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Supplementary Information

Al pairing in 8-membered rings drives superior methanol amination on CHA zeolites

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1. Experimental section

1.1 Materials and chemicals

Fumed silica (Xuzhou Tiancheng Chlor_alkali Co., Ltd), tetraethyl orthosilicate (Sinopharm Chemical Reagent Co., Ltd), aluminum isopropoxide (Tianjin Fuchen), pseudoboehmite (Sasol, 72.7 wt.%), phosphorate acid (Tianjin Jindongtianzheng Precision Chemical Reagent Factory, 85%), sodium hydroxide (Tianjin Tiantai Chemical Co., Ltd, 98%), potassium hydroxide (Tianjin Xinbote Chemical Co., Ltd, 85%), cesium hydroxide monohydrate (Aladdin, 95%), ammonium fluoride (Macklin, 98%), *N,N,N*-Trimethyladamantan-1-aminium hydroxide (TMAdaOH, Kente Catalysts

Inc., 25%), morpholine (Tianjin Fuchen Chemical Reagent Factory), ammonium acetate (Xilong Scientific, 98%), cobalt nitrate hexahydrate (Macklin, 99%), deionized water.

1.2 Synthesis of SAPO-34 and SSZ-13 seeds

SAPO-34 seeds were synthesized following the procedure described in *Verified Synthesis of Zeolitic Materials, 3rd revised edition* published by the Synthesis Commission of the International Zeolite Association (IZA).[1] In a 100 mL glass beaker, 45.63 g of deionized water, 10.27 g of phosphoric acid, and 5.89 g of pseudoboehmite were combined and stirred at room temperature for 2 h. Subsequently, 2.73 g of fumed silica and 7.73 g of morpholine were added, followed by stirring for another 2 h. The resulting mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept at 38 °C for 24 h. Hydrothermal treatment was then carried out at 200 °C for 24 h. The solid product was recovered by filtration, washed with 500 mL of deionized water, and dried at 80 °C overnight.

Commercial SSZ-13 (Si/Al = 7.8) was obtained from China Catalyst Holding Co., Ltd. Both SAPO-34 and SSZ-13 were calcined in air at 600 °C for 10 h to remove the organic structure-directing agent (OSDA). The calcined products are denoted as c-SAPO-34 and c-SSZ-13, respectively.

1.3 Synthesis of pure silica CHA seeds

Pure silica **CHA** (PS-CHA) seeds were synthesized based on a reported procedure with slight modifications.[2] In a 50 mL plastic beaker, 4.50 g of tetraethyl orthosilicate, 7.99 g of *N,N,N*-trimethyl-1-adamantyl ammonium hydroxide solution, and 5.40 g of deionized water were mixed and stirred at room temperature until the water completely evaporated. The beaker was sealed and placed in a lyophilizer for freeze-drying over two days. The dried solid was ground, mixed with 0.37 g of ammonium fluoride, and homogenized by further grinding. The mixture was then transferred to a 15 mL Teflon-lined stainless-steel autoclave and crystallized at 150 °C for 7 days. The product was washed with deionized water, centrifuged, and dried. Finally, PS-CHA was calcined in air at 600 °C for 10 h, yielding c-PS-CHA.

1.4 Synthesis of CHA zeolites

CHA zeolites were synthesized using gels with the molar composition: 20 SiO_2: 1 Al_2O_3: 6 Na_2O: (1 Na_2O or 1 K_2O or 1 Cs_2O): 2000 H_2O: 20% seeds (relative to SiO_2).

The synthesis proceeded as follows: deionized water, alkali, and aluminum isopropoxide were mixed according to the target gel ratio and stirred for 4 h until a clear solution formed. Fumed silica was then added and stirred for another 2 h. Seed crystals (SAPO-34, SSZ-13, or PS-CHA; 20 wt.% of SiO_2) were introduced and stirred for 1 h. The mixture was transferred into a 25 mL Teflon-lined stainless-steel autoclave and crystallized at 160 °C for 24 h under static condition.

