Gas Permeation Characteristics of Silica/Alumina Composite Membrane Prepared by Chemical Vapor Deposition

Sung-Soo Kim[†] **and Bong-Kuk Sea***

Dept. of Environmental Engineering, Catholic University of Pusan, Pusan 609-757, Korea
*Department of Chemical System Engineering, The University of Tokyo, Tokyo 113-8656, Japan

Abstract−Amorphous silica membranes were deposited by thermal decomposition of tetraethoxysilane at 600-650 °C on a porous α-alumina tube with pore size of 110-180 nm or γ-alumina coated α-alumina tube with pore size of 6-8 nm. The forced cross-flow through the porous wall of the support was very effective in plugging macropores. The membranes formed on γ-alumina coated α-alumina tube showed H_2 permeances much higher than the SiO_2 membranes formed on the α-alumina tube. This indicated that the γ-alumina film was effective in improving the H_2 permeance and H_2/N_2 selectivity. The permeation tests with CO_2, N_2, CH_4, C_3H_8 and i-C_4H_{10} showed that a very small number of mesopores remained unplugged by the CVD. Permeation of hydrogen was explained by activated diffusion, and that of the other gases by Knudsen diffusion through the unplugged pores. Thus, the total permeance was composed of permeances due to the activated and Knudsen diffusion mechanisms. The contribution of Knudsen diffusion pores decreased to 0.02 when the γ-alumina film was modified at 650 °C until P_{fe}=50 Pa.

Key words: Silica, Membrane, Gas Permeation, CVD, Hydrogen Permselectivity

INTRODUCTION

Among inorganic membranes developed to date, amorphous silica membranes are attractive for gas separation at elevated temperatures because they are stable under crucial conditions where polymeric membranes cannot be applied. Gavalas and coworkers [1989] first succeeded in plugging pores of a Vycor glass tube, having a pore size of about 4 nm, with silica produced by a chemical vapor deposition (CVD) method. The silica membranes exhibited an H_2 permeance of the order of 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and a H_2/N_2 selectivity of 100-1000 at permeation temperatures of 400-600 °C [Ioannides et al., 1993; Tsapatsis et al., 1994; Kim et al., 1995]. Jiang et al. [1995] improved the H_2 permeance and H_2/N_2 selectivity to 4× 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and 1000 at 600 °C, respectively, by introducing temporary carbon barriers in pores of the Vycor support tube. To improve stability and permselectivity, deposition of silica in the presence of O_2 or O_3 was studied [Ha et al., 1993; Nakao et al., 2000]. Wu et al. [1994] prepared a silica-modified membrane on a γ-alumina support tube by a CVD method with TEOS and oxygen. Their membrane exhibited an H_2 permeance higher than 10^{-6} mol·m^{-2}·s^{-1}·Pa^{-1} and a H_2/N_2 selectivity of 26 at 600 °C. The sol-gel process was also used for silica membrane preparation. Asaeda et al. [1993] coated an α-alumina porous tube with a fine silica sol and further modified it by CVD with TEOS. The CVD method was applied to plug relatively large pores left on the sol-gel derived membrane. This combined method was effective to raise the H_2/N_2 selectivity to 500-1000 at 400-600 °C. H_2 permeance was above 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}. However, the CVD-modified membrane was unstable in humid air,

although it was stable in dry gas. Multi-step pore modification technique using sol-gel and deposition method was often used to enhance the permselectivity [So et al., 1999; Jung et al., 1999]. de Lange et al. [1995a, b] prepared silica and silica-titania membranes by a sol-gel method, using a mesoporous γ-alumina support with a pore diameter of 4-10 nm. Hydrogen permeance was higher than 10^{-6} mol·m^{-2}·s^{-1}·Pa^{-1} at 200 °C, but H_2/N_2 selectivity was of the order of ten. Recently, in sol-gel process, organic template approaches with alkoxides and surfactants were utilized to create controlled micropores [Ramman et al., 1995; Kusakabe et al., 1999; Tsai et al., 2000]. These sol-gel techniques using organic templates were quite effective in controlling pore size. Morooka and coworkers [Morooka et al., 1995; Aoki et al., 1996] 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.

For practical application, current needs require high performance membranes which possess a higher permeance and selectivity. Since permeance is normally enhanced through the sacrifice of selectivity, a balance between permeance and selectivity is essential to achieving optimum performance. Requirements for high permselective separation membrane include 1) thin and defect-free active layer, 2) negligible resistance through a support layer, and 3) mechanical and chemical stability. Therefore, 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.

In this study, to develop a highly permselective membrane, a porous α-alumina tube is coated with a mesoporous γ-alumina layer, and the composite tube is used as the support. In addition, to investigate the effect of pore size and distribution of the support on permselectivity of the membrane formed on a porous support tube,

[†]To whom correspondence should be addressed.
E-mail: sskim@cup.ac.kr
*Present address: Membranes & Separation Research Center, Korea Research Institute of Chemical Technology, Daejeon 305-600, Korea
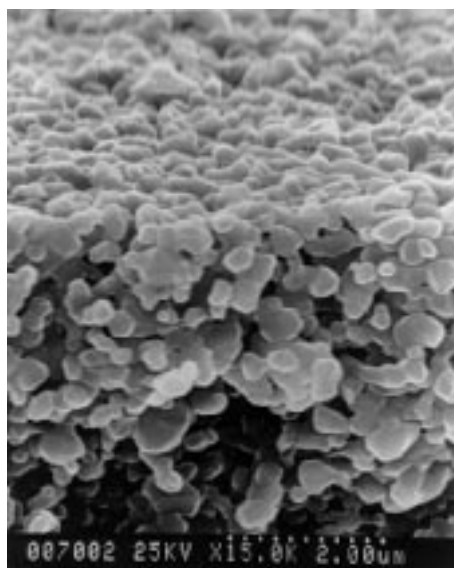
Fig. 1. Fractured surface of a porous α-alumina support tube.

