Chinese Journal of Catalysis 35 (2014) 1800–1810

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Article

Mechanism of seeding in hydrothermal synthesis of zeolite Beta with organic structure-directing agent-free gel

Bumei Zheng [a], Yufeng Wan [a], Weiya Yang [b], Fengxiang Ling [b], Hong Xie [a], Xiangchen Fang [b], Hongchen Guo [a,*]

[a] *State Key Laboratory of Fine Chemicals, Department of Catalytical Chemistry and Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China*

[b] *Fushun Research Institute of Petroleum and Petrochemicals, SINOPEC, Fushun 113001, Liaoning, China*

ARTICLE INFO

Article history:
Received 1 March 2014
Accepted 21 March 2014
Published 20 November 2014

Keywords:
Organic structure-directing agent-free synthesis
Zeolite Beta
Seeding
Seed residues
Dissolved seed fragment

ABSTRACT

The organic structure-directing agent-free synthesis of zeolite Beta was carried out using several zeolite Beta seeds that differed in SiO_2/Al_2O_3 ratio and crystal size. The synthesis was studied using X-ray diffraction, X-ray fluorescence, scanning electron microscopy, transmission electron microscopy, ultraviolet-Raman spectroscopy, infrared spectroscopy, and N_2 physisorption. Synthesis was successful using different zeolite Beta seeds including pure silica seeds. During the induction period, the seeds underwent dissolution. The SiO_2/Al_2O_3 ratio and crystal size, pretreatment (calcination), and seed addition time had a significant influence on seed dissolution behavior, crystallization process, and product. Morphological studies revealed that the seed residues produced by dissolution (except for pure silica) resulted in the formation of “immobilized” surface nuclei, which allowed for the dense growth of fresh small zeolite Beta crystals. The dissolved small seed fragments yielded dispersed nuclei, which formed relatively scattered small zeolite Beta crystals thought to be the main nuclei source of the pure silica seed. It is suggested that the use of an appropriately high SiO_2/Al_2O_3 ratio, small size, and precalcined zeolite Beta seed is helpful for the synthesis of highly crystalline and pure zeolite Beta from the organic structure-directing agent-free gel.

1. Introduction

High-silica zeolite Beta (BEA) has three-dimensional intersected channels and 12-membered ring pore openings [1,2]. These properties make it useful as a catalyst in aromatic alkylation, isomerization, alkene hydration, aromatic acylation, and nitration syntheses in petrochemical industries [3–9].

Formation of the zeolite Beta structure was achieved originally using tetraethylammonium hydroxide (TEAOH) as an organic structure-directing agent (OSDA) [10]. However, its use has increased the zeolite Beta cost significantly, thereby limiting its industrial application. For this reason, recent studies related to zeolite Beta have focused mainly on low-cost synthesis using more affordable OSDAs such as tetraethylammonium bromide (TEABr) [11–14]. Xie et al. [15] demonstrated for the first time that zeolite Beta could be synthesized by adding calcined nanocrystalline zeolite Beta seeds into OSDA-free aluminosilicate gel. This synthesis route attracted much attention [16–23]. Iyoki et al. [22,23] proposed that the key factor in successful zeolite synthesis in the absence of OSDA was the common composite building unit contained in both the seeds and zeolite obtained from the gel after heating without seeds. Majano et al. [16] showed that zeolite Beta could be obtained at low crystallization temperature with non-calcined seeds. They

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* Corresponding author. Tel/Fax: +86-411-84986120; E-mail: hongchenguo@163.com

DOI: 10.1016/S1872-2067(14)60089-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 11, November 2014

believe that the active surface of the as-synthesized seeds promoted crystallization while calcination of the seeds would be harmful because of seed surface deactivation. Kamimura et al. [17,18] reported that zeolite Beta synthesized with OSDA-free gel could be used as a seed to generate more zeolite Beta. They concluded that the seed was partially dissolved during the initial stage in the hydrothermal environment and that subsequent crystallization took place on the surface of the residual Beta seeds exposed to the liquid. They also observed that zeolite Beta with SiO_2/Al_2O_3 ratio greater than 52 could not be used as seeds because of their complete dissolution in the initial stage in the hydrothermal environment. Xie et al. [19] showed that the residues partially dissolved Beta seeds rather than the dissolved species of Beta seeds helped crystallization. They proposed a core–shell growth mechanism to describe the crystallization of OSDA-free gel on the surface of partially dissolved Beta seeds.

