Electronic Supplementary Information (ESI)

Ultrafast Synthesis of Nano-sized Zeolite SAPO-34 with Excellent MTO Catalytic Performance

Qiming Sun,* Ning Wang,* Guanqi Guo,* and Jihong Yu**

* State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, P. R. China
Contents

1. Experiment section
2. Characterizations
3. Catalytic tests and carbon deposit analyses.
4. Supplementary Figures and Tables
1. **Experiment section**

1.1 **Reagents.** The reagents used were aluminum iso-propoxide (Al(OPr)₃, 99.5 wt%, Beijing Reagents Company), phosphoric acid (H₃PO₄, 85 wt%, Beijing Chemical Works), tetraethylammonium hydroxide solution (TEAOH, 35 wt%, Alfa Aesar), colloidal silica (40 wt%, Aldrich).

1.2 **Description of the stainless steel tubular reactor.** Figure S1 shows the stainless steel tubular reactor, which is made from stainless steel tube with an outer diameter of 12.0 mm and an inner diameter of 9.0 mm. The length of the stainless steel tubular is 100 mm, and it is sealed with two end caps (SS-12TC) at both ends. The volume of the stainless steel tubular reactor is 6.5 ml.

1.3 **Synthesis of nano-sized SAPO-34 zeolite seeds.** The nano-sized SAPO-34 zeolite seeds were synthesized under conventional hydrothermal conditions from the starting gel with the molar composition of 1.0Al₂O₃: 1.2P₂O₅: 2.0TEAOH: 0.6SiO₂: 40H₂O as reported in our previous work. Typically, the finely ground Al(OPr)₃ was firstly mixed with TEAOH solution and deionized water at room temperature until dissolved completely. Phosphoric acid was then added dropwise to the resultant solution, followed by a continuous stirring for 2 h. Finally, colloidal silica was added slowly. The reaction mixture was further stirred for 1 h, and was then transferred into a 100 ml Teflon-lined stainless steel autoclave. The crystallization was conducted in a conventional oven at 170 °C for 3 days under static conditions. The as-synthesized solid products were centrifuged, washed with water and ethanol for several times, and then dried at 80 °C in the oven overnight, followed by calcination at 550 °C for 6 h.

1.4 **Preparation of the initial synthesis gel.** The synthesis gel has the same molar compositions as that of nano-sized SAPO-34 zeolite seeds. In the seed-assisted synthesis, after all of the raw materials were added into the gel and stirred uniformly, a specific amount (6.5 wt%, based on Al₂O₃) of SAPO-34 seeds were added into the synthesis gel, and then further stirred continuously for 2 h until the seeds were completely dissolved.

1.5 **Synthesis in the stainless steel tubular reactor.** 5g of initial synthesis gel was transferred into the stainless steel tubular reactor and the reactor was sealed tightly to ensure that the liquid will not overflow. And then the reactor was immersed into the oil bath at 200 °C. After a specific synthesis time, the stainless steel tubular reactor was taken out from oil bath and quenched at the air. The as-synthesized solid products were centrifuged, washed with water and ethanol for several times, and then...
dried at 80 °C in the oven overnight, followed by calcination at 550 °C for 6 h. To avoid the presence of residual sources that could act as seeds in the subsequent synthesis, after each synthesis the tubular reactor was boiled with 5 ml 10M NaOH solution at 140 °C for 12 h in the oven followed by thorough washing with water.

1.6 **Synthesis in the stainless steel autoclave.** 5g of initial synthesis gel was added into the 15 ml stainless steel autoclave and then heated in an oven at 200 °C. After a specific synthesis time, the stainless steel tubular reactor was cooled down at the air. The as-synthesized solid products were centrifuged, washed with water and ethanol for several times, and then dried at 80 °C in the oven overnight, followed by calcination at 550 °C for 6 h.

1.7 **Calculation of product yields.** The yields were calculated by the formula below based on the Al$_2$O$_3$:

\[
\text{Yield} = \frac{\text{Weight of calcined sample}}{\text{Theoretical weight of SAPO - 34}}
\]

The theoretical weight of SAPO-34 was calculated according to the mole of aluminum iso-propoxide and the framework composition of samples.

