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ScienceDirect
Catalysis Today 132 (2008) 182–187
CATALYSIS TODAY
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Selective permeation and separation of steam from water–methanol–hydrogen gas mixtures through mordenite membrane

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Abstract

Separation properties of a mordenite membrane for water–methanol–hydrogen mixtures were studied in the temperature range from 423 to 523 K under pressurized conditions. The mordenite membrane was prepared on the outer surface of a porous alumina tubular support by a secondary-growth method. It was found that water was selectively permeated through the membrane. The separation factor of water/hydrogen and water/methanol were 49–156 and 73–101, respectively. Even when only hydrogen was fed at 0.5 MPa, its permeance was as low as 10^{-9} mol m^{-2} s^{-1} Pa^{-1} up to 493 K, possibly suggesting that water pre-adsorbed in the micropores of mordenite hindered the permeation of hydrogen. The hydrogen permeance dramatically increased to 6.5×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 503 K and reached to 1.4×10^{-6} mol m^{-2} s^{-1} Pa^{-1} at 523 K because of the formation of cracks in the membrane. However, the membrane was thermally stabilized in the presence of steam and/or methanol.

Keywords: Zeolite membrane; Mordenite; Membrane reactor; Methanol synthesis; Gas separation

1. Introduction

Methanol has been used as a feedstock for bulk organic chemicals such as formaldehyde, acetic acid, and methylamine. In addition, since methanol can also be used as clean fuel with sufficient stability and easiness to transport, the demand for methanol is expected to accelerate with future growth in the alternate fuel sectors, driven by both strategic and environmental considerations. In industrial processes, methanol synthesis from syngas, a mixture of H_2, CO, and CO_2, is performed at 473–573 K and 5–10 MPa according to the following reactions [1]:

$$CO + 2H_2 \rightarrow CH_3OH \quad \Delta H_{298\,K} = -90.7\,kJ\,mol^{-1} \tag{1}$$

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \quad \Delta H_{298\,K} = -49.5\,kJ\,mol^{-1} \tag{2}$$

$$CO_2 + H_2 \rightarrow H_2O + CO \quad \Delta H_{298\,K} = 41.2\,kJ\,mol^{-1} \tag{3}$$

As one-pass methanol yield is limited by thermodynamic equilibrium, unconverted syngas is recycled after product separation by condensation. Continuous, *in situ* removal of methanol and/or water from a reactor would allow us to overcome the equilibrium limitation and to achieve an energetically efficient and cost-effective process by improving the level of conversion, downsizing a reactor, and minimizing energy consumption to recycle unconverted gases. Struis et al. [2–4] first studied application of membrane reactor to methanol synthesis using a Li-Nafion membrane through which products, methanol and water, preferentially permeated ($\alpha_{water/hydrogen} = 32$ and $\alpha_{methanol/hydrogen} = 5.6$ at 473 K). These results suggested a

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doi:10.1016/j.cattod.2007.12.005

possible application of membrane to methanol synthesis. Nafion membrane is, however, difficult to be applied above 478 K due to a lack of thermal stability.

Inorganic membranes are superior to organic membranes in terms of thermal resistance, chemical inertness, and mechanical strength. Chen and Yuan [5] investigated silicon rubber/ceramic composite membranes for separation of methanol and water from hydrogen. The membranes showed high thermal stability but poor separation performance ($\alpha_{\text{water/hydrogen}} = 2.5$ and $\alpha_{\text{methanol/hydrogen}} = 0.8$ at 503 K). For these reasons, development of membrane with high separation performance at high temperature and high pressure is demanded for developing a methanol synthesis membrane reactor.

Zeolite membranes have unique properties such as shape selectivity and selective adsorption, in addition to high thermal, chemical and structural stability. They are, thus, attractive candidates as membrane material to be applied at temperatures and pressures for syngas conversion processes like methanol synthesis. Gaullucci et al. [6] investigated performance of a zeolite membrane reactor for methanol synthesis using an A-type zeolite membrane. Their zeolite membrane reactor showed an improved conversion of syngas in comparison with that of traditional reactor at 479 K but its superiority was relatively poor at higher temperatures, compared with the performances expected by the mathematical modeling study by Barbieri et al. [7]. This may be due to a lack of thermal stability of A-type zeolite membrane. An A-type zeolite membrane reported by Aoki et al. [8] showed high separation factors ($\alpha_{\text{water/hydrogen}} > 160$ at 303–473 K) though its stability above 473 K has been unknown yet. Zhu et al. reported that heating a zeolite-4A membrane at 453 K in the absence of water vapor caused irreversible defects formation [9].

