

Electronic Supplementary Information

Transcription-induced formation of paired Al sites in high-silica CHA-type zeolite framework using Al-rich amorphous aluminosilicate

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Experimental

1. Reagents

All the reagents and gases listed here were used as-received without further purification. Tetraethyl orthosilicate (TEOS; Kojundo Chemical Laboratory), propylene glycol (PG; FUJIFILM Wako Pure Chemical), an aqueous HNO₃ solution (1 M, FUJIFILM Wako Pure Chemical), Al(NO₃)₃•9H₂O (FUJIFILM Wako Pure Chemical), Al(OH)₃ (Sigma-Aldrich), citric acid (CA; anhydrous, Nacalai Tesque), ethylene glycol (EG; FUJIFILM Wako Pure Chemical), silica gel (Carplex BS-304F, DSL, Japan), fumed silica (Cab-O-Sil M5, Cabot), an aqueous NaOH solution (8 M, FUJIFILM Wako Pure Chemical), an aqueous *N,N,N*-trimethyl-1-adamantylammonium hydroxide solution (TMAdaOH, 25 wt%, SACHEM) and NH₄NO₃ (FUJIFILM Wako Pure Chemical) were the reagents for synthesizing the Al-rich amorphous aluminosilicate and **CHA**-type zeolites. All gases were obtained from Taiyo Nippon Sanso. For the quantitative analysis for Si and Al in each sample as well as Sr²⁺ in ion-exchange experiments, an aqueous HF solution (50 wt%, FUJIFILM Wako Pure Chemical) was used. In the ion-exchange experiment for Sr²⁺, SrCl₂•6H₂O (FUJIFILM Wako Pure Chemical) was used as a solute.

2. Synthesis of Al-rich amorphous aluminosilicate via polymerized complex method

The Al-rich amorphous aluminosilicate samples that were employed as precursors to zeolites in the hydrothermal process were prepared via the polymerized complex method.^{S1,S2} To prevent the undesired evaporation and hydrolysis of TEOS, this compound was initially converted to propylene glycol-modified silane (PGMS),^{S3} which ensured ease of handling. Thus, a mixture of 0.1 mol of TEOS and 0.4 mol of PG was stirred in an oil bath at 353 K for 24 h. Then, 1 mL of an aqueous HNO₃ solution (1 M) was added into the mixture, which was stirred further at 353 K for 1 h. The colorless, transparent solution was transferred into a 200 mL volumetric flask and diluted with deionized water to obtain a 0.5 M aqueous PGMS solution.

The thus-prepared aqueous PGMS solution, EG, and CA were charged into a 500 mL beaker and mixed at 333 K until a transparent solution was obtained. Then, Al(NO₃)₃•9H₂O was added, and the entire mixture was stirred at the same temperature until all solids were completely dissolved. The molar ratio of PGMS, Al(NO₃)₃•9H₂O, CA, and EG was 2/1/16/48. The mixture was heated at 373 K for *ca.* 1 h to remove water, and subsequently at 423 K to induce condensation between EG and CA, yielding a resin containing Si and Al atoms. Afterwards, the temperature was increased gradually from 423 to 723 K to carbonize the resin. The resulting black powder, a composite of aluminosilicate and carbonized resin, was calcined in an electric furnace in air at 1073 K for 12 h to remove the carbonized resin. The actual Si/Al ratio of the thus-prepared amorphous aluminosilicate specimen was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) to be 2.5 after complete dissolution in an aqueous HF solution (the detailed procedure for ICP-AES is described below).^{S2}