2. **Characterizations**

The crystallinity and phase purity of the samples were characterized by powder X-ray diffraction on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal size and morphology were measured by transmission electron microscopy (TEM) using a Tecnai F20 electron microscope. Thermogravimetric (TG) analysis was performed on a TA company TGA Q500 unit in air at a heating rate of 10 °C min$^{-1}$ from room temperature to 800 °C in air. Chemical compositions were determined with an X-ray fluorescence (XRF) spectrometer (PANalytical, AXIOS). Nitrogen adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer at 77.35 K after the samples were degassed at 350 °C under vacuum. The temperature-programmed desorption of ammonia (NH$_3$-TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. $^{29}$Si NMR experiments were performed on Varian Infinity plus 400WB spectrometer with BBO MAS probe operating at a magnetic field strength of 9.4 T. The resonance frequencies in this field strength was 79.5 MHz. Chemical shifts was referenced to 2,2-dimethyl-2-ilapentane-5-sulfonate sodium salt (DSS) for $^{29}$Si.
The spinning rates of the samples at the magic angle was 4 kHz.

3. **Catalytic tests and carbon deposit analyses.**

Methanol conversion was performed in a quartz tubular fixed-bed reactor at atmospheric pressure. The catalyst (300 mg, 40-60 mesh) loaded in the quartz reactor (6 mm inner diameter) was activated at 773 K in a N₂ flow of 30 mL/min for 1 h before starting each reaction run and then the temperature was adjusted to reaction temperature of 673 K. The methanol was fed by passing the carrier gas (15 mL/min) through a saturator containing methanol at 40 °C, which gave a WHSV of 2.0 h⁻¹. The reaction products were analyzed using an on-line gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and Plot-Q column (Agilent J&W GC Columns, HP-PLOT/Q 19091P-Q04, 30m × 320µm × 20µm). The conversion and selectivity were calculated on CH₂ basis and dimethyl ether (DME) was considered as reactant in the calculation.

The amount of generated coke in SAPO-34 catalysts after the MTO reactions was determined by thermal analysis (TG) on a TGA Q500 at a heating rate of 10 °C min⁻¹ from room temperature to 800 °C under air flow. The organic species retained in the nano-sized SAPO-34 catalysts after methanol conversion were analyzed by GC-MS (Thermo Fisher Trace ISQ, equipped with TG-5MS column, 60m × 320µm × 25µm).
4. Supplementary Figures and Tables

**Fig. S1** Photograph of the stainless steel tubular reactor for the synthesis of SAPO-34.

**Fig. S2** XRD patterns of nano-sized SAPO-34 crystals synthesized without seeds heated in oil bath at different crystallization times.
Fig. S3  XRD patterns of nano-sized SAPO-34 crystals synthesized with seeds heated in oven at different crystallization times.

Fig. S4  XRD patterns of nano-sized SAPO-34 crystals synthesized without seeds heated in oven at different crystallization times.
**Fig. S5** TEM images of nano-sized SAPO-34 zeolite seeds synthesized in a conventional oven at 170 °C for 3 days under static conditions with different scan bars (a) 1 µm; (b) 500 nm; (c) 200 nm; (d) 100 nm.
Fig. S6  TEM images of nano-sized SAPO-34 crystals synthesized with seeds in oil bath at different crystallization times. 0 min (a, b, c); 2 min (d, e, f); 5 min (g, h, i); 10 min (j, k, l); 20 min (m, n, o); 40 min (p, q, r); 60 min (s, t, u); 120 min (v, w, x).
**Fig. S7** TEM images of nano-sized SAPO-34 crystals synthesized without seeds heated in oil bath at different crystallization times. 20 min (a, b, c); 40 min (d, e, f); 60 min (g, h, i); 90 min (j, k, l); 120 min (m, n, o); 180 min (p, q, r).
Fig. S8  TEM images of nano-sized SAPO-34 crystals synthesized with seeds in oven at different crystallization times. 40 min (a, b, c); 60 min (d, e, f); 90 min (g, h, i); 120 min (j, k, l); 180 min (m, n, o); 240 min (p, q, r); 360 min (s, t, u); 720 min (v, w, x).
Fig. S9 TEM images of nano-sized SAPO-34 crystals synthesized without seeds in oven at different crystallization times. 60 min (a, b, c); 120 min (d, e, f); 180 min (g, h, i); 240 min (j, k, l); 360 min (m, n, o); 720 min (p, q, r).
Fig. S10  NH$_3$-TPD profiles of as-synthesized nano-sized SAPO-34 zeolites.

