Supporting information for

Creation of Hollow SAPO-34 Single Crystals by Alkaline or Acid Etching

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Experimental Section

1. Chemical reagents

All chemical reagents were used without further purification. Orthophosphoric acid (85 wt%), diethylamine (DEA), NaOH and HCl (37 wt%) were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.. Tetraethylammonium hydroxide (TEAOH, 35 wt%), tetrabutylammonium hydroxide (TMAOH, 25 wt%) and tetrapropylammonium hydroxide (TPAOH, 25 wt%) were purchased from Runjing Chemical Co., Ltd.. The other chemical reagents used in the experiments included fused silica (Shenyang Chemical Co., Ltd.), pseudoboehmite (67.5 wt%, CHINALCO), tetramethyl ethylenediamine (TMEDA, Sinopharm Chemical Reagent Co., Ltd.).

2. Preparation of SAPO molecular sieve precursors

**Synthesis of SAPO-34 (SP34-P):** an initial gel with a molar composition of 2.0 TEAOH / 0.5 TMEDA / 1.0 Al₂O₃ / 1.2 P₂O₅ / 1.0 SiO₂ / 60 H₂O was prepared by mixing pseudoboehmite, water, orthophosphoric acid, fused silica, TEAOH and TMEDA in sequence. Milled SAPO-34 seeds (1 % gel weight) were finally added into the gel under stirring. The crystallization was conducted in a stainless steel autoclave at 200 °C for 16 h under rotation. The as-synthesized product was recovered through filtration, washed, and dried at 110 °C overnight.

**Synthesis of SAPO-20:** an initial gel with a molar composition of 1.5 TMAOH / 1.0 TMEDA / 1.0 Al₂O₃ / 1.0 P₂O₅ / 1.0 SiO₂ / 60 H₂O was prepared by mixing pseudoboehmite, water, orthophosphoric acid, fused silica, TMAOH and TMEDA in sequence. Milled SAPO-34 seeds (1 % gel weight) were finally added into the gel under stirring. The crystallization was conducted in a stainless steel autoclave at 200 °C for 24 h under rotation. The as-synthesized product was recovered through filtration, washed, and dried at 110 °C overnight.

3. Alkaline or acid treatments

All the alkaline or acid treatments conditions were listed in Table 1. Typically, for alkaline treatment, 1 g SAPO-34 precursor was added to 12 g of 0.6 mol/L TEAOH solution. Then the mixture was mixed and heated in an autoclave at 180 °C for 1 h under rotation. The product was recovered through filtration, washed, and dried at 110 °C overnight. For acid treatment, the procedure was similar to the above.

4. Characterization

The powder X-ray diffraction (XRD) data were recorded on a PANalytical X’Pert PRO X-ray diffractometer with Cu Kα radiation (λ = 1.54059Å) operating at 40 mA and 40 kV. The crystal morphology was observed by field emission scanning electron microscopy (Hitachi SU8020).
Transmission electron microscopy (TEM) images were recorded with a JEM-2100 electron microscope. The bulk and surface compositions of samples were determined with Philips Magix-601 X-ray fluorescence (XRF) spectrometer and VG ESCALAB MK2 X-ray photoelectron spectrometer (XPS). Textural properties of the calcined samples were determined by N₂ adsorption/desorption at -196 °C on a Micromeritics ASAP 2020 system. All the solid state NMR experiments were performed on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet. The resonance frequencies were 156.4, 242.9 and 119.2 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-silapentane-5-sulfonate sodium salt (DSS) for ²⁹Si. ²⁷Al and ³¹P MAS NMR experiments were performed on a 4 mm MAS probe with a spinning rate of 12 kHz. ²⁷Al MAS NMR spectra were recorded using one pulse sequence. A 200 scans were accumulated with a π/8 pulse width of 0.75 μs and a 2 s recycle delay. ³¹P MAS NMR spectra were recorded using high-power proton decoupling. A 32 scans were accumulated with a π/4 pulse width of 2.25 μs and a 30 s recycle delay. ²⁹Si CP/MAS NMR spectra were recorded with a 4 mm MAS probe with a spinning rate of 8 kHz. A 4096 scans were accumulated with a contact time of 3 ms and a recycle delay of 2 s. The temperature-programmed desorption of ammonia (NH₃-TPD) was carried out with an Autochem 2920 equipment (Micromeritics). The calcined samples (100 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).

