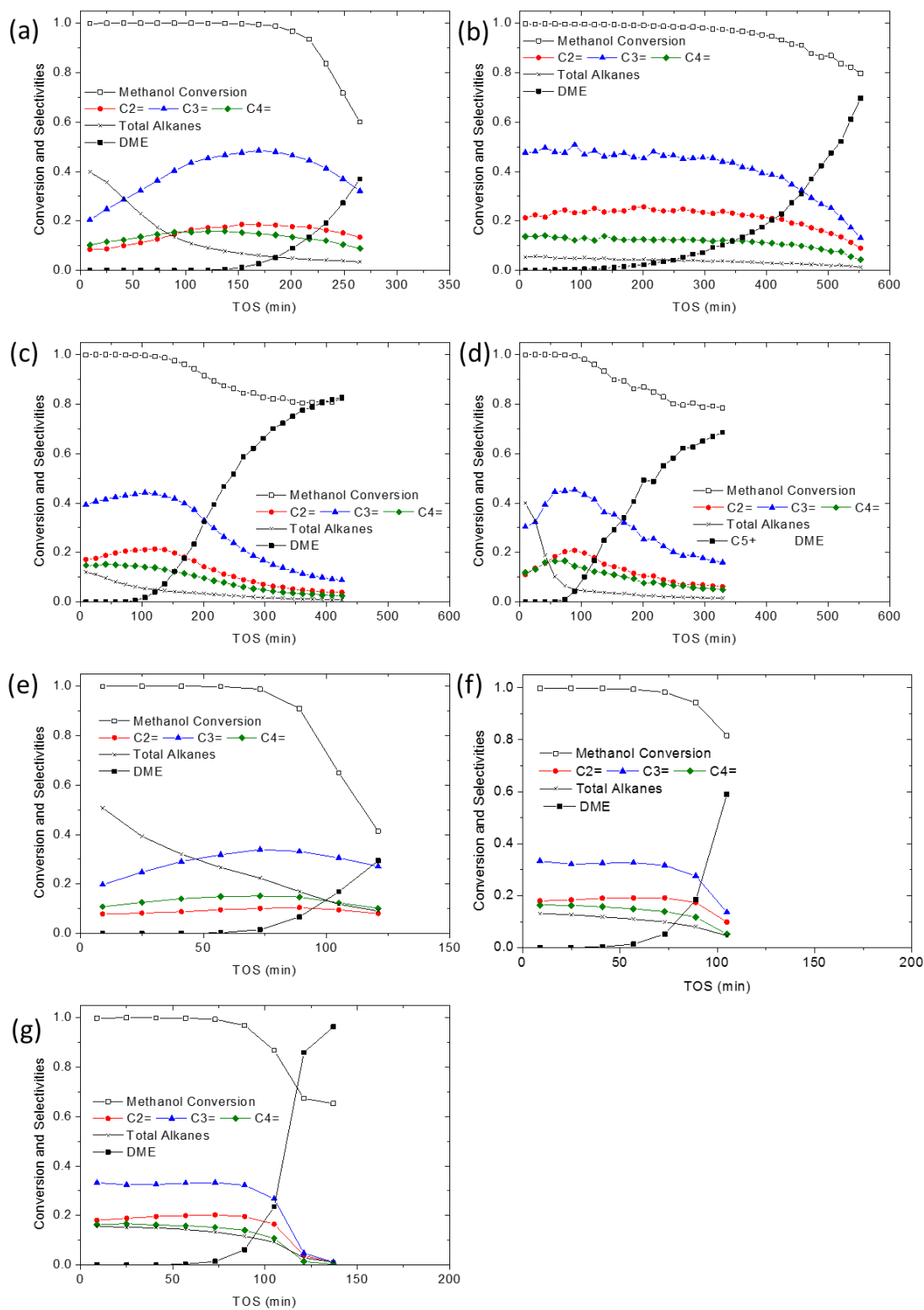


Figure S12. MTO-reaction time-on-stream profiles of: (a) SSZ-39, (b) SAPO-18, (c) CoAPO-18, (d) MgAPO-18, (e) zeolite RTH, (f) STA-7(1), and (g) STA-7(2)

