A Rapid and Eco-friendly Approach for the Synthesis of Low-silica SAPO-34 with Excellent MTO Catalytic Performance

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Experimental

Materials

The SAPO-34-based mother liquid, which was obtained after evaporation to remove organics and concentration by mechanical vapor recompression (MVR), was acquired from the scale-up platform of DICP for molecular sieves synthesis. Note that the use of concentrated mother liquid can increase its addition amounts (based on inorganic oxides) for each batch.

The chemical regents used include silica gel (27.3 wt% SiO_2, Shenyang Chemical Industry Co., Ltd.), phosphoric acid (80 wt% H_3PO_4, Sichuan Xianfeng Chemical Co.), pseudo boehmite (67.5 wt% Al_2O_3, Shandong aluminum Co., Ltd.). Tetraethylammonium hydroxide (35 wt% TEAOH), diethylamine (DEA, 99 wt%), triethylamine (TEA, 99 wt%) and morpholine (MOR, 99 wt%) were purchased from Tianjin cameo chemical reagent Co., Ltd.

Synthesis of SAPO-34 by utilization of recycled mother liquid

The gel molar composition for SAPO-34 synthesis with the addition of recycled mother liquid was $1.0Al_2O_3$:$1.0P_2O_5$:0.1-$0.6SiO_2$:$50H_2O$:xR(template). The amount of mother liquid added in the gel varied from 10 g to 40 g.

The typical synthesis procedure for mother liquid addition of 40 g was as follows. Mother liquid (40 g), H_2O (6.74 g), silica sol (2.08 g), pseudo boehmite (3.59 g) and phosphoric acid (5.56 g) were added in sequence into a beaker under stirring. The mixture was stirred for 20 min at room temperature. After further addition of organic amines (TEA: 10.12 g, DEA: 3.66 g) and stirring for 20 min, a final gel mixture can be obtained, which has a molar composition of $1.0Al_2O_3$:$1.0P_2O_5$:$0.25SiO_2$:$2.0TEA$:$1.0DEA$:$50H_2O$. The gel mixture was transferred into a 100 mL stainless steel autoclave, sealed, placed in an oven. Subsequently, the autoclave was heated to the designed temperature in 120 min under rotation and kept for a certain time. After crystallization, the autoclave was cooled immediately. The solid product was washed with deionized water, separated by centrifugation, and then dried at 120 $^{\circ}$C. The samples were calcined at 550 $^{\circ}$C for 6 h to remove the organics before characterization and catalytic test.

The ratio of $\text{Mass}_{\text{(dry inorganic oxides from mother liquid)}}$/$\text{Mass}_{\text{(total dry inorganic oxides)}}$ for the above synthesis (mother liquid addition of 40 g) was 52.2 wt%.

The sample yields are calculated based on the following formula: yield (wt%) = $M_{sample} \times 0.85 \times 100/(M_{inorganic\ oxides})_{gel}$, where M_{sample}, 0.85 and $(M_{inorganic\ oxides})_{gel}$ stand for sample weight, an estimated value of inorganic framework in the samples, and dry mass of inorganic oxides in the starting gels, respectively.

Characterization

X-ray diffraction (XRD) patterns of the samples were measured on a Panalytical X'Pert PRO X-ray diffractometer, which uses Cu Kα radiation (λ =1.5418 Å) at 40 mA and 40 kV. The relative crystallinity of the samples was calculated according to the sum of the peak height at 2θ = 9.48°, 16.02° and 20.56°. For each recipe, the sample with the highest value was defined as standard sample with a relative crystallinity of 100%.

Elemental composition was measured using a Panalytical AXios X-ray fluorescence (XRF) spectrometer. Scanning electron microscopy (SEM) images of the samples were acquired with a Hitachi

SU8020 scanning electron microscope.

Textural properties of the calcined samples were determined by N_2 adsorption at -196 °C on a Micromeritics ASAP 2020 system. Each sample was pretreated in vacuum at 350 °C for 6 h. 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.

The surface element compositions of the samples were measured using X-ray photoelectron spectroscopy (XPS) on a Thermo fisher ESCALAB 250Xi XPS instrument, which was provided by a monochromatic Al Kα (1486.6 eV, 15 kV, 10.8 mA) X-ray excitation source. The surface atomic concentrations were determined from the photoelectron peak areas of Si 2p, Al 2p and P 2p.

NH_3-TPD was determined using a Micromertics Autochem Model 2920 Chemisorber. Prior to the measurement, ~0.1 g of calcined sample was pretreated under He at 650 °C for 1 h. Then, the sample was cooled down to 100 °C, exposed in NH_3 (2% NH_3 in He) for 0.5 h and purged by He for 1 h to remove physically adsorbed NH_3. The measurement was conducted from 100 to 650 °C with a heating rate of 10 °C/min under He flow (30 mL/min).

