High Temperature Separation of Water/Hydrogen Mixtures through Mordenite Membrane

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ABSTRACT
Separation properties of mordenite membrane for water-methanol-hydrogen mixtures were studied in the temperature range from 150 to 250°C under pressurized conditions. Mordenite is a kind of large pore zeolites with a pore diameter of 0.65 x 0.70 nm. Mordenite membrane was prepared on the outer surface of a porous alumina tubular support by a secondary-growth method. We found that water was selectively permeated through the membrane. The separation factors of water/hydrogen and water/methanol were 49 and 73, respectively, at 250°C. When only hydrogen was fed at 5 atm, its permeance was as low as 10^-9 mol m^-2 s^-1 Pa^-1 up to about 220°C, possibly suggesting that water pre-adsorbed in the micropores of mordenite hindered the permeation of hydrogen. The hydrogen permeance, however, dramatically increased to 6.5 x 10^-7 mol m^-2 s^-1 Pa^-1 at 230°C and reached to 1.4 x 10^-6 mol m^-2 s^-1 Pa^-1 at 250°C owing to the formation of cracks in the membrane. It was, however, found that the membrane was thermally stabilized in the presence of steam and/or methanol.

KEYWORDS
Mordenite, Zeolite membrane, Water-methanol-hydrogen Separation, Methanol synthesis

INTRODUCTION
Methanol has traditionally been used as a feedstock for bulk organic chemicals such as formaldehyde, acetic acid, and methyamine. In addition, since methanol can also be used as a clean fuel with enough 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 H2, CO and CO2, is carried out at 200-300°C and 5-10 MPa according to the following reactions:

\[
\begin{align*}
\text{CO} + \text{2H}_2 &= \text{CH}_3\text{OH} - 90.7 \text{ kJ mol}^{-1} (\Delta H_{298K}) \\
\text{CO}_2 + \text{3H}_2 &= \text{CH}_3\text{OH} + \text{H}_2\text{O} - 49.5 \text{ kJ mol}^{-1} (\Delta H_{298K}) \\
\text{CO}_2 + \text{H}_2 &= \text{H}_2\text{O} + \text{CO} + 41.2 \text{ kJ mol}^{-1} (\Delta H_{298K})
\end{align*}
\]

As methanol yield is limited by the thermodynamic equilibrium, unconverted syngas is
recycled after product separation by condensation. Continuous, in situ removal of methanol and water from a reactor can overcome the equilibrium limitation and achieve an energy-efficient and cost-effective process by improving the level of conversion, downsizing the synthesis reactor, and minimizing energy consumption to recycle unconverted gases.

Struis et al. (1996, 2000 and 2001) first studied the application of a membrane reactor to methanol synthesis using Li-Nafion membrane that allowed preferential permeation of products, methanol and water ($\alpha_{\text{water/hydrogen}} = 32$ and $\alpha_{\text{methanol/hydrogen}} = 5.6$ at 200°C). These results showed that membrane reactor gave a methanol yield higher than that in a traditional type of reactor. Nafion membrane is, however, difficult to be applied over 205 °C 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 et al. (2004) investigated silicon rubber/ceramic composite membranes for a membrane reactor for methanol synthesis. The membranes had high thermal stability but showed poor separation performance ($\alpha_{\text{water/hydrogen}} = 2.5$ and $\alpha_{\text{methanol/hydrogen}} = 0.8$ at 230°C).

For these reasons, development of membrane with high separation performance at high temperature and high pressure is essential for realizing 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 for a methanol synthesis membrane reactor. An A-type zeolite membrane reported by Aoki et al. (2000) showed high separation factor ($\alpha_{\text{water/hydrogen}} > 160$ at 30 – 200°C) though its stability over 200°C has been unknown yet. Gallucci et al. (2003) investigated the performance of a zeolite membrane reactor for methanol synthesis using A-type zeolite membrane. Their zeolite membrane reactor showed an improved conversion of syngas in comparison with that of traditional reactor at 206°C but its superiority was lost at higher temperatures. The mathematical modeling study reported by Barbieri et al. (2002) suggested that the performance of the membrane reactor should be much improved with a membrane having better permselectivities to water and methanol. Recently, we reported the synthesis of thin mordenite and ZSM-5 zeolite membranes by the secondary-growth method in the absence of organic structure-directing agents (Li et al., 2003). The objective of this study was to evaluate water/methanol/hydrogen separation properties of the mordenite membranes at temperatures as high as 250°C under pressurized conditions.

