

Preparation of a Water-Selective Ceramic Membrane on a Porous Stainless Steel Support by Sol-Gel Process and Its Application to Dehydration Membrane Reactor

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Abstract: We developed a water-selective ceramic composite membrane for use as a dehydration membrane reactor for dimethylether (DME) synthesis from methanol. The membranes were modified on the porous stainless steel support by the sol-gel method accompanied by a suction process. The improved membrane modification process was effective in increasing the vapour permselectivity by removal of defects and pinholes. The optimized alumina/silica composite membrane exhibited a water permeance of 1.14×10^{-7} mol/m².sec.Pa and a water/methanol selectivity of 8.4 at permeation temperature of 250°C. The catalytic reaction for DME synthesis from methanol using the membrane was performed at 230°C, and the reaction conversion was compared with that of the conventional fixed-bed reactor. The reaction conversion of the membrane reactor was much higher than that of the conventional fixed-bed reactor. The reaction conversion of the membrane reactor and the conventional fixed-bed reactor was 82.5 and 68.0%, respectively. This improvement of reaction efficiency can last if the water vapour produced in the reaction zone is removed continuously.

Keywords: membrane reactor, ceramic membrane, water permselectivity, sol-gel process, dimethylether

1. Introduction

Membrane reactor combined the permselectivity of a membrane with a catalytic reaction is a good candidate as a new approach to increase the efficiency in the conventional chemical processes. With permselective membrane, the products formed at the catalyst can be immediately removed from the reaction side. This can drive the reaction to completion even at a lower temperature and pressure. In addition, the integration of the two unit operations (reaction and separation) offers many advantages such as system simplification, lower capital cost, yield improvement and selectivity enhancement[1].

Dimethylether (DME), a prospective alternative fuel for diesel engine, is being spotlighted as a clean transportation energy. DME emits much less nitrogen ox-

ides than gasoline and diesel oils while still having thermal efficiency comparable to theirs[2-4]. In this regard, establishment of an effective and stable mass-production system is drawing much attention. At present, DME, the future clean fuel, is produced by the catalytic dehydration of methanol at around 290°C and 10 atm, and thus a large amount of water in the reaction is produced. If water vapour generated by the catalytic reaction can be selectively removed from the reaction zone, decrease in the catalytic activity can be prevented. Thus a good reaction yield can be obtained even in a mild temperature condition. Moreover, the reaction can be forced to completion by removing the water. Therefore, a membrane reactor combined the permselectivity of a membrane with catalytic reaction is a good candidate for a new approach to increase the conversion in the DME synthesis. With the water-selective membrane, the water vapor formed at the

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catalyst can be immediately removed from the reaction side. This can drive the reaction to completion even at a lower temperature and pressure.

Several studies on the membrane reactors for removing water vapour from the catalytic reaction at high temperature have been recently reported. Struis et al. studied the feasibility of Nafion hollow fiber membrane in methanol synthesis[5,6]. Water permeance of the membrane was $5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 200°C , and the membrane was effective in increasing the reaction conversion for the methanol synthesis. Gallucci et al.[7] applied a zeolite membrane reactor to methanol synthesis from carbon dioxide and hydrogen and obtained higher conversion of carbon dioxide and higher methanol selectivity.

Hydrophilic membranes such as zeolite and silica were developed for water separation from organic mixtures. Some ceramic membranes for dehydration was developed and applied to separation of organic mixtures by pervaporation[8,9], but the studies on the inorganic membrane for water separation at high temperature of over 200°C are very few. It is known that separation of water from methanol/water mixture is quite difficult because of the very low thermodynamic activity coefficient of methanol in water[10].

Among the inorganic membranes developed to date, silica and alumina membranes are attractive for gas separation at elevated temperatures because they are stable under crucial conditions where polymeric membranes cannot be applied[11-14]. So far the most widely used inorganic membranes are alumina membranes. In addition, the alumina membranes are expected to show a high water permselectivity by their hydrophilicity and porosity.

