

Electronic Supplementary Information

Exclusive SAPO-seeded synthesis of ZK-5 zeolite for selective synthesis of methylamines

Rui Wu,^{‡a} Jinfeng Han,^{‡a} Yunzheng Wang,^a Mengyang Chen,^a Peng Tian,^b Xue Zhou,^c Jun Xu,^c Jia-Nan Zhang^d and Wenfu Yan^{a,*}

^a State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China. E-mail: yanw@jlu.edu.cn

^b National Engineering Laboratory for Methanol to Olefins, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China

^c National Centre for Magnetic Resonance in Wuhan, State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics, Wuhan Institute of Physics and Mathematics, Chinese Academy of Sciences, Innovation Academy for Precision Measurement Science and Technology, Chinese Academy of Sciences, Wuhan, 430071, China

^d College of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, China

[‡] These authors contributed equally to this work.

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Fig. S14 Conversion of methanol (■) and selectivity for MMA (▲), DMA (●), TMA (▼) on H-ZK-5 catalyst, and conversion of methanol (□) and selectivity for MMA (△), DMA (○), TMA (▽) on H-ZK-5 (K, Cs) catalyst at 350 °C (NH₃/CH₃OH molar ratio = 2/1 and methanol WHSV = 0.813 h⁻¹).

Table S1 Element analysis of as-synthesized ZK-5.

References

1. Experimental section

Materials and chemicals

All materials were used without further purification. Fumed silica (Xuzhou Tiancheng Chlor_alkali Co., Ltd), sodium aluminate ($\text{Al}_2\text{O}_3 \cong 41.0\%$, Sinopharm Chemical Reagent Co., Ltd), and potassium hydroxide (85%, Beijing Chemical Works) were used to synthesize ZK-5 and low-silica CHA in the presence of SAPO-34 seed. Phosphoric acid (85 wt% H_3PO_4 , Beijing Chemical Works), pseudoboehmite (72.7% Al_2O_3 , Sasol), fumed silica (Xuzhou Tiancheng Chlor_alkali Co., Ltd), and morpholine (Tianjin Fuchen Chemical Reagents Factory) were used to synthesize SAPO-34 seed. Potassium hydroxide (85%, Beijing Chemical Works), cesium hydroxide (50%, Aladdin), aluminium hydroxide (76.5 wt%), and Ludox AS-40 (Aladdin; 40%, suspension in water) were used to synthesize ZK-5 (K, Cs) zeolite. Ammonium chloride (Tianjin Fuchen Chemical Reagents Factory) was used to prepare NH_4^+ form zeolites.

Synthesis of SAPO-34 seed

SAPO-34 seed was synthesized by following the recipe in “verified synthesis of zeolitic materials 3rd revised edition” released by the Synthesis Commission of the International Zeolite Association (IZA).¹ In detail, the mixture A solution was prepared by mixing 21.0 g deionized (DI) water, 11.53 g phosphoric acid, and 6.9 g pseudoboehmite. The mixture B solution was prepared by mixing 3.07 g fumed silica, 8.72 g morpholine, and 11.25 g DI water. Subsequently, the mixture B solution and 18.0 g DI water were added into the mixture A solution in turn under continuous stirring. The mixture became homogeneous after 7 h stirring and then was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The reaction mixture was incubated for 24 h at 38 °C, followed by the hydrothermal treatment at 200 °C for 24 h. After filtering and washing with 500 mL DI water, the resultant sample was dried at 80 °C overnight. Calcined SAPO-34 (denoted as SAPO-34-C) was obtained by calcining the dried sample at 700 °C for 7 h in air. The experimental XRD pattern and the SEM image of as-synthesized SAPO-34 are displayed in Fig. S1.

