Evolving mechanism of organotemplate-free hierarchical FAU zeolites with house-of-cards-like structure

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28th May 2019

Note added after first publication: this Supplementary Information file replaces that originally published on 7th August 2018 in which the Experimental section was omitted.

Experimental

Synthesis. The hydrothermal synthesis was conducted in an autoclave under static condition. Aluminosilicate homogeneous gel was obtained by mixing freshly prepared aluminate and silicate solutions together in the molar ratio 1.43 Na_2O: 1.0 Al_2O_3: 2.39 SiO_2: 74.45~95.23 H_2O. Typically, an aluminosilicate gel containing 0.5 g of NaOH, 1.2 g of $NaAlO_2$, 6.7 g of H_2O and 3.88 g of water glass was used. The homogeneous gel was then transferred into an autoclave and hydrothermally crystallized at 70 °C. The powder products were recovered by filtration, washed with DI water until pH<8, and then dried at 80 °C for 12 h.

Characterizations. X-ray diffraction data (XRD) were obtained on a Bruker D8 Advance diffractometer with Cu Kα. radiation (40kV and 200 mA). Data was collected from 2 θ= 4 ° to 40 ° with a step of 0.02 ° and a scanning rate of 0.1 ° s^{-1}. The particle size and morphology of samples was examined by scanning electron microscopy (SEM) images on a field emission SU-70 electron microscope and transmission electron microscopy (TEM) images on JEOL JEM2010 electron microscope. The chemical composition of the solid samples was determined with an X-ray fluorescence (XRF) spectrometer (AXIOS). Nitrogen absorption and desorption isotherms at the temperature of liquid nitrogen (77 K) were measured using ASAP 2020 system after degassing the sample at 573 K under vacuum at least for 4 h. The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) equation and the amount of micropores was calculated by t-plot analysis.

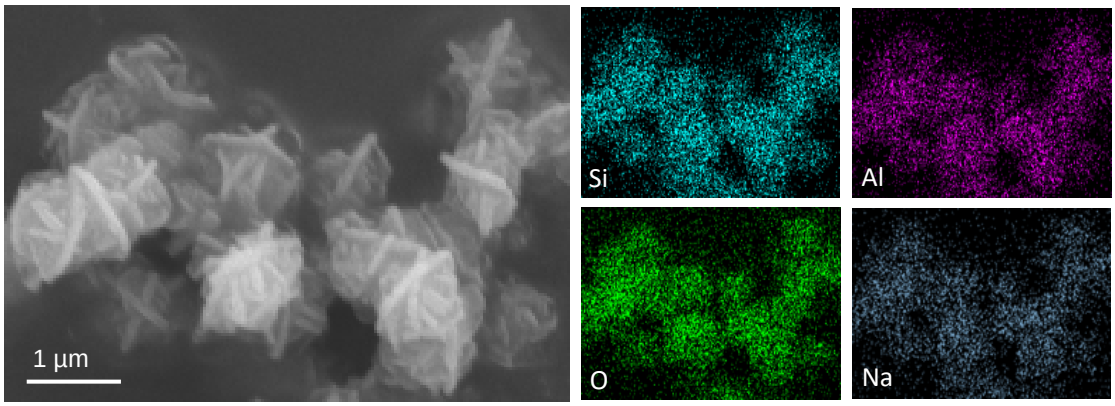

Fig. S1. SEM-EDS mapping images of HCL-NaX showing the elements of Al, Si, Na, and O are all well-distributed over the entire scanning region.