## Category IV

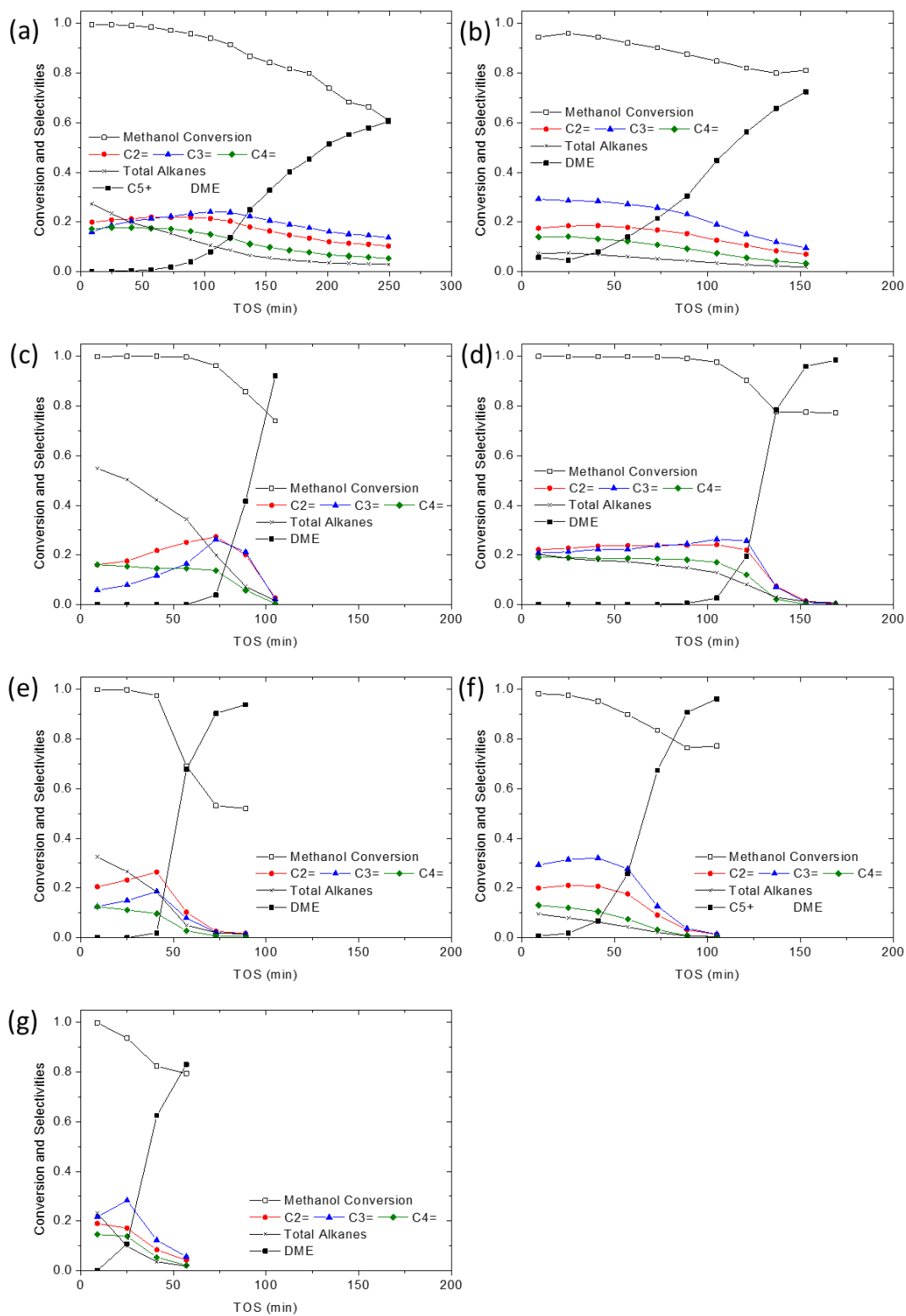


Figure S13. MTO-reaction time-on-stream profiles of: (a) zeolite LTA, (b) SAPO-42, (c) zeolite RHO, (d) DNL-6, (e) zeolite KFI, (f) STA-14, and (g) UZM-5