Thermal stability of zeolite generally increases with increasing Si/Al ratio in the framework, while its hydrophilicity decreased. Thus, we supposed that zeolite with medium Si/Al ratios would be preferred for separating methanol and water from syngas. Mordenite has large channels of 0.67 nm × 0.70 nm and a medium range of Si/Al ratio around 5, and shows high stability, strong hydrophilicity. So far, we reported the synthesis of a thin mordenite membrane by the secondary-growth method in the absence of organic structure-directing agents [10–12] and showed mordenite membranes highly separated water from IPA or acetic acid [11].

The objective of this study was to evaluate water–methanol–hydrogen separation properties of mordenite membrane at temperatures as high as 523 K under pressurized conditions.

2. Experimental

2.1. Membrane preparation

A mordenite membrane was prepared on the outer surface of supports by secondary-growth method, following the procedure described by Li et al. [11,12]. Porous α-alumina tube (i.d. = 8 mm, o.d. = 10 mm, length = 30 mm, NGK Insulators, LTD) was used as support with an asymmetric structure. The average pore size in the outer surface of support was 0.1 μm. These supports were cleaned successively in acetone and distilled water each for 20 min under ultrasonication, and dried at 383 K before use.

The colloidal suspension of mordenite crystals was prepared as follows. Commercially available H-modenite powder (Si/Al = 5.1, Tosoh Co.) was crushed in an agate mortar. The crushed powder was mixed with an appropriate amount of water in a beaker to form slurry. This slurry was then treated in an ultrasonic bath. Finally this slurry was kept at 293 K for several days. While due to the gravitational effect lager particle were settled down to the bottom of the beaker, smaller particle were dispersed in the upper part of the slurry to form a colloidal suspension. Suspension with the solid content of ca. 1.8 g l^{-1} was used for seeding.

To minimize the growth of zeolite crystals on the inner side of support surface, the inside of tube support was plugged with a Teflon rod during seeding and hydrothermal crystallization. The seeding was carried out as follows: the support was dipped in the colloidal suspension for 1 min, withdrawn vertically at 3 cm s^{-1}, and then dried over 30 min at 453 K. This process was run twice.

The seeded tube support was immersed vertically in a 50 ml Teflon-lined stainless steel autoclave and filled with a synthesis mixture. The synthesis mixture with the molar composition of $10Na_2O{:}0.15Al_2O_3{:}36SiO_2{:}960H_2O$ was prepared by dissolving 0.214 g of sodium aluminate (31.0–35.0 wt.% Na_2O, 34.0–39.0 wt.% Al_2O_3, Kanto Chemical) in an aqueous sodium hydroxide solution (3.93 g NaOH and 64.2 g distilled H_2O). Then, 36.8 g of colloidal silica ST-S (30–31 wt.% SiO_2, <0.6 wt.% Na_2O, Nissan Chemical) was slowly added to the sodium aluminate solution under stirring. The gel formed became a clear solution after stirring at 323 K for 4 h. Hydrothermal treatment was carried out at 453 K for 4–6 h. After the crystallization, the sample was carefully washed with distilled water and dried at ambient conditions.

2.2. Membrane characterization

The morphology of the zeolite layer was examined by means of a field emission scanning electron microscope (FE-SEM, Hitachi S4500S) operated at 15 KeV. The crystalline phase of the zeolite layer formed on the support surface was determined using an X-ray diffractometer (XRD, Rigaku RINT 2100) equipped with a Cu Kα radiation source at 40 kV and 20 mA. Average Si/Al ratio of prepared membranes was determined by X-ray photoelectron spectroscope (XPS). Water desorption pattern of the mordenite membrane was analyzed by temperature-programmed desorption (TPD). The amount of water desorbed from a fresh mordenite membrane was measured while the temperature was raised by 100 K in a stepwise manner.

