Supporting Information for

Strontium Ions Function as Both an Accelerant and Structure-Directing Agent of Chabazite Crystallization

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METHODS

Materials. The following reagents were purchased from Sigma-Aldrich: aluminum sulfate hydrate $(Al_2(SO_4)_3 \cdot H_2O, 98\%)$, potassium hydroxide solution (KOH, 40%), potassium hydroxide pellets (KOH, 85%), LUDOX AS-40 colloidal silica (SiO₂, 40%), and aluminum isopropoxide $(Al[OCH(CH_3)_2]_3, 98\%)$. Strontium hydroxide octahydrate (Sr(OH)₂·8H₂O, 99%) was purchased from Alfa Aesar. Commercial zeolites CBV 760 (Si/Al = 30, hydrogen form of zeolite Y) and CBV 28014 (Si/Al = 140, ammonium form of ZSM-5 used only as a Si reference in ²⁹Si MAS NMR experiments) were purchased from Zeolyst. Deionized (DI) water was produced with an Aqua Solutions RODI-C-12A purification system (18.2 M Ω). All reagents were used as received without further purification.

Zeolite synthesis. Low-silica chabazite (CHA-type) zeolites synthesized with strontium (CHA(Sr)) were prepared by modifying a reported protocol¹ using a molar composition of 5 SiO_2 :1.0 Al₂O₃:10.2 K₂O:0.05 SrO:1030 H₂O. In a typical synthesis, potassium hydroxide solution and strontium hydroxide octahydrate were mixed in DI water until fully dissolved. To this solution was added aluminum sulfate hydrate, followed by continuous stirring until the mixture was homogenous. LUDOX AS-40 colloidal silica was then added as the silica source.

Conventional chabazite (labelled sample CHA(K)) was prepared using a molar composition of 5.4 SiO₂: 1.0 Al₂O₃:13.6 K₂O:1093 H₂O, starting with the dissolution of potassium hydroxide pellets in DI water. To this solution was added aluminum isopropoxide, which was then mixed until homogenous, followed by the addition of LUDOX AS-40 colloidal silica. Seed-assisted synthesis of chabazite was performed using a molar composition of 5 SiO₂:1.0 Al₂O₃:10.2 K₂O:*n* SrO:1030 H₂O (where *n* = 0 or 0.05) with seed crystals of faujasite (Zeolyst CBV760) or chabazite (prepared by faujasite seeded growth; sample fCHA). The growth solutions were prepared following the procedure used in the synthesis of CHA(Sr), except that 10 wt% SiO₂ (dry basis) of crystal seed was mixed in the growth solution after the addition of LUDOX AS-40 colloidal silica.

Growth solutions were aged for 24 h at room temperature prior to being transferred to a 60 mL polypropylene (PP) laboratory bottle (VWR) for syntheses at 85 °C or 23 mL Teflon-lined metal autoclave (Parr Instruments) for syntheses at higher temperatures. The synthesis temperature was maintained at 85 – 140 °C using a Thermo Fisher Precision oven and reaction vessels were heated under static conditions (i.e. without rotation). Containers were removed after heating times ranging from 6 h to 21 d. Upon removal from the oven, the container was quenched to room temperature in a water bath. Solids were recovered by three cycles of centrifugation, each at 5 °C and 13,000 rpm for 5 min using a Beckman Coulter Avanti J-E centrifuge and washings with DI water. The recovered product was dried in air at 50 °C overnight prior to analysis. A selected sample was washed additionally for 24 h and 72 h by contacting with DI water under continuous stirring (using 100 mL water per 0.1 g solid).

Characterization. The phase purity of the zeolite samples was determined by powder X-ray diffraction (XRD) using a Rigaku diffractometer with Cu K α radiation (40 kV, 44 mA). Scanning electron microscopy (SEM) was conducted on a FEI-235 Dual-Beam Focused Ion Beam instrument operated at 15 kV and a 5 mm working distance. Samples for SEM analysis were prepared by affixing dried crystals to a SEM sample holder with carbon tape. Elemental analysis was performed by energy dispersive X-ray spectroscopy (EDX) and inductively coupled plasma atomic emission spectroscopy (ICP-OES) using a JEOL JSM 6330F field emission scanning electron microscope at a working distance of 15 mm and voltage of 15 kV and an Agilent 725 ICP-OES with the sample digested by lithium metaborate. Solid-state NMR experiments were performed at 11.7 T on a JEOL ECA-500 spectrometer, equipped with a 3.2 mm field gradient magic angle spinning probe. ²⁷Al MAS NMR spectra were obtained at a spinning frequency of 12.5 kHz, pulse of $\pi/12$, relaxation delay of 0.8 s, and 2 K scans. The ²⁷Al chemical shift was referenced using 1.0 M Al(NO₃)₃ aqueous solution. ²⁹Si MAS NMR spectra were obtained at a spinning frequency of 12.5 kHz, pulse of $\pi/8$, relaxation delay of 10 s, and 4 K scans. The ²⁹Si chemical shift was referenced using commercial zeolite ZSM-5 (Zeolyst CBV28014).

