

Supporting Information

Unique Crystallization Behavior in the Zeolite Synthesis under External High Pressure

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1. Apparatus and its operation

Warm isostatic press (Dr. CHEF, KOBELCO) was used as the pressurization equipment, where silicone oil was used as the pressure-transmitting fluid. The maximum achievable temperature was 150 °C, and the pressure 980 MPa. Nylon-lined polyethylene vacuum-sealing bags were used as the reaction vessels. The reaction mixture was packed and heat-sealed in the plastic bag. In order to reduce the error in pressure introduced by the high compressibility of air, remaining air in the bag reactors were minimized. The sealed bag reactors were further rolled up with Teflon® sheets or rubber sheets, and sealed in plastic bags again, in order to physically mitigate the heat expansion. Such individually packed reaction mixtures were immersed in the pre-heated silicon oil bath of the warm isostatic press, and after adjusting the height of the liquid, the piston exerted uniaxial force on the silicon oil, which conveyed the pressure to the reactors by the Pascal's Law.

2. Experimental

2.1 Materials

Water glass (50%, Wako), fumed silica Cab-O-Sil M5 (Cabot) and colloidal silica LUDOX HS-40 (Sigma-Aldrich) were used as silica sources. Sodium aluminate (molar ratio Al/NaOH=0.79, Wako) and aluminum hydroxide (Wako) were used as Al sources. NaOH (97%, Wako) and KOH (85%, Wako) were used in the pellet form as received. All chemicals were used without further purification. Deionized (DI) water was used throughout the experiment.

2.2 Zeolite synthesis recipes

2.2.1 EDI/BPH case

In a typical run, 7.0 g solid KOH was dissolved in 8.4 g of DI water in a polypropylene bottle. 0.7 g of aluminum hydroxide was added in the solution, and the mixture was heated at 80 °C until a clear solution was obtained. After the solution was cooled down to room temperature, 2.0 g of LUDOX HS-40 was added drop-by-drop under vigorous stirring to obtain the synthesis mixture with a molar composition of 1.0 SiO₂: 0.33 Al₂O₃: 4.0 K₂O: 44 H₂O.

2.2.2 EMT/FAU case

In a typical run, 0.85 g 50 wt% KOH aqueous solution was added into 2.0 g of DI water, and 1.3 g of sodium aluminate was dissolved into the resultant alkali solution. After the solid fully dissolved, the Al solution was poured onto 5.0 g of 50% water glass. The mixture was hand mixed with spatula with the help of vortex shaker for 5 minutes. The final composition was 1.0 SiO₂: 0.14 Al₂O₃: 0.50 Na₂O: 0.12 K₂O: 8.0 H₂O.

2.2.3 LTA/FAU case

In a typical run, 3.0 g of NaOH pellet was dissolved in 14 g of DI water. Half of the solution was used to dissolve 1.2 g of sodium aluminate, and the rest was used to dissolve 1.0 g of Cab-O-Sil M5 fumed silica. The two mixtures were heated until all solids dissolved. After cooling down to room temperature, the Al solution was added to the Si solution drop-by-drop under vigorous stirring. The final composition was 1.0 SiO₂: 0.25 Al₂O₃: 2.5 Na₂O: 48 H₂O.

2.2.4 SOD/LTN case

In a typical run, 6.1 g of NaOH pellet was dissolved in 14 g of DI water. Half of the solution was used to dissolve 1.2 g of sodium aluminate, and the rest was used to dissolve 1.0 g of Cab-O-Sil M5 fumed silica. The two mixtures were heated until all solids dissolved. After cooling down to room temperature, the Al solution was added to the Si solution drop-by-drop under vigorous stirring. The final composition was 1.0 SiO₂: 0.25 Al₂O₃: 4.8 Na₂O: 48 H₂O.

2.2.5 SOD/CAN/FAU case

In a typical run, 1.0 g of 50 wt% NaOH aqueous solution, 0.85 g of 50 wt% KOH aqueous solution, and 1.25 g of DI water was mixed together to dissolve 2.5 g of sodium aluminate. The solution was heated until all solid dissolved. After cooled down to room temperature, the solution was poured onto 5.0 g of 50% water glass. The mixture was hand mixed with spatula with the help of vortex shaker for 5 minutes. The final composition was 1.0 SiO₂: 0.25 Al₂O₃: 0.86 Na₂O: 0.12 K₂O: 8.0 H₂O.

