Preparation of Microporous Silica Membranes for Gas Separation

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Abstract—Microporous silica membranes for hydrogen separation were prepared on a γ-alumina coated α-alumina tube by sol-gel method. The reactants of sol-gel chemistry were tetraethoxysilane (TEOS) and methacryloxypropyl-trimethoxysilane (MOTMS). The silane coupling agent, MOTMS, was added as a template in order to control the pore structure to the silicon alkoxide, TEOS. In particular, the microporous membranes were prepared by changing the molar ratio of MOTMS with respect to other substances, and their pore characteristics were analyzed. Then, the effects of thermal treatment on the micropore structure of the resulting silica membranes were investigated. The pore size of the silica membrane prepared after calcination at 400-700 °C was in the range of 0.6-0.7 nm. In addition, permeation rates through the membranes were measured in the range of 100-300 °C using H_2, CO_2, N_2, CH_4, C_2H_6, C_3H_6 and SF_6. The membrane calcined at 600 °C showed a H_2 permeance of 2×10^{-7}-7×10^{-7} $molm^{-2}s^{-1}Pa^{-1}$ at permeation temperature 300 °C, and the separation factors for equimolar gas mixtures were 11 and 36 for a H_2/CO_2 mixture and 54 and 132 for a H_2/CH_4 mixture at permeation temperatures of 100 °C and 300 °C, respectively.

Key words : Gas Separation, Silica Membrane, Sol-Gel Method, Hydrogen Permeance

INTRODUCTION

Inorganic membranes have attracted considerable attention for use in gas separation processes under conditions where organic polymer membranes cannot be used. Among others, porous inorganic membranes that possess molecular-sieving permeation characteristics offer potential advantages over polymeric membranes for the separation of gases either at elevated temperatures or in the presence of organic vapors [Burggraaf and Cot, 1996]. Inorganic membranes also offer considerable promise in applications to catalytic membrane reactors [Sarocco et al., 1994; Zaman and Chakma, 1994].

The important mechanisms of gas separation via a porous membrane are Knudsen flow and surface diffusion. Knudsen flow occurs when the mean free path of the gas molecule is sufficiently larger than the pore diameter and the collisions between the permeating gas molecules and the pore wall are the dominant transport mechanism. Gas flux due to Knudsen flow is inversely proportional to the square root of molecular weight. Thus separation is limited by the ideal separation factor, which is too low for practical applications. When the interactions between the permeating gas molecules and the pore wall become significant, the adsorption of gas molecules on the pore wall becomes important, and molecules adsorbed on the porous solid surfaces may have considerable mobility. This gives rise to an additional contribution to gas transport [Uhlhorn et al., 1989; Cho et al., 1995]. The surface diffusion rates are determined by the surface diffusion coefficient and adsorption equilibrium, both of which are related to the interactions between adsorbates and pore surfaces [Yamasaki and Inoue, 1991]. Moreover, surface diffusion becomes important as the pore size becomes as small as the permeating gas molecules, since physicochemical interactions between the pore wall and the permeating molecules become pronounced. It is thus important to reduce the pore size to a nano-scale without pinholes or cracks.

Amorphous silica with pores smaller than 1 nm is suitable as a material for highly selective membranes. However, diffusion through such narrow pores is usually slow. In order to improve both the permeance and the selectivity of silica membranes, a number of studies have been reported on attempts to control the pore structure. Chemical vapor deposition (CVD), which is one of the methods used for preparation of such membranes, provides pore properties that are appropriate for gas separation. The modification of mesoporous membranes by a CVD technique results in very high separation factors. Specifically, Tsapatsis and Gavalas [1991, 1994] prepared a CVD-modified membrane, of which the H_2/N_2 selectivity was as high as 750, and the H_2 permeation was 10^{-8} $molm^{-2}s^{-1}Pa^{-1}$ at 600 °C. Yan et al. [1994] also reported on the preparation of silica membranes with high selectivities and permeabilities. So et al. [1998, 1999], Jung et al. [1999] and Lee et al. [1994, 1995a, b] prepared silica-alumina composite membranes within α-alumina supports for hydrogen separation by the multi-step pore modification. The α-alumina supports they used were ultrafiltration membranes and were composed of two distinctively different layers: a dense skin layer with small pores and a coarse support layer with relatively large pores. The composite membrane was formed as an intermediate layer in the vicinity of the interphase between the dense skin layer and the coarse support layer. The preparation proceeded by two consecutive steps: *in situ* silica sol-gel reaction followed by soaking and vapor deposition. However, amorphous silica mem-

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branes formed by CVD using TEOS were not capable of permeating molecules larger than CO_2.

