Microporous and Mesoporous Materials 225 (2016) 210–215

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Polytype distributions in low-defect zeolite beta crystals synthesized without an organic structure-directing agent

Yukichi Sasaki [a, *], Yoko Yoshida [b], Craig A.J. Fisher [a], Takuji Ikeda [c], Keiji Itabashi [d, e], Tatsuya Okubo [d]

[a] Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan
[b] Aichi Center for Industry and Science Technology, 1267-1 Akiai, Yakusa-cho, Toyota 470-0356, Japan
[c] Research Center for Compact Chemical Systems, National Institute of Advanced Industrial Science and Technology, 4-2-1 Miyagino-ku, Sendai 983-8551, Japan
[d] Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[e] Unizeo Co., Ltd., 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form
5 December 2015
Accepted 10 December 2015
Available online 19 December 2015

Keywords:
Zeolite beta
OSDA-Free
Transmission electron microscopy
Polytype

ABSTRACT

Design of efficient and environmentally benign zeolitic materials at the nanoscale is becoming increasingly important for a range of industrial applications. Here we report a high resolution transmission electron microscopy investigation of the atomic level structure of zeolite beta synthesized without an organic structure-directing agent (OSDA). Direct visualization of zeolite beta crystals confirmed them to be essentially defect free, with domain boundaries the only disruption to the pore channel network. Direct visualization enabled the distribution of BEA and BEB polytype subdomains to be quantified, and the overall abundance ratio was calculated to be BEA:BEB = 9:11. By assuming this ratio corresponds to the probability of forming a new BEA or BEB layer on a (001) surface at the tip of a crystal, the experimentally observed polytype distributions can be described by a simple probability function, suggesting that epitaxial crystal growth occurs stochastically in a state close to chemical equilibrium.

1. Introduction

Micron- and nanometer-sized zeolite crystallites are used in many catalytic and adsorption applications, and the efficient design of such materials and optimization of their synthesis parameters require an atomic level understanding of their crystal structures, growth mechanisms, and properties [1]. In addition to the development of more powerful analytical and synthesis techniques [1,2], theoretical modeling is playing an increasingly critical role in achieving this goal [3].

The unusual structural and chemical properties of zeolite beta make it an important material in diverse applications such as catalytic cracking, isomerization, aromatic alkylation with alkenes, and isobutene alkylation with *n*-butene [4]. Although one of the first zeolites ever synthesized, its structure has only recently been adequately elucidated because it consists of a disordered intergrowth of different polytypes [5,6]. Its three distinct polytypes, labeled A, B and C (corresponding to framework types BEA, BEB, and BEC, respectively), have different structures, but these differ only in the stacking sequence of their periodic building units, forming three-dimensional networks of 12-membered ring (12 MR) channels connected by smaller 4-, 5- and 6-membered rings. Their structures are compared in Fig. 1.

The different polytype structures of zeolite beta can be described in terms of the stacking arrangement of layers of the 12 MR channels: *ababab* in BEA, giving an enantiomorphic tetragonal unit cell; *abcabc* in BEB, with monoclinic symmetry and no chirality; and *aaaaaa* in BEC, which also has cubic symmetry, but is non-chiral [7]. BEA is of particular interest because of its potential for enantioselective catalysis and associated applications, but this is hampered by the difficulty of isolating it from the other polytypes. While the intergrowth of BEA and BEB layers in synthesized crystals does not affect the connectivity of the channels in two crystallographic directions, in the direction of stack faulting, *i.e.*, perpendicular to the multimembered ring layers, the channels become more tortuous than in either of the isolated ideal frameworks,

* Corresponding author. Tel.: +81 52 871 3500; fax: +81 52 871 3599.
E-mail address: sasaki@jfcc.or.jp (Y. Sasaki).

