



Organotemplate-free synthesis of hierarchical beta zeolites

Ke Zhang*, Sergio Fernandez, Jeremy T. O'Brien, Tatiana Pilyugina, Sarah Kobaslija, Michele L. Ostraat

Aramco Services Company, Aramco Research Center - Boston, 400 Technology Square, Cambridge, MA 02139, United States

ARTICLE INFO

Keywords:

Beta zeolite
Hierarchical
Mesoporous
OSDA-free
Base leaching

ABSTRACT

This paper reports a straightforward approach to synthesizing hierarchical beta zeolites by exposing microporous zeolites to hydrothermal conditions amenable for beta crystallization, which simultaneously creates hierarchical pore structure while maintaining crystallinity and framework integrity without the use of organic structure-directing agents, pore-directing agents, or mesoporous templates. The obtained hierarchical beta zeolites possess enlarged mesopores and exhibit improved catalytic performance for the conversion of bulky molecules in the liquid-phase conversion of benzyl alcohol with mesitylene. A sequential hierarchical structure formation and recrystallization mechanism is proposed to elucidate the creation of mesopores in beta zeolites with excellent preservation of acidity and microporosity.

1. Introduction

Zeolites are extensively used in the petrochemical and chemical industries for applications including catalytic cracking, alkylation, and isomerization etc [1–5]. The industrial interest in zeolites is due to a combination of several favorable properties, including high surface area, good ion-exchange capability, strong acidity, and high thermal and hydrothermal stability. To address the challenges of diffusion limitation and coke formation in reactions involving bulky molecules, hierarchical zeolites were conceived with the purpose of introducing additional porosity, usually in the mesopore range, by either top-down or bottom-up approaches [6–12]. The top-down approach uses microporous zeolites that are post-synthetically modified to create hierarchical structures [13–16], while bottom-up approaches often involve more complicated templating-based synthesis routes, such as hard- or soft-templating strategies [17–20].

Zeolite beta is a large-pore, low-Al microporous material that features an intergrowth of two or more polymorphs comprising a three-dimensional, 12-membered ring channel system. For hierarchical beta zeolites, if the bottom-up approach is applied, the hierarchical structures are usually obtained under hydrothermal conditions that are similar to microporous zeolite synthesis, i.e. at temperatures above 100 °C and under high autogenous pressures in a contained space, with the presence of various expensive microporous and/or mesoporous templates. Besides cost concerns, the use of templating materials also increases energy consumption and the level of environmental pollution since they have to be removed by a calcination step [21]. On the other

hand, if the top-down approach is used, hierarchical beta zeolites are usually obtained in alkaline solutions at atmospheric pressure and at low temperatures (e.g. ~65 °C) because it is assumed that the beta zeolite framework would be excessively leached and dissolved at higher temperatures, leading to significant crystallinity loss and/or amorphous materials without the preferred catalytic acid sites. Even under optimized conditions, the resulting hierarchical zeolites synthesized with top-down methods have lower crystallinity, total acidity or activity due to partial framework destruction by desilication. Moreover, for beta zeolites, the average mesopore sizes created by top-down approaches are usually limited to the range of 2–6 nm [22–25].

Here, we report an approach for synthesizing hierarchical zeolite beta with enlarged mesopores by simultaneously utilizing the advantages of top-down (economical and simple) and bottom-up (favorable for crystallization) routes by hydrothermal synthesis in aqueous alkaline solutions using microporous zeolite beta under hydrothermal conditions with autogenous pressures. This approach does not involve usage of any micropore organic structure-directing agent (OSDA), any mesopore templates, or any pore-directing agent (PDA) that are usually required for the protection of zeolite framework from excessive dissolution during top-down base leaching [26]. The resulting hierarchical beta zeolites exhibited well-preserved crystallinity, high acidity, and considerably improved catalytic performance for the conversion of bulky molecules.

* Corresponding author.

