

## SUPPORTING INFORMATION

### **Promoted Crystallization of Silicoaluminophosphate Zeolites: an Efficient Way to Accelerates Crystallization Rate and Increases Solid Yield**

Delin Yuan,<sup>\*a</sup> Qianjin Wang,<sup>b</sup> Yunshan Shang,<sup>a</sup> Hua Liu<sup>a</sup> and Aihua Xing<sup>\*a</sup>

## Experimental Section

### *Chemical agents*

Pseudoboehmite (70.0 wt.% Al<sub>2</sub>O<sub>3</sub>) was supplied from China Aluminum Corporation Shandong Branch. Silica sol (30.0 wt.% SiO<sub>2</sub>) was supplied from Qingdao Ocean Chemical Co., Ltd. H<sub>3</sub>PO<sub>4</sub> (85.0 wt.%), Triethylamine (TEA, 99.0%) and Diethylamine (DEA, 99.0%) were supplied from Tianjin Guangfu Fine Chemical Research Institute. Dipropylamine (DPA, 99.0%), Diisopropylamine (DIPA, 99.5%), N,N-Diisopropylethylamine (99.0%), citric acid (99.5%), oxalic acid (99.0%), acetic acid (99.0%), hydrochloric acid (HCl, 99.0%), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>, 99.0%) and nitric acid (HNO<sub>3</sub>, 99.0%) were supplied from Aladdin Chemistry Co., Ltd.

### *Synthesis of SAPO-34 with conventional route*

As a typical run, pseudoboehmite, phosphoric acid and silica sol were used as the sources of aluminum, phosphorus and silicon. TEA and DEA were used as the structure-directing agent. In a typical synthesis, pseudoboehmite was added to the diluted phosphoric acid solution, which was then stirred for 1 h until a uniform gel was obtained. Then, silica sol was added to the solution. After stirring continuously for another 1 h, TEA and DEA were added to the precursor solution, and the stirring was maintained for 1 h to form a uniform reaction mixture. The composition of the gel was 1.0 Al<sub>2</sub>O<sub>3</sub>:1.0 P<sub>2</sub>O<sub>5</sub>:0.25 SiO<sub>2</sub>: 2.5 TEA: 1.0 DEA: 40 H<sub>2</sub>O. The resulting gel was aged for 8 h. Then, the homogeneous gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 200 °C under autogeneous pressure for 12 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of conventional SAPO-34 was obtained.

The solid yield of the samples was calculated by the following formula: yield (%) =  $m_s / (m_{\text{Al}_2\text{O}_3} + m_{\text{P}_2\text{O}_5} + m_{\text{SiO}_2}) \times 100\%$ , where  $m_s$  stand for the weight of the products after calcination (650°C, 5 h) and  $m_{\text{Al}_2\text{O}_3}$ ,  $m_{\text{P}_2\text{O}_5}$ , and  $m_{\text{SiO}_2}$  stand for the dry mass of inorganic oxides in the raw material. The yield of the following molecular

sieve refers to the above calculation method.

#### *Synthesis of SAPO-34 with acid-assisted route*

In a typical synthesis, pseudoboehmite was added to the diluted phosphoric acid solution, which was then stirred for 1 h until a uniform gel was obtained. Then, silica sol was added to the solution. After stirring continuously for another 1 h, TEA and DEA were added to the precursor solution, and the stirring was maintained for 1 h to form a uniform reaction mixture. The resulting gel was aged for 8 h. Then, the acid AC (AC= citric acid, oxalic acid, acetic acid, hydrochloric acid, sulphuric acid or nitric acid) was added to the aged gel. The composition of the gel was 1.0 Al<sub>2</sub>O<sub>3</sub>:1.0 P<sub>2</sub>O<sub>5</sub>:0.25 SiO<sub>2</sub>: 2.5 TEA: 1.0 DEA: x AC 40 H<sub>2</sub>O (x=0.1~1.0). The gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 200 °C under autogeneous pressure for 12 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of acid-assisted SAPO-34 was obtained.

#### *Synthesis of SAPO-5 with conventional route*

As a typical run, pseudoboehmite, phosphoric acid, silica sol were mixed as the sources of aluminum, phosphorus and silicon. And then TEA was added as the structure-directing agent. The composition of the gel was 1 Al<sub>2</sub>O<sub>3</sub>:1 P<sub>2</sub>O<sub>5</sub>:0.40 SiO<sub>2</sub>: 1.2 TEA: 53 H<sub>2</sub>O. The resulting gel was stirred for 4 h. Then, the homogeneous gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 200 °C under autogeneous pressure for 24 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of conventional SAPO-5 was obtained.

#### *Synthesis of SAPO-5 with acid-assisted route*

As a typical run, pseudoboehmite, phosphoric acid, silica sol were mixed as the

sources of aluminum, phosphorus and silicon. And then TEA was added as the structure-directing agent. The resulting gel was aged for 4 h. Then, the citric acid was added to the aged gel. The composition of the gel was 1 Al<sub>2</sub>O<sub>3</sub>:1 P<sub>2</sub>O<sub>5</sub>:0.40 SiO<sub>2</sub>: 1.2 TEA: *x* citric acid: 53 H<sub>2</sub>O. The gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 200 °C under autogeneous pressure for 24 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of acid-assisted SAPO-5 was obtained.

#### *Synthesis of SAPO-11 with conventional route*

As a typical run, pseudoboehmite, phosphoric acid, silica sol were mixed as the sources of aluminum, phosphorus and silicon. And then DPA and DIPA were added as the structure-directing agent. The composition of the gel was 1 Al<sub>2</sub>O<sub>3</sub>:1 P<sub>2</sub>O<sub>5</sub>:0.30 SiO<sub>2</sub>: 0.6 DPA: 0.9 DIPA: 50 H<sub>2</sub>O. The resulting gel was stirred for 4 h. Then, the homogeneous gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 200 °C under autogeneous pressure for 24 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of conventional SAPO-11 was obtained.

#### *Synthesis of SAPO-11 with acid-assisted route*

As a typical run, pseudoboehmite, phosphoric acid, silica sol were mixed as the sources of aluminum, phosphorus and silicon. And then DPA and DIPA were added as the structure-directing agent. The resulting gel was aged for 4 h. Then, the citric acid was added to the aged gel. The composition of the gel was 1 Al<sub>2</sub>O<sub>3</sub>:1 P<sub>2</sub>O<sub>5</sub>:0.30 SiO<sub>2</sub>: 0.6 DPA: 0.9 DIPA: *x* citric acid: 50 H<sub>2</sub>O. The gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 200 °C under autogeneous pressure for 24 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of acid-assisted SAPO-11 was obtained.

### *Synthesis of SAPO-18 with conventional route*

As a typical run, pseudoboehmite, phosphoric acid and silica sol were mixed as the sources of aluminum, phosphorus and silicon. And then N,N-Diisopropylethylamine was added as the structure-directing agent. The composition of the gel was 1 Al<sub>2</sub>O<sub>3</sub>:1 P<sub>2</sub>O<sub>5</sub>:0.30 SiO<sub>2</sub>: 2.0 N,N-Diisopropylethylamine: 50 H<sub>2</sub>O. The resulting gel was stirred for 4 h. Then, the homogeneous gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 170 °C under autogeneous pressure for 36 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of conventional SAPO-18 was obtained.