5. Catalytic testing

Alkylation of benzene with benzyl alcohol was performed in autoclave. 0.15 g of the catalyst was transferred to the 100 ml Parr reactor; Then 29.8 g benzene (99.5%) and 0.52 g benzyl alcohol (98%) were added in sequence resulting in a molar ratio of benzene to benzyl alcohol of 80. The reactor was purged with nitrogen and maintained a permanent pressure of 20–25 bars during the reaction, so the reactants could keep in the liquid phase at the reaction temperature of 140 °C. The mixture was stirred at 300 rpm throughout the run, which was determined to be sufficiently fast. After 1 h reaction, a small amount of liquid sample were withdrawn and analyzed by using GC–MS equipped with a capillary HP-5 (Agilent Technologies) column.
### Table S1. Conditions for base and acid treatments of SAPO molecular sieves

<table>
<thead>
<tr>
<th>Sample</th>
<th>Reagent</th>
<th>C</th>
<th>LSR</th>
<th>T(℃)</th>
<th>t(h)</th>
<th>R (r/min)</th>
<th>Product</th>
<th>Solid yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP34-TEAOH</td>
<td>TEAOH</td>
<td>0.6</td>
<td>12</td>
<td>180</td>
<td>1</td>
<td>60</td>
<td>CHA</td>
<td>35%</td>
</tr>
<tr>
<td>SP34-TPAOH</td>
<td>TPAOH</td>
<td>0.6</td>
<td>12</td>
<td>180</td>
<td>1</td>
<td>60</td>
<td>CHA</td>
<td>38%</td>
</tr>
<tr>
<td>SP34-TMAOH</td>
<td>TMAOH</td>
<td>0.9</td>
<td>12</td>
<td>180</td>
<td>1</td>
<td>60</td>
<td>CHA</td>
<td>39%</td>
</tr>
<tr>
<td>SP34-DEA</td>
<td>DEA</td>
<td>1</td>
<td>10</td>
<td>180</td>
<td>1</td>
<td>60</td>
<td>CHA</td>
<td>42%</td>
</tr>
<tr>
<td>SP34-NaOH</td>
<td>NaOH</td>
<td>0.63</td>
<td>20</td>
<td>80</td>
<td>6</td>
<td>60</td>
<td>amorphous</td>
<td>48%</td>
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<tr>
<td>SP34-HCl</td>
<td>HCl</td>
<td>0.58</td>
<td>10</td>
<td>80</td>
<td>3</td>
<td>60</td>
<td>CHA</td>
<td>25%</td>
</tr>
<tr>
<td>SP34-HCl-i</td>
<td>HCl</td>
<td>0.96</td>
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<td>180</td>
<td>1</td>
<td>60</td>
<td>amorphous</td>
<td>27%</td>
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<td>SAPO-20-TMAOH</td>
<td>TMAOH</td>
<td>0.5</td>
<td>10</td>
<td>200</td>
<td>16</td>
<td>10</td>
<td>SOD</td>
<td>38%</td>
</tr>
<tr>
<td>SAPO-20-HCl</td>
<td>HCl</td>
<td>0.9</td>
<td>11</td>
<td>180</td>
<td>1</td>
<td>60</td>
<td>SOD+amorphous</td>
<td>22%</td>
</tr>
</tbody>
</table>

*a The concentration of base or acid aqueous solution (mol/L).  
b Liquid to solid ratio (ml/g).  
c The tumbling speed during treatment.

### Table S2. Bulk and surface compositions of the sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Product composition</th>
<th>R c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk a</td>
<td>Surface b</td>
</tr>
<tr>
<td>SAPO-20</td>
<td>Si0.299Al0.435P0.357</td>
<td>Si0.488Al0.284P0.228</td>
</tr>
</tbody>
</table>

*a Determined by XRF.  
b Determined by XPS.  
c R=[Si/(Al+P+Si)]_surface/[Si/(Al+P+Si)]_bulk
Figure S1. The XRD patterns of the samples.

Figure S2. The TEM images of the base-treated samples: (a) SP34-TPAOH, (b) SP34-TMAOH, (c) SP34-DEA.
Figure S3. The SEM (left) and TEM (right) images of SP34-NaOH and SP34-HCl-i.

Figure S4. The N$_2$ adsorption-desorption isotherms of the samples.
Figure S5. The $^{29}$Si MAS NMR (a, c) and $^1$H→$^{29}$Si CP MAS NMR (b, d) spectra of SP34-HCl and SP34-HCl-i.

Figure S6. The $^{27}$Al and $^{31}$P MAS NMR spectra of the samples.
Figure S7. The XRD patterns of SAPO-20 and its acid/base-treated samples.
Figure S8. The SEM and TEM images of SAPO-20 and its acid/base-treated samples.
Figure S9. The $^{29}$Si MAS NMR spectra of SAPO-20 and its acid/base-treated samples.

Figure S10. Results of alkylation of benzene with benzyl alcohol (BA) over the samples (DPM: diphenyl methane, DBE: dibenzyl ether, DBB: dibenzyl benzene).
Figure S11. NH₃-TPD curves of the samples.