The solids were recovered by filtration, washed with deionized water, and dried at 80 °C overnight. The use of different seed types yielded samples denoted as CHA-S34-3.4, CHA-S13-4.1, and CHA-PS-4.3 in the Na–Cs system. To vary the Si/Al ratio, the aluminum isopropoxide content was adjusted, producing CHA-S34-3.8 and CHA-PS-3.8. The numbers in the sample names represent the Si/Al ratio.

Owning to the presence of OSDAs, the samples CHA-PS-4.3 and CHA-PS-3.8 were subjected to calcination at 600 °C for 6 h in air to eliminate the organic species. All five synthesized **CHA** zeolites were ion-exchanged three times with 1 mol/L CH_3COONH_4 solution (solid-to-liquid ratio 1: 50) at 80 °C for 4 h per cycle. After each exchange, the solids were filtered, washed, and dried at 80 °C, followed by calcination at 550 °C in air for 4 h. The final products were designated as H-CHA-S34-3.4, H-CHA-S13-4.1, H-CHA-PS-4.3, H-CHA-S34-3.8, and H-CHA-PS-3.8.

1.5 Co-exchange

The five **CHA** zeolites were first converted to the Na^+ form by ion exchange with 1 mol/L NaCl solution at 80 °C for 2 h, repeated twice. The resulting Na-CHA samples were then exchanged twice with 0.5 mol/L $Co(NO_3)_2$ solution at 80 °C for 6 h. The exchanged products were filtered, washed with deionized water, and dried at 80 °C overnight. The Co content of the dehydrated samples was determined by ICP-OES.

1.6 Characterization

Powder X-ray diffraction (PXRD) was performed on a Rigaku D/Max 2550 diffractometer using Cu Kα radiation ($\lambda = 1.5418$ Å) over the range of $2\theta = 4$–$40°$ at a scan rate of 12 °/min. The relative crystallinity corresponds to:

$$Relative\ Crystallinity = \frac{\sum A(characteristic\ peaks)}{\sum A(characteristic\ peaks\ of\ reference\ sample)} \times 100\%$$

where A is the peak area of a characteristic peak.

Characteristic peaks of **CHA** zeolite at $2\theta = 9.8°$, 13.2°, 20.9°, 23.4°, 25.2°, 28.4°, 31.0°, 31.4°, 31.9°, and 33.7° were taken into account for the calculation of relative crystallinity of **CHA** zeolite. Morphology and microstructure were examined by field emission scanning electron microscopy (SEM, JSM-7800F). Thermogravimetric (TG) analysis was carried out on a TA TGA Q500 with a heating rate of 10 °C/min in air. Chemical compositions were determined using a Thermo Scientific iCAP 7600 DUO ICP-OES. N_2 adsorption–desorption isotherms were measured at 77 K on a BSD-660M A6MB6M analyzer. Surface area, external surface area, and micropore volume were derived using the Brunauer-Emmett-Teller (BET) equation and t-plot method. Total pore volume was calculated from the amount of N_2 adsorbed at $P/P_0 = 0.99$.

Solid-state ^{27}Al, ^{29}Si, and ^{31}P magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were collected on a Bruker Avance NEO spectrometer at 14.09 T. Spectra were deconvolved with Gaussian functions. The Si/Al ratio was calculated from the NMR data using the following formula:

$$\left(\frac{Si}{Al}\right)_{NMR} = \frac{\sum_{n=0}^{n=4} I_{Si(nAl)}}{\sum_{n=0}^{n=4} 0.25nI_{Si(nAl)}}$$

Temperature-programmed desorption of ammonia (NH_3-TPD) experiments were carried out on a Micromeritics AutoChem II 2920. Fourier Transform infrared spectroscopy (FT-IR) spectra were recorded on a Bruker VERTEXV 80V spectrometer using KBr pellets, with baseline correction applied after measurement. Diffuse reflectance ultraviolet-visible (UV–vis) spectra were collected on a PerkinElmer Lambda 950 in the range of 200–800 nm and deconvolved with Gaussian functions. Prior to measurement, all samples were dehydrated at 400 °C for 1 h in air. Elemental analysis was carried on using an Elementar Vario MACRO cube CHNS analyzer.

1.7 Catalysis

Methylamine synthesis was evaluated in a fixed-bed quartz tubular reactor under atmospheric pressure. Zeolite catalysts were pelletized, crushed, and sieved to 40–60 mesh, then activated at 350 °C for 1 h under a nitrogen flow of 50 mL/min.