Fig. 2. Experimental apparatus for membrane modification by CVD with forced cross-flow.

a. MFC	f. Alumina support tube
b. TEOS	g. Electric furnace
c. Water bath	h. Quartz tube reactor
d. Pirani gauge	i. Soap film flow meter
e. Ribbon heater	j. Vacuum pump

we used a porous α-alumina support with macropores. Silica membranes were then formed by CVD with TEOS on the α-alumina or γ-alumina layer. During the membrane preparation, forced cross-flow technique through the pores of the support was used. Gas permeation through the silica membrane was characterized by permeance test for hydrogen, carbon dioxide, nitrogen, methane, propane and i-butane. The permeation of these gases was analyzed by activated and Knudsen diffusion mechanisms, and the gas permeation kinetics was discussed.

EXPERIMENTAL

1. Porous Support Tube

A porous α-alumina tube supplied by NOK Corp. (Japan) was used as the support. Fig. 1 shows the fractured section of the α-alumina tube. The properties of the tube were as follows: outer diameter, 2.5 mm; inner diameter, 1.9 mm; pore size, 110-180 nm; 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.

The γ-alumina was prepared from a boehmite sol (γ-AlOOH) prepared by the procedure of Yoldas [1975]: A boehmite sol was formed at 80 °C by adding aluminum isopropoxide ($Al(iso-OC_3H_7)_3$, Wako Chemical Co., Japan) in water. The concentration of aluminum in the sol was 0.6 mol·l^{-1}. The suspension was then peptized by adding an aqueous solution of nitric acid at the final concentration of $Al/H^+=10$. The α-alumina support tube, the lower end of which was closed, was dipped in the boehmite sol for 2 min and the outside of the tube was coated. After dipping, the membrane was dried overnight in air. It was then heated to 750 °C at a rate of 60 °C per hour. This dipping-drying-firing procedure was repeated three times. Details of this procedure have been reported in a previous study [Kim et al., 2000].

2. Membrane Preparation

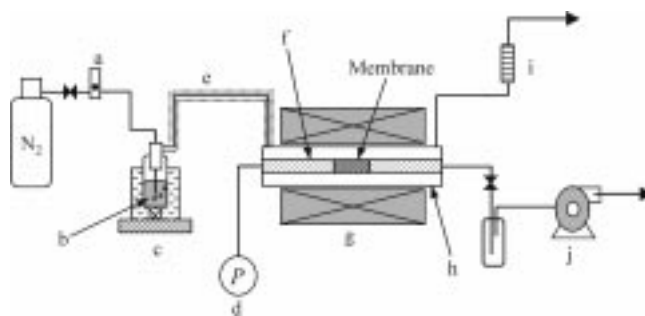Fig. 2 shows a schematic diagram of the apparatus used for thermal decomposition of TEOS with a forced cross-flow. The support tube of 200 mm length was coaxially fixed in a quartz tube of 9.8 mm i.d. and 150 mm length and was placed in an electric tubular furnace. After the system was evacuated with 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, 600-650 °C, at a rate of 15 °C·min^{-1}, and then maintained at that temperature for the duration of the experiment. The flow rate of nitrogen was maintained at 3.4×10^{-3} mol·s^{-1}, and the flow rate of TEOS was 7.9×10^{-5} mol·s^{-1}. During the membrane modification, the gases were continuously evacuated from the outside end of the support tube by 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, where the pressure was always atmospheric. When macropores of the support were plugged with SiO_2, the pressure inside the tube was reduced to 10-100 Pa, which was denoted as P_{fe}. The value of P_{fe} was affected by the balance between nitrogen flow permeated through the membrane and evacuation flow and was dependent on the reactor system and reactants used. However, P_{fe} served as a practical indicator of the completeness of pore plugging.

3. Membrane Characterization

Modified membranes were subjected to observation with a field emission scanning electron microscope (SEM, Hitachi S-900). The average pore size of the γ-alumina support tube was determined with a BET unit (Micromatris, ASAP 2000).

Gas permeation experiments were performed at 30-600 °C by using single-component hydrogen, carbon dioxide, nitrogen, methane, propane and i-butane. With these permeation test results, the pore structure of silica membrane was characterized. Fig. 3 shows details of the test unit. 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 2000 Pa by dilution with the sweep gas. The flow rate was measured with a soap-film flow meter, and gas compositions were analyzed by using a gas chromatograph (Hewlette Packard, HP5890-II) with a thermal conductivity detector.
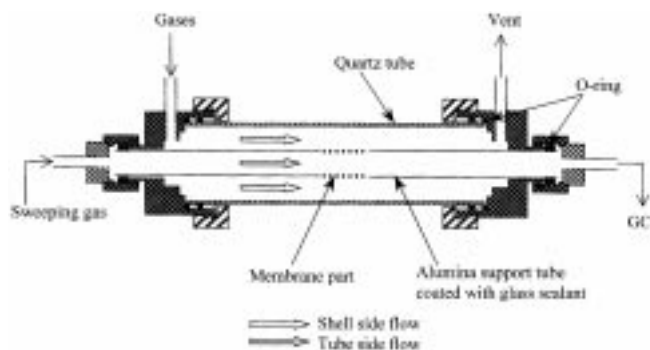
Fig. 3. Details of gas permeation test unit.

