

특별강연 II

고온 기체 분리회수를 위한 실리카 막

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Highly Permselective Silica Membranes for Elevated Temperature Gas Separation

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1. Introduction

Among inorganic membranes developed to date, amorphous silica membranes are attractive for gas separation at elevated temperatures. Gavalas and coworkers[1] first succeeded in plugging pores of a Vycor glass tube, having a pore size of about 4nm, with silica produced by a chemical vapor deposition (CVD) method. The silica membranes exhibited a H_2 permeance of the order of $10^{-7} \text{ mol} \cdot \text{m}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ and a H_2/N_2 selectivity of 100-1000 at permeation temperatures of 400-600°C[2-5]. de Lange et al.[6,7] prepared silica and silica-titania membranes by a sol-gel method, using a mesoporous γ -alumina support with a pore diameter of 4-10nm. Hydrogen permeance was higher than $10^6 \text{ mol} \cdot \text{m}^2 \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at 200, but H_2/N_2 selectivity was of the order of ten. Morooka and coworkers[8,9] showed that the step coverage of deposition was drastically improved by evacuating the reactant through the porous wall during CVD modification. This technique was especially effective in plugging the macropores of a support tube which possessed a wide pore-size distribution.

In this study, amorphous silica membranes are produced for the purpose of hydrogen recovery from a mixture containing steam produced by thermochemical water decomposition process[10]. Silica is deposited on a porous α -alumina support by thermal decomposition of tetraethoxysilane (TEOS) with a forced cross-flow through the porous

support wall. To get a higher permselective membrane, the α -alumina support is coated with γ -alumina layer and the composite tube is used as the support. Silica membranes are produced using phenyl-substituted ethoxysilanes as the Si source for the CVD process to enlarge the micropore size of silica-based membranes. Permeation of the silica membrane is then determined using hydrogen and nitrogen. The stability of the silica membrane is also evaluated in a steam-containing mixture at elevated temperatures.

2. Experimentals

2-1. Membrane preparation

A porous α -alumina tube supplied by NOK Corp. was used as the support. The properties of the tube were: outer diameter, 2.5mm; inner diameter, 1.9mm; pore size, 110-180nm in diameter; and porosity, 0.42-0.55. The outer surface of the support tube other than the central portion of 10-15 mm was glazed with a SiO_2 -BaO-CaO sealant calcined at 1100°C. An α -alumina tube coated with γ -alumina layer which possesses the pore diameters of 6-9nm is also used as a support. The sol-gel process for γ -alumina modification has been described elsewhere in detail[11].

The silica membrane is prepared in the macropores of the alumina support by chemical vapor deposition of tetraethoxysilane (TEOS) with a forced cross-flow. **Figure 1** shows details of the reactor cell for CVD modification. The support tube was coaxially fixed in a quartz tube of 9.8 mm i.d. and 150 mm length and was placed in an electric tubular furnace.

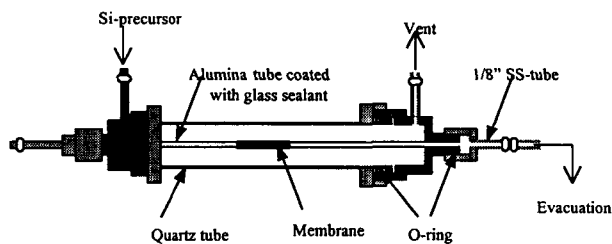


Fig. 1. Details of reactor cell for CVD modification.

After the system was evacuated with a rotary pump, the silicon source, TEOS (Shin-Etsu Chemical Co.), was vaporized at 40°C and introduced into the reactor (shell side) with a nitrogen carrier. The temperature of

the reactor was increased to a reaction temperature, 550–650°C and then maintained at that temperature for the duration of the experiment. During the membrane modification, the gases were continuously evacuated from the outside end of the tube using a rotary pump. In the initial stage of modification, the pressure measured with a Pirani gauge at the exit was 1.7–1.8 kPa, and about 30% of the total gas flow was drawn through the porous tube wall to the outside. The remainder of the gas was directed from the reactor to the outside. When macropores of the support were plugged with SiO₂, the pressure inside the tube was reduced to 10–2000Pa, which was denoted as P_{fe} . Modified membranes were subjected to observation with a field emission scanning electron microscope (SEM, Hitachi S-900).

Figure 2 shows the fractured section of a silica membrane formed on the γ -alumina coated α -alumina tube at P_{fe} =50Pa. The silica modified layer was extended to a depth of 200–300nm, and the tube surface had no pinholes. It was shown that silica was actually deposited in the pores of the support. The silica top layer thickness was not greatly affected by the final evacuation pressure. A computer

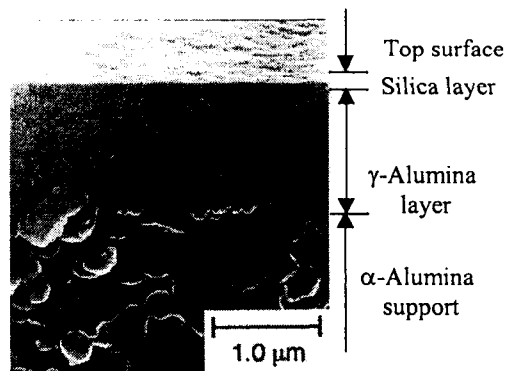


Fig. 2. Fractured section of silica membrane formed on γ -alumina coated α -alumina tube by CVD.

simulation by Morooka et al.[12] describes the mechanism of pore plugging and the role of convective cross flow in this process. Details of this preparation and membrane morphology have been reported previously[11,13].