### *Synthesis of SAPO-18 with acid-assisted route*

As a typical run, pseudoboehmite, phosphoric acid, silica sol were mixed as the sources of aluminum, phosphorus and silicon. And then N,N-Diisopropylethylamine was added as the structure-directing agent. The resulting gel was aged for 4 h. Then, the citric acid was added to the aged gel. The composition of the gel was 1 Al<sub>2</sub>O<sub>3</sub>:1 P<sub>2</sub>O<sub>5</sub>:0.30 SiO<sub>2</sub>: 2.0 N,N-Diisopropylethylamine: *x* citric acid: 50 H<sub>2</sub>O. The gel was transferred into a 150 ml Teflon lined stainless steel autoclave and hydrothermally treated at 170 °C under autogeneous pressure for 36 h. After filtrating with water at room temperature and drying at 110 °C, a crystalline product of acid-assisted SAPO-18 was obtained.

### *Characterization*

The powder XRD patterns of the samples were recorded on a Bruker D8A (Bruker AXS GmbH, Karlsruhe, Germany) with monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The chemical composition of the sample was determined by X-ray fluorescence (XRF) on a XRF-ZSX Primus II spectrometer (Rigaku Co., Tokyo, Japan). The crystal size and morphology of the samples were observed by scanning electron microscopy (SEM) at NOVA Nano SEM 450 scanning electron microscope (FEI. Co., Czech Republic). <sup>13</sup>C NMR of liquid sample was performed on a NMR 400

M system (Bruker, Switzerland), and Solid State NMR experiments of  $^{27}\text{Al}$ ,  $^{29}\text{Si}$  and  $^{31}\text{P}$  of as-synthesis samples were performed with hydrated samples on a Bruker Avance III 400WB spectrometer (Bruker, Germany) at resonance frequencies of 104.3, 79.5 and 161.9 MHz, respectively. The nitrogen adsorption isotherms were obtained using an automatic volumetric adsorption measurement system (Tristar II). Samples were evacuated at 350°C for 3 hours before exposing them to nitrogen gas at 77 K.

#### *Catalyst evaluation*

MTO reaction was performed to test the catalytic performance of SAPO-34 zeolites in a quartz tubular fixed-bed reactor at atmospheric pressure. Prior to the start of the experiment, 0.80 g calcined catalyst was loaded into the reactor and pretreated at 450 °C under  $\text{N}_2$  flow ( $140 \text{ mL min}^{-1}$ ) for 30 min. Then the reactant methanol (80% aqueous methanol solution), which was vaporized by a preheater, entered the reactor bottom through a distribution and contacted the catalyst. The weight hourly space velocity (WHSV) was  $3.5 \text{ h}^{-1}$ . The product was detected using online gas chromatography (GC) employing flame ionization detector.

## Supporting Figure Captions

**Fig. S1** XRD patterns of sample 1 (conventional synthesis) and sample 6 (acid-assisted synthesis).

**Fig. S2** SEM images of SAPO-34 synthesized with Citric acid/ $\text{Al}_2\text{O}_3$ = A) 0, B) 0.2, C) 0.3, D) 0.5, E) 1.0.

**Fig. S3** Solution  $^{13}\text{C}$  NMR spectra of mother liquor with different crystallization time.

**Fig. S4** The plot of the zeolite yield versus the pH value of the starting gel. A: synthesized with different acids including inorganic acids and organic acids. B: synthesized with inorganic acids. C: synthesized with organic acids.

**Fig. S5** XRD patterns of samples synthesized with different crystallization methods at three levels of temperature namely 180, 190, and 200°C. A: conventional hydrothermal (Sample 1) and B: acid-assisted hydrothermal treatment (Sample 6).

**Fig. S6** Schematic representation of crystallization curve of zeolite SAPO-34.

**Fig. S7** Arrhenius plots for SAPO-34 samples synthesized with different crystallization methods of induction period (A) and crystal growth period (B).

**Fig. S8**  $^{31}\text{P}$  MAS NMR spectra of sample 1 and sample 6 obtained at different synthesis time.

**Fig. S9**  $^{27}\text{Al}$  MAS NMR spectra of sample 1 and sample 6 obtained at different synthesis time.

**Fig. S10**  $^{29}\text{Si}$  MAS NMR spectra of sample 1 and sample 6 obtained at different synthesis time.

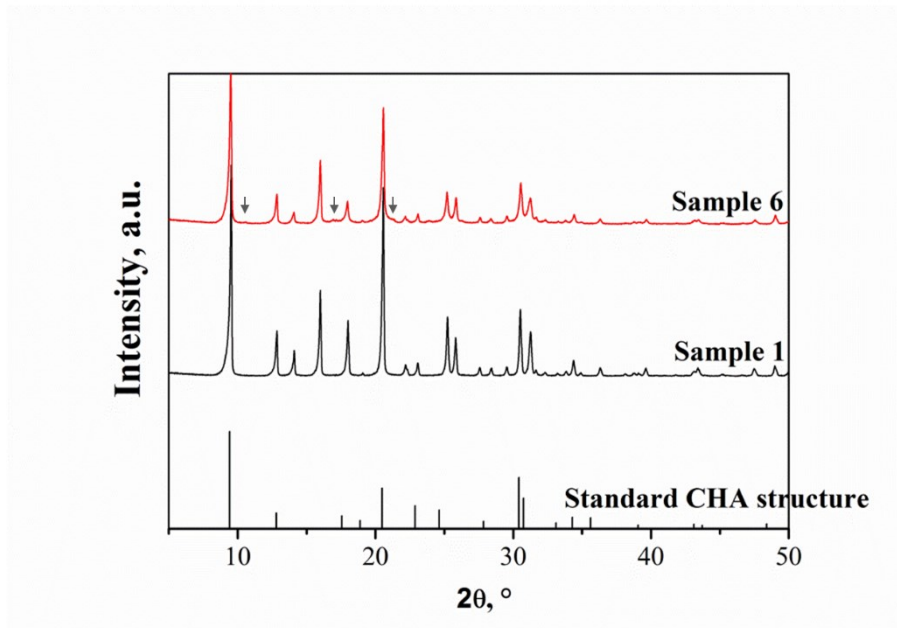
**Fig. S11** Nitrogen adsorption/desorption isotherms (A) and BJH pore size distribution (B) of synthesized SAPO-34s with or without citric acid.

**Fig. S12** Methanol conversion variation and yields of hydrocarbons in the MTO reaction with time-on-stream over the SAPO-34 catalysts.