Synthesis of ZK-5 zeolite

ZK-5 zeolite was synthesized from the initial mixture with the optimal molar composition of 8.5 K_2O : 1.4 Na_2O : 1.0 Al_2O_3 : 23.4 SiO_2 : 1248 H_2O in the presence of SAPO-34 seed (as-synthesized SAPO-34). Firstly, 0.40 g KOH was dissolved in 8.0 g DI water, followed by adding 0.075 g NaAlO_2 . Until the solid had been thoroughly dissolved, 0.5 g fumed silica was added to the mixture. After homogenizing for 5 h, 10 wt% as-synthesized SAPO-34 seed referring to SiO_2 was added to this aluminosilicate mixture. The final mixture was transferred into a Teflon-lined stainless-steel autoclave and heated at 100 °C for 5 d or at 160 °C for 1 d. The solid product was collected by centrifugation, washed with DI water, and dried at 80 °C overnight.

Traditional ZK-5 (K, Cs) zeolite was synthesized according to the conventional method using K^+ and Cs^+ as the inorganic structure-directing agents.² Typically, 3.8 g KOH, 2.5 g CsOH (50%), and 8.3 g DI water were mixed and stirred at ambient temperature for 1 h. Then 3.19 g aluminium hydroxide and 9.38 g colloidal silica were added to the solution under stirring for 2 h. Subsequently, the mixture was transferred into a stainless-steel autoclave and kept at 100 °C for 6 d. The solid sample was recovered by centrifugation and dried at 80 °C overnight.

As-synthesized ZK-5 (SAPO-34 directed) and ZK-5 (K, Cs) (traditional) zeolites were ion-exchanged in 1 mol/L NH_4Cl solution at 80 °C for 3 times. The time for single ion-exchange process was 2 and 12 h for ZK-5 and ZK-5 (K, Cs), respectively. H-ZK-5 and H-ZK-5 (K, Cs) were obtained by calcining NH_4^+ form ZK-5 and ZK-5 (K, Cs) zeolites at 550 °C for 5 h.

Synthesis of aluminosilicate CHA seed

Aluminosilicate CHA seed was synthesized by performing the similar process described in the synthesis of ZK-5 zeolite. The molar composition of the reaction mixture was 8.5 K_2O : 1.4 Na_2O : 1.0 Al_2O_3 : 18.7 SiO_2 : 1248 H_2O . The Si/Al ratio of the resultant CHA zeolite was 3.0, which was denoted as CHA(3.0).

2. Characterizations

Powder XRD patterns were recorded on a Rigaku D/Max 2550 X-ray diffractometer equipped with copper $\text{K}\alpha$ radiation in the 2θ scanning range from 4° to 40°. Elemental analyses were carried out on a Thermo Scientific iCAP 7000 Series ICP-OES or on an Elementar vario MICRO cube analyzer. The morphologies of

the samples were investigated by a JEOL JSM-7800F field emission scanning electron microscope. Nitrogen adsorption and desorption measurement was performed at 77K on a Micromeritics 2020 analyzer. TG analysis was carried out from ambient temperature to 800 °C (SAPO-34 seed) or 900 °C (ZK-5) with a heating rate of 5 °C·min⁻¹ on a TA Q-600 analyzer. The temperature-programmed desorption of ammonia (NH₃-TPD) measurements were carried out on a Micromeritics AutoChem II 2920. The ²⁷Al, ²⁹Si, and ³¹P MAS NMR spectra of as-synthesized SAPO-34 and the initial mixture were obtained using an 11.7 T Bruker AVANCE-III spectrometer with a 4 mm probe at a spinning rate of 10 kHz. ²⁷Al MAS NMR spectra were recorded by small-flip angle technique with a pulse length of 0.27 μs (<π/12) and a recycle delay of 1 s. Single-pulse ²⁹Si MAS NMR spectra with high power proton decoupling were recorded with π/2 pulse of 5.2 μs and a recycle delay of 80 s. Single-pulse ³¹P MAS NMR spectra with high power proton decoupling were recorded with π/2 pulse of 2.95 μs and a recycle delay of 45 s. As-synthesized ZK-5 was dissolved in the mixed acid solution of H₂SO₄ and HF. The liquid ³¹P NMR spectrum of the dissolved ZK-5-containing solution was obtained on a Bruker AVANCE NEO 400 system with 9.4 T magnetic field intensity, recorded with π/2 pulse of 8 μs and a recycle delay of 2 s, using D₂O as solvent.