2.3. Separation tests

Fig. 1 shows the schematic diagram of experimental apparatus for permeation tests. Vapor or gas permeation measurements were performed using a stainless steel tube

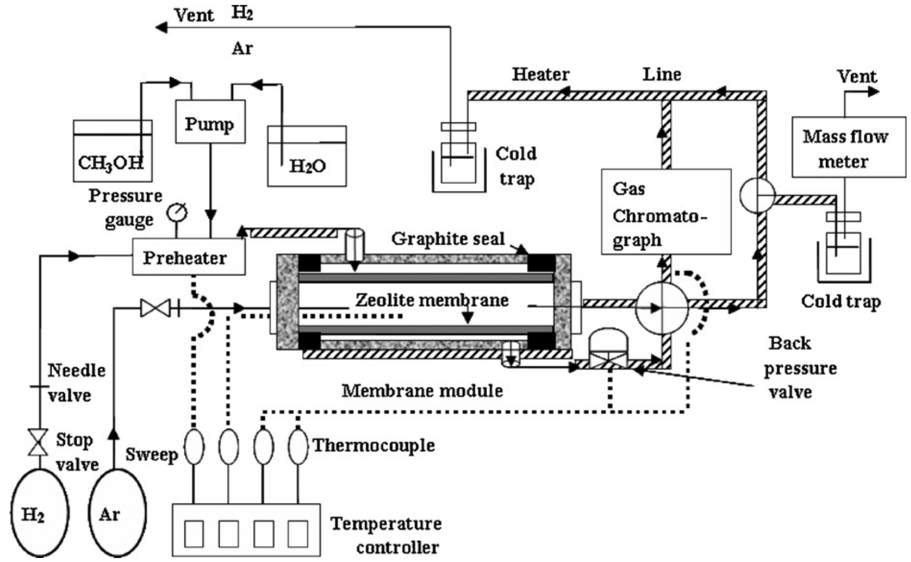

Fig. 1. Schematic diagram of the experimental apparatus for $H_2O/CH_3OH/H_2$ separation through a zeolite membrane.

module cell. The membrane tube was placed inside the module cell and sealed using graphite cylindrical rings at both ends. A thermocouple was inserted into the module cell and placed close to the inner surface of membrane. The effective membrane area was 6.28 cm^2. Both permeate and retentate were condensed in cold traps. Before permeation experiment, the membrane was dried at 423 K for 3 h. Hydrogen was fed into the retentate side of membrane at 300 cm^3 (STP) min^{-1}. A mixture of water and methanol was introduced into the stream and then mixed with hydrogen. The permeation side was swept with carrier gas, Ar, at 100 cm^3 (STP) min^{-1}. The pressure of retentate side of the membrane was controlled with a back pressure regulator, and that of permeation side was atmospheric. The compositions of permeate and retentate were determined by means of an on-line gas chromatography (Shimazu GC-8A). Separation factor was calculated from the following equation:

$$\alpha_{1/2} = \frac{(X_1/X_2)_{\text{permeate}}}{(X_1/X_2)_{\text{feed}}} \tag{4}$$

where X represents the mole fraction of gases 1 and 2.

3. Results and discussion

3.1. Membrane characterization

Fig. 2 shows the XRD patterns for the crystal layer produced and commercially available mordenite powder. The diffraction pattern of the crystal layer was identical to that of the mordenite powder. The reflection peaks of alumina also appeared in the XRD pattern of membrane, suggesting the formation of mordenite thin layer on the top of tubular alumina support.

Fig. 3 shows typical FE-SEM images of the surface of a porous α-alumina support before and after seeding. It can be seen that mordenite seeds of ca. 100 nm nicely filled the voids among the alumina particles in the support. Fig. 4 shows surface and cross-sectional typical FE-SEM images of the seeded support after hydrothermal treatment for 4 h. These FE-SEM observations reveal that after the hydrothermal treatment the surface of support was fully covered with highly intergrown crystals. The thickness of top crystal layer was about 1.5–2.0 μm, judging from cross-sectional FE-SEM images. The XPS measurements revealed the average Si/Al ratio of the surface of prepared membranes was about 5, which is similar to that of seed crystals (Si/Al ratio = 5.1).