2-2. Gas permeation test

Gas permeation experiments were performed at 30–600°C using single-component hydrogen, nitrogen and carbon dioxide, methane,

propane, n-butane, i-butane and sulfur hexafluoride(SF₆). Argon was used as the sweep gas on the permeate side, and ambient pressure was maintained on both sides of the membrane. The partial pressure of the feed gas on the permeate side was maintained at less than 2000Pa by dilution with the sweep gas. The flow rate was measured with a soap-film flow meter, and gas compositions were analyzed using a gas chromatograph (Shimadzu, GC-8A) with a thermal conductivity detector.

3. Results and discussion

3-1. Gas permeance

Figure 3 shows permeances to single-component H₂ and N₂, as well as H₂/N₂ selectivity, for the silica membranes produced on the α -alumina tube at 650°C. The membranes prepared at $P_{fe}=200$ -2000 Pa showed H₂ and N₂ permeances, which were approximately independent of permeation temperatures of 30-600°C. The H₂/N₂ selectivity of the membranes was 4-5,

which was close to the value estimated from the Knudsen diffusion mechanism, 3.7. The silica membranes prepared at $P_{fe}=10$ -50Pa permeated hydrogen by the activated diffusion mechanism, and the H₂ permeance increased with increasing

permeation temperature. The permeance to N₂ was not affected by permeation temperature. The H₂/N₂ selectivity was higher than 100 at permeation temperatures of 400-600°C. The membranes prepared at $P_{fe}=10$ and 20Pa did not permeate nitrogen within the detection limit, 10⁻¹¹ mol m⁻² s⁻¹ Pa⁻¹.

Figure 4 shows single-component H₂ and N₂ permeances through the silica membranes formed with TEOS alone at 650°C in the

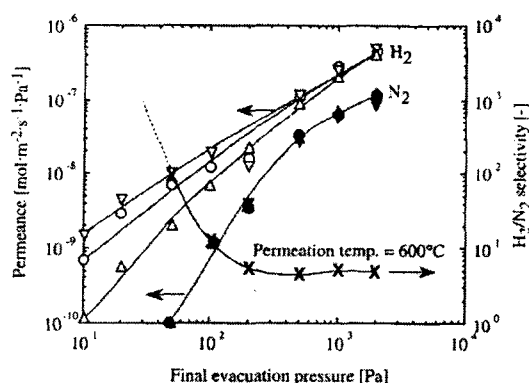


Fig. 3. Gas permeance of silica membrane formed on α -alumina tube at 600-650°C.

mesopores of the γ -alumina film at $P_{fe}=20, 50$ and 200Pa . Hydrogen permeance increased with increasing permeation temperature and reached $3 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ at 600°C for the membrane prepared with $P_{fe}=200\text{Pa}$.

The nitrogen permeance slightly decreased with increasing permeation temperature, and H_2/N_2 selectivity was larger than 100 at 600°C . The hydrogen permeance of the membranes prepared on the γ -alumina film was equivalent to that of Asaeda et al. [14] and de Lange et al. [7]. Both of them prepared membranes by the sol-gel process,

repeating the dip-coating. The result indicates that the CVD method is capable of providing H_2 permeances as high as the sol-gel method when the CVD membrane is formed on the γ -alumina layer. The CVD method is much easier than the sol-gel method because the former needs no repeated coating process after the substrate is prepared. As indicated in Figure 4, N_2 permeance decreased with decreasing P_{fe} , while H_2 permeance was less affected by P_{fe} . The hydrogen permeances of the membranes formed on the γ -alumina coated α -alumina tube were one or two orders higher than those formed on the α -alumina tube described in Figure 3. The H_2/N_2 selectivity was larger than 100 for all cases. Thus, the γ -alumina layer drastically improved the permeance of the membrane without sacrificing of selectivity.

