Synthesis of Dense and Pinhole-free Y-zeolite for Separation Membrane Using a Modified Hydrothermal Method

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Dense zeolite membrane without defects such as pinholes and cracks was synthesized on a porous alumina support by a newly modified hydrothermal technique, i.e., double-layered capsule hydrothermal method.

Zeolite is a porous crystalline material with highly uniform micropores on a molecular level. It has been anticipated to be useful for various applications as catalyst carrier and gas separation membranes due to potential advantages of well-defined sub-nanometer micropore structure. Their application has been, however, restricted, since these microporous zeolites are generally obtained only as a powder.[1–6] Thus, many attempts have been made of powder consolidation and construction of thin film for expansion of applications of microporous zeolites. Because microporous zeolite membranes for gas and liquid separation have better thermal properties, resistance to pressure and chemical resistance compared to organic polymer membranes, the development of high performance zeolite membranes is recently desirable for application to gas separation such as CO_2 separation at high temperatures. However, uniform and dense zeolite membranes without grain boundaries and structural defects are significantly difficult to obtain through conventional techniques, for example, hydrothermal synthesis, chemical vapor deposition, physical vapor deposition, seeding method, and dry gel conversion.[1–5]

Recently, we reported that the dense bulky Y-zeolite and mesoporous silica (MCM and FCM) were successfully synthesized using a hydrothermal hot-pressing (HHP) method.[6–17] This HHP method could densify oxide ceramics and glasses because of its dissolution and deposition by means of increasing the rate of dissolution and solubility of particles into water under hydrothermal conditions. Based on this HHP technique, we attempted to develop a newly coating technique, a double-layered capsule hydrothermal method, which is an isostatic hydrothermal process. Consequently, the newly developed hydrothermal method led to the successful synthesis of dense zeolite coating without pinholes and cracks on porous alumina suports.

A schematic illustration of this new double-layered capsule hydrothermal method is drawn in Figure 1. Sample preparation was as described below. First, 5 M NaOH and Y-zeolite powder (Toso Corporation: 320NAA, $SiO_2/Al_2O_3 = 5.5$ and $840\,m^2\,g^{-1}$) were mixed in various proportions (1–15 wt % zeolite). A porous alumina support (porosity 35%, particle size of alumina 0.5–2 µm, and pore size 5–10 µm) was coated with a slurry of this mixture and placed into a tube made of polyfluoroethylene (FEP). Both ends of the FEP tube were mechanically sealed, and subsequently the FEP tube was further encapsulated using a poly(vinylidene chloride) (PVC) film. The capsule prepared using the PVC film was sealed using a thermocompression method, as shown in Figure 1. Next, the capsule was put into a batch high temperature and pressure vessel for hydrothermal treatment. Subsequently, samples were pressed with an isostatic pressure of 40 MPa and heated for 2 h at 423 K. Components of obtained samples were evaluated by XRD. Microstructures of these samples were observed with SEM. Existence of pinholes or cracks was evaluated by water and ethanol dropping test.

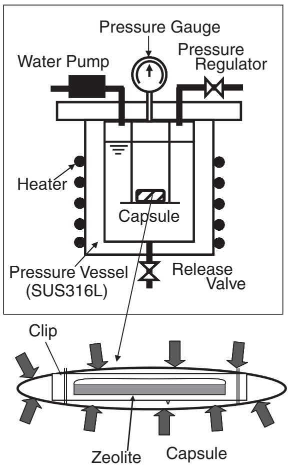

Figure 1. Schematic drawing of the double-layered capsule hydrothermal method and the cross-sectional view of a capsule.

Figure 2 shows the result of XRD. From XRD, all products were identified as Y-zeolite without chemical composition change and impurities, although the intensities of the diffraction peaks gradually increased with increasing concentration of the mixture. SEM images of surface and cross-sectional view of the zeolite coating prepared by the double-layered capsule hydrothermal method are shown in Figure 3. The presence of Y-zeolite particles was observed at the surface of the coating using 1 wt % zeolite mixture (Figure 3a). A uniform zeolite coating was not obtained on the porous alumina support, because zeolite particles were not well coated on the alumina support due to low concentration of the mixture. However, it could be seen that the pores near the surface of the alumina support were filled with Y-zeolite particles, as shown in Figure 3d. Meanwhile, the zeolite coating became denser and the number of the cavities was decreased with increasing concentration of the mixture, as shown in Figures 3b and 3c. Denser coating was obtained with 7 and 15 wt % zeolite mixture, compared to 1 wt % zeolite. SEM observations of a surface prepared using 15 wt % zeolite show that a significantly dense coating without defects as pin-

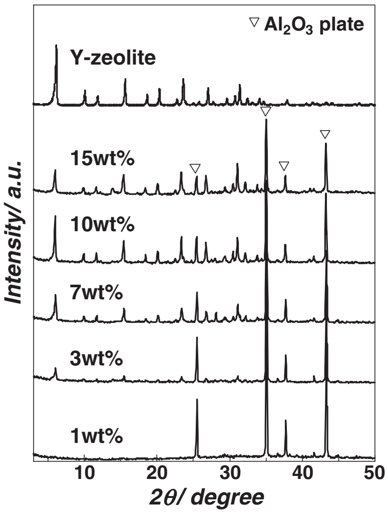

Figure 2. XRD of Y-zeolite membranes prepared by the double-layered capsule hydrothermal method with various concentration mixtures.