**Fig. S13** XRD patterns of SAPO-5 and SAPO-5 synthesized with acid-assisted route.

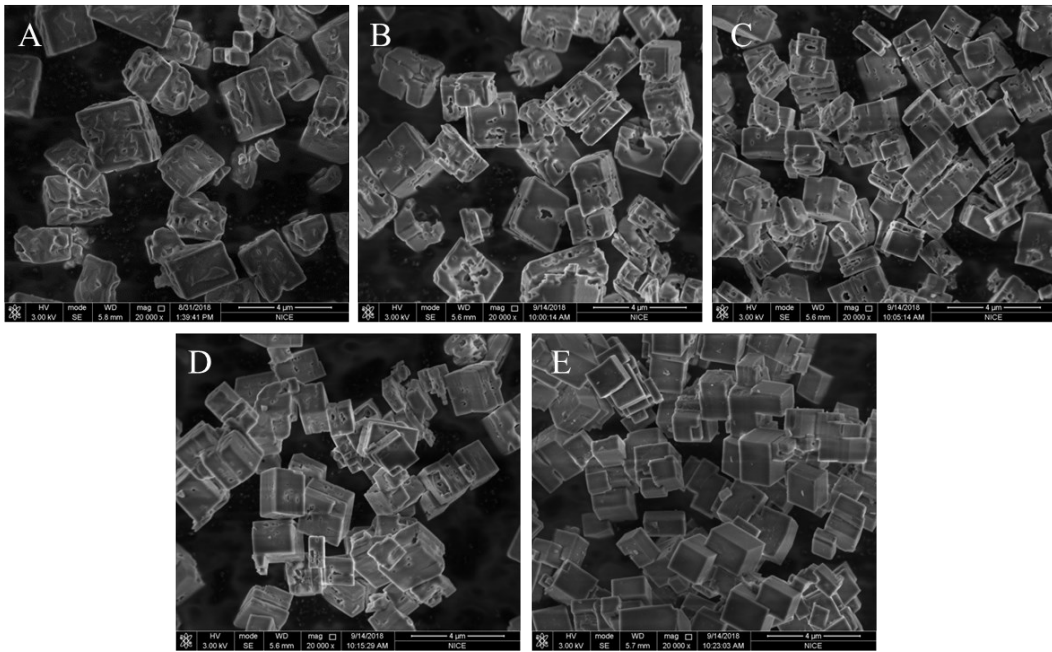
**Fig. S14** XRD patterns of SAPO-11 and SAPO-11 synthesized with acid-assisted route.

**Fig. S15** XRD patterns of SAPO-18 and SAPO-18 synthesized with acid-assisted route.

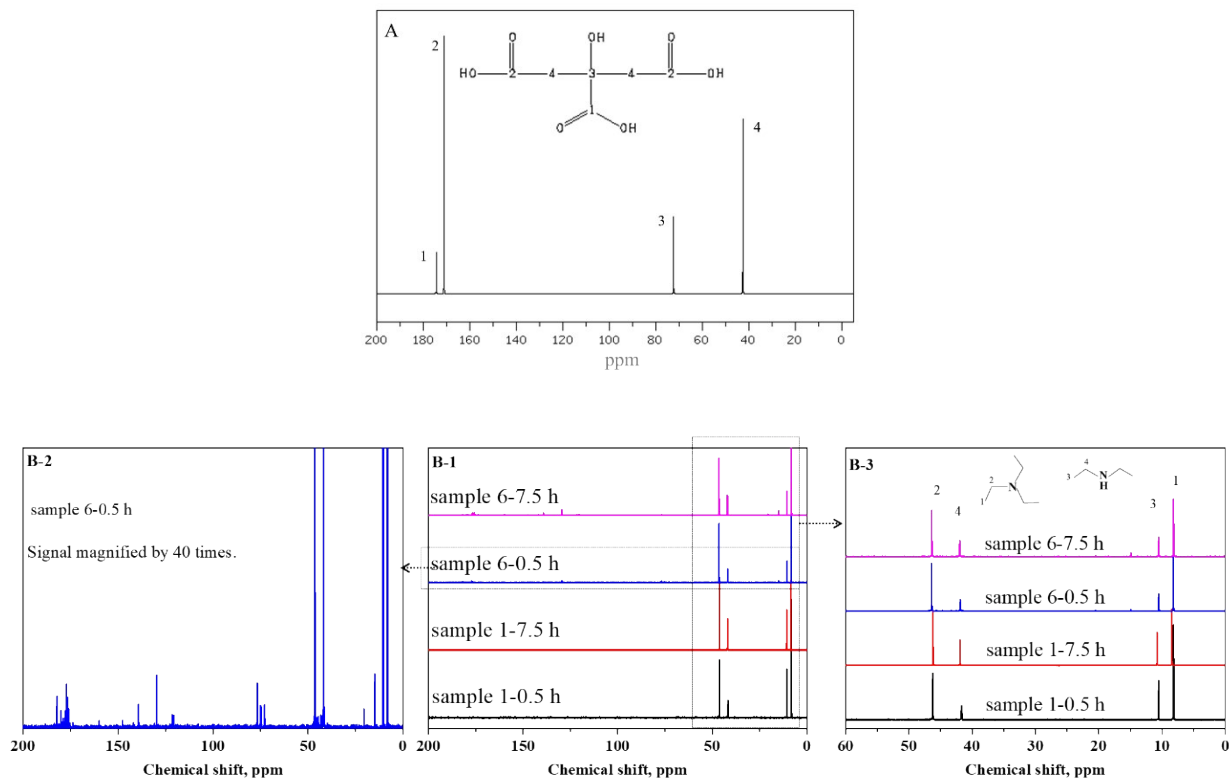


**Fig. S1** XRD patterns of sample 1 (conventional synthesis) and sample 6 (acid-assisted synthesis). For Sample 6, three small peaks (7°, 11°, 21° marked with arrows) indicates the presence of a very small amount of SAPO-18 crystal. It is speculated that the addition of citric acid reduces the pH value of the gel, thus leading to the formation of the impure phase (the pH value of the synthesis environment of SAPO-18 is lower than that of SAPO-34).