EXPERIMENTAL

Membrane preparation

Mordenite membranes were prepared on the outer surface of support by a secondary-growth method. Support used in this study was porous $\alpha$-alumina tube (i.d.= 8 mm, o.d.= 10 mm, length = 30 mm, NGK Insulators, LTD) with an asymmetric structure. The average pore size in the outer surface of support was 0.1 $\mu$m. These supports were cleaned successively in acetone and distilled water each for 20 min under ultrasonication, and dried at 110°C.

Colloidal suspension of mordenite crystals was prepared as follows. Commercially available mordenite powder ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio = 10.2, Tosoh Co.) was first crushed in an agate mortar. The crushed powder was then 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 20°C for several days. Due to the gravitational effect, bigger particles were settled down to the bottom of the beaker, while smaller particle were dispersed in the upper part of the slurry to form a colloidal suspension. A suspension with the solid content of ca. 1.76 g L$^{-1}$ was used for seeding.
To minimize the growth of zeolite crystals on the inner surface of the support, the inside of the 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\textsuperscript{-1}, and then dried over 30 min at 180°C. 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\textsubscript{2}O:0.15Al\textsubscript{2}O\textsubscript{3}:36SiO\textsubscript{2}:960H\textsubscript{2}O was prepared by dissolving 0.214 g of sodium aluminate (31.0-35.0 wt% Na\textsubscript{2}O, 34.0-39.0 wt% Al\textsubscript{2}O\textsubscript{3}, Kanto Chemical Co. Inc.) in an aqueous sodium hydroxide solution (3.93 g NaOH and 64.2 g distilled H\textsubscript{2}O). Then 36.8 g of colloidal silica ST-S (30-31 wt% SiO\textsubscript{2}, <0.6 wt% Na\textsubscript{2}O Nissan Chemical Ind. LTD.) was slowly added to the sodium aluminate solution under stirring to obtain a gel. The gel became a clear solution after stirring at 50°C for 4 h. Hydrothermal treatment was carried out at 180°C for 4 h. After the crystallization, the samples were washed with distilled water and dried at ambient conditions.

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 K\textalpha\ radiation source at 40 kV and 20 mA at a scanning speed of 2\textdegree min\textsuperscript{-1}.

Water desorption pattern of the mordenite membrane was analyzed by temperature-programmed desorption (TPD). The amount of water desorbed from an un-calcined mordenite membrane was measured while the temperature was increased by 100°C in a stepwise manner.

Hexane porosimetry was used to analyze the contributions of micropores (e.g., zeolite pores) and defects to the overall flux through the membrane (Deckman, 2001). In this method the He permeance through the mordenite membrane was measured while the activity (p/p\textsubscript{0}) of hexane was increased in a stepwise manner as listed in Table 1 (p is the partial pressure and p\textsubscript{0} is the saturated vapor pressure of n-hexane). The pressure on both sides of the membrane was atmospheric (Wicke-Kallenbach regime). The temperature at the membrane was kept at 30°C.

<table>
<thead>
<tr>
<th>Point</th>
<th>p/p\textsubscript{0}</th>
<th>Kelvin diameter / nm</th>
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<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>0.13</td>
<td>1.7</td>
</tr>
<tr>
<td>4</td>
<td>0.58</td>
<td>6.4</td>
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*Kelvin equation: 
D\textsubscript{K}= -4\nu\sigma\cos\theta / RT\ln(p/p\textsubscript{0}), where D\textsubscript{K}, \nu, \sigma, and \theta are Kelvin diameter, the molar volume, surface tension, and contact angle, respectively.

Permeation of Water/Methanol/Hydrogen mixtures

Fig. 1 shows the schematic diagram of the experimental apparatus for water/methanol/hydrogen separation. Vapor or gas permeation measurements were performed using a stainless steel tube module cell. The membrane tube was placed inside the module cell and sealed using graphite cylindrical rings at both ends. The stainless steel module cell was heated with a ribbon heater. A thermocouple was
inserted into the module cell and placed close to the inner surface of the membrane. The effective membrane area was 6.28 cm². Both permeate and retentate were condensed in cold traps cooled by ice. Before running an experiment, the membrane was dried at 150°C over 3 h. Hydrogen was fed into the retentate side of the membrane at 300 cm³ (STP) min⁻¹. A mixture of water and methanol was vaporized in a pre-heater at 240°C, and then mixed with hydrogen. Permeate side was swept with a carrier gas, Ar, at 100 cm³ (STP) min⁻¹. The pressure on the retentate side of membrane was controlled with a back pressure regulator. The permeate side of the membrane was kept at atmospheric pressure. The compositions and flow rates of both permeate and retentate were determined by means of a gas chromatography (Shimazu GC-8A) and mass flow measurements. Separation factor was calculated from the following equation,