In this study, we developed water-selective ceramic composite membranes as a dehydration membrane reactor for DME synthesis from methanol. The membranes were modified on the porous stainless steel support by the sol-gel method accompanied by a suction process. The modified membrane was characterized by the permeation test of water-methanol-DME mixture at 250°C . The catalytic reaction for DME synthesis from methanol using

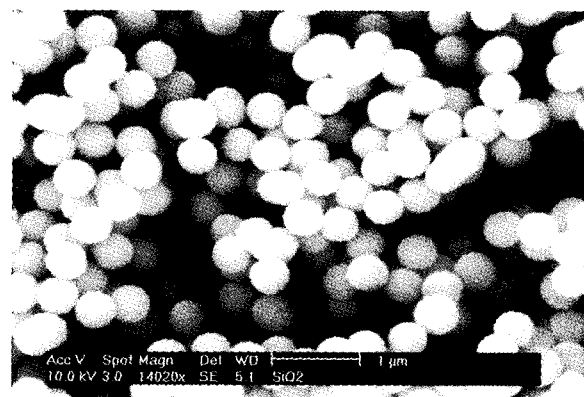


Fig. 1. FE-SEM image of the SiO_2 xerogel with 500 nm-sized particles.

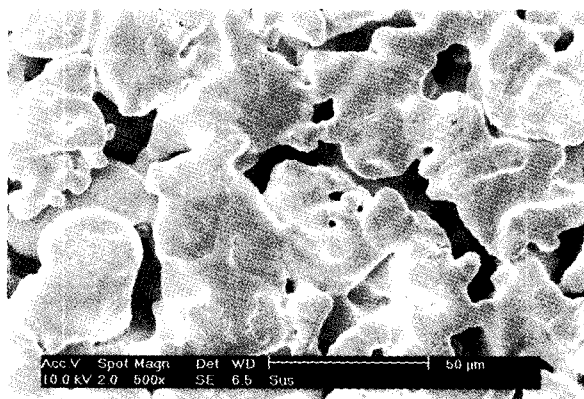


Fig. 2. FE-SEM image of the top surface of SUS support before the modification.

the membrane was performed at 230°C , and the reaction conversion was compared with that of conventional fixed-bed reactor.

2. Experimental

A porous stainless steel tube (SUS316) manufactured by Mott Co. (US) was used as the support to give the membrane mechanical strength. A top surface of the SUS support is shown in Figure 1. The properties of the tube are outer diameter, 1/4 inch; pore size, 0.5-1.0 μm ; and porosity, 0.3-0.4. The macropores of the support tube were modified by packing silica xerogel (500 nm) with a press under 10 MPa and by coating the intermediate layer of gamma alumina. The surface morphology of the silica xerogel is shown in Figure 2.

