Supporting Information

Tuning the distribution of Al atoms in the framework of Beta zeolite and impact on the alkylation of phenol

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Experimental Procedures

Materials

The chemical regents used in present research involve JN-30 silica sol (30 wt%, Qingdao Haiwan Chemical Co., Ltd), sodium aluminate (53 wt% Al_2O_3, 42 wt% Na_2O, Macklin), Tetraethylammonium hydroxide (TEAOH, 35 wt%, Macklin), Tetraethylammonium chloride (TEACl, 98%, Macklin), Tetraethylammonium nitrate ($TEANO_3$, 98%, Macklin), sodium hydroxide (NaOH, 96%, Macklin), ammonium chloride (NH_4Cl, 99 wt%, Tianjin Damao Chemical Reagent Co.), cobaltous nitrate ($Co(NO_3)_2 \cdot 6H_2O$, 99 wt%, Macklin), phenol (99.5%, Macklin), *tert*-butanol (AR, Macklin), n-dodecane (AR, Macklin), cyclohexane (AR, Macklin), pyridine (AR, Macklin), 2,4,6-trimethylpyridine (AR, Macklin), deionized water.

Catalyst characterization

The crystal structures of prepared zeolites were characterized by X-ray diffraction (XRD) analyzer that was conducted on a Bruker-AXS D2 PHASER Advance diffractometer with Cu Kα radiation. The morphology of the zeolites was observed by a TDCLS-4800 scanning electron microscope (SEM). The amounts of silicon, aluminum and cobalt in the zeolite materials were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). The textural parameters of Beta zeolites were measured by Micromeritics ASAP 2460 devices at 77 K, and zeolites were pretreated under the condition of 473 K and vacuum for 6 h. The total surface area of the resultant samples was determined by the Brunauer-Emmett-Teller (BET) model, while the pore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) model based on N_2 desorption isotherm. The total density of acid sites was determined by Fourier transform infrared spectroscopy with the probe molecules of pyridine, using a Bruker VERTEX 70 spectrometer. The zeolites were firstly degassed at 723 K for 2 h before the measurements, then pyridine was adsorbed on the zeolites for 0.5 h at 298 K. Secondly, the temperature was raised to 423 K at 1 h to remove the weakly bound pyridine molecules. Thirdly, the acid density of resultant zeolites was measured by infrared spectroscopy at 32 scans and a resolution of 2 cm^{-1} when these samples were cooled to 298 K. In the Py-IR spectra, the characteristic peak of Brønsted acid and

Lewis acid sites for zeolite are at 1545 cm^{-1} and 1455 cm^{-1}, respectively. The molar extinction coefficient of 2.22 cm μmol^{-1} and 1.67 cm μmol^{-1} were used to calculate the density of Brønsted acid sites and Lewis acid sites, respectively. In the FT-IR spectra of adsorbed 2,4,6-trimethylpyridine, the characteristic peak of Brønsted acid sites is at 1636 cm^{-1}, corresponding to a molar extinction coefficient of 10.1 cm μmol^{-1}.[1, 2] In addition, the acidity of obtained samples were also measured by temperature programmed desorption of ammonia (NH_3-TPD) on an AutoChem 2920 instrument equipped with a thermal conductivity detector (TCD). The high-resolution ^{27}Al MAS NMR characterizations were performed to determine the Al coordination environment on a Bruker Avance Neo 400WB spectrometer equipped at a resonance frequency of 104.3 MHz. The measurements were performed on non-hydrated samples using a pulse length of 3.84 μs and a power of 95 .91 W. The spectral data were fitted and analyzed using the Mastrenova.15. Diffuse reflectance ultraviolet-visible (UV-vis) spectra of the dehydrated Co-Beta-H, Co-Beta-C, and Co-Beta-N samples were measured against $BaSO_4$ in the range of 200-600 nm on a Shimadzu UV3700i spectrometer. Before each measurement, the hydrated Co-Beta-X samples were dehydrated for 3 h at 10^{-1} Pa and 723 K in order to eliminate the influence of divalent cobalt species with H_2O or hydroxyl groups.[3]

Catalytic tests

The catalytic performances of resultant Beta zeolites in the alkylation of phenol with *tert*-butanol were evaluated in a three-necked round-bottom flask under atmospheric pressure at 353 K. In a typical reaction, 0.2 g of zeolite was employed, the molar ratio of phenol and *tert*-butanol was 1:2. Specially, the cyclohexane was served as the solvent, while *n*-dodecane was functioned as the internal standard substance. The reaction mixture was periodically taken and analyzed by gas chromatograph equipped with an HP-5 column and a flame ionization detector.

