Electronic Supplementary Information

Fluoride-Free Synthesis of Beta Zeolite with Enrichment of Polymorph B from a Solvent-Free Route

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Experimental Section

Materials

Sodium hydroxide (AR, 96%, Sinopharm Chemical Reagent Co., Ltd.), sodium aluminate (Sinopharm Chemical Reagent Co., Ltd.), solid silica gel (Qingdao Haiyang Chemical Reagent Co., Ltd.), tetraethylammonium bromide (AR, 98%, Aladdin Chemistry Co., Ltd.), tetraethylammonium hydroxide (*ca.* 35 wt.%, provided by Kente), ammonium nitrate (NH_4NO_3, AR, 99%, Beijing Chemical Reagent Co., Ltd.) were used without further purification.

Syntheses of samples

In a typical run for the synthesis of pure silica Beta zeolite with enrichment of

polymorph B, 3.2 g of SiO_2, 0.6 g of NaOH, 2.0 g of TEABr, 2.2 g of TEAOH and 0.08 g of seeds were added into a mortar one by one and mixed together. After grinding for 5 minutes, the powder was transferred to an autoclave and sealed. After heating at 140 ^oC for 5 d, the sample was fully crystalline. This sample was designated as JXM-1 (Jiaxing Material No. 1). Notably, original seed crystals are synthesized from the recent literature (*Catal. Today*, **2020**, *339*, 174). Once the JXM-1 is synthesized, the obtained JXM-1 could also be used as seed crystals.

In a typical run for the synthesis of aluminosilicate Beta zeolite with enrichment of polymorph B, 3.2 g of SiO_2, 0.04 g of $NaAlO_2$, 0.6 g of NaOH, 2.0 g of TEABr, 2.2 g of TEAOH and 0.08 g of seeds were added into a mortar one by one and mixed together. After grinding for 5 minutes, the powder was transferred to an autoclave and sealed. After heating at 140 ^oC for 5 d, the sample was fully crystalline. This sample was designated as Al-JXM-1 (Jiaxing Material No. 1).

Characterization

X-ray powder diffraction (XRD) patterns were measured with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using CuKα (λ=1.5406 Å) radiation. The N_2 sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2020M. The sample composition was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) with a Perkin-Elmer 8000 OES. Transmission electron microscopy (TEM) images were performed on a JEM-2100F electron microscopy (JEOL, Japan) with an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) experiments were performed on Hitachi SU-1510 electron microscopes. ^{29}Si, ^{13}C, and ^{27}Al MAS NMR spectra were recorded on a Bruker AVANCEIII 500WB spectrometer.

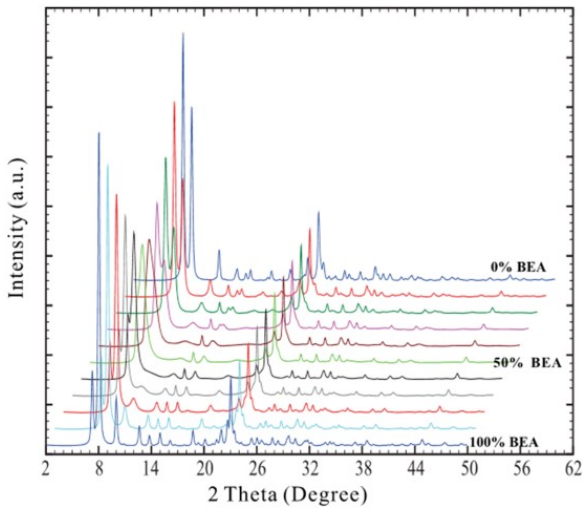

Figure S1. Simulated PXRD patterns of Beta zeolite with different ratios of polymorphs A/B.

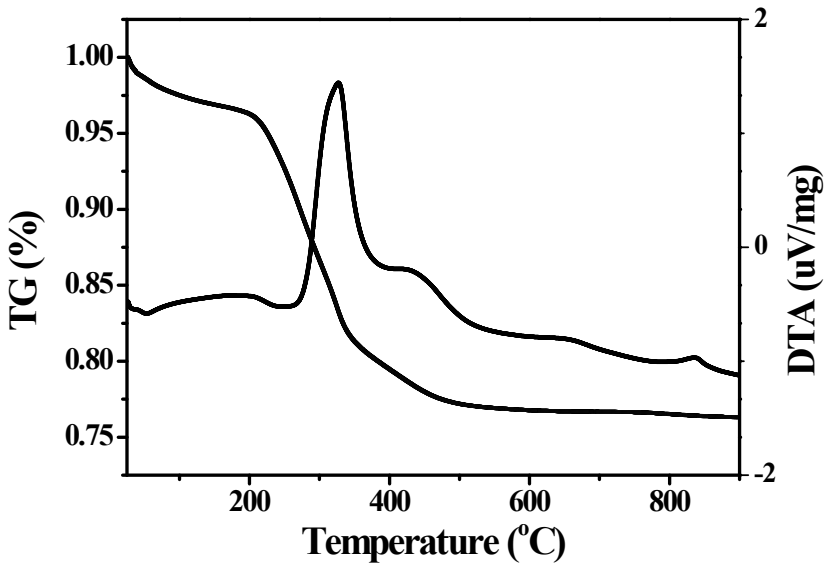

Figure S2. TG-DTA curves of as-synthesized JXM-1 sample.

