Supporting Information

Steam-Assisted Crystallization of Highly Dispersed Nanosized Hierarchical Zeolites from Solid Raw Materials and Their Catalytic Performance in Lactide Production

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This Supporting Information Includes:

Details for experiments, characterizations and catalytic tests

Figures S1-S31

Tables S1-S2

Experimental Details

Materials

All chemicals and reagents were supplied by commercial suppliers and used without further purification: Solid silica gel (SiO_2, 100%, Qingdao Haiyang Chemical Reagent Co, Ltd.), sodium aluminate ($NaAlO_2$, CP, Sinopharm Chemical Reagent Co, Ltd.) tetraethyl ammonium bromide (TEABr, AR, 99%, Tianjin Guangfu Chemical Reagent Co, Ltd.), Tetrapropyl ammonium bromide (TPABr, AR, 99%, Tianjin Guangfu Chemical Reagent Co, Ltd.), sodium hydroxide (NaOH, AR, 98%, Tianjin Yongsheng Chemical Reagent Co, Ltd.), H-Beta zeolite (Si/Al = 12.5, Alfa Aesar Company), H-ZSM-5 zeolite (Si/Al = 20, JALON Micro-nano Co, Ltd.), tetraethylorthosilicate (TEOS, 28 wt%, Tianjin Fuchen Chemical Reagent Co, Ltd.), tetrapropylammonium hydroxide solution (TPAOH, 25 wt%, Sinopharm Chemical Reagent Co, Ltd.), lactic acid (LA, 105 wt%, Zhejiang Hisun Biomaterials Company), toluene (99.5%, Tianjin Xintong Chemical Reagent Co, Ltd.).

Synthesis of nanosized hierarchical Beta-x-BM-SAC zeolites with various Si/Al ratios

A mixture with a molar composition of 1.0 SiO_2: (0.0125–0.05) Al_2O_3: (0.117–0.167) Na_2O: 0.28 TEABr: 3 H_2O was set for the synthesis of nanosized hierarchical Beta with different Si/Al ratios. Details synthetic conditions are listed in Table S1. Typically, solid silica gel, $NaAlO_2$, TEABr, NaOH, H-Beta and H_2O were mixed into ball-milling jar. The ball milling process was carried out with a planetary ball mill (QM-3SP04, Nanjing university instrument factory) at 30 HZ. After mechanical mixing for 5 h, 1.0 g of the powder mixture was transferred into a 50 mL Teflon liner, and 2.0 mL water was added into the bottom of the liner without contacting the powder mixture. The crystallization was conducted at 140 ^oC for 72 h under static conditions. The as-synthesized solid products were centrifuged, washed with water and ethanol several times, and then dried at 80 ^oC in the oven overnight, followed by calcination at 550 ^oC for 6 h. The as-prepared samples are denoted as Beta-x-BM-SAC, where x indicates the Si/Al ratio. To obtain the H-type Beta, the samples were ion-exchanged three times in 1 M NH_4NO_3

solution at 80 ºC for 3 h, and then calcined at 500 ºC for 6 h. The obtained samples are denoted as Beta-10-BM-SAC, Beta-20-BM-SAC, and Beta-40-BM-SAC with Si/Al ratios of 10, 20, and 40, respectively.

Synthesis of Beta-20-BM-SAC zeolites with various mixing methods and crystallization approaches

To investigate the effect of mixing methods and crystallization approaches on the morphologies and structures of as-prepared Beta zeolites, the molar composition of the mixture was set to 1.0 SiO_2: 0.025 Al_2O_3: 0.133 Na_2O: 0.28 TEABr: 3 H_2O. The synthesis procedure was exactly the same as above, except that the crystallization approach was adjusted as heating treatment at 140 ºC for 72 h. The as-prepared sample is denoted as Beta-20-BM-HT, where BM indicates the ball-milling and HT indicates the heating treatment. When the mechanical ball-milling was replaced by the manual grinding for 20 min, then followed the steam-assisted crystallization at 140 ºC for 72 h, the as-prepared sample is denoted as Beta-20-MG-SAC. Similarly, Beta-20-MG-HT sample was prepared via heating treatment from manual grinded solid mixture, and the condition of HT and MG was exactly the same as above.

Synthesis of Beta-20-BM-SAC-y zeolites with various H_2O/SiO_2 ratios

To investigate the effect of the H_2O/SiO_2 ratios on the morphologies and structures of as-prepared Beta zeolites, the molar composition of the mixture was set to 1.0 SiO_2: 0.025 Al_2O_3: 0.133 Na_2O: 0.28 TEABr: (0-6) H_2O for the synthesis of Beta-20-BM-SAC with different H_2O/SiO_2 ratios. The synthesis procedure was exactly the same as above, except that the H_2O/SiO_2 ratios were adjusted from 6 to 1.5 and 0. The as-prepared samples are denoted as Beta-20-BM-SAC -y, where y indicates the H_2O/SiO_2 ratios. After ion-exchange and calcination, the obtained samples are denoted as Beta-20-BM-SAC -6, Beta-20-BM-SAC-1.5, and Beta-20-BM-SAC-0 with H_2O/SiO_2 ratios of 6, 1.5 and 0, respectively. The detailed synthesis conditions are listed in Table S1.

Synthesis of Beta-20-BM-SAC-z zeolites with various seed additions

To investigate the effect of amount of seed additions on the morphologies and structures of as-prepared Beta zeolites, the molar composition of the mixture was set to

1.0SiO_2: 0.025 Al_2O_3: 0.133 Na_2O: 0.28 TEABr: 3 H_2O for the synthesis of Beta-20-BM-SAC with different amount of seed additions. The synthesis procedure was exactly the same as above, except that the seed additions were adjusted from 20 wt% to 5 wt% and 0 wt%. The as-prepared samples are denoted as Beta-20-BM-SAC-z, where z indicates the seed addition. After ion-exchange and calcination, the obtained samples are denoted as Beta-20-BM-SAC-20wt% and Beta-20-BM-SAC-5wt%, and Beta-20-BM-SAC-0wt% with seed addition of 20 wt%, 5 wt% and 0 wt%, respectively. The detailed synthesis conditions are listed in Table S1.

Synthesis of Beta-20-BM-SAC-m zeolites under various ball-milling time

To investigate the effect of the ball-milling time on the morphologies and structures of as-prepared Beta zeolites, the molar composition of the mixture was set to 1.0 SiO_2: 0.025 Al_2O_3: 0.133 Na_2O: 0.28 TEABr: 3 H_2O for the synthesis of Beta-20-BM-SAC with different ball-milling time. The synthesis procedure was exactly the same as above, except that the ball-milling time was adjusted to 1/3 h, 1 h and 8 h. The as-prepared samples are denoted as Beta-20-BM-SAC-m, where m indicates the ball-milling time. After ion-exchange and calcination, the obtained samples are denoted as Beta-20-BM-SAC-8, Beta-20-BM-SAC-1, and Beta-20-BM-SAC-1/3 with ball-milling time of 8 h, 1 h and 1/3 h, respectively. The detailed synthesis conditions are listed in Table S1.

Synthesis of nanosized hierarchical ZSM-5-20-BM-SAC zeolite

A mixture with molar composition of 1.0SiO_2: 0.025 Al_2O_3: 0.083 Na_2O: 0.28 TPABr: 3 H_2O was set for the synthesis of nanosized hierarchical ZSM-5 zeolites. Details synthetic conditions are listed in Table S1. Typically, solid silica gel, $NaAlO_2$, TPABr, NaOH, H-ZSM-5 and H_2O were mixed into ball-milling jar. After mechanical mixing for 5 h, 1.0 g of the powder mixture was transferred into a 50 mL Teflon liner, and 2.0 mL water was added into the bottom of the liner without contacting the powder mixture. The crystallization was conducted at 160 °C for 72 h under static conditions. The as-synthesized solid products were centrifuged, washed with water and ethanol several times, and then dried at 80 ^oC in the oven overnight, followed by calcination at 550 ^oC for 6 h. To obtain the H-type ZSM-5, the sample was ion-exchanged three times

in 1 M NH_4NO_3 solution at 80 ^oC for 3 h, and then calcined at 500 ^oC for 6 h. The obtained sample is denoted as ZSM-5-20-BM-SAC.

Synthesis of conventional ZSM-5 zeolite under hydrothermal condition

A mixture with a molar composition of 1.0 SiO_2: 0.30 TPAOH: 0.025 Al_2O_3: 0.015 Na_2O: 50 H_2O was set for the synthesis of conventional ZSM-5 zeolite under hydrothermal condition. Typically, TEOS, TPAOH, and deionized water were mixed at room temperature under stirring until TEOS was hydrolyzed completely, followed by the addition of $NaAlO_2$ and NaOH. The gel mixture was kept on stirring for 1 h and then transferred into a Teflon liner for crystallization at 170 °C for 72 h under static conditions. The next procedure was exactly the same as ZSM-5-20-BM-SAC, and the obtained sample is denoted as ZSM-5-20-Con.

