Supplementary Information

New mechanism for the nucleation and growth of large zeolite X crystals in the presence of triethanolamine

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1. Chemicals used in the synthesis.
Fumed silica (Cab-O-Sil® M5).
Sodium aluminate (Sigma-Aldrich, technical anhydrous).
Sodium hydroxide (Sigma-Aldrich, ≥98% reagent grade, pellets).
Triethanolamine (Sigma, ≥99%).

2. Synthesis method.
Zeolite X was synthesized using a modified version of the hydrothermal synthesis procedure developed by Warzywoda et al. \(^1\) The molar ratio of the chemicals in the gel used was 4.76\( \text{Na}_2\text{O} : 1.0\text{Al}_2\text{O}_3 : 3.5\text{SiO}_2 : 454.0\text{H}_2\text{O} : 8.0\text{TEA}. \) Fumed silica was suspended in 5/11 of the amount of water. Sodium aluminate powder was dissolved in a hot aqueous sodium hydroxide solution using the remaining water and then allowed to cool before the addition of triethanolamine. Both solutions were stirred overnight and then mixed briefly. The mixed solution was added to autoclaves in portions of 15 mL. The autoclaves were placed in a convection oven at 100°C for the required period of time, 1, 2, 3, 4, 5, 8, 14 days, followed by cooling down to room temperature. The colourless crystalline products were recovered by filtering, washing with deionized water and drying at 100°C for 3 h.


3. Characterisation methods.
Powder X-ray diffraction (XRD) patterns were collected on a STOE STADIP diffractometer operated in Debye-Scherrer geometry using 0.7 mm quartz capillaries over a period of 1.5 h for a fast scan and 10 h for a slow scan. Scanning electron microscopy (SEM) images were recorded using three different microscopes: a Jeol-JSM-6700F, a Jeol-JSM-5600, and a FEI Scios Dualbeam. Different microscopes were used depending on the information required from the sample. The Jeol-JSM-6700F and the FEI Scios Dualbeam were used primarily for imaging, and the Jeol-JSM-5600 was used for collecting energy dispersive X-ray spectroscopy (EDX)
data. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained on a Jeol JEM-2100 electron microscope, operated at 200 kV.

4. Structure refinement of zeolite X from single crystal XRD data

 Single crystal XRD was performed at -180 °C using a Rigaku FRX (Mo radiation) rotating anode generator with Dectris P200 detector. The structure was solved by dual-space methods (SHELXT), and refined by full-matrix least-squares against F2 (SHELXL-2016).

 An octahedral crystal (0.03 x 0.03 x 0.03 mm) was selected for single crystal XRD experiment. It is confirmed that the crystal is zeolite X. The refined structure is cubic with the unit cell parameter $a = 24.846(6)$ Å, space group: Fd$^3$m based on 7200 measured reflections, with 715 uniq (Rint 0.0973) leading to R1 0.0943, wR2 0.3546. The Al/Si positions were all treated as Si and no H atoms were included in the refinement.

Fig. S1 Refined structural diagrams of zeolite X viewed in the (a) [100], (b) [110] (c) [111] directions.

Table S1 Atomic coordinates from single crystal X-Ray study.

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<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
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</table>
Fig. S2 SEM images of (a) the 1 day sample showing irregular aggregates of precipitate, (b) the 3 days sample showing a large proportion of spherical particles.

Fig. S3 TEM images of nanorods formed on the surface of spherical particles and the corresponding SAED patterns. The long axes of the nanorods are indicated by the arrows. The SAED patterns are indexed to the structure of zeolite P with the cubic unit cell parameter of about 10.0 Å viewed down the (a) [001] and (b) [01\̅1] zone axes.
**Fig. S4** Linear EDX analysis from the centre to the surface of a spherical particle in the 3 days sample.

**Fig. S5** EDX spectra of particles dried at room temperature, (a) a spherical particle from the 3 days sample, and (b) an octahedral particle from the 3.75 days sample. The atomic percentages of the elements are (a) 29.9% C, 55.2% O, 5.18% Na, 4.08% Al, 5.67% Si; (b) 18.0% C, 58.7% O, 6.76% Na, 6.71% Al, 9.88% Si.
Fig. S6 Powder XRD patterns of the specimens with different reaction times from 3 days to 4 days.

Fig. S7 Measured particle sizes in diameter, (a) zeolite P-containing spheres and (b) zeolite X octahedra.
Fig. S8 SEM images of spherical particles in (a,b,d) the 14 days sample and (c) the 8 days sample. (a,b) A phase separation into four layers marked by A, B, C, D. (c) Disconnection of the zeolite P crust from a spherical core. (D) Top view of the zeolite P microrods. The circle indicate a cross-shaped end of a single microrod.

Fig. S9 SEM images of octahedral zeolite X crystals, (a) still connected to a sphere and (b) separated from a sphere. EDX spectra from surfaces of (c) spherical (zeolite P) and (d) octahedral (zeolite X) particles.
Fig. S10 Single crystal XRD pattern from an octahedral particle of zeolite X. The exposure time is 160 seconds, which is much longer than normal time.