3. Hydrothermal synthesis of CHA-type zeolites from Al-rich amorphous aluminosilicate

CHA-type zeolites were synthesized hydrothermally using an Al-rich amorphous aluminosilicate under seed-assisted conditions. Initially, silica gel (Carplex BS-304F), as an additional Si source to control the Si/Al ratio in the synthesis gels, an aqueous NaOH solution, an aqueous TMAdaOH solution, as an organic structure-directing agent, and deionized water were charged into a Teflon-lined high-pressure reactor (Model 4749 General Purpose Acid Digestion Vessels, Parr Instrument Company, inner volume 23 mL) with molar ratios of Si/Al/NaOH/TMAdaOH/H₂O = 1/0.10/0.44/0.20/30. The mixture was stirred at room temperature for t_1 hours. After the addition of the amorphous aluminosilicate into the mixture as a source of both Si and Al, the resulting synthesis gel was further aged at room temperature for t_2 hours. Note that in all cases, the total aging time (*i.e.*, $t_1 + t_2$) was kept constant at 48 h. Just before the hydrothermal treatment, a seed crystal (whose loading corresponded to 5 wt% against the total weight of SiO₂) was added into the mixture. The hydrothermal process was conducted using an electric furnace (HIRO Company, pre-heated at 443 K to minimize the temperature ramp time) at a tumbling speed of 40 rpm at 443 K for 5 days. After cooling to room temperature, the solid product was separated and washed with deionized water by centrifugation at 15,000 rpm (this washing process was performed three times), dried at 333 K overnight, and calcined in air at 873 K for 12 h to remove TMAdaOH and obtain CHA-type zeolites.

4. Hydrothermal synthesis of CHA-type zeolites (SSZ-13) from SiO₂ and Al(OH)₃

A control CHA-type zeolite specimen, labeled SSZ-13, was synthesized via a previously reported approach using fumed silica (Cab-O-Sil M5) and Al(OH)₃ as starting reagents.^{S4} Into a Teflon-lined high-pressure reactor, deionized water, an aqueous NaOH solution, an aqueous TMAdaOH solution, Al(OH)₃, and fumed silica were charged in a stepwise manner. The mixture was aged at room temperature for 1 h. After the addition of a seed crystal (whose loading corresponded to 5 wt% against the total weight of SiO₂), the hydrothermal process was conducted in an electric furnace (pre-heated at 443 K to minimize the temperature ramp time) at a tumbling speed of 40 rpm at 423 K for 5 days. After cooling to room temperature, the solid product was separated and washed with deionized water through centrifugation (this washing process was performed three times), dried at 333 K overnight, and calcined in air at 873 K for 6 h to obtain SSZ-13.

5. Characterization of synthesized samples

The Si and Al contents were determined by ICP-AES (SPECTRO ARCOS, AMETEK). Prior to analysis, each sample was dissolved completely in 3 mL of an aqueous HF solution (50 wt%) at room temperature, followed by the addition of 47 mL of deionized water and a further 10-fold dilution. The crystal structure was analyzed by powder X-ray diffraction measurement (XRD; Ultima IV, Rigaku,

equipped with a semiconductor detector, Cu K α radiation at 40 kV and 40 mA, scan speed 2.0° min⁻¹). The porous structure and surface area based on the Brunauer-Emmett-Teller (BET) equation were determined by N₂ physisorption measurement in a relative pressure (p/p_0) range of 0.005–0.995 at 77 K using an automated apparatus (BELSORP-mini II, MicrotracBEL). Before physisorption measurements, each sample was heat-treated at 423 K for 4 h below 10 Pa. The nature of the Al and Si atoms was elucidated by solid-state ²⁷Al magic angle spinning nuclear magnetic resonance (²⁷Al MAS NMR) and ²⁹Si MAS NMR with/without the cross polarization (CP) technique using an NMR spectrometer (JNM-ECA600, JEOL, ²⁷Al 156 MHz, ²⁹Si 119 MHz, MAS frequency 15 kHz). The ²⁹Si MAS NMR spectra were deconvoluted by the mixed Gaussian-Lorentzian functions using the OriginPro 2020b version 9.7.5.184 software.