Dynamic light scattering (DLS) analysis of the mother liquid was measured with Malvern Zetasizer Nano.

Liquid-state NMR experiments were performed on a Bruker AVANCE III 400 instrument equipped with a 5.0 mm liquid probe at a ^1H observed frequency of 400.23 MHz. The resonance frequencies of ^{27}Al, ^{29}Si, and ^{31}P were 104.2, 79.4, and 161.9 MHz respectively. The chemical shift of the ^{27}Al, ^{29}Si, and ^{31}P nucleus was referenced to 1 M aqueous $Al(NO_3)_3$ (0 ppm), TMS (0 ppm), and 85% H_3PO_4 (0 ppm), respectively.

All solid-state NMR experiments were performed using a 4 mm MAS probe at a spinning rate of 12 kHz over Bruker Avance NEO 500 spectroscopic instrument equipped with an 11.7 T wide-aperture magnet. The ^{27}Al MAS NMR spectra were recorded using a single π/18=0.50 μs pulse sequence with a recycle delay of 1 s. The $^1H–^{29}Si$ cross-polarization (CP) MAS measurements were performed with a contact time of 3 ms and a recycle delay of 1 s. The ^{31}P MAS NMR spectra were conducted with high-power proton (^1H) decoupling using a π/2 pulse of 2.8 us and a recycle delay of 60 s. The chemical shifts of the ^{27}Al, ^{29}Si, and ^{31}P nucleus were externally referenced to 1 M aqueous $Al(NO_3)_3$ (0 ppm), kaolinite (−91.5 ppm), and $NH_4H_2PO_4$ (1 ppm), respectively.

MTO catalytic activity

The MTO reactions were performed in a fixed bed reactor at atmospheric pressure. In a typical procedure, the calcined catalyst (0.3 g, 40–60 meshes) was loaded in the reactor and was activated at 500 °C for 2 h under N_2 at a flow rate of 42 mL/min before starting each reaction, and then was adjusted to the reaction temperature of 450 °C. The methanol was fed by passing the carrier gas through a saturator containing methanol, which gave a WHSV of 3.65 h^{-1}. The reaction products were analyzed using an on-line gas chromatograph (Agilent GC 7890N) equipped with a flame ionization detector (FID) and a capillary column of Pora PLOT Q-HT. The conversion was calculated on a CH_2 basis, and dimethyl ether (DME) was considered as a reactant. The distribution of the product was determined by mass percent and the total hydrocarbon was 100%. Catalyst lifetime was defined as the duration of methanol conversion over 99%.
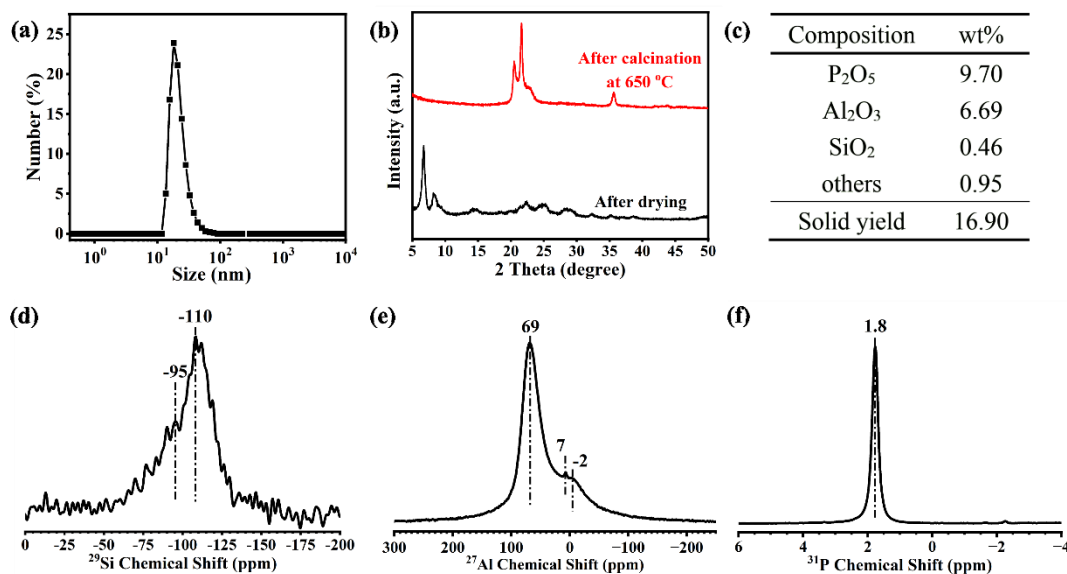
Figure S1. (a) Particle size distribution of the diluted mother liquid, (b) XRD patterns and (c) inorganic compositions of the dried and calcined mother liquid. (d) Liquid ^{29}Si, (e) ^{31}P and (f) ^{27}Al NMR spectra of the diluted mother liquid.