Subsequently, their stability and lifetime were further investigated through a fixed-bed reactor, and a 10 mm diameter reactor tube was used. The reaction was carried out under atmospheric pressure at 413 K. All Beta zeolite catalysts were pelletized to a size of 20-40 mesh and activated at 673 K for 4 h prior to testing. The molar ratio of phenol

to *tert*-butanol was 1:2 and a total weight hourly space velocity (WHSV) was 5 h^{-1}, these products were collected every 2 h and analyzed by gas chromatography as mentioned above. Prior to testing, all Beta zeolites were ion-exchanged three times at 353 K for 12 h, using 1.0 mol L^{-1} NH_4Cl aqueous solution, and these Beta zeolites were transformed into H^+ form.[4] The conversion of phenol and the selectivity of 4-TBP were calculated according to specific formulas[2]:

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

$$Selectivity\ of\ 4\text{-}TBP = (\frac{n_{4-TBP}}{n_{TBPE} + n_{2-TBP} + n_{4-TBP} + n_{2,4-DTBP} + n_{2,6-DTBP} + n_{2,4,6-TTBP}}) \times 100\% \quad (2)$$

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_{TBPE}, $n_{4\text{-TBP}}$, $n_{2\text{-TBP}}$, $n_{2,4\text{-DTBP}}$, $n_{2,6\text{-DTBP}}$ and $n_{2,4,6\text{-TTBP}}$ are the molar amounts of TBPE(*tert*-butyl phenyl ether), 4-TBP (4-*tert*-butyl phenol), 2-TBP (2-*tert*-butyl phenol), 2,4-DTBP (2,4-Di-*tert*-butyl phenol) 2,6-DTBP (2,6-Di-*tert*-butyl phenol) and 2,4,6-TTBP (2,4,6-tri-*tert*-butyl phenol) in the reaction mixture, respectively.

Figures and Tables

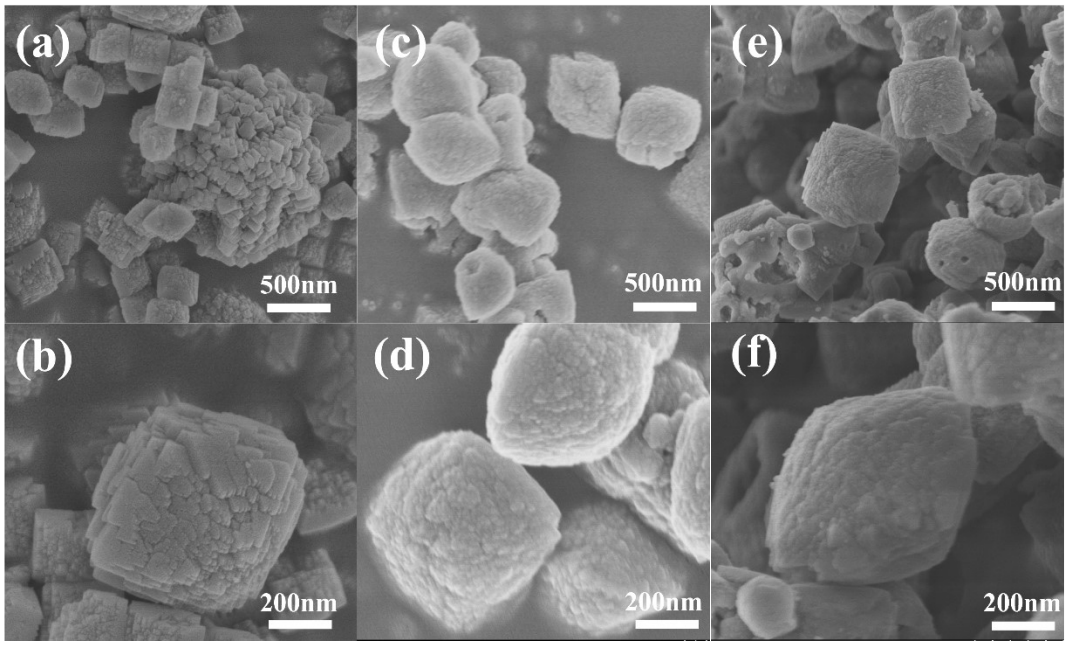


Figure S1. SEM images of Beta-H (a and b), Beta-C (c and d), Beta-N (e and f).