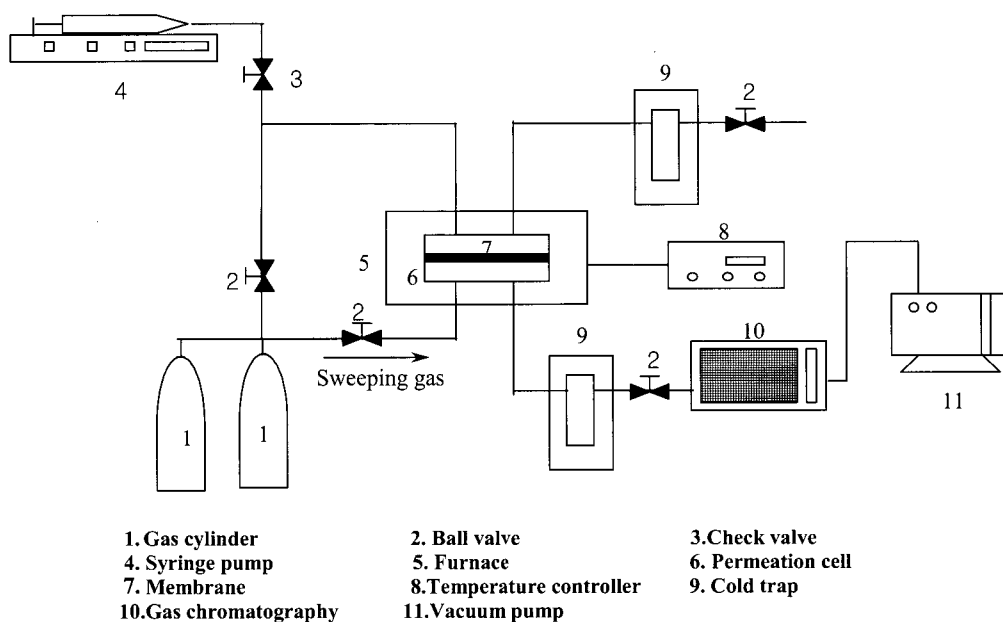


Fig. 3. Schematic diagram of the vapor permeation apparatus.

A mesoporous γ -alumina layer was coated on the SUS support tube from a boehmite sol (γ -AlOOH)[15] by the dipping-drying-firing procedure. After this coating process was repeated three times, the thickness of the γ -alumina layer was 2-3 μm , and the top surface was smooth and defect free. After the film was heat-treated at 700°C for 1 h in air, the typical adsorption-desorption isotherm for the γ -alumina film was of type IV corresponding to the mesoporous solid (2-50 nm pore diameters). The average pore size of the γ -alumina coating layer was determined with a BET unit (Micromeritics, ASAP 2200) and was about 5-7 nm in diameter. To improve the gas permselectivity, the γ -alumina layer was modified with polymeric silica sol by the suction method suggested by Lee et al.[16]. To improve the water selectivity, the silica membranes modified with γ -alumina layer were treated in air at 900°C for 1 h. Thus, the formation of silica-alumina, which has more acid sites than silica and alumina, was expected. Details of these procedures for SUS support modification and membrane preparation have been reported in our previous studies[17-20]. The gas permselectivity of the prepared membranes was investigated at 250°C using single-component water, DME and methanol as

well as the binary mixture of water and methanol (water/methanol = 1). The gas permeance ($\text{mol}/\text{m}^2\cdot\text{sec}\cdot\text{Pa}$) was calculated from the following equation:

$$\text{Permeance} = \frac{\text{mole of gas permeated per unit time}}{(\text{membrane area}) (\text{partial pressure difference})}$$

Figure 3 shows the schematic illustration of membrane reactor system for DME synthesis and gas permeation test. The membrane was coaxially fixed in a SUS tube of 1/2 in. O.D. and 300 mm length, and it was placed in an electric tubular furnace. For the DME synthesis experiments, the reactor was filled with alumina-based catalyst for dehydration of methanol (50 to 70 meshes; γ -alumina catalyst; Nikki Co.) to about 1cm of height. The reactor was heated at 350°C for 4 h under nitrogen atmosphere to activate the catalyst. Then, methanol was injected into the reactor along with nitrogen carrier gas using a HPLC pump. The DME synthesis reaction was conducted at reaction temperature of 230°C and LHSV (liquid hourly space velocity) of 0.36 h^{-1} . The products were analyzed by on-line gas chromatography (Shimadzu Co. Japan, GC-14B) with a thermal conductivity detector (TCD) and a flame ionization detector (FID) at an interval of 20

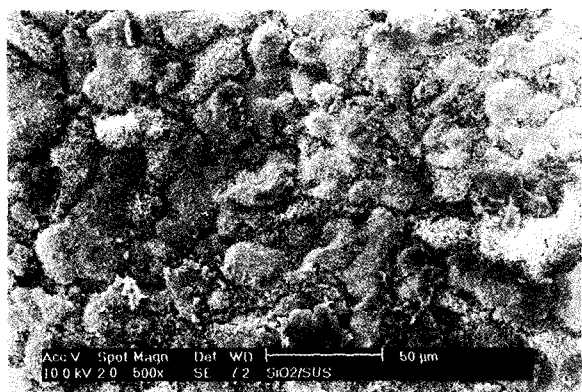
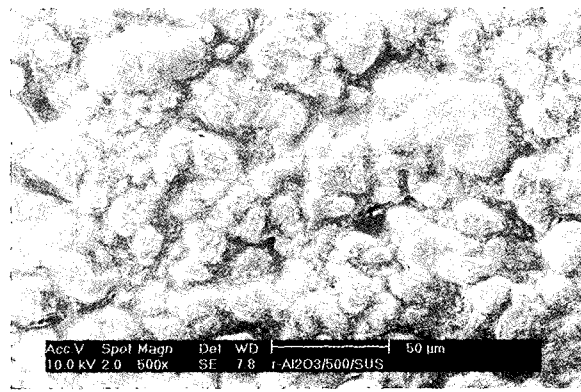


Fig. 4. FE-SEM image of the top surface of SiO_2 (500 nm)/SUS support.