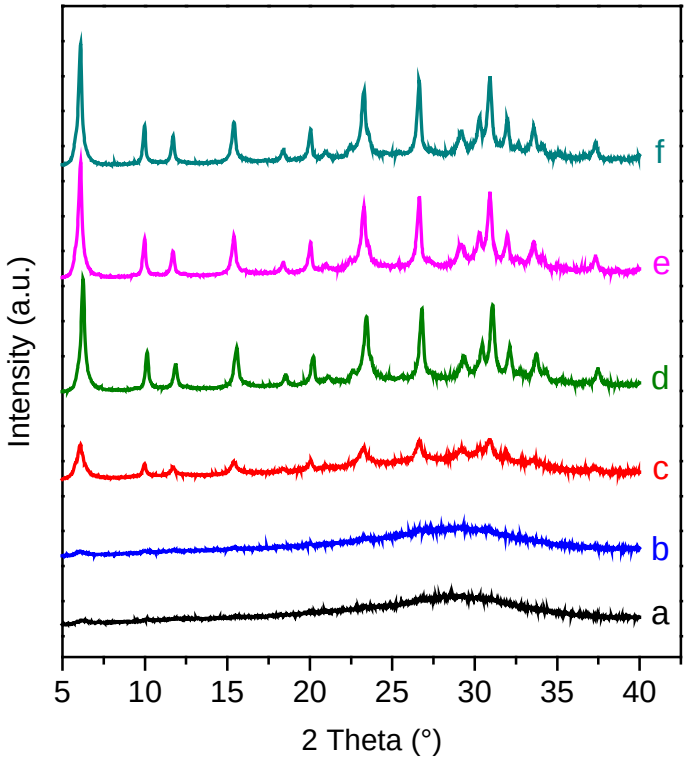

Fig. S2. XRD patterns of the products prepared at 70 ºC for (a) 4 h, (b) 5 h, (c) 6 h, (d) 12 h, (e) 24 h, and (f) 48 h.

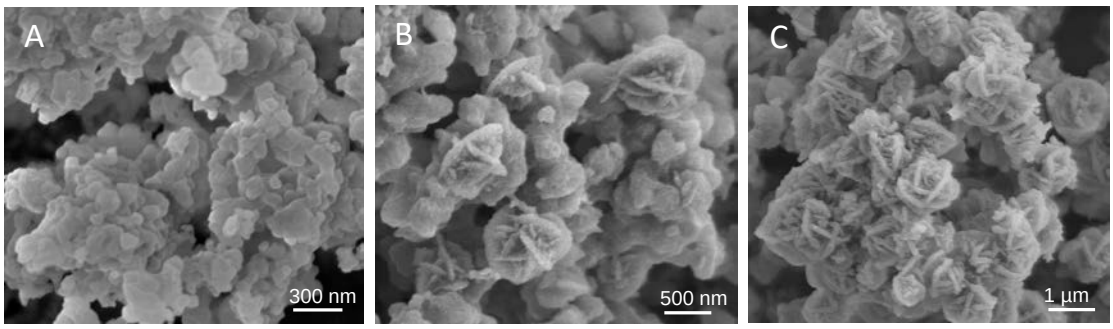

Fig. S3. SEM images of the products prepared at 70 °C for (A) 4 h, (B) 6 h, (C) 24 h.

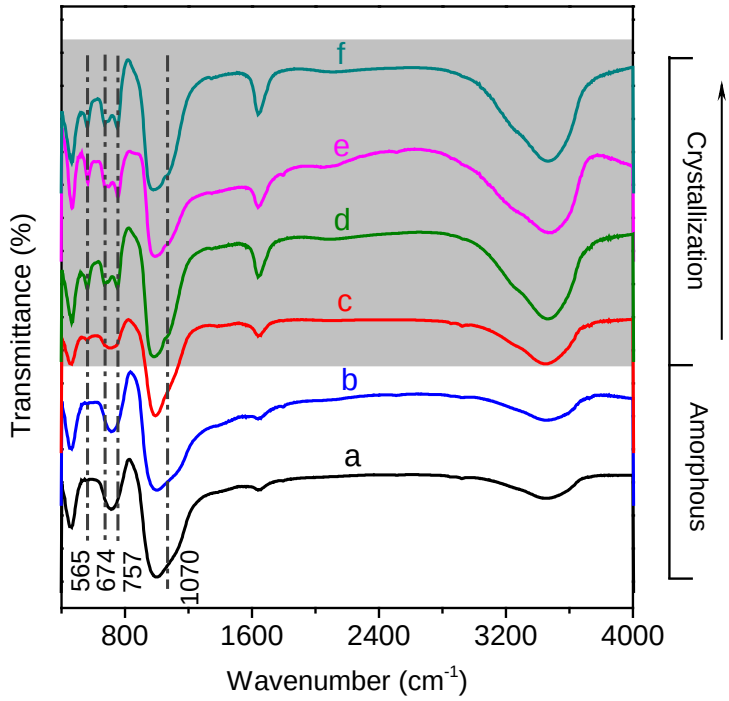

Fig. S4. FTIR spectra of the products prepared at 70 °C for (a) 4 h, (b) 5 h, (c) 6 h, (d) 12 h, (e) 24 h, and (f) 48 h, confirming the FAU zeolites are formed after 6 h of reaction. Typically, two peaks appearing at 674 and 757 cm^{-1} belong to the symmetric stretching band of FAU framework; The peak at 565 cm^{-1} is attributed to the double-ring vibration; The peak around 1070 cm^{-1} is assigned to the asymmetric telescopic vibrational band (Microporous and Mesoporous Materials, 2011, 142, 139–146).