An evidently broadened resonance band centered at -108 ppm is observed in the ^{29}Si spectrum, which can be owing to Si(OAl)$_n$(OSi)$_m$(OH)$_{4-n-m}$ ($0 \leq m \leq 4$, $0 \leq n \leq 4$, $0 \leq m+n \leq 4$) species and implies the heterogeneous environments of Si nuclei. In the ^{31}P spectrum, the distinct signal at 1.07 ppm can be ascribed to HPO$_4^{2-}$ ions bonded to aluminum species in the aluminophosphate complexes.[1,2] In the ^{27}Al spectrum, the predominant resonance centered at 68.5 ppm should mainly arise from penta-/tetra-coordinated Al that are oxygen-bridged to phosphorus. The weak shoulder band between 20 and -40 ppm is likely due to octahedral Al species bonded to HPO$_4^{2-}$ ions. The above results suggest that the silicon and aluminum environments are highly diverse and heterogeneous, whereas the status of phosphorus appears relatively uniform in the mother liquid.
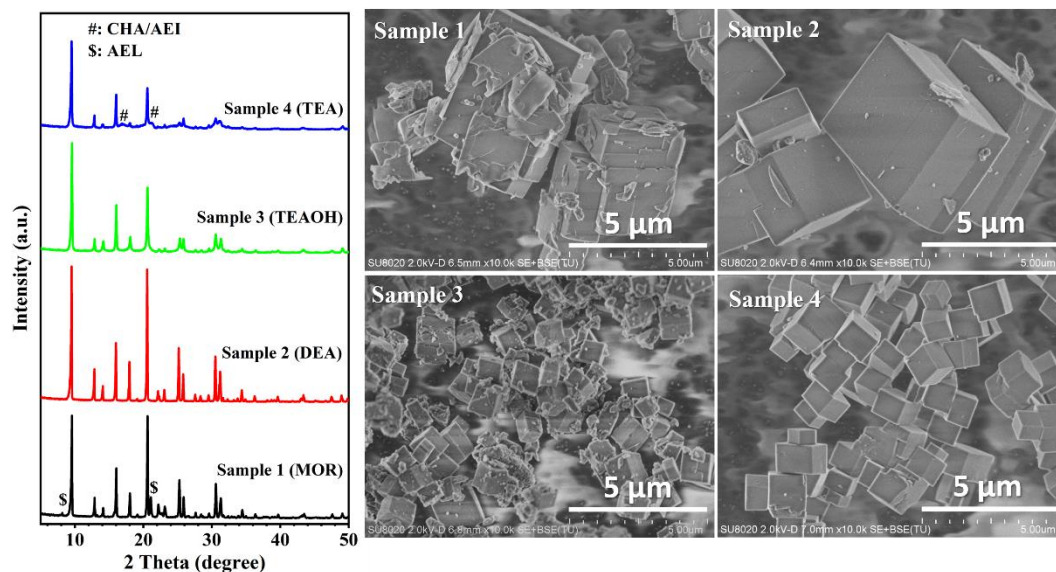
Figure S2. XRD patterns and SEM images of the samples synthesized with different organic amines as the template. The final gel molar composition was $1.0Al_2O_3$:$1.0P_2O_5$:$0.25SiO_2$:xR(template):$50H_2O$ (220 °C, 5 h, mother liquid addition of 40 g).
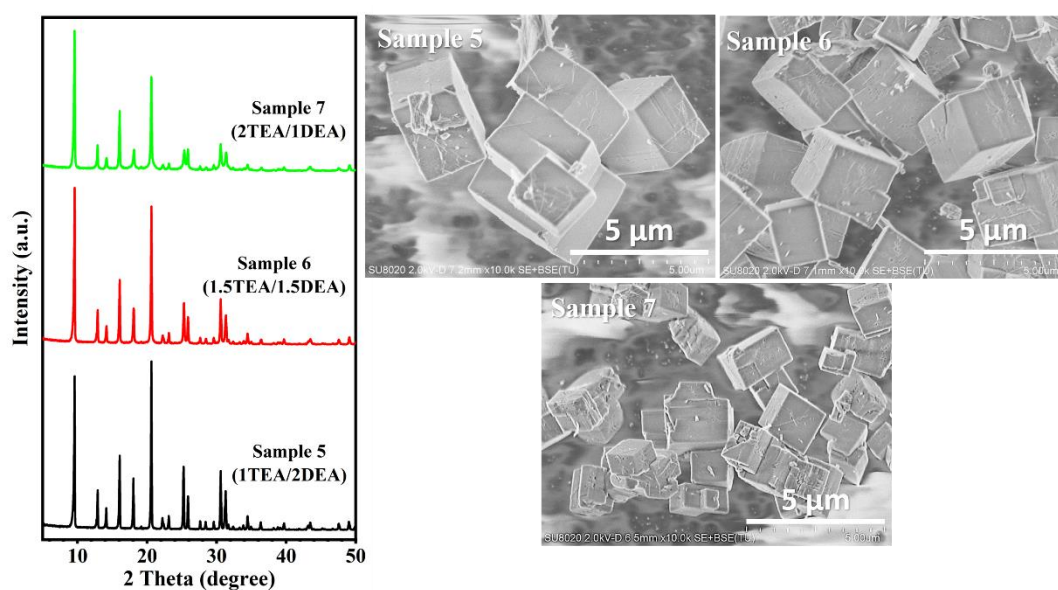

