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Synthesis of Giant Zeolite Crystals by a Bulk-Material Dissolution Technique**

Shinichi Shimizu* and Hideaki Hamada

Zeolites are crystalline microporous materials that are attracting much attention owing to their applications as high-performance catalysts, in separation processes, and in optical, magnetic, and electronic devices.[1] Major efforts have been undertaken to synthesize large single crystals with a well-defined habit, because some applications require large zeolite crystals to allow effective use of their micropores. In 1971 Charnell synthesized zeolite Na-A (LTA) crystals (ca. 65μm) and zeolite Na-X (FAU) crystals (ca. 140 μm) under hydrothermal conditions from gels of sodium metasilicate, sodium aluminate, and triethanolamine, which were purified to remove particles by a precision filtration technique.[2] In 1993 a novel method to synthesize zeolites in nonaqueous media was developed to obtain giant zeolite crystals by controlling the release and solubility of reactive solution species in organothermal systems.[3] Giant crystals of dodecasil-3C, a clathrasil having the MTN framework, were prepared by using a combination of silica rods and fumed silica by Klemperer and Marquart.[4] Other attempts to obtain large zeolite crystals have also been made.[5]

Recently, we developed a novel technique for synthesizing giant zeolite crystals in aqueous media by controlling the solubility in hydrothermal systems. Both silicalite-1 (all-silica MFI) and analcime (ANA) crystals with sizes of about 3 mm, which were unknown until now, were successfully synthesized by using bulk materials as the silica and alumina sources (bulk-material dissolution (BMD) technique). The compositions of the reaction mixtures and the experimental results are summarized in Table 1. A typical procedure is as follows: A piece of quartz glass tube (ca. 24 mm long, 10 mm external and 8 mm internal diameter; 25.2 mmol SiO_2) was placed in a PTFE sleeve (capacity 23 mL) equipped for an autoclave. The sleeve was filled with an aqueous solution containing tetra-*n*-propylammonium hydroxide (TPAOH) and hydrogen fluoride (HF). The experimental setup is illustrated in Figure 1.

Table 1. Synthesis of zeolite crystals by the BMD technique.

Zeolite framework (Figure)	Bulk source [mmol]	Liquid phase [mmol]	T [°C]	t [d]	Maximum crystal size [μm]
MFI (2, 3)	SiO_2 tube SiO_2 (25.2)	TPAOH (8.9) HF (9.7) H_2O (870)	200	25	$2000 \times 1000 \times 1000$
MFI (4)	SiO_2 tube SiO_2 (18.4)	TPAOH (8.9) HF (14.6) H_2O (885)	200	46	$3200 \times 2800 \times 2600$
ANA (5)	ceramic boat SiO_2 (12.1) Al_2O_3 (3.0)	NaOH (20.3) H_2O (847)	200	31	$3000 \times 2800 \times 2500$
JBW & CAN (6)	ceramic tube SiO_2 (12.6) Al_2O_3 (9.6)	NaOH (51.2) H_2O (683)	200	7	$640 \times 320 \times 100$ (JBW) $300 \times 5 \times 5$ (CAN)
CAN	ceramic boat SiO_2 (11.4) Al_2O_3 (2.8)	NaOH (99.0) H_2O (832)	200	13	$100 \times 20 \times 20$
SOD	ceramic boat SiO_2 (11.0) Al_2O_3 (2.7)	NaOH (51.0) H_2O (833)	100	19	$60 \times 60 \times 60$
SOD	ceramic tube SiO_2 (21.7) Al_2O_3 (11.7)	NaOH (98.7) H_2O (697)	200	12	$120 \times 120 \times 120$

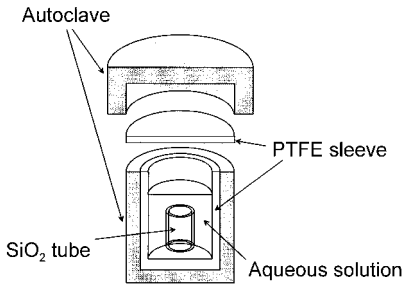

Figure 1. Schematic illustration of the experimental setup for BMD crystallization.

