Microstructure and Pore Size Control of Silica Membrane for Gas Separation at Elevated Temperatures

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Abstract: Among ceramic membranes developed to date, amorphous silica membranes are attractive for gas separation at elevated temperatures. Most of the silica membranes can be formed on a porous support by sol-gel or chemical vapor deposition (CVD) process. To improve gas permselectivity of the membrane, well-controlled pores having desired size and chemical affinity between permeates and membrane become important factors in the preparation of membranes. In this article, we review the literature and introduce our technologies on the microstructure to be solved and pore size control of silica membranes using sol-gel and CVD methods.

1. Introduction

Porous inorganic membranes which contain angstrom range pores represent an attractive approach for separating gas mixtures. 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. Generally, microporous silica membranes can be formed on a porous support tube by sol-gel or chemical vapor deposition (CVD) process.

Size and distribution of pores are major factors that determine separation performance in a porous membrane for separating gases. For example, majority of gas molecules may simultaneously pass through a membrane having pores of dozens of nanometers. A membrane having mesopores (i.e., pores of several nanometers) preferentially permeates gas molecules with low molecular weight (not smaller molecules)

according to Knudsen diffusion mechanism. As shown in Table 1, theoretical separation coefficient, which is determined by molecular weight (not by molecule size), are known to be very low. Therefore, the pores in a membrane for gas separation should be controlled at the level of nanometers to prepare a molecular sieve that separates gas molecules based on the molecule size. "Molecular sieving effect", which refers to a separation mechanism based on a molecule size, may be accomplished by a membrane having pores of molecule size. A molecular sieve is ideal with respect to separation coefficient because molecules bigger than pores cannot permeate.

In addition to the separation performance, permeation rate or permeation flux is one of the important factors to consider before applying it in an industrial process. To maintain separation performance and also increase permeation flux, it requires a control of molecular-sieve pore and an improvement of chemical affinity between permeates and membrane surface. That is, size control in the range of smaller than nanometers and hydrophilicity of the membrane surface is necessary for increasing both separation performance

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Table 1. Separation factors by Knudsen Diffusion and Gas Molecular Size

A \ B	Separation factor, (A/B) [a] [-]					Molecular size [b] [nm]
	H_2	CO_2	N_2	CH_4	C_3H_8	
H_2	-	4.69	3.74	2.83	4.69	0.26
CO_2	0.21	-	0.80	0.60	1.00	0.33
N_2	0.27	1.25	-	0.76	1.25	0.36
CH_4	0.35	1.66	1.32	-	1.66	0.38
C_3H_8	0.21	1.00	0.80	0.60	-	0.43

a. Separation factor by Knudsen diffusion, $(A/B) = [(mw.) B/(mw.)A]^{1/2}$ in where $mw.$ is molecular weight.

b. Molecular size based on Lennard-Jones potential (Breck[28]).

and selectivity toward water vapor. Therefore, uniformly-distributed pores having desired size and chemical affinity between permeates and membrane become serious problems to be solved.

Since the size and distribution of pores decisively affect the separation performance of a porous membrane for separating gases, they remain as serious technical problems to be resolved to introduce a membrane that can serve as a layer for selective separation because of controlled pore size in the range of molecule size and uniform pore distribution. Especially, for selectively controlling target materials, the improvement in chemical affinity between permeates and membrane surface are also important. Therefore, it is in urgent need to develop a novel technique capable of controlling pore size and chemical affinity between permeates and membrane surface.

In this article, we introduce the literature review and our technologies on the microstructure and pore size control of silica membranes for gas separation at high temperatures. This review contains the CVD and sol-gel techniques to improve gas permselectivity of the silica membrane.

2. Gas Permeation In Porous Membrane

Permeation rate and permselectivity of inorganic membranes depend, to a large extent, on the microstructural features of membrane/support composites such as pore size and its distribution, porosity and tortuosity. In the case of porous membranes, pore size control and sur-
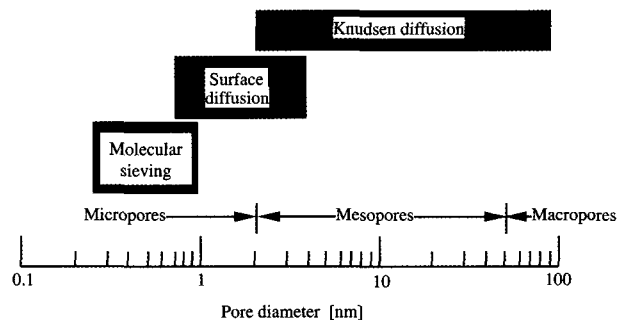
Fig. 1. Relationship between pore size and permeation mechanism.

face modification of pores are critically important for the effective separation of gaseous mixtures. As shown in Figure 1, four different types of transport mechanism are distinguished; Knudsen diffusion; surface diffusion; capillary condensation; and molecular sieving[1].