Figure S3. XRD patterns and SEM images of SAPO-34 synthesized with dual template (TEA-DEA). The final gel molar composition was $1.0Al_2O_3$:$1.0P_2O_5$:$0.25SiO_2$:xTEA:yDEA:$50H_2O$ (220 °C, mother liquid addition of 40 g). The crystallization time was 5 h for samples 5 and 6, while 3 h for sample 7.
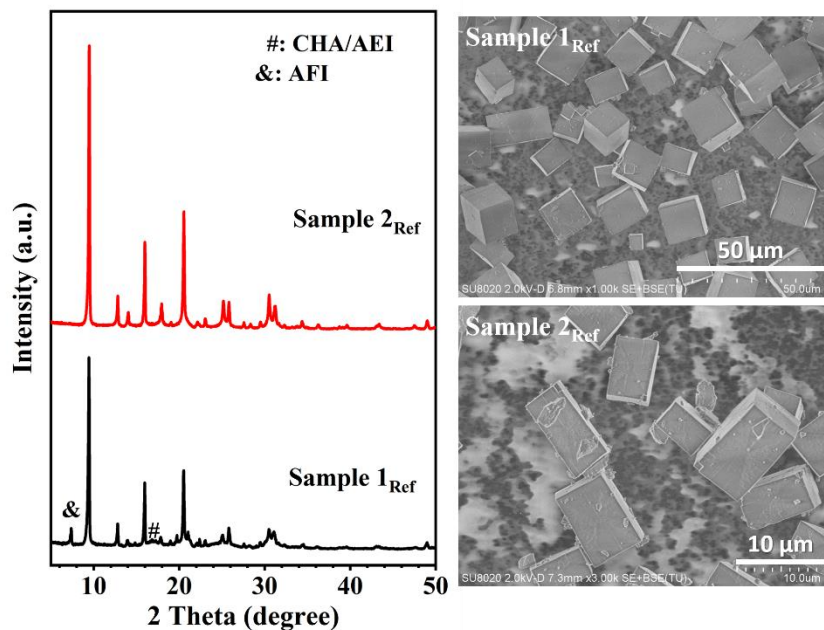
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Figure S4. XRD patterns and SEM images of samples 1_{Ref} and 2_{Ref} synthesized without the addition of mother liquid.

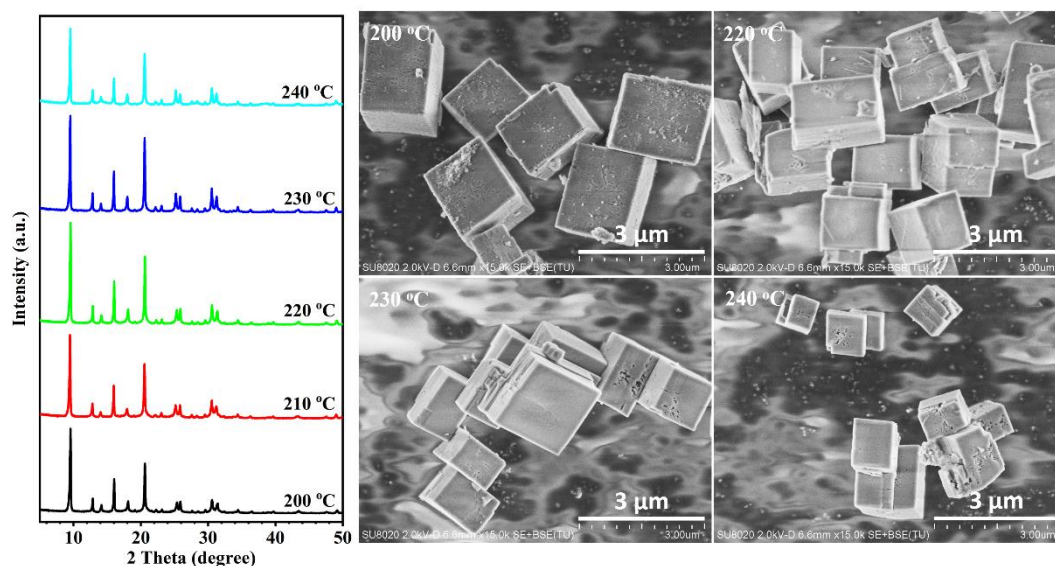|	Final gel molar composition	Solid yield (wt%)
Sample 1_{Ref}	$1.0Al_2O_3$:$1.0P_2O_5$:**0.25**SiO_2:$2.0TEA$:$1.0DEA$:$50H_2O$ (220 °C, 3 h)	74.8
Sample 2_{Ref}	$1.0Al_2O_3$:$1.0P_2O_5$:**0.20**SiO_2:$2.0TEA$:$1.0DEA$:$50H_2O$ (200 °C, 12 h)	53.4