2.3 Synthesis procedure under external high pressures

All experiments were carried out at 80 °C. Crystallization time varied from 10 min to 3 h, and pressure varied from ambient pressure to 800 MPa. The two-step pressurization experiment in the LTA/FAU case was also carried out. After the reactor was immersed in the silicone oil, the pressure vessel was left open to air for 5 min at 80 °C, and then the pressure was applied as usual.

Timing of the reaction started once the pressure stabilized at the designated value, which generally took a few minutes. After the reactant was treated at desired temperature and pressure for the desired period of time, the pressure was released, and reactors were taken out from the warm isostatic pressure. Then the bag reactors were cooled down with running tap water. The obtained products were centrifuged and washed with DI water until pH was under 8. The solid products were then dried in 80 °C oven overnight before further characterization.

2.4 Characterizations

Powder X-ray diffraction patterns were collected from 3 to 40° in 2θ with an Ultima IV X-ray diffractometer (Rigaku) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$, 40 kV, 40 mA). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted with an iCAP-6300 ICP-AES analyzer (Thermo Fisher Scientific) to determine the Si/Al ratio of the samples. Samples were completely dissolved in a KOH aqueous solution prior to the ICP-AES measurement. Solid-state ^{27}Al magic angle spinning (MAS) NMR spectra were acquired with ECA-600 (JEOL RESONANCE) at 156.4 MHz with a $\pi/2$ pulse length of 1.3 μs , a relaxation delay of 5 s, and a MAS spinning frequency of 25 kHz. The ^{29}Si MAS NMR spectra were acquired with ECA-300 (JEOL RESONANCE) at 59.7 MHz with a $\pi/2$ pulse length of 1.0 μs , a relaxation delay of 130 s, and a MAS spinning frequency of 7.5 kHz. A JSM-7000F (JEOL) scanning electronic microscope (SEM) was used to observe the morphology of the products at an accelerating voltage of 10 kV.

3. Supporting Figures

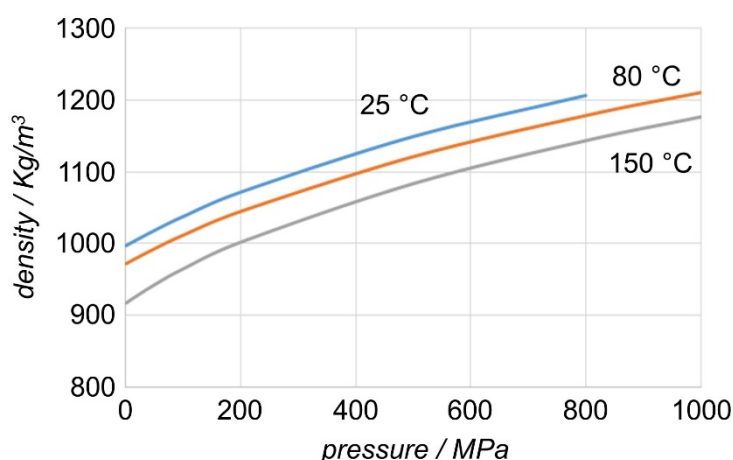


Figure S1 | Water density under high pressures.

Figure S1 shows that water density changes significantly upon increasing the pressure. At 150 °C, water density at 1000 MPa increases by about 30% compared to that under ambient pressure.

