Electronic Supplementary Information

High-temperature synthesis of high silica zeolite Y with good crystallinity in the presence of *N*-methylpyridinium iodide

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Synthesis

***N*-methylpyridinium iodide (NMP).** Methyl iodide (12 mL, 0.2 mol) was added dropwise to a solution of pyridine (16 mL, 0.2 mol) in alcohol (20 mL). After stirring for 24 h at room temperature in a dark place, a solid product was formed. After filtration and washing with alcohol at room temperature, dryness at 50 °C for 24 h under vacuum conditions, the target compound (white crystals) was obtained.

NMP-Y samples. As a typical run, $NaAlO_2$ (0.471 g) was dissolved in water, followed by addition of NMP iodide (1.326 g) and NaOH (0.35 g) solids, forming a clear solution. After stirring for 20 min, silica sol (3.21 mL, 31.5 wt %) was added into the above clear solution, giving an aluminosilicate gel containing NMP SDA. The molar ratio of the gel was 10 SiO_2/1.0 Al_2O_3/3.58 Na_2O/3.0 NMP/202 H_2O. After stirring for 2 h, the gel was transferred to a Teflon-lined stainless steel autoclave and heated at 120-130 °C for 48 h. The product was collected by filtrating and washing with deionized water at room temperature and drying at 80 °C for 24 h. The products obtained were designated as NMP-Y-*x*-*y*, where *x* stands for the crystallization temperature, and *y* stands for SiO_2/Al_2O_3 ratios in the gels.

NaY sample. NaY zeolite was hydrothermally synthesized in a Teflon-lined stainless steel autoclave statically at the temperature of 100 °C for 24 h from an aluminosilicate gel with a molar ratio of 10 SiO_2/1.0 Al_2O_3/4.76 Na_2O/202 H_2O. The product was collected by filtrating and washing with deionized water at room temperature and drying at 80 °C for 24 h. For comparison, the NaY was obtained from Sinopec Co, which was designated as Na-SP-Y.

H-form and NH_4-form NMP-Y zeolites. H-form zeolites were prepared from ion-exchange of NH_4NO_3 solution, followed by calcination. In a typical run, 0.5 g of as-synthesized zeolite was ion-exchanged with 100 mL of NH_4NO_3 solution (0.5 mol/L) at 80 °C for 5 h. After washing with deionized water and drying at 100 °C for 12 h, the ion-exchanged zeolite was calcined at 500 °C for 3 h. This process was repeated for one time.

NH_4-form zeolites were prepared from ion-exchange of calcined NMP-Y zeolite and as-synthesized NaY zeolite with NH_4NO_3 solution.

Hydrothermal treatment. Hydrothermal treatment of the NH_4-form zeolites was performed in a homemade system. The NH_4-form zeolites were placed in the reactor and were heated in 100 % steaming vapor at temperature of 750 °C. The samples were designated as zeolites-HT.

Characterizations.

The X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα (λ=1.5418 Å) radiation (40 kV, 200 mA). The step size was 0.02 °, and the scanning speed was 12 °/min. The relative crystallinity was estimated by the reflection intensities of the peaks (3 3 1), (5 1 1), (4 4 0), (5 3 3), (6 4 2), and (5 5 5) of the samples.[1] The sample morphology was observed with a field emission scanning electron microscope (SEM, JEOS JSM 6700F). N_2 sorption isotherms of the samples were measured with nitrogen sorption isotherms at -196 °C using a micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 200 °C before the measurements. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was measured with Perkin-Elmer 3300

DV. ^{27}Al, ^{29}Si and ^{13}C solid MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer. ^{13}C liquid NMR spectrum was recorded on a Bruker Avance 500 spectrometer using a 5 mm QNP probe equipped with z-gradient coil. DTA-TG analysis was carried out a NETZSCH STA 449C in air at a heating rate of 10 K/min from room temperature to 900 °C. FT-IR spectra were recorded using a Bruker 66V FT-IR spectrometer. The sorption isotherms of H_2O, acetone, and n-hexane were tested from MB-300G (VTI Scientific Instruments). Usually, the samples were activated at 150 °C and the sorption isotherms were measured at 25 °C.

