Synthesis of Dense Y-zeolite Bulks with Large Surface Area Using a Hydrothermal Hot-pressing (HHP) Process

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Highly dense and large bulk Y-zeolites (1.5 mm in thickness and 20 mm in diameter) with a significantly large surface area over 700 m^2/g were obtained by a short-term hydrothermal hot-pressing (HHP) treatment at 423 K for 2 h, comparable with the Y-zeolite powder.

The synthesis of zeolitic films, membranes, coatings, as well as bulk using various methods, such as CVD etc.,[1–4] has received a great attention for various applications (gas separation etc.)[4–8] However, using these methods, it is difficult to avoid the introduction of voids, pinholes, and amorphous phases between aggregated zeolite crystals. As a result, the materials are mechanically weak and also their activity, selectivity, and permeability are often reduced by the discontinuity of a micropore channel network between zeolite crystals and grain boundaries. Also, much attention has been paid to the synthesis of large zeolite single crystals, since pure zeolite single crystals without amorphous phase and defects possess an excellent activity, selectivity, and permeability due to their large surface area, internal adsorption and diffusion properties through its micropore channels.[5–8] However, large zeolite single crystals are difficult to obtain, since the growth of several hundred microns by hydrothermal synthesis generally takes a few months.

We attempted to synthesize a large, dense, and pure zeolite polycrystals with a large surface area through a continuous micropore channel network inside the zeolite bulk, as well as zeolite single crystals in order to achieve a high activity, selectivity, and permeability by using the hydrothermal hot-pressing (HHP) technique developed by Yamasaki et al.,[9,10] similar to the crystallization of the amorphous phase at grain boundary of ceramics. This HHP is a unique method to solidify oxide ceramic powders at low temperatures (i.e. below 773 K) for several hours under a compressive pressure, similarly to the formation of sedimentary solids in a long-term hydrothermal process.

Y-zeolite (Tosoh Corporation: 320NAA, $SiO_2/Al_2O_3 = 5.5$, 840 m^2/g) was used as a starting material. This zeolite powder has the average particle size of 0.4 μm. HHP treatments were carried out as follows. Y-zeolite (0.75 g) was put in a stainless mold.[9] 9, 17, and 29 wt % of NaOH solution (0.1, 1, 5, and 10 M) were added to the Y-zeolite powder in the mold (ϕ 20 mm). Subsequently, samples were pressed with a uniaxial pressure of 40 MPa and heated for 2 h at 423 K. HHP-treated samples were cooled to room temperature. After HHP treatment, samples were sufficiently washed with deionized water and subsequently dried at 343 K. Components of these bulk Y-zeolites were evaluated by XRD. Microstructures were observed with SEM. Specific surface area was measured using N_2 gas absorption equipment.

Figure 1 shows the outside appearance of a bulky Y-zeolite after HHP treatment at 423 K. All bulk Y-zeolites were strongly solidified. Only HHP-treated samples upon adding 17 wt % of 5 M NaOH possessed the translucency after HHP treatments (Figure 1a), while HHP-treated samples with 17 wt % of 0.1 and 1 M NaOH did not show translucency (Figure 1b). This successful synthesis of large zeolite bulks with translucency may lead to new applications, such as photocatalysts, sensors, dielectric and electronic devices. XRD results showed that all products were identified as Y-zeolite, whereas HHP-treated samples with a 17 and 29 wt % of 5 M NaOH solution showed a lower crystallinity than HHP-treated with 9 wt % of 5 M NaOH. Also, an increasing NaOH concentration tended to decrease the intensity of diffraction peaks. Accordingly, it was found that adding an excessive NaOH solution into the Y-zeolite powder lowered the crystallinity in Y-zeolites solidified upon HHP treatments.

The density of HHP-treated bulk Y-zeolites at 423 K with 17 wt % NaOH solutions of different NaOH concentrations was measured. The theoretical density of Y-zeolite was reported as 1.9 g/cm^3 by Sasaki et al.[11] For comparison, the density of Y-zeolite compacted at the same pressure of 40 MPa without a HHP treatment resulted in approximately 50% of the theoretical density. Relative densities increased with the concentration of NaOH solution upon HHP treatments. Especially, HHP-treated bulk Y-zeolites with 5 M NaOH showed a significantly high density, i.e. >98%. However, adding 10 M NaOH slightly decreased the relative density of bulk Y-zeolites (results not shown). Also, the relative density increased with increasing content of 5 M NaOH, although saturated over 9 wt % of 10 M NaOH. Thus, densification of Y-zeolite powders can be sufficiently achieved upon HHP treatments by adding NaOH solution.

Figure 2 shows cross sections of HHP-treated samples. SEM observation showed that bulk Y-zeolites were composed of dense zeolite crystals. HHP-treated samples with 17 wt % of 0.1 M and 1 M NaOH show microstructures with fine equiaxis zeolites (~0.5 μm). However, HHP-treated samples with 9, 17, and 29 wt % of 5 M NaOH consist of elongated zeolite grains,

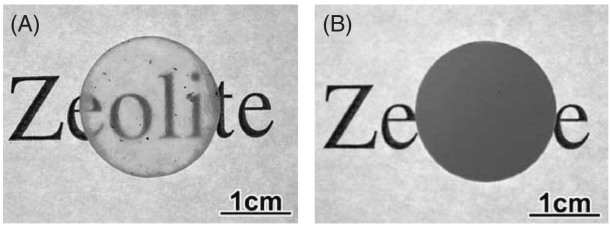

Figure 1. Photographs of bulk Y-zeolite samples prepared by HHP treatment at 423 K for 2 h with 40 MPa with approximately 1.1 mm in thickness and 20 mm in diameter. (A) 17 wt % of 5 M NaOH after HHP-treatment. (B) 17 wt % of 1 M NaOH after HHP-treatment.