Characterizations

The crystallinity and phase purity of the as-prepared samples were carried out by powder X-ray diffraction (PXRD) on a Rigaku D-Max 2550 diffractometer using Cu Kα radiation (λ = 1.5418 Å). The crystal sizes and morphologies were measured by scanning electron microscopy (SEM) using a JSM-7800F electron microscope, low-voltage high-resolution scanning electron microscopy (LV-HR-SEM) using a JSM-7900F electron microscope, and transmission electron microscopy (TEM) using a Tecnai G2 S-Twin F20 electron microscope. High-resolution TEM (HRTEM) and scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) were obtained using JEM-2100F field emission electron microscope. High-resolution scanning transmission electron microscopy-secondary electron imaging (STEM-SEI) was obtained using JEOL JEM-F200 electron microscope. The electron tomography was collected on a JEOL JEM-F200 microscope equipped with a 200 kV field-emission electron gun. Data collection and following reconstruction, visualization was done assisted with TEMography software package. The Si/Al ratios were determined with inductively coupled plasma (ICP) analyses carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Nitrogen adsorption/desorption measurements were performed on a Micromeritics 2020 analyer at 77.35 K after the samples were

degassed at 350 ^{o}C under vacuum. Solid-state ^{29}Si NMR and ^{27}Al NMR experiments were determined on Bruker Avance Neo 600Mz WB spectrometer with BBO MAS probe operating at a magnetic field strength of 14.1 T. The temperature-programmed desorption of ammonia (NH_3-TPD) experiments were performed using a Micromeritics AutoChemII 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. Proton nuclear magnetic resonance spectroscopy (^{1}H-NMR) analysis was conducted on Bruker Varian 300.

Catalytic Tests

In a typical reaction, 1.0 g of 105 wt%, 1.0 g zeolite catalyst and 20 mL of toluene were added in a 25 mL round bottom flask under magnetic stirring. On top of the round bottom flask, a phase-settler/solvent reflux trap was installed, filled beforehand with the same reaction solvent as in the flask (approximate volume of 20 mL). On top of the phase-settler, a condenser was put in place via ground joints. This setup assures reflux of toluene while trapping water. The solvent floats on top and moves to the flask while the water sinks to the bottom of the trap where it accumulates. The oil bath was held at 140 ^{o}C to assure reflux of toluene. Under continuous stirring, 0.4 mL of the products was taken out at different period varying between 0.2 h and 5 h. The withdrawn mixture was added with excess acetonitrile, and placed for three hours. Then the mixture was filtered with Syringe Filter (PTFE, 0.2 μm) to isolate the solid zeolites. The filtered solution was dried under vacuum at room temperature to remove toluene and acetonitrile solvents for ^{1}H-NMR analysis.

Figures

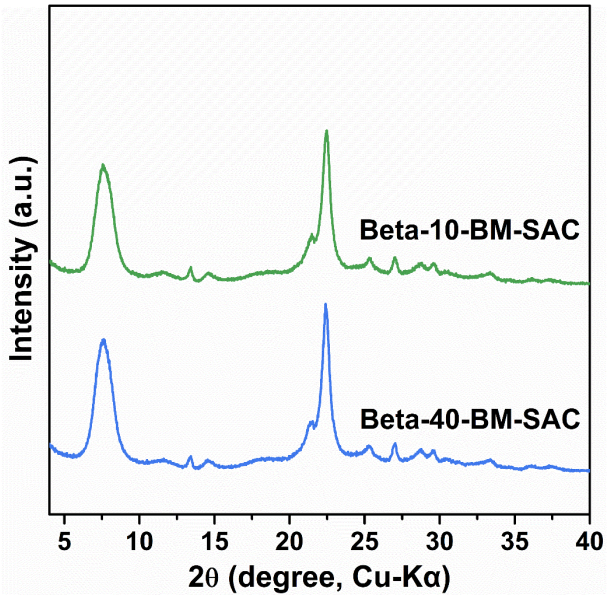

Fig. S1 PXRD patterns of nanosized hierarchical Beta zeolites synthesized with different Si/Al ratios.

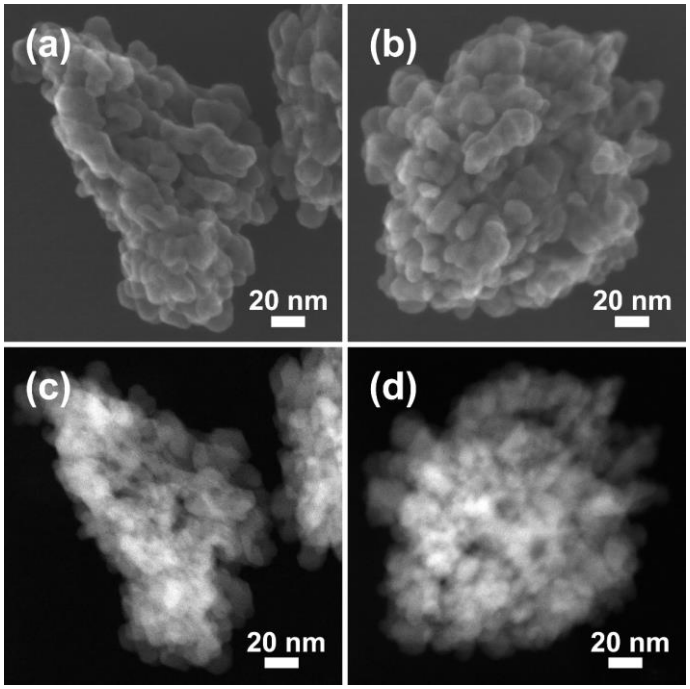

Fig. S2 (a, b) High-magnification STEM-SEI images and (c, d) high-magnification STEM-HAADF images of nanosized hierarchical Beta zeolites: (a, c) Beta-10-BM-SAC and (b, d) Beta-40-BM-SAC.

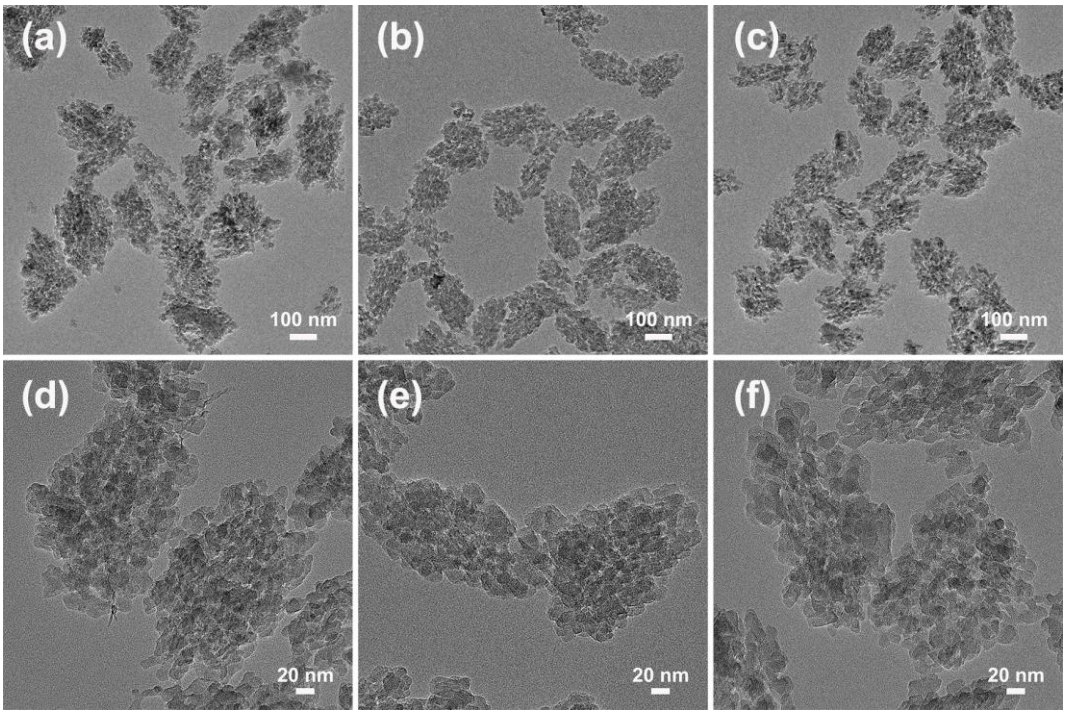

Fig. S3 (a, b, c) Low-magnification TEM images and (d, e, f) high-magnification TEM images of nanosized hierarchical Beta zeolites with different Si/Al ratios: (a, d) Beta-10-BM-SAC, (b, e) Beta-20-BM-SAC, and (c, f) Beta-40-BM-SAC.

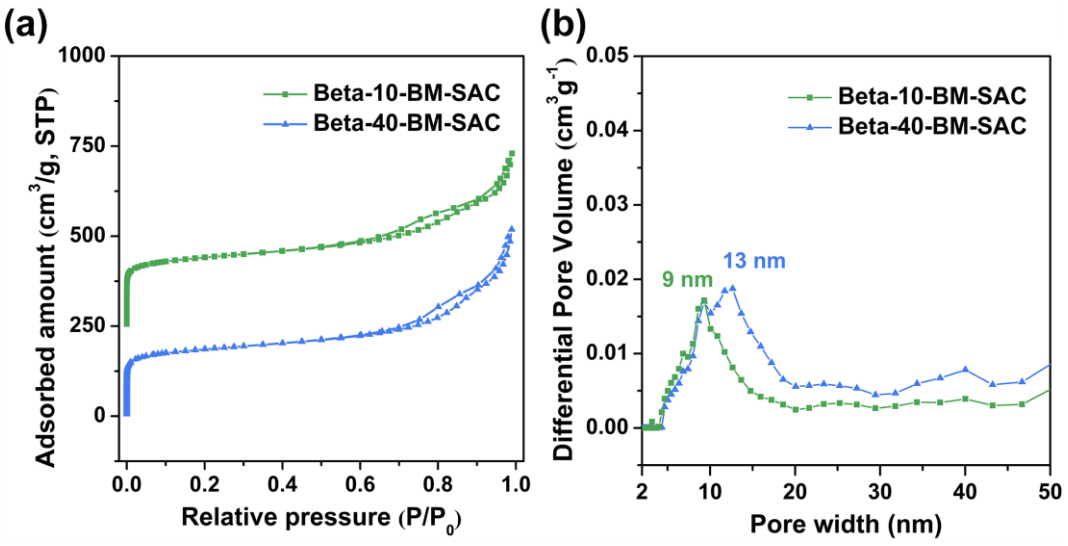

Fig. S4 (a) N_2 adsorption/desorption isotherms and (b) Pore size distributions of nanosized hierarchical Beta zeolites with different Si/Al ratios.