Catalytic cumene cracking

Cumene cracking was carried out at 300 °C by pulse injection at atmospheric pressure. 0.025 g of catalyst was placed in a fixed reactor and nitrogen was used as the carrier gas at a flow rate of 55 mL/min. 0.2 μL of cumene (99.5 %) was injected for each run. The reaction products were analyzed on-line by a Shimadzu GC-8A equipped with a TCD detector.

References

(1) I. C. Neves, G. Botelho, A. V. Machado and P. Rebelo, *Mater. Chem. Phys.*, 2007, **104**, 5.

Supporting Figures

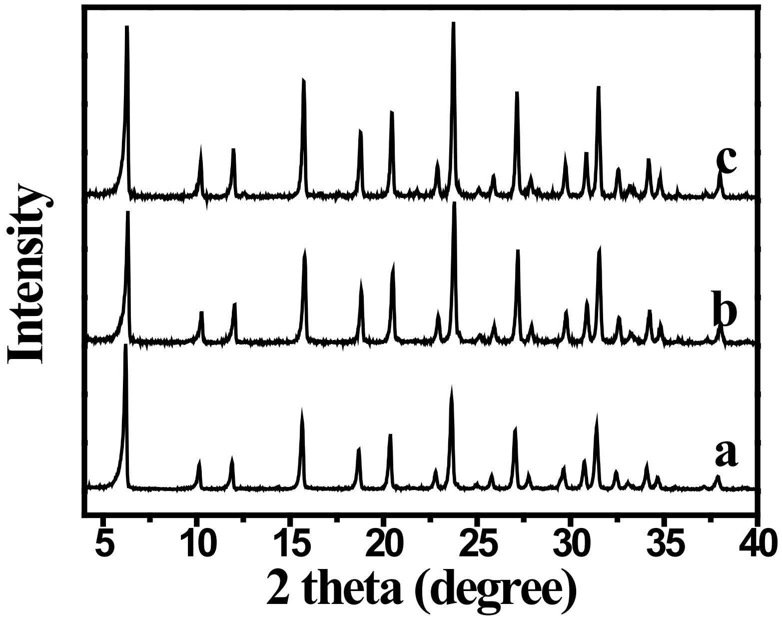

Figure S1. XRD patterns of (a) NMP-Y-120-13.6, (b) NMP-Y-130-10, and (c) NMP-Y-130-13.6.

