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Abstract

Organosilica membranes for gas separation were prepared by plasma-enhanced chemical vapor deposition (PECVD) using three different types of silicon precursors: hexamethyldisiloxane (HMDSO), trimethylmethoxysilane (TMMOS), and methyltrimethoxysilane (MTMOS). Based on gas permeation measurement, the MTMOS-derived membrane showed the highest He/N₂ selectivity, followed by the TMMOS-derived and HMDSO-derived membranes. FT-IR characterization indicated that the HMDSO-derived membrane had the highest content of methyl group and the lowest Si-O-Si, while the methyl group content for the MTMOS-derived membrane was the lowest and Si-O-Si was the highest. These results suggest that the pore size of organosilica membranes could be tuned by changing the chemical structure of the silicon precursor. The MTMOS-derived membrane was further heat-treated to determine the effect of thermal annealing on gas-permeation properties. The gas permeances were drastically improved by the thermal annealing. After heat-treatment at 500°C, the membrane showed a high H₂ permeance of 6.5×10^{-7} mol/(m² s Pa) with a H₂/SF₆ selectivity of 410 at 200°C, and 5.6×10^{-7} mol/(m² s Pa) with a H₂/SF₆ selectivity of 360 at 50°C.

Keywords: Plasma-enhanced chemical vapor deposition; Organosilica membrane; Gas separation; Pore size control

Introduction

Amorphous silica has received considerable interest as a material for microporous inorganic membranes. Because of the small pore openings that result from the siloxane-bond networks, amorphous silica

membranes are capable of separating H_2 molecules by size sieving.^[1-5] Moreover, amorphous silica membranes are generally more stable than conventional organic polymer membranes, and thus can be applied to the separation processes which are required to be operated at higher temperatures and/or in a chemically harsh environment, such as hydrogen separation,^[1, 2] pervaporation dehydration,^[3] and membrane reactor applications.^[4-6] In addition, the size tuning of membrane pores has recently been achieved by, for example, introducing organo-functional groups into siloxane-bond networks.^[7, 8] Such organosilica membranes are reported to have a loose structure with a larger pore-size compared with pure silica membranes, and therefore, usually exhibit higher permeability.^[9, 10] Organosilica membranes are demonstrated to be promising for various separation applications such as carbon dioxide separation,^[11] purification of hydrocarbons,^[12] reverse osmotic water production,^[13, 14] and nanofiltration in organic solvents.^[15]

For the fabrication of both amorphous silica and organosilica membranes, chemical vapor deposition (CVD)^[1, 5] and sol-gel^[2-4, 6-15] have been the methods of choice for many years. As an alternative to the conventional approach, siloxane-based membranes have been fabricated by means of plasma polymerization or plasma-enhanced chemical vapor deposition (PECVD) and are reported in the literature.^[16-18] This deposition technique involves a series of gas phase and surface reactions of volatile precursors induced by plasma discharge to deposit a separation active layer on the surface of support materials. Because of the high reactivity of the species in the plasma, the resulting membranes usually have a highly cross-linked structure that is attractive for molecular separation.^[16, 17] Moreover, compared with conventional CVD and sol-gel methods operated at 500-600°C, PECVD offers a lower processing temperature, even at room temperature, so that it can be applied to the deposition of siloxane-based membranes not only on ceramic supports but on temperature-sensitive polymer supports.^[19-21] In addition, although the deposition processes are operated at low temperatures, the PECVD-derived membranes are found to be stable at high temperatures due to their highly cross-linked structure.

Several research groups have reported the preparation of siloxane-based membranes via PECVD by using silicon precursors such as hexamethyldisiloxane (HMDSO) and octamethylcyclotetrasiloxane (OMCTS).^[17-20] Typical PECVD-derived siloxane-based membranes have shown only a moderate selectivity (e.g. H_2/N_2 selectivity of <10 at 25°C),^[19] probably because of a high content of the remaining organo functional groups in the plasma deposited layer, which makes the structure of the membrane to become flexible and loose. In order to improve the selectivity of PECVD-derived membranes, in our previous work, a 2-step PECVD sequence, which involves HMDSO/Ar-PECVD followed by HMDSO/O₂-PECVD, was proposed.^[22, 23] The

2-step PECVD-derived membranes showed a high He/N₂ selectivity of several thousands probably due to the conversion of the top layer from an organo-rich structure to a rigid silica-like structure in the second HMDSO/O₂-PECVD step. Those results suggested that gas permselectivity of PECVD-derived siloxane-based membranes could be tuned by controlling the content of organo functional groups such as methyl groups. In our previous work, the content of organo functional groups in the PECVD-derived membranes were successfully controlled via the oxidative reactions during the second HMDSO/O₂-PECVD.^[23] Another possible method to control the content of organo functional groups and improve the permeation characteristics of plasma-deposited membranes is to use the silicon precursors with different chemical structure.

