Molecular Sieve Silica Membrane Synthesized in Mesoporous γ-Alumina Layer

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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.

Microporous silica membranes are producible by modification of mesoporous (pore size of 1-25 nm) support with polymeric silica sols which are prepared by sol-gel process. The sol-gel process is attractive for multilayer deposition which can lead to a controlled structure, composition and activity for the membrane. Most of the sol-gel derived membranes reported in the literature have been obtained as microporous thin layers on top of a porous support. Burggraaf and coworkers[1,2] prepared a silica membrane by modifying a porous support with a polymeric silica sol. The amorphous microporous top-layer thickness was of the order of 60-100 nm, and selectivities among gases were improved by the modification. Raman and Brinker[3,4] coated a hybrid organic-inorganic sol, prepared by co-polymerization of TEOS (tetraethoxysilane) and methyltriethoxysilane, on a porous alumina support. The calcined membrane was further modified by dip-coating and pyrolysis of diluted TEOS monomer. Gas permeation rate and selectivity through these sol-gel derived membranes are usually high. However, both the microporous and mesoporous membranes calcined or sintered at relatively low temperature and for a short time show the thermal and hydrothermal instability due to pore growth, grain coarsening and defect development above 400-500 °C.[5]

Gavalas *et al*.[6] 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. Generally, the CVD method is much simpler and easier than wet processes such as sol-gel process and hydrothermal synthesis. Amorphous silica membranes produced by dry process have been a major target for investigator in gas separation area.[7-12] These CVD derived silica membranes were able to separate hydrogen from other gases larger than CO_2 with selectivities of 100-1000. However, Molecules larger than CO_2 permeated the silica membranes by the Knudsen diffusion mechanism through a small number of mesopores left in CVD process.

In this study, molecular sieve silica membrane is synthesized for the purpose of gas separation at elevated temperature. Since permeance is normally enhanced through the sacrifice of selectivity, a balance between permeance and selectivity is essential to achieve optimum performance. 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. We deposited silica on a porous γ-alumina coated α-alumina support by thermal decomposition of tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$ Aldrich chemical co.) with a forced cross-flow through the porous support wall.

Figure 1(a) shows a porous α-alumina tube manufactured by NOK Corp. (Japan), which was used as the support to give the membrane mechanical strength. The properties of the tube are; outer diameter, 2.3 mm; inner diameter, 1.9 mm; pore size, 110-180 nm; and porosity, 0.42-0.55.

The γ-alumina as an intermediate layer was prepared from a boehmite sol (γ-AlOOH) prepared by the procedure of Yoldas[13]: A boehmite sol was formed at 80 °C by adding aluminum isopropoxide ($Al(iso\text{-}OC_3H_7)_3$, Yakuri pure chemical co., Japan) in distilled water. The concentration of aluminum in the sol was 0.6 $mol\cdot l^{-1}$. The α-alumina support tube, the lower end of which was capped with silicon rubber, was dipped in the boehmite sol for 1 min. and outside of the tube is coated. The tube was then pulled out of the sol at a rate of *ca*. 3 mm/s. After dipping, the membrane was dried at 20 °C for 24h. It was then heated to 700 °C at a rate of 60 °C per hour. This dipping-drying-firing procedure was repeated three times. The thickness of the γ-alumina layer was 1.0-1.5 μm, and the top surface was smooth and defect free. After the film was heat-treated at 700 °C for 1h in air, diffraction peaks corresponding to γ-alumina were recognized as indicated in Figure 2. A typical adsorption-desorption isotherm for the γ-alumina coated α-alumina tube was of type IV corresponding to a mesoporous solid (2-50 nm pore diameters). The average pore size of the γ-alumina coated α-alumina support tube was determined with a BET unit (Micromeritics, ASAP 2200) and was about 5-7 nm in diameter. The pore size distribution calculated from the desorption isotherm was quite narrow. Hydrogen permeance of γ-alumina coated α-alumina tube was 5×10^{-6} $mol\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-1}$ and slightly decreased with permeation temperature. The selectivity of H_2/N_2 was close to the values estimated from the Knudsen diffusion mechanism, 3.74. The γ-alumina layer with a large amount of mesopores is able to act as a intermediate layer.