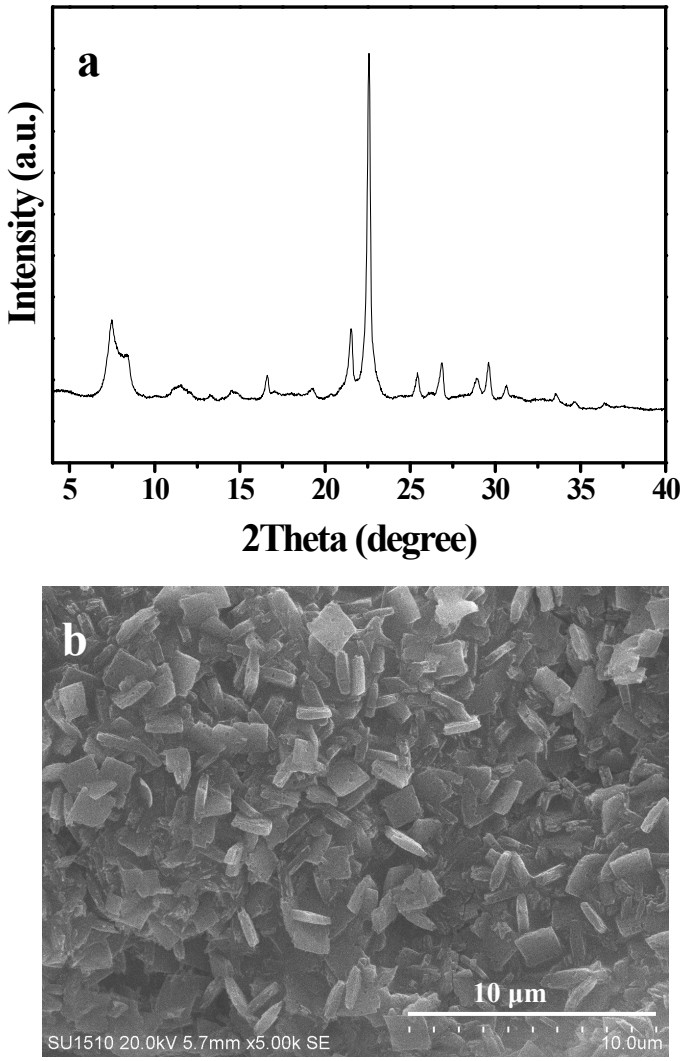

Figure S3. (a) XRD pattern and (b) SEM image of as-synthesized Al-JXM-1 sample with a Si/Al ratio of 72.

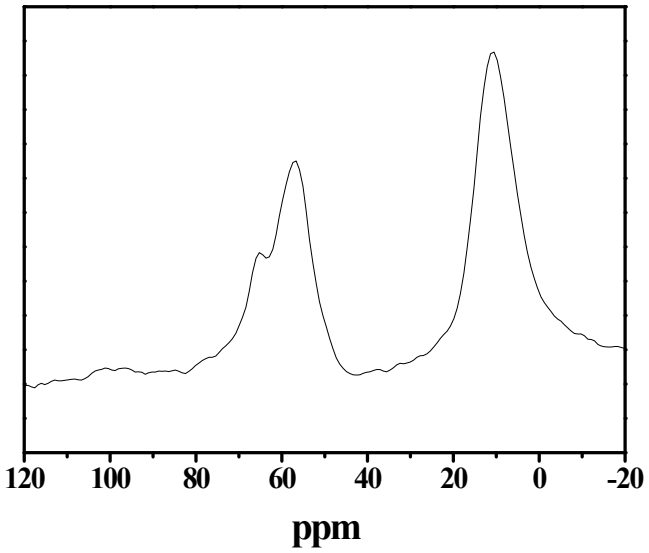

Figure S4. ^{27}Al MAS NMR spectrum of Al-JXM-1 sample.