Although it is well known that seeding is useful for the synthesis of many zeolites, the mechanism by which this occurs has been interpreted in various ways: some believe that seeds behave as crystal nuclei supplying a surface for the crystallization of amorphous aluminosilicate gel; others suggest that the seeds dissolve partially and then the residual seed, or dissolved species, or both form nuclei [23,24]. An investigation into the seeding mechanism therefore holds significance not only for OSDA-free synthesis of zeolite Beta but also for improving synthesis techniques of other zeolites.

In this work, we carried out a detailed study on the OSDA-free synthesis of zeolite Beta using different seeds. X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), and ultraviolet (UV)-Raman spectroscopy were used to characterize the solid products obtained before and during the synthesis. Emphasis was given to the structure-directing effect of different seeds, key aspects of the seed that influence the structure-directing effect, and the seeding mechanism.

2. Experimental

2.1. Synthesis of zeolite Beta seeds

Al-containing zeolite Beta seeds were synthesized as follows. First, silica sol (SiO_2, 30 wt%, Qingdao Haiyang Chemical Co.) or fumed silica (Shenyang Chemical Co.) was mixed with OSDA solutions, which included a TEAOH solution (20 wt%, Hejian Qingfeng Shimian Chemical Co.), TEABr solution (99 wt%, Jintan Huadong Chemical Research Institute), ammonia and NaOH, or solution of TEABr and TEAOH. A $NaAlO_2$ solution (Al_2O_3, 41 wt%, Sinopharm Chemical Reagent Co.) was added to the mixture with vigorous stirring for 40 min. The mixture was transferred to an autoclave and crystallized at 145 °C under static or stirred conditions for ~3–6 d.

Pure silica zeolite Beta seed was synthesized as follows. Fumed silica was mixed with the TEAOH solution (40 wt%, condensed in laboratory). Next, NH_4F was added and the mixture stirred thoroughly. The sticky gel obtained was placed in a Teflon-lined stainless steel autoclave and crystallized at 150 °C for 4 or 5 d.

All solid products were filtered, washed, dried overnight at 110 °C, and calcined in air at 540 °C for 6 h to remove the OSDA before they were used as seeds.

2.2. Seed-assisted synthesis of OSDA-free zeolite Beta

A gel with molar composition $Na_2O:Al_2O_3:SiO_2:H_2O$ = 11.4:1:40:640 was prepared as follows. Fumed silica was dissolved in the NaOH solution before addition of the $NaAlO_2$ solution under vigorous stirring. Calcined zeolite Beta was then added as seed (10 wt% in relation to silica source). The mixtures were agitated to form a homogenous gel. The gel was transferred into a 100-ml autoclave and crystallized statically at 140 °C. Sampling was conducted at time intervals. The solid product was isolated from the resultant mixture by filtration, washed with deionized water, and dried at 110 °C for characterization.

2.3. Characterization

XRD patterns were collected on a Rigaku D/max-2004 diffractometer using Cu K_α radiation (40 kV, 100 mA) and a scanning rate of 0.02°/min (2θ). The crystallinity of the obtained Beta phase was calculated based on the intensity of the peak at reflection (3 0 2) ($2\theta = \sim22.4°$).

FE-SEM micrographs were recorded on a Hitachi S-4800 microscope. TEM micrographs were obtained on a JEOL JEM-2100 electron microscope operating at 200 kV with a point resolution of 0.23 nm. TEM samples were dispersed in ethanol and a droplet of this mixture was deposited on a Cu grid.

FT-IR spectra in the hydroxyl region were obtained on a Nicolet iS10 FTIR instrument according to the following procedure. The sample was pressed into a self-supporting wafer and placed into a quartz IR cell with CaF_2 windows. The FT-IR spectra were recorded with a resolution of 4 cm^{-1} at room temperature. Prior to measurement, the sample was dehydrated under vacuum at 400 °C for 4 h.

UV-Raman spectra were recorded on a DL-2 Raman spectrometer. The 244-nm line of a LEXEL LASER was used as the excitation source. An Acton triple monochromator was used as a spectrometer for Raman scattering. Spectra were collected using a Prinston charge-coupled device detector. The power of the laser line at the sample was below 3 mW.

Elemental analyses were performed using a Bruker SRS 3400 X-ray fluorescence spectrometer.

N_2 adsorption-desorption isotherms were recorded at –196 °C on a Micromeritics ASAP 2000 instrument after activating the sample under vacuum at 350 °C for at least 6 h. The surface area was evaluated using the BET method. The external surface area, micropore surface area, and micropore volume were calculated using the t-plot method. The total pore volume was determined from the amount adsorbed at a relative pressure of approximately 0.99, and the mesopore volume was calculated from the difference between the total and micropore volume.