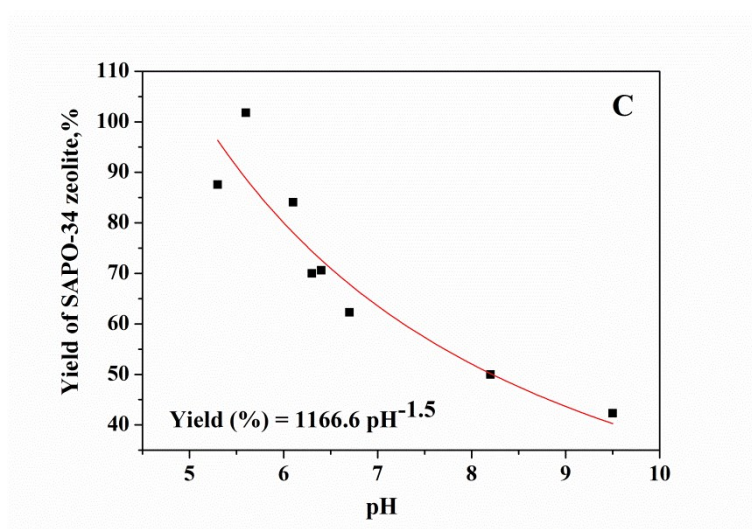
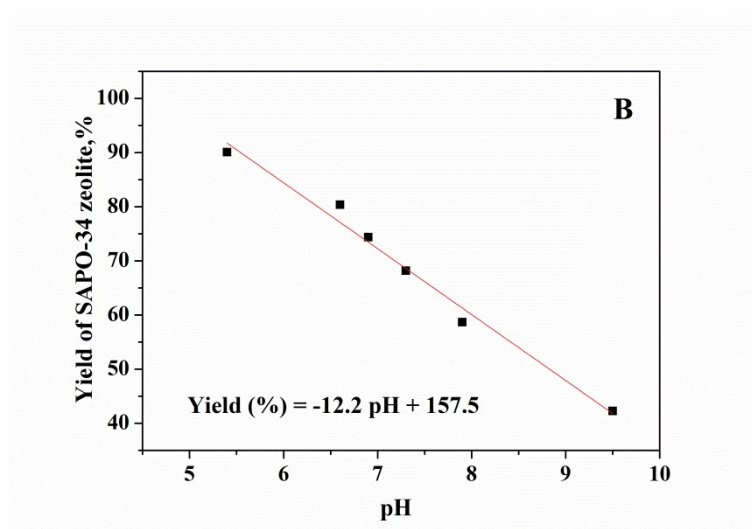
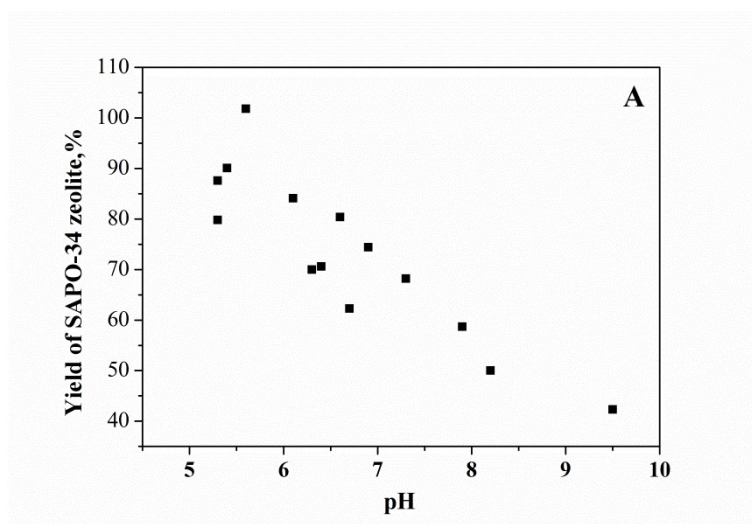




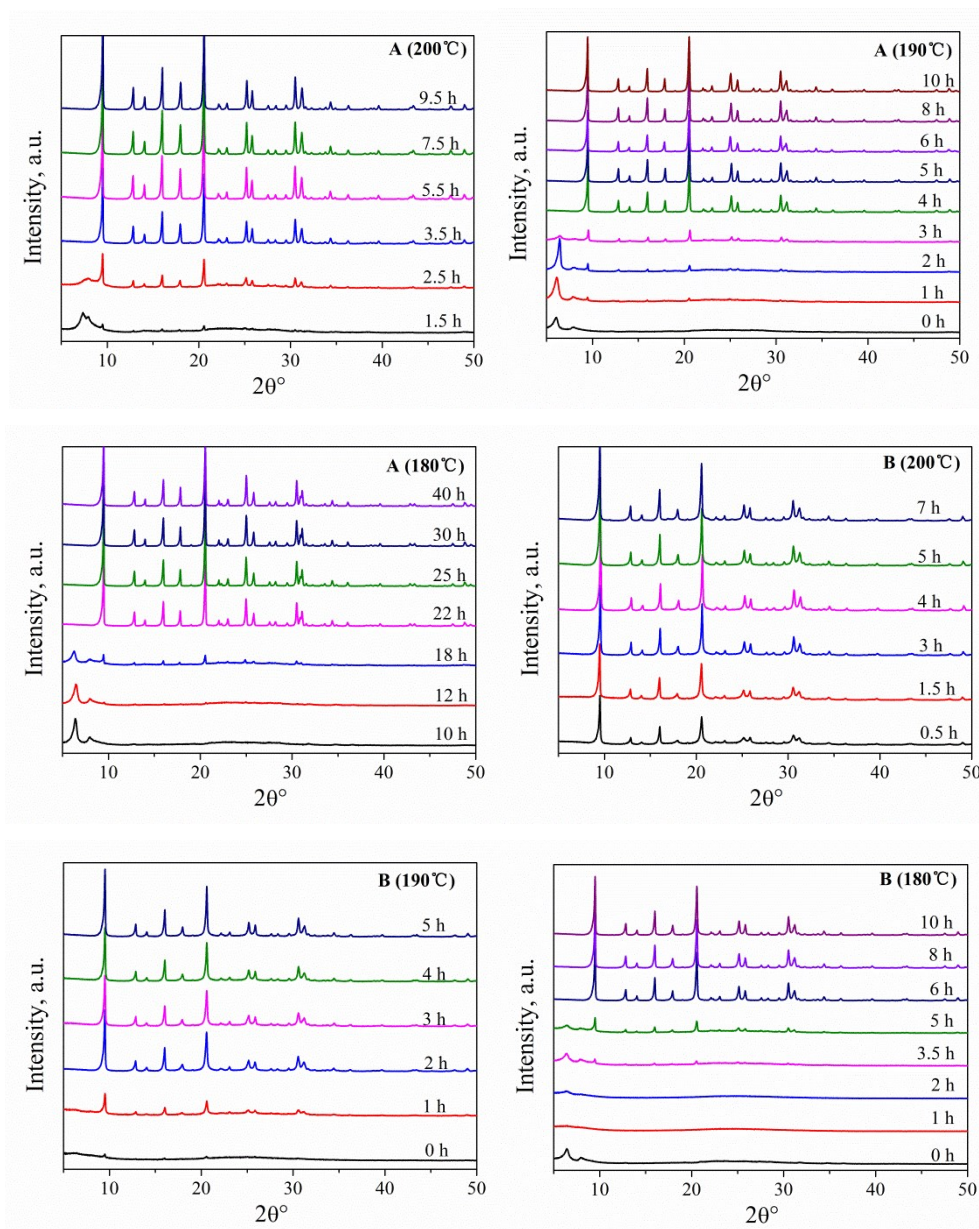
**Fig. S2** SEM images of SAPO-34 synthesized with Citric acid/ $\text{Al}_2\text{O}_3$ = A) 0, B) 0.2, C) 0.3, D) 0.5, E) 1.0.



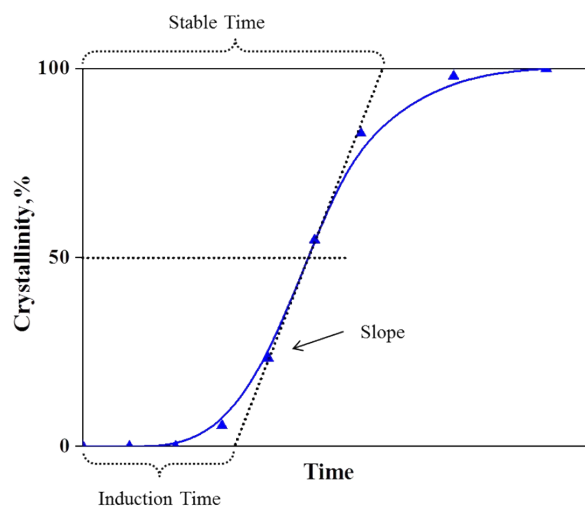
**Fig. S3** Standard  $^{13}\text{C}$  NMR spectra of citric acid (A); Solution  $^{13}\text{C}$  NMR spectra of mother liquors with different crystallization time (B).