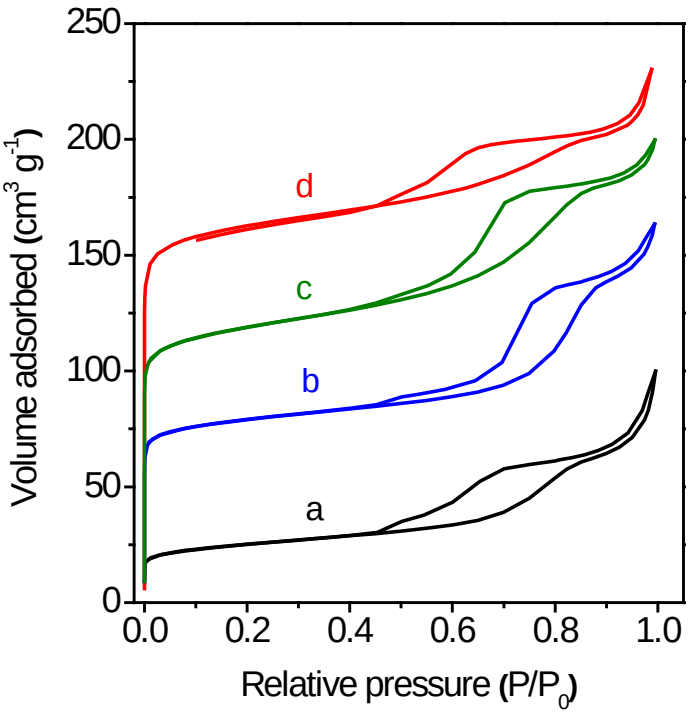

Fig. S5. N_2 adsorption/desorption isotherms of the products prepared at 70 °C for (a) 6 h, (b) 12 h, (c) 24 h, and (d) 48 h.

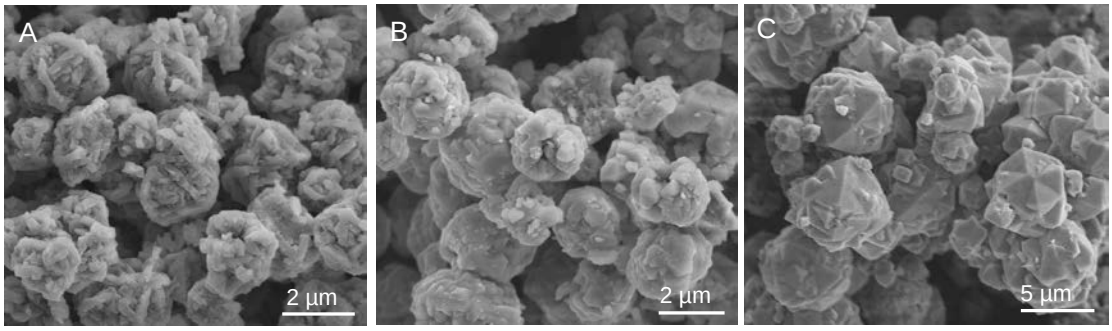

Fig. S6. SEM images of the products synthesized at 70 °C for 48 h with different H_2O/Al_2O_3 molar ratios of (A) 80.04, (B) 87.64, and (C) 95.23.