[*] Dr. S. Shimizu[+]
Joint Research Center for Harmonized Molecular Materials
Japan Chemical Innovation Institute
1-1, Higashi, Tsukuba, Ibaraki 305-8565 (Japan)
Fax: (+81) 298-50-4103
E-mail: shinichi@nimc.go.jp
Dr. H. Hamada
National Institute of Materials and Chemical Research
1-1, Higashi, Tsukuba, Ibaraki 305 – 8565 (Japan)
[+] Present address:
Advanced Technology Laboratory
Kubota Corporation
5-6, Koyodai, Ryugasaki, Ibaraki 301-0852 (Japan)
Fax: (+81) 297-64-7266
E-mail: si-simiz@kubota.co.jp

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After 25 d of crystallization at 200 °C, some crystals were found on the surface of the residual quartz-glass tube, and others at the bottom of the PTFE sleeve (Figure 2). Most of

Figure 2. Giant crystals of all-silica MFI zeolite were synthesized at 200 °C for 25 d from SiO_2, TPAOH, HF, and water (25.2, 8.9, 9.7, and 870 mmol, respectively). a) Giant MFI crystals formed at the bottom of the PTFE sleeve. The finest notch on the ruler indicates 0.1 mm. b) The MFI crystals formed on the tubular source. One block on the grid indicates 1 cm^2.

the product crystals are larger than about $1 \times 1 \times 1$ mm^3. They were identified as all-silica MFI zeolite by powder X-ray diffraction (XRD) (Figure 3a). The XRD reflections were also collected from one of the giant MFI crystals with its

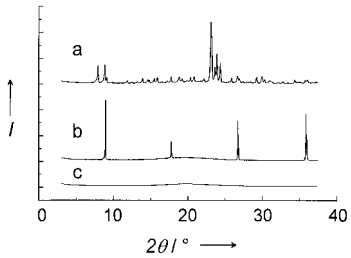

Figure 3. XRD patterns of the giant crystals of all-silica MFI zeolite. a) XRD pattern of the powder obtained by grinding some of the crystals in an agate mortar. b) XRD pattern of reflections from one crystallographic plane parallel to the surface of the giant MFI crystal fixed on the specimen holder by aluminum adhesive tape. c) Blank pattern of the specimen holder equipped with aluminum adhesive tape. I = intensity.

surface parallel to the horizontal plane of the specimen holder (Figure 3b). The reflections were assigned as those from the (h00) or the (0k0) planes ($h = 2, 4, 6, 8$; $k = 2, 4, 6, 8$). No reflections from other crystallographic planes emerged in the XRD pattern. These XRD measurements indicate that the MFI crystals are single crystals. The largest of the MFI crystals shown in Figure 4 has dimensions of about $3.2 \times 2.8 \times 2.6$ mm^3. It was synthesized at 200 °C for 46 d (Table 1). When the solution was stirred in the PTFE sleeve, no MFI crystals larger than 0.5 mm were obtained from a similar reaction mixture.