The sensitivity for nitrogen was of the order of 10^{-11} mol·m^{-2}·s^{-1}·Pa^{-1}. Permeance to the i-component, F_i [mol·m^{-2}·s^{-1}·Pa^{-1}] is defined as;

$$F_i = Q_i/[2\pi r_m l_m (P_{f,i} - P_{p,i})] = J_i/\Delta P_i \tag{1}$$

where Q_i is the permeation rate of the i-component, r_m is the outer membrane radius, l_m is the membrane length, $P_{f,i}$ and $P_{p,i}$ are the partial pressure of the i-component in the feed (shell) and permeate sides, respectively, and J_i is the permeation flux of the i-component. ($P_{f,i}$ −

$P_{p,i}$) is the logarithmically averaged value of the partial pressure difference along the tube length. The selectivity of i-component to j-component is given as F_i/F_j.
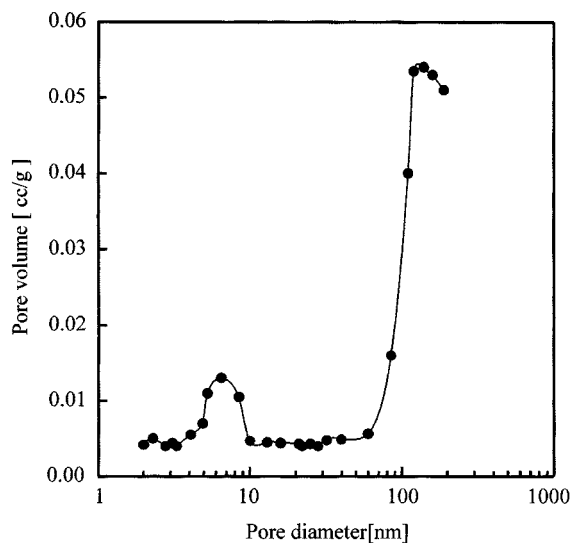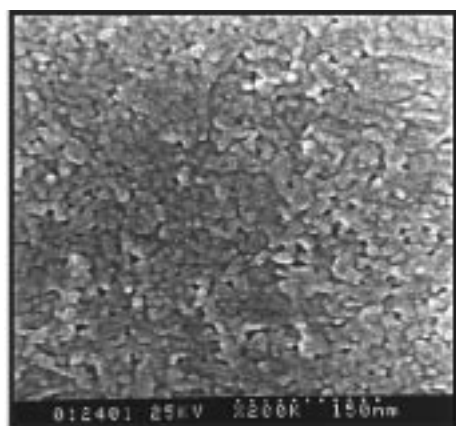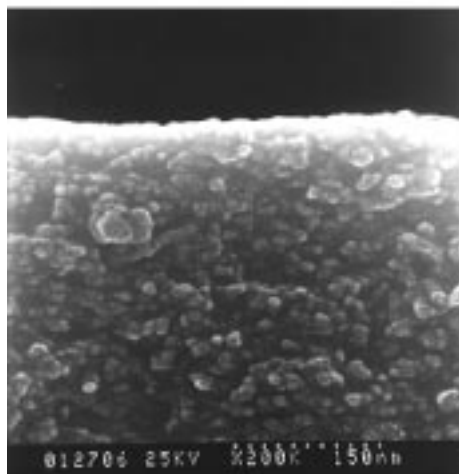

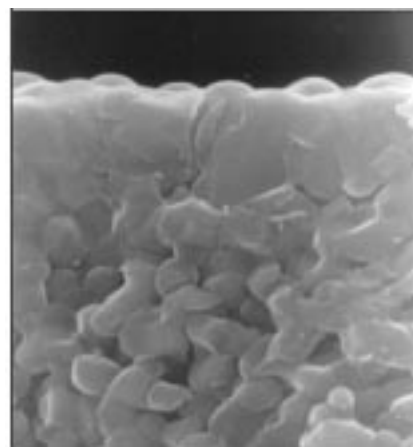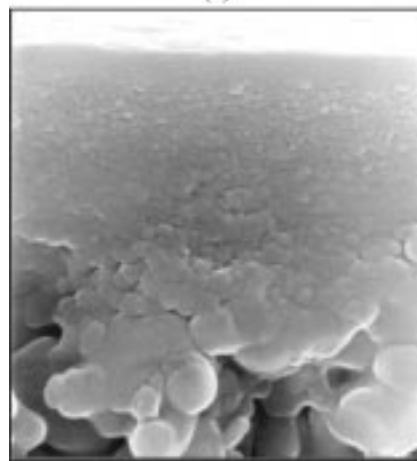**Fig. 5. Pore size distribution of γ-alumina coated α-alumina tube.**

Fig. 4. Scanning electron micrograph of γ-alumina membrane.
(a) top surface, (b) fractured section

Fig. 6. Fractured surface of silica membranes formed on (a) α-alumina tube and (b) γ-alumina coated α-alumina tube.

