

Supporting Information

Hydrothermal synthesis of single-crystalline mesoporous Beta zeolite assisted with N-methyl-2-pyrrolidone

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Raw materials

All reagents were used without any further purification. Fumed silica (SiO₂) was purchased from Shenyang Chemical Company (China). NaOH and NaAlO₂ were supplied by Beijing Chemical Reagent Company (China). N-methyl-2-pyrrolidone (NMP) was obtained from Tianjin Chemical Reagent Company (China). Tetraethylammonium hydroxide (TEAOH, 25 wt %) was bought from Hangzhou Greenda Chemical Co., Ltd. (China).

Experimental

Mesoporous Beta (M-Beta) was hydrothermally synthesized from an aluminosilicate sol with the molar composition of $0.048\text{Na}_2\text{O}/0.023\text{Al}_2\text{O}_3/\text{SiO}_2/15.6\text{H}_2\text{O}/0.636\text{TEAOH}/\text{NMP}$. In a typical synthesis, 0.04 g of NaOH and 0.075 g of NaAlO_2 were dissolved into 7.5 g of TEAOH (25 wt. % aqueous solution), afterwards 2 g of NMP and 1.2 g of fumed silica were added in turn. The resultant sol was transferred into an autoclave and crystallized at 140 °C for 12 h. After cooling down at room temperature for 6 h, the mixture was further recrystallized for 48 h (140 °C). Finally, the product was collected by filtration, dried at 70 °C, and then calcined at 550 °C for 6 h to remove the organic template. For comparison, conventional Beta zeolite was synthesized in the absence of NMP by a similar procedure.

H form Beta zeolites were achieved through ion exchange of calcined samples with 1 M NH_4NO_3 solution under 80 °C followed by calcinations (550 °C, 6 h).

Characterization

X-ray diffraction (XRD) data were recorded on a Rigaku D/MAX-2550 diffractometer (50 kV, 200 mA) using Cu $K\alpha$ Radiation ($\lambda=1.5418 \text{ \AA}$). The morphologies of samples were performed on a JEOL JSM-6700F scanning electron microscopy (SEM) and JEOL JSM-3010 transmission electron microscopy (TEM). The spectra of solid-state ^{13}C and ^{27}Al NMR were collected on Varian Infinity Plus 400 spectrometer. Nitrogen absorption-desorption isotherms were tested on a Micromeritics ASAP 2020M instrument at 77 K. The specific surface areas were

evaluated employing the Brunauer-Emmett-Teller (BET) equation, and the external surface area was calculated from t-plot method. The pore size distribution of mesopores was obtained by Barrett-Joyner-Halenda (BJH) model. The amounts of Si and Al in zeolites were quantified by inductively coupled plasma (ICP) with a Perkin-Elmer 3300DV spectrometer. Temperature-programmed desorption of ammonia (TPD-NH₃) curve was examined on a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD). The adsorption of ammonia on the sample was performed at 100 °C for 30 min, followed by removal of physical adsorption of ammonia at 100 °C for 1.5 h in pure flowing helium.

Catalytic tests

The catalytic performances of M-Beta and conventional porous catalysts (ZSM-5, Beta and Al-MCM-41) were evaluated in aldol condensation of benzaldehyde with n-butyl alcohol and α -pinene isomerization reactions.

Aldol condensation of benzaldehyde with n-butyl alcohol reaction was performed in a three-necked flask equipped a reflux condenser under N₂ atmosphere. For a typical run, benzaldehyde (5.3 g, 0.05 mol), n-butyl alcohol (14.8 g, 0.2 mol), and catalyst (0.2 g) were mixed with continuous stirring. After being stirred for several minutes at ambient temperature (~25 °C), the reaction system was raised to and kept at 78 °C. The reaction products were collected periodically by a microsyringe, and analyzed on a gas chromatograph (GC-17A) equipped with a flame ionization detector (FID) until the composition was basically unchanged.