In this work, organosilica membranes were prepared by using three different organosilanes as silicon precursors with different O/Si atomic ratios and different molecular structure: hexamethyldisiloxane (HMDSO), trimethylmethoxysilane (TMMOS), and methyltrimethoxysilane (MTMOS). We investigated the effect of the molecular structures of the silicon precursors on the gas permeation properties, focusing particularly on the effect of the atomic ratio of oxygen to silicon in the precursors. The chemical structures of the resulting films were determined by FTIR analysis and discussed together with single gas permeation results in order to reveal the effect of the precursor species on the membrane structure and the gas permeation properties. In order to achieve further improvement of gas permeation properties of PECVD membranes, thermal annealing of the membranes was conducted. The effect of the thermal annealing temperature and the gas permeation properties at high temperatures are also discussed.

Experimental

Organosilica membranes were fabricated according to the previously reported method with some modifications.^[22-24] Briefly, a porous α -alumina capillary tube (average pore size, 150 nm; outer diameter, 3 mm; length, 50 mm; kindly supplied by NOK, Corp.) was used as a supporting substrate. Prior to the plasma-deposition of organosilica layers, intermediate layers were prepared on the porous α -alumina supports via a sol-gel method. The procedure for the preparation of intermediate layers was as follows. First, a TiO₂ sol solution was coated onto the surface of a porous support, and the support was fired at 550°C for 15 min to form a TiO₂ intermediate layer. Subsequently, a SiO₂-ZrO₂ (Si/Zr = 1/1) sol was coated onto the TiO₂ intermediate layer and fired at 550°C to form a SiO₂-ZrO₂ intermediate layer. The pore size distributions of the intermediate layers were evaluated by the nanoporimetry technique.^[25] The average pore size of the substrates with the SiO₂-ZrO₂ intermediate layer, which was defined at 50% of dimensionless permeability,

was approximately 1 nm.

Organosilica layers were then deposited onto the intermediate layers by means of PECVD. A schematic diagram of the experimental setup is shown in Figure 1. A radio frequency (RF) plasma reactor (SAMCO Inc., Japan) consisted of a quartz tube surrounded by a RF coil. The substrate was placed 5 cm downstream from the RF coil, and both the retentate and the permeate of the substrate were connected to each vacuum system. The silicon precursors were introduced to the reactor at a fixed flow rate of 1 sccm. In the present study, three different organosilicons, HMDSO, TMMOS and MTMOS, as shown in Figure 2, were employed as silicon precursors. Argon, as the working gas, was also fed to the reactor at fixed flow rate of 10 sccm. A plasma was produced at room temperature using a 13.56 MHz RF generator (AX-300III, AD-TEC, Japan) with a RF power of 30 W. During the deposition, the pressure inside the reactor was maintained at approximately 150 Pa. The chemical structures of plasma-deposited films were determined by Fourier transform infrared spectroscopy (FT/IR-4100, JASCO, Japan). The film samples were prepared on silicon wafer under the same deposition conditions used for the membrane preparation.

---(Figure 1)---

Figure 1. Schematic diagram of the PECVD experimental setup.

---(Figure 2)---

Figure 2. Molecular structures of hexamethyldisiloxane (HMDSO), trimethylmethoxysilane (TMMOS), and methyltrimethoxysilane (MTMOS).

The gas permeation properties of the PECVD-derived organosilica membranes were evaluated using the same apparatus as that used for the plasma-deposition. The gas permeances for He (kinetic diameter, $d_i = 0.26$ nm), H_2 (0.289 nm), N_2 (0.364 nm), and SF_6 (0.55 nm) were measured using the constant-volume variable-pressure method with a constant feed pressure, p_1 , of 105 kPa. The permeate was vacuumed to 10 Pa prior to measurement, and the pressure in the permeate, p_2 , was measured with a pressure transducer (MKS Baratron type 722A). The fixed volume of the permeate side, V_2 , including the glass balloon, was 5.05×10^{-4} m³. By measuring the time course of the pressure in the permeate, the single gas permeance, P , was determined from the following equation:

$$P = \frac{V_2}{ART} \frac{1}{(p_1 - p_2)} \frac{dp_2}{dt} \quad (1)$$

where A is the surface area of the membrane, R is the gas constant, and T is the temperature of gas balloon. Since the feed pressure, p_1 , was constant, Eq. (1) can be integrated as follows:

$$P = \frac{V_2}{ART\Delta t} \ln \frac{(p_1 - p_{2,1})}{(p_1 - p_{2,2})} \quad (2)$$

where $p_{2,1}$ and $p_{2,2}$ were the permeate pressure at $t = 0$ and $t = \Delta t$, respectively.