6. Ion exchange of Sr²⁺ over CHA-type zeolites

To prevent the effects of a class of counter cations, each CHA-type zeolite sample was subjected to ion-exchange treatment prior to the Sr²⁺ adsorption experiment. Thus, 100 mg of CHA zeolite was dispersed in 100 mL of an aqueous NH₄NO₃ solution (2 M). The suspension was ultrasonicated for 1 min to achieve a better dispersion of the adsorbent particles, and stirred at 353 K for 3 h. After separation and washing with deionized water by centrifugation, the resulting sample was treated in the same manner once more. After drying at 333 K overnight and calcination at 873 K for 6 h, a CHA-type zeolite sample containing H⁺ as counter cation was obtained.

For the ion exchange of Sr²⁺ over CHA-type zeolites, 100 mg of the thus-prepared CHA zeolite was dispersed in 10 mL of an aqueous SrCl₂ solution (50 mM). After ultrasonication to improve the dispersion of CHA zeolite particles, the suspension was stirred at room temperature for 24 h. After centrifugation, the thus-treated CHA zeolite was washed three times with 45 mL of deionized water using a centrifuge to remove physisorbed species. The resulting sample was treated in the same manner once more. After drying at 333 K overnight, the solid was dissolved in an aqueous HF solution in the same manner as described in Experimental section 4. The resulting solutions were analyzed by ICP-AES to directly quantify the uptake of Sr²⁺ introduced on the surface of each CHA zeolite.