After activation, the catalysts were exposed to a feed mixture of ammonia and methanol carried by nitrogen. Reactions were conducted at 350–400 °C with a methanol weight hourly space velocity (WHSV) of 0.813–4.3 h^{-1}. Products were analyzed online using an Agilent 7890A gas chromatograph equipped with a flame ionization detector and a CP-Volamine capillary column. Data collection began immediately upon introduction of the feed and continued for 0.5 h. Methanol conversion and methylamine selectivity were calculated accordingly:

$$MeOH\ conversion = \frac{moles\ of\ MeOH\ (in)\ -\ moles\ of\ MeOH\ (out)}{moles\ of\ MeOH\ (in)} \times 100\%$$

$$selectivity\ of\ MMA = \frac{moles\ of\ MMA}{moles\ of\ products\ detected} \times 100\%$$

$$selectivity\ of\ DMA = \frac{moles\ of\ DMA}{moles\ of\ products\ detected} \times 100\%$$

$$selectivity\ of\ TMA = \frac{moles\ of\ TMA}{moles\ of\ products\ detected} \times 100\%$$

$$selectivity\ of\ DME = \frac{moles\ of\ DME}{moles\ of\ products\ detected} \times 100\%$$

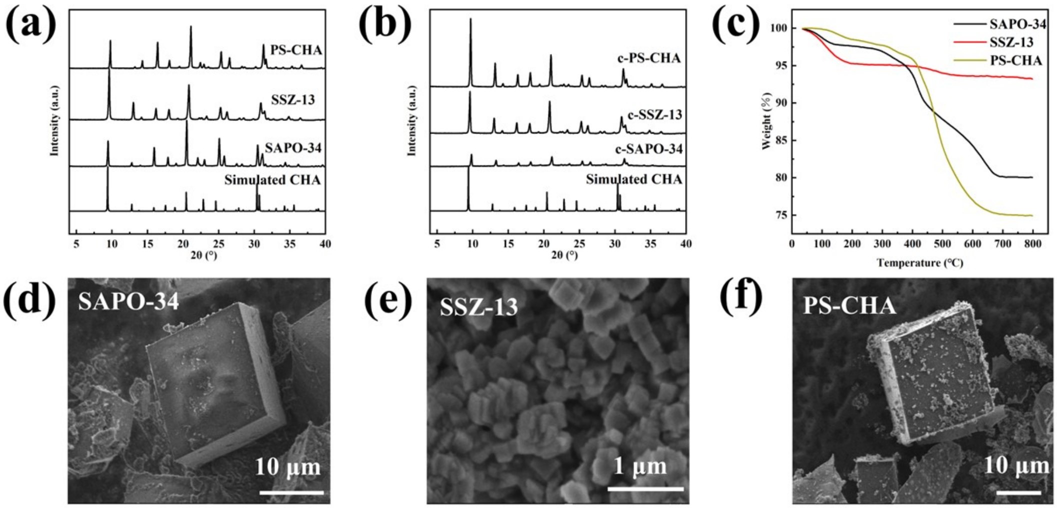

Fig. S1 XRD patterns of (a) three kinds of seed crystals and (b) calcined seed crystals, (c) TG curves of three kinds of seeds, SEM images of (d) SAPO-34, (e) SSZ-13, and (f) PS-CHA.