Results and discussion

FTIR analysis

Figure 3 shows the Fourier transform infrared (FTIR) spectra of the plasma-deposited films derived from HMDSO, TMMOS, and MTMOS. The most intense absorption band peaked at around 1040 cm^{-1} in the FTIR spectrum of the HMDSO film was assigned to the asymmetric stretching vibrations related to Si-O-Si bonding. The absorption peaks located at 1410 and 1260 cm^{-1} were, respectively, from the asymmetric and symmetric CH_3 bending vibrations in $\text{Si}(\text{CH}_3)_x$,^[26] and that at 1460 cm^{-1} was from the bending vibration of methylene (CH_2) groups. The absorption peaks at $870\text{-}750\text{ cm}^{-1}$ were assigned to the rocking vibrations of CH_3 .^[26] More specifically, the peak located at 840 cm^{-1} was from $\text{Si}(\text{CH}_3)_3$, and that at 800 cm^{-1} was from $\text{Si}(\text{CH}_3)_2$. The peaks at around $3000\text{-}2800\text{ cm}^{-1}$ were due to the stretching vibrations of the saturated C-H bonds.^[27] In particular, the asymmetric and symmetric C-H₃ stretching vibrations at 2960 and 2900 cm^{-1} , respectively, could be identified in the spectrum of the HMDSO film. A broad band located at 2150 cm^{-1} corresponded to the stretching vibrations of Si-H, which is often found in plasma-deposited siloxane-based films.^[28] The absorption peak for Si-OH groups at 900 cm^{-1} was also observed. A substantial level of absorption intensity for the $\text{Si}(\text{CH}_3)_2$ structure (800 cm^{-1}), which does not exist in the HMDSO monomer structure, indicated that the plasma-deposited HMDSO-film was mainly composed of the dimethyl-siloxane backbone formed in the plasma-induced cationic polymerization.^[29] A weak peak at 1350 cm^{-1} might be ascribed to the CH_2 scissoring and wagging vibrations in Si-CH₂-Si.^[30] The signal for Si-CH₂-Si at 1350 cm^{-1} was reported to be very weak, and was usually observed with a much stronger absorption due to the wagging vibrations of CH_2 at around 1060 cm^{-1} .^[30] However, this signal was not determined in the spectrum of HMDSO-film because it overlapped with the absorption band of Si-O-Si asymmetric stretching. By comparison with the intensities of peaks at 1350 and 1060 cm^{-1} in an oxygen-free silazane polymer spectrum reported in the literature,^[30] although the intensity of the peak at 1350 cm^{-1} in the HMDSO-film was very small, it was a significant indication of the existence of the Si-CH₂-Si structure. The presence of the Si-CH₂-Si structure indicated that the cross-linking via Si-CH₂-Si contributed as a part of the film deposition in the HMDSO/Ar-PECVD.

---(Figure 3)---

Figure 3. FTIR spectrum of plasma-deposited films prepared using (a) HMDSO, (b) TMMOS, and (c) MTMOS. The spectra are normalized to the maximum absorption peak height and shifted vertically.

Compared with the HMDSO-film, the FTIR spectrum of the TMMOS-film showed some new characteristic peaks in addition to all the peaks observed in the HMDSO-film. New peaks at 2840 and 1190 cm^{-1} corresponded, respectively, to the C-H stretching and the Si-O-C stretching from the methoxy groups.^[31] A high-wavenumber shoulder at around 1100 cm^{-1} on the signal of Si-O-Si asymmetric stretching was also observed. When compared with the spectra of the HMDSO and TMMOS-films, the FTIR spectrum of MTMOS-film showed a decreased in the intensity of the peaks related to $\text{Si}(\text{CH}_3)_x$ at 1260 and 800 cm^{-1} , which indicated a lower carbon content. Furthermore, the peak location of the absorption band for Si-O-Si asymmetric stretching was shifted to a higher wavenumber at 1080 cm^{-1} .