3. Catalysis

Selective synthesis of methylamines was carried out under atmospheric pressure in a fixed-bed quartz tubular reactor. The H-ZK-5 and H-ZK-5 (K, Cs) zeolites were pelletized, crushed, sieved into 20~60 mesh, and activated at 370 °C for 1 h under a N₂ flow. After the pre-treatment, the catalysts were exposed to a feed gas composition of a 2:1 in mole mixture of ammonia and methanol (carried into the reactor by N₂). The reaction temperature was 350 °C and the weight hourly space velocity (WHSV) of methanol was 0.813 h⁻¹. An Agilent 7890A gas chromatograph equipped with a flame ionization detector and a CP-Volamine capillary column recorded the products on-line.

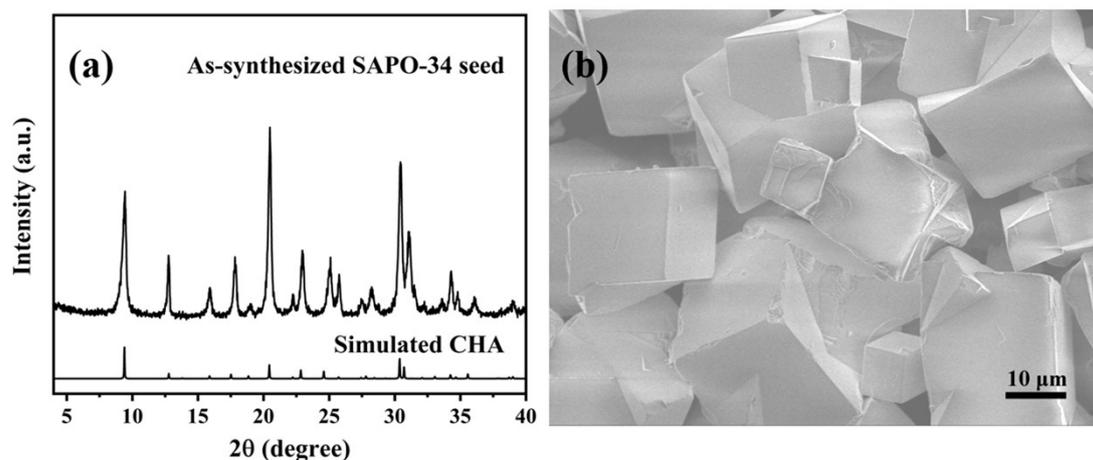


Fig. S1 XRD pattern (a) and SEM image (b) of as-synthesized SAPO-34 seed.

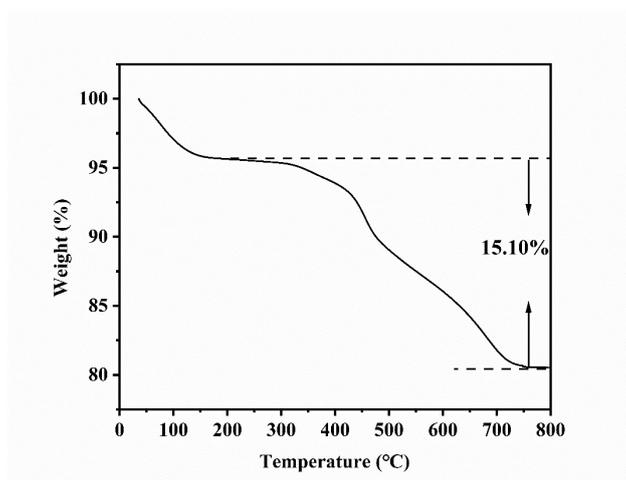


Fig. S2 TG curve of as-synthesized SAPO-34 seed.

