Desalination and Water Treatment
www.deswater.com

17 (2010) 288–293
May

1944-3994/1944-3986
doi: 10.5004/dwt.2010.1731

Preparation of silica hybrid membranes for high temperature gas separation

Mikihiro Nomura*, Keita Momma, Yoshio Negishi, Emi Matsuyama, Sayuka Kimura

Department of Applied Chemistry, Shibaura Institute of Technology, Toyosu, Koto-ku, Tokyo 135-8548, Japan
Tel. +81358598160; Fax +81358598160; email: Lscathy@shibaura-it.ac.jp

Received 23 July 2009; accepted 25 November 2009

ABSTRACT

A molecular sieve silica hybrid membrane was successfully prepared by using a counter diffusion chemical vapor deposition (CVD) method. Propyltrimethoxysilane (PrTMOS) was employed for a silica precursor. O_3 was used as an oxidizer. Effects of deposition temperatures on permeation properties through the silica membranes were investigated. H_2 (0.29 nm), N_2 (0.36 nm) and SF_6 (0.55 nm) permeances were measured at the deposited temperatures through the membranes. H_2/N_2 permeances ratios decreased sharply with increasing the deposition temperatures from 200°C to 400°C. In addition, H_2 permeance through the membrane deposited at 400°C was very high (4.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1}) with a low H_2/N_2 permeances ratio (3.4). This shows that silica was not deposited at 400°C due to O_3 decomposition at the high temperature deposition. On the other hand, N_2/SF_6 permeances ratios increased with increasing the deposition temperatures upto 320°C. The maximum value of N_2/SF_6 permeances ratio was 110 at 320°C deposition. This is much larger than that of Knudsen diffusion separation (2.3). According to the kinetic diameters of N_2 and SF_6, the pore sizes of the membrane were estimated at about 0.5 nm. These results show that the pore size of silica membranes can be controlled by changing the deposition temperatures. The decomposition reactions of propyl groups on silica hybrid materials were also investigated by TG and IR measurements. Propyl groups on silica hybrid materials decomposed at around 300°C and 400°C. Decomposition at around 300°C was C_2H_4 removal from the surface to remain methyl groups on the surface. Thus, we conclude that the high selective membrane deposited at 320°C was a silica hybrid membrane having methyl groups in the silica deposition.

Keywords: Silica hybrid membrane; Counter diffusion CVD; Pore size control

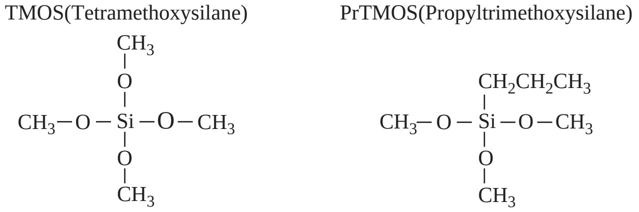
1. Introduction

High temperature gas separation through an inorganic membrane is one of the important techniques for efficient energy utilization. Metal membranes, zeolite membranes, silica membranes and so on have been developed. Silica membrane prepared by using a sol–gel method [1–3] or a chemical vapor deposition method (CVD) [4–7] have been studied for high temperature hydrogen separation. Hydrogen is considered to be separated by a molecular-sieve mechanism. Thus, pore size of the silica membranes must be about 0.3 nm. These hydrogen permselective silica membranes were applied to membrane reactors for steam reforming reaction of methane [8–10]. Pore size control of a membrane should be required for hydrocarbons separation at high temperature. Several groups have been investigated molecular sieve silica membranes by using a sol–gel method. Raman and Brinker [11] fabricated molecular sieve silica membranes using a hybrid organic–inorganic sol that was prepared by copolymerization of tetraethoxysilane and methyltriethoxyilane. This

---

*Corresponding author

Presented at the Fifth Conference of the Aseanian Membrane Society Aseania 2009 "Recent Progress in Membrane Science and Technology", 12–14 July 2009, Kobe, Japan.