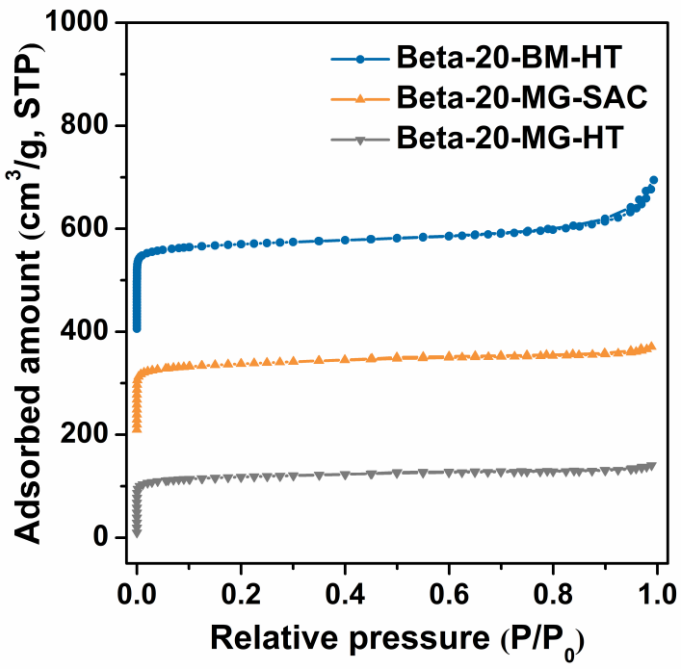

Fig. S5 N_2 adsorption/desorption isotherms of Beta zeolites prepared by different synthesis methods.

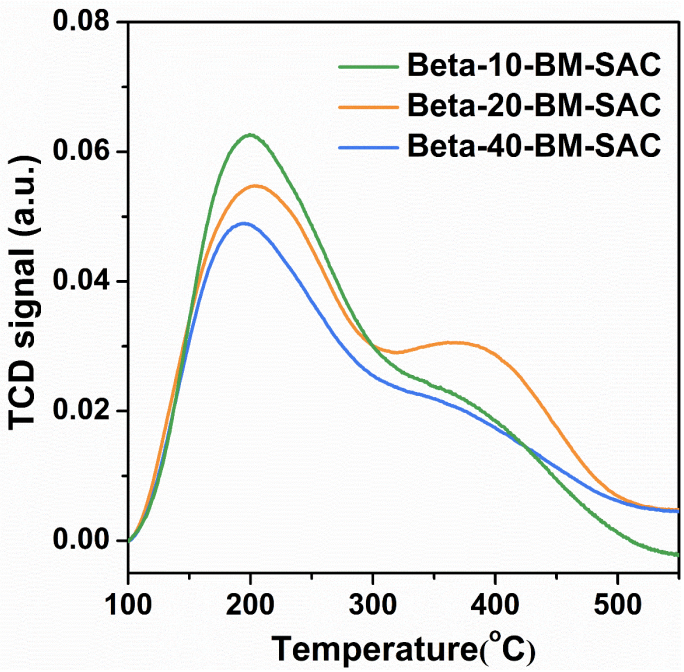

Fig. S6 NH_3-TPD profiles of nanosized hierarchical Beta zeolites with different Si/Al ratios.

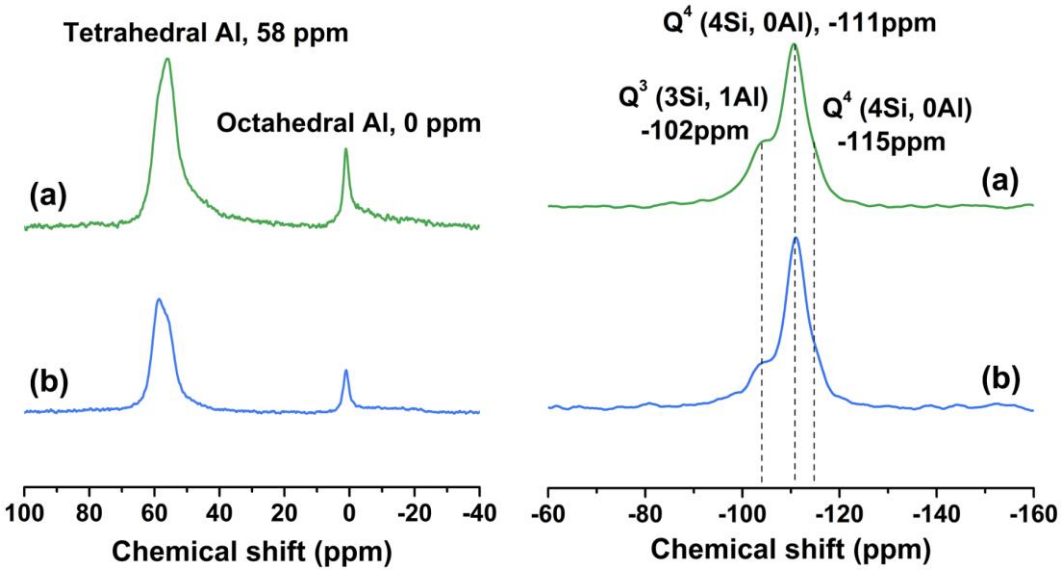

Fig. S7 ^{27}Al (left) and ^{29}Si (right) solid-state MAS NMR spectra for (a) Beta-10-BM-SAC and (b) Beta-40-BM-SAC.

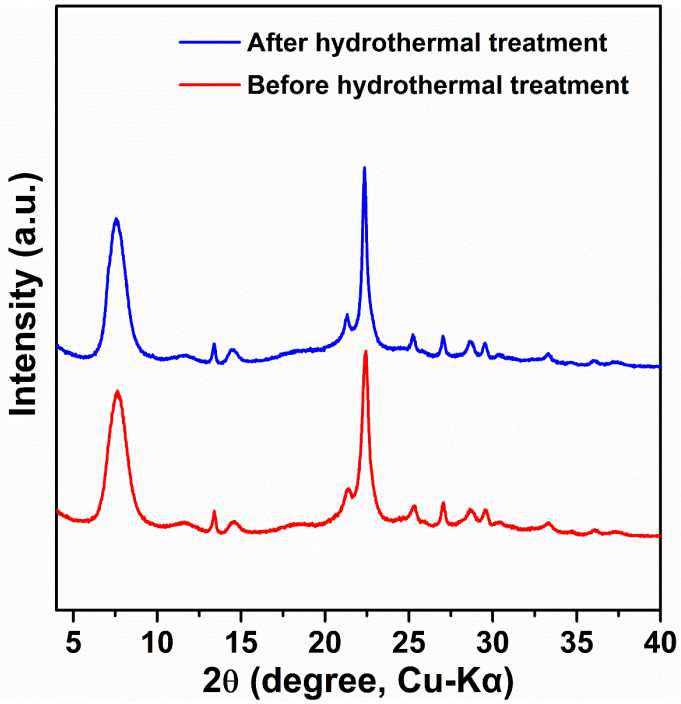

Fig. S8 XRD patterns of Beta-20-BM-SAC before and after 10% steam treatment at 750 °C for 3 h.

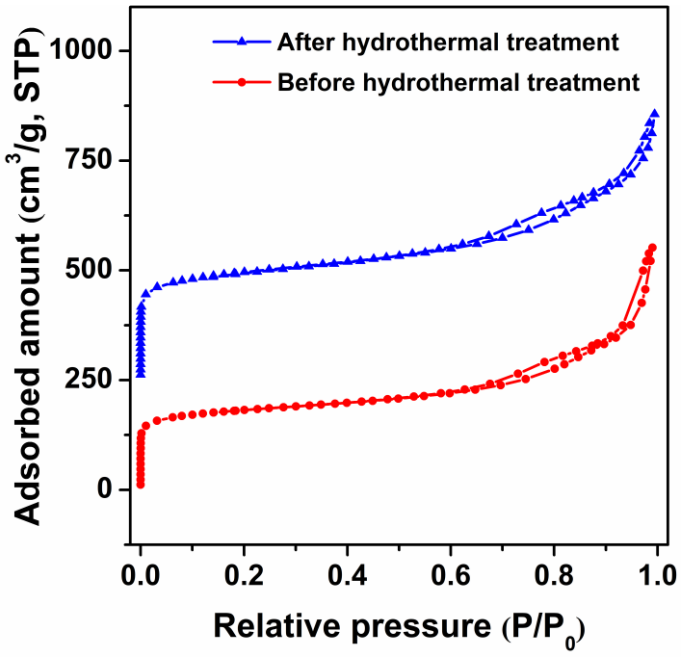

Fig. S9 N_2 adsorption/desorption isotherms of Beta-20-BM-SAC before and after 10% steam treatment at 750 °C for 3 h.