3.2. Separation properties

Separation properties of mordenite membrane for water–methanol–hydrogen mixtures were studied in the temperature range from 423 to 523 K under the pressurized conditions (i.e. partial pressures of water, methanol, and hydrogen in feed were 0.37, 0.10, and 0.23 MPa, respectively). Fig. 5 shows the permeances of water, methanol, and hydrogen for water–methanol–hydrogen ternary-component through the mordenite membrane. The water permeance was 1.3–1.8 × 10^{-8} mol m^{-2} s^{-1} Pa^{-1} while the methanol and hydrogen

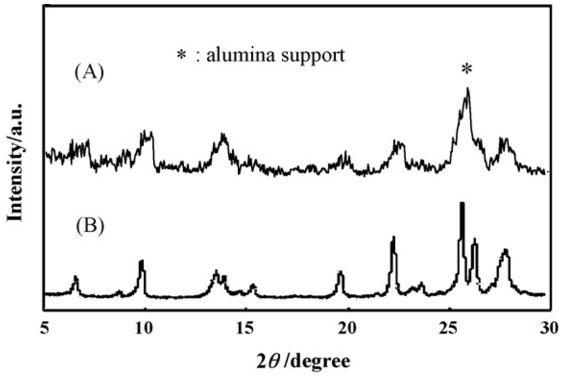

Fig. 2. XRD pattern for (A) the mordenite membrane grown on a seeded α-alumina support at 453 K for 4 h and (B) mordenite powder.

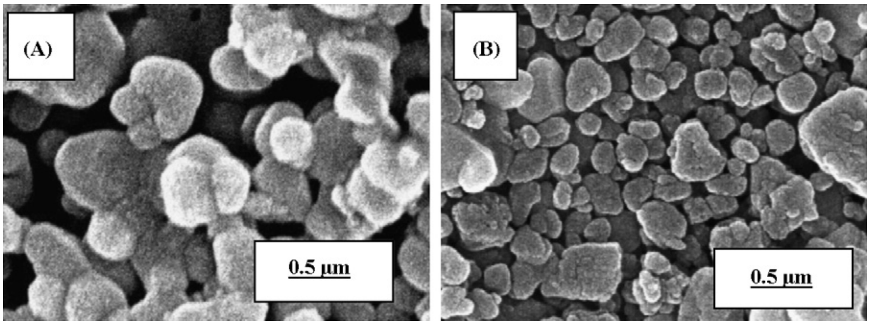

Fig. 3. FE-SEM images for (A) surface of a porous α-alumina support and (B) surface of a seeded porous α-alumina support.

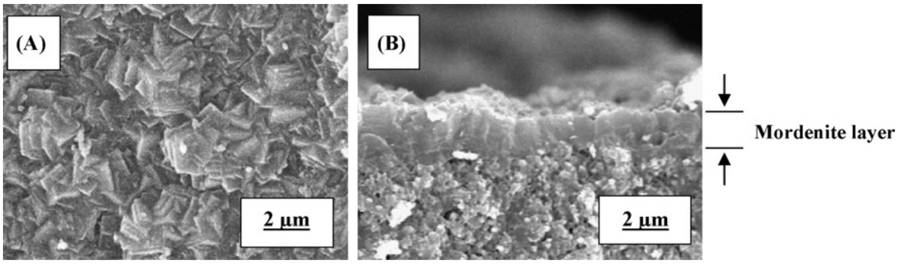

Fig. 4. FE-SEM images for (A) the top surface and (B) the cross-section of the mordenite membrane grown on a seeded α-alumina support at 453 K for 4 h.

permeances were about 10^{-10} mol m^{-2} s^{-1} Pa^{-1}, indicating that water was selectively permeated through the mordenite membrane. As shown in Fig. 6, the separation factors were $\alpha_{\text{water/hydrogen}} = 49$ and $\alpha_{\text{water/methanol}} = 73$ at 523 K.

Since water (ca. 0.30 nm [13]), methanol (ca. 0.38 nm [13]), and hydrogen (ca. 0.29 nm [14]) molecules are smaller than the pore size of mordenite zeolite (0.65 nm × 0.70 nm), molecular sieving seems difficult to control the separation of water from methanol and hydrogen. Therefore, selective water permeation at a high temperature of 523 K would be mainly due to strong, selective adsorption of water on the mordenite membrane.