Knudsen diffusion occurs when the average pore size of a membrane, through which the molecules diffuse, is smaller than the mean free path of the molecules. Each molecule undergoes more collisions with the pore wall than with other molecules and, as a result, flows through the pores independently of other gases.

Surface diffusion is a mechanism where molecules are adsorbed on the pore walls and diffuse on the surface. Condensation mechanism is useful for separation of gases including a condensable vapor. Pores are often blocked with a liquid, which prevents the permeation of noncondensable components. Both surface diffusion and condensation mechanisms become less effective at higher permeation temperatures. When the pore size is of molecular dimensions, gases are transported by molecular sieving mechanism. This is the most desirable separation with respect to selectivity, but permeation rates are usually very low. Diffusion in molecular sieving pores is enhanced by increasing permeation temperature. When the activation energy of permeance is positive, the permeation is referred to as based on the activated diffusion mechanism.

In many cases, molecules permeate through a membrane by different mechanisms working at the same time. Knudsen diffusion gives low separation selectivities and high permeation rates, compared to surface

diffusion and molecular sieving diffusion. Thus, selectivity depends strongly on pore size distribution, and interaction between gases and pore walls. In order to improve permselectivities of larger molecules, strict control of micropore size is required.

Requirements for gas separation membranes are; 1) thin active layer, 2) defect free active layer, 3) negligible resistance through a support layer, and 4) mechanical and chemical stability. A multi-layered asymmetric membrane is often used for gas separation. Typical preparation methods of porous membranes are sol-gel and CVD process.

3. Sol-gel Derived Silica Membranes

Microporous silica membranes are producible by modification of mesoporous (pore size of $1\sim25$ nm) membranes with polymeric silica sols which are prepared by sol-gel process. 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[2-5] 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 $60\sim100$ nm, and selectivities among gases were improved by the modification. They also prepared silica-based membranes that were selective to H_2, CO_2 and CH_4 using sol-gel process. Hydrogen permeance was higher than 10^{-6} mol $\cdot$ m$^{-2}\cdot$s$^{-1}\cdot$Pa^{-1} at 200°C, but H_2/N_2 selectivity was only of the order of ten. Separation factors for H_2/CH_4 and H_2/i-C_4H_{10} were in the order of 50 and 200 at 200°C, respectively.

The size of micropore is more successfully controlled by the sol-gel process than by the CVD method. Raman and Brinker[6,7] demonstrated that a sol-gel process with organic templates lead to a microporous silica membrane, which exhibited both high permeance and permselectivity for mixtures of carbon dioxide and methane. They 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. The CO_2 permeance was of the order of 10^{-7} mol $\cdot$m$^{-2}\cdot$s$^{-1}\cdot$Pa^{-1}, and the CO_2/CH_4 selectivity of the membranes was 71.5. Asaeda et al.[8] prepared silica membrane on a porous α-alumina support by sol-gel process and separated C_3H_6/C_3H_8 mixture by surface diffusion mechanism. Recently, they prepared Ni-doped porous silica membranes by the sol-gel techniques for separation of H_2 at high temperature around 500°C[9].

The sol-gel process is attractive for multilayer deposition which can lead to a controlled structure, composition and activity for the membrane. Gas permeation rate and selectivity through these sol-gel derived membranes are usually high. However, these membranes calcined or sintered at relatively low temperature for a short time show the thermal and hydrothermal instability due to pore growth, grain coarsening and defect development above $400\sim500$°C[10].

