Supporting Information

Selective Alkylation of Phenol and tert-butanol Using Zr

Containing Beta Zeolite

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Experimental Procedures Materials

Fumed silica (SiO₂, Aladdin), aluminum isopropoxide (99.8%, Macklin), cetyltrimethylammonium bromide (99%, Macklin), tetraethylammonium hydroxide (35% in H₂O, Aladdin), ammonium chloride (99.5%, Macklin), phenol (99.5%, Macklin), dodecane (AR, Macklin), tert-Butanol alcohol (AR, Macklin), icosylcyclohexane (AR, Macklin), zirconium nitrate (AR, Macklin), deionized water, pyridine (AR, Macklin).

Catalyst characterization

The crystal structures of the prepared zeolites were characterized by X-ray diffraction instrumentation equipped with a Bruker-AXS D2 PHASER Advance diffractometer with Cu Ka radiation. The silicon, aluminum and zirconium loadings of the zeolite materials were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The pore structure parameters of Beta zeolites were measured by Micromeritics ASAP 2460 devices at 77 K. Zeolite were pretreated under the condition of 473 K and vacuum for 6 h. The total surface area of the resulting samples was determined by the Brunauer-Emmett-Teller (BET) model, while the pore size distribu-tion was obtained by the Barrett-Joyner-Halenda model based on N2 desorption isotherm. The total acidity was determined by Fourier transform infrared spectroscopy with the probe molecules of pyridine, respectively, using a Bruker VERTEX 70 spectrometer. The zeolites were first degassed at 723 K for 2 h before the measurements, Pyridine was then adsorbed on the above zeolites for 0.5 h at 298 K. The temperature of the sample was raised to 423 K or 623 K at 1 h to get rid of the weakly bound pyridine molecules. After the samples were cooled to 298 K, the acidity of zeolites was measured by infrared spectroscopy at 32 scans and a resolution of 2 cm⁻¹. In the Py-IR spectra, the characteristic peak of Brønsted acid and Lewis sites of zeolite is at ~1545 cm⁻¹ and 1455 cm⁻¹, corresponding to a molar extinction coefficient of 2.22 cm /µmol and 1.67 cm $/\mu$ mol¹. The morphology of the zeolites was observed by a TDCLS-4800 scanning electron microscope (SEM). Transmission electron microscopy (TEM) imaging was performed with a JEM-2100F TEM (200 kV) microscope, equipped with an Energy

Dispersive X-ray Spectroscopy (EDX) analysis were taken using a JEM-F200 system. Diffuse reflectance ultraviolet-visible (UV-vis) spectra of the dehydrated zeolite samples were measured against BaSO₄ in the range of 200-600 nm on a Varian Cary 300 UV-vis spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB Xi⁺ (ThermoFisher Scientific) with an Al K α X-ray. All binding energy (BE) values were calibrated to the C 1s peak of adventitious carbon at 248.8 eV.

Catalytic tests

The catalytic performance of resultant Beta zeolites in the alkylation of phenol with *tert*-Butanol were evaluated within a micro-fixed-bed reactor under atmospheric pressure at 413 K. All Beta zeolites catalysts were pelletized with a size of 20–40 mesh and activated at 673 K for 4 h prior to test. The molar ratio of phenol and *tert*-butanol was 1: 2, and dodecane was used as an internal standard. The total weight hourly space velocity (WHSV) was 5 h⁻¹, and the products were collected at every 2 h interval and analyzed by gas chromatograph equipped with a HP-5 column and an FID detector. The conversion of phenol and the selectivity of 2,4-DTBP were calculated as follow²:

Conversion of Phenol =
$$(1 - \frac{C_A}{C_{A,0}}) \times 100\%$$
 (1)

Selectivity of 2,4-DTBP =
$$\left(\frac{n_{2,4-DTBP}}{n_{2-TBP} + n_{4-TBP} + n_{2,4-DTBP} + n_{2,6-DTBP} + n_{2,4,6-TTBP}}\right)$$
 (2)

where $C_{A,0}$ is the initial concentration of phenol in the mixtures (mmol L⁻¹) and C_A is the concentration of phenol after reaction at a certain moment (mmol L⁻¹). The n_{4-TBP} , n_{2-TBP} , $n_{2,4-DTBP}$, $n_{2,6-DTBP}$ and $n_{2,4,6-TTBP}$ are the molar amounts of 4-TBP (4-*tert*-butyl phenol), 2-TBP (2-*tert*-butyl phenol), 2,4-DTBP (2,4-Di-*tert*-butyl phenol) and 2,6-DTBP (2,6-Di-*tert*-butyl phenol), 2,4,6-TTBP (2,4,6-tri-*tert*-butyl phenol) in the reaction mixture, respectively.

