Electronic Supplementary Information for

Carboxylic acids to butyl esters over dealuminated-realuminated Beta zeolites

for removing organic acids from bio-oils

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Supplementary characterizations methods

Nitrogen physisorption measurements were conducted on a Micromeritics ASAP 2420 instrument to characterize the textural properties of the samples. Specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) method and pore volumes were estimated from nitrogen adsorption-desorption isotherms. Mesopore diameters corresponding to the maxima of the pore size distribution curves were obtained from the adsorption isotherms using the Barret-Joyner-Halenda (BJH) method.

X-ray powder diffraction (XRD) patterns of the samples were recorded on a PANalytical Cubix X'Pert Pro diffractometer with Cu Kα radiation (λ = 1.5418 Å) and in the 2θ range between 5° and 50°. The relative crystallinities of the samples were determined by comparing the (302) peak intensities of the modified samples with that of the parent H-Beta zeolite which was considered to be 100% in crystallinity.

The crystal morphology and sizes of the samples were observed by field-emission scanning electron microscopy (FESEM) on a FEI Quanta 200F microscope.

The Si and Al elemental analyses of the samples were made by X-ray fluorescence spectroscopy (XRF) on a ZSX-100e 4580 instrument.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher ESCALAB 250Xi spectrometer (UK) with monochromatic Al Kα radiation (E = 1486.74 eV). Before test, the samples were ground to powders and then pressed into thin self-supporting wafers with a diameter of 9 mm and a thickness of 1 mm. A small piece of each sample was introduced into the vacuum chamber for analysis. The spectra were collected with a pass energy of 30 eV under ultrahigh vacuum condition. The binding energies were calibrated by the internal

standard method using the C1s peak at 284.8 eV. The compositions and chemical surrounding of the sample surfaces were investigated on the basis of the areas and binding energies of Al 2p, Si 2p and O 1s photoelectron peaks.

Infrared (IR) spectra were obtained on a VERTEX 80v instrument (Bruker Co., Germany) in the wavenumber range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. The samples, each 20 mg, were extruded into the self-supported 13 mm diameter circular wafers; subsequently, the samples were dehydrated at 673 K for 1 h under a vacuum of 1.33×10^{-3} Pa, followed by the adsorption of purified pyridine vapor at room temperature for 20 min; and finally, the system was evacuated at different temperatures and pyridine-adsorbed IR (Py-IR) spectra were recorded. Total Lewis (L) acidity and total Brönsted (B) acidity, medium and strong L acidity and medium and strong B acidity were calculated from the IR measurement results of pyridine adsorption at 473 and 623 K, respectively.[1]

Temperature-programmed desorption of ammonia (NH_3-TPD) was carried out on a PCA-1200 chemical adsorption instrument (Beijing Biaode Electronic Technology Co., Ltd., PR China) with a thermal conductivity detector (TCD). First, 100 mg of a sample were pretreated at 773 K in a N_2 stream for 30 min and then cooled down to 373 K; afterwards, pure NH_3 was adsorbed at 373 K for 15 min, followed by N_2 purging at 373 K for 15 min; and finally the desorption of NH_3 was monitored in the range of 373-873 K at a ramp rate of 10 K/min.

^{27}Al multiple quantum magic angle spinning nuclear magnetic resonance (MQ MAS NMR) was used to determine the coordination of aluminum atoms in zeolites. With this technique pure isotropic spectra with high resolution could be obtained without anisotropic quadrupolar broadening by making a correlation between the multiple and single quantum transitions in a two-dimensional mode.[2] Both ^{27}Al MAS NMR and MQ MAS NMR experiments were

performed on a Bruker Avance III 500 WB (11.75 T) spectrometer operated at a frequency of 130.39 MHz for ^{27}Al. A DVT triple resonance 4 mm o.d. Bruker CP/MAS probe was used with a spinning frequency of 12.0 kHz. ^{27}Al MAS NMR spectra were recorded with a single pulse excitation using a short pulse length (0.18 μs) to obtain quantitative results, and a recycle delay of 0.5 s (the RF field strength was 160 kHz and the tip angle was π/18). ^{27}Al MQ MAS experiments were performed using the two-pulse z-filtered procedure. The excitation pulse was a π pulse, and the conversion pulse was a π/3 pulse. ^{27}Al chemical shifts were referenced using a Al(NO$_3$)$_3$ solution (1 M) as the external reference (0 ppm).