SUPPORTING FIGURES



Figure S1. Powder X-ray diffraction patterns of as-synthesized samples in Figure 3 that were prepared at 100 °C for various heating times required to reach full crystallinity. For comparison, we include references patterns of chabazite and merlinoite (labelled as CHA(ref) and MER(ref), respectively) provided by the International Zeolite Association Structure Database.²



Figure S2. Powder X-ray diffraction patterns of as-synthesized CHA(Sr) samples prepared at 140 °C and extracted after various time periods of hydrothermal treatment.



Figure S3. Powder X-ray diffraction patterns of as-synthesized CHA(Sr) samples prepared at 100 °C and extracted after various time periods of hydrothermal treatment.



Figure S4. Powder X-ray diffraction patterns of as-synthesized CHA(Sr) samples prepared at 85 °C and extracted after various time periods of hydrothermal treatment.



Figure S5. Scanning electron micrographs of solids extracted from synthesis mixtures used to prepare CHA(Sr) samples for Figure 2D after heating at 140 °C for (A) 6 h, (B) 12 h, (C) 24 h, (D) 36 h, and (E) 48 h. All scale bars equal 1 μ m.



Figure S6. Scanning electron microscopic images of solids extracted from synthesis mixtures used to prepare CHA(Sr) samples for Figure 2D after heating at 100 °C for (A) 6 h, (B) 12 h, (C) 24 h, (D) 36 h, and (E) 48 h. All scale bars equal 1 μ m.



Figure S7. Scanning electron microscopic images of solids extracted from synthesis mixtures used to prepare CHA(Sr) samples for Figure 2D after heating at 85 °C for (A) 6 h, (B) 12 h, (C) 24 h, (D) 36 h, and (E) 48 h. All scale bars equal 1 μ m.



Figure S8. Phase(s) of solids extracted from synthesis mixtures after heating for 6 - 48 h at three Sr/Al molar ratios: 0.015, 0.025, and 0.035. Color coding: chabazite (red), amorphous (white), and mixtures of chabazite and amorphous product (split red/white).



Figure S9. Elemental analysis (EDX) of the Si/Al molar ratio of solids extracted from a growth solution after 24 h of aging at ambient temperature. Each sample was prepared with a molar composition of 10.2 K₂O:5 SiO₂:1.0 Al₂O₃:2*x* SrO:1030 H₂O (where x = Sr/Al with values spanning from 0 to 1).



Figure S10. Scanning electron microscopic images of as-synthesized fully crystalline chabazite prepared at 100 °C using synthesis protocols for the following products: (A) CHA, (B) CHA(Sr), (C) cCHA, (D) cCHA(Sr), (E) fCHA, and (F) fCHA(Sr). All scale bars equal 2 µm.



Figure S11. ²⁷Al MAS NMR spectra of as-synthesize CHA-type samples prepared at 100 °C showing the presence of tetrahedral (framework) Al and the absence of octahedral (extra-framework) Al, which if present would appear at 0 ppm. A conventional synthesis in the absence of seeds or alkaline earth metal (CHA(K)) is compared with syntheses employing 10 wt% chabazite seeds in the absence (cCHA) and presence of 0.02 wt% Sr²⁺ ions (cCHA(Sr)), as well as syntheses employing 10 wt% faujasite seeds in the absence (fCHA) and presence of 0.02 wt% Sr²⁺ ions (fCHA(Sr)).

SUPPORTING TABLES

Si/Al Ratio			K/Al				Viald 6		
Sample	NMR ^a	EDX	ICP ^b	Average	As-made	24 h wash	72 h wash	Sr/Al	(%)
CHA(K)	2.2	1.5	1.67	1.8 ± 0.4	1.94				32
CHA(Sr)	2.2	1.8	2.12	2.0 ± 0.2	1.37 ^b	1.33 ^b	1.31 ^b	0.15 ^b	35
cCHA		1.9	2.17	2.0 ± 0.2	1.57				51
cCHA(Sr)		2.0	2.05	2.03 ± 0.04	1.38			0.13	67
fCHA	1.9	2.0	2.14	2.0 ± 0.1	1.59				34
fCHA(Sr)	2.0	2.1	2.14	2.08 ± 0.07	1.50			0.04	46

Table S1. Elemental composition and yield of as-synthesized samples.

a. Determined from ²⁹Si MAS NMR spectra (Figure 4B); b. Performed by Galbraith Laboratories; c. Calculated as the mass of as-synthesized product (subtracting the quantity of K^+) divided by the total mass of starting reagent (silica + alumina)

Speciation	CHA(K) (%)	CHA(Sr) (%)	fCHA (%)	fCHA(Sr) (%)
Q ⁴ (0A1)	10	3	2	3
$\hat{Q}^4(1Al)$	22	30	19	18
$Q^4(2Al)$	46	51	47	58
$Q^4(3Al)$	22	16	29	16
$Q^4(4Al)$	<1	<1	4	6

Table S2. Aluminum speciation from the deconvolution of ²⁹Si MAS NMR spectra.

REFERENCES

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