Fig. S11  $^{29}$Si MAS NMR spectra of as-synthesized nano-sized SAPO-34 zeolites.
Fig. S12  Products distribution of nano-sized SAPO-34 catalyst (5 min-S-Oil) synthesized with seeds in oil bath in 5 minutes in MTO reaction. Experimental conditions: WHSV = 2 h\(^{-1}\), T = 673 K, catalyst weight = 300 mg.

Fig. S13  Products distribution of nano-sized SAPO-34 catalyst (10 min-S-Oil) synthesized with seeds in oil bath in 10 minutes in MTO reaction. Experimental conditions: WHSV = 2 h\(^{-1}\), T = 673 K, catalyst weight = 300 mg.
Fig. S14  Products distribution of nano-sized SAPO-34 catalyst (20 min-S-Oil) synthesized with seeds in oil bath in 20 minutes in MTO reaction. Experimental conditions: WHSV = 2 h⁻¹, T = 673 K, catalyst weight = 300 mg.

Fig. S15  Products distribution of nano-sized SAPO-34 catalyst (40 min-S-Oil) synthesized with seeds in oil bath in 40 minutes in MTO reaction. Experimental conditions: WHSV = 2 h⁻¹, T = 673 K, catalyst weight = 300 mg.
Fig. S16  Products distribution of nano-sized SAPO-34 catalyst (60 min-S-Oil) synthesized with seeds in oil bath in 60 minutes in MTO reaction. Experimental conditions: WHSV = 2 h⁻¹, T = 673 K, catalyst weight = 300 mg.

Fig. S17  Products distribution of nano-sized SAPO-34 catalyst (120 min-S-Oil) synthesized with seeds in oil bath in 120 minutes in MTO reaction. Experimental conditions: WHSV = 2 h⁻¹, T = 673 K, catalyst weight = 300 mg.
Fig. S18  Products distribution of nano-sized SAPO-34 catalyst (120 min-N-Oil) synthesized without seeds in oil bath in 120 minutes in MTO reaction. Experimental conditions: WHSV = 2 h⁻¹, T = 673 K, catalyst weight = 300 mg.