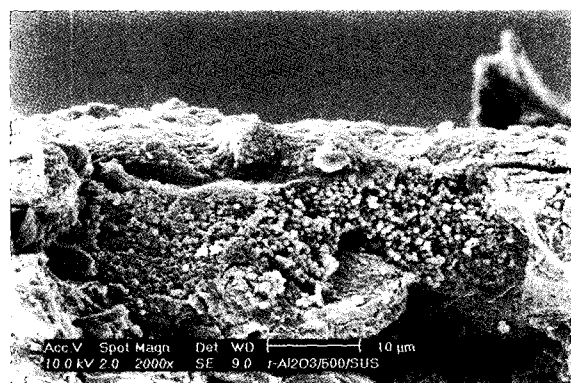
min. Methanol collected from both the tube and the shell side effluent stream was measured to establish the reaction conversion.

3. Results and Discussion

It is expected that the presence of an intermediate layer between the active layer and the support tube improves both permeance and selectivity of the membrane. One of attractive candidates for the intermediate layer is a γ -alumina film. First, SUS supports were modified using silica xerogel of 500 nm-sized in order to reduce pore size and surface roughness of the SUS support. Figure 4 shows a SEM image of the SUS support modified by silica xerogel. Pore size and surface roughness of the SUS support were definitely reduced. SiO_2 /SUS support was modified again with AlOOH sols by soaking-rolling method. A SEM image of the support modified with AlOOH sols is shown in Figure 5. Modification with AlOOH sols had the pore size of the SiO_2 /SUS support reduced more due to penetration of AlOOH sols into the macropores of the modified SUS support with silica xerogels. The SiO_2 (500 nm) particles are surrounded by the γ - Al_2O_3 . As shown in Figures 4 and 5, the macropores of the SUS support, which has very rough surface and wide pore size distribution, were successfully diminished by the well-packed silica xerogel and sol-gel procedure accompanied by a soaking-rolling method. The top surface of



(a)



(b)

Fig. 5. FE-SEM image of the (a) top surface and (b) cross-section of γ - Al_2O_3 / SiO_2 (500 nm)/SUS support by modification.

the membranes was quite smooth and showed no pin-holes.

For the dehydration membrane reactor, water-selective membranes were chosen among the membranes prepared under optimized conditions in previously studies. Table 1 shows permeation characteristics of water, methanol and DME for the titania, silica or alumina modified membranes in the γ -alumina and silica xerogel coated SUS support. During the gas permeation test, the total pressure on both sides of the membrane was maintained at the atmospheric pressure. As shown in Table 1, separation of water/methanol was very severer than that of water/DME because of the similar thermodynamic properties between water and methanol vapors[10]. Titania membrane[20], which is calcined at 450°C , showed a water selectivity to methanol as low

Table 1. Water Permselectivities of Ceramic Membranes Prepared on a Porous SUS Support

Membrane top layer ²	Permeance (mol/m ² ·sec·Pa) ¹			Selectivity	
	H ₂ O	Methanol	DME	H ₂ O/Methanol	H ₂ O/DME
TiO ₂	6.78 × 10 ⁻⁸	5.65 × 10 ⁻⁹	2.65 × 10 ⁻⁹	1.2	25.6
SiO ₂	4.09 × 10 ⁻⁸	5.68 × 10 ⁻⁹	-	7.2	-
Al ₂ O ₃	9.15 × 10 ⁻⁹	8.32 × 10 ⁻¹⁰	-	10.9	-
Al ₂ O ₃ /SiO ₂	1.14 × 10 ⁻⁷	1.36 × 10 ⁻⁸	1.81 × 10 ⁻⁹	8.4	62.9