α -pinene isomerization reaction was carried out in a round bottom flask with a reflux condenser at atmospheric pressure. In a typical procedure, 0.10 g of catalyst and 2.0 mL of α -pinene were charged into a 25 mL flask, and kept at 70 °C for 30 min under magnetic stirring. After being cooled to the room temperature rapidly, the supernatant was collected by centrifugation, and then analyzed on a gas chromatograph (GC-17A) equipped with a flame ionization detector (FID).

Supporting Figures

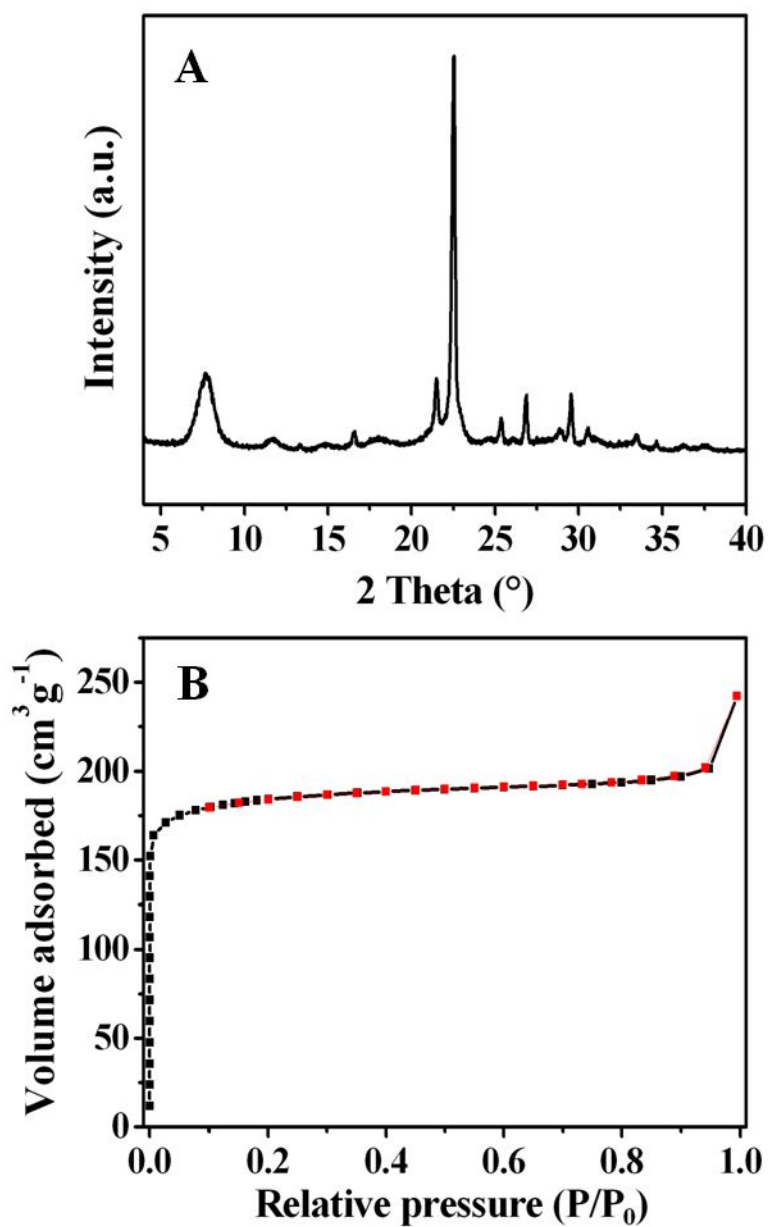


Figure S1. (A) XRD pattern and (B) N₂ adsorption-desorption isotherms of conventional Beta zeolite. Image (B) shows that no hysteresis loop emerges at moderate relative pressures, reflecting the lack of mesoporosity in conventional Beta zeolite.