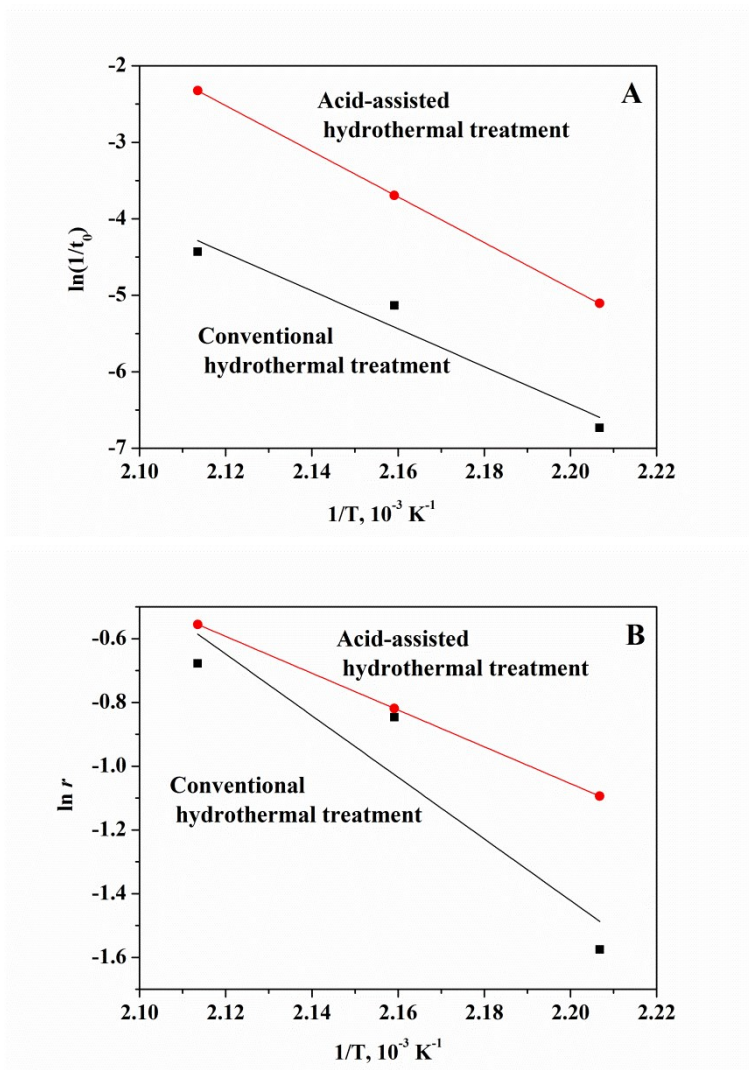
**Fig. S4** The plot of the zeolite yield versus the pH value of the starting gel. A: synthesized with different acids including inorganic acids and organic acids. B: synthesized with inorganic acids. C: synthesized with organic acids.



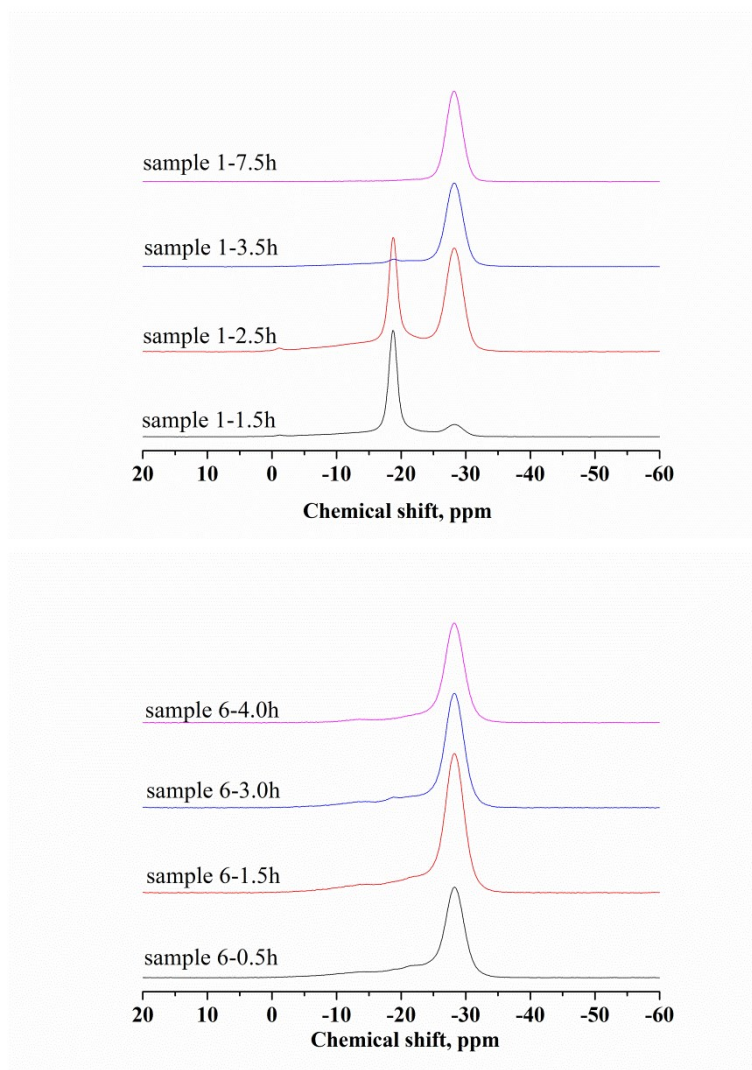
**Fig. S5** XRD patterns of samples synthesized with different crystallization methods at three levels of temperature namely 180, 190, and 200°C. A: conventional hydrothermal (Sample 1) and B: acid-assisted hydrothermal treatment (Sample 6).