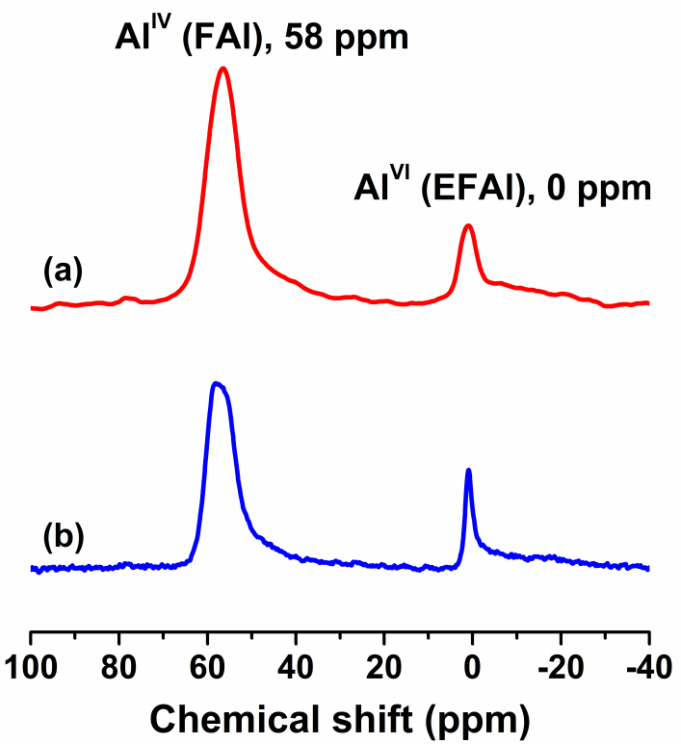

Fig. S10 ^{27}Al solid-state MAS NMR spectra of Beta-20-BM-SAC before (a) and after (b) 10% steam treatment at 750 °C for 3 h.

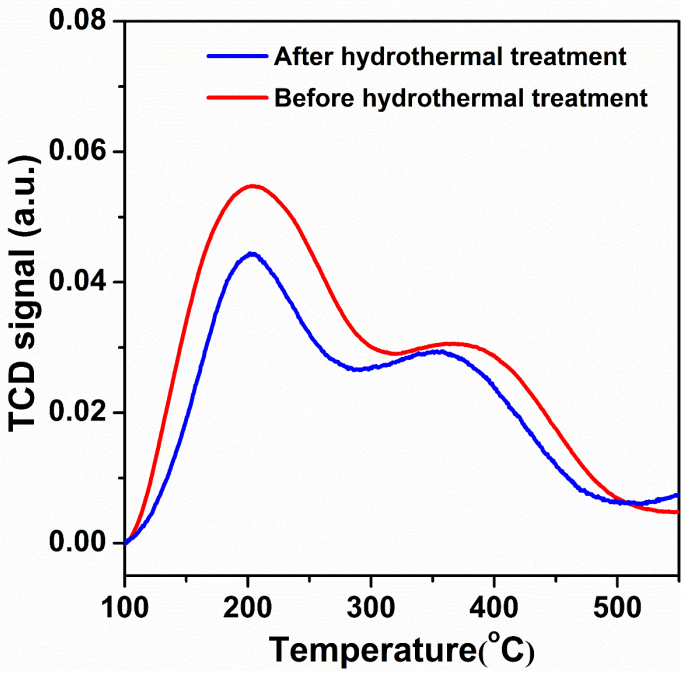

Fig. S11 NH_3-TPD profile of Beta-20-BM-SAC before and after 10% steam treatment at 750 °C for 3 h.

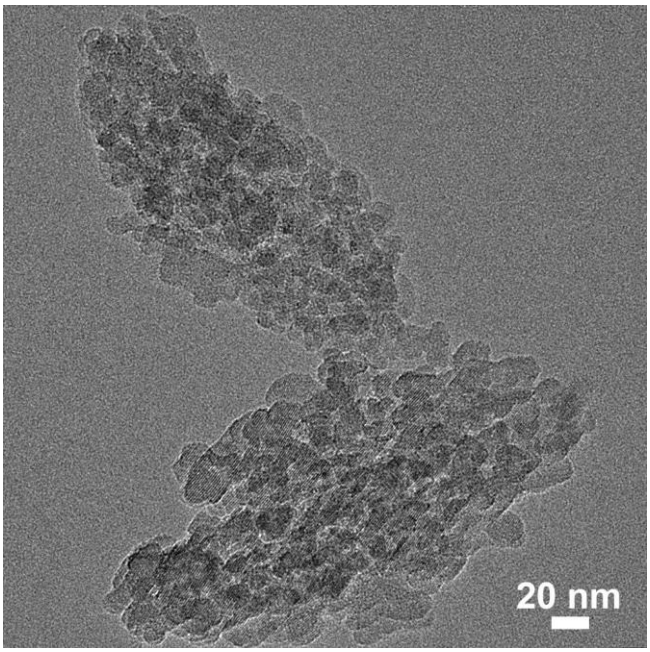

Fig. S12 TEM image of Beta-20-BM-SAC after 10% steam treatment at 750 °C for 3 h.

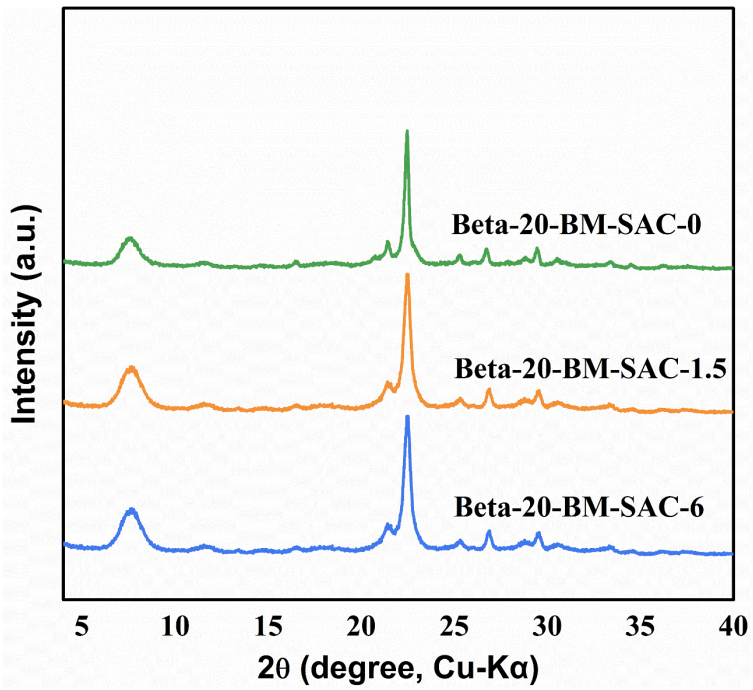

Fig. S13 PXRD patterns of Beta zeolites synthesized with different H_2O/SiO_2 ratios.

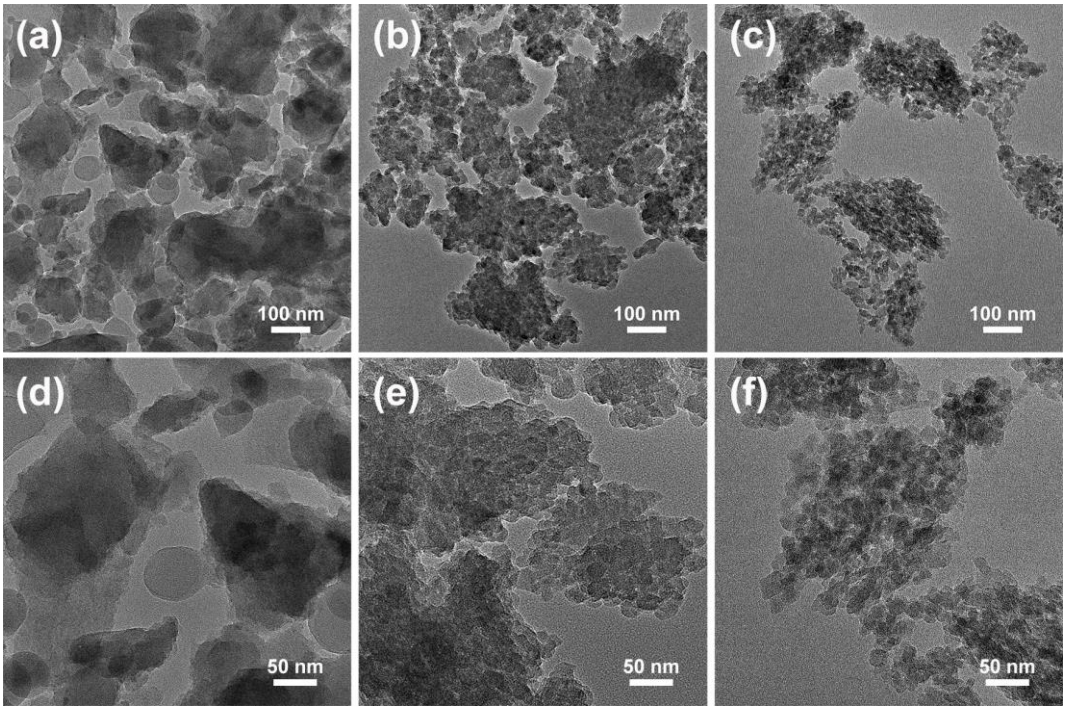

Fig. S14 TEM images of Beta zeolites synthesized with different H_2O/SiO_2: (a, d) Beta-20-BM-SAC-0, (b, e) Beta-20-BM-SAC-1.5, and (c, f) Beta-20-BM-SAC-6.