RESULTS AND DISCUSSION

1. Membrane Morphology

Fig. 4 shows the top surface and fractured section of the γ-alumina coated α-alumina tube. The thickness of the γ-alumina layer was 1.0-1.5 μm, and the top surface was smooth and defect free. The average pore size of the γ-alumina coated α-alumina support tube was determined with a BET unit and was about 6-8 nm in diameter as shown in Fig. 5. Fig. 6 shows the fractured sections of silica membranes formed in pores of (a) α-alumina tube and (b) the γ-alumina film coated on the α-alumina tube. The CVD was carried out until the evacuation pressure reached 30 Pa. In a high resolution view, we found that the silica-modified layer was extended to a depth of 1.0 μm and 200 nm for Fig. 6(a) and (b), respectively. The silica film formed on the γ-alumina layer was thinner and smoother than that of α-alumina support. The top surface of the membranes was quite smooth and showed no pinholes. Silica was actually deposited in the macropores of the α-alumina support or the mesopores of the γ-alumina film coated on the α-alumina support. However, the silica top layer thickness was not greatly affected by the final evacuation pressure, P_{fe}, for the same support. The thickness of the silica layer formed in the γ-alumina layer is decided by competition between reaction and infiltration in the pores. When the reaction rate increases, silica will be deposited in pores near the surface. However, an excessive increase in reaction temperature may cause heterogeneous nucleation in the gas phase, resulting in the formation of defects. A computer simulation by Morooka et al. [1995] describes the mechanism of pore plugging and the role of convective cross-flow in the CVD process using the aid of evacuation. The forced cross-flow through the porous wall of the support was very effective in plugging macropores. The final evacuation pressure was an important factor for the quality of membranes prepared although it was also dependent on the apparatus used and other experimental conditions.

2. Gas Permeance

Fig. 7 shows H_2, N_2 and CO_2 permeances of γ-alumina coated α-alumina support. Each gas permeance was slightly decreased with
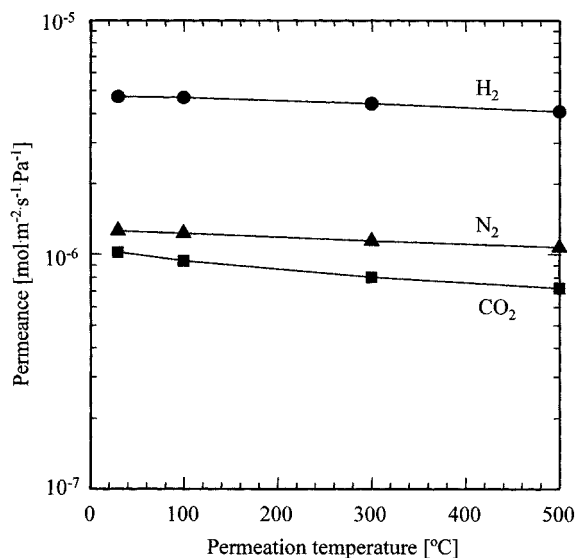

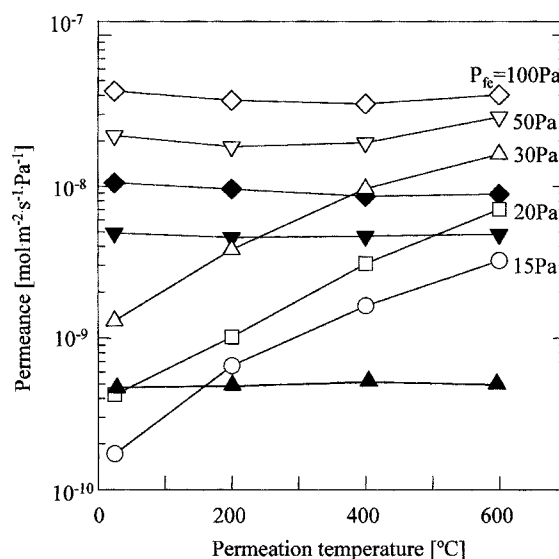Fig. 8. Permeances of silica membranes formed on α-alumina tube. Open keys, hydrogen; closed keys, nitrogen.

permeation temperature, and the selectivity of H_2/N_2 and N_2/CO_2 was 3.6-3.8 and 1.2-1.5, respectively. These selectivities are close to the values estimated from the Knudsen diffusion mechanism, $H_2/N_2=3.74$ and $N_2/CO_2=1.25$ [Noble and Stern, 1995].

Fig. 8 shows permeances of silica membranes formed on α-alumina support tube at $P_{fe}=15\text{-}100$ Pa. The membranes prepared at $P_{fe}=50$ and 100 Pa showed that H_2 permeance was $2\text{-}5 \times 10^{-8}$ mol·m^{-2}·s^{-1}·Pa^{-1} and the H_2/N_2 selectivity was low as 4-7. The H_2 and N_2 permeances were nearly independent of the permeation temperature of 30-600 °C. For the membranes prepared at $P_{fe}=15\text{-}30$ Pa, however, the H_2 permeance was increased with the permeation temperature and H_2/N_2 selectivity of membrane of $P_{fe}=30$ Pa was increased to 35 at 600 °C. This indicates that hydrogen is permeated mainly by activated diffusion mechanism. The N_2 permeances of

Fig. 7. Permeances of γ-alumina coated α-alumina tube.

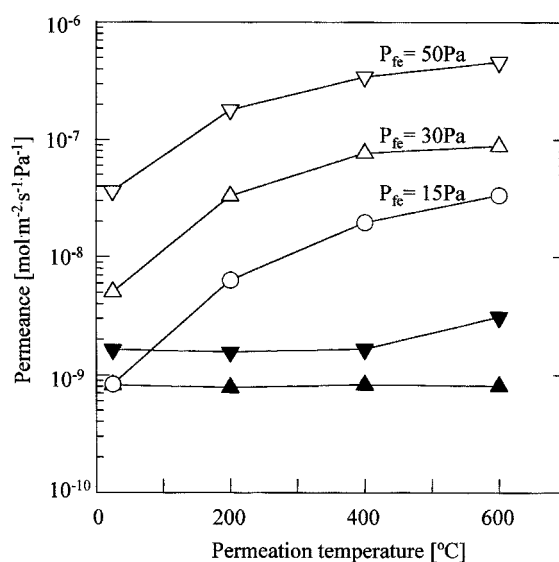

Fig. 9. Permeances of silica membranes formed on γ-alumina coated α-alumina tube. Open keys, hydrogen; closed keys, nitrogen.

membranes of P_{fe}=15 and 20 Pa were lower than detection limit, 10^{-11} mol·m^{-2}·s^{-1}·Pa^{-1}.