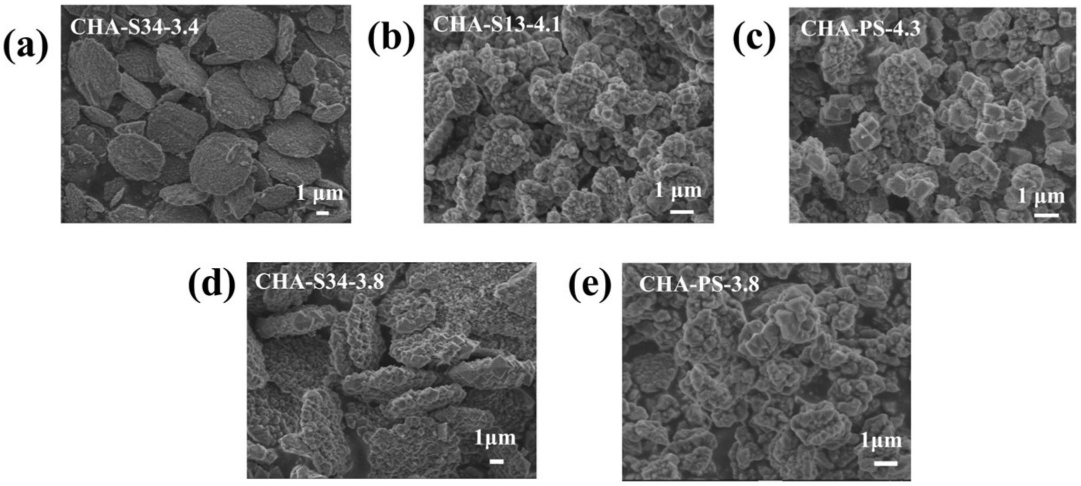

Fig. S2 SEM images of (a) CHA-S34-3.4, (b) CHA-S13-4.1, (c) CHA-PS-4.3, (d) CHA-S34-3.8, and (e) CHA-PS-3.8.

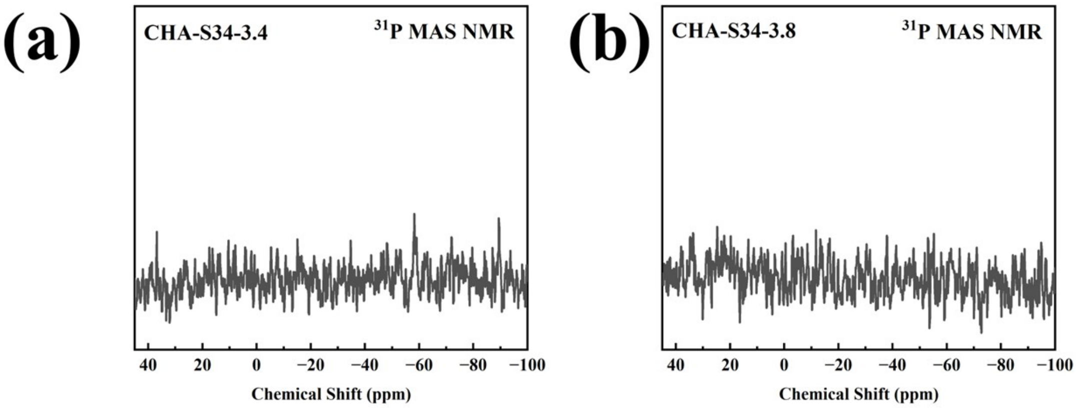

Fig. S3 ^{31}P MAS NMR spectrum of (a) CHA-S34-3.4 and (b) CHA-S34-3.8.