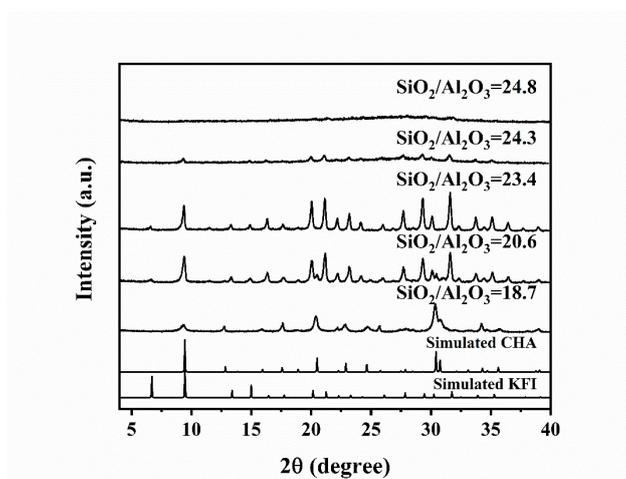


Fig. S3 Simulated XRD patterns of CHA and KFI and the experimental ones of the products crystallized from the initial mixtures with the molar composition of 8.5 K₂O: 1.4 Na₂O: 1.0 Al₂O₃: X SiO₂: 1248 H₂O at 100 °C for 5 d, where X = 18.7, 20.6, 23.4, 24.3, and 24.8.

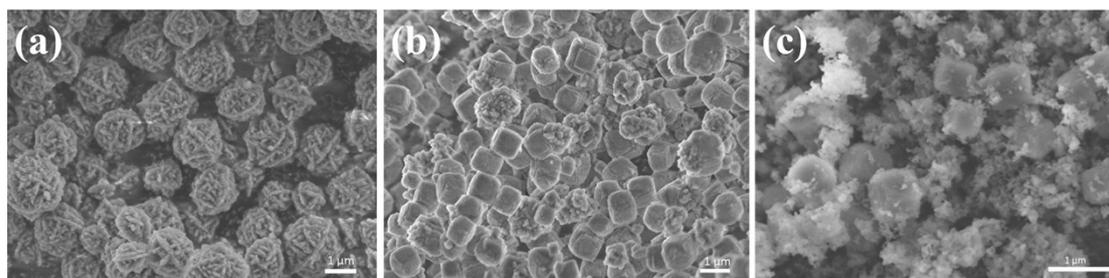


Fig. S4 SEM images of the products crystallized from the initial mixtures with the molar composition of 8.5 K₂O: 1.4 Na₂O: 1.0 Al₂O₃: X SiO₂: 1248 H₂O at 100 °C for 5 d, where X = 18.7 (a), 20.6 (b), and 24.3 (c).

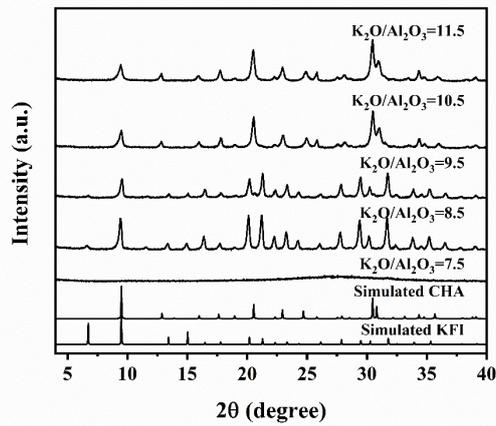


Fig. S5 Simulated XRD patterns of KFI and CHA and the experimental ones of the products crystallized from the initial mixtures with the molar composition of $Y \text{ K}_2\text{O}:1.4 \text{ Na}_2\text{O}:1.0 \text{ Al}_2\text{O}_3:23.4 \text{ SiO}_2:1248 \text{ H}_2\text{O}$ at 100°C for 5 d, where $Y = 7.5, 8.5, 9.5, 10.5,$ and 11.5 .

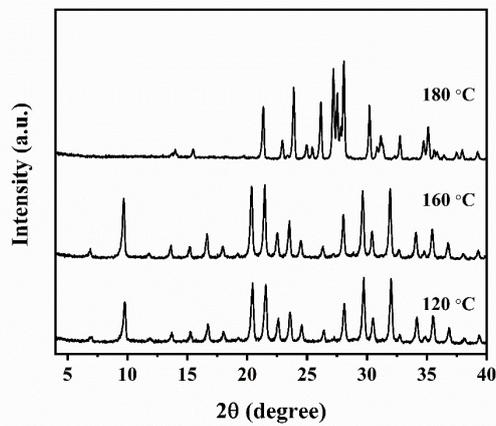


Fig. S6 XRD patterns of the products crystallized from the initial mixtures with the optimal molar composition of $8.5 \text{ K}_2\text{O}:1.4 \text{ Na}_2\text{O}:1.0 \text{ Al}_2\text{O}_3:23.4 \text{ SiO}_2:1248 \text{ H}_2\text{O}$ at 120, 160, and 180°C for 5 d.