$Si(OCH_3)_4$; $CH_3CH_2CH_2Si(OCH_3)_3$

Fig. 1. Chemical formulas of the silica precursors.

hybrid sol was calcined at 550°C, methyl group in the hybrid sol was fired to obtain uniform micropores. In this study, we had employed a CVD method to prepare silica hybrid membrane. There are two types of CVD methods classified by the differences of providing geometries of reactants for a porous substrate. One is a one side geometry that all reactants are provided from only one side of the porous substrate. The other is a counter diffusion CVD method that two reactants are provided from the opposite side of the porous substrate. Deposition reaction occurs in the pores of the substrate and the reaction stops due to the diffusion limitation of the reactants by the deposited silica. Recently, silica membranes with an excellent hydrogen permselective were prepared by the counter diffusion CVD method [12]. Sea et al. [13] had prepared a silica membrane by pyrolysis of phenyltriethoxysilane (PTES) and diphenyldiethoxysilane (DPDES). The permeances ratio of N_2/SF_6 at 200°C through the PTES membrane and the DPDES membrane were 11.3 and 19.0, respectively. These results indicate that these membranes had larger micropores than that of the TEOS-derived silica membrane. Phenyl groups in the membranes were removed during the deposition procedures. We had investigated that pore size was controlled by using a counter diffusion CVD method [14]. N_2/SF_6 permeances ratio was 30 through a silica membrane prepared by using propyltrimethoxysilane (PrTMOS), indicating that pore size was controlled at about 0.5 nm. However, reproducibility of the membranes was not good. In this study, deposition conditions including deposition temperatures are investigated to control pore size of a molecular sieve silica membrane.

2. Experimental

Tetramethoxysilane (TMOS) and PrTMOS were used as a silica precursor (Shin-Etsu Chem. Co.). Fig. 1 shows the chemical formulas of the silica precursors. One methoxy group of TMOS is changed for one propyl group for PrTMOS. Fig. 2 shows the schematic diagram of a counter diffusion CVD method. Porous γ-alumina capillary substrates (effective length: 50 mm, ϕ:2.8 mm, pore size: 4 nm) were provided by NOK Co. The γ-alumina substrate was placed in a membrane module in a furnace. Both sides of the substrate are sealed by viton o-rings. The deposition temperatures was kept between 200°C and 600°C that was controlled by the thermocouple placed in the center of the membrane module. The temperature of the precursor bottle was kept at 45°C, and the precursor vapor was bubbled by nitrogen at the rate of 0.2 L min^{-1}. The precursor vapor was provided to outside of the substrate. O_2 or O_3 (2.1–3.0 mol m^{-3}) was introduced into the inside of the substrate at the rate of 0.2 L min^{-1}. O_3 was produced by using an O_3 generator (ZOS-YB-6G, SYOKEN Co.). CVD was carried out for 90 min. Single gas permeances of H_2 (0.29 nm), N_2 (0.36 nm) and SF_6 (0.55 nm) were measured at the deposited temperatures of the membranes.

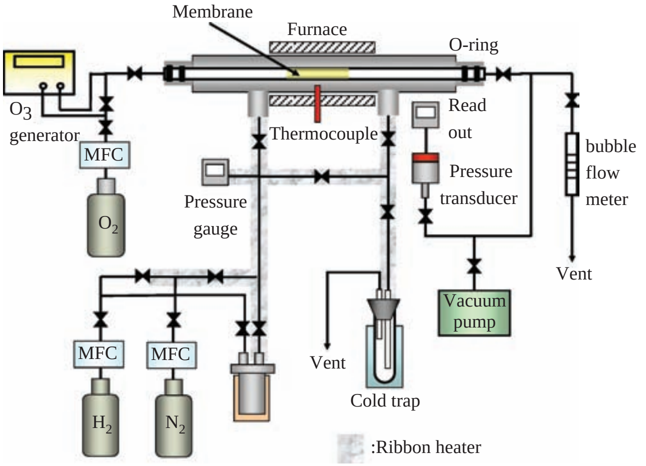


Fig. 2. A schematic diagram for a counter diffusion CVD apparatus.

