Supporting Information for Publication

A quasi solid-phase approach to activate natural minerals for zeolite synthesis

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This Supporting Information for Publication includes 3 tables and 5 figures, a total of 12 pages.

Supplementary Methods

Characterizations

The chemical compositions of the different kaolin and diatomite samples were determined by X-ray fluorescence (XRF) conducted on a Bruker S4 Explorer instrument.

The phase structures of the samples were characterized by X-ray diffraction (XRD) conducted on a Bruker AXS D8 Advance X-ray diffractometer. The instrument used Cu Kα radiation and was operated at 40 kV, 40 mA, and 2θ in the range of 0.5~5° or 5~50°. The relative crystallinities of the NaA and NaY zeolites were calculated according the ASTM D-5357-03 and ASTM D-3906-03 standards, respectively.

Fourier transform infrared (FTIR) spectroscopy spectra of the samples in the range of 4000-400 cm^{-1} with a resolution of 1 cm^{-1} were recorded on a Nicolet Magna-IR 560 ESP spectrometer.

^{29}Si and ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy characterizations were performed on a Bruker DSX 500 MHz spectrometer with a spinning rate of 14 kHz and a π/8 pulse length of 1 ms.

Field-emission scanning electron microscopy (FESEM) images of the samples were obtained on a FEI Quanta 200F machine. High-resolution transmission electron microscopy (HRTEM) images were taken on a FEI Tecnai F20 (200 kV) instrument by mounting the sample to be measured on a C-flat TEM grid.

The textural properties of the samples were examined by N_2 adsorption-desorption experiments at -196 ^oC on a Micromeritics ASAP 2420 instrument. Specific surface areas of the samples were calculated by the BET method, while the external surface areas and micropore volumes were estimated using the de Boer t-plot method.

The thermogravimetric-differential scanning calorimetric (TG-DSC) analysis was performed on a Netzsch STA409PC thermogravimetric analyzer (Germany).

X-ray photoelectron spectroscopy (XPS) characterization was conducted on a Thermo Scientific K-Alpha instrument with a beam size of 400 μm.

The strength distributions of acid sites of the samples were studied by temperature-programmed desorption of ammonia (NH_3-TPD) conducted in a home-made apparatus. First, one of the H-form zeolite samples (200 mg) was heated from room temperature to 600 ^oC at a ramping rate of 10 ^oC/min and then cooled down to 100 ^oC in a pure N_2 flow; then, the sample was exposed to a NH_3 flow for adsorption at 100 ^oC for 10 min; subsequently, the sample was purged by a flowing N_2 stream at 100 ^oC for 1 h to remove excessive and physically adsorbed NH_3; and finally, the sample was heated from 100 to 600 ^oC at a ramping rate of 10 ^oC/min in a pure N_2 flow and the desorption patterns were recorded.

Catalyst preparation

NH_4^+-form zeolites were prepared by successive ion exchanges with a NH_4Cl aqueous solution (1 M) at 90 ℃ and a solution-to-zeolite ratio of 10 mL/g for 2 h. After the ion exchange step, an ultra-stabilization treatment was carried out in 100% steam at 600 ℃ for 2 h. The ultra-

stable Y zeolites (USYs) derived from QSP-Y, HCA-Y and the commercial Y were named as QSP-USY, HCA-USY and Com-USY, respectively. A series of model fluid catalytic cracking (FCC) catalysts designated as QSP-Cat, HCA-Cat and Com-Cat were prepared by first preparing a homogeneous slurry consisting of one of the above USYs (25 wt%), HZSM-5 (10 wt%), kaolin (50 wt%), silica gel (15 wt%) in dry basis and an appropriate amount of water, calcinating the slurry at 500 ^{o}C for 4 h, and finally crushing the resulting lumps into particles of 70-150 μm in size. To simulate the commercial deactivation process, the model FCC catalysts prepared were deactivated with 100% steam at 800 ^{o}C for 10 h.