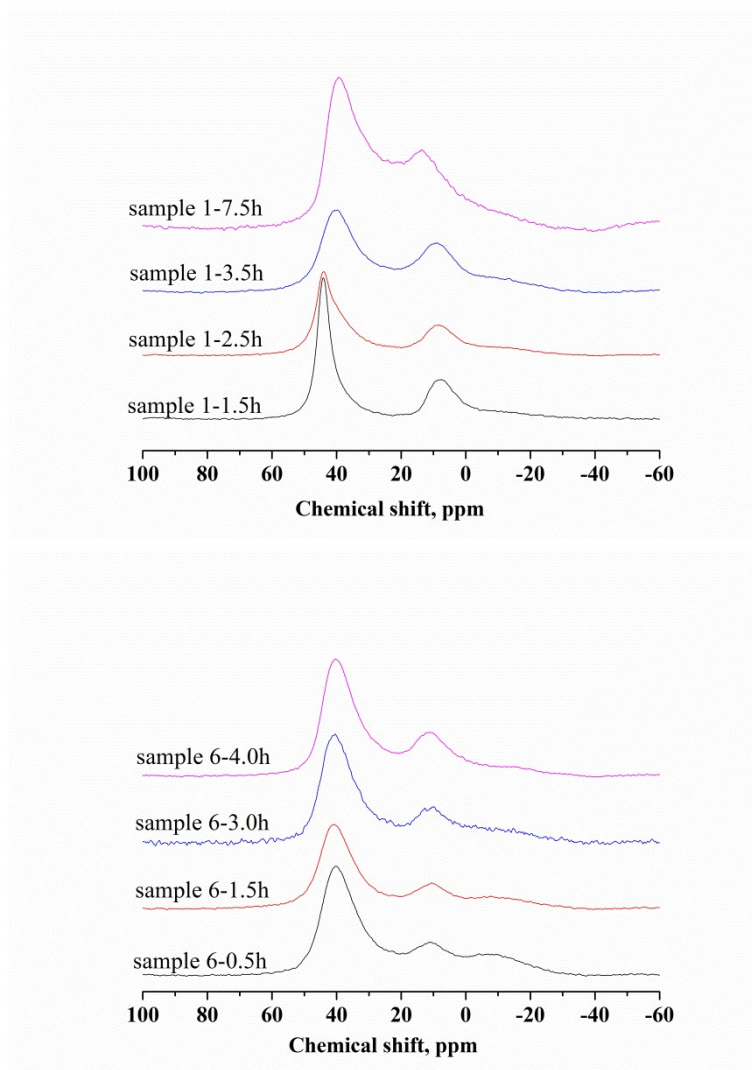
**Fig. S6** Schematic representation of crystallization curve of zeolite SAPO-34.



**Fig. S7** Arrhenius plots for SAPO-34 samples synthesized with different crystallization methods of induction period (A) and crystal growth period (B).