Lee and coworkers of Korea research institute of chemical technology (KRICT) prepared silica membrane in a macroporous stainless steel support using a modified sol-gel method[11-14]. To improve the thermal stability of the membranes, the composite membranes were prepared by the new technique of the soaking-rolling method as shown in Figure 2. The soaking process leads to the penetration of the coating layer into pores of porous stainless steel support and the interstitial voids among colloidal silica particles of the intermediate layer, and the rolling process following the soaking process contributes to the removal of concentrated surface gel layer formed during the soaking process. Therefore the soaking-rolling method gives rise to the minimization of the interface between coating layer and stainless steel surface. The silica composite membrane prepared by the new technique of the soaking-rolling method is structurally different from that prepared by dip-coating method as schematically shown in Figure 3. For the composite membrane prepared by dip-coating method, the coating layers such as polymeric silica or α-alumina consist of vertically only one layer, and the contact area bet-
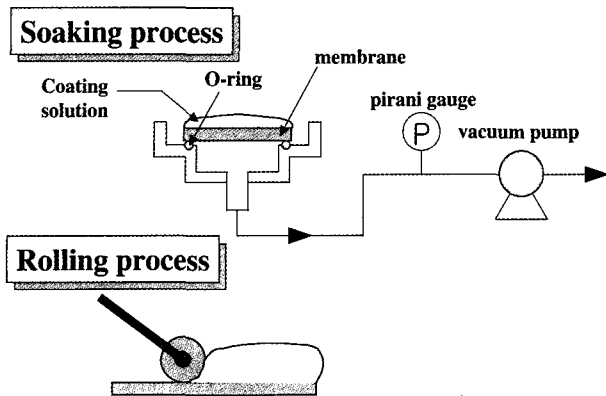
Fig. 2. Soaking-rolling process for membrane preparation.

ween the coating layer and the stainless steel is much larger than that of the membrane prepared by the soa king-rolling method. For the soaking-rolling method, however, the coating materials deeply penetrate into the inner pores of the stainless steel and the interstitial voids among colloidal silica particles, resulting in minimization of interface between the coating layer and the stainless steel. The coating layer has vertically multilayered structure divided by the walls of the stainless steel, and even top layer includes colloidal silica particles.

Figure 4 shows the SEM images of cross-section of the silica composite membranes prepared by the soaking-rolling and dip-coating method. The morphologies of the membranes are consistent with the expected structures are shown in Figure 3. Comparing with the membrane prepared by dip-coating method, the skin layer fabricated by the soaking-rolling method penetrated into the stainless steel substrate and included the colloidal silica particles. It is well-known that, for dip-coating method, capillary filtration occurs when the dry support comes into contact with a sol and the pore surface is wetted by the sol, followed by capillary suction of the support. For the soaking-rolling method, forced suction combined with capillary suction is applied by a vacuum pump during the soaking procedure, and concentrated gel layer formed on surface of the support is removed by the rolling process. That is the reason why the soaking-rolling method makes the skin layer deeply penetrate into the inner pores of the
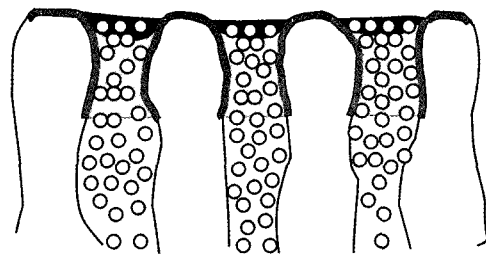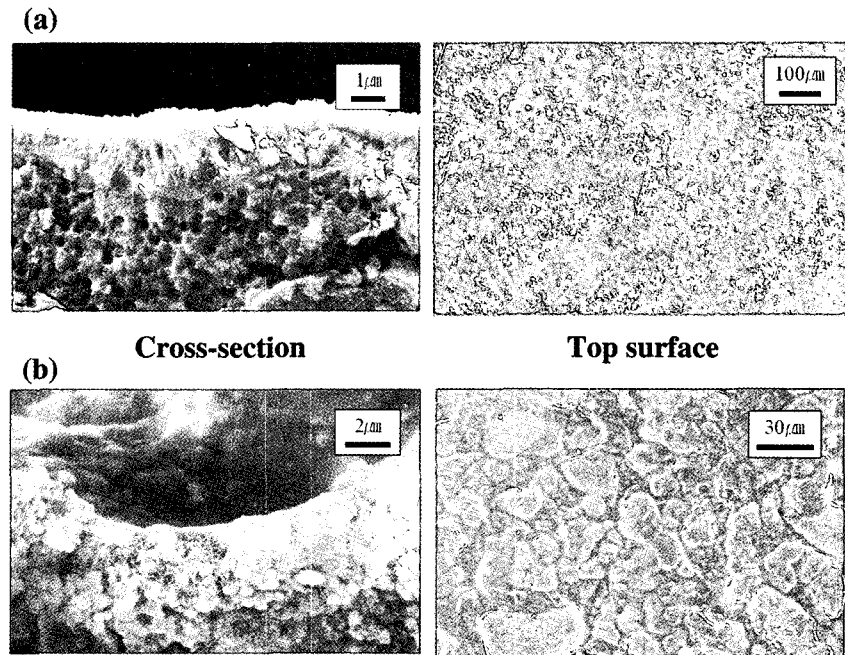
Dip-coating method
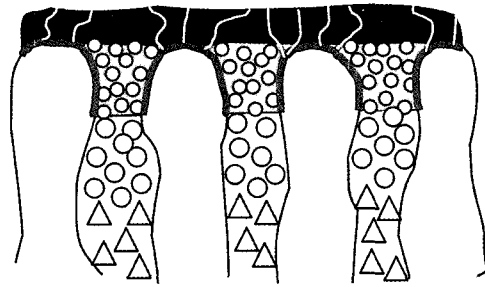
Soaking-rolling method