E-mail address: ke.zhang@aramcoservices.com (K. Zhang).

<https://doi.org/10.1016/j.cattod.2017.11.033>

Received 18 September 2017; Received in revised form 27 October 2017; Accepted 29 November 2017
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Table 1
Porous properties of parent microporous beta (B1) and hierarchical beta zeolites (B2, B3) synthesized at different conditions..

	NaOH/Si	H ₂ O/Si	T/°C	time/h	V _{mic} /cm ³ g ⁻¹	V _{tot} /cm ³ g ⁻¹	S _{ext} /m ² g ⁻¹	S _{BET} /m ² g ⁻¹	d _p /nm
B1	–	–	–	–	0.29	0.33	114	647	^a
B2	0.35	97	150	21	0.28	0.59	191	594	10.2
B3	0.53	97	150	21	0.24	0.49	175	565	14.4

^a the pore size distribution of B1 indicates the existence of small amounts of mesopores in the parent beta crystals that is likely due to the intercrystalline spaces created by the aggregation of the zeolite crystals and/or intracrystalline spaces on the parent beta crystals.

2. Experimental

2.1. Synthesis

The parent beta zeolite (H-form), provided by TOSOH Corporation, has a nominal Si/Al ratio of 14 and is referred to as B1. The Si/Al ratio is confirmed by an Energy Dispersive X-Ray Spectroscopy (EDX) analysis. The Si/Al ratio is also confirmed by an Inductively Coupled Plasma (ICP) analysis (completed by Galbraith Laboratories, Inc.). The hierarchical beta zeolites were synthesized by adding 0.37 g of B1 in 10 ml of either 0.2 M (hierarchical beta B2) or 0.3 M (hierarchical beta B3) NaOH solutions to make the initial zeolite suspension with NaOH/Si ratio of 0.35 and 0.53 (as shown in Table 1), and a resulting H₂O/Si ratio of 97. The initial zeolite suspensions were then transferred into a Teflon-lined autoclave and heated in an oven at 150 °C for 21 h. After the synthesis, the autoclave was quenched to room temperature and the zeolites were obtained by centrifugation and washing. The as-synthesized hierarchical beta zeolites were transformed to the protonic form by a 3-fold ammonium-exchange in 0.8 M NH₄NO₃ (Fisher) and a subsequent calcination at 550 °C for 5 h at a heating rate of 10 °C/min. The yield is about 65 wt% of the added parent zeolites.

2.2. Characterization

Powder X-ray diffraction (XRD) measurements were taken using a Bruker D8 Discover diffractometer equipped with a Copper tube ($\lambda = 0.15418$ nm) and a VANTEC-500 2-D detector. Data were recorded in the range of 5–40°. Scanning electron microscopy (SEM) imaging was determined using a JEOL JSM-7100F equipped with an Oxford Energy Dispersive X-Ray Spectroscopy (EDS) system. Images were taken using an operating voltage of 15 kV. Transmission electron microscopy (TEM) was carried out in a JEOL 2010F TEM/STEM operated at 200 kV and equipped with a Gatan OneView 4k × 4k camera. To prepare TEM samples, a few drops of the sample suspended in ethanol were drop casted on a carbon-coated copper grid and allowed to evaporate at ambient conditions. Argon (Ar) sorption isotherms were performed at –186 °C on a Micromeritics ASAP 2460. Prior to the measurements, all samples were degassed at 350 °C overnight under vacuum in a Micromeritics Smart VacPrep. The apparent surface areas were determined with the Brunauer-Emmett-Teller (BET) method in the range between P/P₀ 0.02–0.10. The mesopore size distribution was obtained by the Barrett-Joyner-Halenda (BJH) model applied to the adsorption branch of the isotherm. The nonlocal density functional theory (NLDFT) method was applied to estimate the micropore volume (V_{mic}) and total pore volume (V_{tot}) using Quantachrome's data reduction software (based on the model of Ar at –186 °C on a zeolite with cylindrical pores). Ammonia temperature-programmed desorption (NH₃-TPD) analysis was performed using a Micromeritics AutoChem II chemisorption analyzer with a flow-through reactor connected to a thermal conductivity detector (TCD). The samples were activated at 560 °C for 1 h followed by the adsorption of NH₃ at 180 °C. The NH₃-adsorbed zeolites were purged in high purity helium flow gas for an extended 5 h to minimize the extent of NH₃ physisorption. Then, the TPD spectra were recorded by heating the samples from 180 to 550 °C at a rate of 15 °C/min in helium flow.

