Supplementary Information

A Reconstruction Strategy to Synthesize Mesoporous SAPO

Molecular Sieve Single Crystals with High MTO Catalytic Activity

Chan Wang,^{a,+} Miao Yang,^{a,+} Mingrun Li,^b Shutao Xu,^a Yue Yang^a Peng Tian,^{a,*} and Zhongmin Liu^{a,*}

^a National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: tianpeng@dicp.ac.cn; liuzm@dicp.ac.cn

^b State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

+ These authors contributed equally to this work.

Sample Preparation

Preparation of milled SAPO-34 precursor

SAPO-34 was first synthesized according to our previous report.¹ The composition of the product is Al_{0.448}Si_{0.200}P_{0.351}O₂. 10.0 g SAPO-34 was calcined at 600 °C for 240 min to remove template. After that, it was dispersed into water and milled in a planetary ball mill (QM-3SP2, Nanjing China) at 550 rpm/min for 420 min. The agate beads have mixed diameters of 3, 6 and 10 mm. After milling, the mud was collected and dried at 110 °C overnight. The XRD pattern of the milled SAPO-34 precursor is shown in Fig. S13.

Synthesis of SP34-MS

TPOAC was first added into deionized water and stirred for 1 h. And then, Al(i-C₃H₇O)₃, DEA, TEOS and H₃PO₄ were added in sequence. The SAPO gel has a molar composition of DEA/Al₂O₃/P₂O₅/TPOAC/TEOS/H₂O = 2.3/1.0/1.0/0.15/0.45/150. After that, 45.5% milled SAPO-34 precursor was added into the mixture and stirred overnight. Finally, the mixture was transferred into a stainless steel autoclave and heated at 200 °C for 4 h under rotation. The products were filtrated, washed and dried in air. Template removal was performed by calcination in air with a temperature profile of 2 °C/min to 600 °C, where it was kept for 2 h. The composition of the product is Al_{0.488}Si_{0.148}P_{0.364}O₂.

The amount of the precursor was calculated by the following formula: Precursor amount (%) = $M_{milled SAPO-34} \times 100 / M_{(Al_2O_3 + P_2O_5 + SiO_2)_{gel}}$, where $M_{milled SAPO-34}$ and $M_{(Al_2O_3 + P_2O_5 + SiO_2)_{gel}}$ stand for the weights of the milled SAPO-34 and the dry mass of three inorganic oxides in the starting mixture, respectively.

Synthesis of SP34-P

The synthetic procedure is the same with SP34-MS except using TEOS as the only silica source. The SAPO gel with a molar composition of DEA/Al₂O₃/P₂O₅/TEOS/H₂O = 2.3/1.0/1.0/0.9/150 was prepared to control the product composition comparable to that of SP34-MS. The amount of the milled SAPO-34 precursor is equal to that of SP34-MS, which is 21.4% calculated by the above formula. The composition of the product is Al_{0.490}Si_{0.151}P_{0.359}O₂.

Synthesis of mesoporous SAPO-11

45.5% milled SAPO-34 precursor was charged into a gel consisted of TPOAC, TEOS, DEA, Al(i- C_3H_7O)₃, H_3PO_4 and H_2O with the composition of DEA/Al₂O₃/P₂O₅/TPOAC/TEOS/H₂O = 1.7/1.0/1.0/0.45/0.15/150. The mixture was hydrothermally crystallized at 200 °C for 36 h. The products were filtrated, washed and dried in air.

Synthesis of mesoporous DNL-6

22.9% milled SAPO-34 precursor was charged into a gel consisted of TPOAC, TEOS, DEA, Al(i- C_3H_7O)₃, H_3PO_4 and H_2O with the composition of DEA/Al₂O₃/P₂O₅/TPOAC/TEOS/H₂O = 3.5/1.0/1.0/0.075/0.225/150. The mixture was hydrothermally crystallized at 180 °C for 3 h. The products were filtrated, washed and dried in air.