Powder samples were prepared in order to discuss surface properties and decomposition procedures of the deposited membrane. TMOS or PrTMOS was stirred at 80°C for 2 h in anhydrous ethanol. Nitric acid or sodium hydroxide solution was added to hydrolyze the precursors. After the stirring, obtained gel was dried at 100°C for 12 h. The molar compositions of the sol are TMOS: EtOH: H_2O: HNO_3 =1: 3.8:6.4:0.085 and PrTMOS: EtOH: H_2O: NaOH=1:3.8:25: 0.94, respectively. The procedures to obtain powder samples were different. However, the decomposition reaction of the surface groups must be the same. The weight loss of the dried gel was measured using a thermogravimetry (TGA 50, Shimadzu Co.) at a rate of 5°C min^{-1} in the nitrogen. FT-IR (FTIR-8400S, Shimadzu Co.) measurements of reflection adsorption were carried out for the as-made samples, the calcined samples at 300°C and the calcined samples at 500°C. KBr disks were formed with 10 wt% of the samples.

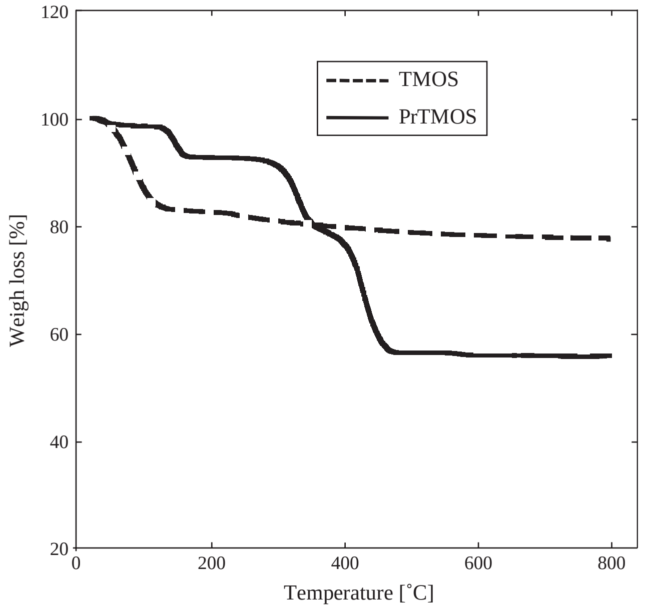


Fig. 3. TGA measurements for the powder samples prepared by using a sol-gel method.

3. Results and discussion

3.1. Decomposition properties of silica precursors

Decomposition properties of the silica precursors were tested using TGA. Fig. 3 shows the weight losses of the TMOS and PrTMOS derived powder samples prepared by using a sol–gel method. Weight losses for both samples at about 100°C must be the desorption of physically adsorbed water. No significant weight loss was found for the TMOS sample above 100°C, showing that hydrolyzation was completely finished for the TMOS sample. On the other hand, there were two weight losses for the PrTMOS sample found at around 300°C and 400°C. These losses are explained by decompositions of propyl groups of PrTMOS powder samples.

Fig. 4 shows FTIR spectra of the PrTMOS samples calcined at 300°C and 500°C. The broad absorption band at 3500 cm^{-1} corresponds to Si–OH group. The peak at around 1,000 cm^{-1} shows SiO_2. The absorption bands at around 3,000 and 1,460 cm^{-1} are C–H bond. These adsorption bonds were found from the PrTMOS samples calcined at 300°C indicating that propyl groups on SiO_2 are not decomposed at 300°C. While an absorption band at around 3,000 cm^{-1} was not observed from the PrTMOS sample calcined at 500°C. These results suggested that propyl groups in the PrTMOS are decomposed between 300°C and 500°C. The pyrolysis reactions considered from TG and IR data are described below.$-\mathrm{Si}-C_3H_7 \rightarrow -\mathrm{Si}-CH_3+C_2H_4$ (ca. 300°C)$-Si-CH_3 \rightarrow -\mathrm{Si}-+CH_3^*$ (ca. 400°C)