The absorption band of the Si-O-Si asymmetric stretching is known to vary according to the structure of the siloxane networks.^[28] As the siloxane chain become longer or branched, the absorption band become broader. Furthermore, the peak location of the Si-O-Si asymmetric stretching mode is related to the bonding nature such as bond angle and length. In general, the smaller the bond angle, the lower the peak

wavenumber. For example, the peak centered at around 1023 cm^{-1} belongs to the linear siloxanes and various types of suboxidized siloxane networks such as a long polymeric chain, a ring structure, or more random ones, which have a Si-O-Si bond angles smaller than 144° . The peak located at around 1070 cm^{-1} can be assigned to a Si-O-Si ring formation and/or network structure, which has a bond angle nearly equal to 144° , and that at 1125 cm^{-1} is Si-O-Si cage structure, which has a bond angle of approximately 150° .^[28] The peaks located at $1020\text{-}1060\text{ cm}^{-1}$ and at $1060\text{-}1080\text{ cm}^{-1}$ are typically identified as Si-O-Si chains and Si-O-Si ring formations, respectively. Accordingly, the high-wavenumber shoulder and/or the peak shift to a higher wavenumber in the Si-O-Si signal indicates the presence of a siloxane ring- and/or cage-type structures.

The adsorption band corresponding to Si-O-Si related bonds between 1000 and 1150 cm^{-1} can be separated by applying a Gaussian distribution fitting. The baseline assumed to be linear and tangent to the sides of the adsorption band. Figure 4 (a) shows the deconvolution of the Si-O-Si asymmetric stretching band of the film derived from HMDSO. The absorption band was separated into three peaks. The dominant peak centered at 1043 cm^{-1} was assigned to the Si-O-Si chain structure, and the two minor peaks at 1112 and 1090 cm^{-1} were due to cage- and ring-type structures, respectively. For the TMMOS-film, as shown in Figure 4 (b), the peak assigned to the Si-O-Si chains was still dominant, but the cage- and ring-type structures become more abundant. In the MTMOS-film, the contribution of the Si-O-Si chain structure decreased relatively, and the Si-O-Si cage structure was dominant.^[26, 27]

---(Figure 4)---

Figure 4. Deconvolution of the Si-O-Si asymmetric stretching band of the film prepared using (a) HMDSO, (b) TMMOS, and (c) MTMOS.

In order to compare the effect of precursors on the film structure, as shown in Figure 5, the ratio of the area of the deconvoluted peak assigned to the Si-O-Si cage structure to the total absorption band of the Si-O-Si asymmetric stretching mode including linear, ring and cage structures (Si-O-Si cage/ Si-O-Si) for plasma-deposited films was plotted as a function of the O/Si atomic ratio of precursor. The Si-O-Si cage/Si-O-Si absorbance ratio appeared to increase with an increase in the O/Si atomic ratio of the precursors. The Si-O-Si cage/Si-O-Si absorbance ratios for the films prepared using HMDSO, TMMOS and MTMOS were 0.03, 0.19, and 0.62, respectively. In contrast, the absorbance area ratio of the bands assigned to the symmetric CH₃ bending vibrations in the Si-CH₃ group at 1260 cm⁻¹ to the asymmetric stretching vibrations of the Si-O-Si bond at 1000-1150 cm⁻¹ (Si-CH₃/Si-O-Si) for plasma-deposited films decreased when the O/Si atomic ratio of the precursor increased. The Si-CH₃/Si-O-Si absorbance ratio for the films prepared using HMDSO, TMMOS and MTMOS were 0.12, 0.09, and 0.05, respectively.

---(Figure 5)---

Figure 5. The peak height ratio of Si-CH₃ and Si-O-Si cage/Si-O-Si peak height ratio for plasma-deposited films as a function of the O/Si atomic ratio of the precursor molecules.

FTIR analysis indicated that the plasma-deposited HMDSO-film was composed of linear dimethylsiloxane chains with a structure that partially cross-linked with the Si-CH₂-Si bridges, and was found

to be the most organic “silicone-like” structure of the three films studied. Regarding the plasma-deposited TMMOS-film, although the FTIR spectrum showed a peak pattern that was similar to that of the HMDSO-film, the broader Si-O-Si absorption bands of the TMMOS-film suggested that siloxane networks were more branched and denser. The MTMOS-film, on the other hand, had the most inorganic “silica-like” structure with rigid micropores that resulted from low carbon content and an abundance of Si-O-Si cage type structures. FTIR analysis revealed that the chemical structure of plasma-deposited films shifted from an organic “silicone-like” structure to an inorganic “silica-like” structure when the O/Si atomic ratio of the precursor was increased. Therefore, the chemical structure of plasma-deposited films could be controlled by changing the chemical structure of the silicone precursor.

