Microporous and Mesoporous Materials 173 (2013) 129–138

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Effect of Si/Al ratio on mesopore formation for zeolite beta via NaOH treatment and the catalytic performance in α-pinene isomerization and benzoylation of naphthalene

Fuping Tian *, Yihui Wu, Qicheng Shen, Xiang Li, Yongying Chen, Changgong Meng

School of Chemistry & State Key Laboratory of Fine Chemicals, Dalian University of Technology, 2 Linggong Road, P.O. Box 288, Dalian 116024, China

ARTICLE INFO

Article history:
Received 7 August 2012
Received in revised form 24 January 2013
Accepted 10 February 2013
Available online 24 February 2013

Keywords:
Zeolite beta
Si/Al ratio
Mesoporosity
Alkaline treatment
Acid catalytic performance

ABSTRACT

Small crystal zeolites beta with molar Si/Al ratios of 21, 30 and 40.5 were successfully obtained by treating parent beta (Si/Al = 14.5) with different oxalic acid concentrations. The influence of Si/Al ratio of zeolite beta on effective mesopore formation via NaOH treatment was studied by investigating the changes in crystallinity, morphology, chemical composition, acidity and textural property of zeolite beta before and after alkaline treatment. The catalytic performance was evaluated in terms of α-pinene isomerization and benzoylation of naphthalene with benzoyl chloride. Substantial mesoporosity could be developed for zeolites beta with molar Si/Al ratios of 14.5–30, coupled with better preserved microporosity. Though the largest mesopore surface area (488 $m^2 g^{-1}$) was achieved when Si/Al = 30, the crystallinity of zeolite beta was partly destroyed. The substantially improved catalytic activity of alkaline treated samples in α-pinene isomerization is mainly attributed to the developed mesoporosity, but the volcano curve change in catalytic activities of alkaline treated samples in benzoylation of naphthalene manifested that both mesoporosity and acid property play important role in a medium strong acid catalyzed reaction.

1. Introduction

Zeolites as the microporous crystalline materials have been widely employed in a large number of industrial processes as environmentally friendly heterogeneous catalysts, ion exchangers and adsorbents due to their high specific surface area, large pore volume, uniform microporous channels, and excellent thermal and hydrothermal stability [1,2]. The microporous channels of zeolites, however, impose diffusion limitations, restrict the access to the active sites in the internal surface, and therefore limit their applications involving bulky compounds [3]. To overcome the disadvantages of microporous zeolites, i.e., to improve the accessibility and molecular transport, a variety of strategies have been taken, for example, the synthesis of extra-large pore zeolite with more than 12–member rings, such as ITQ-21[4], SU-M [5]; the preparation of nanocrystalline zeolites to shorten diffusion path length [6,7]; and the creation of mesopores within the zeolite crytals to yield a network of connected mesopores and micropores [8–26]. Of these strategies, the last one leads to the preparation of micro/mesoporous zeolites charateristic of hierarchical structure and includes several preparation methods: post-synthesis treatment [8–20], recrystallization of amorphous aluminosilicate deposited onto hard templates [21], zeolite synthesis by using carbon materials as hard templates [22–24] or surfactants as soft templates [25,26]. Thereinto, the post-synthesis treatments and the use of carbon templates have proved to be most reliable for creating mesoporous zeolites with fully crystalline pore walls. However, mass production of micro/mesoporous zeolites via carbon template route is often a major issue due to the complicated synthesis procedures involved and the hydrophobicity of carbon templates. The post-synthesis treatments of zeolites, including dealumination or desilication, have been widely investigated as more simple, feasible and highly effective methods [27,28].

Dealumination by steam treatment or acid leaching could form extraporosity by creating defect sites in zeolite framework, but it unavoidably affects the acidic properties of zeolites [29,30]. Desilication with alkaline solution has been proved to be a more effective post treatment method to improve the porosity of zeolites through selective extraction of silicon atoms from the framework without distinct change in the acidity and crystallinity [28,31]. So far, the effectiveness of mesoporosity introduction via desilication has been investigated on several widely used zeolites, such as FER [8], beta [8–11], ZSM-22 [12], mordenite [13] and ZSM-5 [14–20]. Among these, ZSM-5 is the most widely and deeply studied material. Early works demonstrated that [15–17] the optimal range for creating mesoporous ZSM-5 is Si/Al ~ 25–50. Based on which, a recent work [20] extended the available Si/Al range to 12–200 by either the addition of external pore-directing agent

---

* Corresponding author. Tel.: +86 411 84708901; fax: +86 411 84706313.
E-mail address: fptian@dlut.edu.cn (F. Tian).