Fig. S19  Products distribution of nano-sized SAPO-34 catalyst (720 min-S-Oven) synthesized with seeds in oven in 720 minutes in MTO reaction. Experimental conditions: WHSV = 2 h⁻¹, T = 673 K, catalyst weight = 300 mg.
Fig. S20  Products distribution of nano-sized SAPO-34 catalyst (720 min-N-Oven) synthesized without seeds in oven in 720 minutes in MTO reaction. Experimental conditions: WHSV = 2 h\(^{-1}\), T = 673 K, catalyst weight = 300 mg.
Fig. S21  GC-MS chromatograms of occluded organic species retained in the nano-sized SAPO-34 catalysts after methanol conversion at 673K. The structures annotated onto the chromatograms are peak identifications in comparison with the mass spectra to those in the NIST database.
### Table S1  MTO results on nano-sized SAPO-34 catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>TOS (min)</th>
<th>Selectivity (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;</td>
<td>C&lt;sub&gt;4&lt;/sub&gt;</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>5 min-S-Oil</td>
<td>186*</td>
<td>1.0</td>
<td>34.8</td>
<td>0.2</td>
<td>43.0</td>
<td>0.5</td>
<td>15.5</td>
<td>5.0</td>
</tr>
<tr>
<td>10 min-S-Oil</td>
<td>606*</td>
<td>1.0</td>
<td>36.6</td>
<td>0.2</td>
<td>42.1</td>
<td>0.2</td>
<td>14.9</td>
<td>5.0</td>
</tr>
<tr>
<td>20 min-S-Oil</td>
<td>606*</td>
<td>1.2</td>
<td>39.4</td>
<td>0.2</td>
<td>40.7</td>
<td>0.3</td>
<td>13.4</td>
<td>4.8</td>
</tr>
<tr>
<td>40 min-S-Oil</td>
<td>586*</td>
<td>1.2</td>
<td>40.2</td>
<td>0.3</td>
<td>40.6</td>
<td>0.5</td>
<td>12.8</td>
<td>4.4</td>
</tr>
<tr>
<td>60 min-S-Oil</td>
<td>686*</td>
<td>1.4</td>
<td>40.4</td>
<td>0.3</td>
<td>40.3</td>
<td>0.5</td>
<td>12.6</td>
<td>4.5</td>
</tr>
<tr>
<td>120 min-S-Oil</td>
<td>666*</td>
<td>1.3</td>
<td>40.2</td>
<td>0.3</td>
<td>40.4</td>
<td>0.4</td>
<td>12.7</td>
<td>4.7</td>
</tr>
<tr>
<td>120 min-N-Oil</td>
<td>606*</td>
<td>1.4</td>
<td>40.4</td>
<td>0.3</td>
<td>40.3</td>
<td>0.5</td>
<td>12.6</td>
<td>4.5</td>
</tr>
<tr>
<td>720 min-S-Oven</td>
<td>566*</td>
<td>1.3</td>
<td>40.2</td>
<td>0.4</td>
<td>39.9</td>
<td>0.6</td>
<td>12.4</td>
<td>5.2</td>
</tr>
<tr>
<td>720 min-N-Oven</td>
<td>586*</td>
<td>1.5</td>
<td>40.1</td>
<td>0.3</td>
<td>39.5</td>
<td>0.5</td>
<td>12.5</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Reaction conditions: WHSV = 2 h<sup>-1</sup>, T = 673 K, catalyst weight = 300 mg.

* Lifetime: the reaction duration with > 99.9% methanol conversion.

### Table S2  The variation of coke formation in methanol conversion over nano-sized SAPO-34 catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Coke (% g/gcat)</th>
<th>TOS(min)</th>
<th>R&lt;sub&gt;coke&lt;/sub&gt; (mg/min)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>P&lt;sub&gt;coke&lt;/sub&gt; (g/gMeOH)&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 min-S-Oil</td>
<td>18.75</td>
<td>186</td>
<td>0.30</td>
<td>0.030</td>
</tr>
<tr>
<td>10 min-S-Oil</td>
<td>19.00</td>
<td>606</td>
<td>0.09</td>
<td>0.009</td>
</tr>
<tr>
<td>20 min-S-Oil</td>
<td>20.45</td>
<td>606</td>
<td>0.10</td>
<td>0.010</td>
</tr>
<tr>
<td>40 min-S-Oil</td>
<td>19.02</td>
<td>586</td>
<td>0.10</td>
<td>0.010</td>
</tr>
<tr>
<td>60 min-S-Oil</td>
<td>21.29</td>
<td>686</td>
<td>0.09</td>
<td>0.009</td>
</tr>
<tr>
<td>120 min-S-Oil</td>
<td>21.18</td>
<td>666</td>
<td>0.10</td>
<td>0.010</td>
</tr>
<tr>
<td>120 min-N-Oil</td>
<td>22.78</td>
<td>606</td>
<td>0.11</td>
<td>0.011</td>
</tr>
<tr>
<td>720 min-S-Oven</td>
<td>23.63</td>
<td>566</td>
<td>0.13</td>
<td>0.013</td>
</tr>
<tr>
<td>720 min-N-Oven</td>
<td>23.01</td>
<td>546</td>
<td>0.13</td>
<td>0.013</td>
</tr>
</tbody>
</table>

<sup>a</sup> R<sub>coke</sub>(mg/min) = coke amount (mg)/reaction time (min);

<sup>b</sup> P<sub>coke</sub>(g/g) = coke amount (g)/methanol feedstock (g).