Sol-gel method is frequently adopted in membrane synthesis or membrane pore modification because of its controllability and homogeneity [Kim et al., 1995; Roh et al., 1999; Lee et al., 1995c]. Gas permeation rates through inorganic membranes prepared by sol-gel process are relatively high, because of the very thin top layers of 50-200 nm thick. The pore structure of the membranes is dependent on the size of the primary sol particles, as well as the three-dimensional polymeric sol network formed by the condensation of precursors. Brinker et al. [1994] and Raman and Brinker [1995] used methyltriethoxysilane (MTES) to modify silica membranes that were formed by using tetraethoxysilane (TEOS) and reported that the resulting membranes showed both high CO_2 permeances and CO_2/CH_4 selectivities. de Vos et al. [1998, 1999] also prepared hydrophobic membranes using MTES. Kusakabe et al. [1999] and Kim et al. [submitted] prepared defect-free silica membranes by sol-gel process using a mixture of TEOS and either octyltriethsysilane (OTES) or dodecyltriethoxysilane. The alkyl groups in the precursors were decomposed during calcination, which permitted a reasonable degree of controlling the size of the micropores. Asaeda et al. [1991] also modified silica membranes by sol-gel technique. However, roles of the chemical structures of the silica precursors in the formation of micropores have not yet been understood.

Fig. 1 represents the organic template approach showing the progressive densification of the inorganic matrix and creation of micropores by temple removal during calcination. Organic ligands embedded in a dense inorganic matrix are removed to create a continuous network of micropores. Ideally, the organic ligand volume fraction is used to control porosity and hence flux, independently of selectivity, which depends on the ligand size and shape. For this approach to be successfully implemented, the following criteria must be satisfied: (1) the organic ligands must be uniformly incorporated in the inorganic matrix without aggregation or phase separation to avoid creating pores larger than the size of the individual ligands; (2) the synthes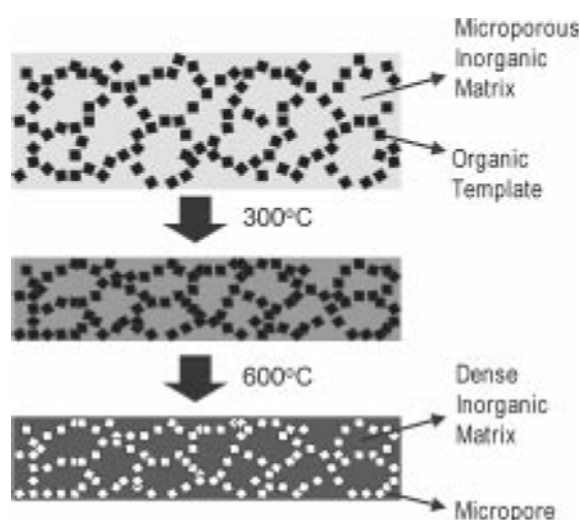is and processing conditions should result in a dense embedding matrix so that pores are created only by template removal; (3) template removal should be achieved without collapse of the matrix, so that the pores created preserve the original size and shape of the template; (4) after the first three criteria are satisfied, pore connectivity may be achieved by exceeding some percolation threshold of the organic ligands.

The key to improving permeability and permselectivity is control of the pore structure of the membrane top layer. In this study, silica membranes were prepared on a γ-alumina coated α-alumina tube via the copolymerization of TEOS and methacryloxypropyltrimethoxysilane (MOTMS) which has organic ligand. In particular, the microporous membranes were prepared by changing the molar ratio of MOTMS with respect to other substances, and their pore characteristics were analyzed. Then, the effects of thermal treatment on the micropore structure of the resulting silica membranes were investigated. For illustrative purposes, the permeance and permselectivity of the membranes for single and binary systems of various gases were examined at elevated temperatures.

EXPERIMENTAL

TEOS and MOTMS were dissolved in anhydrous ethanol at 60 °C, followed by stirring for 2 hr. HCl and water were then added dropwise to the solution at 60 °C to hydrolyze the ligands, after which the mixture was stirred additionally for 2 hr. The composition of the final solution was MOTMS:TEOS: $EtOH:H_2O:HCl=$ x:(1−x):9:1:0.2 on a molar basis. In the present study, the mole fraction of MOTMS, x, was varied in the range of 0-0.3. Unsupported silica was prepared by casting a sol on a glass plate and then allowing it to dry overnight in ambient air. The dried gel was calcined at 500, 600 and 700 °C for 2 hr. Temperature was increased at a rate of 1 °C/min. The pore size distribution of the silica powders was determined from Ar sorption isotherm for micropore and N_2 for mesopore (ASAP2010/ASAP2000, Shimadzu Micromeritics). The thermal behavior of the gel powders in air was determined by thermo-gravimetry analysis (TGA) and differential thermal analysis (DTA) using a heating rate of 5 °C/min (Shimadzu TGA-50).