Fig. 9 shows single-component H$_2$ and N$_2$ permeances through the silica membranes formed in the mesopores of the γ-alumina film at P_{fe}=15, 30 and 50 Pa. Hydrogen permeance increased with increasing permeation temperature and reached 4×10^{-7} mol·m^{-2}·s^{-1}· Pa^{-1} at 600 °C for the membrane prepared with P_{fe}=50 Pa. The nitrogen permeance slightly decreased with increasing permeation temperature, and H$_2$/N$_2$ selectivity was larger than 150 at 600 °C. 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. Thus, the γ-alumina layer drastically improved the permeance of the membrane without sacrificing selectivity. The hydrogen permeance of the membranes prepared on the γ-alumina film was equivalent to that of Asaeda et al. [9] and de Lange et al. [10]. Both of these groups 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. Generally, the CVD method is much easier than the sol-gel method because the former needs no repeated coating process after the substrate is prepared.

The relationships between H$_2$ permeance and H$_2$/N$_2$ selectivity of silica membranes modified by CVD are summarized in Fig. 10. The data were obtained at permeation temperature of 600 °C. Generally, hydrogen selectivity to nitrogen tends to decrease with increasing of hydrogen permeance. In practical application, high selectivity is advantageous to reducing feed loss and recompression cost, but high permeance is also necessary to get commercially satisfactory production rates. That is, both high selectivity and high permeance are equally important. In this research, the H$_2$ permeance and H$_2$/N$_2$ selectivity were improved simultaneously by introducing a γ-alumina film as intermediate layer and controlling micropores of silica membrane through evacuating reactant during CVD modification. The performance of membrane obtained in this study was better than that of other membranes in the applicability.
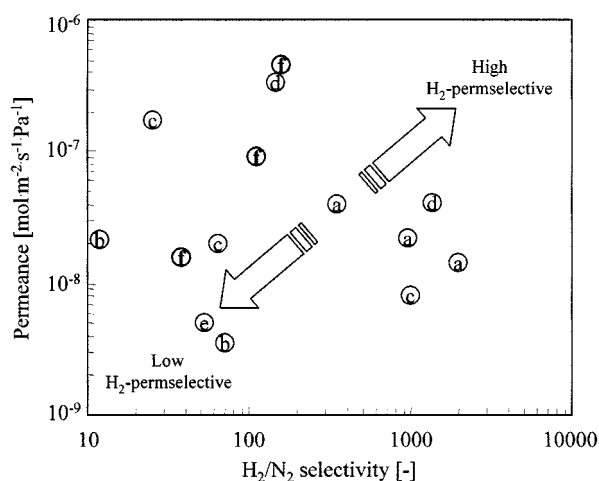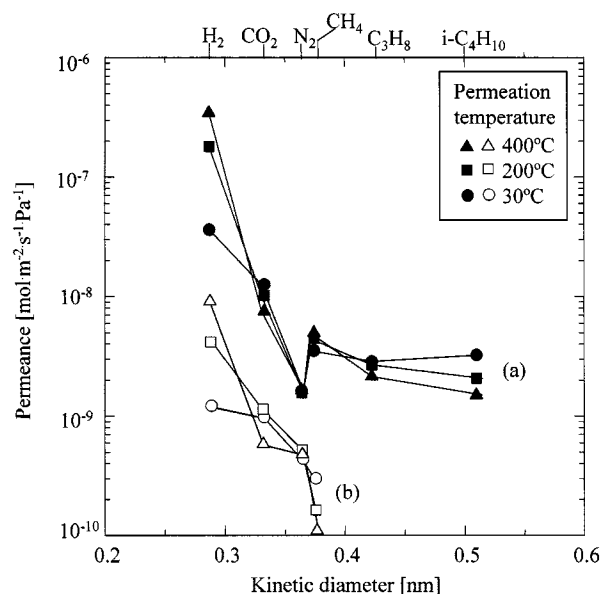

Fig. 11. Permeances as a function of kinetic diameters in silica membranes formed on (a) γ-alumina coated α-alumina and (b) α-alumina tube.

Fig. 11 shows the permeances to gases as a function of their molecular kinetic diameters, which are cited from the literature [Breck, 1974]. According to the support of the membrane, the gas permselectivity is quite different. This indicates that the properties of the underlying support affect the performance of the top selective microporous membrane. When a silica membrane was prepared with a P_{fe} value lower than 50 Pa, large pores were fundamentally plugged. Molecules larger than hydrogen leaked through a small number of mesopores, which were left unplugged in the membrane. In the case of silica membrane formed on γ-alumina layer, H$_2$, CO$_2$ and N$_2$ are separated by molecular sieve effect, and N$_2$, CH$_4$, C$_3$H$_8$ and i-C$_4$H$_{10}$ are permeated by Knudsen diffusion mechanism, with lighter gas permeating preferentially. In the case of silica membrane formed on α-alumina support, on the other hand, the gases are separated by molecular size and the molecular sieve mechanism is dominant. Since gases larger than CH$_4$ were not detected, no mesopores existed in the membrane. At low temperature, CO$_2$ permeance is enhanced by surface diffusion. The low H$_2$ permselectivity implies that the silica membrane formed on α-alumina support possesses larger micropores than those of the silica membrane formed on γ-alumina layer, and the number of micropores is smaller. From these permeance data, the gas permeation kinetics in CVD-derived silica membranes is analyzed.