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

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

RESULTS AND DISCUSSION

Characterization by FE-SEM and XRD

Surface FE-SEM images shown in Fig.1 reveal that the surface of the support was well covered with highly intergrown zeolite crystals. The thickness of the zeolite layer was about 1.5 µm, judging from cross-sectional FE-SEM image. Fig. 2 shows the XRD patterns for the zeolite membrane and commercially available mordenite zeolite powder. The diffraction pattern of the membrane was identical to that of mordenite.
Fig. 2 FE-SEM images of (A) top surface and (B) cross section of a zeolite membrane (M1) grown on a seeded α-Al₂O₃ support at 180°C for 4 h in a gel with molar composition of 10Na₂O:0.15Al₂O₃:36SiO₂:960H₂O.

Permeation of water/methanol/hydrogen ternary mixtures

The separation property of mordenite membrane for water-methanol-hydrogen mixtures was studied in the temperature range from 150 to 250°C. Fig. 3 shows the permeances of water, methanol, and hydrogen through membrane. The water permeance was 1.3-1.8 x 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ while the methanol and hydrogen permeances were about 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹, indicating that water was selectively permeated through the mordenite membrane. The separation factors at different
temperatures were shown in Fig. 4: \( \alpha_{\text{water/hydrogen}} = 49 \) and \( \alpha_{\text{water/methanol}} = 73 \) at 250°C and at a total pressure of 0.8 MPa. Since water (ca. 0.28 nm), methanol (ca. 0.38 nm), and hydrogen (ca. 0.29 nm) molecules are smaller than the pore size of mordenite zeolite (0.65 x 0.70 nm), molecular sieving did not control the separation of water from methanol and hydrogen. Therefore, high water-separation performance at a high temperature of 250°C would be mainly due to the strong, selective adsorption of water on the mordenite membrane.

**Thermal stability of mordenite membranes**

Fig. 5 shows the effect of co-existing water and/or methanol on the hydrogen permeance through the mordenite membrane. When only hydrogen was fed at 5 atm, its permeance was as low as 10^{-9} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} up to about 220°C, suggesting that water pre-adsorbed in the micro-pores of mordenite hindered the permeation of hydrogen. The hydrogen permeance, however, dramatically increased to 6.5 x 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} at 230°C and reached to 1.4 x 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} at 250°C. After cooling the membrane down to 150°C, the permeance remained very high, approximately 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}. Even after the membrane was immersed in water, the hydrogen permeance decreased only to 9.1 x 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}, indicating that the cracks were formed on the membrane. When hydrogen was fed with water and methanol vapor, hydrogen permeance hardly changed at least up to 250°C, indicating that mordenite membranes stably blocked the hydrogen permeation and cracks were not formed. It can be concluded that thermal stability of the mordenite membrane was enhanced under the conditions where water and/or methanol vapor co-existed.
H₂O-TPD measurement

High water-separation performance at high temperature above 200°C and enhancement of thermal stability of mordenite membrane in the presence of water and methanol seem to be related to the water adsorption property of the mordenite membranes. Fig. 6 shows the result of H₂O-TPD measurement. A large desorption peak of water was observed by heating the membrane up to 150°C, being due to the desorption of physically adsorbed water on the surface of membrane. After the desorption of water finished at 150°C, the membrane was heated to 250°C. The peak of water desorption was again observed upon heating, indicating that strongly adsorbed water which could not be desorbed at 150°C

Fig. 6 Effect of H₂O (MeOH) on H₂ permeation through mordenite membranes grown on a seeded α-Al₂O₃ support at 180°C for 6 h in a gel with molar composition of 10Na₂O:0.15Al₂O₃:36SiO₂:960H₂O. Partial pressures in feed: P₉₂ = 5.0 atm under dry conditions (□, M2); P₂H₂O = 0.5 atm, P₆MeOH = 0.2 atm, and P₈H₂ = 3.3 atm under wet ① conditions (◇, M3); P₂H₂O = 2.4 atm, P₆MeOH = 0.6 atm, and P₈H₂ = 1.0 atm under wet ② conditions (○, M4).