3.3. Thermal stability of mordenite membranes

Fig. 7 shows the effect of co-existing water on hydrogen permeance through the mordenite membrane. When only hydrogen was fed at 0.5 MPa, its permeance was as low as 10^{-9} mol m^{-2} s^{-1} Pa^{-1} up to about 493 K, presumably suggesting that water pre-adsorbed in the micropores of mordenite hindered the permeation of hydrogen. Hydrogen permeance, however, dramatically increased to 6.5×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 503 K and reached to 1.4×10^{-6} mol m^{-2} s^{-1} Pa^{-1} at 523 K. After cooling the membrane down to 423 K, the permeance of hydrogen remained very

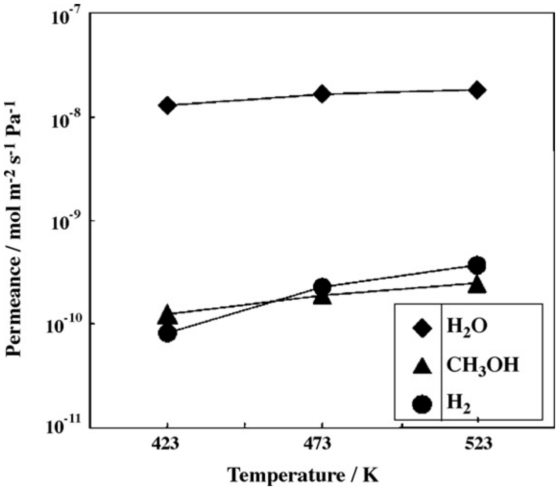

Fig. 5. Permeation of H_2O, MeOH, and H_2 through the mordenite membrane grown on a seeded α-alumina support at 453 K for 4 h. Partial pressures of H_2O, CH_3OH, and H_2 in feed were 0.37, 0.10, and 0.23 MPa, respectively.

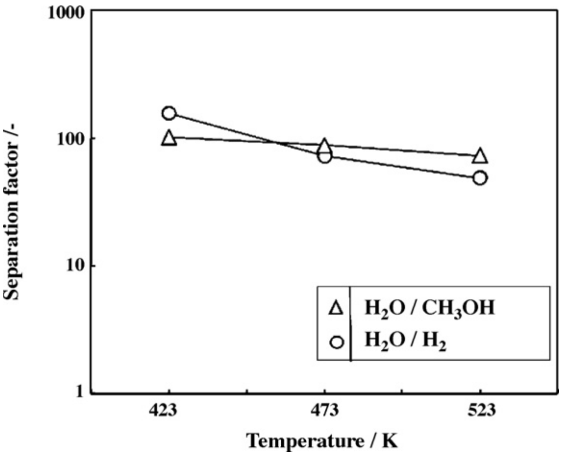

Fig. 6. Separation factors of H_2O/CH_3OH and H_2O/H_2 through the mordenite membrane grown on a seeded α-alumina support at 453 K for 4 h. Partial pressures of H_2O, CH_3OH, and H_2 in feed were 0.37, 0.10, and 0.23 MPa, respectively.

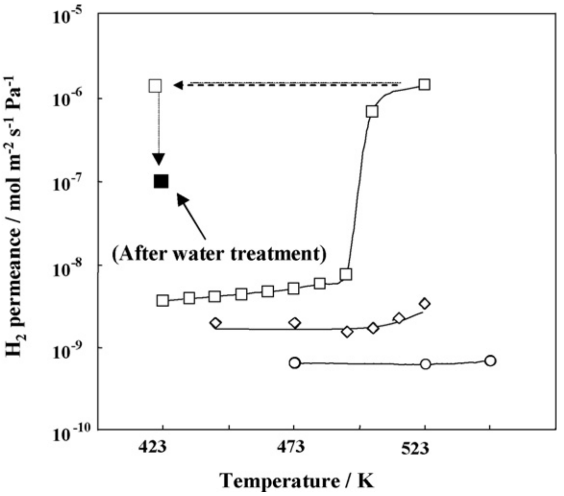

Fig. 7. Effect of H_2O on H_2 permeation through mordenite membranes grown on a seeded α-alumina support at 453 K for 6 h. Partial pressures in feeds (□), $P_{H_2} = 0.50$ MPa; (◇), $P_{H_2O} = 0.05$ MPa; $P_{CH_3OH} = 0.02$ MPa and $P_{H_2} = 0.33$ MPa; (○), $P_{H_2O} = 0.24$ MPa; $P_{CH_3OH} = 0.06$ MPa, and $P_{H_2} = 0.10$ MPa.