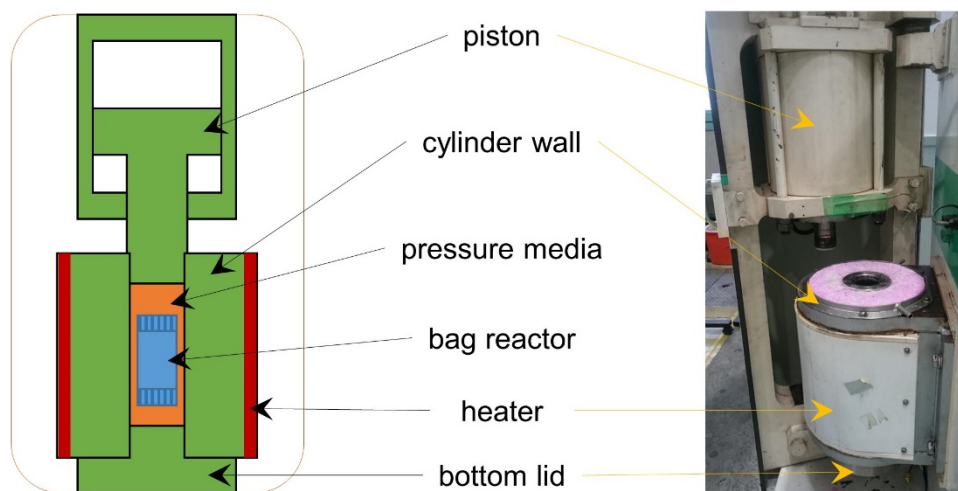


Figure S2. Schematic illustration and a photo of the warm isostatic press apparatus used for the synthesis of zeolites under high pressures. (Pressure media and bag reactor are not arrowed in the photo as they are inside the cylinder.)

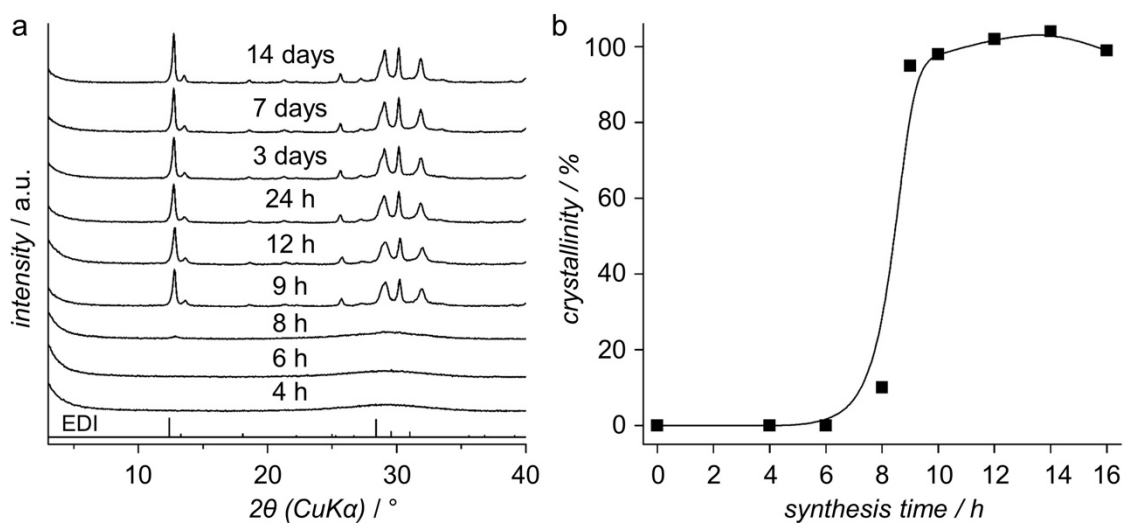


Figure S3 | Synthesis of EDI zeolite under autogenous pressure. a), XRD patterns of the products synthesized under autogenous pressure over different periods of time. b), Crystallinity curve for the EDI synthesis under autogenous pressure.

Figure S3 indicates that it took about 9 h to obtain fully crystalline EDI zeolite under autogenous pressure and that the product remained to be EDI even the synthesis period was prolonged to 14 days. On the contrary, it took only 1 h to synthesize EDI zeolite under 400 MPa, and at 800 MPa, the product turned to be a mixture of EDI and BPH (note that the latter is a large pore zeolite featuring 12MR, see Figure 1e). The results clearly demonstrate that applying external high pressure remarkably fastened the crystallization rate, and that larger pore zeolite tended to be generated upon elevating the synthesis pressure.