3. Permeation Kinetics

In a porous inorganic membranes, the gas transport is often explained by activated diffusion, Knudsen diffusion and Poiseuille flow [Lange et al., 1995a; Way et al., 1992]. In the case of silica membrane formed on γ-alumina layer with mesopores, there are few macropores of Poiseuille flow regime. Therefore, in Fig. 11, permeation through the silica membrane formed on γ-alumina layer is dominated by both activated and Knudsen diffusion mechanisms. Thus, total permeance, F_T, can be expressed as;

$$F_T = F_A + F_K \qquad (2)$$

Fig. 10. Relationships between H$_2$ permeance and H$_2$/N$_2$ selectivity of silica membranes prepared by CVD.

a. Gavalas group	d. Sea et al.
b. Wu et al.	e. Hwang et al.
c. Morooka group	f. this study

where F_A and F_K are the permeances due to activated diffusion and Knudsen diffusion, respectively.

The activated diffusion prevails when the pore size of the membrane is close to molecular dimensions and increases with increasing permeation temperature.

$$F_A = C_A \exp[-E_A/(RT)] \qquad (3)$$

where C_A is the coefficient related to the amorphous structure of the membrane, and E_A is the apparent activation energy for activated diffusion. When the pore size is between the small and large molecules, the permeation is performed by the molecular sieving mechanism. The pore size is usually distributed, however, and the strictness of the molecular sieving mechanism is lost. The term of activated diffusion mechanism in this research indicates the separation mode where the membrane at least partially differentiates molecules by their sizes.

Permeance due to the Knudsen diffusion mechanism is expressed as

$$F_K = 2\varepsilon v r_p/(3\tau RTL) \qquad (4)$$

with average molecular velocity, $v = (8RT/\pi M)^{0.5}$. Permeance is then given by

$$F_K = C_K (MT)^{-0.5} \qquad (5)$$

where C_K is the coefficient related to porosity and tortuosity of the pores.

Permeances to gases except hydrogen and carbon dioxide are plotted against $(MT)^{-0.5}$ in Fig. 12. The slopes of lines connecting data obtained for each permeant at different permeation temperatures are smaller than the slope of the straight line which coincides with the origin. This indicates that these gases are principally transported by the Knudsen diffusion mechanism but that the activated diffusion mechanism works to some extent. C_K was obtained from the slope of the straight solid line in Fig. 12, and F_K for hydrogen was calculated from Eq. (5). The F_A for hydrogen was then calculated by subtracting F_K from F_T. As shown in Fig. 13, the activation energy for hydrogen permeance by activated diffusion was deter-

Fig. 13. Arrhenius plots of hydrogen permeances, F_T and F_A.

Table 1. Contribution of activated diffusion and Knudsen diffusion mechanisms for hydrogen permeation in silica membrane formed on γ-alumina coated α-alumina tube (P_{fe}= 50 Pa)

	Permeance×10^8 [mol·m^{-2}·s^{-1}·Pa^{-1}]			E_A [kJ·mol^{-1}]
	30 °C	200 °C	400 °C	
F_T	3.8	19.1	33.8	9.8
F_A	2.6	18.0	33.2	11.9
F_K	1.2	0.99	0.81	-
F_K/F_T	0.32	0.05	0.02	-

mined from an Arrhenius plot of F_T to be 9.8 kJ·mol^{-1}, while that of the total hydrogen permeance, F_A, was 11.9 kJ·mol^{-1}. The silica membrane formed on α-alumina support showed an activation energy of 9.5 kJ·mol^{-1} for total hydrogen permeance. The values of the activation energy were slightly lower than the reported ones for high performance silica membranes [Kim et al., 1995; Jiang et al., 1995; Lange et al., 1995; Shelekhin et al., 1995]. Table 1 shows F_T, F_A, F_K and E_A for hydrogen. The ratio of the permeance due to the Knudsen diffusion to the total hydrogen permeance, F_K/F_T, decreased with a permeation temperature, and the contribution of the Knudsen diffusion to the total permeance was about 2% at a permeation temperature of 400 °C.

Permeance through a membrane with a thickness L is given as

$$F_T = D_{eff}/(RTL) \qquad (6)$$

where L is the membrane thickness. D_{eff} is the effective diffusivity of permeate in the membrane and includes the adsorption equilib-
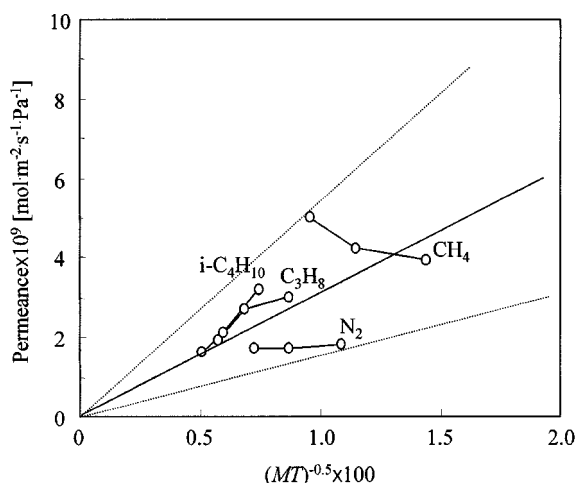

