Preparation of nano-zeolite X by bead-milling and post-milling recrystallization

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A top-down approach has been applied for the preparation of nano zeolite X using a combination of bead milling and post-milling recrystallization. This gives nano zeolite X approximately 60 nm in size with high crystallinity without using specific organic compounds. Pair distribution function analysis by high-energy X-ray diffraction showed that the ring structure of zeolite framework is distorted and/or destroyed by bead milling, and the crystallinity returned to close to the original level after recrystallization treatment.

Key-words: Recrystallization, Amorphization, Milling, Zeolite X, Amorphous

1. Introduction

Zeolite are crystalline microporous high surface area solids that find applications as heterogeneous catalysts or separation media for gases, liquids and ions.1,2 So far, much interest has been paid in the synthesis of nano zeolites3-6 since zeolites with nanometer size particles allow greater access to the internal pore sites due to their high external surface area. In general, the fabrication of nano zeolites has been achieved by hydrothermal synthesis, that is, controlling zeolite nucleation and crystal growth. These efforts have yielded the synthesis of many types of nano zeolites, including zeolite X and Y.7-9 They have an average size less than 100 nm and come from homogeneous clear solutions containing a large amount of an organic template like tetramethylammonium hydroxide to control crystallization. The use of organic compounds has resulted in many advances but suffers from a number of drawbacks, such as high production cost and low crystalline yield.10 Therefore, a new method of synthesizing nano-zeolite without organic templates is strongly desired.

This report focuses on a top-down approach for the fabrication of nanosized zeolites.11,12 Recently, Wakihara et al.13,14 reported on a new method for the production of nanosized zeolite powder by a top-down approach. In those papers, nano-sized zeolite A and ZSM-5 (LTA and MFI type structures, respectively) were prepared by milling and subsequent recrystallization treatment. The characteristic point of this method is that the outer portion of the zeolite framework was destroyed by milling method; however, the damaged parts can be recrystallized by the use of dilute aluminosilicate or silicate solutions after bead milling. From the combined bead milling and post-milling recrystallization, nanosized zeolites with an average size less than 100 nm were obtained. This method has yet to be applied to the preparation of other nanosized zeolites. The preparation of nanosized zeolite X is also of interest since it is one of the most representative zeolites and is widely used as an adsorbent, catalyst and in ion-exchange.15 In this study, therefore nano zeolite X has been prepared by bead milling and subsequent recrystallization from a dilute aluminosilicate solution. Nano zeolite X approximately 60 nm in average size with high crystallinity was successfully obtained without the use of an organic template.

2. Experimental

Commercial zeolite X (LSX, FAU type zeolite, Si/Al = 1.0, Cation: K+:Na+ = 1:1. Tosoh Co., Japan) was used in this study (raw zeolite X). First, the zeolite X was ion-exchanged to the Na+ form by conventional methods. It was then processed in a bead mill (Minicer, Ashizawa Finetech, Ltd., Tokyo, Japan). Sixty grams of raw zeolite X was dispersed in 350 mL of distilled water using an ultrasonic vibrator (VCX 600, Sonic & Materials Inc., USA) and the slurry was pulverized for 120 min using zirconia beads 300 μm in diameter followed by an additional milling for 120 min using zirconia beads 100 μm in diameter. An agitation speed of 3000 rpm was used to shear and exert force on the zeolite agglomerates. After milling, the slurries were dried overnight in an oven at 373 K. The recovery rate of the zeolite powder after bead milling was nearly 100%. Recrystallization of the milled zeolite X was performed using dilute aluminosilicate solution with the composition of 405Na2O:1Al2O3:51SiO2:2990H2O. This particular ratio is important in that it gives a solution nearly in equilibrium with zeolite X. This means that zeolite X is in neither macroscopic growth nor dissolution mode.16 In these conditions poorly crystalline parts of the milled zeolite X are more easily dissolved than the more crystalline parts. Recrystallized back onto the zeolite X then gives greater crystallinity. First, 100 mL of the aqueous solution was heated to 363 K using an oil bath. 3 g of milled zeolite was then added to...
the heated solution with stirring. After a period of 120 min, the slurry was centrifuged and the supernatant liquid was decanted off. The residual solid was washed with distilled water several times. The phases present, and the morphology of the products were identified by conventional X-ray diffractometry (XRD, Multriflex, Rigaku, Tokyo, Japan), field emission scanning electron microscopy (FE-SEM, S-5200, Hitachi, Tokyo, Japan) and field emission transmission electron microscopy (FE-TEM, 2100F, JEOL Tokyo, Japan). The composition of each sample was also measured using X-ray fluorescence spectrometry (XRF, JSX-3202, JEOL, Tokyo, Japan).