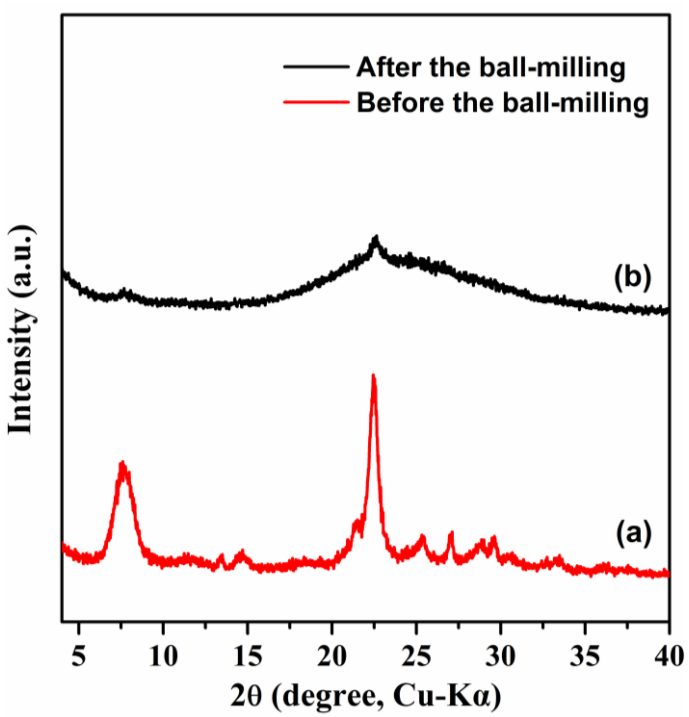

Fig. S15 XRD patterns of Beta-Com before and after the ball-milling for 5 h.

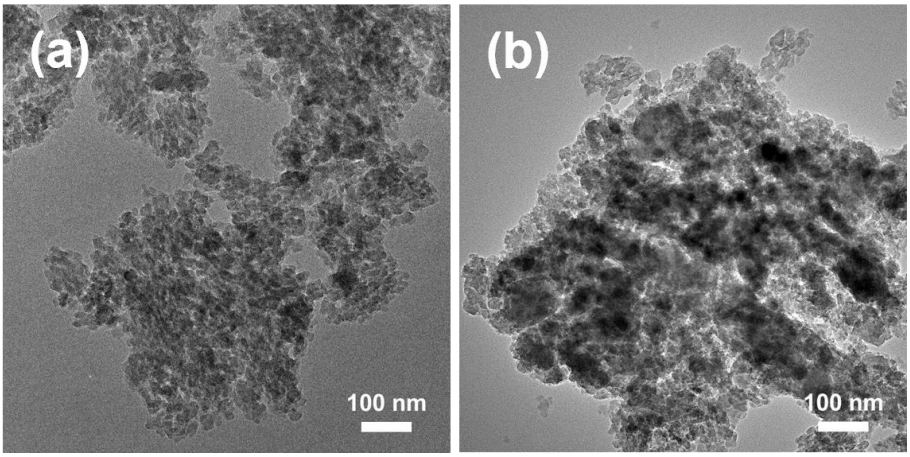

Fig. S16 TEM images of Beta-Com before (a) and after (b) the ball-milling for 5 h.

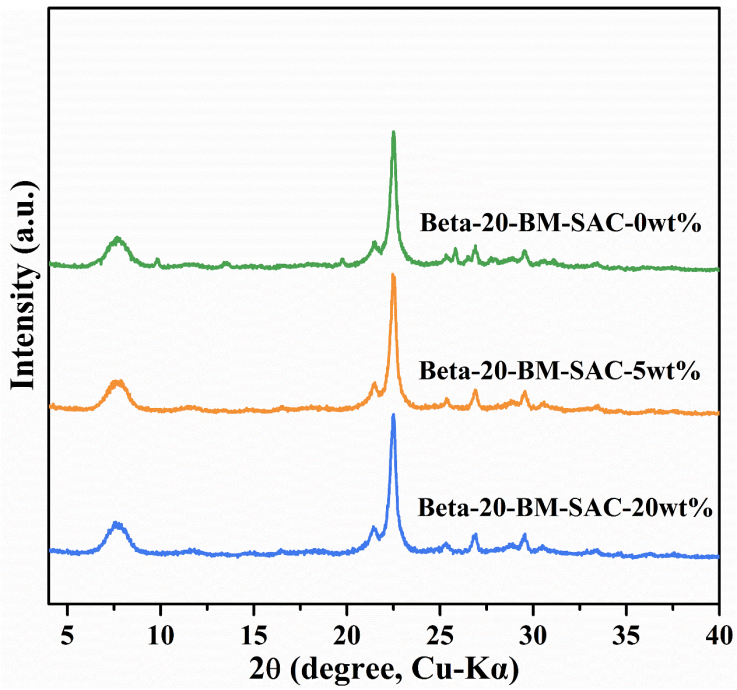

Fig. S17 PXRD patterns of Beta zeolites synthesized with different amount of seed addition.

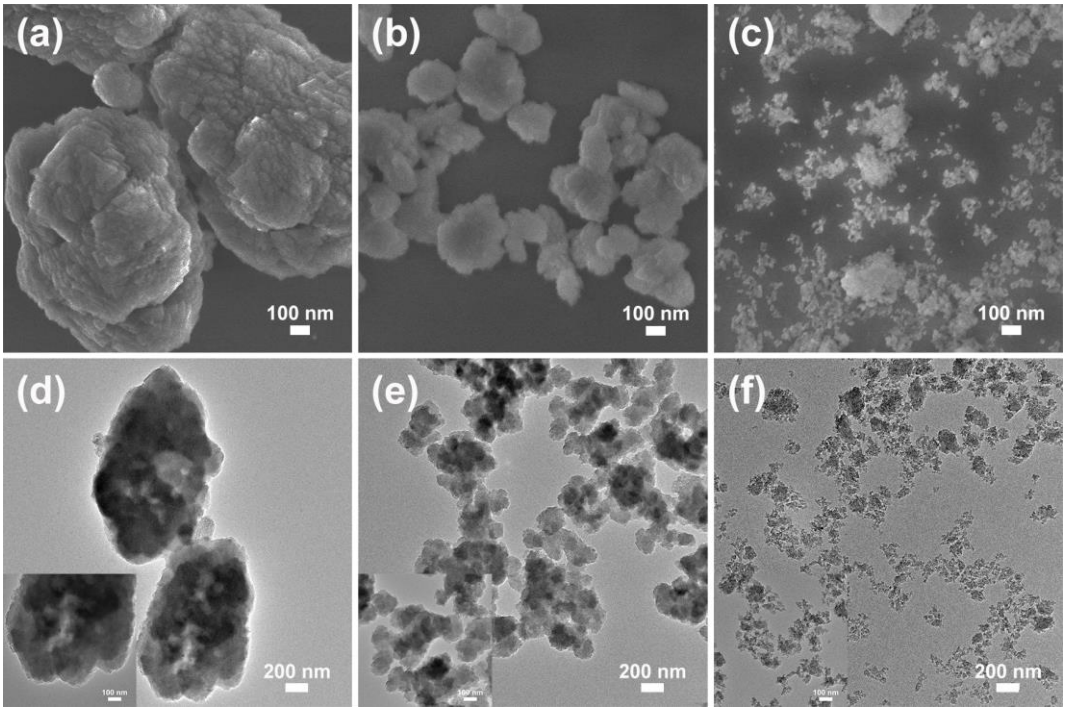

Fig. S18 (a, b, c) SEM images and (d, e, f) TEM images of Beta zeolites synthesized with different amount of seed addition: (a, d) Beta-20-BM-SAC-0wt%, (b, e) Beta-20-BM-SAC-5wt%, and (c, f) Beta-20-BM-SAC-20wt%.

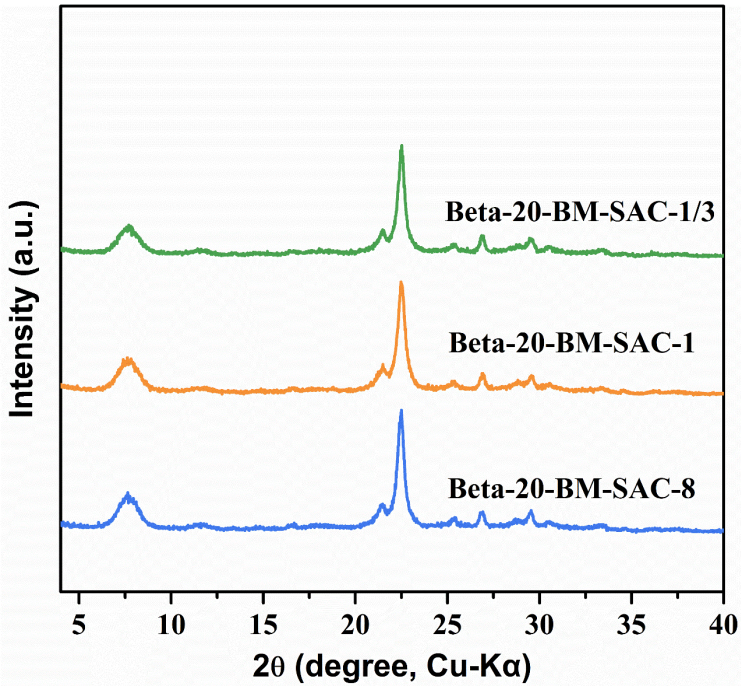

Fig. S19 PXRD patterns of Beta zeolites synthesized with different ball-milling time.