Figure S5. XRD patterns and SEM images of SAPO-34 synthesized at different temperatures. The final gel molar composition was $1.0Al_2O_3$:$1.0P_2O_5$:$0.25SiO_2$:$2.0TEA$:$1.0DEA$:$50H_2O$ (3 h, mother liquid addition of 40 g).
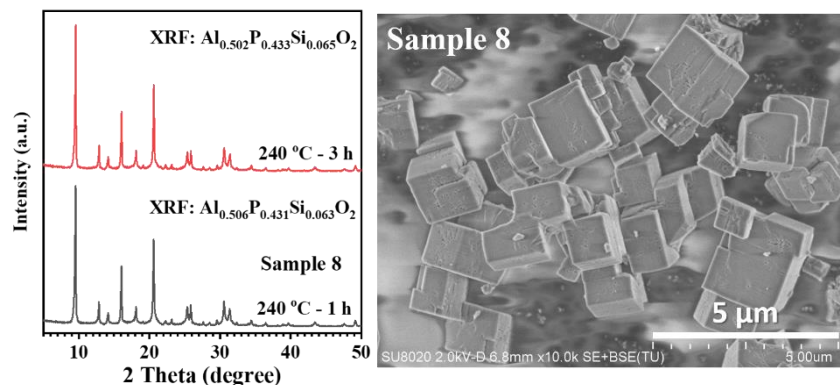
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Figure S6. XRD patterns and SEM image of the sample synthesized at 240 ^{o}C. The final gel molar composition was $1.0Al_2O_3:1.0P_2O_5:0.25SiO_2:2.0TEA:1.0DEA:50H_2O$ (mother liquid addition of 40 g).
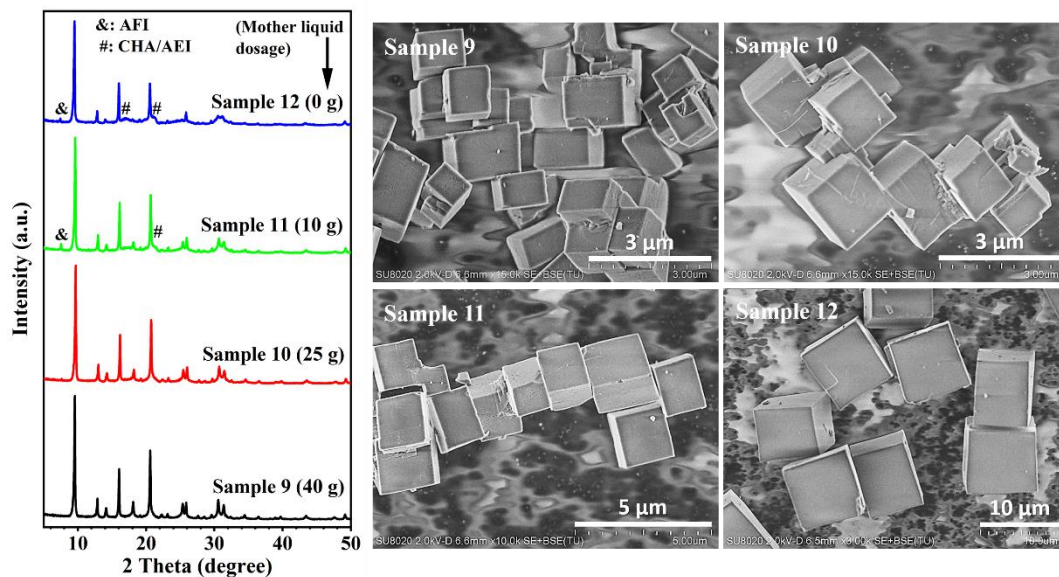