Catalytic tests

The catalytic tests were conducted in a standard confined fluidized-bed reactor under the following typical conditions: 525 ^{o}C, feedstock injection time 45 s, mass ratio of catalyst to oil 6.5, mass ratio of water to oil 0.3, and catalyst loading 50 g. During the reaction and stripping processes, the liquid products were collected in a glass receiver kept in an ice-bath, and the gaseous products were collected in a burette by water displacement. An Agilent 6890 gas chromatograph (GC) equipped with the ChemStation software was used for the quantitative determination of the components in the gaseous products. A simulated distillation GC was used to analyze the liquid products as described in the ASTM D-2887 standard. A coke analyzer was used to determine the coke content in catalyst.

Supplementary Tables

Table S1. Chemical compositions of the kaolin mineral, the diatomite mineral, QSP-Y, QSP-A, the commercial NaY and NaA zeolites.

	Component (wt%)	Na_2O	Al_2O_3	SiO_2	P_2O_5	SO_3	MgO	K_2O	CaO	TiO_2	Fe_2O_3
1	kaolin	0.3	44.2	52.7	0.4	0.9	0.1	0.6	0.2	0.3	0.3
2	diatomite	0.2	2.3	95.2	0.1	0.2	0.2	0.6	0.2	0.2	0.8
3	QSP-Y	12.5	20.8	65.2	-	-	0.1	0.6	0.2	0.2	0.4
4	commercial Y	15.7	21.3	62.6	-	-	0.1	0.1	0.1	-	0.1
5	QSP-A	17.4	37.0	43.9	-	0.1	0.2	0.5	0.3	0.3	0.3
6	commericial A	17.3	37.7	43.8	-	-	0.2	0.3	0.6	-	0.1

Table S2. Physicochemical properties of the as-synthesized and commercial NaY zeolites.

	sample	QSP-Y	HCA-Y	commercial Y
1	BET area (m^2/g)	631	604	691
2	micropore area (m^2/g)	580	562	657
3	external surface area (m^2/g)	51	42	34
4	pore volume (cm^3/g)	0.36	0.32	0.34
5	micropore volume (cm^3/g)	0.28	0.27	0.32
6	mesopore volume (cm^3/g)	0.08	0.05	0.02
7	crystal size (μm)	0.3~0.5	0.5~0.7	1.5~1.8
8	relative crystallinity (%)	91	86	100
9	framework SiO_2/Al_2O_3 molar ratio	5.0	5.0	5.0
10	bulk density (g/ml)	0.41	0.41	0.38

Table S3. Properties of the Xinjiang vacuum gasoil.

	item	Xinjiang vacuum gasoil
1	density (20 ^{o}C) (kg/m^{3})	898.40
2	kinematic viscosity at 100 ^{o}C (mm^{2}/s)	12.05
3	average molecular weight (g/mol)	449
4	conradson carbon residue (CCR) (wt%)	0.39
5	lumped composition (wt%)	
6	saturated alkanes	76.59
7	aromatics	21.01
8	resins	4.08
9	asphaltenes	0.17
10	element composition (wt%)	
11	C	86.02
12	H	13.13
13	N	0.12
14	S	0.64