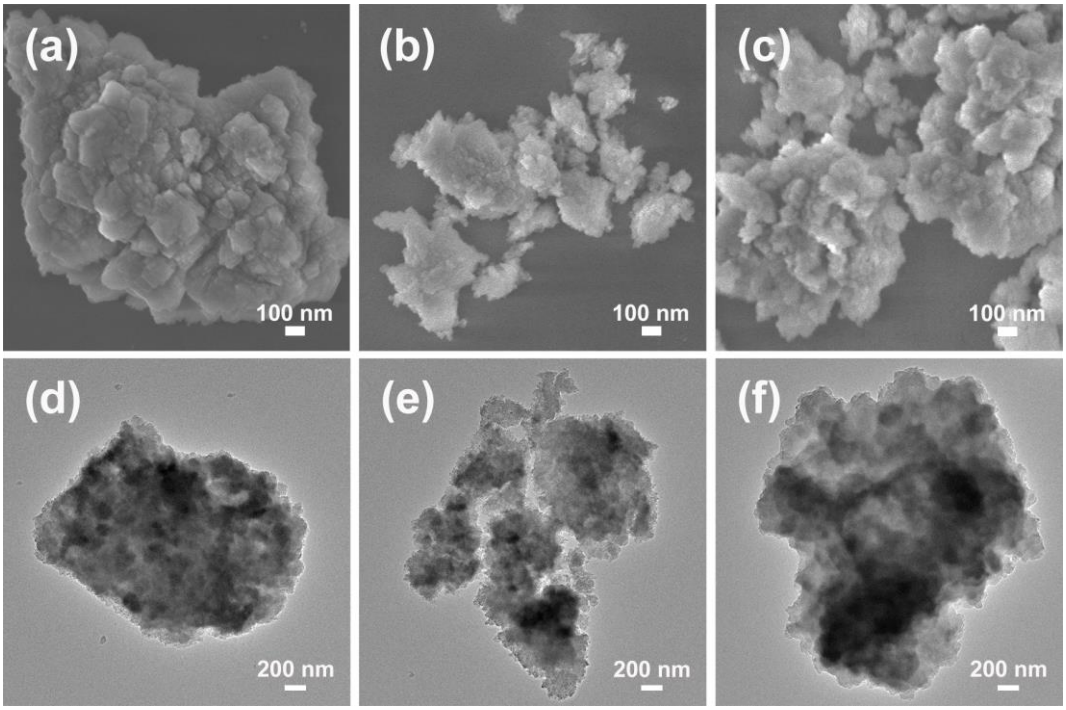

Fig. S20 (a, b, c) SEM images and (d, e, f) TEM images of Beta zeolites synthesized with different ball-milling time: (a, d) Beta-20-BM-SAC-1/3, (b, e) Beta-20-BM-SAC-1, and (c, f) Beta-20-BM-SAC-8.

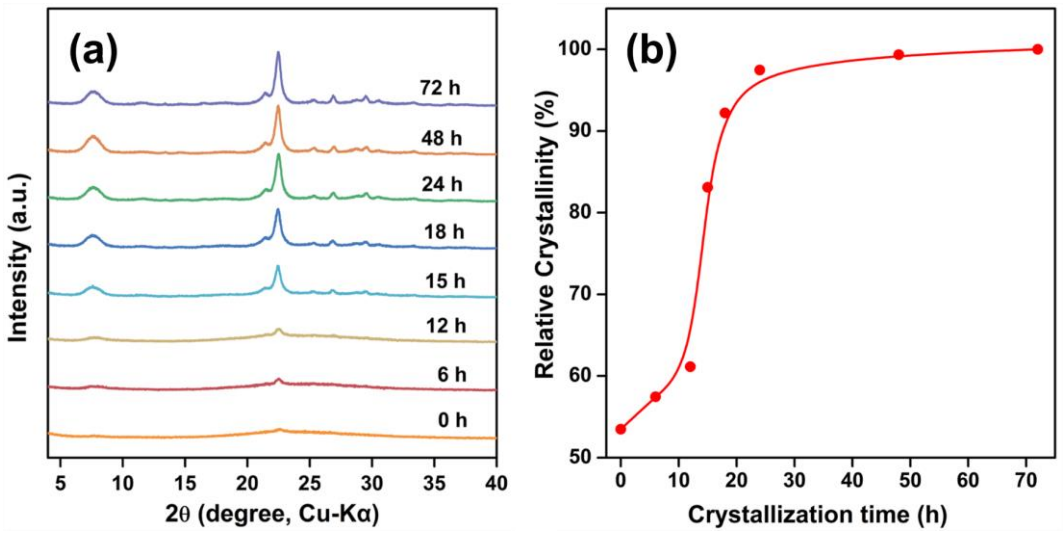

Fig. S21 (a) PXRD patterns of Beta-20-BM-SAC sample crystallized at 0 h, 6 h, 12 h, 15 h, 18 h, 24 h, 48, and 72 h, respectively. (b) Relative crystallinities over crystallization time, calculated according to the intensity of the peaks at 2θ of 7.6° and 22.6°. The crystallinity of Beta-20-BM-SAC reached its maximum at the time of 72 h, which is set at 100% and is considered as the reference.

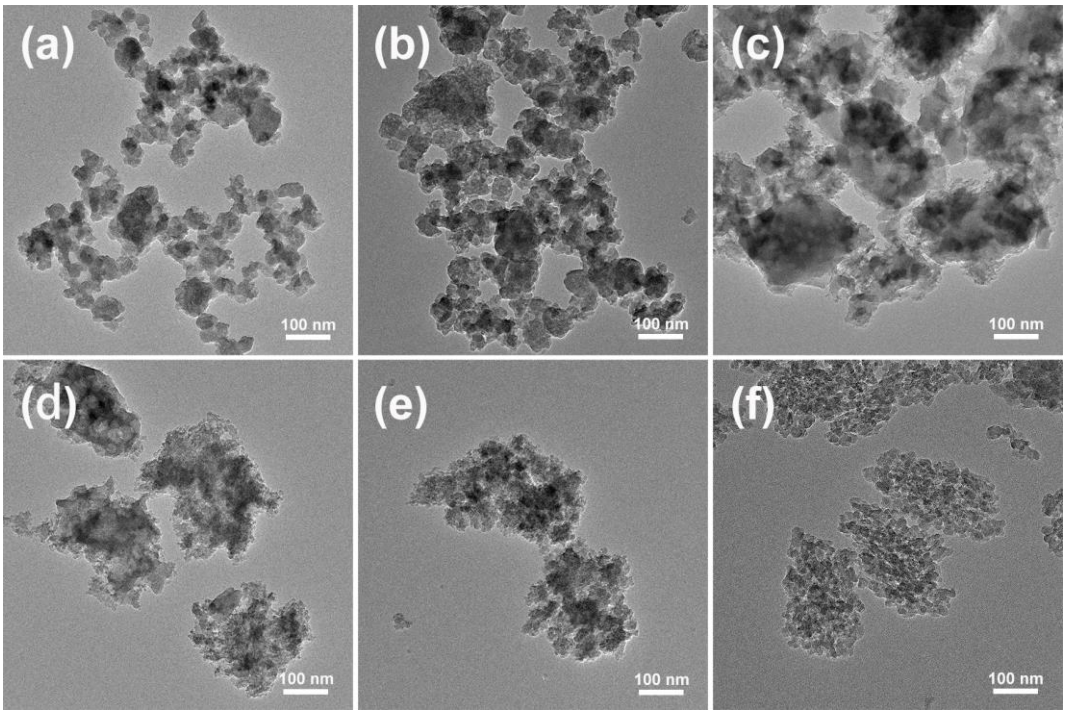

Fig. S22 TEM images of Beta-20-BM-SAC crystalline evolved under 140°C at different periods: (a) 0 h, (b) 6 h, (c) 12 h, (d) 15 h, (e) 18 h, and (f) 72 h.

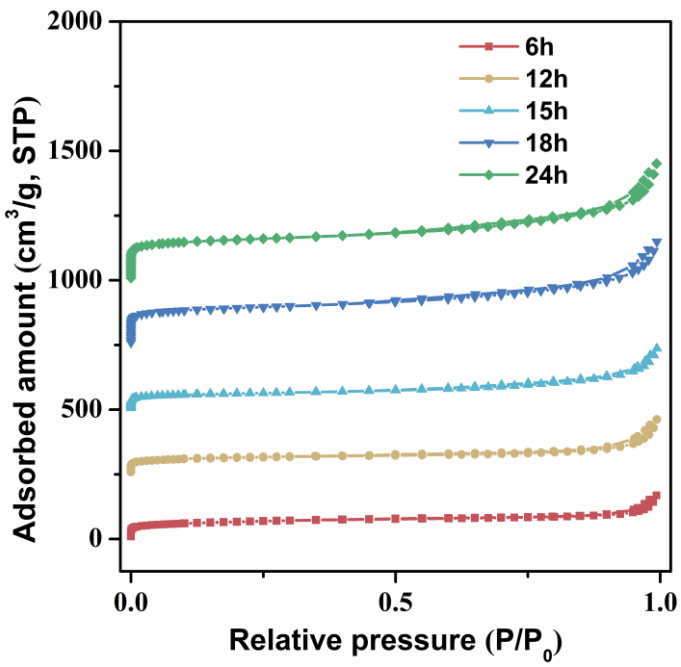

Fig. S23 N_2 adsorption/desorption isotherms of Beta-20-BM-SAC sample crystallized at 6 h, 12 h, 15 h, 18 h and 24 h, respectively.