A porous α-alumina tube was used as a support (outer diameter: 2.1 mm, inner diameter: 1.9 mm, porosity: 0.39, average pore size: 150 nm) provided by NOK Co., Japan. Except for the permeation portion, which was approximately 12 mm in length, the outer surface of the tube was sealed with a glass sealant. The support tube was dipped in a boehmite sol for several minutes and pulled out at the rate of 14 cm/min. The dip-coated membrane was then dried overnight in ambient air. The green layer was calcined at 800 °C in air for 1 hr, resulting in γ-alumina layer. After this process was repeated three times, the γ-alumina coated α-alumina tube was dipped in the silica sol, air-dried overnight, and then calcined at 400, 500, 600 and 700 °C for 2 hr. Temperature was increased at a rate of 1 °C/min, and the samples were maintained at each maximum temperature for 2 hr. This dipping-calcinating process was repeated three times, to give a silica membrane. The morphology of the membranes was observed by scanning electron microscopy (SEM, Hitachi S-900).

Fig. 2 shows a schematic diagram of the permeation test apparatus used. Each end of the membrane was connected to a stainless steel tube. Permeation rates through the membranes were deter-
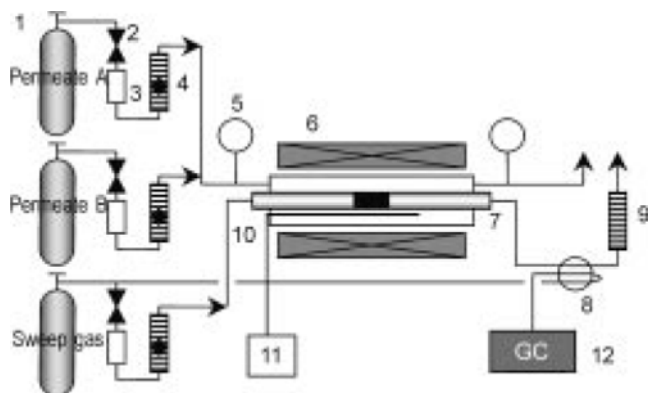

Fig. 1. Organic template approach showing the progressive densification of the inorganic matrix and creation of micropores by temple removal during calcination.

Fig. 2. Schematic diagram of gas permeation apparatus.

1. Gas cylinder	7. Membrane
2. Stop valve	8. Six-way valve
3. Mass flow controller	9. Soap film
4. Flow meter	10. Thermocouple
5. Pressure gauge	11. Thermo-regulator
6. Electronic furnace	12. Gas chromatograph

mined in the range of 100-300 °C by using H_2, CO_2, N_2, CH_4, C_2H_6, C_3H_8 and SF_6. Argon was introduced as the sweep gas into the permeate side, with the result that the partial pressures of permeants on the permeate side were negligible. The total pressure on both sides of the membrane was maintained at ambient pressure. Gas flow rates were determined by using bubble flow meters, and the compositions were determined by using a TCD-Gas Chromatograph (Shimadzu, GC-8A). The permeance to the i-component, P_i, is defined as follows:

$$P_i = \frac{(\text{moles permeated})}{(\text{membrane area})(\text{partial pressure difference})} \quad (1)$$

The partial pressure difference of the permeant between the feed and permeate sides was calculated by logarithmically averaging the differences at the inlet and outlet. Permeances to equimolar mixtures were also determined for systems composed of H_2/CO_2, CO_2/N_2, CO_2/CH_4, H_2/CH_4 and H_2/SF_6. The selectivity of the i-component to the j-component was defined as the ratio of permeances, P_i/P_j.

RESULTS AND DISCUSSION

1. Structure of Silica

Sol formation was strongly influenced by the addition of templating reagents. Since hydrolysis and condensation rates of the templates were higher than those of TEOS, aggregation occurred during the sol formation [1975]. However, hydrophilic bonds of the templating reagents served to form clear sols at a fraction of x=0.1. This is due to the hydrophilicity of the substituents of the templating reagents. Hereafter, sols were prepared at x=0.1, if not otherwise specified.

The organic components embedded in a dense inorganic matrix were removed by calcination. Fig. 3 shows the weight loss, as determined by TGA, for the gel prepared with x=0.1. The initial weight change is caused by the vaporization of residual water and ethanol. Densification occurs mainly due to continued condensation reactions that expel water from the gel network up to about 320 °C. The
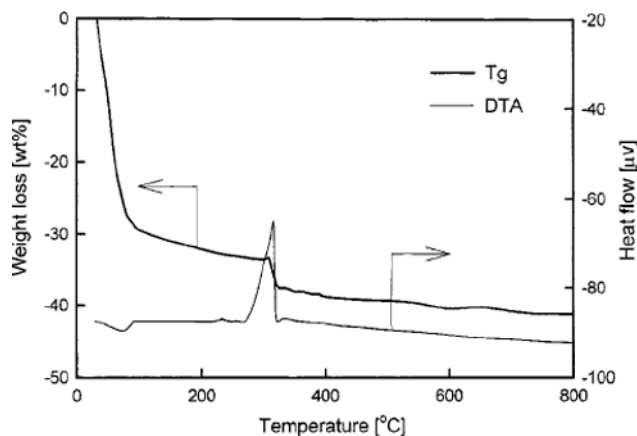
Fig. 3. Weight loss of the gel prepared with x=0.1.