To improve the gas selectivity, the mesopores of Knudsen diffusion regime distributed in the γ-alumina layer were

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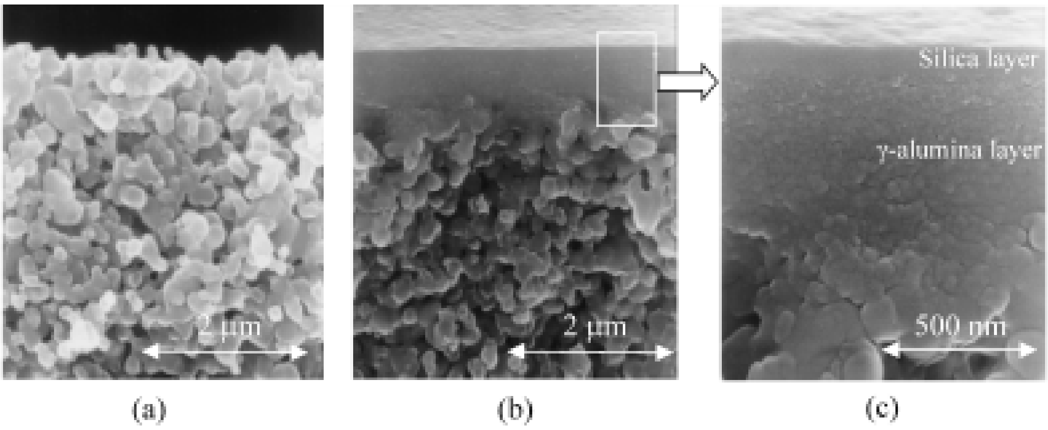

Figure 1. Fractured surface of (a) porous α-alumina support tube, (b) silica membrane formed on γ-alumina coated α-alumina tube and (c) high resolution view of silica/γ-alumina composite layer.

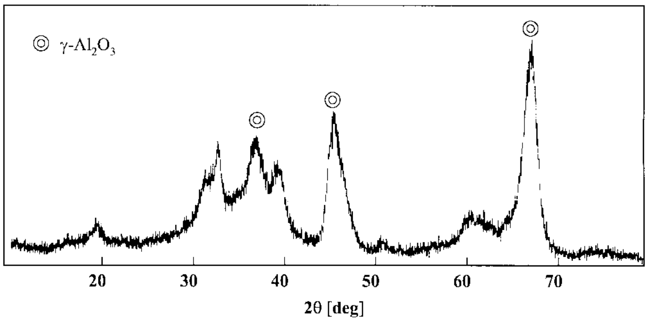

Figure 2. XRD spectra of γ-alumina film formed from boehmite sol.

modified by chemical vapor deposition of TEOS at 600 °C. 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 was vaporized at 40 °C and introduced into the reactor shell side with a nitrogen carrier. During the membrane modification, the gases were continuously evacuated from the outside end of the support tube using a rotary pump. When mesopores of the support were plugged with SiO_2, the pressure inside the tube was reduced to final evacuation pressure.

Figure 1(b) shows the fractured sections of silica membranes formed in pores of the γ-alumina film coated on the α-alumina tube. The final evacuation pressure measured with a Pirani gauge was 4 torr. In a high resolution view, Figure 1(c), we found that the silica modified layer was extended to a depth of 150 nm. The silica film formed on the γ-alumina layer was thin and the top surface of the membranes was quite smooth and showed no pinholes. Silica was actually deposited in the mesopores of the γ-alumina film coated on the α-alumina 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.*[14] 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 mesopores.

To characterize the separation performance of the silica membrane, gas permeation experiments were conducted at 250-450 °C using single-component water, hydrogen, carbon dioxide, nitrogen and methane. Argon was used as the sweep gas on the permeate side, and ambient pressure was maintained on both sides of the membrane. The flow rate was measured with a soap-film flow meter, and gas compositions were analyzed using a gas chromatograph (Shimazu, GA-14) with a thermal conductivity detector. Permeance to the i-component, $\boldsymbol{G(i)}$ [$\mathrm{mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}}$] is defined as;

$$\boldsymbol{G(i)} = Q\mathrm{i} / [A\Delta \mathrm{P(i)}]$$

where Q_i is the permeation rate of the i-component [mol/s], A is the membrane area [m^2], ΔP(i) is the partial pressure difference [Pa] along the tube length of the i-component between the feed (shell) and permeate sides, respectively. The selectivity of i-component to j-component is given as