Figures and Tables



Fig. S1 XRD patterns of resultant Beta zeolites



Fig. S2 SEM images of (a) Beta-30 (b) Zr(2)-Beta-30 (c) Zr(6)-Beta-30 (d) Zr(8)-Beta-30



Fig. S3 Nitrogen adsorption-desorption isotherms (a) and BJH pore size distributions (b) of obtained Beta zeolites with different Si/Al ratios

Note: The nitrogen adsorption-desorption isotherms of various Beta zeolites with different Si/Al ratios are shown in Fig. S3. It's observed from Fig. S3a that all Beta samples show the characteristics of type IV isotherms with hysteresis looping, indicating the existence of mesopores due to the stacking of nanocrystalline Beta zeolite. In Fig. S3b, the resultant Beta zeolites exhibit obvious mesopores with 3-4 nm based on the BJH pore size distribution, which are attributed to the intracrystalline mesopores generated by CTAB³.



Fig. S4. FT-IR spectra of pyridine adsorption of different Beta zeolite samples

Note: The Brønsted and Lewis acidity of Beta zeolites with various Si/Al ratios are analyzed by Fourier transform infrared spectroscopy (FT-IR) of pyridine adsorption on Beta zeolites. The molecular diameter of pyridine is 0.54 nm⁴, which is smaller than the size of Beta zeolite $(0.66 \times 0.67 \times 0.57 \text{ nm})$, so pyridine molecules can enter into the channels along the *a*, *b*, and *c* axes⁵⁻⁷⁻⁷. The absorption peaks at positions 1545 cm⁻¹ and 1455 cm⁻¹ in Fig. S5 are attributed to the adsorption of pyridine molecules at Brønsted acid sites and Lewis acid sites, respectively¹.



Fig. S5 Conversion of Phenol with time-on-stream on synthesized zeolite (Test condition: reaction temperature = 413 K; pressure = 0.1 MPa; phenol/*tert*-butyl alcohol mole ratio = 0.5; WHSV = 5 h⁻¹)





Beta-50



Fig. S7 GC-MS Spectrogram of (a) spent Beta-30 and (b) spent Zr(8)-Beta-30

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Catalysts	Si/Al ^a	S_{BET}^{b} $[m^2g^{-1}]$	S _{ext} [m ² g ⁻¹]	S _{micro} [m ² g ⁻¹]	V_{tol}^{c} [cm ³ g ⁻¹]	V _{micro} d [cm ³ g ⁻¹]	V _{meso} ^e [cm ³ g ⁻¹]	Relative Crystalli zation %
Beta-20	12.3	553	128	405	0.399	0.216	0.183	89.1
Beta-30	14.3	558	164	394	0.434	0.210	0.224	100
Beta-40	21.9	513	115	398	0.336	0.213	0.123	93.9
Beta-50	26.1	533	129	403	0.362	0.216	0.146	86.3

Table S1 Textural properties of resultant Beta zeolites

^aSi/Al ratio of samples was determined by ICP-OES. ^bTotal surface of area was obtained by Brunauer–Emmett–Teller (BET) method. ^cDetermined from desorbed volume at P/P₀ = 0.99. ^d Determined from t-plot method. ^eV_{meso} = V_{tol} - V_{micro.}

Note: It can be seen from Table S1 that these Beta zeolites with different Si/Al ratios display a similar BET surface area, but the external surface area (S_{ext}) and mesopore volume (V_{meso}) of Beta-20, Beta-40, and Beta-50 samples slightly reduce compared with Beta-30.

Table 52 Acid site density of Beta Zeoffie Catalysis						
Catalysta	Acids	sites ^a				
Catarysts	B (mmol g ⁻¹)	$L \pmod{g^{-1}}$				
Beta-20	0.0351	0.335				
Beta-30	0.0474	0.216				
Beta-40	0.0392	0.366				
Beta-50	0.0339	0.267				
C-Beta	0.0190	0.152				
Na-Beta-30	0.0032	0.257				

Table S2 Acid site density of Beta zeolite catalysts

^aMeasured by FT-IR spectra of adsorbed pyridine

Note: The acidity of resultant Beta zeolites is given in Table S2, the C-Beta exhibits the lowest density of total Brønsted acid sites due to its condensed structure, which reduces the accessibility of acid sites. While the Beta-30 shows the highest density of total Brønsted acid sites since it possesses the optimized Si/Al ratio.

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