

Supporting Information

Synthesis of Linear Alkylbenzenes over Beta Zeolites with Enhanced Transport and Surface Activity

Weijian Lu[†], Jianwen Zhang[†], Shiqi Zhang[†], Chen Ji[†], Ying Wu[‡], Huiyong

Chen[#], Yanxiong Fang[†], Jinxiang Dong^{†,§} and Baoyu Liu^{*,†}

[†]School of Chemical Engineering and Light Industry, Guangdong Provincial Key Laboratory of Plant Resources Biorefinery, Guangzhou Key Laboratory of Clean Transportation Energy Chemistry, Guangdong University of Technology, Guangzhou, 510006, P.R. China

[‡]School of Chemistry and Chemical Technology, South China University of Technology, Guangzhou, Guangdong 510640, P.R. China

[#]School of Chemical Engineering, Northwest University, Xi'an, Shaanxi, 710069, China

[§] College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan, 030024, P.R. China

*Corresponding author:

Prof. Baoyu Liu

Email: baoyu.liu@gdut.edu.cn

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Experimental Procedures

Catalyst Characterization

The Powder X-ray diffraction (PXRD) patterns were obtained on a Bruker D8 ADVANCE Diffractometer equipped with Cu K α radiation at Bragg angles 2θ of 5°-55°. Nitrogen adsorption-desorption isotherms performed to obtain the textural properties were measured on Micromeritics ASAP2010 instrument at -196 °C. Prior to analysis, all the samples were outgassed at 200 °C for 12 h. The Brunauer-Emmett-Teller (BET) equation and t-plot method were employed to analyze the surface areas of the sample, while the pore size distribution of the samples were analyzed by the Barrett-Joyner-Halenda (BJH) model. Kinetic adsorption experiment was performed in BEISHIDE Vacuum Vapor Sorption analyzer. Before starting the measurement, the sample was degassed at 100 °C for 3 h in vacuum, and the fractional transient uptakes of benzene on Beta zeolites was carried out under 303 K and 4.78 KPa (relative pressure $P/P_0=0.3$). Scanning electron microscopy (SEM) images were performed using a Hitachi S4800 electron microscope at an acceleration voltage of 10 kV with a metal coating. The contents of Si and Al in zeolite samples were measured with inductively coupled plasma optical emission spectroscopy (ICP-OES) on Optima 7000DV (PerkinElmer) spectrometer. The acidity of the calcined zeolites was investigated by infrared spectroscopy with adsorption/desorption of pyridine (Py) and 2,6-di-tert-butyl pyridine (DTBPy) as probe molecules monitored on a Vertex 70 FTIR apparatus. Prior to the measurements, the samples were outgassed for 2 h at 550 °C. Pyridine or

2,6-di-tert-butyl pyridine was adsorbed on the degassed samples for 1 h at ambient temperature. The sample was heated to 150 °C for 1 h to remove the weakly bound pyridine species. After cooling to room temperature, IR spectra were recorded with 30 scans and 2 cm⁻¹ resolution. The concentrations of total Brønsted acid sites, total Lewis acid sites and external Brønsted acid sites of zeolites¹⁻² were calculated by integrating absorbance peak at $\nu = 1545\text{ cm}^{-1}$ with $\epsilon = 1.88\text{ cm}^2\text{ }\mu\text{mol}^{-1}$, at $\nu = 1455\text{ cm}^{-1}$ with $\epsilon = 1.42\text{ cm}^2\text{ }\mu\text{mol}^{-1}$ and at $\nu = 1616\text{ cm}^{-1}$ with $\epsilon = 2.84\text{ cm}^2\text{ }\mu\text{mol}^{-1}$, respectively.³

Catalytic Tests

Alkylation of benzene with 1-dodecene was performed to evaluate the catalytic performance of prepared Beta zeolites at atmospheric pressure in a two-necked glass flask with stirring, which was impregnated in a temperature-controlled oil bath and equipped with a reflux condenser. Prior to the catalytic tests, all of the zeolite catalysts were activated at 100 °C for 5 h and the reactants benzene and 1-dodecene were dehydrated by 4A zeolite. Typically, 112 mmol of benzene, 7.2 mmol ethylcyclohexane (as internal standard) and 100 mg catalysts was added into a two-necked flask (25 ml). After stabilizing at 80 °C in oil bath for a desired time under stirring, 12.8 mmol 1-dodecene was injected quickly. This moment was considered as the initial reaction time. The mixture was withdrawn periodically and analyzed in a gas chromatograph (Agilent 7820A) equipped with a HP-5 column (Agilent, 30 m \times 0.320 mm, 0.25 micron) connected to a flame ionization detector (FID). For the recycling experiment, zeolite catalysts after cycle were filtered and

dried at 100 °C for 12 h, then they were used to evaluate the catalytic performance in next cycle without any treatment.