http://dx.doi.org/10.1016/j.micromeso.2015.12.022
1387-1811/

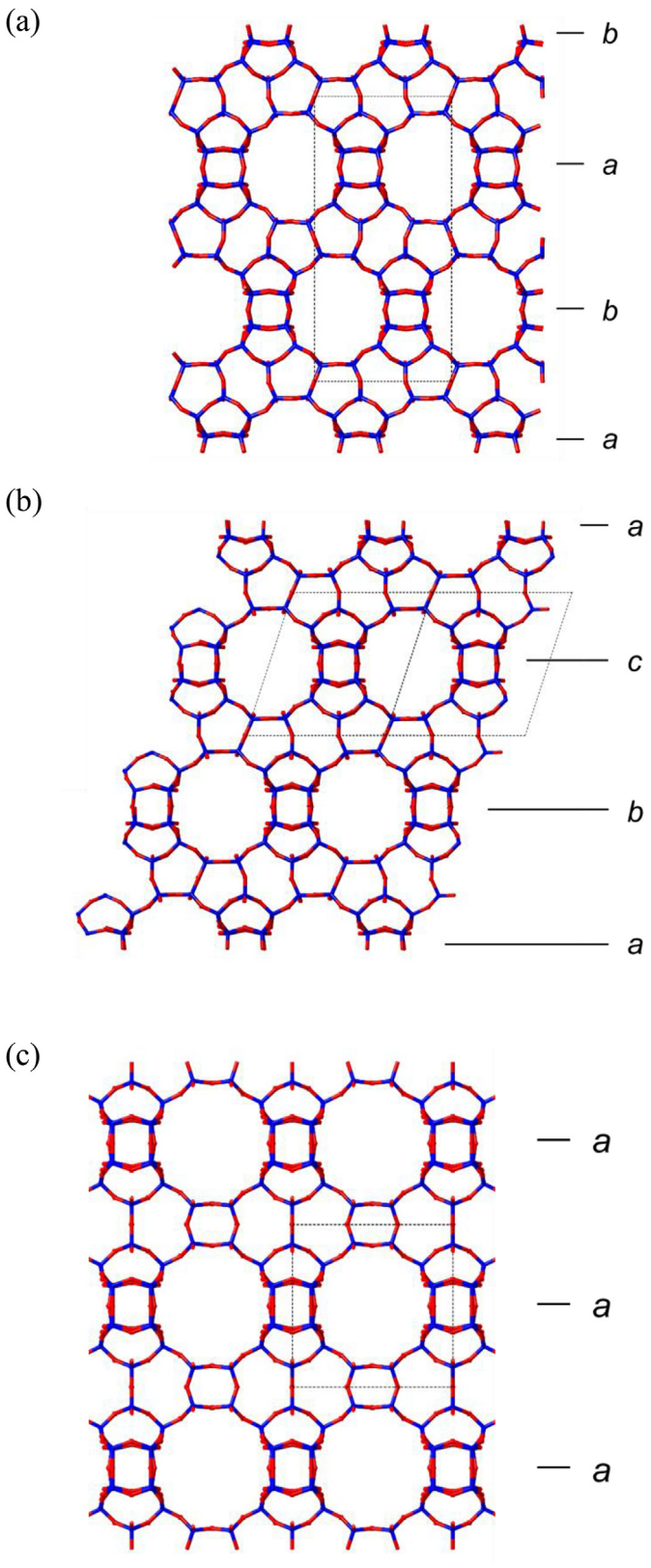

Fig. 1. Crystal structures of zeolite beta polytypes comparing stacking order of the periodic building units (12-ring pore channels): (a) BEA ($P4_122$), (b) BEB ($C12/c1$), and (c) BEC ($P4_2/mmc$). Dotted lines demarcate a single unit cell in each case.

which may affect their permeability to different organic molecules and even their catalytic behavior. An understanding of the formation mechanisms and relative stabilities of the different polytypes may aid in the search for techniques of synthesizing BEA-rich materials with the desired Si/Al ratios and counter-cation contents.

In practice, many zeolites can only be synthesized using organic structure-directing agents (OSDAs) such as quaternary ammonium compounds. In the case of zeolite beta, some OSDAs, if chosen carefully, can increase the proportion of a given polytype [8–10], but the OSDA must be removed afterwards by calcination before the zeolite can be used. This often leads to microscopic cracks and other defects (such as dealumination, distorted-ring formations, and residual organic impurities) in the zeolite crystals, which also strongly affect the performance of the catalyst or separation membrane in which they are used [11,12].

Growth of zeolites from seed particles without using an OSDA is an attractive alternative for producing commercially useful zeolites. This method has recently been applied successfully to a number of zeolite systems [11–17]. Zeolite beta particles synthesized without the use of an OSDA exhibit characteristic crystal habits with a truncated octahedral morphology similar to that of tschernichite, a natural analog of zeolite beta [18]. Moreover, nuclear magnetic resonance and specific surface area measurements suggest such particles contain far fewer defects than OSDA-derived zeolite beta [14,15]. Consequently, OSDA-free zeolites generally exhibit excellent durability and thermal stability [19].

In this study, we combine X-ray diffraction (XRD) and electron microscopy analysis of zeolite beta crystals with first-principles calculations of the pure polytype structures in an effort to better understand the complex atomic-scale and microstructural features of this material. OSDA-free zeolite beta crystals were chosen for this because their high crystallinity enables the stacking sequences and hence regions of different polytypes to be identified readily from high-resolution transmission electron microscopy (HRTEM) images. By doing this over a wide region for a large number of crystals, abundance ratios of BEA and BEB polytypes, as well as their distributions, could be determined directly. Comparison of these results with macroscale XRD analysis and theoretical calculations suggests that crystals in this system grow by a stochastic mechanism.

2. Methods

High-quality zeolite beta crystals were synthesized by adding calcined OSDA-derived beta seeds (Si/Al = 12.0; Na/Al = 0.04) 100–400 nm in diameter to an OSDA-free Na aluminosilicate gel with molar composition $13Na_2O{:}Al_2O_3{:}40SiO_2{:}1000H_2O$ [15,20]. Hydrothermal treatment was performed at 140 °C for 40 h under static conditions and autogeneous pressure. The yield of the fully crystallized sample was ca. 26% [20].

Powder XRD measurements before and after hydrothermal treatment were performed at room temperature using a D8 Advance Vαrio1 diffractometer (Bruker AXS) with Cu Kα radiation between 5 and 60° 2θ. The volumetric ratio of BEA to BEB in dehydrated samples was calculated using the DIFFaX+ program [21], an extension of the original DIFFaX program [22] that allows a greater number of instrumental, structural, and microstructural parameters to be refined in accordance with the experimental diffraction data.

Crystals were also observed using state-of-the-art high-resolution transmission electron microscopes. HRTEM samples were prepared by dispersing zeolite particles in ethanol, and then depositing them on a Cu micro-grid mesh without mechanical grinding. As low beam irradiation conditions were necessary to avoid damage to the zeolite structure, observations were performed using a JEOL JEM-3000F microscope at an accelerating voltage of 300 kV. Images were processed using the fast Fourier transform method.