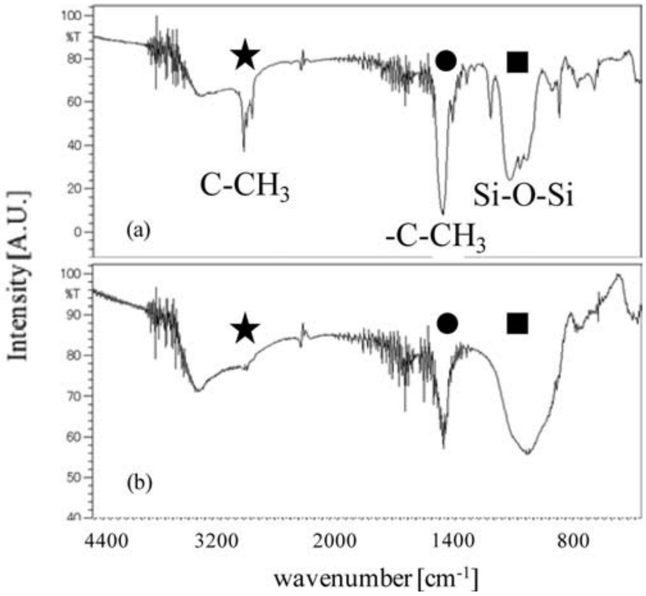


Fig. 4. FT-IR spectra of the PrTMOS powders calcinated at 300°C and 500°C. (a) calcined at 300°C (b) calcined at 500°C ★:C-CH_3 $_{vas}$ ●:C-CH_3 δas ■: Si–O–Si $\nu_{Si\text{-}O}$.

First, C_2H_4 was removed at around 300°C to remain methyl groups on the surface of the sample. Next, the remained methyl groups were decomposed at around 400°C. The weight loss at around 400°C was smaller than that at around 300°C. This might be explained that all propyl groups were not on the surface of the powder samples. A part of the decomposed gas must be captured in the sample and released at the higher temperature. Detailed measurements are required for the further discussions. In order to increase pore size of the deposited silica hybrid materials, the reaction should be operated at the first decomposition temperature. Thus, the deposition temperatures should be investigated at around 300°C to obtain larger pores by the decomposition of propyl groups from the deposited membranes.

3.2. Effects of O_2 and O_3

Effective reactants for the PrTMOS membranes were investigated by changing deposition temperatures. PrTMOS membranes were prepared by using O_2 or O_3 (2.1 mol m^{-3} in O_2) as a reactant. Fig. 5 shows H_2 permeances through the deposited membranes between 200°C and 500°C. Permeation measurements were performed at the deposition temperatures. H_2 permeances through a γ-alumina substrate were also plotted in the figure. H_2 permeances decrease from those through a γ-alumina substrate due to the deposited silica in the pores of the substrate. H_2 permeance

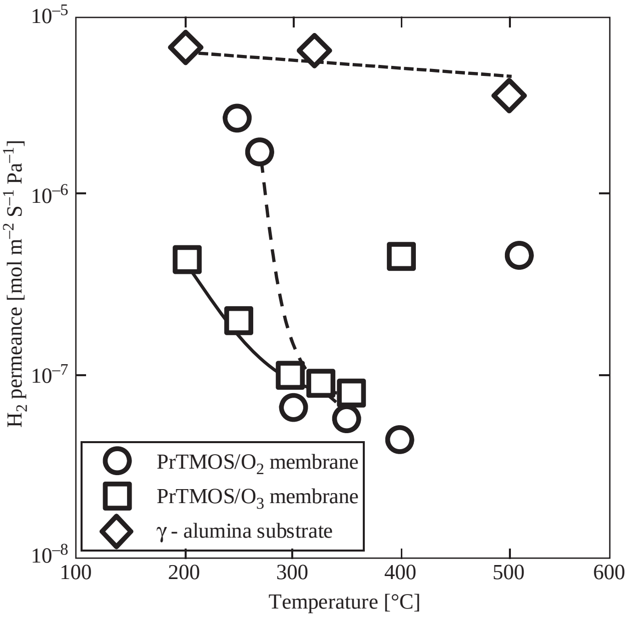


Fig. 5. H_2 permeances through the deposited membranes between 200°C and 500°C.