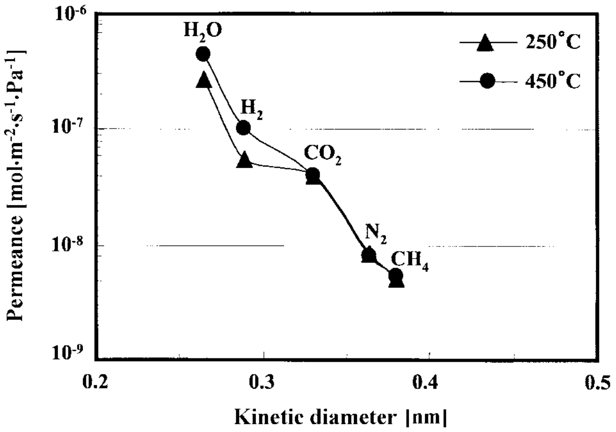

Figure 3. Gas permeance of silica membrane formed on γ-alumina coated α-alumina tube.

Table 1. Gas permeance and selectivity of silica membrane

Permeation temperature [°C]	Permeance $\times 10^{-9}$ mol·m^{-2}·s^{-1}·Pa^{-1}					Selectivity [–]			
	H_2O (0.27)[a]	H_2 (0.29)	CO_2 (0.33)	N_2 (0.36)	CH_4 (0.38)	H_2O/CH_4 (0.94)[b]	H_2/N_2 (3.74)	H_2/CH_4 (4.69)	CO_2/N_2 (0.79)
250	274	55	39	8.28	5.19	52.8	6.6	10.6	4.7
450	438	100	40	8.06	5.25	83.4	12.4	19.1	4.9

[a] Kinetic diameter of gas molecular [nm].[15] [b] Theoretical selectivity by Knudsen diffusion mechanism, $(A/B)=[(mw.)_B/(mw.)_A]^{1/2}$ in where *mw.* is molecular weight.

$\boldsymbol{G(i)/G(j)}$.

Figure 3 shows the permeances to gases as a function of their molecular kinetic diameters, which are cited from the literature.[15] If there are unplugged mesopores in the top layer, molecules larger than hydrogen leaked through the mesopores. The gases are permeated by Knudsen diffusion mechanism, lighter gas permeate preferentially. In the case of silica membrane synthesized in this study, however, the gases are separated by molecular size and the molecular sieve mechanism is dominated as shown in Figure 3. The permeances of the membrane gradually decreased with increasing size of molecules and recognized the gas molecules of CO_2, N_2 and CH_4 which are even in the narrow range of 0.33-0.38 nm. We succeeded in strict controlling micropores of silica membrane by CVD with a forced cross-flow and intermediate γ-alumina layer with a high quality. Gas permeances and selectivities through the silica membrane are summarized in Table 1. Hydrogen permeance increased with increasing permeation temperature and reached the order of 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} at 450 °C. The hydrogen selectivities to nitrogen and methane were also high as 12.4 and 19.1, respectively. In other hand, the CO_2/N_2 selectivity hardly increased with permeation temperature because the surface diffusion mechanism works to some extent in the permeation of these gases.[16] The selectivities among gases larger than H_2 were higher than those of Knudsen diffusion regime, but the values were not sufficient. In order to increase both flux and selectivity of large molecules through silica membranes, a stricter control of micropore size is required. Computer simulation of a carbon membrane indicates that pores narrower than four molecules are highly desirable, and that the chemical affinity between pore walls and permeating molecules need to be properly modified.[17] In practical application, long-term stability of the membrane in the mixture system of high temperature is very important. In the H_2-N_2 mixture of 450 °C, hydrogen permeance and H_2/N_2 selectivity of the silica membrane were not changed for 100 hours and the membrane was stable.

In conclusion, a molecular sieve silica membrane was formed in a mesoporous γ-alumina film coated on the α-alumina tube by chemical vapor deposition of TEOS at 600 °C. The forced cross flow through the porous wall of the support was very effective in plugging mesopores. We obtained very thin and defect free silica top layer in the mesopores of γ-alumina layer. Permeation tests with H_2O, H_2, CO_2, N_2 and CH_4 showed that the silica membrane possesses high molecular-sieving properties permeating according to the gas molecular size.

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