Hydrothermal transformation of magnetically orientation-controlled seed layer into orientation-retained dense, continuous film in clear reaction solution

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Randomly-oriented and b-axis oriented mordenite seed layers, which were pre-fabricated out of and in a strong 12 T magnetic field, were hydrothermally treated in clear reaction solutions with molar ratios of 6Na2O:Al2O3:30SiO2:3500H2O (x = 1500, 3500 and 10000). Crystal growth of the seed particles only slightly occurred in the solution of x = 10000, but occurred in the solutions of x = 1500 and 3500, giving rise to densified films. However, the films treated with x = 1500 were composed of two layers with different morphologies; i.e., the precipitation of crystals from the solution was considered to induce the upper layer in the bilayered films. Homogenized films were formed in the solutions of x = 3500. The initial orientation of the seed layer was retained in the continuous films treated at x = 3500. Thus, dense, continuous mordenite films with random and b-axis orientations were successfully fabricated from random and b-axis oriented seed layers by hydrothermal treatment in the clear reaction solutions at the molar ratio of 6Na2O:Al2O3:30SiO2:3500H2O.

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1. Introduction

Studies on synthetic zeolites having molecular sieve activity began in the middle of 1940s. After that, commercially-used zeolites had been limited in the form of granules, and their function had been limited to either an adsorptive separation process or a catalytic action. In 1987, composite membrane having a surface layer of an ultrathin film of a zeolite and the production processes were first patented by Suzuki.3) Since then, much interest has focused on films of zeolites, which are often referred to as molecular sieves, because of their potential applications such as gas-separation membranes, chemical sensors and optoelectronic devices.2)–4) Although various film-formation processes have been reported, most of the zeolite films available today are randomly oriented even though a preferred orientation is often desired. The secondary growth of seed particles pre-deposited on substrates is an effective way to make oriented zeolite films.5)–7) The film-formation based on the secondary growth is performed in the following two steps: the first step is seeding of the zeolite or precursor particles onto substrates and the second step is transformation of the seed particles into a continuous film via hydrothermal treatments in reaction solutions with the appropriate molar ratios. Therefore, controlling both of these steps is important for the formation of oriented zeolite films during the film-formation process based on the secondary growth.

Very recently, the authors have proposed a magneto-scientific seeding process using a strong magnetic field.9) Since the fundamental concepts of the proposed new seeding process are based on the anisotropies of the magnetic properties of the asymmetric crystal structures,9)–14) the process can be applied to various types of zeolites except for cubic zeolites. The authors applied the magneto-scientific process to an actually-used zeolite, mordenite, which is a very important catalysis, adsorption and separation material widely used in the petroleum refining and fine-chemical industries.15)–18) The unit cell of mordenite is orthorhombic with Cnmc symmetry,19) and two different types of pore channels exist in the structure: one is composed of a 12-membered ring running along the c-axis, and the other is an 8-membered ring along the b-axis. A previous study disclosed that the b- and c-axes of mordenite are easy- and hard-magnetization axes, respectively.5)–7) The authors have already succeeded in controlling the orientation of mordenite using a strong magnetic field of 12 T, obtaining the b- and c-axes oriented mordenite compacts which are merely packed mordenite particles.9) The present study has attempted to prepare oriented mordenite membrane by the secondary growth from the oriented seed layers prepared using the magneto-scientific seeding process. This paper deals with the hydrothermal treatments of randomly-oriented and the b-axis oriented mordenite seed layers in reaction solutions with controlled chemical compositions.

2. Experimental

A commercially-available highly siliceous H-type mordenite zeolite (HSZ-640HOA, Tosoh Co., Ltd.; SiO2/Al2O3 = 230) was used as the starting material in this study. The powders were dispersed in distilled water by ultrasonic vibration for 10 min using an ultrasonic homogenizer. The prepared suspensions were left...
for 72 h without stirring for sedimentation classification. The detailed sedimentation classification procedure has been reported elsewhere.\textsuperscript{21} The obtained supernatant suspensions were poured into bottomless, cylindrical glass vessels placed on porous substrates of zirconia which were prepared by sintering compacted disks of commercial powder (TS-8Y, Tosoh Co., Ltd.) at 900°C for 5 h in air. The slip casting was performed in or out of the static 12 T magnetic field. A superconducting magnet with the room temperature bore of 100 mm (JASTEC Inc., JMTD-12T100NC5) was used for applying the magnetic field. The magnetic field was vertically applied to the suspension, that is, the direction of applied magnetic field was parallel to the slip casting.