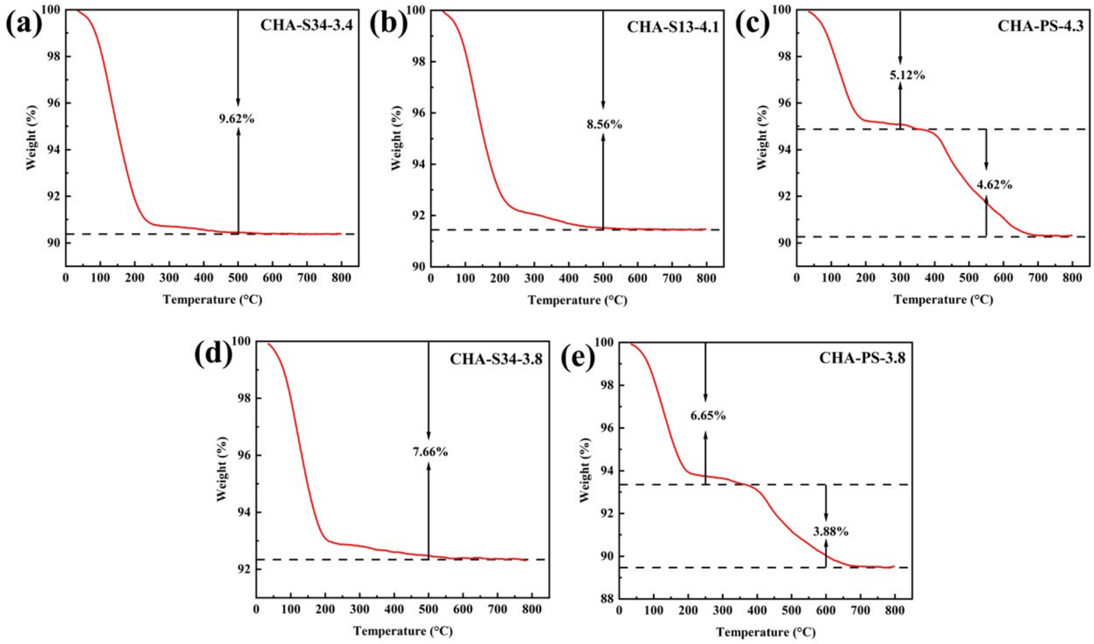

Fig. S4 TG curves of (a) CHA-S34-3.4, (b) CHA-S13-4.1, (c) CHA-PS-4.3, (d) CHA-S34-3.8, and (e) CHA-PS-3.8.

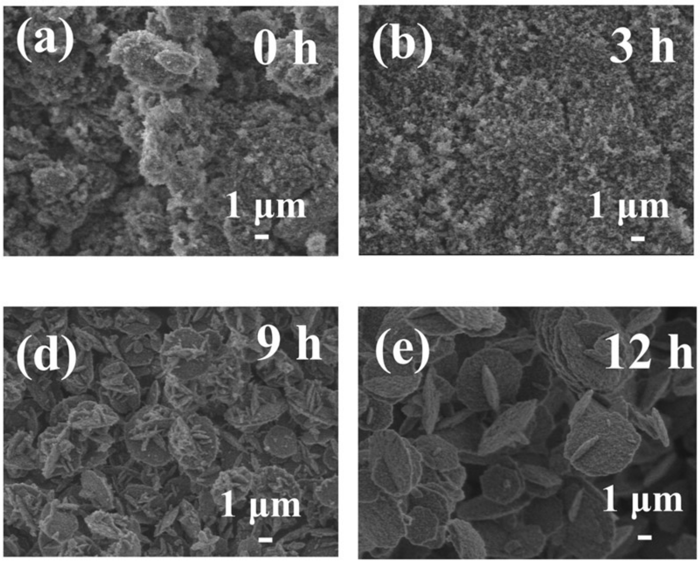

Fig. S5 SEM images of the CHA-S34-3.4 solid products extracted at periodic times: (a) 0 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h, and (f) 18 h.

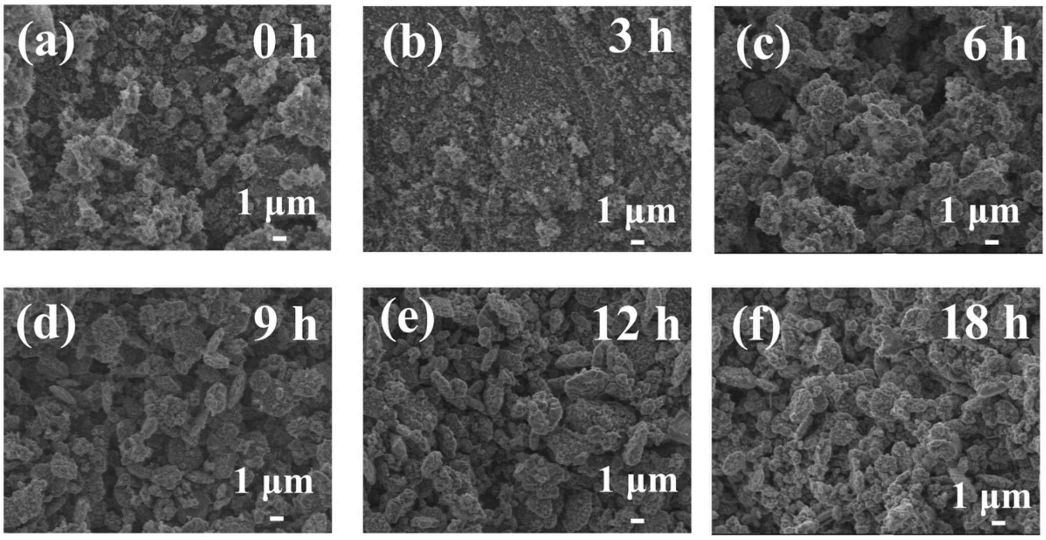

Fig. S6 SEM images of the CHA-S13-4.1 solid products extracted at periodic times: (a) 0 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h, and (f) 18 h.