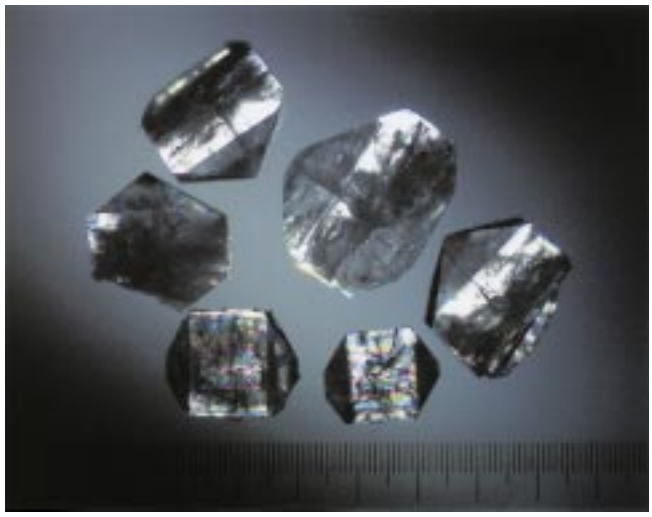

Figure 4. Giant crystals of MFI zeolite synthesized at 200 °C for 46 d from SiO_2, TPAOH, HF, and water (18.4, 8.9, 14.6, and 885 mmol, respectively). The finest notch on the ruler indicates 0.1 mm.

We also investigated a small ceramic boat, which is usually used as a container for combustion of a specimen, as an aluminosilicate source for zeolites. The ceramic boat weighed 1.036 g and was found to contain 12.1 mmol of SiO_2 and 3.0 mmol of Al_2O_3 ($SiO_2/Al_2O_3 = 4.0$) by X-ray fluorescence analysis. The boat was placed in a PTFE sleeve (capacity 23 mL) equipped for an autoclave, and the sleeve was filled with an aqueous solution of sodium hydroxide. The crystals obtained after heating the reaction mixture at 200 °C for 31 d in a convection oven were identified as ANA zeolite by XRD measurements. The largest ANA crystal had approximate dimensions of $3.0 \times 2.8 \times 2.5$ mm^3 (Figure 5).

When a ceramic tube with composition ($SiO_2/Al_2O_3 = 1.3$) different from that of the ceramic boat was used as an aluminosilicate source, different crystals were obtained. In this case, crystallization was carried out by heating a reaction mixture consisting of a piece of the ceramic tube, NaOH, and water at 200 °C for 7 d. The product consisted of large parallelopipedal crystals and fine needlelike crystals, and was identified as a mixture of JBW and CAN zeolites by powder XRD measurements. The larger crystals were identified as JBW by single-crystal XRD analysis. The largest JBW (ca. $640 \times 320 \times 100$ μm^3) and CAN crystals (ca. $300 \times 5 \times 5$ μm^3) are shown in Figure 6.

We believe that the BMD technique with glassy or sintered bulk material is one of the most attractive techniques for synthesizing large crystals of all-silica and aluminosilicate

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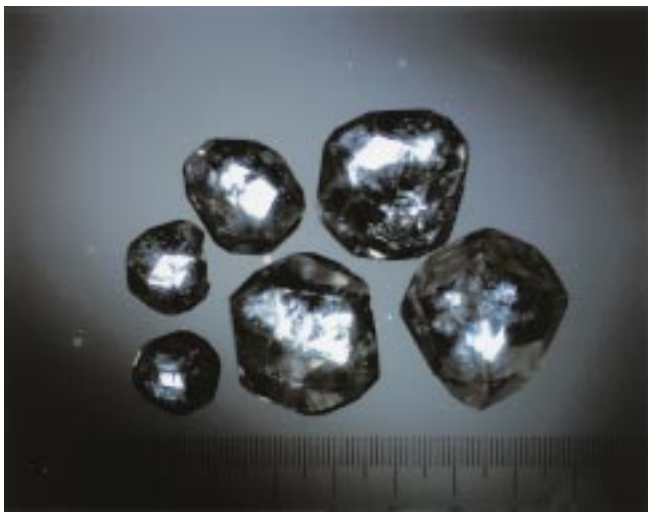

Figure 5. Giant crystals of ANA zeolite synthesized at 200 °C for 31 d from SiO_2, Al_2O_3, NaOH, and water (12.1, 3.0, 20.3, and 847 mmol, respectively). The finest notch on the ruler indicates 0.1 mm.