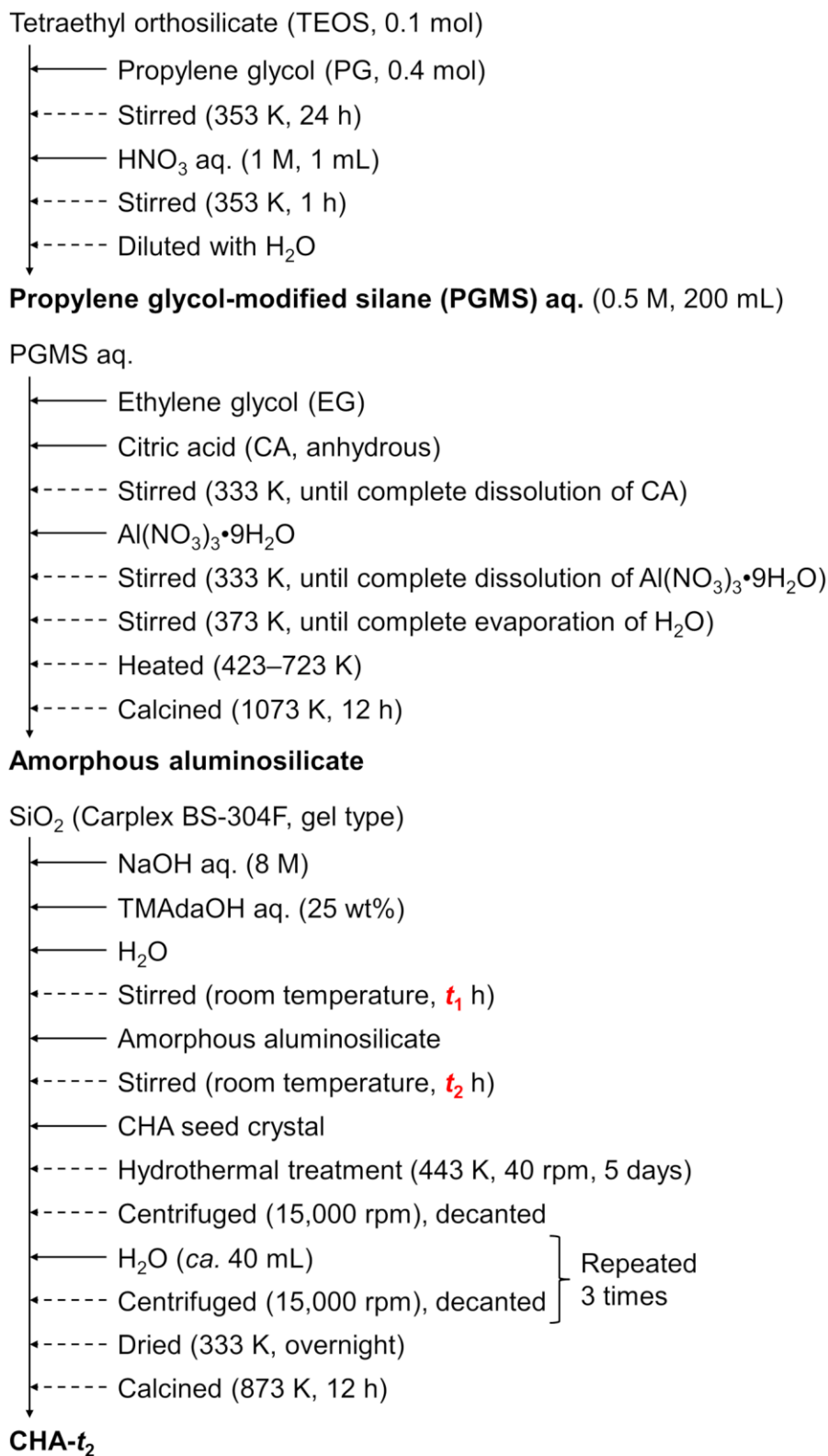


Fig. S1 Procedure for synthesizing CHA-*t*₂ samples.

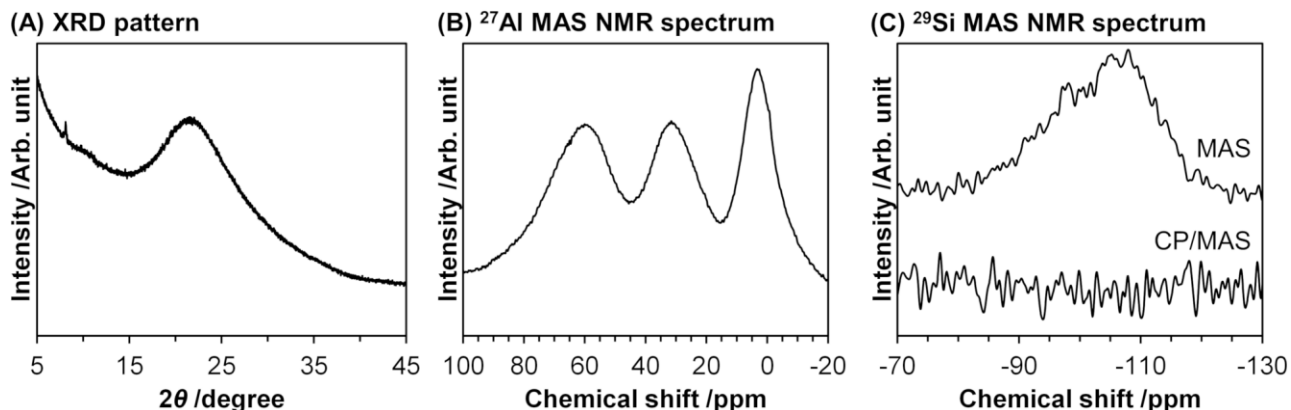


Fig. S2 Textural properties of Al-rich aluminosilicate prepared via the polymerized complex method, determined by (A) powder XRD, (B) ²⁷Al MAS NMR, and (C) ²⁹Si MAS NMR with/without the CP technique. These data were taken from our previous paper (Ref. S2).