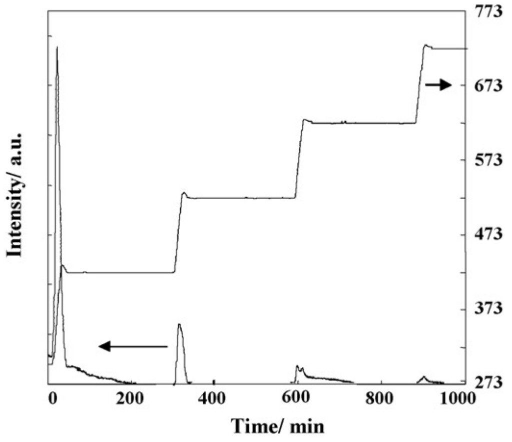

Fig. 8. H_2O-TPD pattern for a mordenite membrane grown on a seeded α-alumina support at 453 K for 6 h.

high, approximately 10^{-6} mol m^{-2} s^{-1} Pa^{-1}. Even the membrane was immersed in water at room temperature, the hydrogen permeance decreased only to 9.1×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, indicating that cracks were formed on the membrane.

When hydrogen was fed with water and methanol vapor, hydrogen permeance was considerably low at least up to 523 K, indicating that mordenite membranes stably blocked hydrogen permeation and cracks were not formed in the membrane. Formation of non-zeolitic pores with increasing temperature was also observed for hydrophilic LTA and FAU zeolite membranes. Recently, Noack et al. [15] discussed three possible reasons: (A) a contraction of the crystal size (B) a contraction of amorphous inter-layer in the grain boundaries between the crystals by drying, and (C) removing of water inter-layer in the grain boundaries between the zeolite crystals in the membrane layer. The cases (B) and (C) are unlikely in our study. It is difficult to imagine that amorphous inter-layer in the grain boundaries (if existed) stably blocked gas permeation at 523 K with steam. In addition, water condensation is not expected in non-zeolitic pores above 473 K under the partial pressures of water employed in this study. Shrink of crystals is probably the reason for crack formation observed in this study. Water in gas phase would prevent the mordenite membrane from dehydration and crack formation.

3.4. Pre-adsorbed water remaining in mordenite micropores

Outstanding water separation performance and the enhancement of thermal stability of mordenite membranes observed in this study seem to be related to the water adsorption property of mordenite membrane. Fig. 8 shows the results of H_2O-TPD measurement. A large water desorption peak was observed upon heating up to 423 K, and would be due to desorption of the water physically adsorbed on the surface of membrane. After the desorption ceased at 423 K, the membrane was again heated to 523 K. The peak of water desorption was again observed, indicating that strongly adsorbed water which could not desorb at 423 K existed in the pore of mordenite membrane. Besides, water desorption was observed during heating from 523 to 623 K and from 623 to 723 K. Such a strong interaction between water and mordenite would cause the appearance of water-selectivity at high temperatures. Hunger et al. [16] reported two kinds of main desorption peaks in the TPD of water from Na-exchanged zeolites: one is the desorption with energy between 42–60 kJ mol^{-1} correlated with the electronegativity of zeolites and average charge of lattice oxygen atoms; the other is the desorption with energy between 60 and 90 kJ mol^{-1} reflecting interactions of water with Na^+ cations. Considering their study, retention of water in mordenite at high temperature seems due to strong interactions between water and Na^+ cation. In Fig. 7, even single hydrogen permeance was very low. Considering the results of H_2O-TPD, a possible explanation would be that strongly pre-adsorbed water could block the permeation of other kinds of molecule through the pore of the mordenite membrane. We suppose that cracks formation with raising temperature is caused by the shrink of crystals with water desorption. The presence of water in gas phase prevented cracks formation and enhanced thermal stability of mordenite membrane.

4. Concluding remarks

In this study, we first found that a mordenite membrane prepared on the outer surface of porous α-alumina tube supports by the secondary-growth method allowed selective permeation of water at high temperatures as high as 523 K. In terms of application to a membrane reactor for methanol synthesis, removal of methanol seems also important though the mordenite membrane allowed only water permeation. Future study should be directed toward controlling selectivity of water and methanol possibly by exchanging a kind of cation and/or using other kind zeolite such as ZSM-5.

Acknowledgements

This work was financially supported by Japan Oil, Gas and Metals National Corporation (JOGMEC) in part. This work was also partially performed under the support of Grant-in-aid for scientific research (B) (No. 19360368) from Ministry of Education, Science, Sports and Culture, Japan and the Global COE program of MEXT "Center for Practical Chemical Wisdom", Japan.

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