1387-1811/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2013.02.021

(in the case of high Si/Al ratio) or the use of higher NaOH concentration followed by acid wash (in the case of low Si/Al ratio). All the literature on ZSM-5 revealed a crucial effect of the molar Si/Al ratio on the effectiveness of mesopore formation. 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 [8]. Zeolite beta is a disordered intergrown hybrid of two distinct but closely related structures that have tetragonal system and clinorhombic system. It possess a three-dimensional pore system containing 12-membered ring apertures and highly framework defects, which makes it more active [32,33]. 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 [9]. To evade the negative effect of inorganic base on the crystallinity owing to the less stability of framework aluminum of zeolite beta, the other two strategies, such as desilication of partial detemplated beta by NaOH solution [10] or treatment with organic base tetramethylammonium hydroxide (TMAOH) [11], were employed to create hierarchically structured zeolite beta with mostly retained crystallinity. It should be noted that the Si/Al ratio of the parent zeolite beta under above investigation is 35 and lies in the optimal range for ZSM-5, but considering the less stability of framework aluminum in zeolite beta, it is necessary to study the optimal conditions, including the efficient base concentration and Si/Al ratio, for mesopore creation in zeolite beta. Our recent work [34] demonstrated that for zeolite beta with Si/Al ratio of 12, the optimal NaOH concentration range is 0.2–0.4 M when aiming at high mesoporosity coupled with better preserved microporosity and acidic properties. This work focuses on the optimal Si/Al ratio range for mesoporous zeolite beta under a fixed condition (0.2 M NaOH, 65 °C, 30 min).

In this study, small crystal zeolites beta with molar Si/Al ratios of 14.5–40.5 were treated by 0.2 M NaOH at 65 °C for 30 min to investigate the effect of Si/Al ratio of zeolite beta on the mesopore creation while maintaining the acidic property and crystallinity. The different Si/Al ratios of zeolites beta were realized by treating the parent beta (Si/Al = 14.5) with 0.03–0.07 M oxalic acid. To the best of our knowledge, though some studies on mesopore creation in zeolite beta have already been made [8–11], no systematic evaluation on the influence of Si/Al ratio of zeolite beta on mesopore formation via alkaline treatment has been reported, from the viewpoint of its unique structural characteristic. The catalytic performances of zeolites beta before and after alkaline treatment were tested using α-pinene isomerization (weak acid catalyzed reaction) and benzoylation of naphthalene with benzoyl chloride (moderate strong acid catalyzed reaction) as probe reactions. It will be shown that additional mesopores are created with the maintenance of crystallinity and microporosity for zeolite beta with molar Si/Al ratio less than 30, which is quite different from the optimal Si/Al range for ZSM-5, and evidently enhanced catalytic performances are observed in both α-pinene isomerization and benzoylation of naphthalene with benzoyl chloride owing to the development of mesoporosity.

2. Experimental

2.1. Catalysts preparation

Parent zeolite H-beta (Si/Al = 14.5, designated as B) purchased from Nankai University Catalyst Factory was firstly treated by oxalic acid solutions of different concentrations to adjust the Si/Al ratio of zeolite beta according to the procedure reported in the literature [35]. Briefly, 3 g of H-beta was dispersed into 60 mL of oxalic acid solution (0.03, 0.05, 0.07 M) at 70 °C under stirring for 3 h. The slurry was filtered, washed thoroughly with deionized water, dried at 110 °C overnight, and calcined at 550 °C (onwards at a rate of 5 °C/min) for 5 h. The resultant sample was denoted as B-*n*OT, where *n* represents the oxalic acid concentration and OT the treatment with oxalic acid solution.

The parent beta (B) and dealuminated samples B-*n*OT were then treated by NaOH solution following the same procedure in our recent work [34]. Briefly, 3 g of zeolite beta was dispersed into 60 mL of 0.2 M NaOH solution at 65 °C under stirring for 30 min. The slurry was filtered, washed thoroughly with deionized water and dried at 110 °C. Finally the product was transformed into protonic form beta by ion-exchanging in 1 mol/L NH_4Cl solution at 70 °C for 2 h and calcination at 550 °C for 5 h. The resultant samples were denoted as B-AT and B-*n*OAT, where AT indicates only alkaline treatment and OAT the sequential treatment with oxalic acid and NaOH solutions.

2.2. Characterization

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

N_2 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.

Scanning electron microscopy (SEM) was carried out in a Hitachi S-5500microscope operated at an accelerating voltage of 1.0 kV.

Transmission electron microscopy (TEM) was carried out in a Hitachi HT7700 microscope operated at 100 kV and equipped with a AMT41B camera. A few drops of the sample suspended in ethanol were placed on a carbon-coated copper grid followed by evaporation at ambient conditions.

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

Self-supporting thin wafers, used in OH-stretching vibration, were pressed and placed in a quartz IR cell with CaF_2 windows. Prior to the measurements, each sample was dehydrated in N_2 flow of ultrahigh purity at 400 °C for 1 h. And then the OH-stretching vibration spectra were collected at the same temperature.

Temperature-programmed desorption of ammonia (NH_3-TPD) was carried out in a TP-5079 unit equipped with a thermal conductivity detector. The sample (200 mg) was pretreated at 400 °C in N_2 flow (30 cm^3/min) for 30 min. Afterwards, pure NH_3 (25 cm^3/min) was adsorbed at RT for 10 min followed by N_2 purging at 100 °C for 1 h. This procedure was repeated three times. Desorption of ammonia was monitored in the range of 100–600 °C using a heating rate of 10 °C/min.

2.3. Catalytic test

The catalytic performances of zeolites beta with different molar Si/Al ratios before and after alkaline treatment were evaluated in α-pinene isomerization and benzoylation of naphthalene with benzoyl chloride. The reaction of α-pinene isomerization was carried out at atmospheric pressure in a glass reactor with a reflux