**Fig. 3.** The schematic comparison of the soaking rolling and dip-coating method.

support.

4. Cvd-Derived Silica Membranes

CVD method is fundamentally much simpler and easier than wet processes such as sol-gel process and hydrothermal synthesis. Usually, amphorous silica membranes formed by the CVD method are hydrogen permselective but often not useful for the separation of larger molecules.

Gavalas et al.[15] 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 a H_2 permeance of the order of 10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and a H_2/N_2 selectivity of $100 \sim 1000$ at permeation temperatures of $400 \sim 600°C$[16-18]. Jiang et al.[18] improved the H_2 permeance and H_2/N_2 selectivity to 4×10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and 1000 at 600°C, respectively, by introducing temporary carbon barriers in pores of

(a)

Cross-section   **Top surface**

(b)

Fig. 4. SEM images of the cross-section of the SiO_2(polymeric)/ γ -Al_2O_3/SiO_2 (500 nm)/SUS membrane prepared by different method (drying condition: 25 °C, RH 60%): (a) the soaking rolling method, (b) dip-coating method.

(a)

Evacuation

(b)
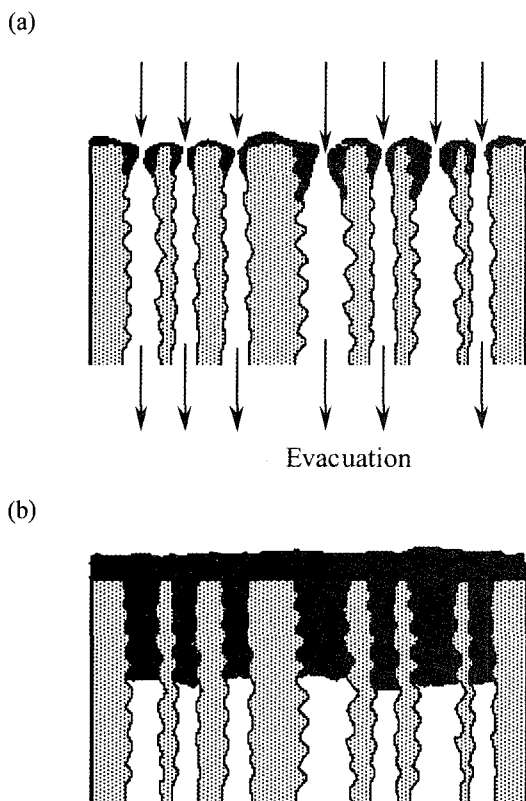
Fig. 5. Pore plugging model by CVD with forced cross-flow.