The computational results

The computational calculations were performed using Sorption module in Materials studio 7.0.⁴ One molecule of 1-dodecene and one molecule of benzene were fixed loaded in BEA zeolite using Metropolis Monte Carlo method.⁵ To fully examine the interaction of 1-dodecene and benzene with the framework of BEA zeolite, both van der Waals and electrostatic interactions were considered. Universal force field⁶ was used to describe the van der Waals interaction between the adsorbates and adsorbent, while the partial charges calculated with QEq method⁷ and summed with Ewald method⁸ were used to model the electrostatic interactions. The cutoff distance of van der Waals interactions was set to 15.5 Å, and Ewald accuracy was set to 1×10^{-4} kcal/mol. During the simulations, the relative probabilities of adsorbate exchange, conformer, rotate, translate and regrow was set to 0.39, 0.20, 0.20, 0.20, 0.02, respectively, for each Monte Carlo step. 1×10^5 steps were used for equilibration, and 1×10^6 steps were for production.

Details for acid sites passivation experiment.

In this part, Beta-0 and Beta-5 were selected for modification and test. Typically, 0.2 g the calcined samples were pressed into self-supporting wafers, respectively. Then it was put in the in-situ cell at room temperature, followed by the pump system to achieve high vacuum environment. After turning off the pump valve and opening the valve between the cell and adsorbed reagent tube, the adsorption of zeolites was

carried out under the flowing pyridine (Py) / 2,6-di-tert-butyl pyridine (DTBPy) stream in the system. The resulted sample was recovered after adsorption at room temperature for 1 h and denoted as Beta-0-x or Beta-5-x, respectively, where x represented the adsorbed reagent. Specific details for alkylation test were consistent with the description in the section of catalytic tests.

Calculation of effective diffusion coefficient

The diffusion coefficient of benzene within beta zeolites was calculated through adsorption kinetic curves. Assuming that the beta zeolite particle is spherical and according to Fick's law, the diffusion equation was:⁹⁻¹⁰

$$\frac{Q_t}{Q_e} = 1 - \frac{6}{\pi} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left(-\frac{D_{eff} n^2 \pi^2}{R^2} t \right) \quad (S1)$$

For a short period of time, equation (S1) could be further written as:¹¹

$$\frac{Q_t}{Q_e} \cong 6 \sqrt{\frac{D_{eff} t}{\pi R^2}} \quad (S2)$$

Where Q_e and Q_t are the adsorption capacity (mg/g) of adsorbent at equilibrium and time t (s), respectively. D_{eff} is the effective diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), R is the particle radius (m). When $\frac{Q_t}{Q_e}$ is plotted versus \sqrt{t} , a straight line with a slope $(6 \sqrt{\frac{D_{eff}}{\pi R^2}})$ can be obtained. Therefore, the diffusion time constant $\frac{D_{eff}}{R^2}$ (s^{-1}) can be found from the slope of the line.

Figures and Tables

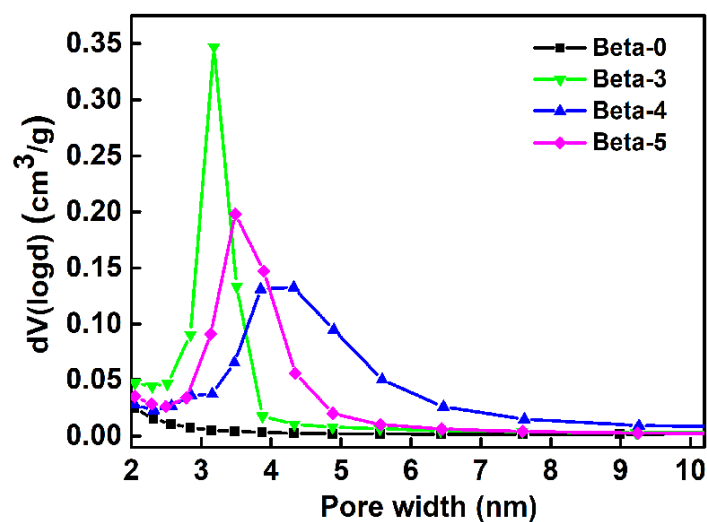


Figure S1. The BJH pore distributions of Beta zeolites.