Supplementary Figures

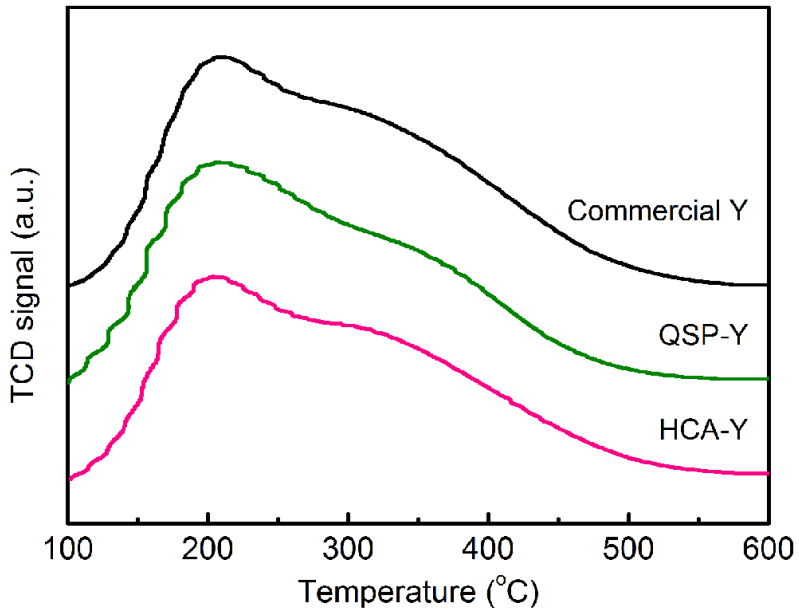

Figure S1. NH_3-TPD curves of the H-form QSP-Y sample, H-form HCA-Y sample and H-form commercial Y zeolite.

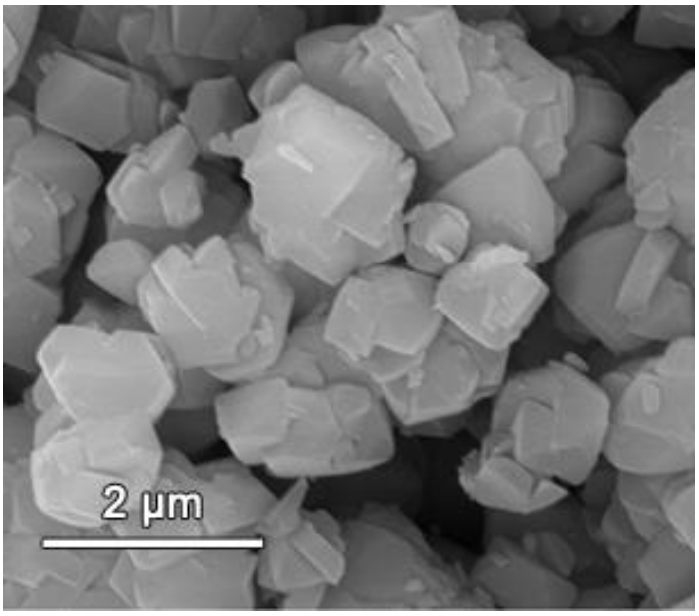

Figure S2. FESEM image of the commercial NaY zeolite.

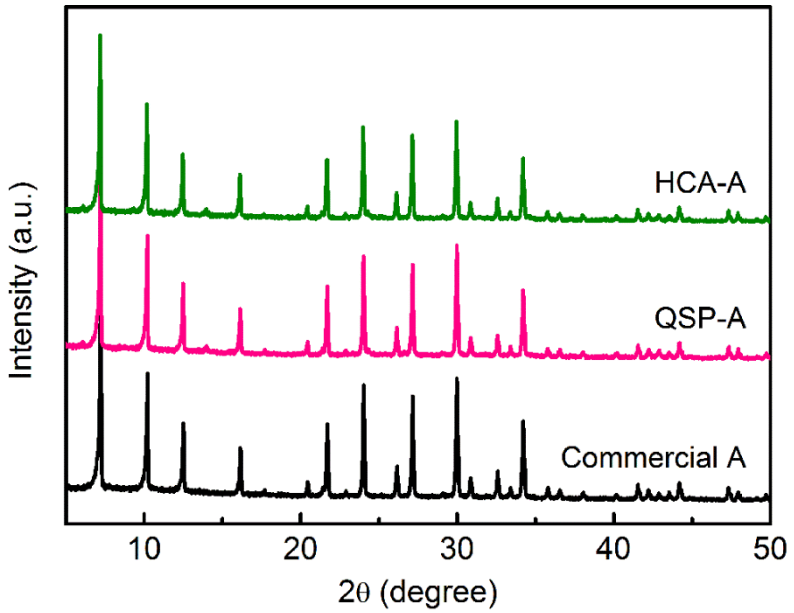

Figure S3. XRD patterns of the NaA zeolites synthesized from the different activated products and the commercial NaA zeolite.