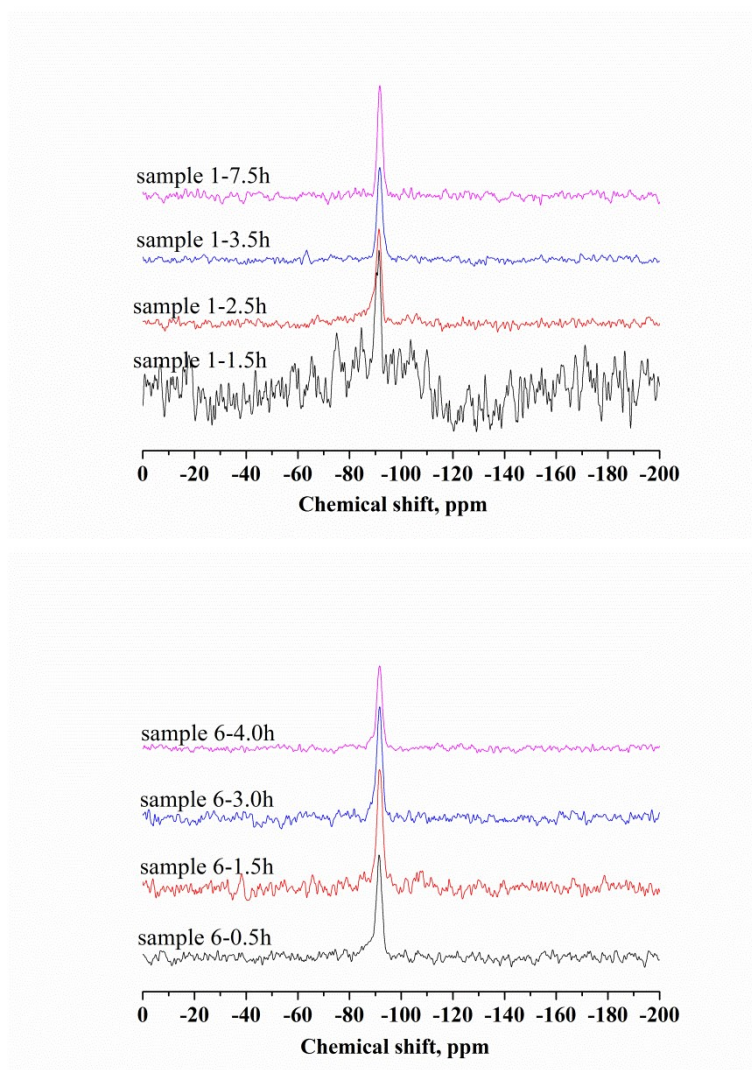


**Fig. S8**  $^{31}\text{P}$  MAS NMR spectra of sample 1 and sample 6 obtained at different synthesis time.

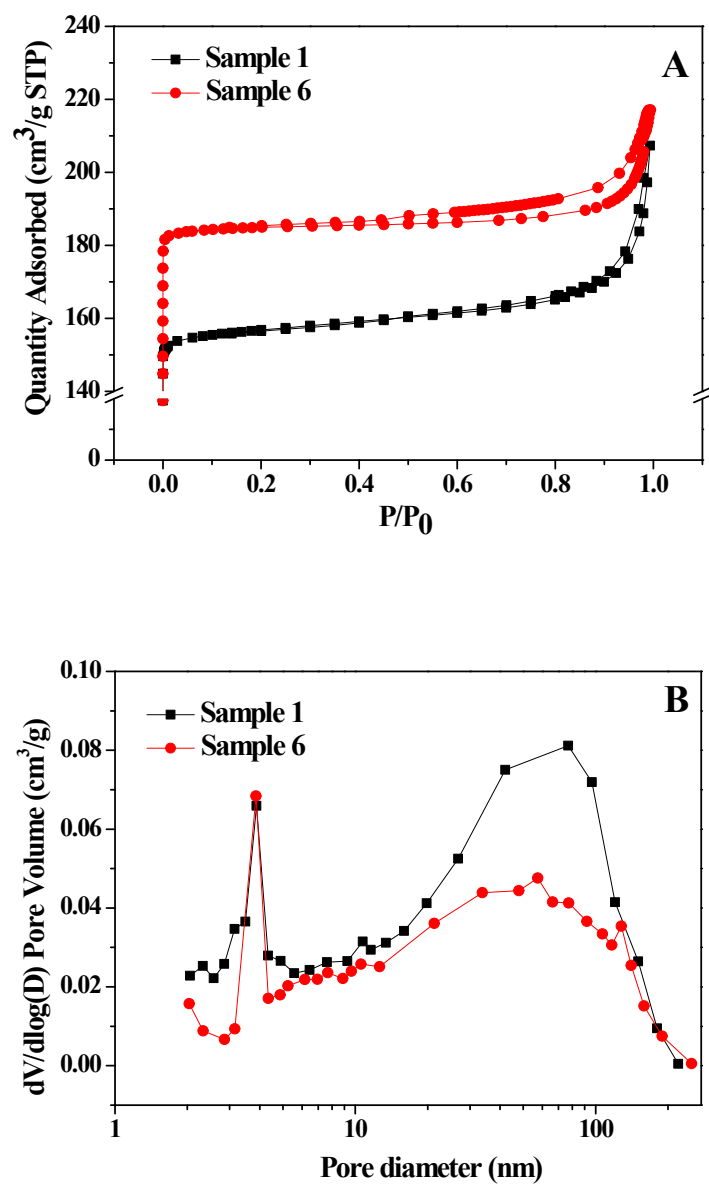


**Fig. S9**  $^{27}\text{Al}$  MAS NMR spectra of sample 1 and sample 6 obtained at different synthesis time.

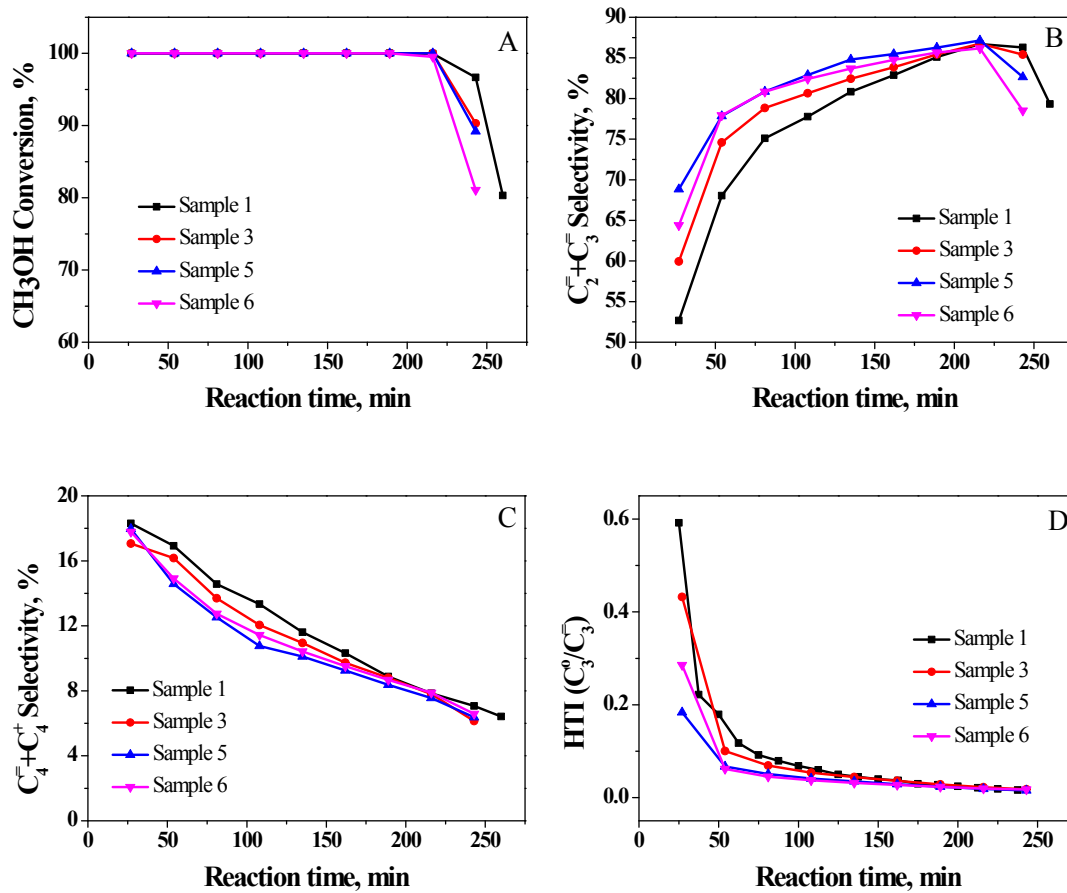




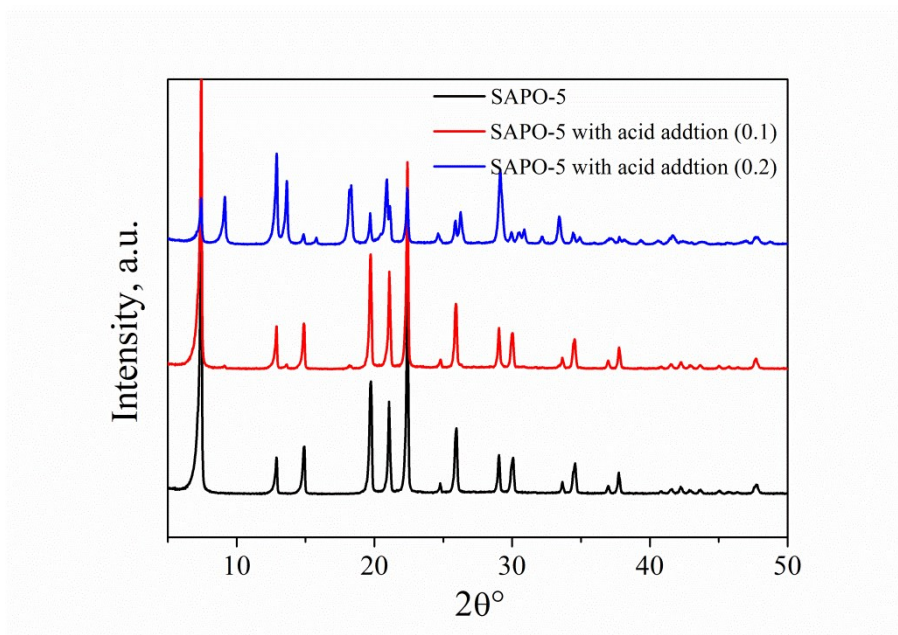
**Fig. S10**  $^{29}\text{Si}$  MAS NMR spectra of sample 1 and sample 6 obtained at different synthesis time.



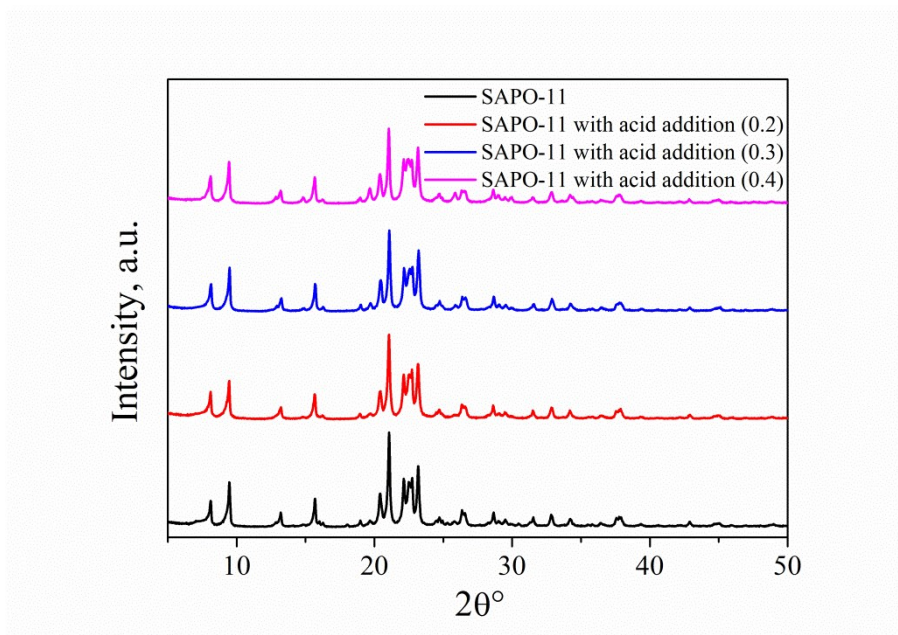
**Fig. S11** Nitrogen adsorption/desorption isotherms (A) and BJH pore size distribution (B) of synthesized SAPO-34s with or without citric acid.