weight loss, which occurs around 320 °C, is attributed to the oxidative pyrolysis of the precursors. The total weight loss after the initial vaporization stage is approximately 9 wt% and is not consistent with the weight loss of the substituents in the precursor molecules. Theoretically, a weight loss of 17.47 is expected if all methyl groups that are initially introduced in the synthesis are removed in this way. De Vos et al. [1999] reported similar behavior for methyltriethoxysilane (MTES). From their work, this behavior can be explained as follows: (1) the relatively low concentration of methyl groups makes it unlikely that all methyl groups can participate in a reaction, which makes not an Si-O-Si bond but Si-CH_2-Si bond; (2) it is unlikely that all methyl groups initially added during synthesis are actually incorporated in the calcined material; (3) the actual condensation mechanism is not clear yet and the formation of, for instance, -CH_2- groups has never been found up to now. In the case of MTESU, the weight loss continued at higher temperatures. However, the DTA results of all samples showed a unique peak at 320 °C, which indicates that the degradation of substituted structure occurs in a narrow range of temperature.

For the pore sizes that fall into a range in which capillary condensation or molecular sieving is dominant, the hyrophilicity becomes important because the separation process is determined by
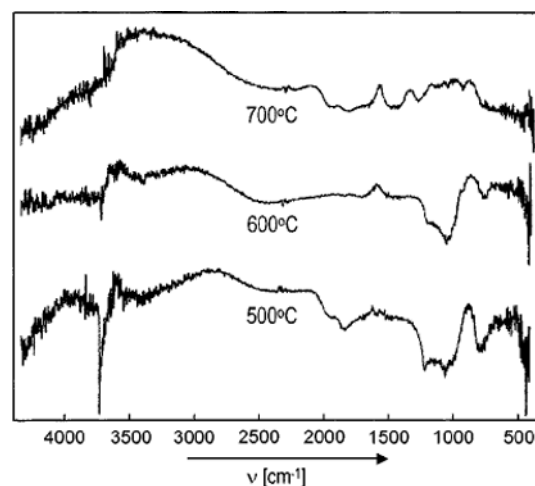

Fig. 4. Comparison of infrared spectra of silica gel calcined at different temperatures.

the affinity between gases and the pore wall. The infrared analyses show that some -OH groups remain in the product up to 700 °C; see Fig. 4. Dehydroxylation begins in the early stage of the thermal treatment and proceeds up to 700 °C. The precise evolution of this phenomenon cannot be established from the TGA curve. The -OH groups are characterized by two absorption bands in the IR spectrum: 3,000-3,800 cm^{-1} and 960 cm^{-1}. It is possible to choose the calcination temperature for the desired quantity of -OH in the final product resulting in the change of hydrophilicity. These results are similar to those obtained by Larbot et al. [1989] and Bertoluzza et al. [1982].

Fig. 5(a) and 4(b) show the micropore size distributions of the membranes prepared in the presence of MOTMS with x=0.1 and in the absence of MOTMS, respectively. All the silica samples show a peak at 0.6-0.7 nm. However, the addition of MOTMS greatly increased the volume of the micropores and narrowed the size distribution. The micropores of the silica sample, which was prepared from TEOS, i.e., x=0, nearly disappeared, when the green film was calcined at 700 °C, while those for the sample with x=0.1 were preserved.