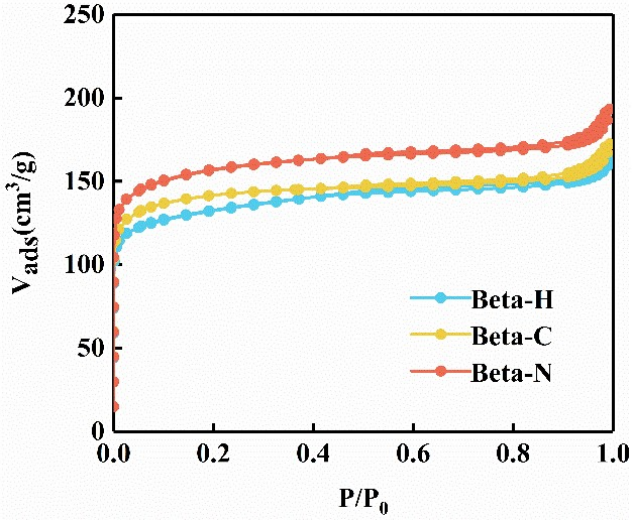


Figure S2. Nitrogen adsorption-desorption isotherms of the obtained Beta zeolites.

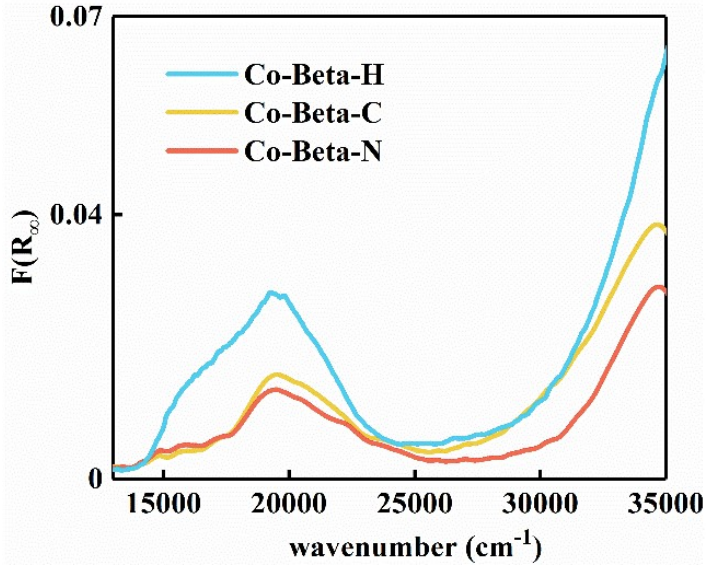


Figure S3. UV-vis spectra of different dehydrated Co-Beta zeolites.

Note: The absorption intensity is calculated by the Schuster Kubelka Munk equation[5, 6], $F(R_\infty) = (1-R_\infty)^2/2R_\infty$.

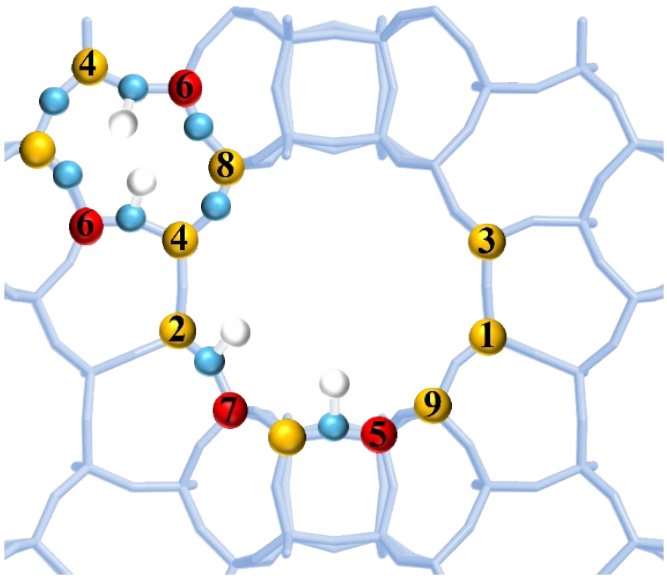
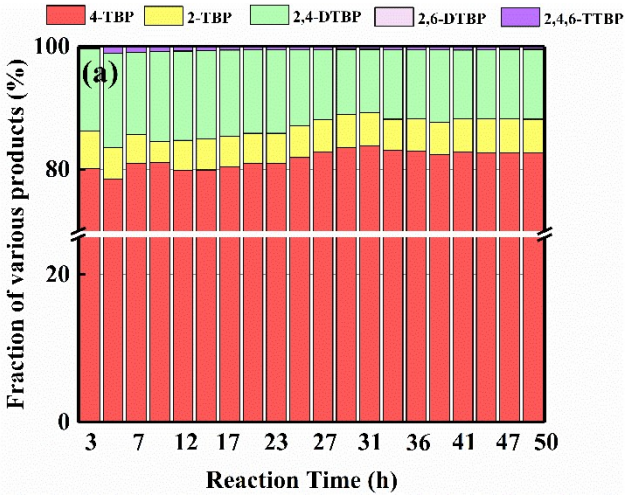