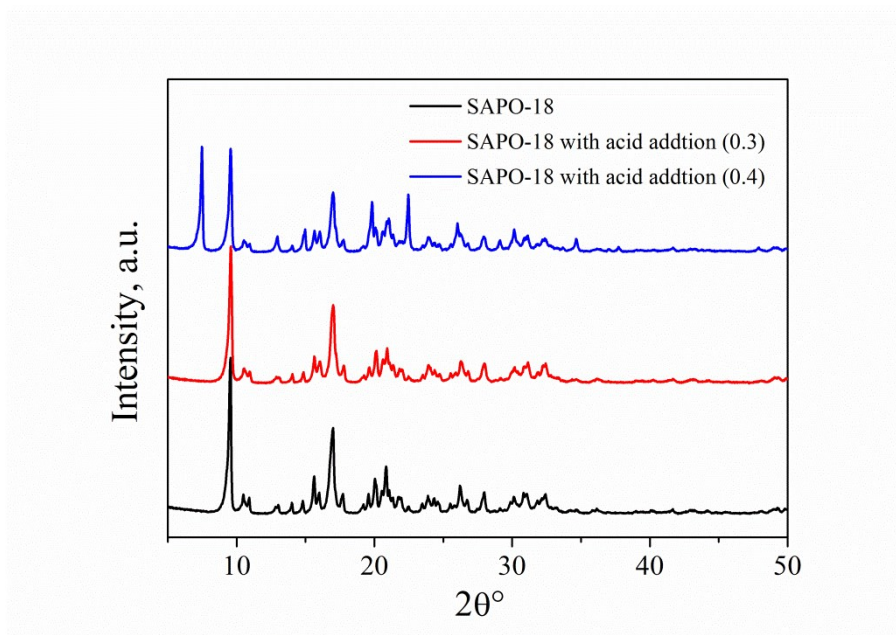
**Fig. S12** Methanol conversion variation and yields of hydrocarbons in the MTO reaction with time-on-stream over the SAPO-34 catalysts. Experimental conditions: WHSV = 3.5 h<sup>-1</sup>, T = 450°C, catalyst weight = 0.80 g.



**Fig. S13** XRD patterns of SAPO-5 synthesized with acid-assisted route. Number in bracket represents citric acid/ $\text{Al}_2\text{O}_3$ .



**Fig. S14** XRD patterns of SAPO-11 synthesized with acid-assisted route. Number in bracket represents citric acid/ $\text{Al}_2\text{O}_3$ .



**Fig. S15** XRD patterns of SAPO-18 synthesized with acid-assisted route. Number in bracket represents citric acid/ $\text{Al}_2\text{O}_3$ .

**Table S1** Comparison of different gel compositions in the synthesis of SAPO-34.

Sample	Gel composition (molar ratio)	T (°C)	Time (days)	Yield (%)	Cost (RMB/kg)
1	1.0 Al <sub>2</sub> O <sub>3</sub> : 1.0 P <sub>2</sub> O <sub>5</sub> : 0.25 SiO <sub>2</sub> : 2.5 TEA: 1.0 TEA: 40 H <sub>2</sub> O	200	0.5	42.3	76.6
2	1.0 Al <sub>2</sub> O <sub>3</sub> : 1.0 P <sub>2</sub> O <sub>5</sub> : 0.25 SiO <sub>2</sub> : 2.5 TEA: 1.0 TEA: 40 H <sub>2</sub> O: 1.0 Citric acid	200	0.5	100	34.3
3	1.0 Al <sub>2</sub> O <sub>3</sub> : 0.9 P <sub>2</sub> O <sub>5</sub> : 0.30 SiO <sub>2</sub> : 7.0 TEA: 15.7 H <sub>2</sub> O	160	6	90.4	59.0
4	2.0 DEA : 1.0 Al <sub>2</sub> O <sub>3</sub> : 0.8 P <sub>2</sub> O <sub>5</sub> : 0.60 SiO <sub>2</sub> : 50 H <sub>2</sub> O	200	2	39.5	60.6
5	1.2 Al <sub>2</sub> O <sub>3</sub> : 0.9 P <sub>2</sub> O <sub>5</sub> : 0.50 SiO <sub>2</sub> : 3.0 DIPA: 40 H <sub>2</sub> O	200	2	85.2	42.6

Sample 1: in this work;

Sample 2: in this work;

Sample 3, 4: D. Fan, P. Tian, S. Xu, Q. Xia, X. Su, L. Zhang, Y. Zhang, Y. He and Z. Liu, *J. Mater. Chem.*, 2012, **22**, 6568-6574.

Sample 5: D. Fan, P. Tian, S. Xu, D. Wang, Y. Yang, J. Li, Q. Wang, M. Yang and Z. Liu, *New J. Chem.*, 2016, **40**, 4236–4244.

**Table S2** Summary of the synthesis of SAPO-34 molecular sieves with different type of acids

Samples	Acid type	Acid/Al <sub>2</sub> O <sub>3</sub>	pH in the starting gel	pH after crystallization	Yield (%)
1	oxalic acid	1.5	6.4	9.1	70.6
2	acetic acid	3.0	5.3	6.7	87.6
3	hydrochloric acid	0.5	6.9	10.1	74.4
4	hydrochloric acid	1.0	6.6	9.8	80.4
5	hydrochloric acid	1.5	5.4	7.0	90.1
6	sulfuric acid	0.5	7.9	9.5	58.7
7	sulfuric acid	1.0	5.3	9.5	79.8
8	nitric acid	1.0	7.3	10.5	68.2



**Table S3** Variation of textural properties of synthesized SAPO-34s with or without citric acid.

	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{micro}}$ ( $\text{m}^2/\text{g}$ )	$S_{\text{ext}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{total}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{micro}}$ ( $\text{cm}^3/\text{g}$ )	$V_{\text{meso}}$ ( $\text{cm}^3/\text{g}$ )
Sample 1	657.7	625.3	32.5	0.32	0.23	0.09
Sample 6	719.8	706.0	13.8	0.33	0.28	0.05

$$V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$$

**Table S4** Summary of the synthesis of SAPO molecular sieves with acid-assisted route

Samples	Citric acid/Al <sub>2</sub> O <sub>3</sub>	Product Phase	Yield (%)
1	-	SAPO-5	66.3
2	0.1	SAPO-5	82.3
3	0.2	SAPO-5+unknown phase	-
4	-	SAPO-11	45.3
5	0.2	SAPO-11	55.1
6	0.3	SAPO-11	70.6
7	0.4	SAPO-11	92.1
8	-	SAPO-18	66.1
9	0.3	SAPO-18	85.0
10	0.4	SAPO-18+SAPO-5	-