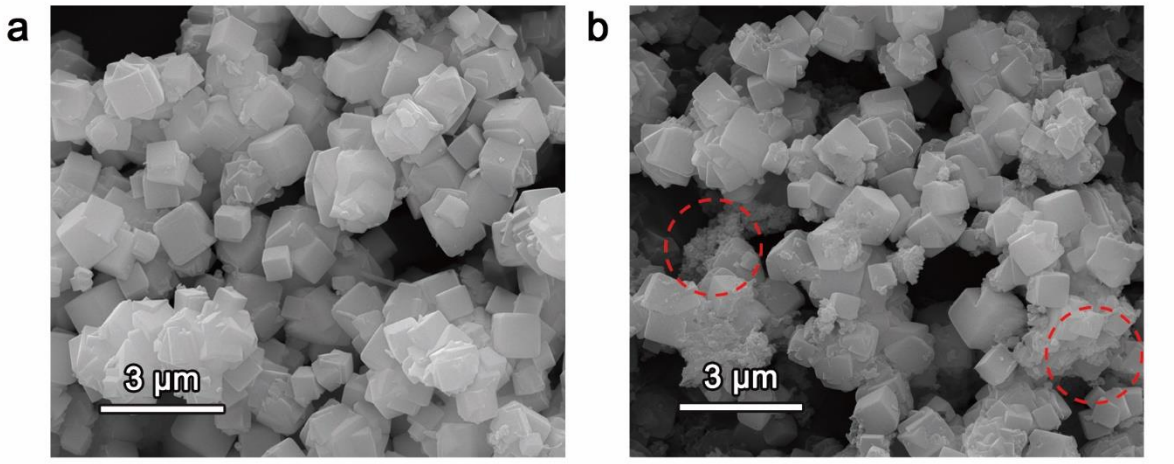

Figure S4. FESEM images of the NaA zeolites synthesized from the different activated products.

(a): QSP-A and (b): HCA-A.

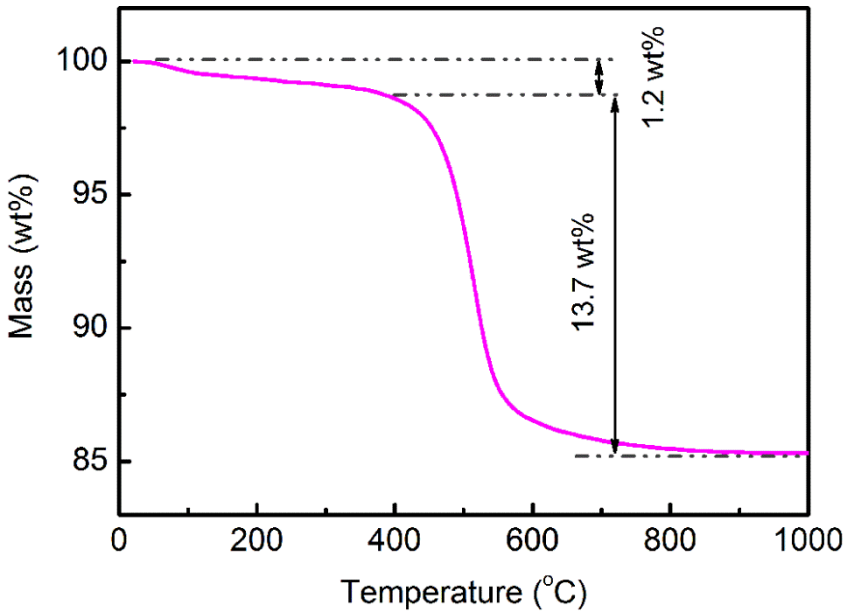

Figure S5. TG curve of the raw kaolin mineral.