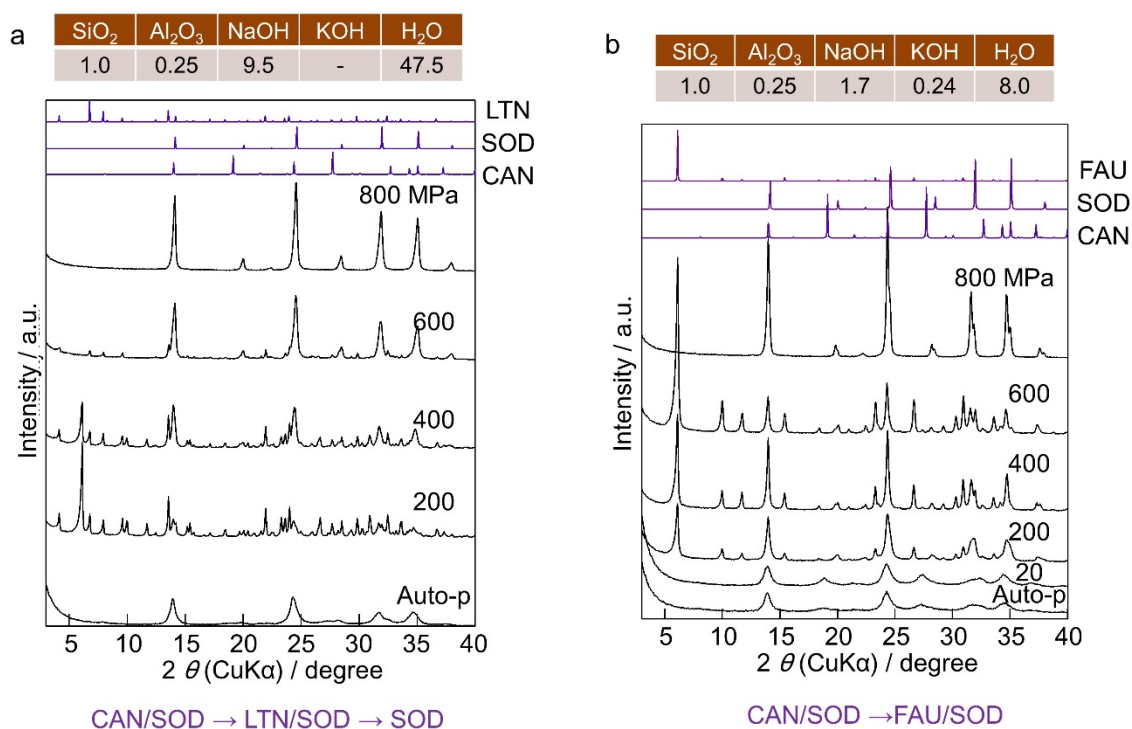


Figure S4 | Additional examples showing the formation of a structure with a different FD_{Si} upon varying the synthesis pressure. a), The SOD/LTN case. b), The SOD/CAN/FAU case.

Figure S4 shows two additional examples of the synthesis under different external pressures with otherwise identical conditions. From the results, we can see that a structure with a different FD_{Si} could be obtained upon varying the synthesis pressure, confirming the influence of external high pressure on the crystallization pathways.

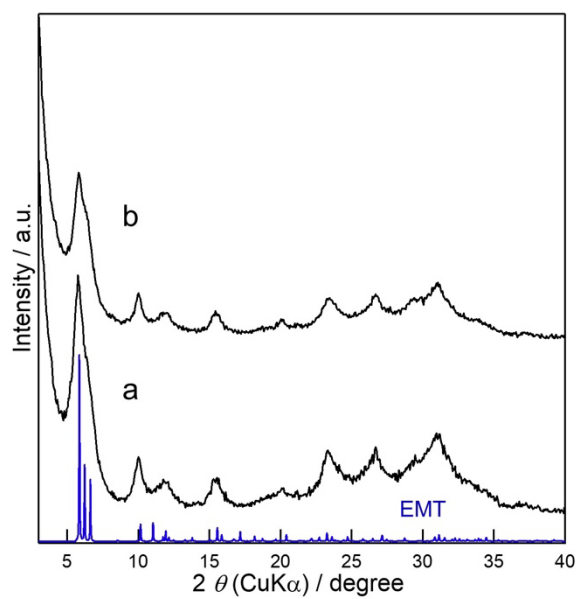


Figure S5 | Synthesis of EMT zeolite under autogenous pressure and 20 MPa. XRD patterns of the EMT samples synthesized under autogenous pressure. **a**, EMT zeolite synthesized at 60 °C for 3 h. **b**, EMT zeolite synthesized at 80 °C for 1 h.

