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Preparation of mordenite membranes on α-alumina tubular supports for pervaporation of water–isopropyl alcohol mixtures

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Mordenite membranes prepared on α-alumina tubular supports by *in situ* hydrothermal synthesis using organic template-free media showed high water permselectivity for pervaporation of water–isopropyl alcohol mixtures.

Zeolite membranes have been widely studied in recent years because of their great potential applications in separations, membrane reactors and sensors. A continuous zeolite layer can be grown on various supports, including α-alumina and stainless steel generally by *in situ* hydrothermal synthesis. Different types of zeolites such as MFI, zeolite A, zeolite Y, mordenite and ferrierite have been synthesized on flat and tubular supports. Research has so far mainly focused on MFI (silicalite and ZSM-5) membranes for gas separation because their pore sizes, which are close to the sizes of gas molecules, allow separation of molecules based on their size. In addition, MFI crystals are easily grown on a support with structure-directing agents (SDAs). Some MFI membranes showing good separation of hydrocarbon isomers such as *n*-butane–isobutane have been reported by several groups.[1–3]

With respect to pervaporation separation, not only the pore sizes of zeolites, but also their surface properties (hydrophobicity and hydrophilicity) play an important role. Hydrophobic MFI membranes exhibit preferential alcohol permeation for pervaporation of a water–alcohol mixture although the molecular size of water is smaller than that of the alcohol.[4] In contrast, water permeated much faster than alcohols through hydrophilic zeolite A and Y membranes.[5,6] Since mordenite zeolite with large channels of 0.67 × 0.7 nm and small channels of 0.26 × 0.56 nm is hydrophilic, mordenite membranes would be selective for permeating water against alcohols.

In 1990, Suzuki *et al.*[7] first claimed the synthesis of a zeolite membrane (mordenite) onto a porous silica–alumina plate using an *in situ* hydrothermal synthesis method. Their membrane, synthesized at 160 °C for 2 days, exhibited Knudsen-diffusion behavior. Matsukata and coworkers[8] applied the vapor-phase transport method to obtain a mordenite membrane on a porous α-alumina disk. Their membranes showed a good separation factor of 160 for pervaporation of a benzene–*p*-xylene mixture. Very recently, Santamaría and coworkers[9,10] synthesized mordenite membranes onto a tubular support by *in situ* hydrothermal synthesis using TEAOH and reported the formation of composite mordenite/ZSM-5/chabazite membranes. They studied the separation of a water–n-propanol mixture through their composite membranes by a sweep gas method. Permeance ratios as high as 70 to 140 for water and *n*-propanol were achieved through their membranes. To our knowledge, the synthesis of mordenite membranes under SDA-free conditions on tubular supports has not been reported. Here we report the synthesis of a mordenite membrane onto a tubular support for pervaporation of a water–isopropyl alcohol mixture.

Mordenite membranes were synthesized on porous 6 cm long α-alumina tubes (NGK, Ltd.) with 0.1 μm diameter pores by *in situ* hydrothermal synthesis. The parent aluminosilicate gel was prepared as follows. An appropriate amount of alumina sulfate (Wako Pure Chem. Ind. Co. Ltd.) was added to a NaOH solution and stirred at room temperature until it dissolved. Colloidal silica containing 30–31 wt% of SiO_2 and 0.6 wt% of Na_2O ST-S, Nissan Chem. Ind. Ltd.) was then added to this solution and stirred vigorously for 1 h to give a gel of molar composition $0.38Na_2O:SiO_2:0.025Al_2O_3:40H_2O$.[7] The tubular support was washed, coated with a water slurry of seed crystals of zeolite mordenite (HSZ600, 70A, Tosoh Co.), SiO_2/Al_2O_3 ratio = 10.2), and then dried at 100 °C for 15 min. The support was then vertically immersed in the gel. Crystallization was carried out at 180 °C for a given period. After the crystallization, the sample was removed, washed carefully with distilled water, and then dried at 100 °C.

The membranes obtained were characterized by X-ray diffraction (XRD) with Cu-Kα radiation (Rigaku RINT2000). Fig. 1 shows the XRD patterns for the products crystallized at 180 °C for 8 and 24 h together with that for the seed powder. These XRD patterns were consistent with the mordenite structure. The XRD patterns of the membranes crystallized for different periods of crystallization showed that the (150) reflection intensity at 22.24°, became dominant with increasing crystallization time. Thus, mordenite crystals appear to grow randomly in the early stages of crystallization, and further crystal growth occurred mainly with the (150) face parallel to the support surface. Mordenite crystals were also grown on an unseeded support and gave almost the same XRD pattern as those on the seeded supports.

