



## Enhanced catalytic isomerization of $\alpha$ -pinene over mesoporous zeolite beta of low Si/Al ratio by NaOH treatment

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### ABSTRACT

Small crystal zeolite beta with Si/Al ratio of 12 was subjected to post-synthesis treatment with NaOH solutions. The effect of alkaline concentration on the crystallinity, pore structures, compositions and acidic properties of zeolite beta was studied by XRD,  $N_2$  sorption, XRF, and FTIR techniques. The catalytic performance of zeolite beta before and after alkaline treatment was investigated in terms of liquid phase isomerization of  $\alpha$ -pinene. No distinct change in the crystallinity was observed after the zeolite was treated by 0.1–0.4 M NaOH solutions. However, mesoporosity was evidently developed; the mesopore surface area up to  $349 \text{ m}^2 \text{ g}^{-1}$  was obtained when 0.4 M NaOH solution was employed. The acidic properties of zeolite beta were mostly preserved when it was treated by 0.1–0.2 M NaOH solutions, but the amount of strong Brønsted acid sites was to some extent reduced when 0.4 and 0.7 M NaOH solutions were employed. The catalytic activities of the samples increase with the development of mesoporosity. The best catalytic performance at  $70^\circ\text{C}$  and 30 min reaction time was observed on zeolite beta containing the largest mesopore volume of  $0.69 \text{ cm}^3 \text{ g}^{-1}$ : 100% conversion of  $\alpha$ -pinene with 85.4% selectivity into camphene, terpinolene,  $\alpha$ - and  $\gamma$ -terpinene as desired products. At the same conditions only 20.3% conversion was obtained over parent zeolite beta containing only  $0.23 \text{ cm}^3 \text{ g}^{-1}$  mesopore volume. This result indicates that the enhanced catalytic activity for  $\alpha$ -pinene isomerization is mainly attributed to the mesopore formation resulting from alkaline treatment.

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### 1. Introduction

Zeolites, the crystalline microporous aluminosilicates, have been widely used in industry as environmentally friendly heterogeneous catalysts and sorption media, especially in oil refining, petrochemistry and the production of fine chemicals [1,2]. Their high specific surface area, large pore volume, uniform microporous channels, and excellent thermal and hydrothermal stability are all catalytically desirable properties. However, their small pores impose diffusion limitations and restrict the access of reactant molecules to the active sites in their internal surface [3]. These drawbacks preclude practical applications involving bulky molecules, like for example the isomerization of  $\alpha$ -pinene. Considerable efforts have been devoted to improve the accessibility of active sites by synthesizing mesoporous molecular sieves with pore sizes between 2 and 50 nm [4–6]. Unfortunately, these materials have usually low thermal and hydrothermal stability and lose most Brønsted acidic sites.

Many strategies have been employed to overcome these difficulties. One example is the synthesis of nanocrystalline zeolites

to increase external surface area and shorten diffusion path length [7–10]. Another example is formation of microporous materials with mesopores to facilitate diffusion to the internal active sites [11–21]. Hierarchically structured zeolites, which have advantages of both microporous and mesoporous molecular sieves, can be obtained in different ways, such as by post-synthesis treatment [11–14], crystallization of amorphous aluminosilicates deposited onto hard templates including certain carbon containing materials [15–19] or by using surfactants as soft templates [20,21], and other methods. Of these strategies, the post-synthesis treatment and the use of solid carbon templates have proved to be most reliable for creating mesoporous zeolites with fully crystalline pore walls. However, the carbon template approach is not suitable for mass production due to the complicated synthesis procedures involved and the hydrophobicity of these templates. The post-synthesis treatments of zeolites, including dealumination and desilication, are more simple, feasible and highly effective methods.

Dealumination by steam or acid solution could create additional porosity by generating defect sites in the zeolite framework; it also affects the acidic properties of zeolites [22–24]. Desilication with alkaline solution proved to be a more efficient post-synthesis treatment method to improve the porosity of zeolites through selective extraction of silicon atoms from the framework without distinct

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change of the acidity and crystallinity [11–13,25–32]. So far, zeolite ZSM-5 has been the most widely and deeply studied material for creating hierarchical structures by desilication in alkaline solution [30–32]. From these studies one can conclude that the Si/Al ratio substantially affects the mesopore formation and the optimum range is Si/Al  $\sim$  25–50. If the Si/Al ratio is too low, the excess framework and extra-framework Al species will inhibit Si extraction and related mesopore formation. If the Si/Al ratio is too high, excess dissolution occurs. Analogously, the optimal conditions and the effectiveness of desilication were investigated in the synthesis of mesoporous ZSM-22 [14], mordenite [26], FER [29] and zeolite beta [11,12,29,33]. Among the reported zeolites that subjected to alkaline treatment, zeolite beta is more susceptible to mesoporosity development than MFI, FER and MOR, since the framework aluminum in zeolite beta is less stable [29,33]. Zeolite beta is a disordered intergrown hybrid of two or more distinct but closely related crystal structures. It possesses a three-dimensional pore system containing 12-membered ring apertures and many framework defects, which makes it more active [34,35]. When zeolite beta with Si/Al ratio of 35 was treated by 0.2 M NaOH solution at 338 K for 30 min, which is the optimal condition for mesoporous ZSM-5, the crystallinity was severely damaged [33]. Therefore, it is necessary to study the possibility of the creation of mesopore in zeolite beta of low Si/Al ratio.