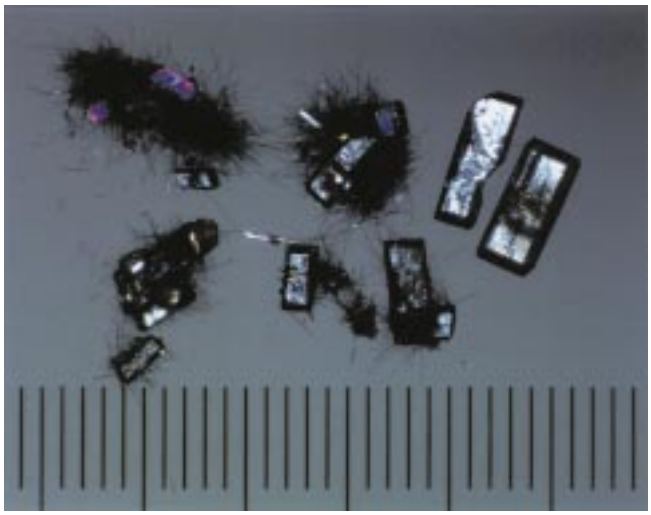

Figure 6. Giant crystals of JBW zeolite synthesized at 200 °C for 7 d from SiO_2, Al_2O_3, NaOH, and water (12.6, 9.6, 51.2, and 683 mmol, respectively). The numerous fine crystals around the JBW crystals were identified as CAN zeolite by XRD measurement. The finest notch on the ruler indicates 0.1 mm.

zeolites. In comparison with conventional hydrothermal synthesis, in which colloidal materials or powders are used as raw materials, the most distinctive feature of this technique is that the total surface area of the bulk raw materials is extremely small. Accordingly, the rate of dissolution of the raw materials in the aqueous phase is much smaller than in the conventional hydrothermal process. When the concentration of the chemical species increases very slowly and reaches a slight supersaturation level, the concentration is considered to remain approximately at the saturation level because of a balance between the consumption by the growing nuclei and the supply from the bulk raw materials. As a result, only a few nuclei are produced in the first stage of the hydrothermal reaction and grow to giant zeolite crystals. It is interesting that no giant zeolite crystals are obtained in the stirred reaction. This suggests that the presence of concentration gradients plays an important role in transferring the chemical species from the bulk raw material to the zeolite nuclei. Consequently, both the small total surface area of the bulk raw materials and the concentration gradient produced in the static crystallization process are assumed to be essential factors in the BMD technique.

Natural zeolites can occur as large single crystals, but it has so far proven difficult to synthesize them in the laboratory. It is believed that the natural crystals were formed from bulk minerals in a static natural process, whereas artificial zeolite crystals are usually synthesized from powdered or colloidal raw materials. The BMD process therefore can be considered to resemble the natural process.

Experimental Section

Powder XRD measurements: The specimen powder was obtained by grinding the crystals in an agate mortar. Powder XRD patterns were measured on a Rigaku Rint 2500 diffractometer with $Cu_{K\alpha}$ radiation with $\theta/2\theta$ scans and 1 deg min^{-1} 2θ scan rate.

XRD measurement on an MFI single crystal: An MFI crystal was fixed at the center of a through-type specimen holder for the Rigaku Rint 2500 diffractometer by aluminum adhesive tape. After the position of the crystal surface was adjusted to the horizontal plane of the holder, the XRD pattern was measured. The reflections were assigned as those from the (h00) or the (0k0) plane (h = 2, 4, 6, 8; k = 2, 4, 6, 8). It is very difficult to distinguish between these reflections in such a simple measurement because the crystallographic cell of the MFI framework is primitive orthorhombic with dimensions: a = 20.022, b = 19.899, and c = 13.383 Å, and these reflections are observed in very similar positions.[6]

Single-crystal XRD measurement on a JBW single crystal: XRD data were collected on a Rigaku AFC5R diffractometer with $Mo_{K\alpha}$ graphite monochromated radiation. The structure of the specimen crystal is orthorhombic, space group $Pna2_1$ (no. 33) with a = 16.457(3), b = 15.009(2), c = 5.234(5) Å, Z = 4, and ρ_{calcd} = 2.400 g cm^{-3}. It is in good agreement with the published structure of JBW.[7]

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