When pinholes or cracks are developed, the selectivity is greatly deteriorated because gas molecules larger than the pore size can
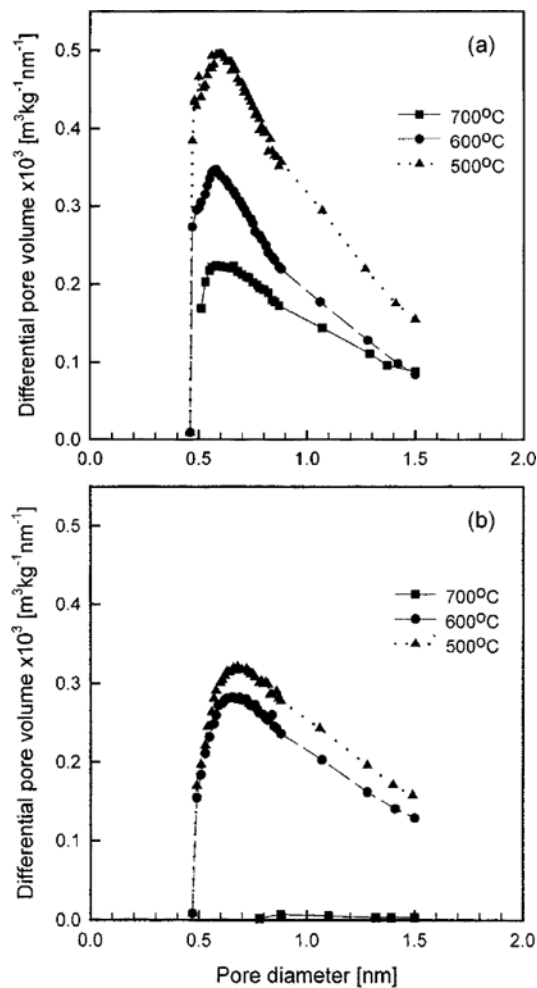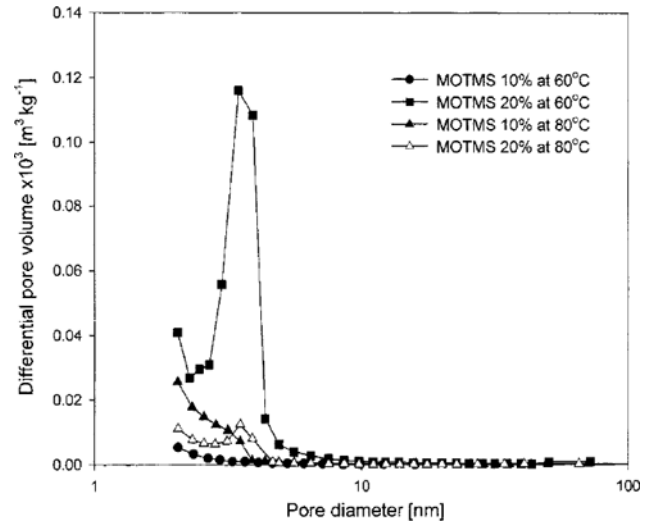

Fig. 6. Mesopore size distribution calcined at 600 °C.

Fig. 5. The effect of calcination temperature on the pore size distributions: (a) x=0.1, (b) x=0.
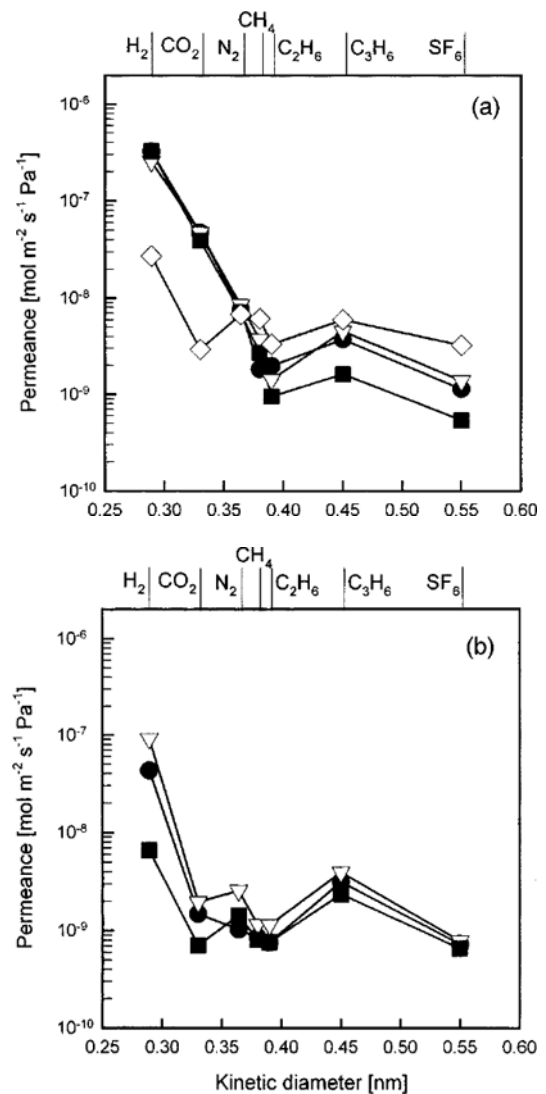

Fig. 7. The effect of calcination temperature on the permeance at 100 °C: (a) x=0.1, (b) x=0. Calcination temperature; ∇= 400 °C, ●=500 °C, ■=600 °C, ◇=700 °C.

pass through the membrane. Fig. 6 shows mesopore distribution of unsupported silica. At x=0.2, an increase of MOTMS/TEOS ratio develops mesopores. An increase in hydrolysis temperature would be expected to promote the hydrolysis reaction. This tends to form smaller particles and pores. Yoldas [1973] showed that the hydrolysis of aluminium alkoxides at a low temperature is unstable and converts to a less condensed state, whereas the hydroxide formed at a high temperature is stable. Thus, at 80 °C, mesopore density was decreased.