Figure S7. XRD patterns and SEM images of the samples synthesized with different amounts of mother liquid. The final gel molar composition was $1.0Al_2O_3:1.0P_2O_5:0.25SiO_2:2.0TEA:1.0DEA:50H_2O$ (230 ^{o}C, 1 h).
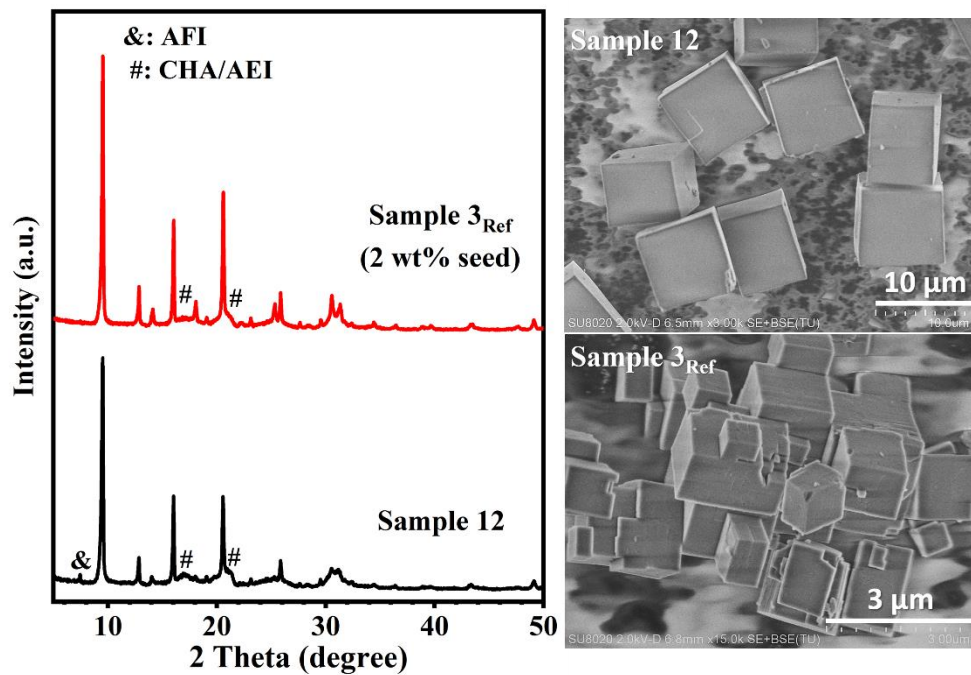
Figure S8. XRD patterns and SEM images of SAPO-34 synthesized without the addition of mother liquid. The final gel molar composition was $1.0Al_2O_3:1.0P_2O_5:0.25SiO_2:2.0TEA:1.0DEA:50H_2O$ (230 ℃, 1 h).
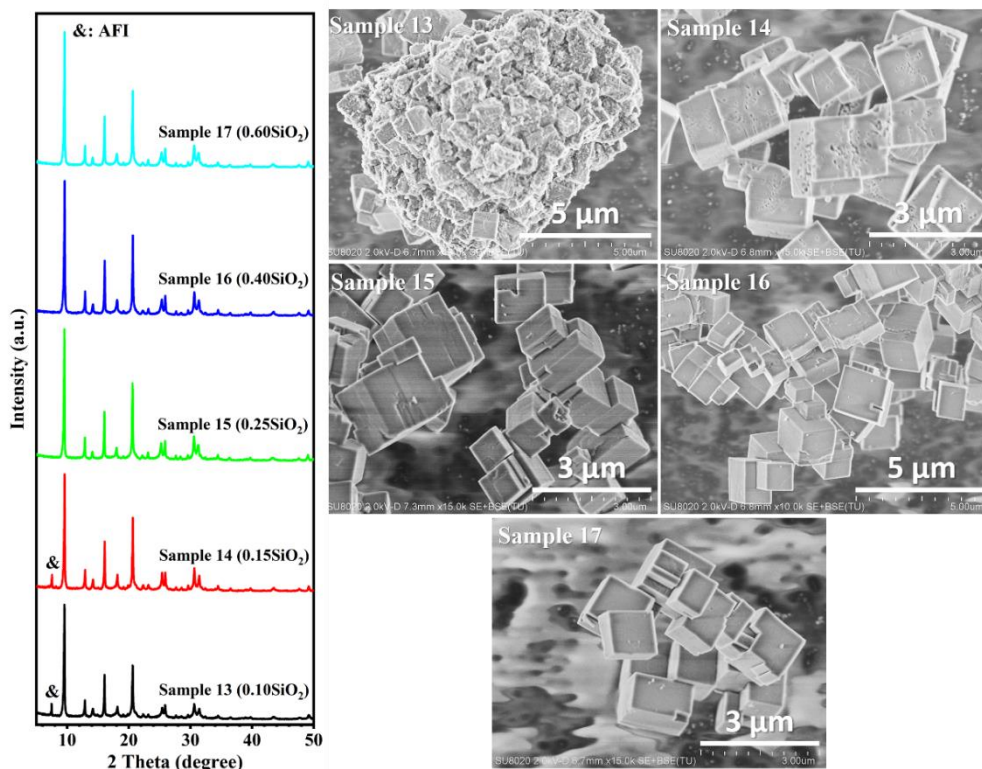