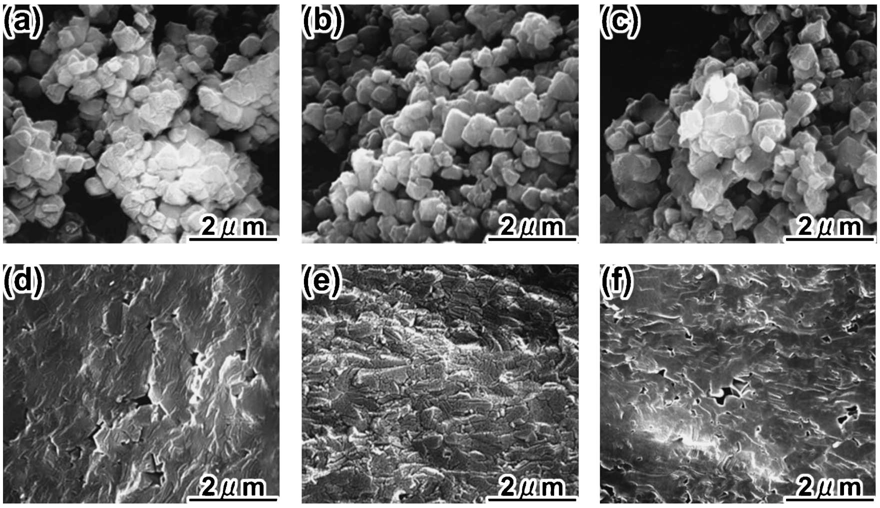

Figure 2. SEM images of bulk Y-zeolites HHP-treated at 423 K for 2 h containing various contents of 0.1, 1, and 5 M NaOH solutions. (a) Y-zeolite as a starting powder, (b) 0.1 M–17 wt %-HHP, (c) 1 M–17 wt %-HHP, (d) 5 M–9 wt %-HHP, (e) 5 M–17 wt %-HHP, (f) 5 M–29 wt %-HHP.

whereas HHP-treated samples with 9 wt % of 5 M NaOH also show some voids, and is consistent with density results as mentioned above. Accordingly, SEM observations suggest that precipitation of zeolite crystals filled up voids in the Y-zeolite matrix. Previous papers[9,10] on the solidification of oxide-ceramics by HHP treatments suggest that crystal growth of oxides are related to various process factors such as temperature, pH, water content, and pressure during the HHP treatment and controlled by a solution-precipitation process of oxide-grains under hydrothermal conditions. This densification of Y-zeolites during HHP is believed to be due to the dissolution from the Y-zeolite matrix and subsequent precipitation of zeolite crystals. Especially, the successful synthesis of bulk translucent HHP-treated samples with 17 wt % of 5 M NaOH is suggested to be attributable to this dense and pinhole-free microstructure consisting of fine zeolite crystals.

HHP-treated samples with 17 wt % of 0.1, 1, and 5 M NaOH were broken into a few smaller pieces (approximately 5–10 mm in dimension) and the specific surface area of these pieces were measured. Y-zeolite bulk HHP-treated with 17 wt % of 5 M NaOH solution had a specific surface area of approximately 700 m^2/g. Also, samples HHP-treated with 17 wt % of 0.1 M and 1 M NaOH showed a higher specific surface area of approximately 800 m^2/g. This significantly high specific surface area of fully dense bulk zeolite solidified upon HHP treatment was comparable with that of the Y-zeolite powder as a starting material. As noted above, XRD results showed that these bulk samples only possess Y-zeolite phase, no other phases. Also, SEM observation for these dense samples exhibit no voids and pinholes between fine Y-zeolite crystals, suggesting that during HHP treatments, zeolite crystals of the matrix dissolved into the NaOH solution and finally precipitated as zeolite crystals between other zeolite crystals. Accordingly, this intergrowth of zeolite crystals during a HHP treatment filled the voids between zeolite crystals and resulted in the successful synthesis of pinhole-free, dense, pure, and large bulk zeolite polycrystal. This resulting large surface area suggests that no amorphous layer exists at the interface (i.e. grain boundary) of zeolite crystals, although a TEM study is under investigation. From these results, it is concluded that these dense bulky zeolite polycrystal solidified upon a HHP treatment possess a significantly large surface area without diminishing continuous micropore channel network inside zeolite polycrystals. Namely, these bulk zeolite polycrystals solidified upon a HHP treatment can be considered to be a large-sized pseudo-single crystal.

In summary, we successfully synthesized single crystal-like bulk zeolite. Furthermore, a translucent bulk Y-zeolite with a large surface area upon a HHP treatment under optimum conditions was also obtained. Thus, it is expected that this HHP process can synthesize a large bulk of various zeolites having dimensions in the mm to cm range for a short time.

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