Supplementary Table

**Table S1.** 2θ values and the corresponding *d* spacings of the main reflections in the XRD patterns in Figure 4.

Sample	Peak 1[a]		Peak 2[a]		Peak 3[a]		Peak 4[a]	
	2θ	*d* (Å)	2θ	*d* (Å)	2θ	*d* (Å)	2θ	*d* (Å)
H-Beta	7.72	11.436	13.44	6.581	22.52	3.945	43.60	2.074
O-Beta	7.88	11.211	13.51	6.549	22.60	3.932	43.79	2.066
M-Beta	7.84	11.266	13.48	6.563	22.54	3.941	43.69	2.070
T-Beta	7.84	11.266	13.47	6.567	22.54	3.941	43.68	2.071

[a] Corresponding to * in Figure 4.

Supplementary Figures
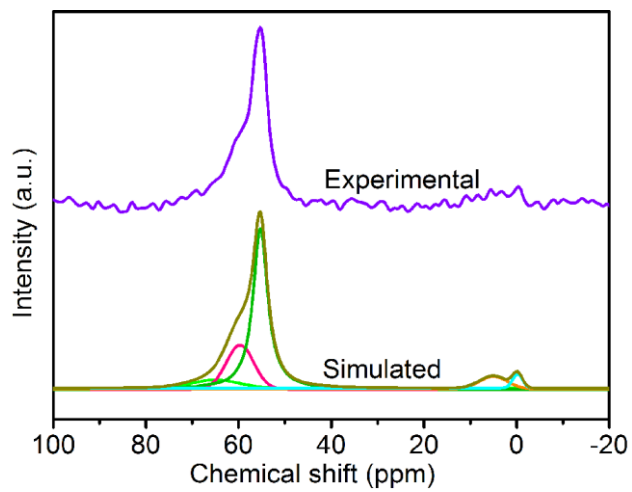
**Figure S1**. Experimental and simulated ^{27}Al NMR MAS spectra of H-Beta.
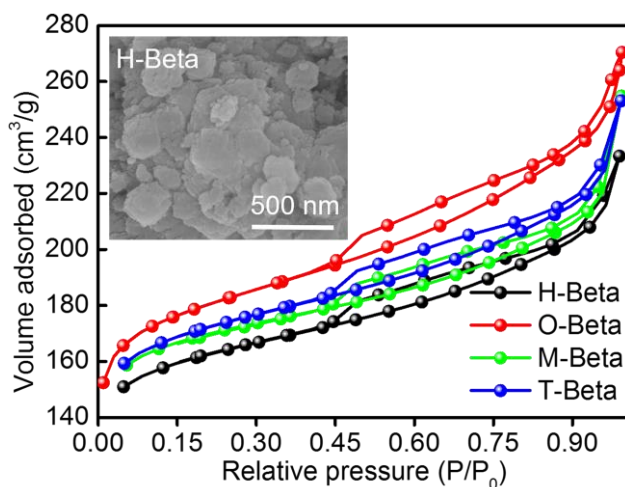
Figure S2. N_2 adsorption/desorption isotherms of H-Beta, O-Beta, M-Beta and T-Beta. Inset shows the SEM image of H-Beta.

