Supporting information

A top-down approach to prepare silicoaluminophosphate molecular sieve nanocrystals with improved catalytic property

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Sample Preparation:

1. Synthesis of conventional SAPO molecular sieves.

Typical synthesis of SAPO-34 precursor: an SAPO gel with a molar composition of diethylamine/Al$_2$O$_3$/P$_2$O$_5$/SiO$_2$/H$_2$O = 2.0/1/1/0.8/50 was prepared by mixing pseudo-boehmite (72.5 wt%), water, phosphoric acid (85 wt%), silica sol (30.1 wt%), and diethylamine in sequence. The crystallization was conducted in a stainless steel autoclave at 200 °C for 48 h under rotation. The as-synthesized product was washed and recovered through filtration, and dried at 110 °C overnight.

Typical synthesis of SAPO-5 precursor: an SAPO gel with a molar composition of triethylamine/Al$_2$O$_3$/P$_2$O$_5$/SiO$_2$/H$_2$O = 1.2/1/1/0.4/60 was prepared by mixing pseudo-boehmite (72.5 wt%), water, phosphoric acid (85 wt%), silica sol (30.1 wt%), and triethylamine in sequence. The mixture was charged into a stainless steel autoclave, sealed, and heated to 200 °C under rotation for 24 h. The as-synthesized product was washed and recovered through filtration, and dried at 110 °C overnight.

Typical synthesis of SAPO-35 precursor: an SAPO gel with a molar composition of hexamethyleneimine/Al$_2$O$_3$/P$_2$O$_5$/SiO$_2$/H$_2$O = 1.5/1/1/0.3/55 was prepared by mixing pseudo-boehmite (72.5 wt%), water, phosphoric acid (85 wt%), silica sol (30.1 wt%) and hexamethyleneimine in sequence. The mixture was charged into a stainless steel autoclave, sealed, and heated to 200 °C under rotation for 48 h. The as-synthesized product was washed and recovered through filtration, and dried at 110 °C overnight.

2. Milling treatment: 6.0 g as-made SAPO-34/5/35 was calcined at 600 °C for 300 min, after that it was dispersed into water and milled at 550 rpm/min for 360 min using a planetary ball mill (QM-3SP2, Nanjing China) with agate beads mixture in diameter of 3, 6 and 10 mm. After milling, the mud was collected and dried at 110 °C overnight.
3. Recrystallization

For SAPO-34: 2.1 g milled sample was charged into 21 g solution consisted of H₃PO₄, pseudo-boehmite (72.5 wt%), triethylamine, and H₂O with the composition of triethylamine/Al₂O₃/P₂O₅/H₂O = 3.5-3.8/1/1/55-150. The mixture was hydrothermally crystallized at 180-200 ºC for 3-24 h. The product was washed and recovered by centrifugation, and dried at 110 ºC overnight.

Recrystallization in mother liquid: a mother liquid was first obtained after the SAPO-34 synthesis from the mixture of triethylamine, pseudo-boehmite (72.5 wt%), H₃PO₄, silica gel, and H₂O with the molar ratio of triethylamine/Al₂O₃/P₂O₅/SiO₂/H₂O = 3.5/1/1/0.3/55. Then, 3.0g milled SAPO-34 precursor was charged into 30.0 g mother liquid. The mixture was hydrothermally crystallized at 180 ºC for 2 h. The product was washed and recovered through centrifugation, and dried at 110 ºC overnight.

For the composition analysis of the mother liquid, 20 g of mother liquid was dried and calcined at 600 ºC for 300 min. The solid was collected and weighted. The solid content was calculated to be 11%. XRF analysis for the solid showed that it consisted of Al₂O₃ 31.3 wt%, P₂O₅ 65.6 wt% and 3.0 wt% SiO₂.

For SAPO-5: 0.25 g milled SAPO-5 precursor was charged into 2.5 g solution consisted of triethylamine, Al₂O₃, H₃PO₄ and H₂O with the composition of triethylamine/Al₂O₃/P₂O₅/H₂O = 1.9/1/1.2/150. The mixture was hydrothermally crystallized at 150 ºC for 2 h. The product was washed and recovered by centrifugation, and dried at 110 ºC overnight.