Figure S4. Representation of Beta zeolite framework in the [010] axis with nine different T-sites substituted by Al^{3+} ion (Si yellow, Al red, O blue, H white).



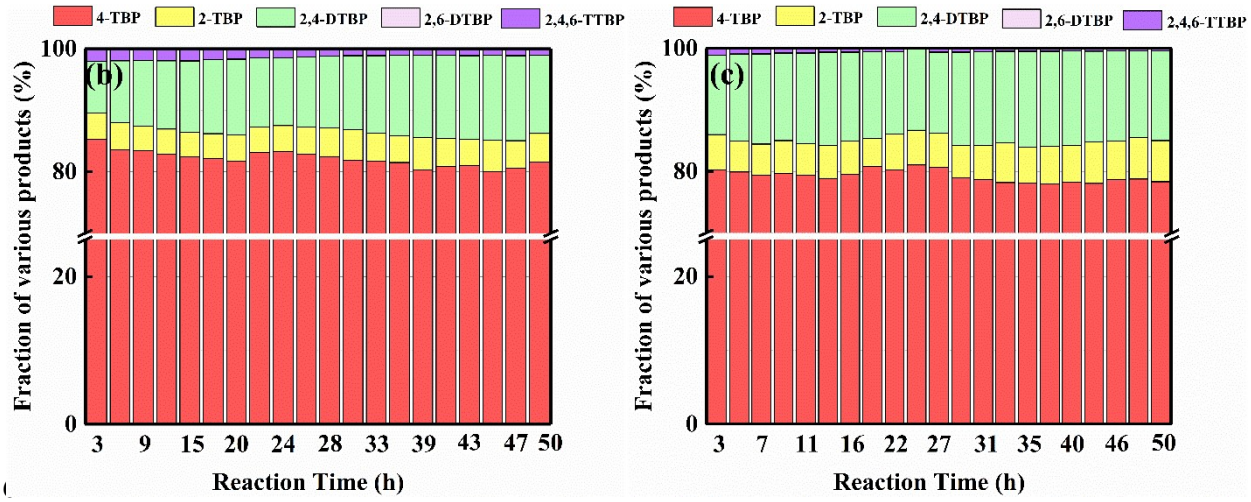


Figure S5. Product distributions with time-on-stream over (a) Beta-H, (b) Beta-C and (c) Beta-N, respectively.

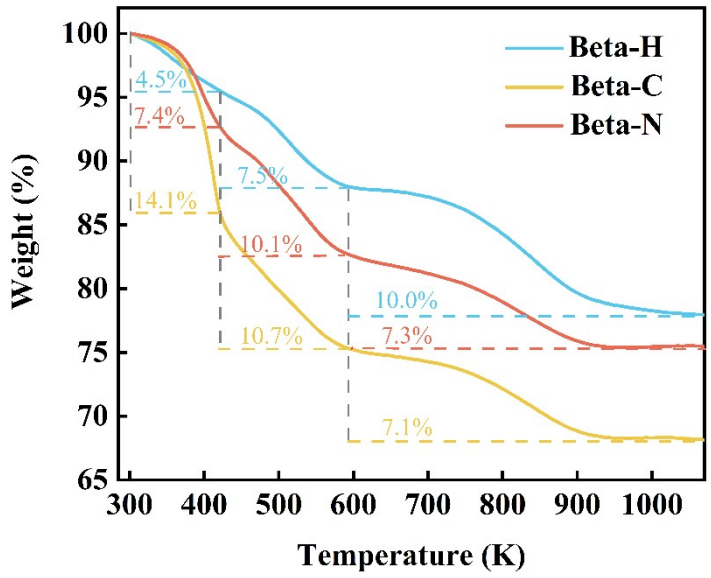


Figure S6. Thermogravimetric (TG) curves of various spent Beta zeolites.