To investigate the changes in the intermediate range order before and after the milling and recrystallization treatments, high-energy X-ray diffraction (HEXRD) measurement was also performed. For HEXRD measurements, 250 mg of the sample was pressed into a disc and the measurements carried out at room temperature. High-energy X-ray diffraction experiments were carried out on a horizontal two-axis diffractometer, optimized for structural measurements in glass and liquid and built at the BL04B2 high-energy monochromatic bending magnet beam line of SPring-8. A bent Si(220) crystal mounted on the monochromator stage fixed at a Bragg angle of 3° in the horizontal plane, provides an incident photon energy of 61.63 keV (wavelength: 0.2012 Å). Pelletized samples were fixed to the sample stage before characterization. The Q<sub>max</sub> collected in this study was 25 Å<sup>-1</sup>. The collected data were subjected to well-established analysis procedures including absorption, background and Compton scattering corrections followed by normalization to the Faber-Ziman total structure factor, S(Q). The pair distribution function, G(r), was derived from Eq. (1).

\[
G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_{Q_{\text{m}}}^{Q_{\text{max}}} \left[ Q[S(Q) - 1] \sin(Qr) \right] dQ
\]

where \( \rho(r) \) is the microscopic pair density and \( \rho_0 \) is the average number density.

3. Results and discussion

XRD patterns of the samples are shown in Fig. 1. The diffraction peaks assigned to an FAU structure in the bead milled samples showed the sample has still crystalline but the peak intensities had decreased, indicating a decrease in crystallinity. After recrystallization, however, the crystallinity returns to close to the original level. There was almost no loss of mass during the recrystallization treatment with the recrystallized product having 94.1% of the mass of the milled starting material. It appears that selective recrystallization occurs at the poorly crystalline parts of the milled zeolite X, where damage has been caused by bead milling. The Si/Al ratio of the samples measured by XRF shows almost no significant changes [Raw(1.0) → Milled(1.0) → Recrystallized (1.1)], indicating that the material balance was maintained during the milling and recrystallization. Changes in the intermediate range order were also investigated by high-energy X-ray diffraction (HEXRD). Figure 2 shows the pair distribution function, G(r), of the zeolite X samples. From the G(r) curves, it is possible to identify distances associated with several features. The first peak in G(r) is related to the Si-O (ca. 1.61 Å) and Al-O (1.71 Å) distances, although the Q range obtained here is not sufficient to resolve the two. Peaks at 2.6–2.7 and 3.0–3.3 Å are related to O-O and Si-Al(Si) distances (T = Si or Al). In the G(r) of raw zeolite, peaks can be seen at 3.7–4.0 and 4.2–4.6 Å, which mainly correspond to the distances from the Si(Al) to the second oxygen in the ring [2nd Si(Al)–O]. It is worth noting that a peak can still be seen but the intensity decreased in the milled zeolite X at 3.7–4.0 and 4.2–4.6 Å, indicating a decrease in crystallinity. This result clearly shows that the ring structure of zeolite framework is distorted and/or destroyed by bead milling. After recrystallization, however, the crystallinity returned to close to the original level. It can be deduced, therefore, that the distorted and/or destroyed part of milled zeolite X has reformed on recrystallization.

Typical FE-SEM images of the samples are shown in Fig. 3. The raw zeolite X powder comes as agglomerates and has smooth spherical features. After bead milling, the zeolite X morphology has changed considerably. The raw zeolite X has an average size of 3.5 μm and has formed agglomerates composed of tiny particles approximately 50–200 nm. After recrystallization, the product has become sharply-defined nanoparticle approximately 30–100 nm across. The average particle size after recrystallization was estimated to be 60 nm from the FE-SEM image. TEM images before and after recrystallization are shown in Fig. 4. As shown in Fig. 4(a), particle is composed of non-crystalline and crystalline part, as was seen in XRD data shown in Fig. 1. On the other hand the zeolite nano particles were highly crystalline after post-milling recrystallization as shown in Figs. 4(b) and 4(c). No residual non-crystalline part or layer was confirmed on the
A top-down approach has been applied to the preparation of nano zeolite X by the combination of bead milling and post-milling recrystallization, giving nano zeolite X approximately 60 nm in size with high crystallinity for the first time. The characteristic point of the present method is that templating organic compounds are not required to control zeolite nucleation and crystal growth. Furthermore, nanosized zeolite can be obtained almost without loss of material. The adsorption and ion-exchange properties of nano zeolite X with various crystalline sizes will be published elsewhere.

**Acknowledgment**

The authors would like to thank Profs. T. Tatsumi and T. Yokoi from the Tokyo Institute of Technology for FE-SEM measurements. This work has been supported partially by a “Grant for Advanced Industrial Technology Development” in 2011 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

**References**