through the PrTMOS/O_2 membrane deposited at 250°C was almost the same with that through a substrate, while H_2 permeance through the PrTMOS/O_3 deposited at 250°C decreased about 64% with that through a substrate. This indicates that the reactant at 250°C is O_3. H_2 permeances through the membranes prepared above 300°C were the similar for the PrTMOS/O_2 system and PrTMOS/O_3 system. H_2/N_2 and N_2/SF_6 peremeances ratios of the PrTMOS/O_3 membrane deposited at 350°C were 13.0 and 18.3, respectively. On the other hand, H_2/N_2 and N_2/SF_6 peremeances ratios of the PrTMOS/O_2 membrane deposited at 350°C were 4 and 2, respectively. These are almost the same as those for the Knudsen diffusion ($H_2/N_2 = 3.7$, $N_2/SF_6 = 2.3$). Thus, we concluded that the effective reactant was O_3 below the 350°C deposition. However, O_3 concentration at the outlet of the membrane module was 0.21 mol m^{-3} at 270°C when the concentration at the inlet was 1.6 mol m^{-3}. O_3 is also decomposed at 270°C. The O_3 concentration at the substrate should be precisely controlled.

3.3. *Effects of deposition temperatures on the membrane properties*

Fig. 6 shows that the single gas permeation results through the PrTMOS/O_3 membranes deposited at between 200°C and 400°C. Permeation measurements were carried out at the deposited temperatures of the membranes. H_2/N_2 permeances ratios decreased with decreasing the deposition temperatures between 200°C and 400°C. Both permeances ratio of H_2/N_2 (3.4) and N_2/SF_6 (2.3) through the membrane deposited 400°C were low, and H_2 permeance was high (4.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1}). This result shows that silica was not deposited in the pores of the substrates at 400°C. This can be explained that deactivation of O_3 at 400°C.

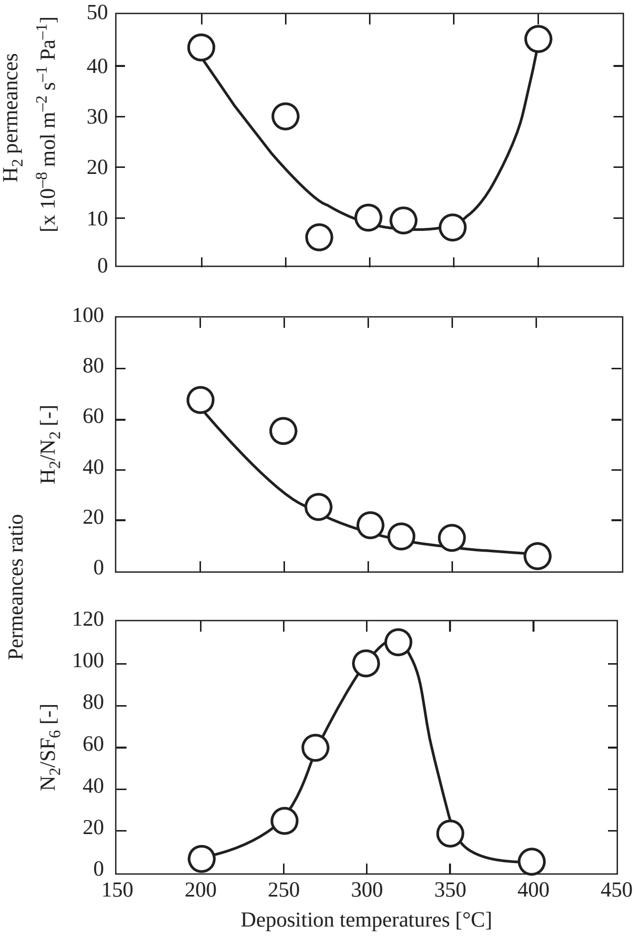


Fig. 6. Single gas permeances through PrTMOS/O_3 membranes by changing deposition temperatures.