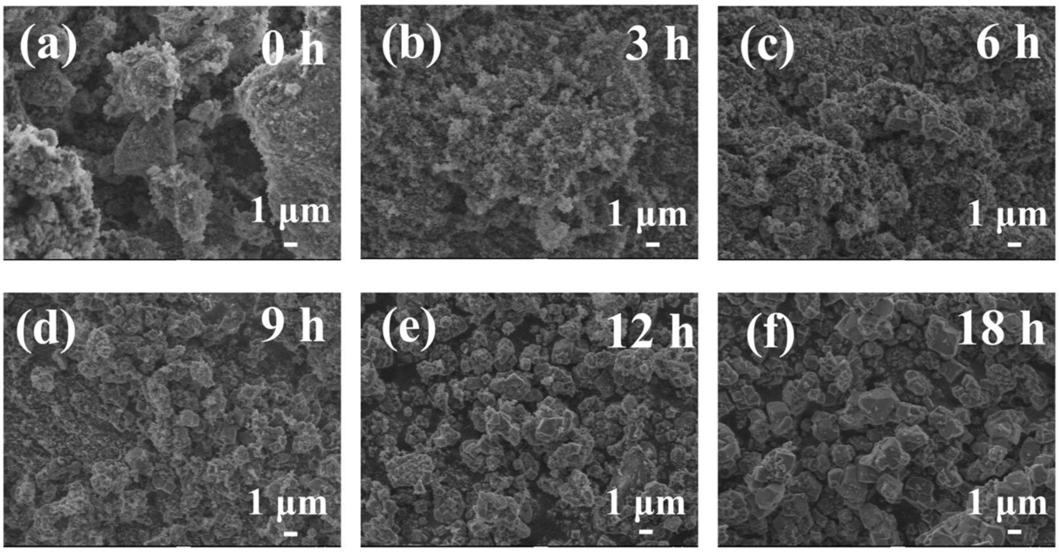

Fig. S7 SEM images of the CHA-PS-4.3 solid products extracted at periodic times: (a) 0 h, (b) 3 h, (c) 6 h, (d) 9 h, (e) 12 h, and (f) 18 h.