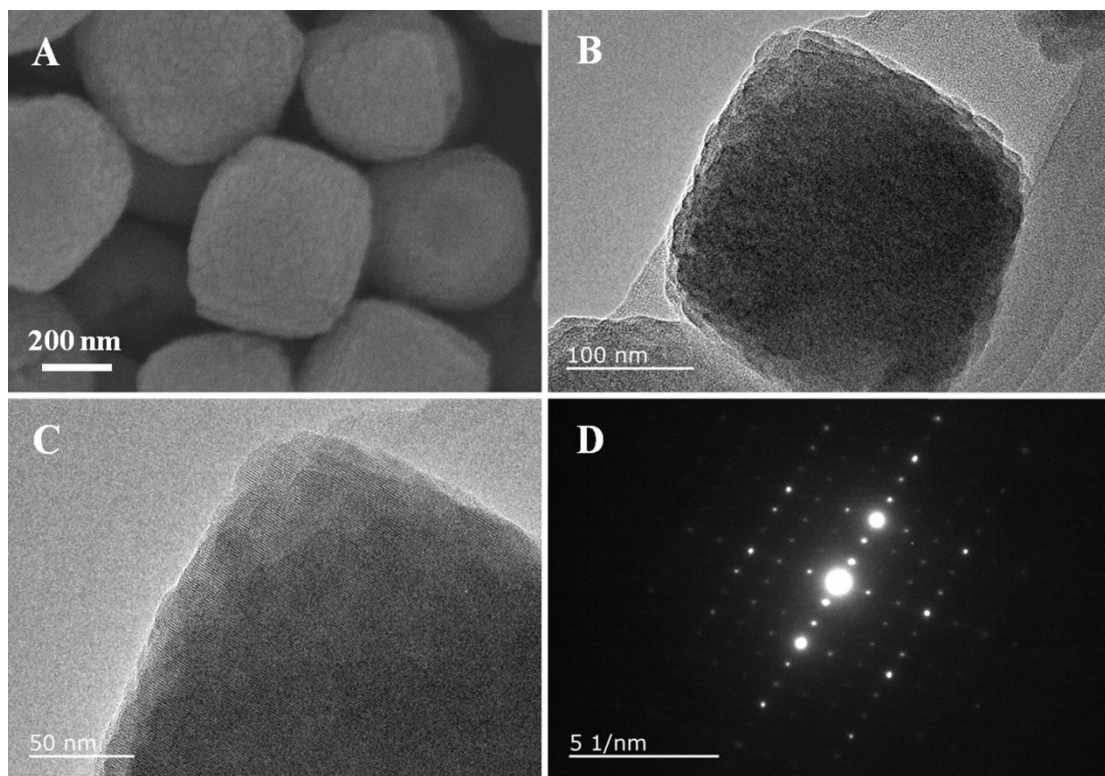


Figure S2. (A) SEM (B) TEM (C) high resolution TEM images of conventional Beta zeolite. (D) Corresponding SAED pattern of image (C). Taken together, these results confirm that conventional Beta zeolites are densely monocrystals, in which mesopore structures barely exist, being in good agreement with N₂ adsorption-desorption isotherms.