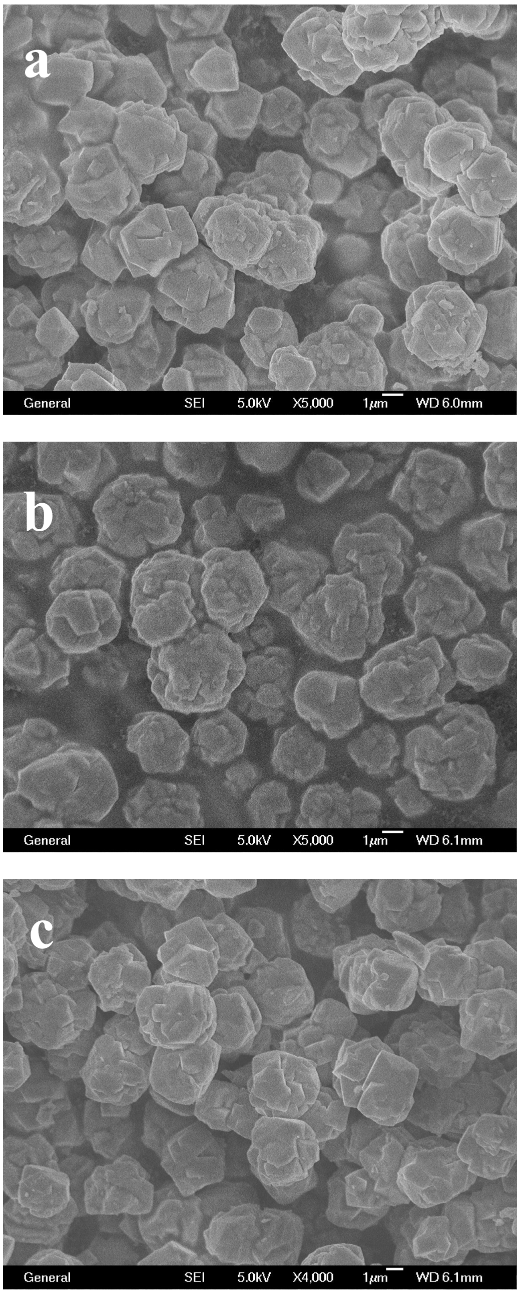

Figure S2. SEM images of (a) NMP-Y-120-13.6, (b) NMP-Y-130-10, and (c) NMP-Y-130-13.6**.** Scale bars are 1 μm.

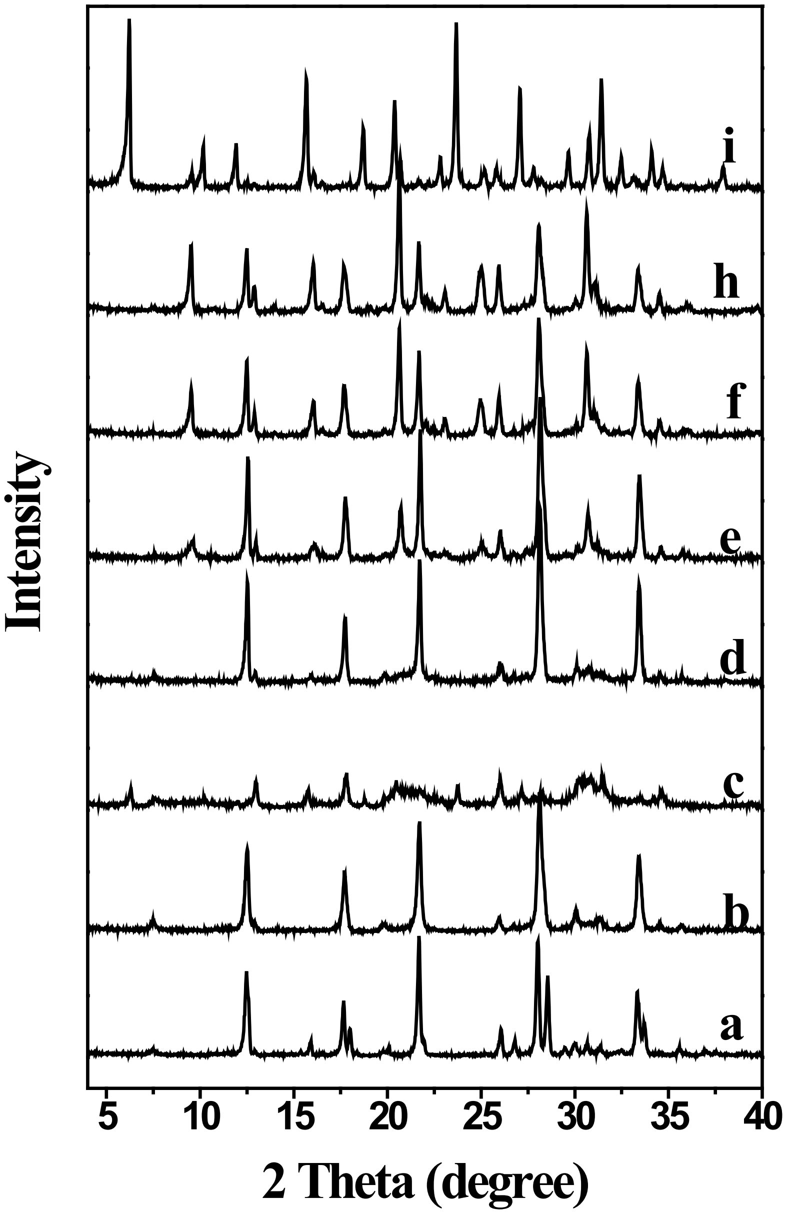

Figure S3. XRD patterns of solid samples synthesized from the starting aluminosilicate gels with molar ratio of 10 SiO_2/1.0 Al_2O_3/2.96-4.76 Na_2O/0-2.5 NMP/202 H_2O at 130 °C for 48 h. Na_2O/Al_2O_3 ratios of (a) 4.76, (b) 3.58, and (c) 2.96 in the absence of NMP; NMP/Al_2O_3 ratios of (d) 0.5, (e) 1.0, (f) 1.5, (h) 2.0, (i) 2.5 and Na_2O/Al_2O_3 ratio of 3.58.