For SAPO-35: 0.2 g milled SAPO-35 precursor was charged into 2.0 g solution consisted of H₃PO₄, hexamethyleneimine, and H₂O with the composition of hexamethyleneimine/P₂O₅/H₂O = 5.8/1/128. The mixture was hydrothermally crystallized at 200 ºC for 2 h. The product was washed and recovered by centrifugation, and dried at 110 ºC overnight.
**Characterization:** The chemical composition of the solid samples was determined with a Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed by scanning electron microscopy TM3000 (Hitachi) and field emission scanning electron microscopy (Hitachi SU8020). The thermal analysis was performed on a TA Q-600 analyzer with a temperature-programmed rate of 10 °C/min under an air flow of 100 ml/min. The powder X-ray diffraction (XRD) data were recorded on a PANalytical X’Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.54059 Å) operating at 40 mA and 40 kV. Textural properties of the calcined samples were determined by N₂ adsorption/desorption at 77 K on a Micromeritics ASAP 2020 system. The total surface area was calculated based on the BET equation. The micropore volume and micropore surface area were evaluated using the t-plot method. Mesopore volume and mesopore surface area were evaluated by Barret–Joyner–Halenda (BJH) method. All NMR experiments were performed on a Varian Infinity plus 400WB spectrometer with BBO MAS probe operating at a magnetic field strength of 9.4 T. The resonance frequencies were 104.2, 161.9 and 79.4 MHz for ²⁷Al, ³¹P and ²⁹Si respectively. Chemical shifts were referenced to 1.0 M Al(NO₃)₃ for ²⁷Al, 85% H₃PO₄ for ³¹P, and 2,2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS) for ²⁹Si. The spinning rates of the samples at the magic angle were 4, 10, and 6 kHz for ²⁹Si, ²⁷Al and ³¹P, respectively. The temperature-programmed desorption of ammonia (NH₃-TPD) was carried out with an Autochem 2920 equipment (Micromeritics). The calcined samples (200 mg, 40-60 mesh) was activated at 650 °C for 60 min (10°C/min) in He, and then cooled down and saturated with ammonia at 150 °C for 30 min. After the samples were purged with He (30 ml/min) for 30 min, the measurements of the desorbed NH₃ were performed from 150 to 650 °C (10°C/min) under He (30 ml/min). X-ray photoelectron spectroscopy (XPS) was used to analyze the change of surface composition measured by VG ESCALAB MK2 X-ray photoelectron spectrometer.

**Catalytic testing:** MTO reaction was carried out with a fixed-bed reactor at atmospheric pressure. 1.2 g of catalyst (20-40 mesh) was loaded into the reactor. The sample was activated in a flow of nitrogen at 550 °C for 1 h, and then the temperature was
reduced to a reaction temperature 450 °C. The methanol solution (weight ratio of \( \text{CH}_3\text{OH/\text{H}_2\text{O}} \) was 40/60) was pumped into the reactor after nitrogen was turned off. The weight hourly space velocity (WHSV) was 4 h\(^{-1}\). The reaction products were analyzed using an online gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and PoraplotQ-HT capillary column. The conversion and selectivity were calculated on CH\(_2\) basis. Dimethyl ether (DME) was considered as reactant in the calculation.
**Fig. S1** SEM image of SAPO-34 recrystallized in a self-made solution with composition of 1.0P₂O₅: 1.0Al₂O₃: 3.5TEA: 55H₂O at 200 °C for 24 h (sample 6).
Fig. S2 TG curve of recrystallized SAPO-34 (sample 2).
**Fig. S3** N$_2$ adsorption (solid) and desorption (empty) isotherms of sample 2 (■, □) and 6(★, ☆).
**Fig. S4** $^{27}$Al and $^{31}$P MAS NMR spectra of SAPO-34 precursor, milled SAPO-34, and recrystallized SAPO-34 (sample 2).
Fig. S5 Methanol conversion and selectivity of C$_2$H$_4$ plus C$_3$H$_6$ in the MTO reaction on the milled SAPO-34. Reaction condition: 450 ºC, WHSV = 4.0 h$^{-1}$, 40 wt% methanol solution.
Fig. S6 NH$_3$-TPD profiles of precursor, milled and recrystallized SAPO-34s (sample 2 and sample 6).
Fig. S7 XRD patterns of SAPO-5 (a) and SAPO-35(b) in the three stages.
**Fig. S8** SEM images of SAPO-5 precursor (a), recrystallized SAPO-5 (b), SAPO-35 precursor (c) and recrystallized SAPO-35 (d).
<table>
<thead>
<tr>
<th>Samples</th>
<th>Lifetime</th>
<th>CH$_4$</th>
<th>C$_2$H$_4$</th>
<th>C$_2$H$_6$</th>
<th>C$_3$H$_6$</th>
<th>C$_3$H$_8$</th>
<th>C$_4^+$</th>
<th>C$_5^+$</th>
<th>C$_2$H$_4$+C$_3$H$_6$</th>
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<tr>
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<td>1.3</td>
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<td>1.6</td>
<td>36.5</td>
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<td>13.1</td>
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<td>Sample 2</td>
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<td>0.6</td>
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<td>Sample 6</td>
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<td>0.5</td>
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<td>SAPO-34-TEA</td>
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<td>2.5</td>
<td>11.2</td>
<td>3.1</td>
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*Reaction conditions: WHSV = 4 h$^{-1}$, T = 450 $^\circ$C, 40 wt% methanol-water solution; *b Lifetime: the reaction duration with >99.5% methanol conversion. *c SAPO-34 hydrothermally synthesized with TEA as a template for compare. Its bulk composition (Al$_{0.486}$Si$_{0.080}$P$_{0.434}$O$_2$) is similar to that of sample 6.
**Table S2** Textural properties of samples

<table>
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<tr>
<th>Samples</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
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<tr>
<td></td>
<td>T-plot</td>
<td>External</td>
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<td>SAPO-34 precursor</td>
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<td>Milled SAPO-34</td>
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<tr>
<td>Sample 2</td>
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<tr>
<td>Sample 6</td>
<td>499.2</td>
<td>41.8</td>
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