For the hydrothermal treatments, reaction solutions with the molar ratios of $6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:30\text{SiO}_2:x\text{H}_2\text{O}$ ($x = 1500, 3500$ and $10000$) were prepared by mixing sodium aluminate, sodium hydroxide and colloidal silica with ultrapure water. The concentrations of sodium hydroxide in the $x = 1500, 3500$ and $10000$ reaction solutions were 0.37, 0.16 and 0.06 M, respectively. Based upon a previous report,\textsuperscript{22} it is expected that such clear reaction solutions diluted with H$_2$O suppress the extraneous precipitation of crystals from the reaction solutions onto the layer during the hydrothermal treatments, but has an effect on the crystal growth of the seed particles. The seed layers obtained on the substrates were fully-immersed in 16 mL of the reaction solutions and hydrothermally treated at 170°C for 24 and 48 h in 27 mL Teflon-lined stainless steel vessels. In the experimental setup, the seeded surfaces of the substrates faced toward the bottom of the vessels. The crystal growth of the seed particles took place in the liquid phase during hydrothermal treatment. The pressure of the vessel at 170°C was estimated to be about 0.98 MPa. These hydrothermally treated seed layers were washed with distilled water and then dried at room temperature. The morphology of the obtained films was observed using a scanning electron microscope (SEM). X-ray diffraction (XRD) with monochromatic Cu-K$_\alpha$ radiation was used to characterize the orientation of the mordenite before and after the hydrothermal treatments.

3. Results and discussion

3.1 Randomly-oriented seed layer

In Fig. 1, SEM photographs of the seed particles contained in the supernatant suspensions and the cross-section of the mordenite layer seeded on the substrate out of the strong 12 T magnetic field are shown. Each primary seed particle had an $a$-$b$ plane developed, $b$-axis elongated shape with a few $\mu$m size in the $b$-axis direction. It was observed that the seed particles were densely packed in the film.

Figure 2 shows an XRD pattern of the mordenite layer seeded on the substrate out of the strong 12 T magnetic field. For comparison, the XRD pattern of the as-received mordenite powder is also shown in the figure. There was no significant difference in the XRD patterns of Figs. 2(a) and 2(b), indicating that the seed layer was randomly oriented. This result also indicated that the directionally-elongated shape of the seed particles did not act on any preferential orientation of the seed layers during consolidation by the slip casting.

Figure 3 shows SEM photographs for the cross-section of the randomly-oriented mordenite films hydrothermally treated for 24 and 48 h in the reaction solutions with the molar ratios of $6\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:30\text{SiO}_2:x\text{H}_2\text{O}$ ($x = 1500, 3500$ and $10000$). Two layers with different morphologies were observed in the films treated with $x = 1500$ for 24 h; the lower layer on the substrate-side of the films consisted of the grown seed particles, whereas the upper layer consisted of elongated particles much larger than the seed particles in size. The thickness of the upper layer seemed to increase with the increasing treatment time. Highly grown prismatic particles were observed in the upper layer after the
treatment for 48 h. Although it is not shown in the results, the XRD patterns of the synthesized films treated for 24 and 48 h were different from that of the seed layer. The obtained films had the most intense peak from the (202) plane probably attributed to the upper layer; however, the reason of the crystal growth has not been clarified. The morphological changes in the upper layer were ascribed to both the enhanced crystal growth of the seed particles in the reaction solutions and the precipitation of the crystals from the solutions. Therefore, it was considered that the solution of $x = 1500$ was rather concentrated. On the other hand, such pronounced morphological changes were not observed for the films treated with $x = 3500$. The seed layer was thoroughly densified in the solution of $x = 3500$, but unfilled voids still remained after the treatment for 24 h. The voids decreased in size and number with further densification after the treatment for 48 h, and the seed layer was eventually transformed into a dense film. The observation of the morphology of the densified films was performed at higher magnifications using an FE-SEM, however, it was difficult to reveal the detailed process of the densification. The thickness of the film was identical in appearance even with an increase in the treatment time. Although one might have noticed in Fig. 3 that the thickness of films increased with the treatment time, the differences in the thickness of the films were due to the poor controlling ability of the film-thickness during the slip casting used in this study. In fact, it was not easy to reproduce seed layers with a controlled thickness on the order of a few $\mu$m using the slip casting even though the experiments were exactly performed. When the solution of $x = 10000$ was applied to the seed layer, no significant morphological changes were observed before and after the treatment for 24 h. With the increasing treatment time from 24 to 48 h, the seed layer was partly densified around the surface; however, the other part of the film became detached from the substrate. Thus, the clear reaction solution with the molar ratio of 6Na$_2$O:Al$_2$O$_3$:30SiO$_2$:3500H$_2$O was appropriate for the hydrothermal transformation of the seed layer composed of densely packed mordenite particles into a dense, continuous film.

The water content of our study was higher than that in previous studies which fabricated mordenite films by the secondary growth process using seed particles. Li and Matsukata et al. used the reaction solutions with the molar ratios of 10Na$_2$O:0.15Al$_2$O$_3$:36SiO$_2$:3H$_2$O ($x = 460$ and 960). The developed microstructures of the films were much thicker than the seed layers probably due to the promoted precipitation of crystals on the seed layer from the solutions in addition to the growth of the seed particles. Matsukata et al. also investigated the crystal formation and growth of mordenite using more diluted solution of $x = 1440$. They observed slight crystal growth of the seed particles from the diluted solution, however, they have not reported further investigation; they might consider that the solution of the diluted concentration was impotent to precipitate new crystals on the seed layer. As opposed to it, the use of diluted solution was preferable for us because it still had the ability to fill the voids between the seed particles without depositing newly-precipitated crystals on the seed layer during the hydrothermal reaction. In the present study, therefore, the densification of the films was performed in reaction solutions with the molar ratios of 6Na$_2$O:Al$_2$O$_3$:30SiO$_2$:1H$_2$O ($x = 1500$ and 3500). The films treated with $x = 1500$ was non-homogenous with two layers of different morphologies, whereas those with $x = 3500$ seemed to be homogenous. Based on the present results, it is considered that the diluted reaction solution with the molar ratio of 6Na$_2$O:Al$_2$O$_3$:30SiO$_2$:3500H$_2$O is effective for the mild intergrowth of the seed particles and suppression of precipitation onto the substrate from the solution during the hydrothermal treatments.