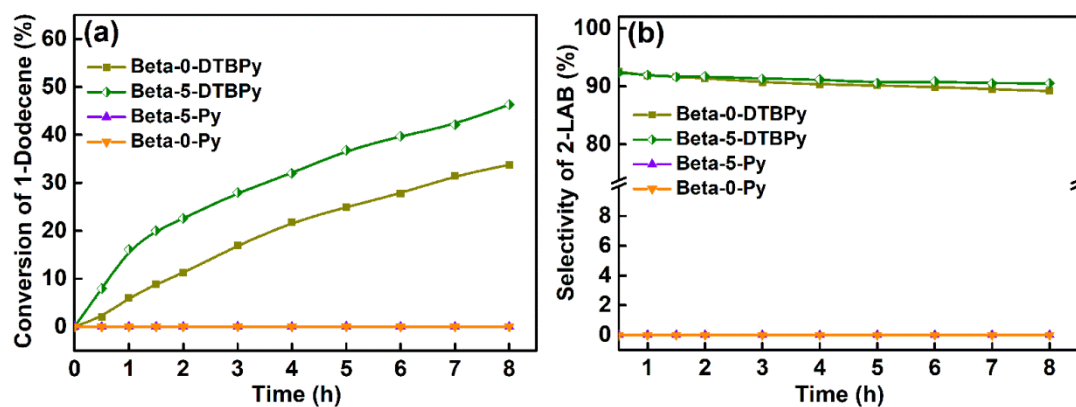


Figure S2. Conversion of 1-Dodecene (a) and Selectivity of 2-LAB (b) of Beta-0 and Beta-5 after adsorbed Py or DTBPy.

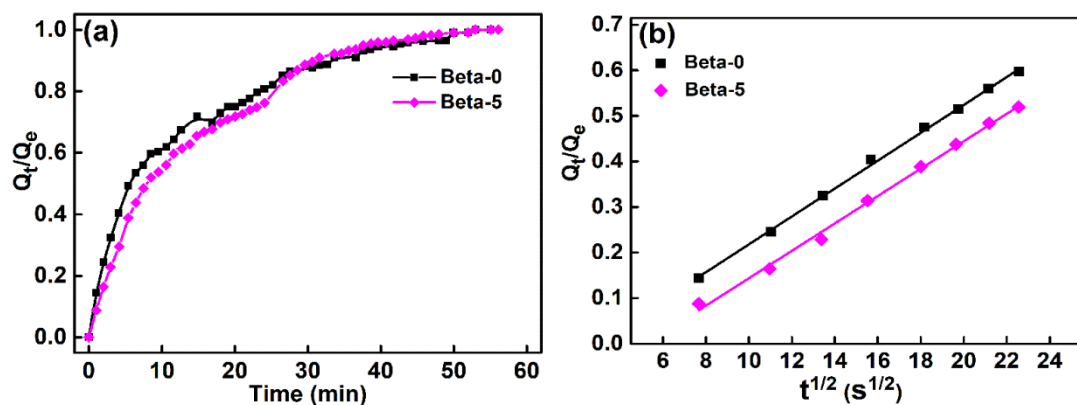


Figure S3. Fractional transient (a) and plots of the fractional adsorption (b) uptakes of benzene on Beta zeolites.