## Ethylene-to-Propylene Ratio by Time-on-Stream

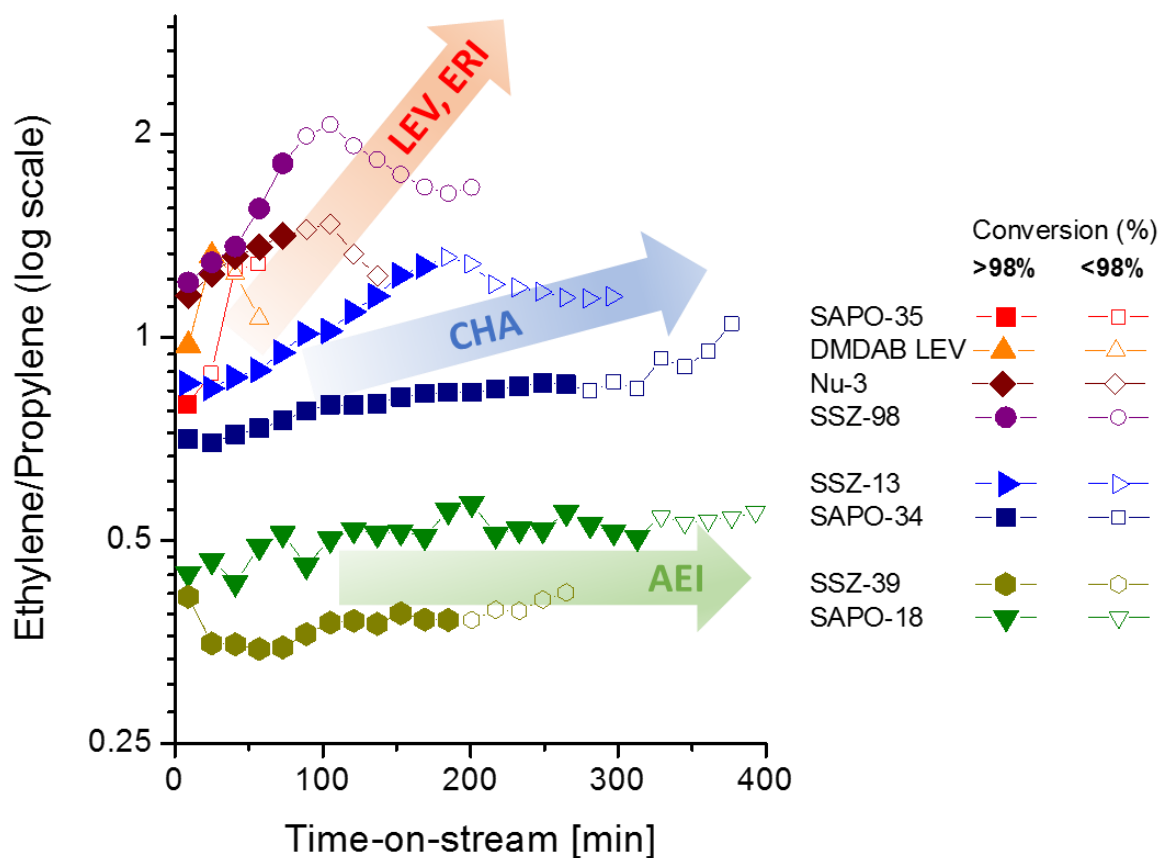


Figure S14. The ratio of ethylene selectivities to propylene selectivities as functions of reaction time-on-stream for selected catalysts.