2. Permeation of Silica Membranes

Fig. 7 shows the permeances to single component gases through the silica membranes, which were prepared in the presence of MOTMS with x=0.1 (a) and in the absence of MOTMS (b). The permeances decreased with increasing the molecular size of the permeant. Permeances to H_2, N_2 and CH_4 at a permeation temperature of 100 °C were 3.2×10^{-7}, 3.9×10^{-8} and 2.7×10^{-9} mol·m^{-2}s^{-1}Pa^{-1}, respectively, for the case of a membrane which was prepared with x=0.1 and calcined at 600 °C. The presence of MOTMS increased the H_2 permeance by approximately 40 times relative to the case without MOTMS. This shows the pore structure developed by pyrolysis of MOTMS at a temperature over 500 °C has pore size small enough to pass only H_2 and CO_2. The increased pore volume shown in Fig. 5 also represents the role of added MOTMS. The permeance to H_2 was approximately five times higher than the highest values obtained for the silica membrane which had been prepared from a sol containing octyltriethoxysilane, as reported in the previous study [Roh et al., 1999]. Fig. 7 also shows the effect of calcination temperature on the permeance. The permeances of both membranes (with x=0.1 and 0) were not greatly changed for the calcination temperatures at 400 and 500 °C. For the case of membranes which were calcined at 700 °C, however, the H_2 permeance for the membrane formed with x=0.1 was considerably decreased.

In Table 1, the permeances for the single component systems are listed. The membrane was prepared with x=0.1 and calcined at 600 °C. As the permeation temperature increased, the permeances to

Table 1. Permeances of a silica membrane formed with x=0.1 for various gases at various temperatures. Calcination temperature is fixed at 600 °C and permeances are in 10^{-9} molm^{-2}s^{-1}Pa^{-1}

System	Gases	100 °C	200 °C	300 °C
Single-component	H_2	240	404	680
	CO_2	20	18	20
	N_2	3.1	4.5	23
	CH_4	1.0	2.2	5.9
	SF_6	0.5	0.4	0.5
H_2/CO_2	H_2	105	183	295
	CO_2	9.7	9.1	8.2
H_2/CH_4	H_2	94	133	248
	CH_4	1.7	1.9	1.9
CO_2/CH_4	CO_2	16	18	24
	CH_4	0.9	2.0	5.0
CO_2/N_2	CO_2	20	20	21
	N_2	1.5	3.3	13
H_2/SF_6	H_2	98	165	293
	SF_6	0.4	0.4	0.4

H_2, N_2, CH_4 increased, while those to CO_2 and SF_6 remained unchanged. The effective activation energy for permeation, E_a, is defined as follows:

$$P = P_o \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

in which E_a is composed of the energy required for diffusion in pores and the heat of adsorption. When the separation of molecules is based on the difference between the molecules and the micropores, E_a has a positive value. If molecules permeate through macropores by a Knudsen diffusion mechanism, E_a may assume a small negative value. When adsorption is dominant in the permeation, E_a can be negative. The values of E_a were 9.1, 0.09, 16.8, 13.7 and 0 kJ for H_2, CO_2, N_2, CH_4 and SF_6, respectively. The small values for CO_2 and SF_6 are due to the adsorptivity of these permeants. Table 1 also shows the permeances to gases for binary mixture systems. The H_2 permeance decreased for the cases of binary systems. This suggests that the diffusion of H_2 molecules through the micropores is hindered by the presence of slowly diffusing molecules. For a mixture of H_2 and CO_2, the CO_2 permeance is also decreased, implying that the adsorption of CO_2 near the entrance of the micropores on the surface of the membrane is decreased, as a result of the collision of H_2 molecules present in the gas mixture.

Table 2 shows the selectivities of the membrane that was used in the tests shown in Table 1. The selectivity is defined as: α_i, the selectivity for single component systems (referred to as the ideal selectivity), and α_m, the selectivity for binary mixtures (referred to as the binary selectivity). When a membrane is used to separate gases, its performance should be evaluated based on the binary selectivity. As shown in Table 2, the binary selectivity increased with increasing the permeation temperature for mixtures of H_2/CO_2, H_2/CH_4, H_2/SF_6, but the trend was the reverse for mixtures of CO_2/CH_4 and CO_2/N_2.

In the case of vapor mixture systems, vapor is condensed into the pore structure at low temperatures. Fig. 8 shows the effect of condensed water for hydrogen and carbon dioxide. The condensed water diffused into the membrane pores with the aid of capillary force, preventing the gases from passing through the membrane. Therefore, low permeation rates were obtained compared to single component systems. As permeation temperature increased, the permeance of a gas was increased and approached the result for the single component system, while vapor was decreased.