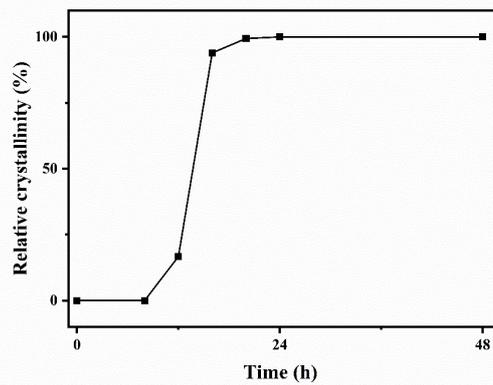


Fig. S7 Crystallization curve of ZK-5 at 160°C .

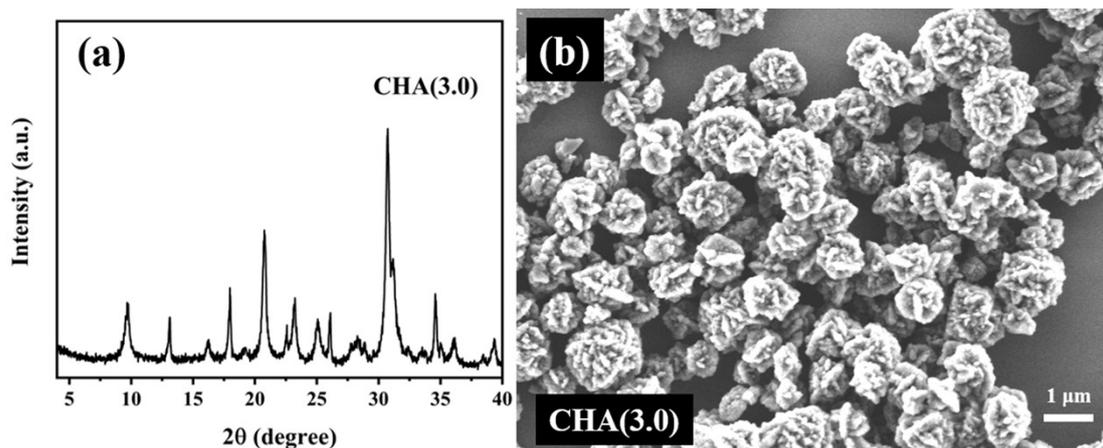


Fig. S8 Experimental XRD pattern (a) and SEM images of CHA(3.0) (b).

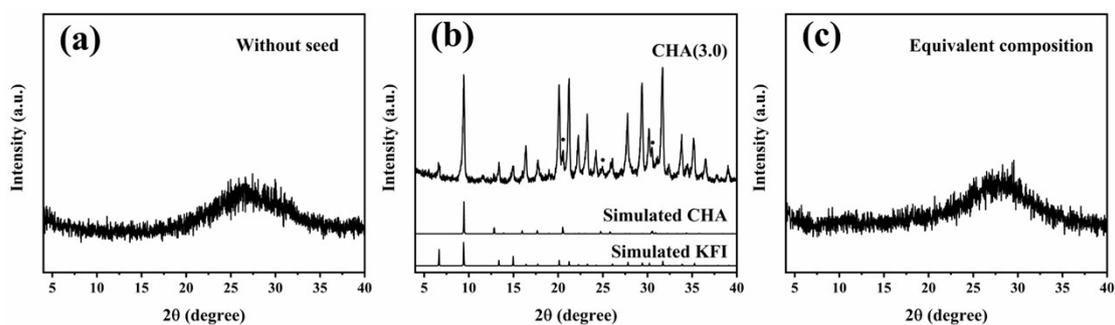


Fig. S9 XRD patterns of the products crystallized from the initial mixtures without seed (a), with CHA(3.0) seed (b), and with the equivalent chemicals of as-synthesized SAPO-34 (c). “•” represents the impurity phase of CHA.