The halo at *ca.* 22° observed in the XRD pattern (Fig. S2A) and the absence of any other diffraction peaks indicated the formation of amorphous aluminosilicate. The peaks at 60, 30, and 0 ppm in the ²⁷Al MAS NMR spectrum in Fig. S2B indicated the presence of tetra-, penta-, and hexa-coordinated Al species, respectively.^{S5,S6} In the ²⁹Si MAS NMR spectrum (Fig. S2C), the broad signal is assignable to Q⁴(0Al) at -115 ppm, Q⁴(1Al) at -108 ppm, Q⁴(2Al) at -102 ppm, Q⁴(3Al) at -95.7 ppm, and Q⁴(4Al) at -87.5 ppm.^{S5} The absence of any peaks in the ²⁹Si CP/MAS NMR spectrum indicated that no Si(OT)_{4-y}(OH)_y (T = Si or Al, 1 ≤ y ≤ 3) species had formed.

Table S1 Proportion of Q⁴(nAl) species in amorphous Al-rich aluminosilicate.^a

Q ⁴ (0Al)	Q ⁴ (1Al)	Q ⁴ (2Al)	Q ⁴ (3Al)	Q ⁴ (4Al)
26	25	19	17	13

^a Examined via deconvolution of ²⁹Si MAS NMR spectrum shown in Fig. S2C.

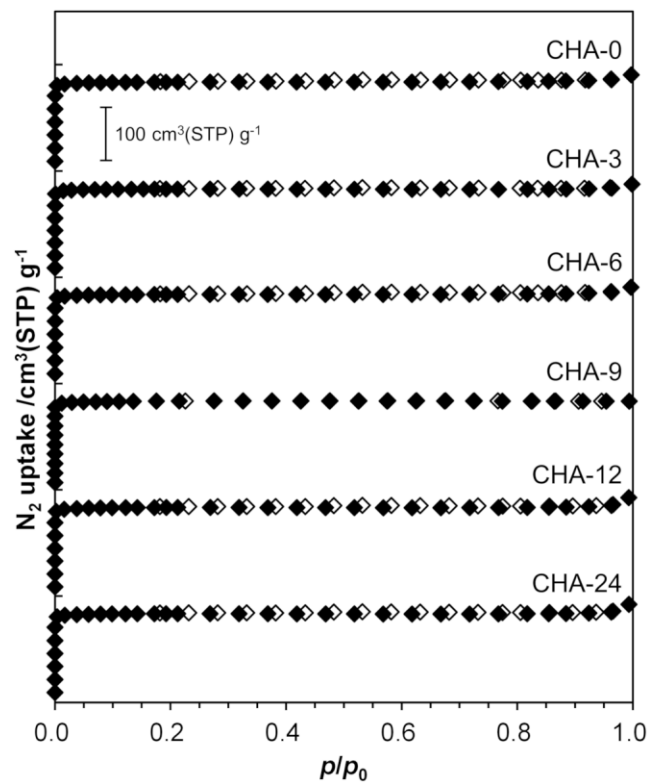


Fig. S3 N₂ physisorption isotherms for CHA-*t*₂, recorded at 77 K. The filled and open dots show the adsorption and desorption branches, respectively.