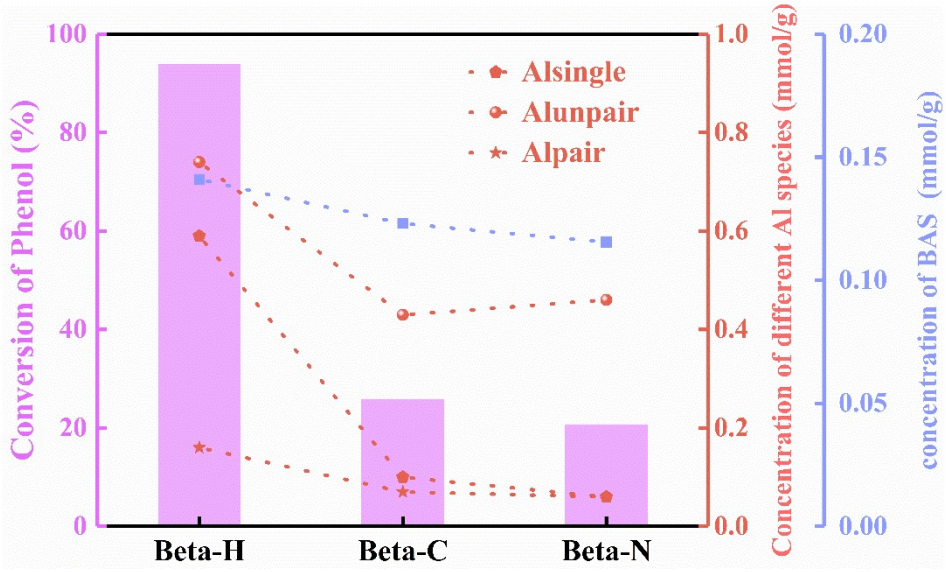


Figure S7. Quantitative relationship between concentrations of different aluminum species and Brønsted acid sites (BAS) and phenol conversion(all provided data were evaluated at 353 K and 1 h, with a ratio of phenol and *tert*-butanol to 2:1）

Table S1. Acid density of Beta zeolite catalysts

Catalyst	Acidity [a] (mmol g^{-1})		
	Weak acid sites [b]	Strong acid sites [c]	Total acid sites [d]
Beta-H	1.18	0.72	1.90
Beta-C	0.92	0.49	1.41
Beta-N	0.93	0.46	1.39

[a] Measured by NH_3-TPD.

[b] The density of weak acid sites are measured at 323–543 K.

[c] The density of strong acid sites are measured at 543–873 K.

[d] The total density of acid sites = the density of weak acid sites + the density of strong acid sites.

Table S2. The distribution of Brønsted acid sites in Beta zeolites

Catalyst	B_{total}[a] (mmol g^{-1})	$B_{a\&b}$[b] (mmol g^{-1})	B_c[c] (mmol g^{-1})	$B_{a\&b}/B_{total}$ (%)
Beta-H	0.141	0.107	0.034	76
Beta-C	0.123	0.073	0.050	59
Beta-N	0.116	0.058	0.058	50

[a] The concentration of total Brønsted acid sites is measured by the Py-IR spectra.

[b] The concentration of Brønsted acid sites in the channels along the *a* and *b* axis is determined by FT-IR spectra of adsorbed 2,4,6-trimethylpyridine.

[c] The concentration of Brønsted acid sites in the channel along the *c* axis is calculated by $B_c = B_{total} - B_{a\&b}$.

Note: Pyridine molecules can enter into all channels of Beta zeolite along the *a*, *b* and *c* axis to determine the total Brønsted acid sites of catalysts, while the 2,4,6-trimethylpyridine with a size of 6.2 × 5.6 Å can only access the pore channels along the *a* and *b* axis.

Table S3. Coke deposit of resultant Beta zeolites.

Catalyst	sample weight (mg)	soft coke [a] (g/g^0 cat)×10^{-2}	hard coke [b] (g/g^0 cat)×10^{-2}	Average coke rate [c] ($mg/g^0.h^{-1}$ cat)
Beta-H	4.5	7.5	10.0	2.56
Beta-C	5.3	10.7	7.1	2.09
Beta-N	4.6	10.1	7.3	1.95

[a] The weight loss from 423 to 593 K.

[b] The weight loss from 593 to 1073 K.

[c] Average coke rate = the weight of hard coke/time.

References

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