Table 2. Selectivities of the silica membrane used in Table 1 at various temperatures

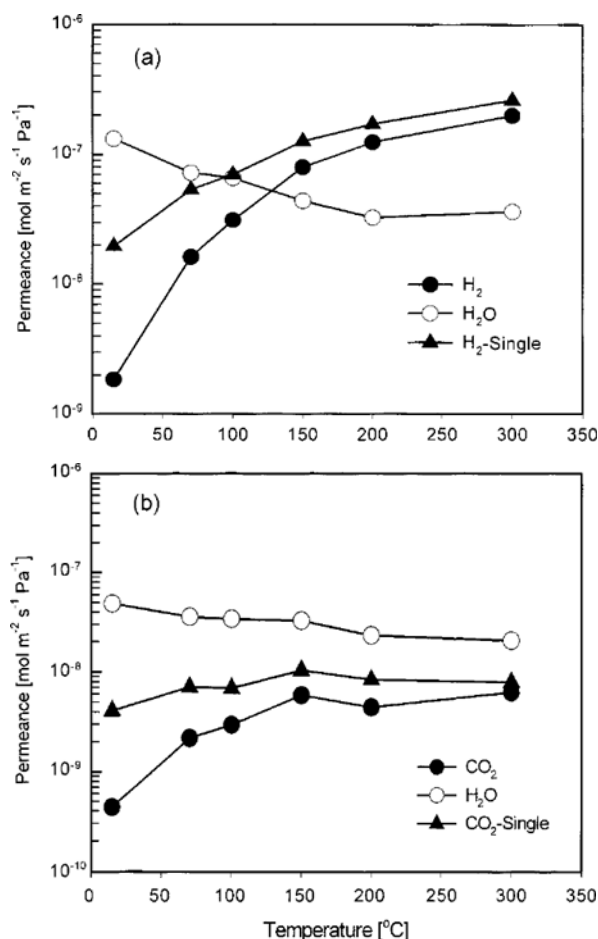| Mixture	Selectivity	100 °C	200 °C	300 °C
H_2/CO_2	α_i	12	22	34
	α_m	11	20	36
H_2/CH_4	α_i	235	185	115
	α_m	54	72	132
CO_2/CH_4	α_i	19	8.5	3.4
	α_m	18	9.0	4.8
CO_2/N_2	α_i	6.1	4.1	0.9
	α_m	13	6.0	1.6
H_2/SF_6	α_i	488	976	1380
	α_m	239	413	792

Fig. 8. The permeance of gas-vapor system as a function of temperature: (a) H_2-H_2O, (b) CO_2-H_2O.

CONCLUSIONS

Microporous silica membranes were prepared by sol-gel method with TEOS as a silica precursor and with MOTMS as a template to control the micropore structure. The presence of MOTMS increased the micropore volume and induced a narrow pore size distribution. The silica membrane prepared by addition of MOTMS with a molar ratio x=0.1 and calcined at 600 °C showed high permeances and selectivities. The binary selectivity increased with increasing the permeation temperature for the mixtures of H_2/CO_2, H_2/CH_4 and H_2/SF_6, and that for the mixture of H_2/CH_4 was as high as 132 at a permeation temperature of 300 °C.

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REFERENCES

Asaeda, M. and Kitao, S., "Inorganic Membranes," Proc. 2nd Intern. Conf. on Inorganic Membranes, 295 (1991).

Bertoluzza, A. Fangnano, C. and Morelli, M. A., "Raman and Infrared Spectra on Silica Gel Evoluting Toward Glass," *J. Non-Cryst. Solids*, **48**, 117 (1982).

Brinker, C. J., Sehgal, R., Hietala, S. L., Deshpande, R., Smith, D. M., Loy, D. and Ashley, C. S., "Sol-gel Strategies for Controlled Porosity Inorganic Materials, Alex Stern Honorary Symposium on Membrane-Based Gas Separations," *J. Membr. Sci.*, **94**, 85 (1994).

Burggraaf, A. J. and Cot, L., "Fundamentals of Inorganic Membrane Science and Technology," Elsevier, Amsterdam (1996).

Cho, Y. K., Han, K. W. and Lee, K. H., "Separation of CO_2 by Modified γ-Al_2O_3 Membranes at High Temperature," *J. Membr. Sci.*, **104**, 219 (1995).

de Vos, R. M. and Verweij, H., "Improved Performance of Silica Membranes for Gas Separation," *J. Membr. Sci.*, **143**, 37 (1998).

de Vos, R. M., Maier, W. F. and Verweij, H., "Hydrophobic Silica Membranes for Gas Separation," *J. Membr. Sci.*, **158**, 277 (1999).