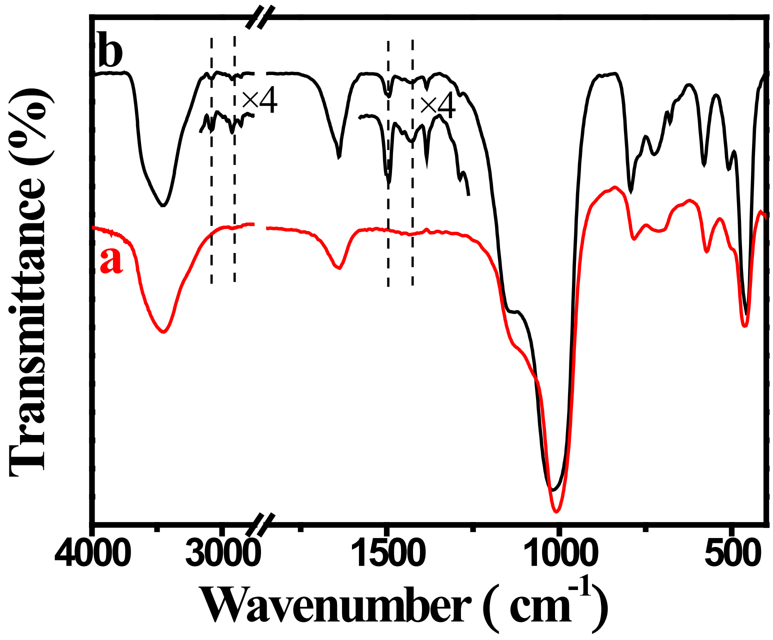

Figure S4. FT-IR spectra of as-synthesized (a) NaY and (b) NMP-Y-120-10.

Table S1. Products synthesized for 48 h under various conditions from the gel (1.0 Al_2O_3/10 SiO_2/202 H_2O).

Run	NMP/Al_2O_3	Na_2O/Al_2O_3	Cryst. temp. (°C)	Products
1	0	4.76	130	GIS+GME
2	0	3.89-3.58	130	GIS+GME
3	0	3.27	130	GME+GIS
4	0	2.96-2.64	130	Amorphous+GME
5	0.5	3.58	130	GME+GIS
6	1.0	3.58	130	CHA+GIS
7	1.5	3.58	130	CHA+GIS
8	2.0	3.58	130	CHA+GIS
9	2.5	3.58	130	Y+CHA

Table S2. Textural properties of NH_4Y, NH_4-SP-Y, and NH_4-NMP-Y-120-10 samples before and after the hydrothermal treatment by 100 % steaming at 750 °C for 2 h.

Samples	Crystallinity (%)[a]	BET surface area (m^2/g)		Micropore volume (cm^3/g)	
		Before	After	Before	After
NH_4Y-HT	19.34	681	79	0.313	0.020
NH_4-SP-Y-HT	77.52	653	475	0.298	0.203
NH_4-NMP-Y-120-10-HT	85.66	675	522	0.292	0.216

[a] As-synthesized NH_4Y, NH_4-SP-Y, and NH_4-NMP-Y-120-10 samples designated as 100 % crystallinity.

Table S3. Textural parameters of H-NMP-Y, H-SP-Y, and HY samples.

Samples	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Total pore volume (cm^3/g)
H-NMP-Y-120-10	834	0.289	0.413
H-NMP-Y-120-13.6	788	0.275	0.389
H-NMP-Y-130-10	767	0.235	0.379
H-NMP-Y-130-13.6	720	0.283	0.361
H-SP-Y	669	0.255	0.346
HY	250	0.100	0.164