Figure S9. XRD patterns and SEM images of the samples synthesized with different silica dosages. The final gel molar composition was $1.0Al_2O_3:1.0P_2O_5:xSiO_2:2.0TEA:1.0DEA:50H_2O$ (230 ℃, 2 h, mother liquid addition of 40 g).
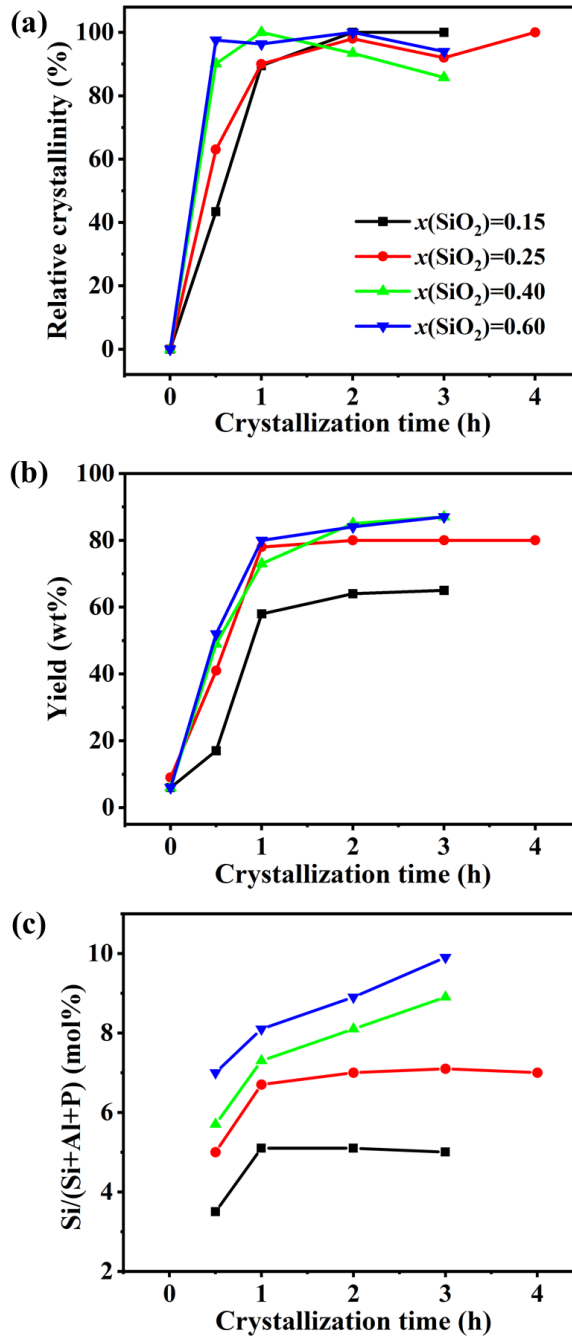
Figure S10. The evolution of (a) relative crystallinity, (b) solid yields and (c) product silica contents during the synthesis of SAPO-34 with different silica dosages.

The final gel molar composition was $1.0Al_2O_3:1.0P_2O_5:xSiO_2:2.0TEA:1.0DEA:50H_2O$ (230 °C, mother liquid addition of 40 g).
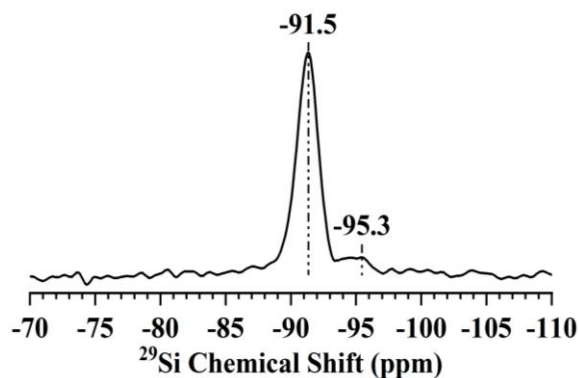
Figure S11. ^{29}Si MAS NMR spectrum of the as-synthesized SAPO-34. The sample was synthesized at 240 °C for 3 h with a final gel molar composition of 1.0Al$_2$O$_3$:1.0P$_2$O$_5$:0.25SiO$_2$:2.0TEA:1.0DEA:50H$_2$O (mother liquid addition of 40 g).
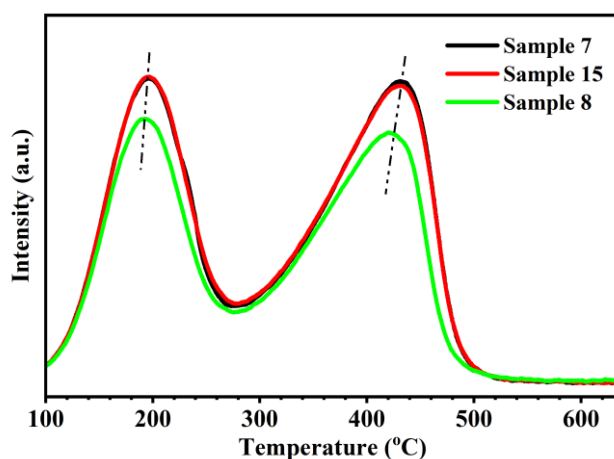
Figure S12. NH$_3$-TPD curves of the rapidly synthesized SAPO-34.