H₂O-TPD pattern for a mordenite membrane (M5) grown on a seeded α-Al₂O₃ support at 180°C for 6 h in a gel with molar composition of 10Na₂O:0.15Al₂O₃:36SiO₂:960H₂O.
existed in the pore of mordenite. This strongly pre-adsorbed water could block the pore of mordenite membrane, which explains why even single hydrogen permeance was small as shown in Fig. 5. Water and methanol would suppress the desorption of water from the micropores of mordenite, possibly preventing a polycrystalline structure of zeolite membrane from crack formation induced by shrinkage of crystals. The thermal stability of mordenite membrane could, thus, be enhanced in the presence of water and methanol. Besides, the peaks of water desorption appeared upon heating from 250 to 350°C and from 350 to 450°C, indicating that there was water strongly interacted with the micropores of mordenite.

Porosimetry

Hexane porosimetry was employed to investigate the effect of pre-adsorbed water on the permeation of gas such as hydrogen. The mordenite membrane was heated to 150°C and dried at the same temperature for 12 h to remove physically adsorbed water on the surface of membrane, as shown in Fig. 6. The membrane was then cooled to 30°C in a stream of Ar and analyzed by the hexane porosimetry. The results were shown in Fig. 7. The He permeance almost unchanged even when hexane activity increased, indicating that He mainly permeated via defects of the membrane. The relative He permeance via zeolitic pores could be evaluated by the following equation:

Relative He permeance via zeolitic pores
\[
= 1 - \frac{\text{He permeance at } p/p_\text{o} = 0.03}{\text{He permeance at } p/p_\text{o} = 0}
\] (5)

Fig. 7 Hexane porosimetry patterns of the mordenite membrane (M6): after heated at 150°C for 12 h (O) and after heated up to 250°C at a rate of 1°C min\(^{-1}\) (◇). The He permeance was measured as a function of hexane activity (p/p\(_{\text{o}}\)). The pressure on both sides of the membrane was atmospheric (Wicke-Kallenbach regime). The temperature at the membrane was kept at 30°C.

Fig. 8 Single \(\text{H}_2\) permeation through the mordenite membrane (M6) grown on a seeded \(\alpha\)-\(\text{Al}_2\text{O}_3\) support at 180°C for 6 h in a gel with molar composition of 10Na\(_2\)O:0.15Al\(_2\)O\(_3\):36SiO\(_2\):960H\(_2\)O. \(\text{H}_2\) partial pressure in feed: P\(_{\text{H}_2}\) = 5.0 atm.
According to equation (5), the relative He permeance through zeolite pores was only 0.56 %, suggesting that the membrane prepared in this study is fairly compact and almost all zeolite pores were filled with pre-adsorbed water, which hindered the He permeation through zeolite pores. Taken the results of hexane porosimetry into the consideration, we consider that hydrogen mainly permeated through defects (inter-crystalline voids) of membrane at 150-220°C. After this porosimetry measurement, the mordenite membrane was heated to 150°C and held at this temperature for 3 h. The membrane was then heated to 250°C at a rate of 1°C min⁻¹ and the single hydrogen permeance was measured at a given temperature. Fig. 8 shows the results of hydrogen permeance measurements. The hydrogen permeance almost unchanged from 150 to 220°C and suddenly increased above 225°C, which is consistent with the results shown in Fig. 5. After being heated to 250°C, the membrane was cooled down to 30°C and then analyzed by the hexane porosimetry again. The result was also shown in Fig. 7., together. The He permeance through defects was substantially enhanced by the heat treatment at 250°C, indicating that sudden increase of hydrogen permeance was mainly due to the defects formation by the desorption of water from mordenite pores at temperatures as high as 250°C.

CONCLUSIONS

Mordenite membrane was prepared on the outer surface of porous α-alumina tube supports by a secondary-growth method. The membrane showed a large permselectivity to water from a gas mixture of water, methanol, and hydrogen even at high temperature up to 250°C possibly due to strong adsorption of water on mordenite membrane. Pre-adsorbed water existing in the pores of mordenite membrane hindered the hydrogen and methanol permeation. Water and/or methanol vapor enhanced thermal stability of the mordenite membrane, resulting from the prevention of defects formation by water desorption from mordenite pores.

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REFERENCES