¹ Permeation temperature = 250°C² Top layers modified on γ -Al₂O₃ and SiO₂ xerogel coated SUS supports.

as 1.2. Silica membrane, which is calcined at 500°C, showed a water/methanol selectivity of 7.2. The water selectivity of the alumina membrane, for which sol-gel coating was repeated two times, increased to ca. 11, but water permeance decreased to the order of 10⁻⁹ mol/m²·sec.Pa. To enhance the water permeance, hydrophilic modification of silica membrane was tried by coating a thin γ -alumina layer and by heat-treating the composite layer at 900°C. As a result, the alumina-silica composite membrane showed a high water permeance of the order of 10⁻⁷ mol/m²·sec.Pa, maintaining a moderate water/methanol selectivity of 8.4. This result is attributed to the formation of silica-alumina, which has more acid sites than silica and alumina[21].

To investigate the water removal effect on the conversion of DME synthesis, the water-selective membrane tube was used as a fixed bed catalytic reactor. The conversion of methanol was determined by analyzing all the collected effluent flow rates and composition data in the gas stream leaving the reactor during a given time. The conventional catalytic reactor was tested in the same dimensions, under the same operating conditions to compare it with the membrane reactor. The methanol yields in the two different modes of reactor operation are summarized in Table 2, where the liquid hourly space velocity (LHSV) is defined as a ratio of the reactant feed rate to the catalyst volume, and LHSV is given in units of h⁻¹. Membranes with low water permselectivity had little effect on the improvement of the reaction conversion for DME synthesis. This is due to insufficient removal of water from the reaction zone during the catalytic reaction.

Table 2. Comparison of Reaction Conversion According to Reactor Mode

Reactor mode	Conversion to DME (%)
Conventional reactor	68.0
Al ₂ O ₃ Membrane reactor	70.5
Al ₂ O ₃ /SiO ₂ Membrane reactor	82.5

LHSV = 0.36 h⁻¹

Reaction temperature: 230°C

On the other hand, the reaction conversion of the alumina-silica membrane reactor and the conventional fixed-bed reactor was 82.5 and 68.0%, respectively, at the reaction temperature of 230°C and LHSV of 0.36 h⁻¹. This improvement of reaction efficiency was made possible by the continuous removal of water vapour produced in the reaction zone. The result clearly exhibits that continuous selective water removal from the reaction region is actually taking place.

To remove water as fast as possible, the permeability of the membrane for water should be at least as large as the water formation. Otherwise, the conversion is again limited by the thermodynamic equilibrium. Therefore, given the higher water permeation rate, the methanol conversion sharply increases beyond the thermodynamic equilibrium value since more water can be removed from the reaction zone, which results in a greater equilibrium shift. In conclusion, this study demonstrated that a ceramic membrane reactor is capable of overcoming the severe thermodynamic limitations on conversion by in situ water separation from a catalytic DME synthesis reaction. Although the feasibility of the ceramic membrane as an effective catalytic reactor was proved, further research is needed to improve and opti-

mize the membrane reactor performance.

4. Conclusions

Alumina-silica composite membranes were prepared on the porous stainless steel support by the sol-gel method accompanied by a suction-rolling process. The improved membrane modification process was effective in increasing the water vapour permselectivity by removing the defects and pinholes. The optimized composite membrane exhibited a water flux of the order of 10^{-7} mol/m².sec.Pa and a water/methanol selectivity of 8 at permeation temperature of 250°C. The water-selective membrane was successfully applied to DME synthesis by methanol dehydration at 230°C, and the reaction conversion of the membrane reactor was much higher than that of the conventional fixed-bed reactor. The reaction conversion of the membrane reactor and the conventional fixed-bed reactor shows 82.5 and 68.0%, respectively. These findings led us to conclude that the dehydration membrane reactor simultaneously separating the water vapour produced in the reaction zone was very effective in increasing the reaction conversion. The water-selective ceramic membrane developed in this study was applicable to the dehydration membrane reactor for improving the reaction conversion.

Acknowledgements

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