When a silica membrane was prepared with a P_{fe} value lower than 200Pa , large pores were fundamentally plugged. Molecules leaked

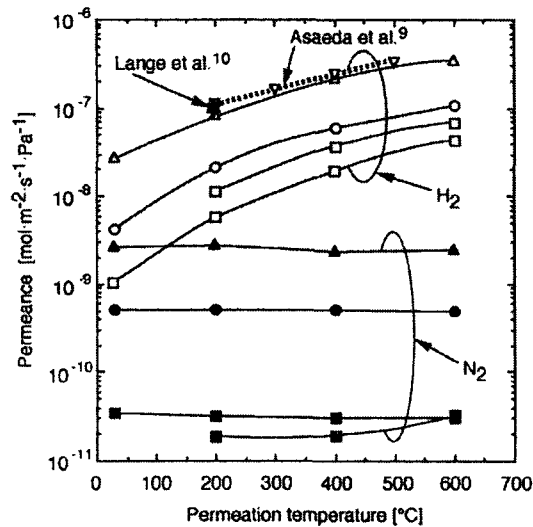


Fig. 4. Gas permeance of silica membrane formed on γ -alumina coated α -alumina tube.

through a small number of mesopores, which were left unplugged in the membrane. Permeation tests with CO_2 , N_2 , CH_4 , C_2H_6 , $n\text{-C}_4\text{H}_{10}$ and $i\text{-C}_4\text{H}_{10}$ showed that a small number of mesopores existed after the CVD modification. Permeation of hydrogen was explained by activated diffusion, and that of the other gases by Knudsen diffusion. The contribution of Knudsen diffusion pores decreased to 0.005 when the γ -alumina film was modified at 650°C until $P_{\text{fe}}=20\text{Pa}$.

Figure 5 shows the effects of molecular size and final evacuation pressure on permeance of silica membranes formed using diphenyldiethoxysilane

(DPDES). The membrane formed with $P_{\text{fe}}=1000\text{ Pa}$ showed only low permselectivities, but the membrane formed with $P_{\text{fe}}=500\text{ Pa}$ exhibited higher molecular-sieving properties than the membranes formed using TEOS. The hydrogen permeance was as high as $7 \times 10^7 \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. At a permeance temperature of 30°C , CO_2 permeance and CO_2/CH_4 selectivity was $8 \times 10^8 \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and 11, respectively. The

permeance of CO_2 in the DPDES-derived membrane was affected by adsorption and increased with decreasing permeation temperature. Permeances to the other species were not significantly dependent on permeation temperature.

Thermal and chemical stability of membrane is important in terms of practical applications. **Figure 6** shows the results of the stability test for the membrane formed on the γ -alumina coated α -alumina support tube using TEOS alone at 650°C . The final evacuation

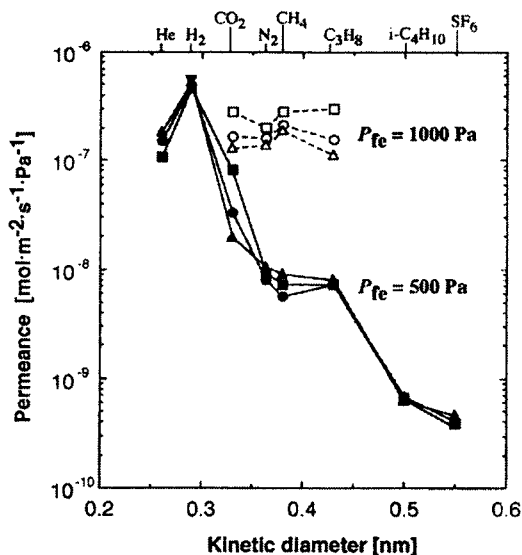


Fig. 5. Gas permeance of membrane prepared by CVD of DPDES at 550°C .

pressure was 40Pa. During the exposure to helium at 600°C, H₂ and N₂ permeances remained unchanged. In a mixture of He and H₂O (20%) at 600°C, H₂ permeance decreased from $4 \times 10^8 \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $2 \times 10^8 \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ after 73h.

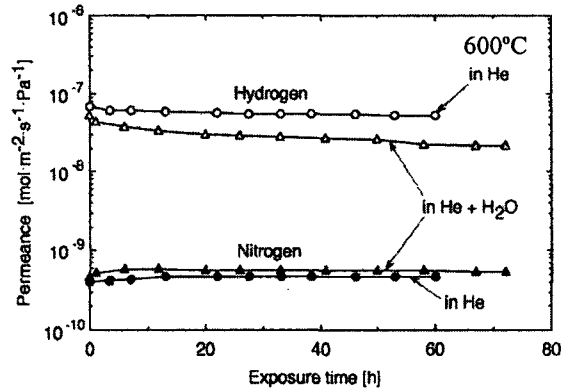


Fig. 6. Change of permeance of silica membrane modified by CVD.

4. Conclusions

Crack-free and thin amorphous silica was deposited by thermal decomposition of TEOS at 550–650°C on a porous α -alumina tube or γ -alumina coated α -alumina tube. The forced cross flow through the porous wall of the support was effective in plugging macropores. All silica membranes formed with TEOS alone on the α -alumina tube were H₂-selective. The membrane formed on γ -alumina coated α -alumina tube showed an H₂ permeance much higher than that of the membrane formed on the α -alumina tube, retaining a high H₂ selectivity. The γ -alumina film was thus effective in improving the H₂ permeance and H₂/N₂ selectivity. Permeation of hydrogen was explained by activated diffusion, and that of the other gases by Knudsen diffusion through a small number of mesopores, which were left unplugged in the membrane. The use of phenyl-substituted ethoxysilanes as the Si source was effective in controlling micropore size and increasing gas permselectivity. All membranes were stable in the steam containing mixture of 400–600°C.

5. References

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