Characterization

The powder XRD patterns were recorded on a PANalytical X' Pert PRO X-ray diffractometer with Cu-K α radiation (λ = 1.54059 Å), operating at 40 kV and 40 mA. The chemical composition of the samples was determined with Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed by scanning electron microscopy (SEM) using a TM3000 (Hitachi) and field emission SEM (Hitachi SU8020). Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were recorded with FEI Tecnai F30 electron microscope. Textural properties of the calcined samples were determined by N₂ adsorption at 77 K on a Micromeritics ASAP 2020 system. The total surface area was calculated based on the BET equation. The micropore volume, micropore surface area and external surface area were evaluated using the t-plot method. Mesopore volume was evaluated from the adsorption isotherm by Barret-Joyner-Halenda (BJH) method. The temperature-programmed desorption of ammonia (NH₃-TPD) was carried out with an Autochem II 2920 equipment (Micromeritics). 0.2 grams of the sample particles (40-60 mesh) were loaded into a U-quartz tube and pretreated at 650 °C for 60 min under He flow. After cooling down to 100 °C, a gas mixture of NH₃ and He flow was introduced to saturate the sample surface with NH₃ adsorption (60 min). After this, He flow was purged through the sample for 30 min to remove the weakly adsorbed NH₃ molecules. The measurement of the desorbed NH₃ was performed from 100 °C to 650 °C (10 °C/min) under He flow (20 ml/min). ²⁹Si magic-angle-spinning (MAS)/cross-polarization (CP) nuclear magnetic resonance (NMR) and ¹³C MAS NMR analyses were carried out on a Bruker AvanceIII 600 spectrometer at 119.2 MHz for ²⁹Si and 150.9 MHz for ¹³C. ²⁹Si CP/MAS NMR spectra were measured with a contact time of 3 ms and a recycle delay of 2 s. ²⁹Si CP/MAS NMR spectra were recorded with a 4 mm MAS probe with a spinning rate of 8 kHz. ¹³C MAS NMR spectra were recorded with a 4 mm MAS probe with a spinning rate of 12 kHz. Chemical shifts were referenced to 4, 4-dimethyl-4-silapentane sulfonate sodium salt (DSS) for ²⁹Si, and adamantane for ¹³C. Laser-hyperpolarized (HP) ¹²⁹Xe NMR experiments were carried out at 110.6 MHz on the Varian Infinity-plus 400 spectrometer using a 7.5 mm probe. Prior to each experiment, samples were pressed, crushed, and sieved into 40-60 mesh particles, then dehydrated at 400 °C under vacuum (<10⁻⁴ Torr) for ca. 20 h. A flow of 1% Xe-1% N₂-98% He gas mixture was delivered at the rate of 148 mL/min to the sample in detection region via plastic tubing. Variable-temperature NMR measurements were performed in the range of 163-293 K. All spectra were acquired with 3.0 μ s π /2 pulse, 100 scans, and 2 s recycle delay. The chemical shifts were referenced to the signal of xenon gas. The two-dimensional exchange experiments (2D-EXSY) were performed at 173 K using a 90°-t₁-90°-t₂ pulse sequence in TPPI mode. Each 2D spectrum was acquired with 32 points in the t₁ dimension and 1024 points in the t₂ dimension. Before Fourier transformation, the t₁ dimension was zero-filled to 256 points. Mixing time was 2 ms. The weight ratio of SAPO-34 and silica in mechanically mixed sample was 3.6/1, and the two parts were blended thoroughly.

Catalyst evaluation

Methanol to olefins (MTO) reaction was performed in a quartz tubular fixed-bed reactor at atmospheric pressure. 300 mg catalyst (40-60 mesh) was loaded in the quartz reactor and activated at 550 °C in a He flow of 30 ml/min for 1 h before starting each reaction run, and then the temperature was adjusted to a reaction temperature of 450 °C. The methanol was fed by passing the carrier gas (42 mL/min) through a saturator containing methanol at 30 °C, which gave a weight hourly space velocity (WHSV) of 3 h⁻¹. The reaction products were analyzed using an online gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and Plot-Q column.

1 G. Y. Liu, P. Tian, J. Z. Li, D. Z. Zhang, F. Zhou and Z. M. Liu, *Microporous Mesoporous Mater.*, 2008, **111**, 143.



Fig. S1 XRD patterns of samples SP34-P, SP34-MS and SP34-MS-HT.



Fig. S2 SEM images of calcined samples (a) SP34-P and (b) SP34-MS.



Fig. S3 (a) N_2 sorption isotherms and (b) pore size distribution curve of mesoporous silica (SiO₂). (c) N_2 sorption isotherms and (d) pore size distribution curve of mechanical mixture of mesoporous silica (SiO₂) and microporous SAPO-34.



Fig. S4 Laser-hyperpolarized ¹²⁹Xe NMR spectra of Xe adsorbed in the (a) mesoporous silica (SiO₂), (b) SP34-P, (c) mechanical mixture and (d) SP34-MS at different temperatures.



Fig. S5 Laser-hyperpolarized ¹²⁹Xe 2D-EXSY NMR spectra of (a) mechanically mixed microporous SAPO-34 and mesoporous silica and (b) SP34-MS at 173 K with mixing time of 2 ms using a 90°-t₁-90°-t₂ pulse sequence in TPPI mode. Each 2D spectrum was acquired with 32 points in the t₁ dimension and 1024 points in the t₂ dimension. Before Fourier transformation, the t₁ dimension was zero-filled to 256 points.



Fig. S6 TEM images and SAED patterns of individual SP34-MS crystals taken along the (a) [100] and (b) [-111] zone axes.



Fig. S7 SEM image of sample SP34-MS-HT.