the Vycor support tube. Wu et al.[19] prepared a silica-modified membrane on a γ -alumina support tube by a CVD method with TEOS and oxygen. Their membrane exhibited a 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. Morooka and coworkers[20,21] showed that the step coverage of deposition was drastically improved by evacuating the reactant through the porous wall during CVD modification, as shown in Figure 5. This technique was especially effective in plugging the macropores of a support tube which possessed a wide pore-size distribution. 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 KRICT, a silica membrane was formed in a porous α -alumina tube by chemical vapor deposition ofTEOS at 600°C[22-24]. Since permeance is normally enhanced through the sacrifice of selectivity, a balance between permeance and selectivity is essential to ac-
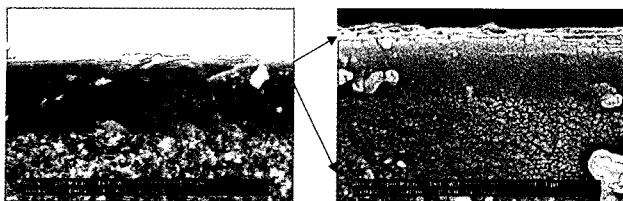
Fig. 6. Fractured section of CVD-modified composite membrane in silica/ γ -alumina layer coated on α -alumina tube.

Fig. 7. Gas permeance of silica membrane formed on γ -alumina coated α -alumina tube.

hieve 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) with a forced cross-flow through the porous support wall. Figure 6 shows the silica membrane formed in a porous alumina support by the CVD method. 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.*[21] 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.

Figure 7 shows the permeances to gases as a function of their molecular kinetic diameters, which are cited from the literature. 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 7. The permeances of the membrane gradually decreased with
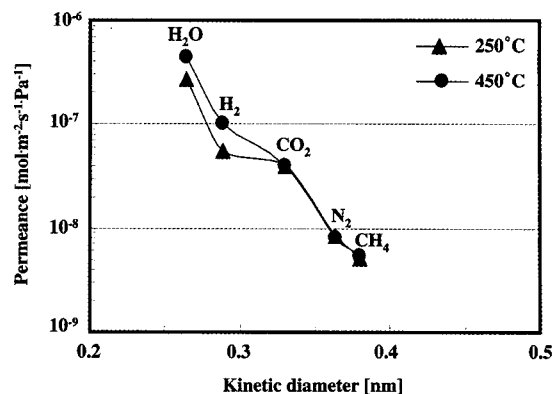
increasing size of molecules and recognized the gas molecules of CO_2, N_2 and CH_4 which are even in the narrow range of 0.33~0.38 nm. We succeeded in strict controlling micropores of silica membrane by CVD with a forced cross-flow and intermediate γ -alumina layer with a high quality. Computer simulation 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[25]. 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.

Sea *et al.*[26] attempt to make the best use of the simplicity of the CVD process as well as to enlarge the micropore size of silica membrane using phenyl-substituted ethoxysilane as the Si-source. Figure 8 shows the synthesis scheme for micropore controlling by phenyl-substituted ethoxysilane. Morphology of a silica membrane was not greatly affected by the Si-precursor, TEOS or PTES. The silica modified layer was expanded to a depth of 200~500 nm, and the top surface contained no pinholes. In the case of TEOS-derived membrane, hydrogen selectivities to N_2, CO_2, CH_4 and C_3H_8 were in the range of 10~15, but selectivities among the gases except hydrogen remained atthe level of theoretical values by Knudsen diffusion, lighter gas being permeated preferentially. Molecules
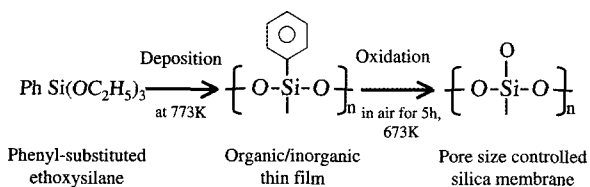
Fig. 8. Schematic illustration for pore size control by phenyl-substituted ethoxysilane.

Fig. 9. Chemical surface modification for dehydration silica membrane.

larger than hydrogen leaked through a small number of mesopores, which were left unplugged in the membrane. On the other hand, the PTES-derived membrane exhibited molecular sieving property. The gas permeance values followed the exact order of the kinetic diameters of the gas molecules. Hydrogen, which has the smallest kinetic diameter (0.29 nm), carbon dioxide (0.33 nm), nitrogen (0.36 nm), methane (0.38 nm) and finally propane (0.43 nm). Permselectivity values for the membrane were also well above the Knudsen diffusion values. The selectivities of carbon dioxide to methane and propane were 5.8 and 13.2, respectively, compared to the Knudsen diffusion values of 0.6 and 1.0. This result is quite different from the permeation of the membrane prepared with TEOS. In addition, the hydrogen permselectivity was dramatically improved: hydrogen permeance of PTES-derived membrane was 4.5 times higher than that of TEOS-derived membrane maintaining a high hydrogen/nitrogen selectivity of 59.5.