Sample	T-time [a]	NH$_3$-TPD (mmol/g)	
		Weak	Moderate + Strong
7	220 °C-3 h	0.48	0.65
15	230 °C-2 h	0.48	0.65
8	240 °C-1 h	0.42	0.54

a: T and time were the crystallization temperature and time, respectively.

Table S1. Product phases, solid yields and silica contents of the samples synthesized with different dosages of mother liquid (230 °C, 1 h).

Sample [a]	M_m/M_{total} [b] (wt%)	Mother liquid added	Product		
			Crystal phase	Yield (wt%)	Elemental composition
9	52.2	40 g	CHA	78.0	$Al_{0.499}P_{0.434}Si_{0.067}O_2$
10	32.8	25 g	CHA	80.0	$Al_{0.500}P_{0.437}Si_{0.063}O_2$
11	13.0	10 g	CHA/AEI + minor AFI	72.3	/
12	0	0 g	CHA/AEI + minor AFI	40.1	/
3$_{Ref}$	0	0 g (2 wt% seed) [c]	CHA/AEI	79.0	$Al_{0.501}P_{0.436}Si_{0.063}O_2$

[a] The final gel molar composition was $1.0Al_2O_3$:$1.0P_2O_5$:$0.25SiO_2$:$2.0TEA$:$1.0DEA$:$50H_2O$.

[b] M_m: mass of dry inorganic oxides from mother liquid. M_{total}: total mass of dry inorganic oxides in the final gel.

[c] The seed was prepared by ball milling method as the previously reported.[3]

Table S2. Product phases, solid yields and silica contents of the samples synthesized with different silica dosages (230 °C, 2 h).

Sample [a]	x SiO$_2$	Product			R [b]
		Crystal phase	Yield (wt%)	Elemental composition	
13	0.10	CHA + minor AFI	/	/	-
14	0.15	CHA+ minor AFI	64.0	$Al_{0.503}P_{0.446}Si_{0.051}O_2$	1.41
15	0.25	CHA	81.0	$Al_{0.500}P_{0.433}Si_{0.070}O_2$	1.19
16	0.40	CHA	85.1	$Al_{0.499}P_{0.420}Si_{0.081}O_2$	0.89
17	0.60	CHA	83.9	$Al_{0.494}P_{0.419}Si_{0.088}O_2$	0.67

[a] The final gel molar composition was $1.0Al_2O_3$:$1.0P_2O_5$:$xSiO_2$:$2.0TEA$:$1.0DEA$:$50H_2O$ (mother liquid addition of 40 g).

Table S3. Textural properties of the rapidly synthesized low-silica SAPO-34 samples.

Sample	T-time[a]	Surface area [b] (m^2/g)			Pore volume [c] (cm^3/g)		
		S_{total}	S_{micro}	S_{ext}	V_{total}	V_{micro}	V_{meso}
7	220 °C-3 h	559.5	556.2	3.4	0.28	0.26	0.02
15	230 °C-2 h	565.7	555.8	9.9	0.27	0.26	0.01
8	240 °C-1 h	541.2	532.8	8.4	0.28	0.26	0.02

a: T and time are crystallization temperature and time, respectively.

b: S_{total}: BET surface area; S_{micro}: t-plot micropore surface area; $S_{ext} = S_{total} - S_{micro}$.

c: V_{total} was evaluated at $P/P_0 = 0.97$; V_{micro}: t-plot micropore volume; $V_{meso} = V_{total} - V_{micro}$.

Table S4. Lifetime and products distribution of the samples in the MTO reaction
(WHSV$_{methanol}$ = 2h^{-1}, T = 450℃, catalyst weight = 300 mg).

Sample	Lifetime [a] (min)	$C_2^=$ (wt%)	$C_3^=$ (wt%)	$C_2^=+C_3^=$ [b] (wt%)
7	378	53.42	32.59	86.01
15	429	54.43	31.03	85.46
8	395	53.45	32.07	85.52
2$_{Ref}$	378	53.14	32.42	85.56

[a] Catalyst lifetime is defined as the reaction·duration with >99 % methanol conversion.

[b] The highest selectivity of $C_2^=$ and·$C_3^=$ under > 99 % methanol conversion.

Reference

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2. R. F. Mortlock, A. T. Bell and C. J. Radke. ^{31}P and ^{27}Al NMR investigations of highly acidic, aqueous solutions containing aluminum and phosphorus, *J. Phys. Chem.* 1993, 97, 767.

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