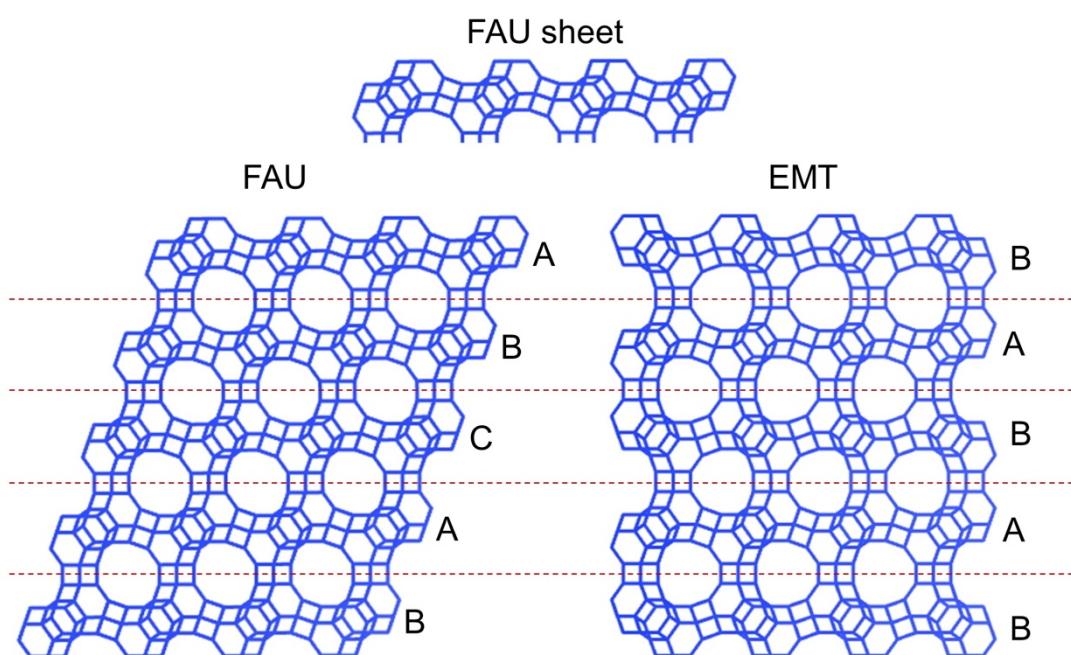


Figure S6 | Comparison of FAU and EMT structures. Structure of the FAU sheet is given on the top of the two structures. Different stacking arrangements of the FAU sheets give FAU (in ABCABC sequence) along the $[110]_c$ and EMT (in ABAB sequence) along the $[100]_h$, respectively (“c” and “h” in the subscripts denote cubic and hexagonal symmetry respectively).

Reference: N. Hanif *et al.* *Phys. Chem. Chem. Phys.* **2000**, 2, 3349.

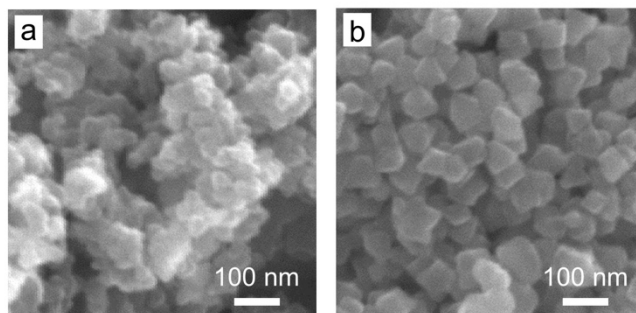


Figure S7 | SEM images of the EMT zeolite and the FAU zeolite. a, SEM images of the EMT zeolite (synthesized at 20MPa). **b,** FAU zeolite (synthesized at 800MPa).

The SEM image in **Figure S7a** indicates that the product synthesized at 20 MPa was nano-sized EMT zeolite, which resembled the one reported in ref. 19. When an external high pressure of 800 MPa was applied, the product turned to be nanosized FAU (**Figure S7b**), which featured well-defined octahedral crystal habit.