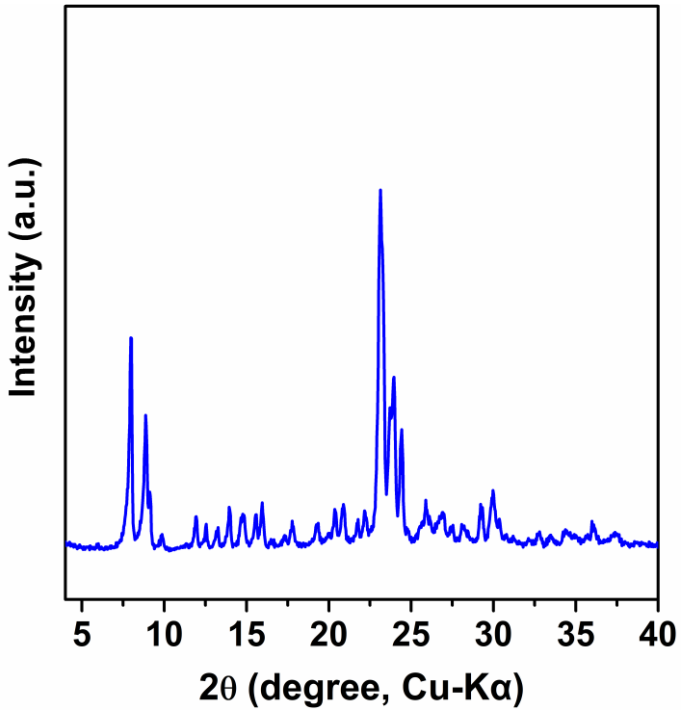

Fig. S24 PXRD pattern of H-ZSM-5 seed (Si/Al=20)

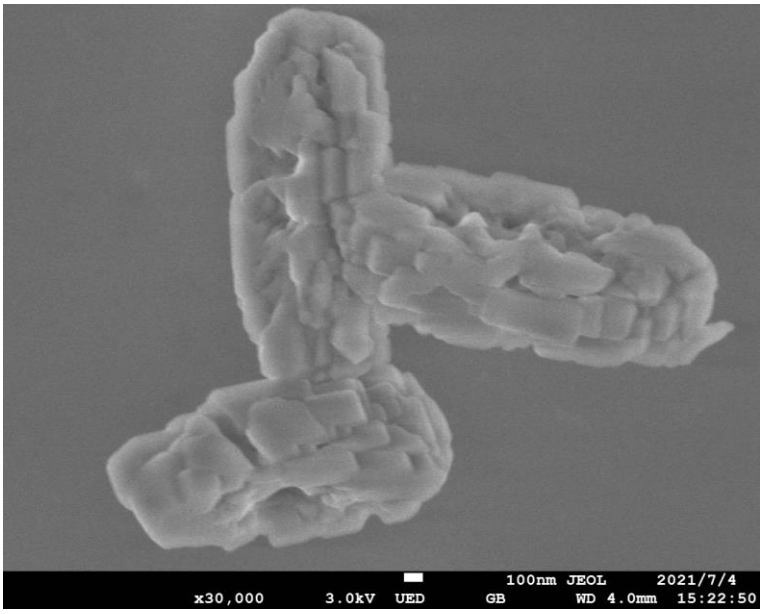

Fig. S25 SEM image of H-ZSM-5 seed (Si/Al=20).

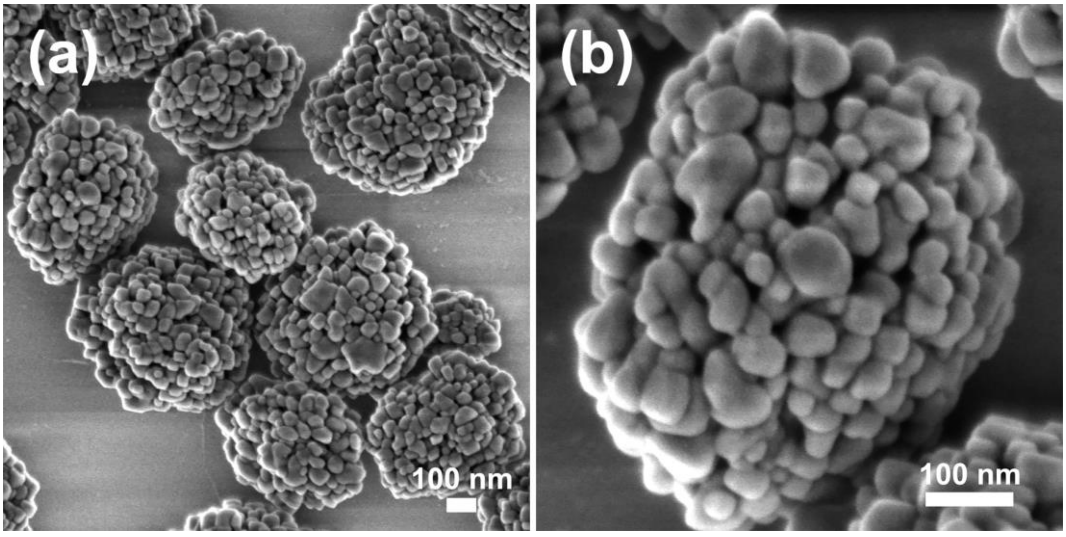

Fig. S26 (a) Low-magnification SEM and (b) high-magnification SEM images of ZSM-5-20-Con zeolite.

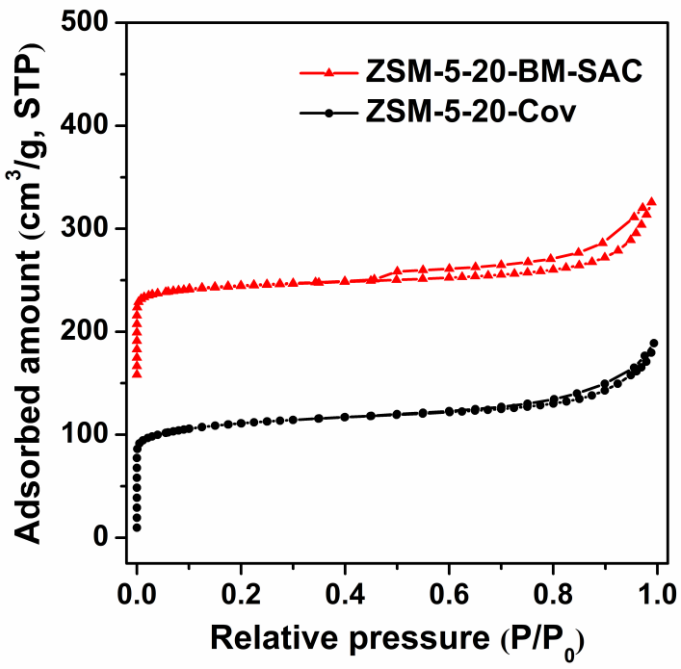

Fig. S27 N_2 adsorption/desorption isotherms of ZSM-5-20-BM-SAC and ZSM-5-20-Con zeolites.

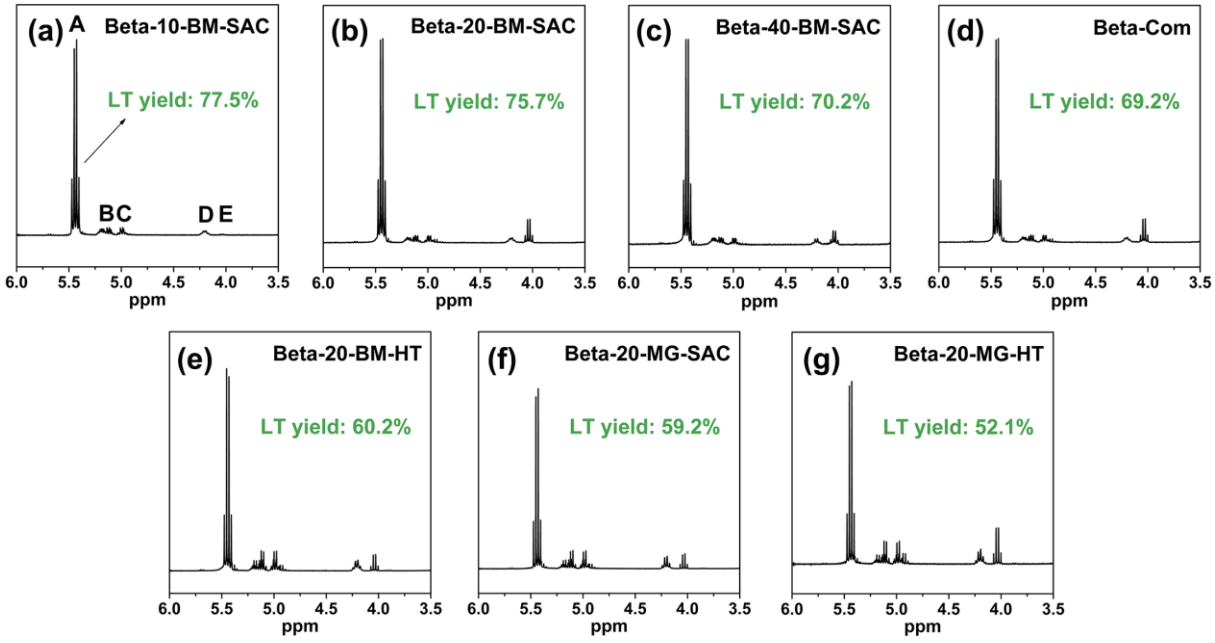

Fig. S28 Typical ^{1}H-NMR analysis (in DMSO-d6) of the reaction mixture after 5 hours over Beta zeolite, methine proton signals of A: lactide (LT), B: centers of oligomers, C: carboxylic end groups of oligomers, D: hydroxyl end groups of oligomers, and E: LA.