The nitrogen adsorption-desorption isotherms of H-Beta and the organic acid leached Beta zeolites are shown in Figure S2. They all exhibit a type IV isotherm with a hysteresis loop. It can be seen that the three acid leached samples have increased volumes of nitrogen adsorbed. The presence of the hysteresis loops in all of the isotherms indicates the presence of mesopores. Actually, the parent H-Beta zeolite used in the present investigation is a material with both microporous and mesoporous structures, as reflected by its isotherm. The size of the crystallites of H-Beta as determined by SEM (Figure S2) is in the range of 200~350 nm, consistent with the XRD results. In the literature,[3] the researchers suggested two phenomena to explain the existence of mesoporosity: the first is the intra-granular mesoporosity because of the existence of mesopores in zeolite particles; and the second is the inter-granular mesoporosity because of the existence of mesopores among packed individual crystals.
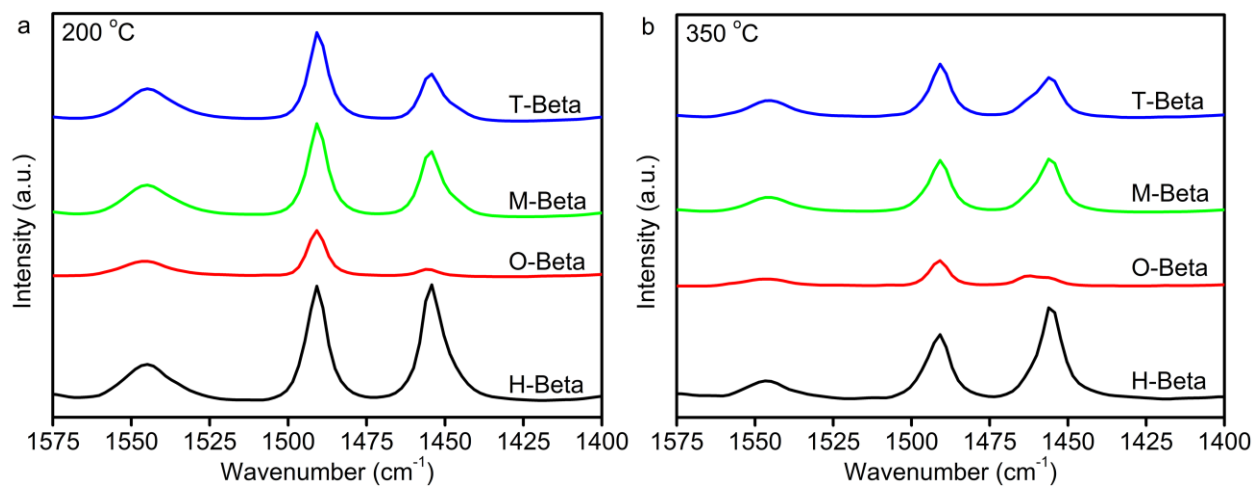
Figure S3. Py-IR spectra of H-Beta, O-Beta, M-Beta and T-Beta at (a) 473 K and (b) 623 K.
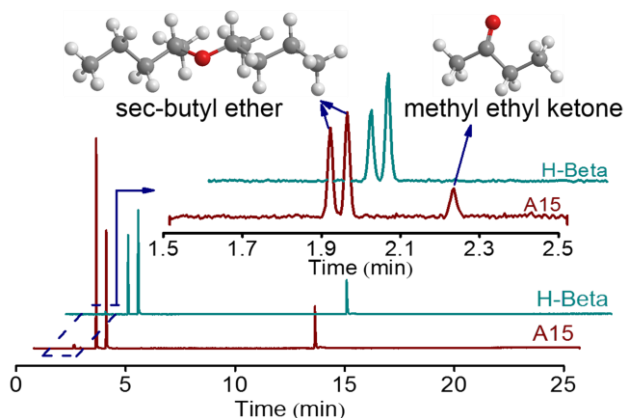
Figure S4. GC-MS spectra of esterification products formed over A15 and H-Beta catalysts.

The GC-MS spectra of the esterification products formed over A15 and H-Beta zeolites were presented in Figure S4. It can be seen that sec-butyl ether was the main by-product in the esterification of sec-butyl alcohol with acetic acid over H-Beta zeolites, while sec-butyl ether and methyl ethyl ketone appeared in the product obtained over A15. Because the concentration of acid sites (H^+) of A15 is 4700 µmol/g, more than 10 times higher than that (410.6 µmol/g) of H-Beta, much more by-products were formed over A15 than over the Beta zeolites.
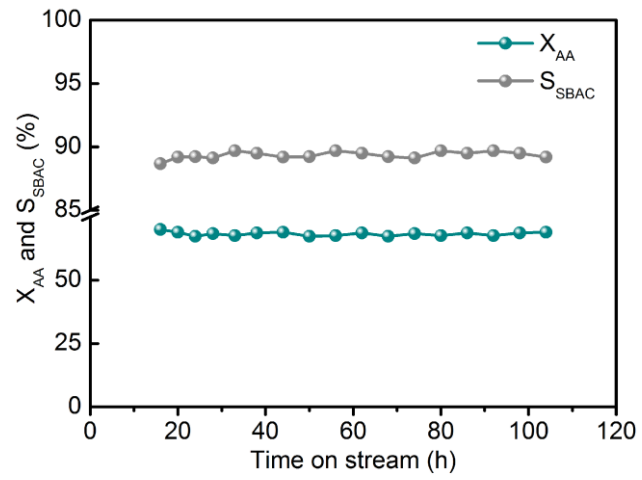
Figure S5. Stability of M-Beta zeolite for the esterification of acetic acid and sec-butanol.

References

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