## References

- (1) Turrina, A.; Garcia, R.; Cox, P. A.; Casci, J. L.; Wright, P. A., *Chem. Mater.* **2016**, 28, 4998-5012.
- (2) Zones, S. I.; Van Nordstrand, R. A., *Zeolites* **1988**, 8, 409-415.
- (3) Xie, D. Synthesis of aluminosilicate LEV framework type zeolites, US Patent 9,708,193B2. 2017.
- (4) Xie, D. Method for Preparing Zeolite SSZ-98, US Patent 9,663,379B2. 2016.
- (5) Schmidt, J. E.; Deimund, M. A.; Xie, D.; Davis, M. E., *Chem. Mater.* **2015**, 27, 3756-3762.
- (6) Boal, B. W.; Schmidt, J. E.; Deimund, M. A.; Deem, M. W.; Henling, L. M.; Brand, S. K.; Zones, S. I.; Davis, M. E., *Chem. Mater.* **2015**, 27, 7774-7779.
- (7) Dusselier, M.; Deimund, M. A.; Schmidt, J. E.; Davis, M. E., *ACS Catal.* **2015**, 5, 6078-6085.
- (8) Chatelain, T.; Patarin, J.; Fousson, E.; Soulard, M.; Guth, J. L.; Schulz, P., *Micropor. Mater.* **1995**, 4, 231-238.
- (9) Kim, J.; Cho, S. J.; Kim, D. H., *ACS Catal.* **2017**, 7, 6070-6081.
- (10) Park, J. W.; Lee, J. Y.; Kim, K. S.; Hong, S. B.; Seo, G., *Appl. Catal. A* **2008**, 339, 36-44.
- (11) Deimund, M. A.; Harrison, L.; Lunn, J. D.; Liu, Y.; Malek, A.; Shayib, R.; Davis, M. E., *ACS Catal.* **2016**, 6, 542-550.
- (12) Ashtekar, S.; Chilukuri, S. V. V.; Prakash, A. M.; Harendranath, C. S.; Chakrabarty, D. K., *J. Phys. Chem.* **1995**, 99, 6937-6943.
- (13) Ashtekar, S.; Prakash, A. M.; Chakrabarty, D. K.; Chilukuri, S. V. V., *J. Chem. Soc. Farad. Trans.* **1996**, 92, 2481-2486.
- (14) Wilson, S. T.; Broach, R. W.; Blackwell, C. S.; Bateman, C. A.; McGuire, N. K.; Kirchner, R. M., *Micropor. Mesopor. Mater.* **1999**, 28, 125-137.
- (15) Pinilla-Herrero, I.; Olsbye, U.; Márquez-Álvarez, C.; Sastre, E., *J. Catal.* **2017**, 352, 191-207.
- (16) Corma, A.; Moliner, M.; Martínez, R. Synthesis of sapo-18 and the catalytic applications thereof, US Patent Application 20170259253A1. 2017.
- (17) Chen, J.; Thomas, J. M., *J. Chem. Soc. Chem. Commun.* **1994**, 603-604.
- (18) Castro, M.; Warrender, S. J.; Wright, P. A.; Apperley, D. C.; Belmabkhout, Y.; Pirngruber, G.; Min, H.-K.; Park, M. B.; Hong, S. B., *J. Phys. Chem. C* **2009**, 113, 15731-15741.
- (19) Su, X.; Tian, P.; Li, J.; Zhang, Y.; Meng, S.; He, Y.; Fan, D.; Liu, Z., *Micropor. Mesopor. Mater.* **2011**, 144, 113-119.
- (20) Nagy, T. F.; Mahanti, S. D.; Dye, J. L., *Zeolites* **1997**, 19, 57-64.
- (21) Momma, K.; Izumi, F., *J. Appl. Crystallogr.* **2008**, 41, 653-658.