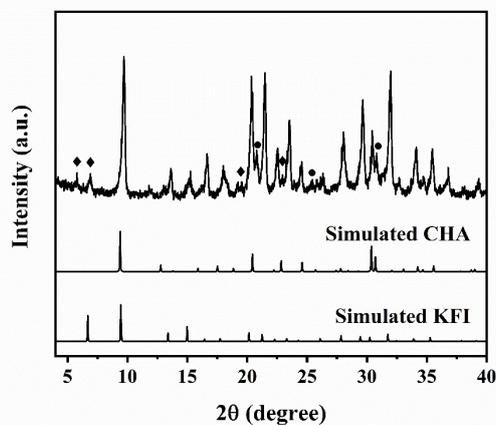


Fig. S10 Simulated XRD patterns of KFI and CHA and the experimental one of the product crystallized with the CHA(3.0) seed at 100 °C for 10 d. “•” represents the impurity phase of CHA. “♦” represents unknown impurity phases.

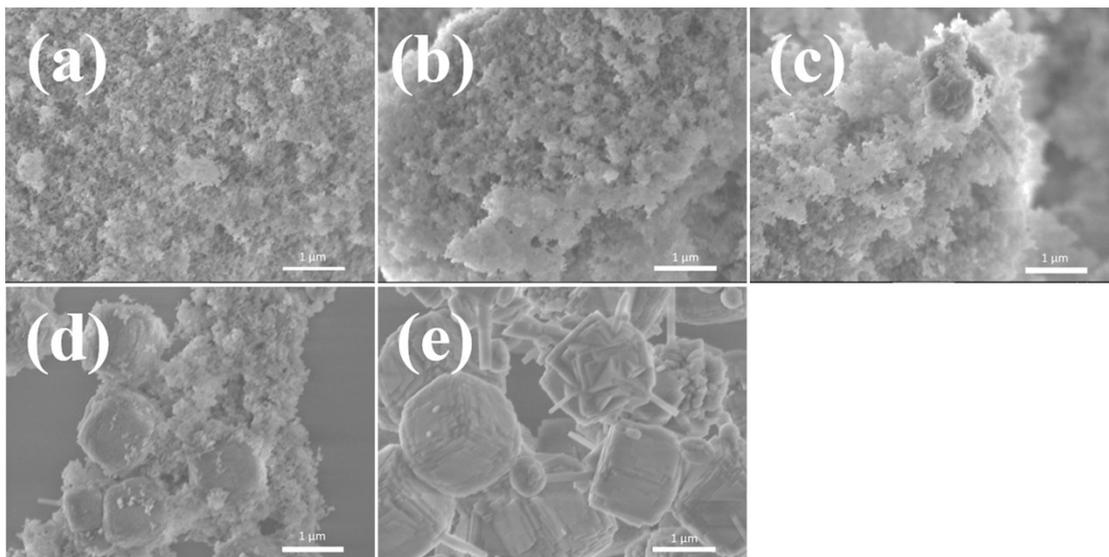


Fig. S11 SEM images of the products crystallized from the initial mixtures with the CHA(3.0) seed for 1 d (a), 2 d (b), 3 d (c), 4 d (d), and 5 d (e).

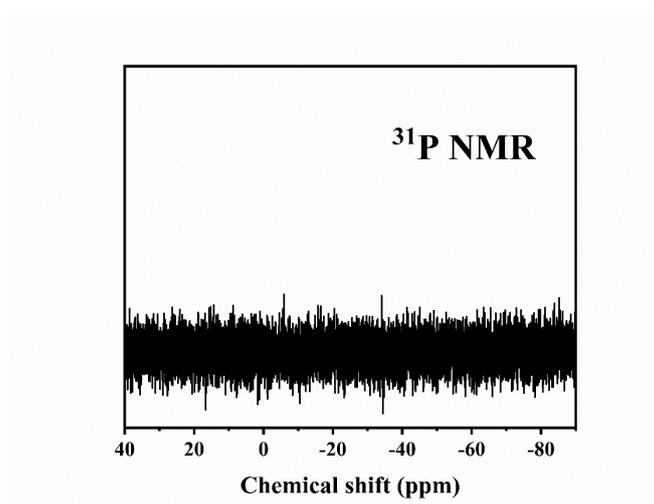


Fig. S12 Liquid ^{31}P NMR spectrum of as-synthesized ZK-5.