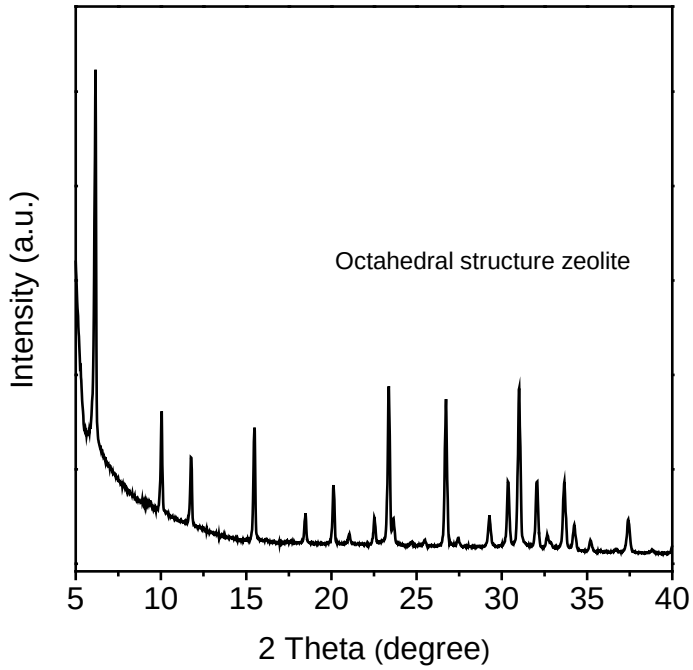

Fig. S7. XRD pattern of octahedral structure zeolite synthesized at 70 ^{o}C for 48 h with the H_2O/Al_2O_3 molar ratio of 95.23.

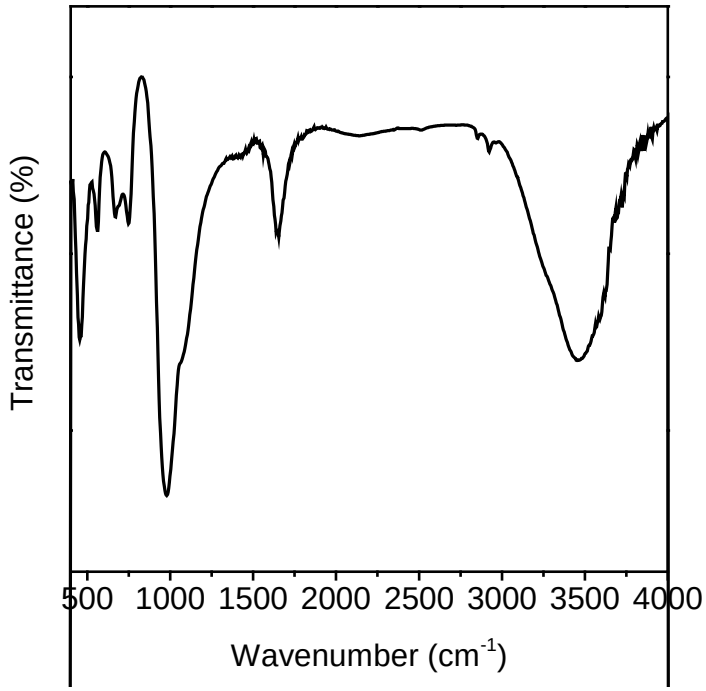

Fig. S8. FTIR spectrum of octahedral structure zeolite synthesized at 70 ^{o}C for 48 h with the H_2O/Al_2O_3 molar ratio of 95.23.