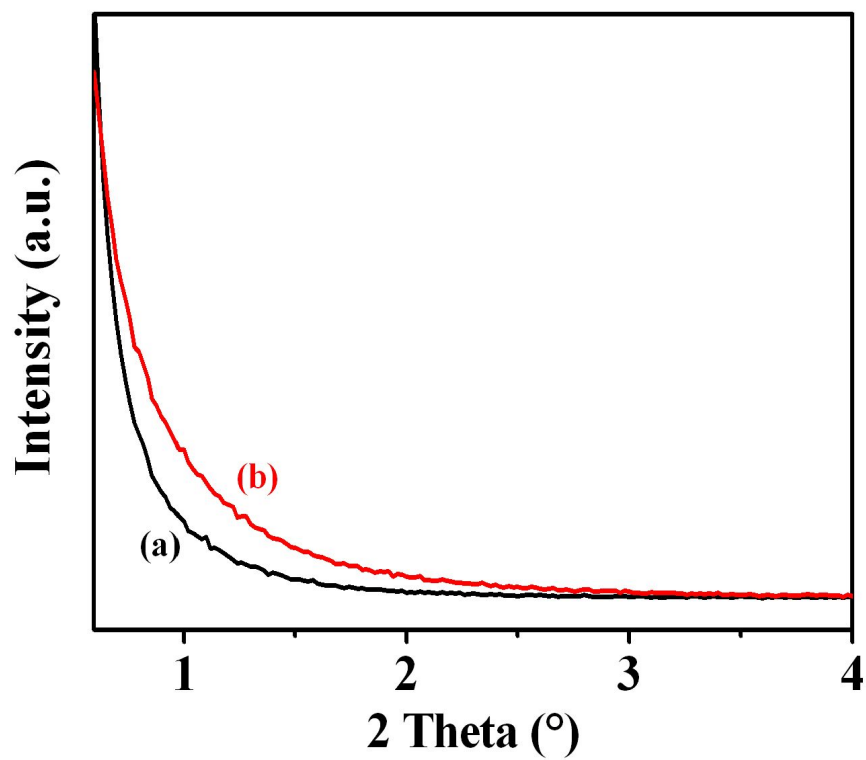


Figure S3. Small-angle XRD patterns of (a) conventional Beta and (b) M-Beta samples recorded in the 2-theta range of 0.6-4 degrees.

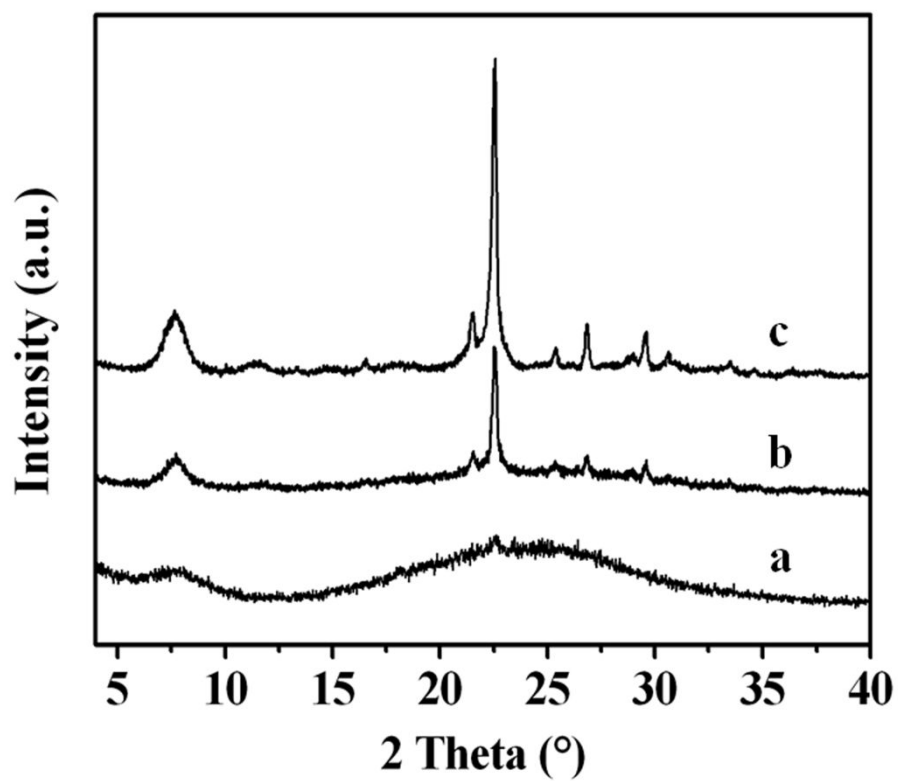


Figure S4. XRD patterns of M-Beta samples crystallized at 140 °C for (a) 3 h (b) 6 h and (c) 12 h.