Figure 4 shows XRD patterns of the randomly-oriented mordenite films treated in the reaction solution with the molar ratio of 6Na$_2$O:Al$_2$O$_3$:30SiO$_2$:3500H$_2$O. As can be seen from a comparison of Fig. 4 and Fig. 2, no significant difference was observed before and after the hydrothermal treatments, indicating that the random oriented structure was retained without any formation of other phases in the treated films.

3.2 Magnetically orientation-controlled seed layer

Based on the above results, it was demonstrated that the dense, randomly-oriented mordenite films could be fabricated with an initial random orientation of the seeds by treating in a reaction solution having the molar ratio of 6Na$_2$O:Al$_2$O$_3$:30SiO$_2$:3500H$_2$O. This process was applied to magnetically orientation-controlled seed layers using the reaction solutions in order to further study the hydrothermal treatment effects.

Figure 5 shows SEM photographs of the cross-section of the magnetically oriented-controlled seed layer before and after the hydrothermal treatments of 24 and 48 h in the reaction solutions. The characteristic elongated axis of the mordenite particles, corresponding to the $b$-axis of mordenite, was preferentially aligned normal to the surface of the substrate. All the particles observed in the seed layer were clear-cut. The seed layers were transformed into a dense film after the hydrothermal treatment for 24 h; however, some voids were observed between the particles. With the increasing treatment time to 48 h, the films became too dense to distinguish the morphology of the individual particles. This tendency was consistent with the results for the randomly-oriented mordenite films.

Figure 6 shows XRD patterns of the magnetically oriented-controlled seed layer before and after the hydrothermal treatments for 24 and 48 h in the reaction solutions. As shown in Fig. 2, the peaks from the 200, 111, 330, 150 and 202 reflections were intense in the XRD patterns of the randomly-oriented films. These peaks, except for the 150 reflection, were considerably depressed in the XRD pattern of the magnetically oriented-controlled seed layer. For the seed layer, the 150 reflection was the most intense, and the peak from the 020 reflection was relatively intense compared to that in the XRD patterns of the randomly-oriented films. The XRD pattern of the seed layer was characterized by the $b$-axis orientation of mordenite, the $b$-axis of which was an easy-magnetization axis. The incomplete orientation must be due to inevitable partial overlapping of the
In this study, the hydrothermal treatments of (b) 24 and (c) 48 h in reaction solutions with the molar ratio of 6Na₂O:Al₂O₃:30SiO₂:3500H₂O.

Edges of the elongated platelet-like particles during the consolidation in the slip casting followed by the shrinkage in air during drying, and the irregularity of the packing of the seed particles can be observed for the seed layer in Fig. 5. The characterful XRD pattern indicating the b-axis orientation was observed after the hydrothermal treatments. These results clearly indicated that the orientation of the mordenite particles in the seed layer was retained during the hydrothermal treatments in the reaction solution for the molar ratio of 6Na₂O:Al₂O₃:30SiO₂:3500H₂O.

In this study, the c-axis-oriented seed layer was not used due to the difficulty in obtaining thin, uniform deposits with the c-axis orientation using the previous experimental condition. However, this effective process would be also applicable to the fabrication of dense, continuous mordenite films with the c-axis orientation after the optimization of the preparation condition of the c-axis oriented seed layers. The application of the process to other types of zeolites with non-cubic crystalline structures would be expected.

4. Conclusions
The present work was undertaken to investigate the hydrothermal transformation of mordenite seed layers with random and b-axis orientations into dense, continuous films using clear reaction solutions with the molar ratios of 6Na₂O:Al₂O₃:30SiO₂:xH₂O (x = 1500, 3500 and 10000), for which the magnetostriuctive technique was applied to from the orientated-controlled seed layer for the mordenite. The seed layer of elongated platelet-like particles was applied on porous YSZ substrates by slip casting in a strong magnetic field. Densified and continuous mordenite films were successfully fabricated in the solutions of x = 3500. For these fabricated films, it was observed that the orientation of the seed layer was retained after the hydrothermal treatments. On the other hand, non-homogeneous films were formed when the solutions of x = 1500 and 10000 were applied; it was considered that the former was concentrated, while the latter was too diluted. Thus, the randomly-oriented and the b-axis oriented mordenite seed layers were successfully transformed into dense, continuous films with the initial orientation structure by hydrothermal treatments using a clear reaction solution having the molar ratio of 6Na₂O:Al₂O₃:30SiO₂:3500H₂O.

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