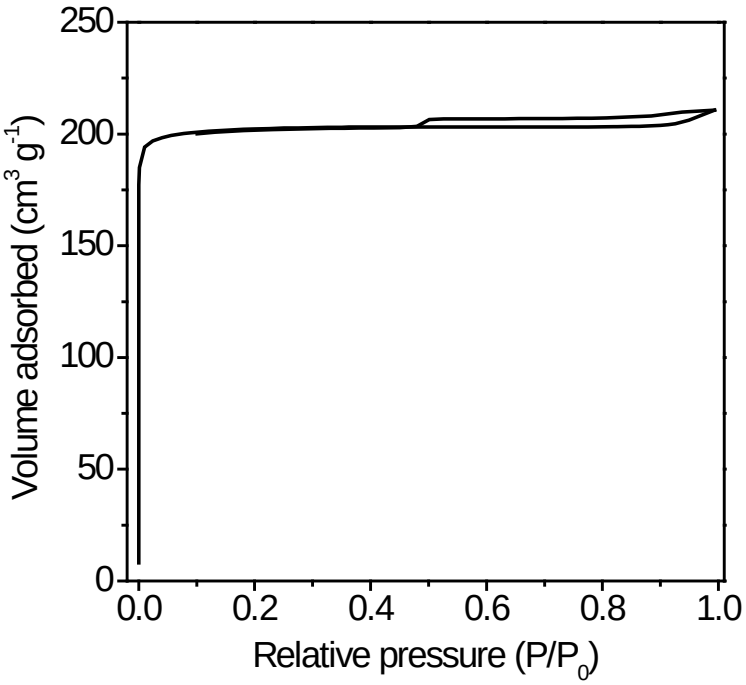

Fig. S9. N_2 adsorption/desorption isotherms of octahedral structure zeolite synthesized at 70 ^oC for 48 h with the H_2O/Al_2O_3 molar ratio of 95.23. The BET surface area is 664 $m^2\ g^{-1}$, in which the external surface area accounts for 27.8 $m^2\ g^{-1}$.

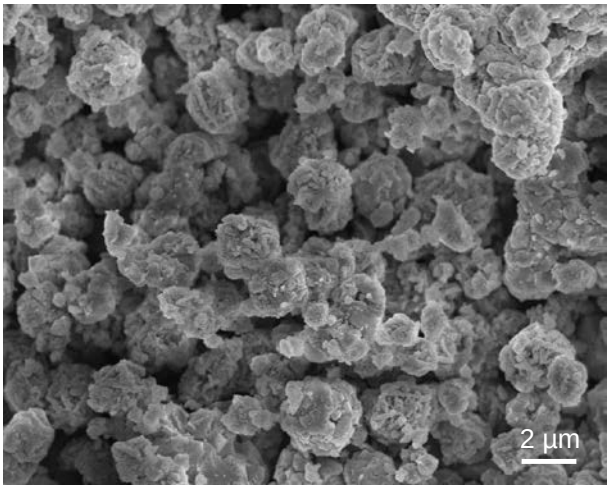

Fig. S10. SEM image of the product synthesized at 70 ^oC for 48 h with the H_2O/Al_2O_3 ratio of 95.23, and with the H_2O/NaOH mol ratio in accordance with that of H_2O/Al_2O_3 mol ratio=74.45.

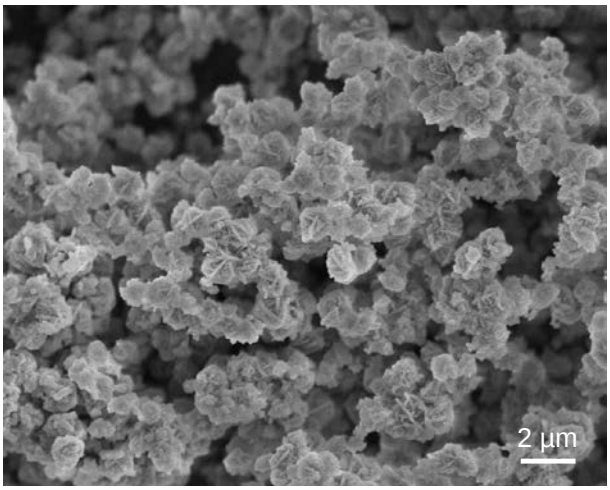

Fig. S11. SEM image of the HCL-NaX product with synthesis scaled up for ten times (70 ^{o}C for 48 h).

Table S1. Structure parameters of the products prepared at 70 ^{o}C for 6 h, 12 h, 24 h, and 48 h.

Sample	Si/Al (-)	S_{BET} [a] (m^2 g^{-1})	S_{ext} [b] (m^2 g^{-1})	d_{meso} [c] (nm)	V_{total} [d] (cm^3 g^{-1})	V_{micro} [e] (cm^3 g^{-1})
HCL-NaX-6	1.33	92	41	9.3	0.14	0.03
HCL-NaX-12	1.35	299	52	12.5	0.24	0.11
HCL-NaX-24	1.38	373	88	9.3	0.30	0.18
HCL-NaX-48	1.31	541	100	7.6	0.37	0.26

[a] $S_{BET,}$ Brunauer–Emmett–Teller (BET) surface; [b] S_{ext}, external surface area; [c] d_{meso}, mean mesopore size; [d] V_{total}, total pore volume; [e] V_{micro}, micropore volume.