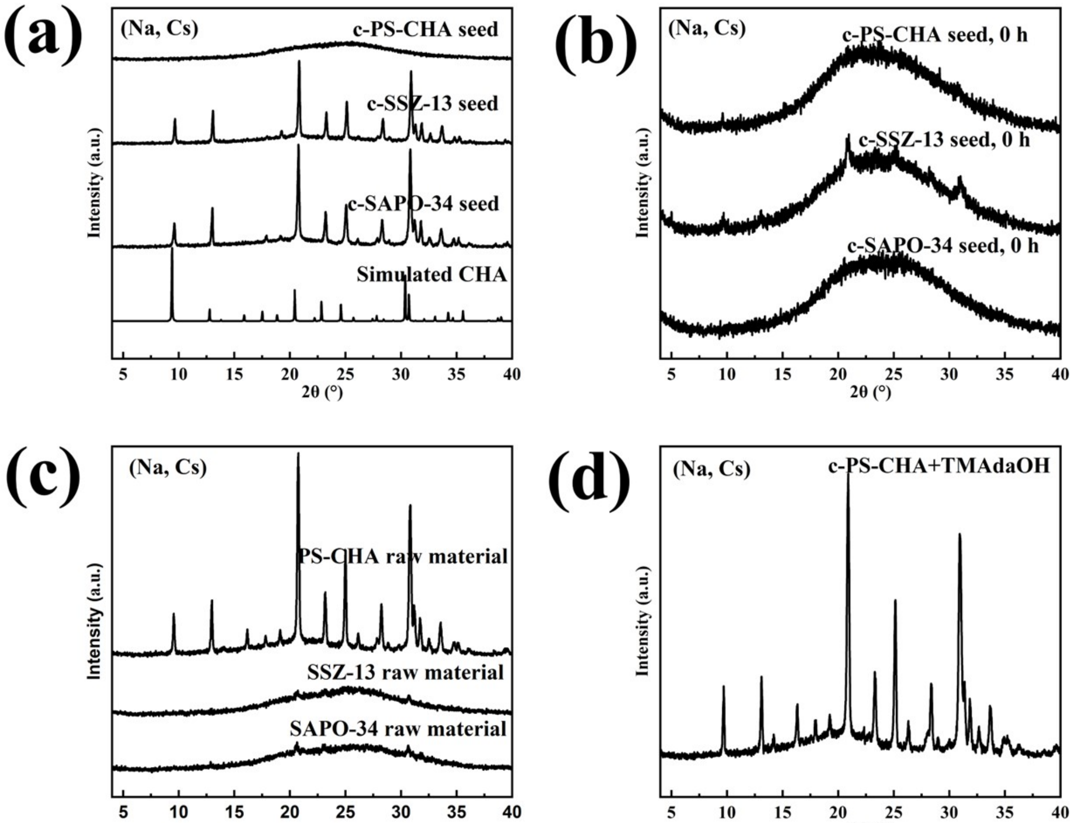

Fig. S8 XRD patterns of the products: (a) after calcination of the three seeds; (b) at 0 h of crystallization using the three seeds; (c) when the seeds were replaced with raw materials; (d) using c-PS-CHA and TMAdaOH instead of PS-CHA.

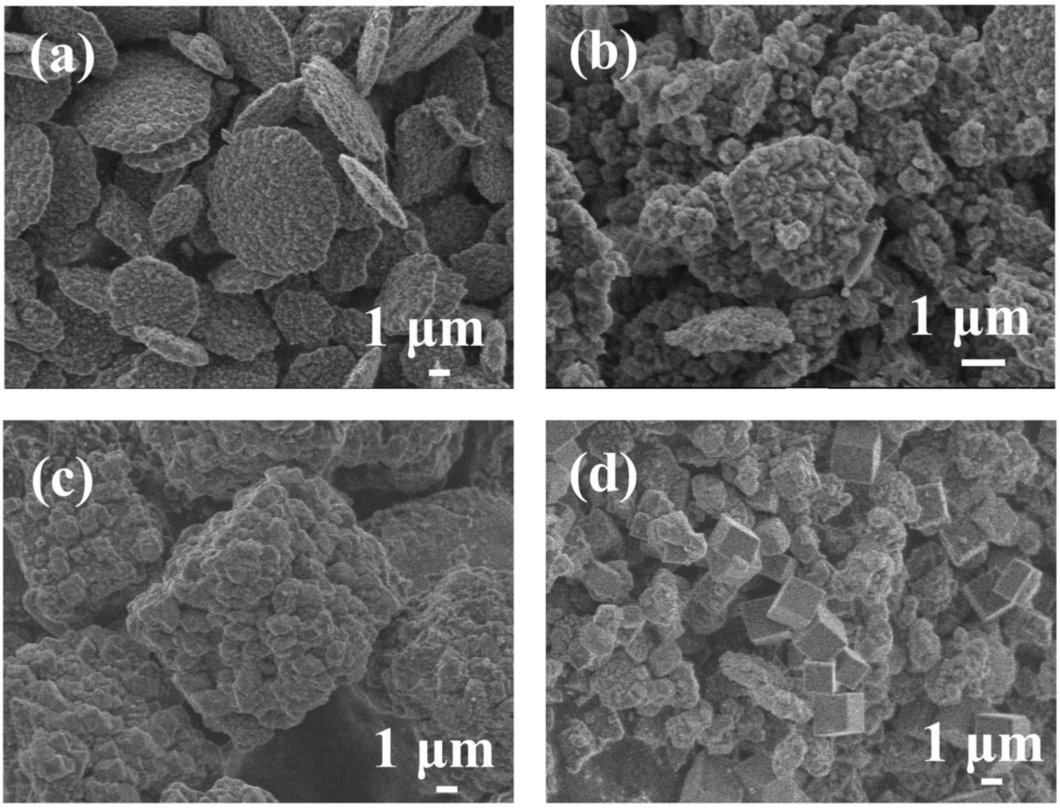

Fig. S9 SEM images of the products obtained under different seeding conditions: (a) calcined SAPO-34, (b) calcined SSZ-13, (c) fumed silica and TMAdaOH replacing PS-CHA, and (d) c-PS-CHA and TMAdaOH replacing PS-CHA.