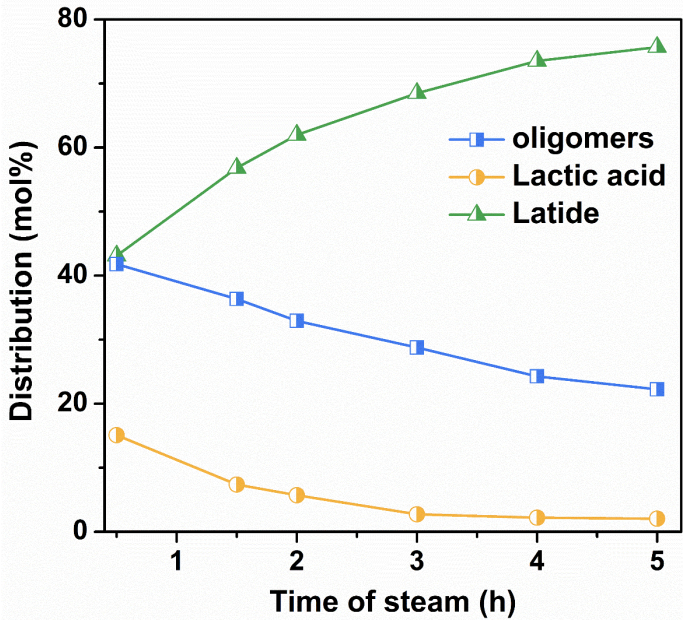

Fig. S29 Typical time profile of a zeolite reaction for Beta-20-BM-SAC based on ^{1}H-NMR analysis.

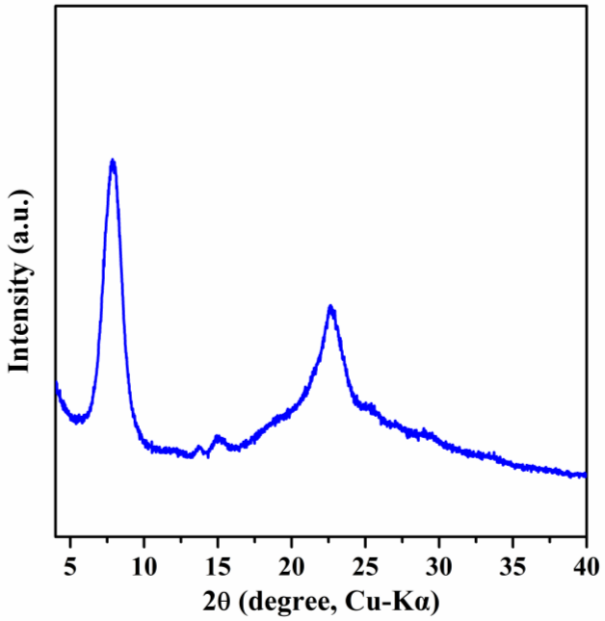

Fig. S30 PXRD pattern of Beta-20-BM-SAC recovered after five catalytic recycles.

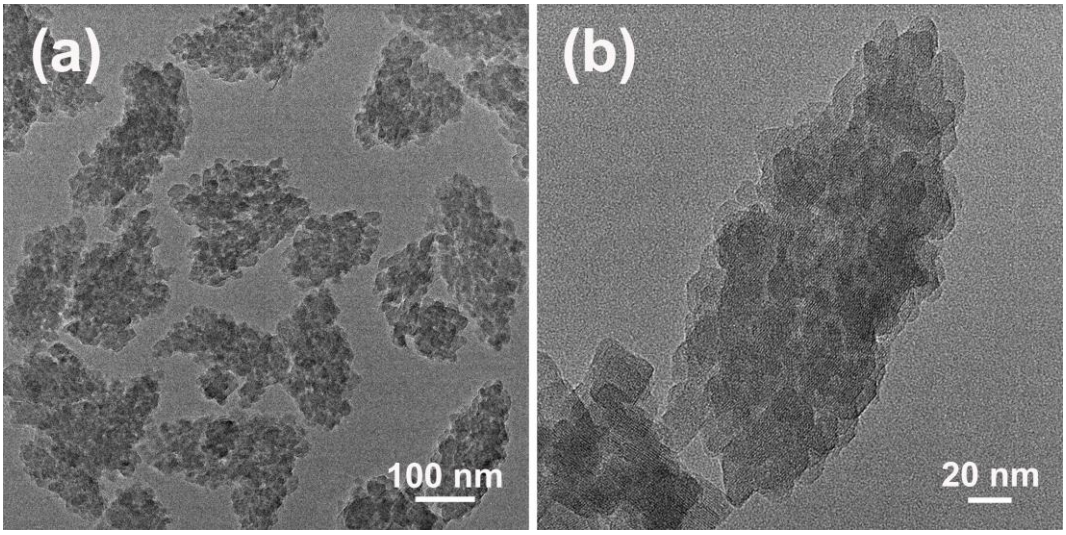

Fig. S31 TEM images of Beta-20-BM-SAC recovered after five catalytic recycles.

Table S1. Molar compositions of the initial mixtures and crystallization conditions of Beta and ZSM-5 zeolites.

Sample	$Si/Al_{initial}$	Si/Al_{ICP}	Na_2O/Si	H_2O/Si	Seed addition (wt%)	Ball-milling Time (h)
Beta-10-BM-SAC[a]	10	9.1	0.167	3	10	5
Beta-20-BM-SAC [a]	20	17.3	0.133	3	10	5
Beta-40-BM-SAC [a]	40	33.4	0.117	3	10	5
Beta-20-BM-SAC-0[b]	20	17.8	0.133	0	10	5
Beta-20-BM-SAC-1.5[b]	20	17.5	0.133	1.5	10	5
Beta-20-BM-SAC-6[b]	20	17.7	0.133	6	10	5
Beta-20-BM-SAC-0wt%[c]	20	18.1	0.133	3	0	5
Beta-20-BM-SAC-5wt%[c]	20	18.0	0.133	3	5	5
Beta-20-BM-SAC-20wt%[c]	20	17.9	0.133	3	20	5
Beta-20-BM-SAC-1/3[d]	20	18.2	0.133	3	10	1/3
Beta-20-BM-SAC-1[d]	20	17.5	0.133	3	10	1
Beta-20-BM-SAC-8[d]	20	18.1	0.133	3	10	8
Beta-20-BM-HT[e]	20	17.5	0.133	3	10	5
Beta-20-MG-SAC[f]	20	18.0	0.133	3	10	-
Beta-20-MG-HT[g]	20	17.9	0.133	3	10	-
ZSM-5-20-BM-SAC	20	17.8	0.083	3	10	5

[a] Initial Si/Al ratios. [b] The H_2O/Si ratio of the mixtures. [c] The Seed addition of the mixtures. [d] The Ball-milling time for the mixtures. [e] Heating treatment after ball-milling. [f] Manual grinding followed by steam-assist crystallization. [g] Heating treatment after manual grinding.

For all the Beta samples, TEA/Si ratio of the initial mixtures was 0.28, crystallization temperature was 140 ºC, crystallization time was 72 h. For ZSM-5-20-BM-SAC sample, TPA/Si ratio of the initial mixtures was 0.28, crystallization temperature was 160 ºC, crystallization time was 72 h.

Table S2. Textural Properties of Beta-20-BM-SAC zeolites crystalline evolved under 140 ^{o}C at different periods (6-24 h).

Sample	Crystallization time (h)	S_{BET}[a] (m^2g^{-1})	S_{micro}[b] (m^2g^{-1})	S_{ext}[b] (m^2g^{-1})	V_{total}[c] (cm^3g^{-1})	V_{micro}[b] (cm^3g^{-1})	V_{meso}[d] (cm^3g^{-1})
Beta-20-BM-SAC-6h	6	211	74	136	0.26	0.04	0.22
Beta-20-BM-SAC-12h	12	207	101	106	0.32	0.05	0.27
Beta-20-BM-SAC-15h	15	196	94	102	0.36	0.05	0.31
Beta-20-BM-SAC-18h	18	443	250	193	0.62	0.14	0.48
Beta-20-BM-SAC-24h	24	486	279	207	0.70	0.15	0.55

[a] S_{BET}: Total surface area, calculated by the BET method. [b] S_{micro}: micropore surface area, S_{ext}: external surface area, and V_{micro}: micropore volume, calculated by the *t*-plot method. [c] Total pore volume of N_2 adsorbed at p/p_0=0.99. [d] V_{meso}: mesopore volume, $V_{meso} = V_{total} - V_{micro}$.