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 Multi Stage Inorganic Membrane," *Korean J. Chem. Eng.*, **16**, 193 (1999).

Kim, H. S., Han, J. W., Chun, K. Y., Shul, Y. G. and Joe, Y. I., "Synthesis of Organic-inorganic Composite Membrane by Sol-gel Process," *Korean J. Chem. Eng.*, **12**, 405 (1995).

Kim, Y. S., Kusakabe, K., Morooka, S. and Yang, S. M., "Characterization of Silica Membranes formed by a Sol-gel Technique with Organic Templating Reagents," *J. Membr. Sci., submitted.*

Kusakabe, K., Sakamoto, S., Saie, T. and Morooka, S., "Pore Structure of Silica Membranes formed by a Sol-gel Technique using Tetraethoxysilane and Alkyltriethosysilanes," *Sep. & Purif. Tech.*, **16**, 139 (1999).

Labot, A., Julbe, A., Guizard, C. and Cot, L., "Silica Membranes by the Sol-gel Process," *J. Membr. Sci.*, **44**, 289 (1989).

Lee, K. H., Cho, Y. K. and Han, K. W., "Manufacture of Alumina Composite Membranes for CO_2 Separation," *HWAHAK KONGHAK*, **33**, 570 (1995c).

Lee, S. J., Cho, I. H., Kim, K. Y., Yang, S. M. and Park, S. B., "Preparation and Characterization of Pd/Al_2O_3 Composite Membrane Supported on Porous Alumina Tube by Sol-gel Method," *HWAHAK KONGHAK*, **33**, 29 (1995a).

Lee, S. J., Yang, S. M. and Park, S. B., "Synthesis of Palladium Impregnated Alumina Membrane for Hydrogen Separation," *J. Membr. Sci.*, **96**, 223 (1994).

Lee, S. Y., Lee, S. J., Kwon, S. J., Yang, S. M. and Park, S. B., "Preparation of Sol-gel Driven Alumina Membrane Modified by Soaking and Vapor Deposition Method," *J. Membr. Sci.*, **108**, 97 (1995b).

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

Roh, H. S., Chang, J. S. and Park, S. E., "Synthesis of Mesoporous Silica in Acidic Condition by Solvent Evaporation Method," *Korean J. Chem. Eng.*, **16**, 331 (1999).

Sarocco, G., Versteeg, G. F. and van Swaaij, W. P. M., "Current Hurdles to the Success of High Temperature Membrane Reactors," *J. Membr. Sci.*, **95**, 105 (1994).

So, J. H., Yang, S. M. and Park, S. B., "Preparation of Silica-alumina Composite Membranes for Hydrogen Separation by Multi-step Modification," *J. Membr. Sci.*, **147**, 147 (1998).

So, J. H., Yoon, K. Y., Yang, S. M. and Park, S. B., "Preparations of

Metal Impregnated Porous Inorganic Membrane for Hydrogen Separation by Multi-step Pore Modification," *Korean J. Chem. Eng.*, **16**(2), 193 (1999).

Tsapatsis, M. and Gavalas, G., "Structure and Aging Characteristics of H₂-permselective SiO₂-Vycor Membranes," *J. Membr. Sci.*, **87**, 281 (1994).

Tsapatsis, M., Kim, S. J., Nam, S. W. and Gavalas, G., "Synthesis of Hydrogen Permselective SiO₂, TiO₂, Al₂O₃ and B₂O₃ Membranes from Chloride Precursors," *Ind. Chem. Res.*, **30**, 2152 (1991).

Uhlhorn, R. J. R., Keizer, K. and Burggaaf, A. J., "Gas and Surface Diffusion in Modified γ-alumina Systems," *J. Membr. Sci.*, **46**, 225 (1989).

Yamasaki, A. and Inoue, H., "Surface Diffusion of Organic Vapor Mixtures Through Porous Glass," *J. Membr. Sci.*, **59**, 233 (1991).

Yan, S., Maeda, H., Kusakabe, K., Morooka, S. and Akiyama, Y., "Hydrogen-selective SiO₂ Membrane formed in Pores of Alumina Support Tube by Chemical Vapor Deposition with Tetraethylorthosilicate," *Ind. Eng. Chem. Res.*, **33**, 2696 (1994).

Yoldas, B. E., "Alumina Sol Preparation from Alkoxide," *J. Membr. Sci.*, **10**, 1956 (1975).

Yoldas, B. E., "Hydrolysis of Aluminium Alkoxides and Bayerite Conversion," *J. appl. Chem. Biotechnol.*, **23**, 803 (1973).

Zaman, J. and Chakma, A., "Inorganic Membrane Reactors," *J. Membr. Sci.*, **92**, 1 (1994).