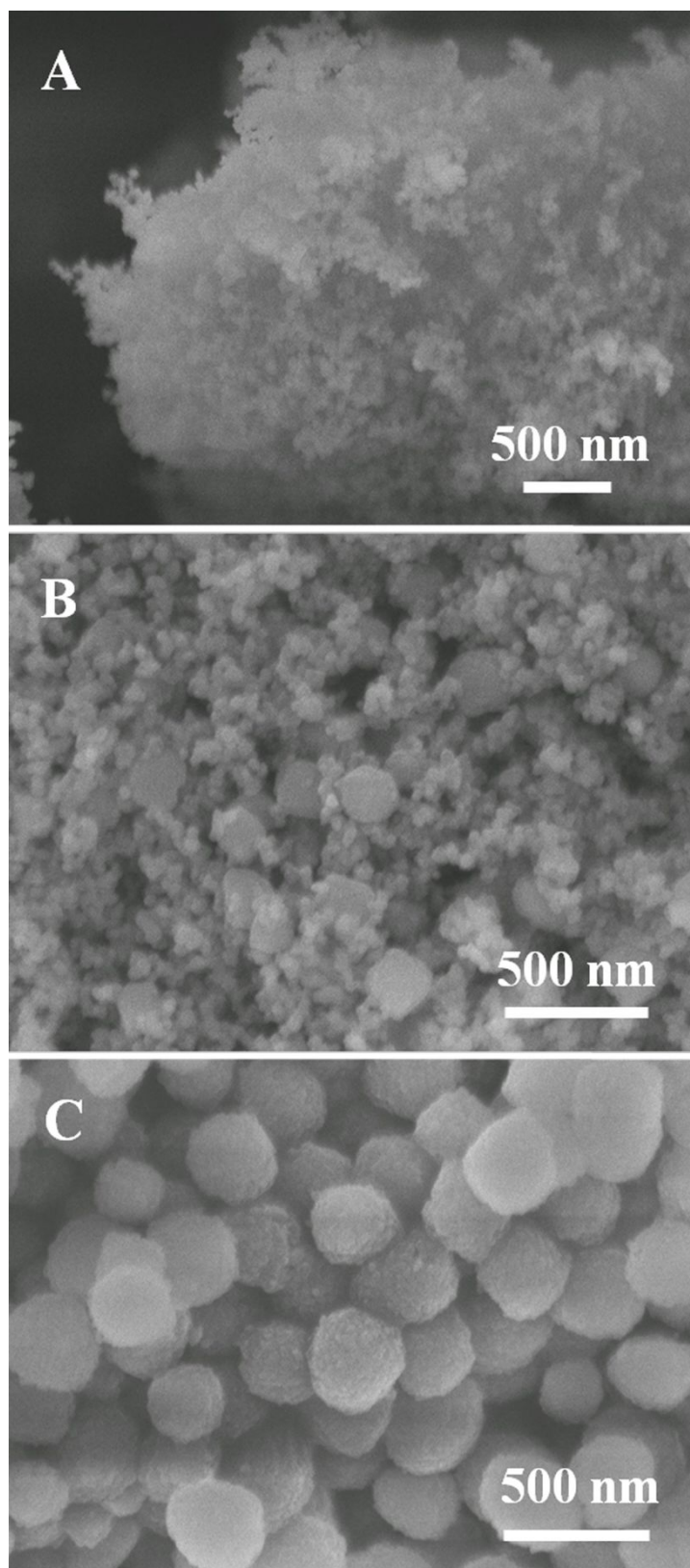


Figure S5. SEM images of M-Beta samples crystallized at 140 °C for (A) 3 h (B) 6 h and (C) 12 h.