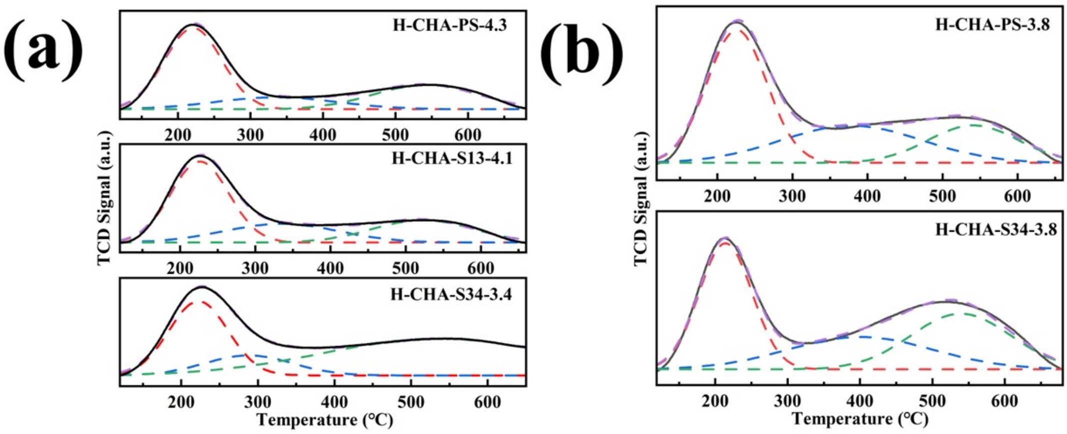

Fig. S10 (a) NH_3-TPD profiles of H-CHA-S34-3.4, H-CHA-S13-4.1, and H-CHA-PS-4.3, (b) NH_3-TPD profiles of H-CHA-S34-3.8, and H-CHA-PS-3.8.

Table S1 Proportion of Si species in five **CHA** zeolites.

	Proportion of Si species (%)		
Sample	Si(4Si,0Al)	Si(3Si,1Al)	Si(2Si,2Al)
CHA-S34-3.4	17.2	52.6	30.2
CHA-S13-4.1	25.8	54.3	19.9
CHA-PS-4.3	28.2	51.4	20.4
CHA-S34-3.8	22.8	54.8	22.4
CHA-PS-3.8	21.2	52.0	26.8

Table S2 The Si/Al ratios of the products with different kinds and different amounts of seeds.

	Si/Al[a]			
Sample	5%	10%	15%	20%
CHA-S34	3.6	3.5	3.4	3.4
CHA-S13	3.6	3.7	3.9	4.1
CHA-PS	3.7	4.0	4.2	4.3

[a] Determined by the ICP analyses.

Table S3 The acidic properties of Acidic properties of five **CHA** zeolites.

	Center of Acid Sites (°C)			Amount of Acid Sites (%)[a]		
Sample	Weak	Medium	Strong	Weak	Medium and Strong	total
H-CHA-S34-3.4	222	287	535	34.4	65.6	100
H-CHA-S13-4.1	226	335	523	41.5	38.7	80.2
H-CHA-PS-4.3	221	336	542	42.6	36.5	79.1
H-CHA-S34-3.8	214	400	539	38.1	58.2	96.3
H-CHA-PS-3.8	226	379	541	39.6	42.9	82.5

[a] The value was calculated by comparing the area of each acid sites with the total area of H-CHA-S34-3.4.

References

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2. E. A. Eilertsen, B. Arstad, S. Svelle and K. P. Lillerud, Single parameter synthesis of high silica **CHA** zeolites from fluoride media, *Microporous Mesoporous Mater.*, 2012, **153**, 94–99.