The PTES-derived membrane thus is believed to have micropores larger than those of the TEOS-derived membrane and all the mesopores were virtually plugged. In addition, the PTES-derived membrane consisted of abundant sub-micropores through which only hydrogen is permeable and a few micropores through which CO₂ and N₂ are barely able to pass one another. This suggests that micropore size in the amorphous silica membranes was well controlled by varying the substituents on silanes. Under the present deposition condition of 773 K, phenyl groups of PTES remained unreacted and decreased the crosslink density, thus leading to a loose amorphous structure after calcination. The BET surface areas of calcined silica powders were, respectively, 193 m²/g and 365 m²/g for TEOS
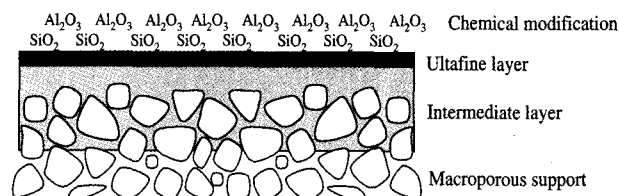
and PTES used as the Si source. Therefore, it is presumed that micropores were more abundant in the membrane formed with PTES than with TEOS. Although there is currently no direct method to measure the pore size distribution of the supported submicron-thick membrane layer in the silica-based membranes, we believe that the large observed differences in the permeance values for gases with only relatively small differences in kinetic diameters indicate that the diameter of most of the pores is below 0.5 nm.

Our group also attempted surface modification approach to develop dehydration silica membrane exhibiting superior water - selectivity and - permeance due to the hydrophilicity on the surface[27]. As shown in Figure 9, the chemical modification of silica surface by alumina may form Si(OH)Al-structured Bronsted acidic site and allow water vapor to preferentially adsorb on the surface, thus increasing the hydrophilicity. The Bronsted acidic site is not a simple composite layer physically formed on the interface between γ - alumina middle layer and silica gas molecular sieve layer. When a silica gas molecular layer is introduced on the γ -alumina middle layer, the physical layer lamination can be achieved without causing any chemical or structural change on the surface because the γ -alumina middle layer requires comparatively high temperature for layer formation. On the contrary, when an active layer of γ -alumina for separation of water vapor is introduced on the silica layer of gas molecular sieve, the active layer of γ -alumina for separation of water vapor requires a relatively higher temperature than those of the surrounding layers, the chemical structure and characteristics on the surface of the silica gas molecular layer. The chemical modification of a silica coating layer with alumina sol increased

water vapor permeation and selectivity by $2\sim3$ times, which means the hydrophilicity of the selective membrane surface is increased by the chemical modification.

5. Perspective and Conclusions

In porous inorganic membranes, generally, permeability is controlled by the volume fraction porosity, whereas selectivity is determined by the pore size and pore size distribution. In order to improve both permeance and selectivity of gas molecules through silica membranes, strict control of micropore size and microstructure of the silica top layer was tried using sol-gel and CVD process.

In order to improve the thermal stability of the stainless steel supported membranes, the composite membranes were prepared by the new technique of the soaking-rolling method. The silica composite membrane prepared by the soaking-rolling method was thermally stable below 450°C due to a decrease in the interface. The improvement of thermal stability of the stainless steel supported silica membrane by the soaking-rolling method is attributed to the minimization of the interface, and colloidal silica particles, included in coating layer, as a barrier of propagation of the cracks derived from the remaining interface between the coating layer and the wall of stainless steel.

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.

A defect free silica membrane was synthesized in a mesoporous γ-alumina film coated on the α-alumina tube by CVD of phenyltriethoxysilane (PTES) at 773 K. The PTES-derived membrane consisted of abundant sub-micropores through which only hydrogen is permeable and a few micropores through which CO_2 and N_2 are barely able to pass one another. Improved membrane performance was obtained by using PTES as a CVD precursor, presumably via fine-tuning of micropores with successful removal of mesopores.

For practical application, despite many studies on the silica membranes, further studies are needed to improve their permselectivity and stability under crucial conditions.

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