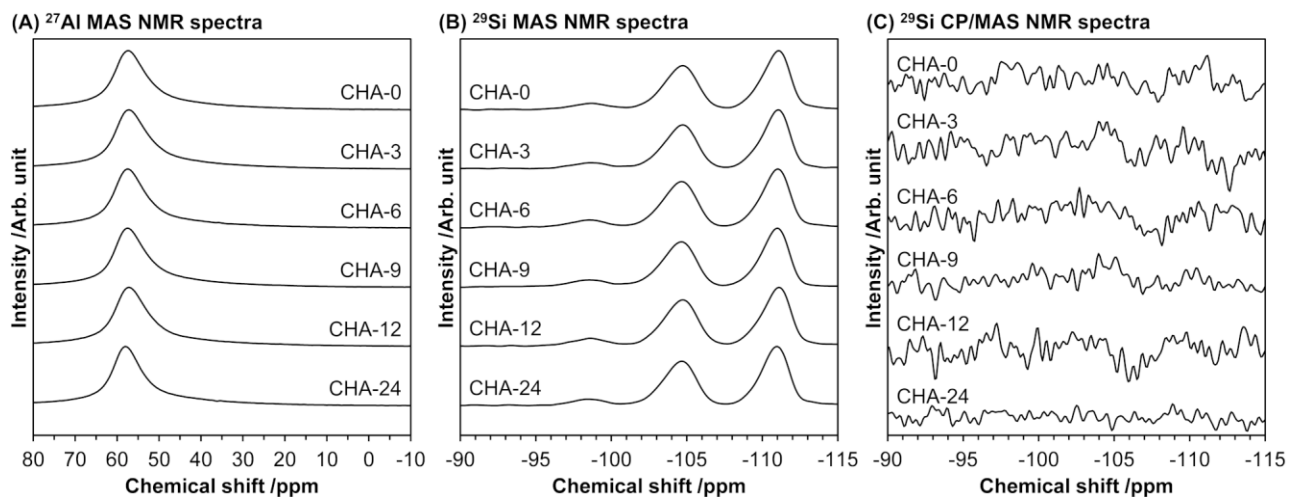


Fig. S4 Coordination structure of Al and Si species involved in CHA-*t*₂, examined by NMR spectroscopy: (A) ²⁷Al MAS NMR spectra; (B) ²⁹Si MAS NMR spectra; and (C) ²⁹Si CP/MAS NMR spectra. The deconvolution results for the ²⁹Si MAS NMR spectra are shown in Fig. S5.