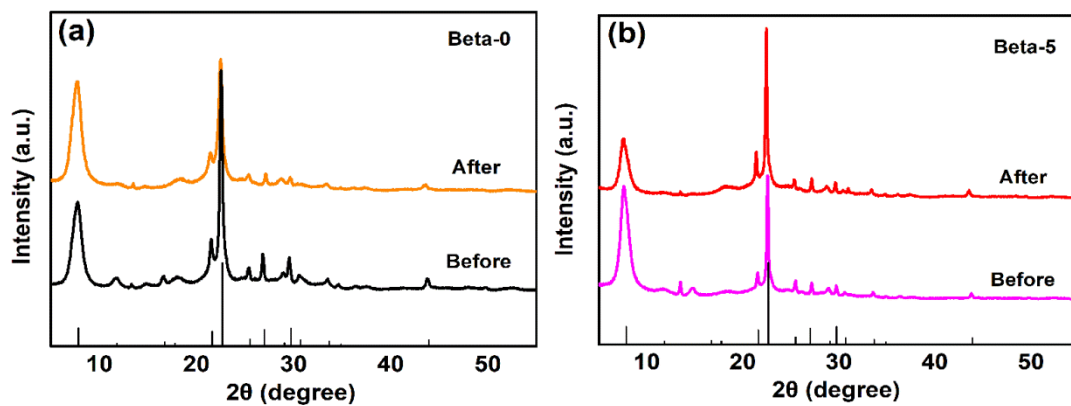


Figure S4. XRD patterns of Beta-0 (a) and Beta-5 (b) before and after catalytic durability experiment.

Table S1. Acidity of resultant Beta zeolite catalysts

Sample	Si/Al ^a	Acid sites ^b		B/L ^d	External acid sites ^c
		B (mmol g ⁻¹)	L (mmol g ⁻¹)		B (mmol g ⁻¹)
Beta-0	31.8	0.1109	0.2311	0.480	0.0325
Beta-3	38.0	0.0795	0.1975	0.403	0.0288
Beta-4	51.0	0.0802	0.2081	0.385	0.0296
Beta-5	52.4	0.0839	0.1457	0.576	0.0298

^a The Si/Al ratios determined by ICP-OES.

^b Measured by FT-IR spectra of adsorbed pyridine.

^c Measured by FT-IR spectra of adsorbed 2,6-di-tertbutylpyridine.

^d B/L= Brønsted acid sites (mmol g⁻¹) : Lewis acid sites (mmol g⁻¹)

Table S2. Diffusion time constant and effective diffusion coefficient of benzene on the samples

Catalysts	D_{eff}/R^2 (s ⁻¹)	R (m)	D_{eff} (m ² s ⁻¹)
Beta-0	8.17×10^{-5}	3.25×10^{-8}	8.63×10^{-20}
Beta-5	7.9×10^{-5}	8.50×10^{-8}	5.71×10^{-19}

R (m) is the particle radius measured from SEM images.

References

- (1) Li, R.; Xing, S.; Zhang, S.; Han, M. Effect of surface silicon modification of H-beta zeolites for alkylation of benzene with 1-dodecene. *RSC Adv.* **2020**, 10, 1006-1016.
- (2) Emeis, C. A. Determination of Integrated Molar Extinction Coefficients for Infrared Absorption Bands of Pyridine Adsorbed on Solid Acid Catalysts. *J. Catal.* **1993**, 141, 347-354.
- (3) Huang, J.; Liu, B.; Liao, Z.; Chen, H.; Yan, K. Fabrication of Cu-Encapsulated Hierarchical MEL Zeolites for Alkylation of Mesitylene with Benzyl Alcohol. *Ind. Eng. Chem. Res.* **2019**, 58, 16636-16644.
- (4) Accelrys *Materials Studio 7.0*, 2013.
- (5) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. Equation of state calculations by fast computing machines. *J. Chem. Phys.* **1953**, 21, 1087-1092.
- (6) Rappé, A. K.; Casewit, C. J.; Colwell, K.; Goddard Iii, W.; Skiff, W. UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations. *J. Am. Chem. Soc.* **1992**, 114, 10024-10035.
- (7) Rappe, A. K.; Goddard III, W. A. Charge equilibration for molecular dynamics simulations. *J. Phys. Chem.* **1991**, 95, 3358-3363.
- (8) Ewald, P. P. Ewald summation. *Ann. Phys.* **1921**, 369, 1-2.
- (9) Zhao, H.; Song, L.; Qin, Y.; Duan, L.; Sun, Z. Adsorption Thermodynamics and Diffusion Kinetics of PX over Na Y Zeolite Synthesized by In-Situ Crystallization from Kaolin Microsphere. *China Pet. Process. Petrochem. Technol.* **2014**, 4, 47-54.
- (10) Xu, F.; Xian, S.; Xia, Q.; Li, Y.; Li, Z. Effect of Textural Properties on the Adsorption and Desorption of Toluene on the Metal-Organic Frameworks HKUST-1 and MIL-101. *Adsorpt. Sci. Technol.* **2013**, 31, 325-340.
- (11) Zhao, Z.; Li, Z.; Lin, Y. S. Adsorption and Diffusion of Carbon Dioxide on Metal-Organic Framework (MOF-5). *Ind. Eng. Chem. Res.* **2009**, 48, 10015-10020.