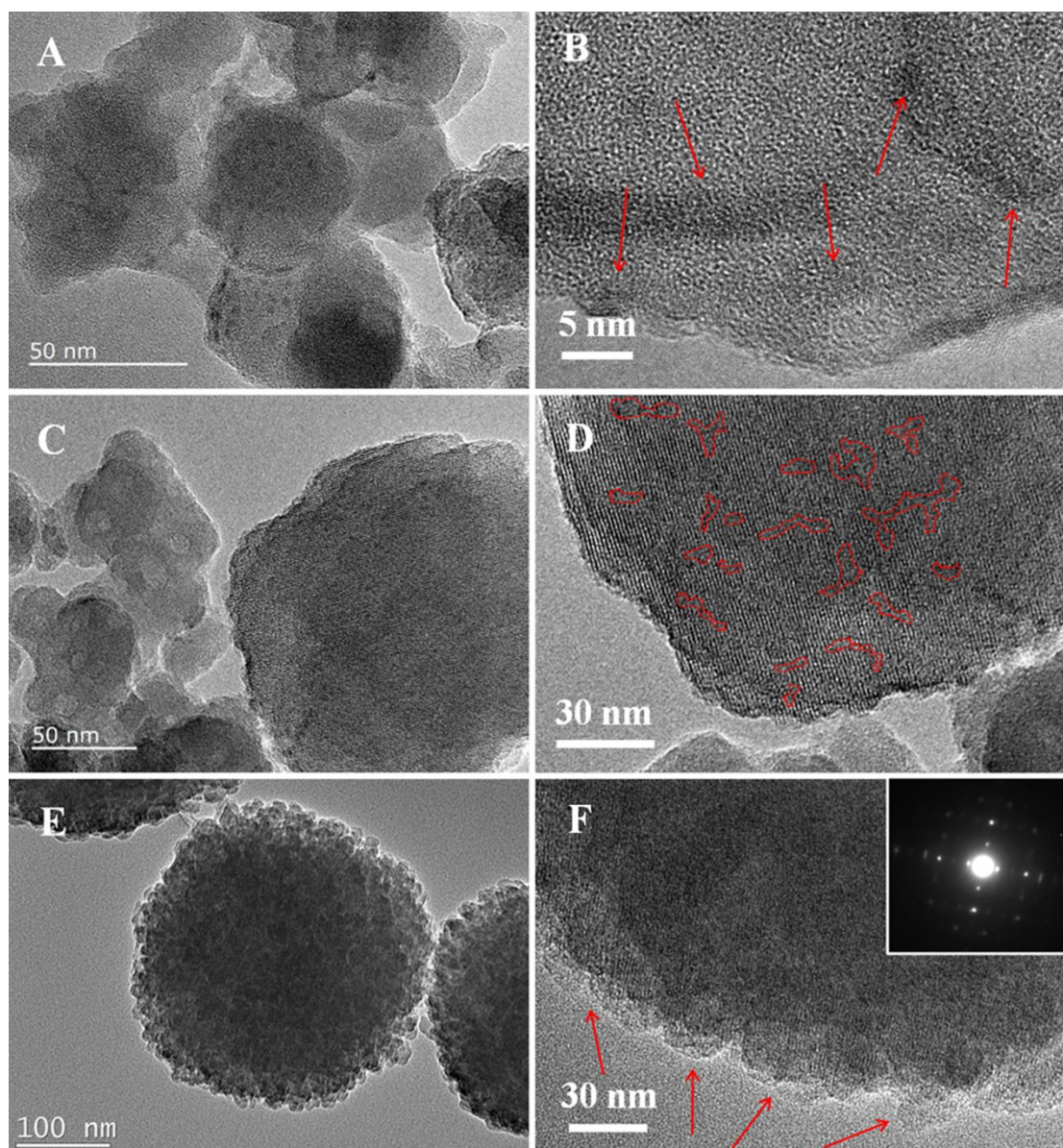


Figure S6. TEM images of M-Beta samples crystallized at 140 °C for (A) 3 h (C) 6 h and (E) 12 h. High resolution TEM images of M-Beta samples crystallized at 140 °C for (B) 3 h (D) 6 h and (F) 12 h. Inset in (F) shows the corresponding SAED pattern. Image (B) shows that there are some Beta nuclei (marked with red arrows) in the sample crystallized for 3 h. Image (D) reveals that quasi-spherical Beta crystal (crystallized for 6 h) is totally a dense single crystal, in which small wormlike intracrystalline mesopores (partly outlined with red lines) exist. Image (F) suggests that mesoporous Beta crystal (crystallized for 12 h) also exhibits a single-crystalline feature, where some amorphous components (marked with red arrows) can be detected, indicating the relatively poor crystallinity of zeolite framework.