Fig. 12. Relationships between permeances and $(MT)^{-0.5}$ for gases larger than carbon dioxide in silica membrane formed on γ-alumina layer at P_{fe}=50 Pa.
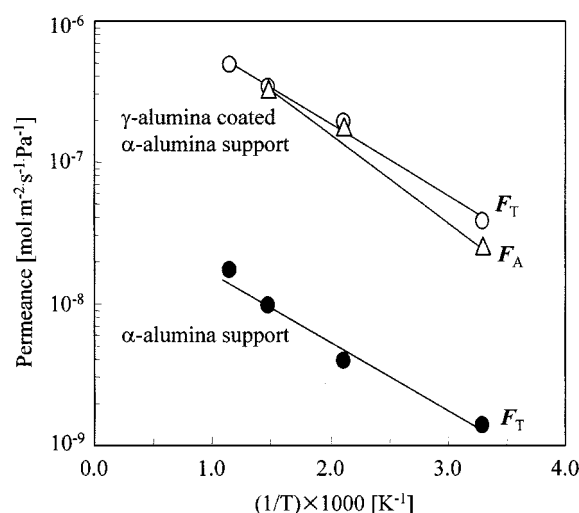
Table 2. Effective diffusivity of silica membrane prepared by CVD

	D_{eff}×10^{12} [m^2·s^{-1}]			
	H_2	CO_2	CH_4	i-C_4H_{10}
30 °C	19	6.6	1.9	1.6
200 °C	150	8.6	3.3	1.7
400 °C	380	8.9	5.6	1.8

rium coefficient of the permeate, K. Thus, the term corresponds to D[(1−ε)/ε]ρK as defined by de Lange et al. [1995a] where D is the micropore diffusivity, and ε and ρ are the porosity and density of the membrane, respectively. Bakker et al. [1996] indicated that the effect of adsorption on diffusivity in an MFI-type zeolite was negligible at permeation temperatures higher than 200 °C for species less adsorptive than n-C_4H_{10} and i-C_4H_{10}. Table 2 shows effective diffusivities calculated for the silica membrane formed on γ-alumina coated α-alumina tube, whose thickness is assumed as 200 nm. The diffusivities calculated in the present study are smaller than those reported by de Lange et al. [1995a] for sol-gel derived silica membranes. Their values are of the order of 10^{-10} m^2·s^{-1} for H_2 and 10^{-11} m^2·s^{-1} for CO_2, CH_4 and i-C_4H_{10} at 25 °C. Thus the permeation properties of micropores are dependent on processes by which membranes are produced.

CONCLUSION

Amorphous silica was deposited by thermal decomposition of TEOS at 600-650 °C on a porous α-alumina tube or γ-alumina film coated on the α-alumina tube. The forced cross-flow through the porous wall of the support was very effective in plugging macropores or mesopores. The membrane formed on the γ-alumina film showed an H_2 permeance much higher than that of the membrane formed on the α-alumina tube, retaining a high H_2 selectivity. The γ-alumina film was thus effective in improving the H_2 permeance and H_2/N_2 selectivity. The results show that the quality of underlying support and stick control of micropores is significant to prepare highly permselective membrane. Permeation tests with CO_2, N_2, CH_4, C_3H_8 and i-C_4H_{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. Thus, the total permeance was comprised of permeances due to the activated and Knudsen diffusion mechanisms. The contribution of Knudsen diffusion to the total hydrogen permeance decreased to 0.02 at a permeation temperature of 400 °C.

NOMENCLATURE

C_A : coefficient defined by Eq. (3)
C_K : coefficient defined by Eq. (5)
D_{eff} : effective diffusivity [m^2·s^{-1}]
E_A : activation energy for activated diffusion [J·mol^{-1}]
F_A : permeance due to activated diffusion [mol·m^{-2}·s^{-1}·Pa^{-1}]
F_K : permeance due to Knudsen diffusion [mol·m^{-2}·s^{-1}·Pa^{-1}]
F_T : total permeance [mol·m^{-2}·s^{-1}·Pa^{-1}]
J_i : permeation flux of the i-component [mol·m^{-2}·s^{-1}]
K   : adsorption equilibrium coefficient
L   : thickness of silica membrane [m]
l_m : membrane length [m]
M   : molar mass of permeate [kg·mol^{-1}]
P_f : partial pressure in the feed side [Pa]
P_p : partial pressure in the permeate side [Pa]
P_{fe} : final evacuation pressure [Pa]
Q_i : permeation rate of the i-component [mol·s^{-1}]
R   : gas constant [J·mol^{-1}·K^{-1}]
r_m : outer membrane radius [m]

r_p : pore radius [m]
T   : permeation temperature [K]

Greek Letters
ε   : porosity
ρ   density of membrane [kg·m^{-3}]
τ   : tortuosity
ν   : average velocity of molecules [m·s^{-1}]

REFERENCES

Aoki, K., Yokoyama, S., Kusakabe, K. and Morooka, S., "Preparation of Supported Palladium Membrane and Separation of Hydrogen," *Korean J. Chem. Eng.*, **13**, 530 (1996).

Asaeda, M., Oki, Y. and Manabe, T., "Preparation of Porous Silica Membranes for Separation of Inorganic Gaseous Mixtures at High Temperatures," Report on Energy Conversion and Utilization with High Efficiency. Science and Technology for Energy Conversion. Ministry of Education, Science, Sports and Culture, Japan, 253 (1993).

Bakker, W. J. W., Kapteijin, F., Poppe, J. and Moulijn, J. A., "Permeation Characteristics of a Metal-Supported Silicalite-1 Zeolite Membrane," *J. Membrane Sci.*, **117**, 57 (1996).