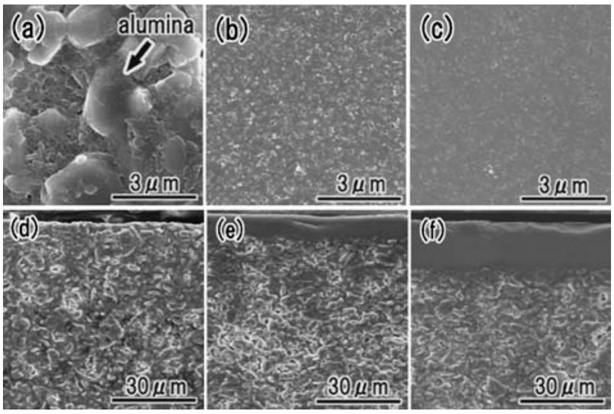

Figure 3. SEM images of Y-zeolite membranes prepared by the double-layered capsule hydrothermal method with various concentration mixtures. Surface: (a) 1 wt % zeolite, (b) 7 wt % zeolite, (c) 15 wt % zeolite. Cross section: (d) 1 wt % zeolite, (e) 7 wt % zeolite, (f) 15 wt % zeolite.

holes and cracks was obtained. Cross sections of these coatings composed of a dense zeolite layer were observed by SEM. The thickness of zeolite coating prepared using 1, 7, and 15 wt % zeolite mixtures were approximately 1, 5, and 23 μm, respectively (Figures 3d–3f). This suggests that the coating thickness can be controlled by adjusting the concentration of the zeolite mixtures. This densification behavior is thought to be due to dissolution and deposition promoting a connection of the zeolite particles under hydrothermal conditions and solidification caused by isostatic pressing.[9,11,13] Next, the presence or absence of defects such as pinholes or cracks in the coating was confirmed by water and ethanol drop tests. In the case of untreated alumina support, liquid drops penetrated into the pores of the alumina in a few second. On the other hand, for samples coated by the double-layered capsule hydrothermal method, drops of water or ethanol remained as liquid on the surface of the zeolite coating for more than several minutes (not shown). This suggested that a high quality zeolite coating without pinholes and cracks was obtained. In addition, there were no cracks or delamination even after Vickers hardness test for the coatings prepared by this modified hydrothermal method. Moreover, the coating did not peel off during a debonding test with the cellophane tape. Thus, it was confirmed that there was very strong bonding between the zeolite coating and alumina substrate.

In summary, a new double-layered capsule hydrothermal method was successfully developed. By this isostatic hydrothermal treatment, high-quality, dense, and uniform zeolite coating with no pinholes was easily obtained in a significantly short time. Moreover, it was possible to control the coating thickness by this process. This modified technique was effective for high performance zeolite coating with good permeability to liquid and gas. Consequently, the double-layered capsule hydrothermal method has some advantages in densification of various meso- and microporous materials for the preparation of dense membranes without defects for many microporous and mesoporous materials.

References

1 T. Sano, H. Yanagishita, Y. Kiyozumi, D. Kitamoto, F. Mizukami, *Chem. Lett.* **1992**, 2413.
2 J. Li, Q. T. Nguyen, L. Z. Zou, T. Wang, Y. C. Long, Z. H. Ping, *Desalinaiton* **2002**, *147*, 321.
3 D. Coutinho, K. J. Balkus, Jr., *Microporous Mesoporous Mater.* **2002**, *52*, 79.
4 Z. Lai, G. Bonilla, I. Diaz, J. G. Nery, K. Sujiaoti, M. A. Amat, E. Kokkoli, O. Terasaki, R. W. Thompson, M. Tsapatsis, D. G. Vlachos, *Science* **2003**, *300*, 456.
5 M. Matsukata, E. Kikuchi, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 2341.
6 N. Yamasaki, K. Yanagisawa, N. Kakiuchi, *J. Mater. Res.* **1990**, *5*, 647.
7 K. Yanagisawa, M. Nishioka, K. Ioku, N. Yamasaki, *J. Mater. Sci. Lett.* **1990**, *9*, 7.
8 A. Nakahira, T. Murakami, T. Onoki, T. Hashida, K. Hosoi, *J. Am. Ceram. Soc.* **2005**, *88*, 1334.
9 A. Nakahira, S. Takezoe, Y. Yamasaki, *Chem. Lett.* **2004**, *33*, 9.
10 S. Takezoe, K. Hosoi, M. Tajika, Y. Yamasaki, A. Nakahira, *Key Eng. Mater.* **2006**, *97*, 317.
11 H. Nagata, M. Takimura, Y. Yamasaki, A. Nakahira, *Mater. Trans.* **2006**, *47*, 2103.
12 M. Takimura, H. Nagata, Y. Yamasaki, A. Nakahira, *Solid State Phenom.* **2007**, *124–126*, 1833.
13 A. Nakahira, S. Takezoe, Y. Yamasaki, Y. Sasaki, Y. Ikuhara, *J. Am. Ceram. Soc.* **2007**, *90*, 2322.
14 A. Nakahira, M. Takimura, Y. Yamasaki, *J. Non-Cryst. Solids* **2007**, *353*, 4203.
15 H. Nagata, T. Kubo, A. Nakahira, *J. Ion Exchange* **2007**, *18*, 594.
16 H. Nagata, N. Hirao, T. Onoki, Y. Baba, Y. Yamasaki, A. Nakahira, *J. Ceram. Soc. Jpn.* **2008**, *116*, 216.
17 A. Nakahira, H. Nagata, T. Onoki, Y. Yamasaki, *Res. Chem. Intermed.* **2008**, *34*, 347.

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