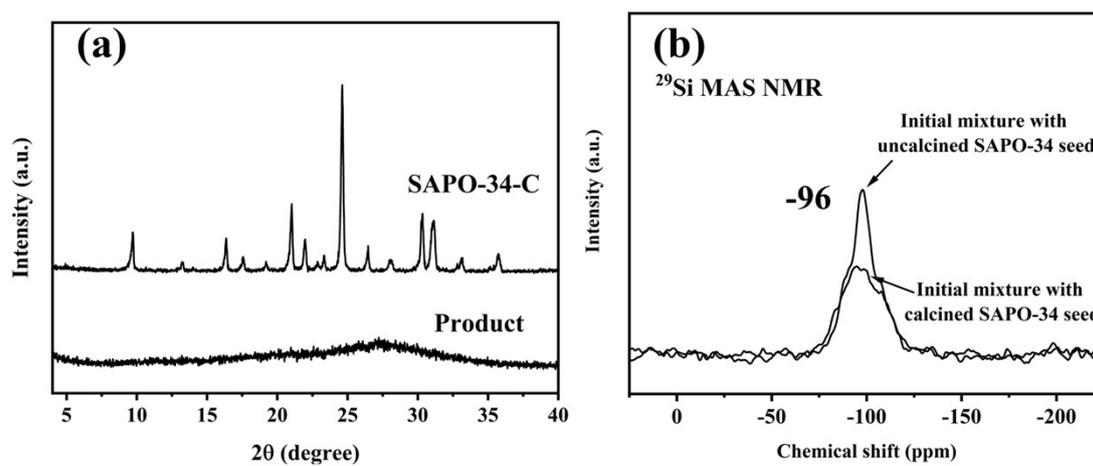


Fig. S13 Experimental XRD patterns of SAPO-34-C seed and the product crystallized from the initial mixture with SAPO-34-C seed at 100 °C for 5 d (a). The ^{29}Si MAS NMR spectra of the initial mixtures with calcined SAPO-34 seed and uncalcined SAPO-34 seed, respectively (b).

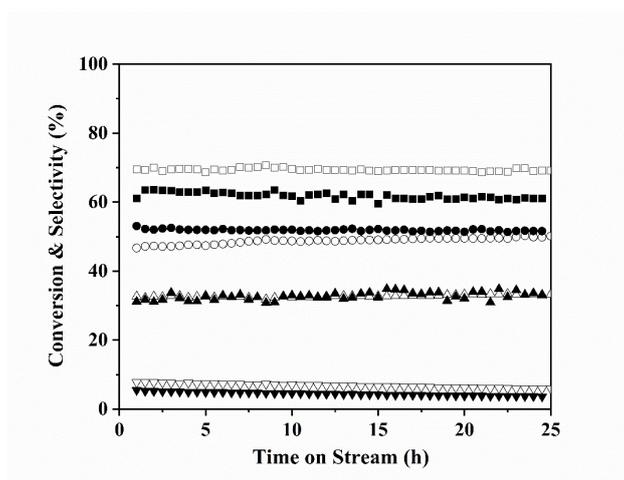


Fig. S14 Conversion of methanol (■) and selectivity for MMA (▲), DMA (●), TMA (▼) on H-ZK-5 catalyst, and conversion of methanol (□) and selectivity for MMA (△), DMA (○), TMA (▽) on H-ZK-5 (K, Cs) catalyst at 350 °C ($\text{NH}_3/\text{CH}_3\text{OH}$ molar ratio = 2/1 and methanol WHSV = 0.813 h^{-1}).

Table S1 Element analysis of as-synthesized ZK-5.

Element	N	C	H
Weight (%)	0.00	0.09	1.60

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