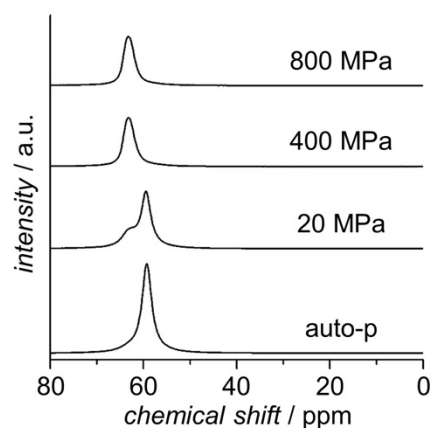


Figure S8 | Solid-state ^{27}Al NMR spectra of the samples synthesized under different pressures (LTA-FAU case).

The ^{27}Al NMR spectra in **Figure S8** show only one peak around 60 ppm, which corresponds to the tetrahedrally coordinated framework Al. No peaks were observed around 0 ppm, indicating the absence of octahedral extra-framework Al species. Note that two peaks were observed for the sample synthesized at 20 MPa, which is due to that the sample was a mixture of LTA and FAU zeolites.

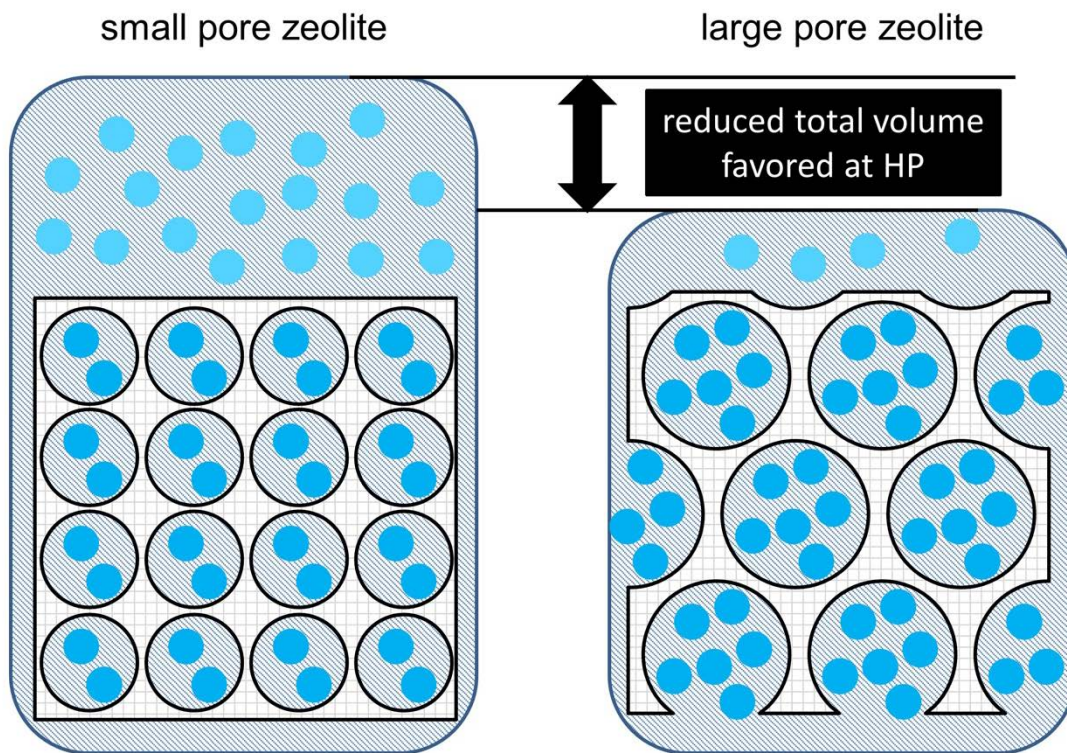


Figure S9 | Illustration of the hypothesis of total volume reduction.

The blue circles and the shadowed circles represent water molecules and zeolite pores. This figure illustrates that larger pores can accommodate more water molecules and thus help reduce the total volume of the system.