The morphology of the mordenite membranes was studied by scanning electron microscopy (SEM) (Hitachi S2150) and Fig. 2 shows SEM images for the surface and cross section of the mordenite membrane crystallized at 180 °C for 24 h. A continuous, intergrown layer fully covers the surface of support. The crystal sizes are *ca.* 6–7 μm, and the thickness of crystal

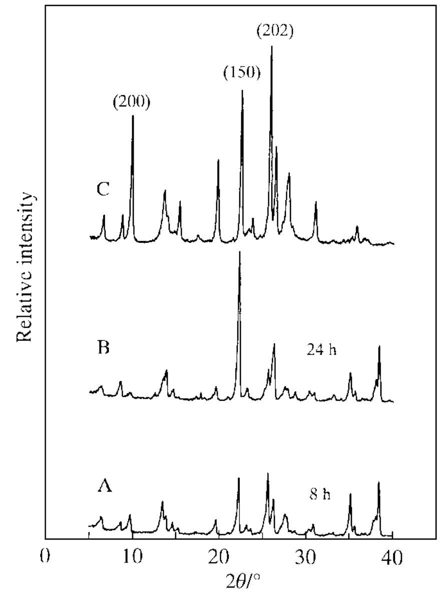

Fig. 1 XRD patterns for mordenite membranes crystallized at 180 °C for (A) 8 and (B) 24 h, and (C) mordenite seed powder.

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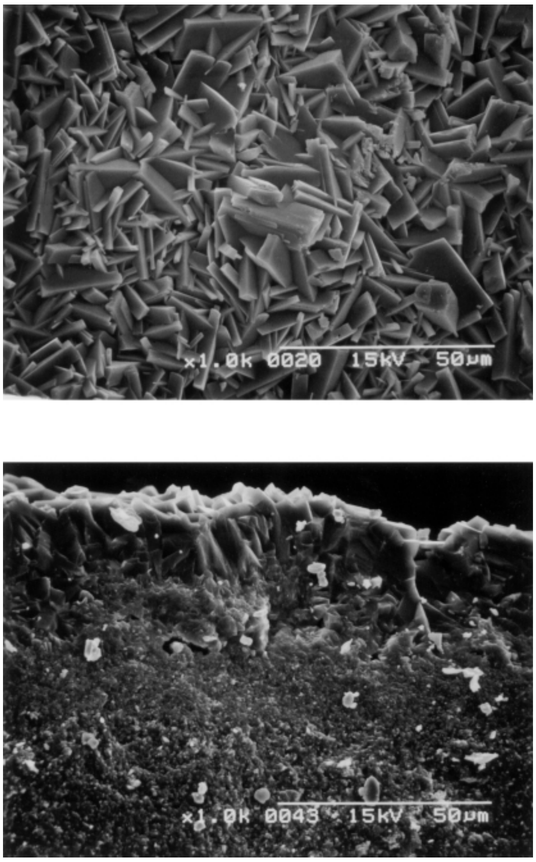

Fig. 2 SEM images for the surface and cross section of the mordenite membrane synthesized at 180 °C for 24 h.

layer is *ca.* 35 μm. The SiO_2/Al_2O_3 ratio of the mordenite zeolites determined by EDAX was *ca.* 12. In addition, the mordenite crystals have a rectangular form.

The pervaporation (PV) tests for water–isopropyl alcohol, and water–n-propanol mixtures were carried out at 75 °C using the pervaporation experimental apparatus described elsewhere.[8] The effective membrane area was *ca.* 15 cm^2 and the permeation side was kept under vacuum. The flux was calculated by weighing the condensed permeate. The separation factor was determined as $\alpha_{A/B} = (Y_A/Y_B)/X_A/X_B)$, where X_A, X_B, Y_A and Y_B denote the mass fractions of components A and B in the feed and permeate sides. The pervaporation results through the mordenite membranes crystallized at 180 °C for 24 h are listed in Table 1 and clearly show that water preferentially permeated through the mordenite membranes. The membrane synthesized on the seeded support exhibited a very high separation factor of 3360 for the water–isopropyl alcohol mixture compared with that of the unseeded support (192). We propose that the seed crystals increased the density of mordenite crystals on the support, resulting in a pinhole-free structure in contrast to the membrane formed on the unseeded support.

Table 1 Pervaporation results through mordenite membranes

Membrane[a]	Feed solution (A/B) (wt% of A)	Separation factor (A/B)[b]	Flux/ kg m^{-2}
M1	Water–n-propanol (10)	1782	0.2
M2	Water–isopropyl alcohol (10)	3360	0.1
M3[c]	Water–isopropyl alcohol (10)	192	0.2

[a] Membranes were crystallized at 180 °C for 24 h; [b] PV carried out at 75 °C. [c] Prepared without seeds.

Mordenite is formed for Si/Al ratios of *ca.* 5–6, higher than those for LTA (Si/Al = 1) and Y (Si/Al ratio = *ca.* 2.5). Thus, in comparison with LTA and Y, mordenite has potential application in acidic solutions under which esterification can occur. In addition, it is known that the effective pore size of mordenite can be precisely controlled in the range of *ca.* 0.3–0.6 nm by ion exchange, possibly leading to a wide variety of applications such as hydrocarbon separation and use as membrane reactors.

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