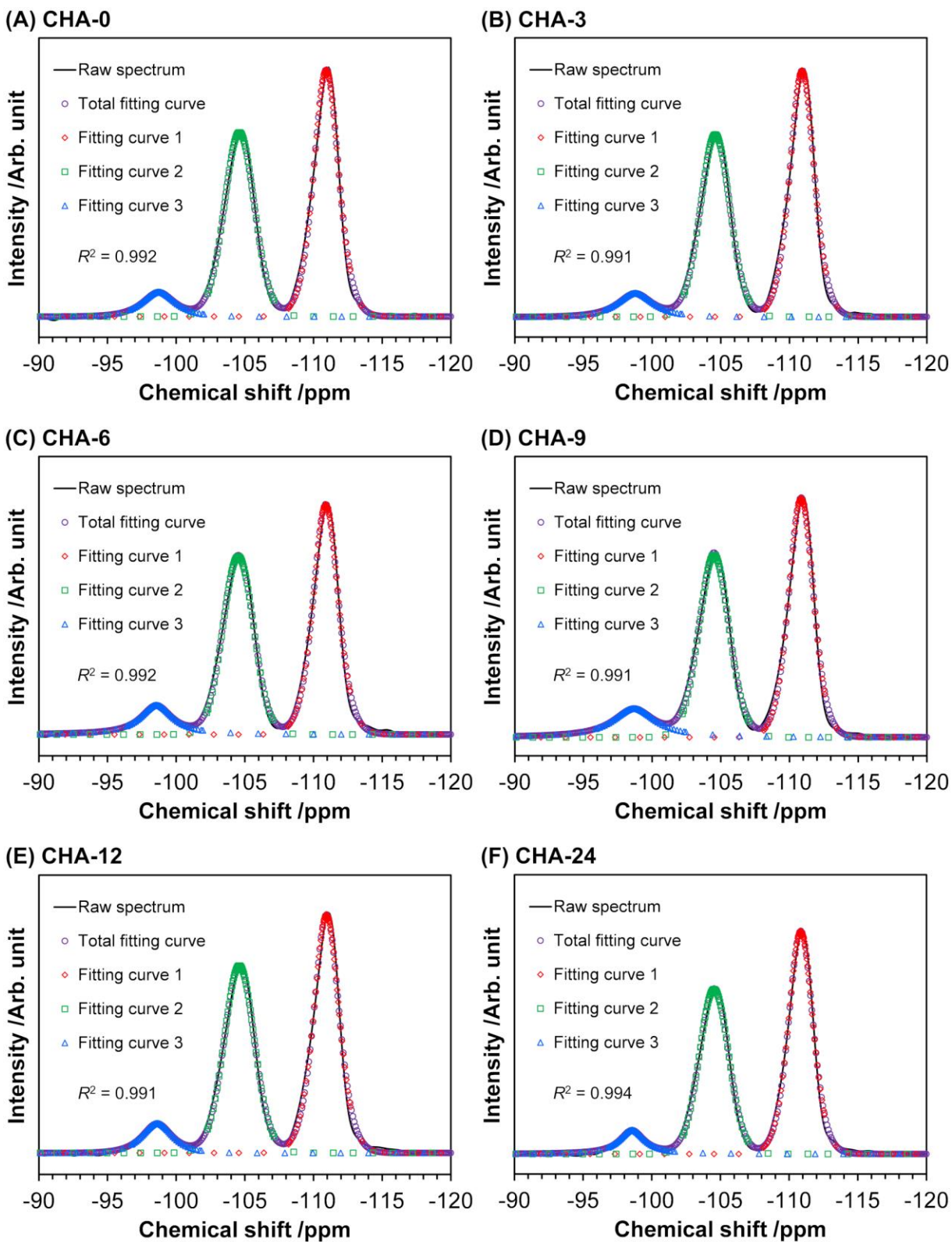


Fig. S5 Deconvolution results for ^{29}Si MAS NMR spectra for CHA- t_2 : (A) CHA-0; (B) CHA-3; (C) CHA-6; (D) CHA-9; (E) CHA-12; and (F) CHA-24.

Table S2 Proportion of Al-containing Q⁴(nAl) species in high-silica **CHA**-type zeolites in reported works.

Sample name in each paper	SDAs	Si/Al ^a	Proportion of Al-containing Q ⁴ (2Al) ^b /%		Reference
			Q ⁴ (1Al)	Q ⁴ (2Al)	
CHA-9	TMAda ⁺ , Na ⁺	5.7	77	23	This work
CHA-4 ^c	TMAda ⁺ , Na ⁺	7.6 ^e	73	27	S7
CHA-F-1.0 ^c	TMAda ⁺ , Na ⁺	13.5 ^f	70	30	S8
CHA-FAU-TEA ^c	TEA ⁺ , Na ⁺ , K ⁺ ^d	6.3 ^f	82	18	S9

^a Molar ratio of Si to Al.

^b Estimated from the areas of each Q⁴(nAl) peak in ²⁹Si MAS NMR spectra: (Proportion of Al-containing Q⁴(nAl) (n = 1 or 2)) = (Peak area for Q⁴(nAl)) / ((Peak area for Q⁴(1Al)) + (Peak area for Q⁴(2Al))).

^c Synthesized via the interzeolite conversion from Al-rich **FAU**-type zeolites.

^d TEA⁺ = tetraethylammonium cation.

^e Determined by ²⁹Si MAS NMR.

^f Quantified by ICP-AES.