2.3. Catalytic testing

The catalytic performance of the hierarchical beta zeolites was evaluated by the liquid-phase conversion of benzyl alcohol in mesitylene, in which benzyl alcohol is consumed simultaneously via alkylation and etherification (Scheme S1). 100 mg of the catalyst were weighed into a 20 ml vial. The powder was heated to 250 °C for 2 h in an oven. Mesitylene (9.56 ml) with dodecane (0.227 ml, 1.0 mmol) was added to the powder. The mixture was stirred for 90 min at 90 °C. Then the mixture was heated to 120 °C and benzyl alcohol (0.208 ml) was added. Aliquots of 0.1 ml were drawn and diluted with 3 ml of toluene. The samples were filtered using a syringe filter and analyzed by gas chromatography-mass spectrometry (GC-MS). To quantify the reaction products and remaining benzyl alcohol, an internal standard, dodecane, was included in the initial reaction mixture. The reaction mixture was sampled, filtered and diluted by 30 × into toluene after 2 h of reaction time. The abundances of this standard as well as the reaction components were measured using a JEOL AccuToF GCx instrument which consists of an Agilent 7890 B GC and a JEOL time of flight (ToF) MS as the detector. A 30-m Restek RTX-1 column was used with a front inlet temperature of 250 °C. The oven program consisted of an initial temperature hold at 75 °C for 6 min followed by a ramp to 225 °C at 20 °C/min and the final temperature was held for 2 mins. The injection split ratio was set to 100. The abundance of each compound was determined by the integrated peak area from the total-ion chromatogram and was converted to concentration based its ratio to the internal standard using a calibration curve. The catalytic activity of zeolites in mesitylene alkylation is represented by benzyl alcohol conversion, while the selectivity of the zeolites is defined as twice the concentration of the ether product divided by the concentration of the alkylation product.

3. Results and discussion

The XRD patterns (Fig. 1A) revealed that the hierarchical beta (B2 and B3) preserved the crystallinity of microporous beta (B1) with sharp characteristic diffraction peaks. In fact, the characteristic beta diffraction peaks in the 2-theta range of 20–30° for hierarchical B2 and B3 are stronger in intensity than the parent beta B1, which is most likely due to the recrystallization of locally disrupted area during the alkaline-solution-mediated mesopore creation. The Ar isotherms display similar initial uptakes at low P/P₀ (< 0.1) for B2 and B3 as compared to B1, which implies well-preserved crystallinity and microporosity (Fig. 1B). The micropore volume is 0.28 and 0.24 cm³/g for B2 and B3, respectively. This represents only less than a 4% decrease in micropore volume for B2 from that of B1. For comparison, the conventional top-down approach for the synthesis of hierarchical beta zeolites using identical parent beta resulted in a 20–30% decrease in micropore volume under the same alkalinity, although at a much lower temperature (65 °C) [23]. The creation of large mesopores is demonstrated by the enhanced Ar uptakes for B2 and B3 at high P/P₀ due to capillary condensation. BJH pore size distribution shows that the peak mesopore size increases significantly to ~25 nm for B2 and ~40–50 nm for B3 with average mesopore sizes of 10.2 and 14.4 nm, respectively (Fig. 1B). The average mesopore sizes of hierarchical beta zeolites from the conventional top-down approach in NaOH solutions are smaller than 5 nm

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