Permeances ratios of H_2/N_2 and N_2/SF_6 through the membrane deposited at 200°C were 67 and 4.0, respectively. This membrane was H_2 permselective membrane. Thus, the pore sizes of membrane were estimated at about 0.3 nm by the kinetic diameter of H_2 and N_2. Atomic ratio of the membrane surface deposited at 270°C was measured. Only Si, Al and O were detected at the surface of the membrane, and no carbon was found. Propyl groups of the silica precursor were completely decomposed by O_3 at 270°C. The O_3 concentration at the outlet of the membrane module increased with decreasing deposition temperatures. The deposited membrane below 270°C might be a silica membrane with H_2 permselectivity.

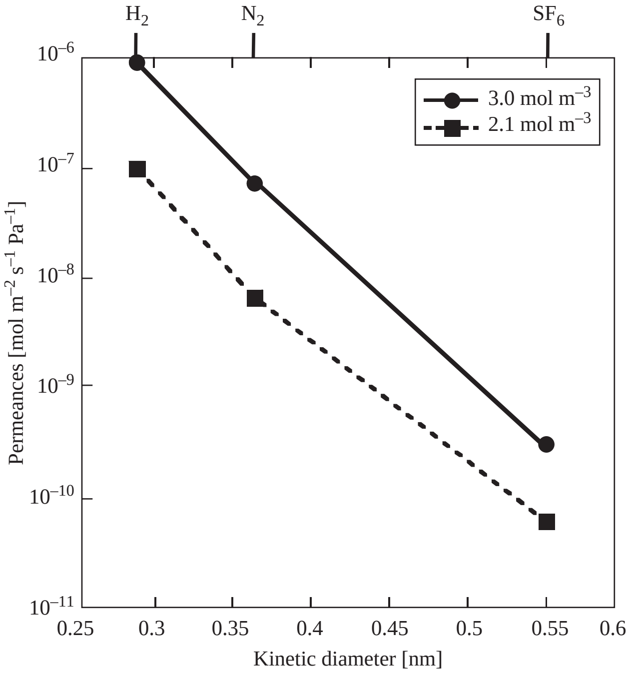


Fig. 7. Effects of O_3 concentrations on the membrane properties (deposition temperature: 320°C).

N_2/SF_6 permeances ratios increased with increasing the deposition temperatures till 320°C deposition. N_2/SF_6 permeances ratio shows the maximum value (110) at 320°C of the deposition. This value is much larger than that of Knudsen diffusion ($N_2/SF_6 = 2.3$). Pore sizes of the membrane deposited at 320°C were controlled at about 0.5 nm. According to the TG measurement of PrTMOS powders (shown in Fig. 3), decomposition of propyl groups on SiO_2 is started at about 300°C. N_2 permselective membranes were obtained from deposition at the decomposition temperatures of propyl groups. Atomic ratio of the membrane deposited at 320°C was measured. Carbon was slightly found on the surface. Propyl groups of the silica precursor must be decomposed at around 320°C during the deposition.

3.4. Effects of O_3 concentrations on the PrTMOS/O_3 membrane properties

Fig. 7 shows that single gas permeances of H_2, N_2 and SF_6 through the PrTMOS/O_3 membrane deposited at 320°C. O_3 concentrations of the inlet of the membrane module were changed from 2.1 to 3.0 mol m^{-3}. H_2 permeances and N_2/SF_6 permeances ratio through the membrane deposited at 2.1 mol m^{-3} of O_3 concentration were 9.8×10^{-8} mol m^{-2} s^{-1} Pa^{-1} and 110, respectively. Those through the membrane deposited at 3.0 mol m^{-3} of O_3 concentration were 9.1×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and 240, respectively. H_2 permeance for 3.0 mol m^{-3} of ozone concentration was about 10 times larger than that for 2.1 mol m^{-3} of O_3 concentration, while N_2/SF_6 permeances ratios were kept at the higher values. This is explained that effective membrane thickness deposited at 3.0 mol m^{-3} of O_3 concentration was thinner than that of the membrane deposited at 2.1 mol m^{-3} of O_3 concentration.