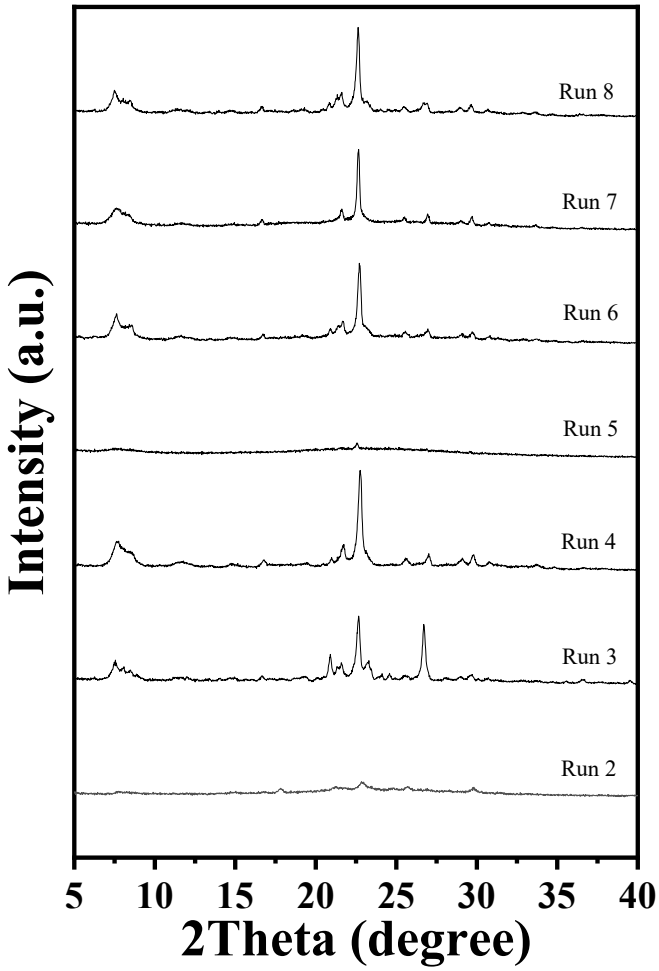

Figure S5. XRD patterns of as-synthesized samples in Run 2-8 of Table 1 under various conditions.

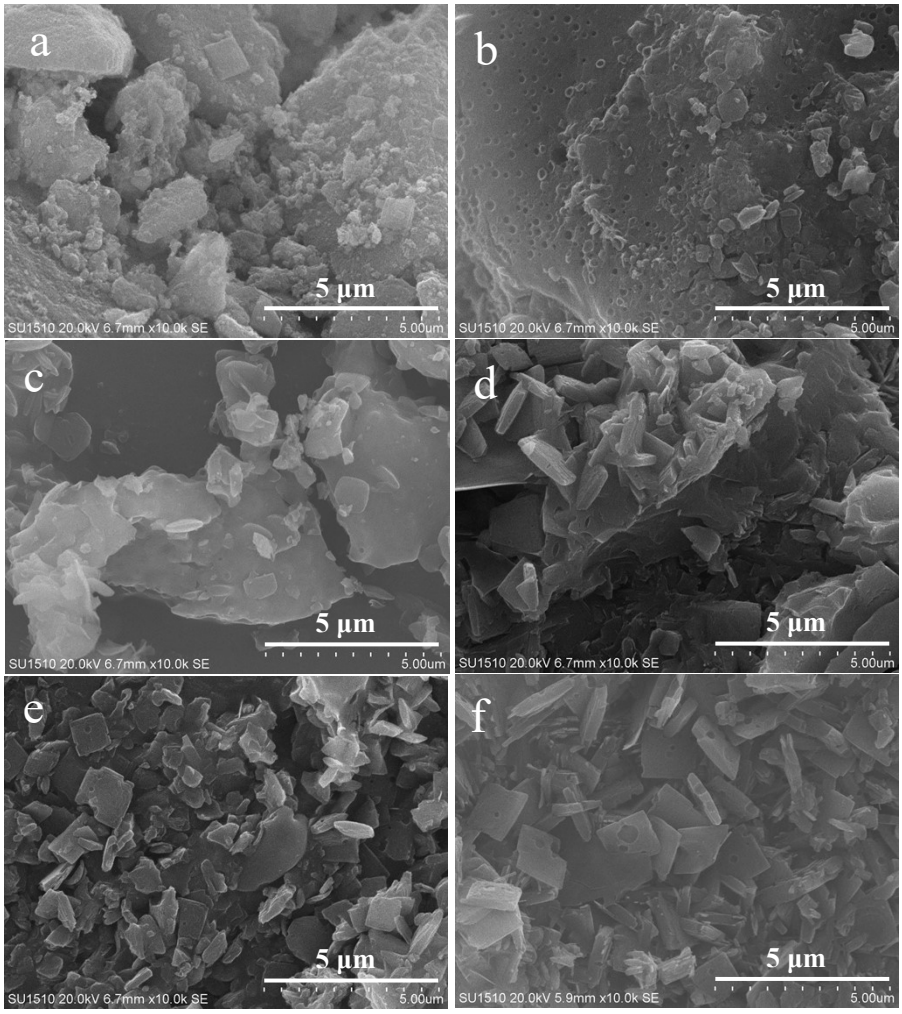

Figure S6. SEM images of JXM-1 samples crystallized for (a) 0, (b) 1, (c) 2, (d) 2.5, (e) 3, and (h) 5 d, respectively.