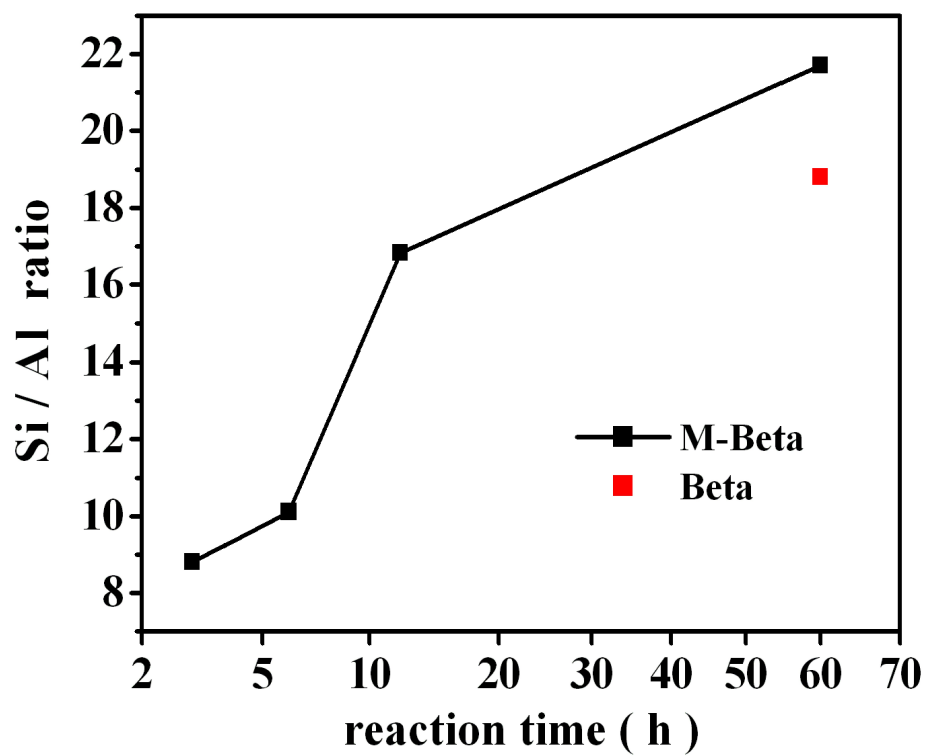


Figure S7. Si/Al ratios of (black) Beta products achieved with different reaction time in the presence of NMP and (red) conventional Beta.

Table S1. Textural parameters of various catalysts.

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)
ZSM-5	15.6	336	65	—	0.15	0.11
Beta	18.8	601	82	—	0.35	0.25
Al-MCM-41	41.6	807	807	2.7	0.88	—
M-Beta	21.7	770	203	9.2	0.59	0.28

^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.

Table S2. Acid strength distributions of M-Beta and conventional Beta zeolites.

Sample	Total acid ($\mu\text{mol g}^{-1}$)	Weak acid ($\mu\text{mol g}^{-1}$)	Medium-strong acid ($\mu\text{mol g}^{-1}$)
M-Beta	1077	615	462
Beta	996	595	401