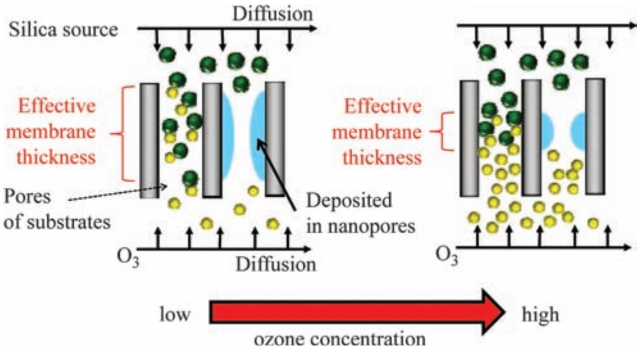


Fig. 8. A schematic diagram of the deposition mechanism by changing O_3 concentrations.

Fig. 8 shows a schematic diagram of the deposition mechanism by changing the O_3 concentrations. Each precursor meets in the pores of the substrate and the reaction occurs in the pores of the substrate. Effective membrane thickness should decrease by increasing O_3 concentrations in the pores.

4. Conclusions

Effects of deposition temperatures were investigated to control pore sizes of the PrTMOS/O_3 membrane. N_2/SF_6 permeances ratio increased with increasing the deposition temperatures. N_2 permselective membrane (N_2/SF_6 = 110) was successfully obtained at 320°C of deposition. Pore sizes of the membrane deposited at 320°C were controlled at about 0.5 nm. O_3 concentration is important parameter to obtain a thin membrane. H_2 permeances and N_2/SF_6 permeances ratio through the PrTMOS/O_3 membrane deposited at 3.0 mol m^{-3} of O_3 concentration were 9.1×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and 240, respectively. H_2 permeance was about 10 times larger by increasing O_3 concentrations from 2.1 to 3.0 mol m^{-3}. Decomposition phenomena of propyl groups on silica materials were investigated by using TG and IR measurement. Propyl groups on silica were decomposed at about 300°C to remain methyl groups.

References

[1] B.N. Nair, T. Okubo and S. Nakao, Membrane, 25 (2000) 73–85.

[2] Y. Yoshino, T. Suzuki, B.N. Nair, H. Taguchi and N. Itoh, J. Membr. Sci., 267 (2005) 8–17.

[3] M. Kanezasi and M. Asaeda, J. Membr. Sci., 271 (2006) 86–93.

[4] G.R. Gavalas, C.E. Megiris and S.-W. Nam, Chem. Eng. Sci., 44 (1989) 1829–1835.

[5] S. Morooka, S.-C. Yan, K. Kusakabe and Y. Akiyama, J. Membr. Sci., 101 (1995) 89–98.

[6] A.K. Prabhu and S.T. Oyama, J. Membr. Sci., 176 (2000) 233–248.

[7] M. Nomura, T. Yamaguchi, I. Kumakiri and S. Nakao, Membrane, 26 (2001) 124–133.

[8] S. Kurungot, T. Yamaguchi and S. Nakao, Catal. Lett., 86 (2003) 270–278.

[9] T. Tsuru, K. Yamaguchi, T. Yoshioka and M. Asaeda, AIChE J., 50 (2004) 2794–2805.

[10] M. Nomura, H. Aida, K. Nakatani, S. Gopalakrishnan, T. Sugawara, S. Nakao, M. Seshimo, T. Ishikawa and M. Kawamura, Ind. Eng. Chem. Res., 45 (2006) 3950–3954.

[11] N.K. Raman and C.J. Brinker, J. Membr. Sci., 105 (1995) 273–279.

[12] M. Nomura, K. Ono, S. Gopalakrishnan, T. Sugawara and S. Nakao, J. Membr. Sci., 251 (2005) 151–181.

[13] B.K, Sea, K. Kusakabe and S. Morooka, J. Membr. Sci., 130 (1997) 41–52.

[14] M. Nomura, T. Nagayo and K. Monma, J. Chem. Eng. Jpn, 40 (2007) 1235–1241.