Breck, D. W., "Zeolite Molecular Sieves," John Wiley, New York, 636 (1974).

Gavalas, G. R., Megiris, C. E. and Nam, S. W., "Deposition of H_2-Permselective SiO$_2$ Films," *Chem. Eng. Sci.*, **44**, 1829 (1989).

Ha, H. Y., Nam, S. W., Hong, S.-A. and Lee, W. K., "Chemical Vapor Deposition of Hydrogen-Permselective Silica Films on Porous Glass Support from Tetraethylorthosilicate," *J. Membrane Sci.*, **85**, 279 (1993).

Hwang, G.-J., Onuki, K. and Shimizu, S., "Separation of Hydrogen from a H_2-H_2O-HI Gaseous Mixture Using a Silica Membrane," *AIChE J.*, **46**, 92 (2000).

Ioannides, T. and Gavalas, G. R., "Catalytic Isobutane Dehydrogenation in a Dense Silica Membrane Reactor," *J. Membrane Sci.*, **77**, 207 (1993).

Jiang, S., Yan, Y. and Gavalas, G. R., "Temporary Carbon Barriers in the Preparation of H_2-Permselective Silica Membranes," *J. Membrane Sci.*, **103**, 211 (1995).

Jung, K. Y., So, J. H., Park, S. B. and Yang, S. M., "Hydrogen Separation from the H_2/N_2 Mixture by Using a Single and Mult Stage Inorganic Membrane," *Korean J. Chem. Eng.*, **16**, 193 (1999).

Kim, S. and Gavalas, G., "Preparation of H_2 Permselective Silica Membranes by Alternating Reactant Vapor Deposition," *Ind. Eng. Chem. Res.*, **34**, 168 (1995).

Kim, S.-S., Choi, H.-K., Park, H.-C., Kim, T.-O. and Sea, B., "CO_2 Separation Using a Surface Modified Silica Membrane," *J. Korean Environmental Sci. Soc.*, **9**, 311 (2000).

Kusakabe, K., Sakamoto, S., Saie, T. and Morooka, S., "Pore Structure of Silica Membranes Formed by a Sol-Gel Technique using Tetraethoxysilane and Alkyltriethoxysilanes," *Sep. and Pruif. Tech.*, **16**, 139 (1999).

Lange, R. S. A., Keizer, K. and Burggraaf, A. J., "Analysis and Theory of Gas Transport in Microporous Sol-Gel Derived Ceramic Membranes," *J. Membrane Sci.*, **104**, 81 (1995a).

Lange, R. S. A., Keizer, K. and Burggraaf, A. J., "Aging and Stability Microporous Sol-Gel-Modified Ceramic Membranes," *Ind. Eng.*

Chem. Res., **34**, 3838 (1995b).

Morooka, S., Yan, S., Kusakabe, K. and Akiyama, Y., "Formation of Hydrogen-Permselective SiO$_2$ Membrane in Macroporous of α-Alumina Support Tube," *J. Membrane Sci.*, **101**, 89 (1995).

Nakao, S., Suzuki, T., Sugawara, T., Tsuru, T. and Kimura, S., "Preparation of Microporous Membranes by TEOS/O3 CVD in the Opposing Reactant Geometry," *Microporous & Mesoporous Materials*, **37**, 145 (2000).

Noble, R. D. and Stern, S. A., "Membrane Science and Technology Series 2, Membrane Separations Technology Principles and Applications," Elsevier Sci. Ltd., Netherlands (1995).

Prabhu, A. K. and Otama, S. T., "Highly Hydrogen Selective Ceramic Membranes: Application to the Transformation of Greenhouse Gases," *J. Membrane Sci.*, **176**, 233 (2000).

Raman, N. K. and Brinker, C. J., "Organic Template Approach to Molecular Sieving Silica Membranes," *J. Membrane Sci.*, **105**, 273 (1995).

Sea, B.-K., Kim, S.-S. and Kim, T.-O., "Pore Size Control of Silica-Coated Alumina Membrane for Gas Separation," *J. Korean Environmental Sci. Soc.*, **8**, 263 (1999).

Shelekhin, A. B., Dixon, A. G. and Ma., Y. H., "Theory of Gas Diffusion and Permeation in Inorganic Molecular-Sieve Membranes," *AIChE J.*, **41**, 58 (1995).

So, J. H., Yoon, K. Y., Yang, S. M. and Park, S. B., "Preparations of Metal Impregnated Porous Inorganic Membranes for Hydrogen Separation by Mulit-Step Pore Modifications," *Korean J. Chem. Eng.*, **16**, 180 (1999).

Tsai, C.-Y., Tam, S.-Y., Lu, Y. and Brinker, C. J., "Dual-layer Asymmetric Microporous Silica Membranes," *J. Membrane Sci.*, **169**, 255 (2000).

Tsapatsis, M. and Gavalas, G., "Structure and Aging Characteristics of H$_2$-Permselective SiO$_2$-Vycor Membranes," *J. Membrane Sci.*, **87**, 281 (1994).

Way, J. D. and Roberts, D. L., "Hollow Fiber Inorganic Membranes for Gas Separations," *Sep. Sci & Tech.*, **27**, 29 (1992).

Wu, J. C. S., Sabol, H., Smith, G. W., Flowers, D. L. and Liu, P. K. T., "Characterization of Hydrogen-Permselective Microporous Ceramic Membranes," *J. Membrane Sci.*, **96**, 275 (1994).

Yoldas, B. E., "Alumina Sol Preparation from Alkoxides," *Ceramic Bull.*, **54**, 289 (1975).