In this work, small crystal zeolite beta with low Si/Al ratio of 12 was selected to investigate the possibility of creating mesopores in it by NaOH treatment while maintaining its acidic property and crystallinity. The effect of NaOH concentration on its structure, acidic property, and catalytic performance in  $\alpha$ -pinene isomerization is also investigated. It will be shown that additional mesopores were created with the maintenance of its crystallinity when the concentration of NaOH solution was below 0.4 M, and significantly enhanced  $\alpha$ -pinene conversion was observed owing to the development of mesoporosity.

## 2. Experimental

### 2.1. Synthesis of parent zeolite beta

Sodium form zeolite beta (Na-beta) used as parent zeolite was prepared using silica sol (SiO<sub>2</sub> 30 wt.%) and Boehmite (Al<sub>2</sub>O<sub>3</sub> 76 wt.%) as silica and alumina sources, respectively. A typical synthesis procedure was as follows: a certain amount of tetraethylammonium bromide (TEABr) was dissolved in concentrated ammonia solution, and then silica sol was added in the solution with stirring to obtain solution A. NaOH, KOH and Boehmite were dissolved in deionized water to get a clear solution B. With vigorous stirring solution B was added in Solution A. Subsequently, crystal seed of zeolite beta was added in above mixture with continuous stirring to obtain a homogeneous gel. The gel was then loaded into an autoclave and heated at 140 °C for 4 days. After the crystallization process, the solid product was cooled, recovered by filtration, washed with deionized water, dried in oven at 120 °C, and calcined in air at 550 °C for 6 h. Primary characterization of the resultant product suggests that the particle sizes are in the range of 200–700 nm (by SEM) and its SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio is 24 (determined by XRF), corresponding to a chemical composition of 2.5Na<sub>2</sub>O·2.5Al<sub>2</sub>O<sub>3</sub>·59SiO<sub>2</sub>.

### 2.2. Treatment of zeolite beta

Na-beta was transformed into H form for the catalytic reaction. Briefly, 3 g of Na-beta was ion-exchanged by refluxing it at 70 °C in 60 mL of 1 mol/L aqueous NH<sub>4</sub>Cl solution for 2 h. The filtered product was thoroughly washed with deionized water, dried overnight,

heated in air at 5 °C/min rate to 550 °C and kept at this temperature for 5 h. This proton-exchanged parent zeolite beta was designated as HB-1.

Alkaline treatment of zeolite beta was carried out using NaOH solution, following the procedure as reported previously [33]. Briefly, 3 g of Na-beta were dispersed into 60 mL of NaOH solution (0.1 mol/L) at 65 °C under stirring for 30 min. The slurry was filtered, washed thoroughly with deionized water and dried at 110 °C. Then the product was treated by NH<sub>4</sub>Cl solution as described above to obtain the protonated form zeolite beta. The resultant sample was designated as HB-2. Samples HB-3, HB-4 and HB-5 were obtained by the same procedure as HB-2 except that the concentration of NaOH solution is 0.2, 0.4 and 0.7 mol/L, respectively.

### 2.3. Characterization

X-ray diffraction (XRD) analysis was carried out by using Japan XD-3A diffractometer with Cu K $\alpha$  monochromatized radiation source ( $\lambda$  = 0.154 nm), operated at 30 kV and 30 mA. The scanning rate was 5°/min and the scanning range was 5–40°. The bulk Si/Al ratio was determined on Bruker SRS 3400 X-ray fluorescence (XRF) elemental analysis spectrometer.

N<sub>2</sub> adsorption and desorption isotherms with multipoint method at –196 °C were measured using Micromeritics ASAP 2020. Prior to the measurements, the samples were evacuated at 300 °C for 4 h. The total surface areas were determined by BET method. The micropore volumes and the micropore surface areas were obtained by *t*-plot method. The BJH model applied to the adsorption branch of the isotherm was used to obtain the mesopore size distribution.

IR spectra were recorded on a Nicolet Avatar 360 FT-IR spectrometer. KBr pellets were pressed from a homogeneous mixture of zeolite (3%) in KBr for the framework vibration investigation at room temperature (RT).

Self-supporting thin wafers, used in OH-stretching vibration and pyridine adsorption studies, were pressed and placed in a quartz IR cell with CaF<sub>2</sub> windows. Prior to the measurements, each sample was dehydrated in N<sub>2</sub> flow of ultrahigh purity at 400 °C for 1 h. And then the OH-stretching vibration spectra were collected at the same temperature. After the pretreatment, the wafer was cooled down to RT and the adsorption of pyridine was carried out for 10 min. Desorption was performed by surging the wafer with N<sub>2</sub> flow at elevated temperatures. The spectra were recorded at 150, 300 and 450 °C, respectively. All the Py-FTIR spectra in this paper were difference spectra.

### 2.4. Catalytic test

All catalysts were tested in the reaction of  $\alpha$ -pinene isomerization. The reaction was carried out at atmospheric pressure in a glass reactor with a reflux condenser under magnetic stirring. For a typical run, 0.10 g of catalyst and 2.0 mL of  $\alpha$ -pinene (Aldrich, 98%) were charged into a glass tube reactor to react at 70 °C for 30 min. After the reaction was finished, the sample was cooled to RT rapidly and filtered to remove the catalyst. The products were analyzed with a gas chromatograph (GC 7890 F with 30 m  $\times$  0.25 mm  $\times$  0.3  $\mu$ m capillary column) equipped with a flame ionization detector (FID). Chemstation software was used to collect and analyze the data. The content of each product was calculated using the area normalization method.

The ingredients of the products were analyzed with HP 6890N-5975B (GC-MS) equipped with EI ion source and quadrupoles detector. The carrier gas was He.

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