Fig. S8 Methanol conversion and selectivity for ethylene and propylene variation with time-onstream over SP34-P, SP34-MS and SP34-MS-HT, experimental conditions: WHSV = 3 h^{-1} , T = 450 °C, catalyst weight = 300 mg.



Fig. S9 NH₃-TPD profiles of SP34-P, SP34-MS and SP34-MS-HT.



Fig. S10 SEM images of samples synthesized with different SiO_2/Al_2O_3 and different amount of milled SAPO-34 precursor: (a) SP34-MS-1, (b) SP34-MS-2, (c) SP34-MS-3, (d) SP34-MS-4, (e) SP34-MS and (f) SP34-MS-5 corresponding to the Table S2.



Fig. S11 (a) XRD pattern (b) N_2 sorption isotherms (c) SEM image (d) TEM image and SAED pattern (insert) of calcined mesoporous SAPO-11.



Fig. S12 (a) XRD pattern (b) N_2 sorption isotherms (c) SEM image (d) TEM image and SAED pattern (insert) of calcined mesoporous DNL-6.



Fig.S13 XRD pattern of the prepared milled SAPO-34 precursor.

Table S1 Textural properties of Mixture

Sample	S _{BET} ^a (m ² /g)	S _{mic} ^b (m²/g)	S _{ext} ^b (m²/g)	V _{mic} ^b (cm ³ /g)	V _{meso} ^c (cm³/g)
Mixture	559	443	116	0.20	0.17

^{*a*} Total surface area is determined by the BET equation. ^{*b*} Micropore surface area, volume and external surface area are determined by the t-plot method. ^{*c*} Mesopore volume is determined from the adsorption isotherm by the BJH method.

Sample	SiO ₂ /Al ₂ O ₃	Precursor ^b (wt%)	Product composition Si/Al/P	S _{BET} ^c (m²/g)	S _{mic} ^d (m²/g)	S _{ext} ^d (m²/g)	V _{mic} ^d (cm ³ /g)	V _{meso} ^e (cm ³ /g)
SP34-MS-1	0.2	49.8	0.106/0.515/0.379	521	438	83	0.20	0.21
SP34-MS-2	0.4	47.6	0.128/0.504/0.368	532	406	126	0.19	0.27
SP34-MS-3	0.6	10.7	0.130/0.500/0.370	517	374	143	0.17	0.22
SP34-MS-4	0.6	21.4	0.140/0.495/0.365	557	427	130	0.20	0.18
SP34-MS	0.6	45.5	0.148/0.488/0.364	567	455	112	0.21	0.17
SP34-MS-5	0.6	64.3	0.150/0.486/0.364	580	488	72	0.23	0.13

Table S2 Synthesis conditions^a, compositions and textural properties of mesoporous SAPO-34s

^{*a*} The initial gel molar composition is 2.3 DEA:1.0 Al_2O_3 :1.0 P_2O_5 :0.2-0.6 SiO₂:150 H_2O , crystallization condition: 200 °C, 4 h. The silica source is a 1/3 molar ratio mixture of TPOAC/TEOS. ^{*b*} Calculation based on the inorganic oxides content. ^{*c*} Total surface area is determined by the BET equation. ^{*d*} Micropore surface area, volume and external surface area are determined by the t-plot method. ^{*e*} Mesopore volume is determined from the adsorption isotherm by the BJH method.

Sample	Precursor ^c (wt%)	Product composition Si/Al/P	S _{BET} ^d (m²/g)	S _{mic} ^e (m²/g)	S _{ext} ^e (m²/g)	V _{mic} ^e (cm ³ /g)	V _{meso} f (cm ³ /g)	
SAPO-11 ^a	45.5	0.135/0.501/0.364	242	137	105	0.06	0.13	
DNL-6 ^b	22.9	0.162/0.478/0.360	731	520	211	0.24	0.38	

Table S3 Synthesis conditions, compositions and textural properties of mesoporous SAPO-11 and DNL-6

^{*a*} The gel molar composition is 1.7 DEA:1.0 Al₂O₃:1.0 P₂O₅:0.6 SiO₂:150 H₂O, crystallization condition: 200 °C, 36 h. The silica source is a 3/1 molar ratio mixture of TPOAC/TEOS. ^{*b*} The gel molar composition is 3.5 DEA:1.0 Al₂O₃:1.0 P₂O₅:0.3 SiO₂:150 H₂O, crystallization condition: 180 °C, 3 h. The silica source is a 1/3 molar ratio mixture of TPOAC/TEOS. ^{*c*} Calculation based on the inorganic oxides content. ^{*d*} Total surface area is determined by the BET equation. ^{*e*} Micropore surface area, volume and external surface area are determined by the t-plot method. ^{*f*} Mesopore volume is determined from the adsorption isotherm by the BJH method.