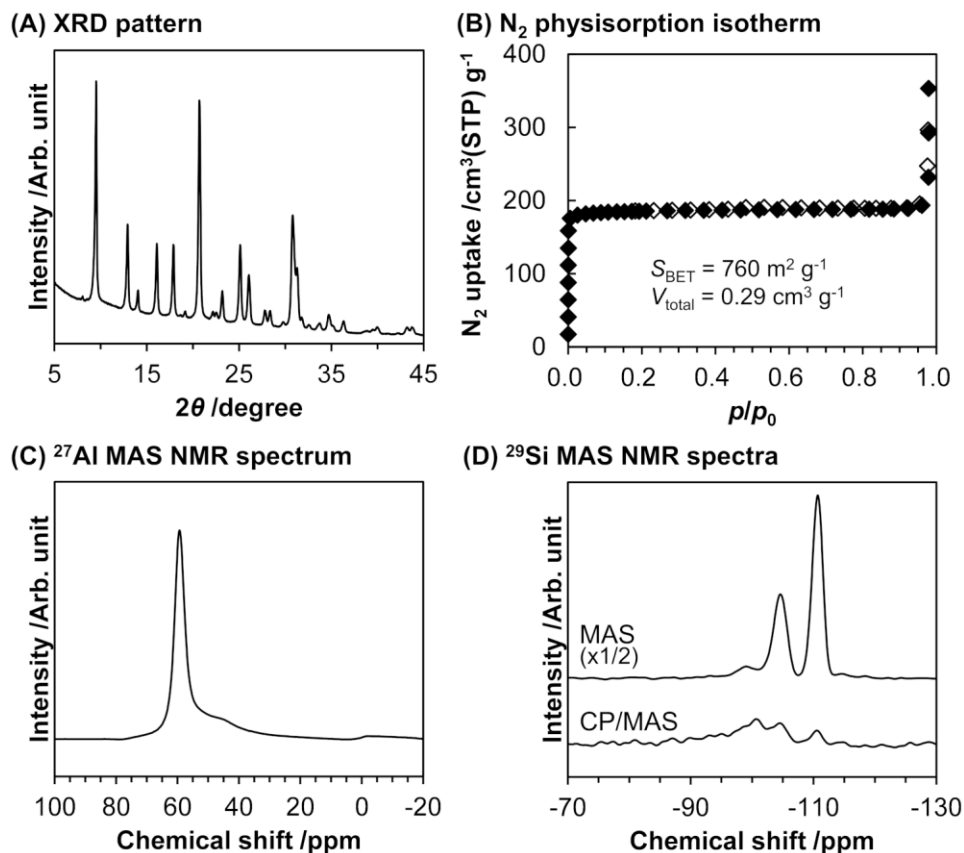


Fig. S6 Characterization data of SSZ-13: (A) XRD pattern, (B) N₂ physisorption isotherm, (C) ²⁷Al MAS NMR spectrum, and (D) ²⁹Si MAS NMR spectra recorded with/without CP technique. In Fig. S6B, the filled and open dots show the adsorption and desorption branches, respectively.

The ICP-AES measurement for SSZ-13, whose framework was confirmed to be **CHA** type by XRD (Fig. S6A), determined its Si/Al ratio to be 7.1. The BET specific surface area and total pore volume of SSZ-13 were 760 m² g⁻¹ and 0.29 cm³ g⁻¹ (Fig. S6B), respectively, both slightly higher than those of CHA-*t*₂ (see Table 1). The ²⁷Al MAS NMR spectrum in Fig. S6C revealed the presence of intra-framework Al species with slight amounts of penta- and hexa-coordinated Al species.^{S5,S6} The ²⁹Si MAS NMR spectrum (the upper spectrum in Fig. S6D) suggested the presence of Q⁴(0Al), Q⁴(1Al), and Q⁴(2Al) species,^{S5} yet the spectrum recorded with the CP technique (the bottom spectrum in Fig. S6D) indicated that a certain amount of Si(OT)_{4-y}(OH)_y (T = Si or Al, 1 ≤ y ≤ 3) species was also involved in SSZ-13 and their peaks overlapped with those of Q⁴(nAl) in the upper spectrum of Fig. S6D, making the accurate evaluation of the Q⁴(2Al) proportion impossible. If we completely ignored such issue, the proportion of Q⁴(2Al) to the total Al-containing Q⁴(nAl) species for SSZ-13 was estimated to be at most 20% (note that the actual value must be lower than 20%), which is lower than the highest value achieved in this study (*i.e.*, 23% for CHA-9, see Table 1).

Supplementary references

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