The plasma-deposited films were further heat-treated in a furnace at 550°C under a N₂ atmosphere in order to investigate the thermal stability of the materials. Figure 6 shows the FTIR spectra for the heat-treated films together with those of the as-deposited films. In the case of the HMDSO-film, as shown in Figure 6 (a), the absorbance for Si-O-Si stretching at around 1040 cm⁻¹, symmetric CH₃ bending vibration in Si(CH₃)_x at 1260 cm⁻¹, and C-H₃ stretching vibrations at 2960 and 2900 cm⁻¹ decreased by half after the heat-treatment at 550°C probably due to the thermal decomposition of the plasma-deposited HMDSO-film. On the other hand, in the case of the MTMOS-film, as shown in Figure 6 (b), the absorbance for Si-O-Si stretching only decreased 8%, suggesting that the MTMOS-film possessed a higher thermal stability than the HMDSO-film. This difference can be explained by the different chemical structures of the two films. As discussed previously, the chemical structures of the films shifted from organic “silicone-like” structures to inorganic “silica-like” structures with increases in the O/Si atomic ratio of the precursor. The higher thermal stability of the MTMOS-film could thus be attributed to its inorganic “silica-like” structure with highly cross-linked siloxane-based networks.

---(Figure 6)---

Figure 6. Effect of thermal annealing at 550°C on the FTIR spectrum of plasma-deposited films prepared using (a) HMDSO and (b) MTMOS. The spectra are normalized to the maximum absorption peak height of as-deposited films and shifted vertically.

Gas permeation characteristics

Figure 7 (a)-(c) shows the deposition time course of single gas permeances at room temperature for three membranes prepared using different silicon precursors, and Figure 7 (d)-(f) shows the corresponding permeance ratios. As shown in Figure 7 (a), for the HMDSO-derived membrane, the single gas permeances of He, H₂ and N₂ decreased significantly at the beginning and reached a plateau at 5 min of deposition, while that of larger molecules, namely the permeance of SF₆, continued to decrease moderately with time. The decrease in the single gas permeance during the first 5 min can be ascribed to the blockage of the pores in the intermediate layer, showing a rapid formation of the plasma-deposited layer on the intermediate layer. The subsequent decrement of the SF₆ permeance can be ascribed to the filling of a few remaining pinholes. The permeances of He and H₂ decreased by approximately two order of magnitude after the deposition, while those of N₂ and SF₆ decreased one or two orders of magnitude more than those of He and H₂. The decreases in single gas permeance during deposition were likely to vary with the molecular size of the permeating species.

The permeance ratios for He/N₂ and He/SF₆, as shown in Figure 7 (d), increased with time and reached steady values of 7.1 and 200, respectively. The observed permeance ratios of He/N₂ and He/SF₆ exceeded those expected from the Knudsen diffusion mechanism (2.64 for He/N₂ and 6.04 for He/SF₆). These results clearly indicate that the HMDSO-derived membrane possessed a molecular sieving characteristic. It should be also noted that, for the case of HMDSO-derived membrane, the permeance ratio of He/H₂ was exactly the same as the Knudsen ratio of 0.71, and was unchanged during deposition. This indicates that the permeation of He and H₂ were unaffected by the molecular sieving effect of the plasma-deposited layer. The membrane prepared using TMMOS as a silicon precursor showed a similar time dependency of single gas permeances (Figure 7 (b)) with slightly higher permeance ratios compared with those observed for the HMDSO-derived membrane (Figure 7 (e)). The maximum values of the permeance ratios of He/N₂ and He/SF₆ for the TMMOS-derived membranes were 7.8 and 260, respectively. For the membrane prepared using MTMOS as a silicon precursor, the time dependency of single gas permeances showed a similar tendency (Figure 7 (c)). The permselective characteristics, however, were different from the former two membranes (Figure 7 (f)). The MTMOS-derived membrane exhibited a He/N₂ permeance ratio of 15, which was almost twice that of the HMDSO-derived membrane, indicating that the MTMOS-derived membrane had a pronounced molecular sieving characteristic. Moreover, the permeance ratio of He/H₂ for the MTMOS-derived membrane was determined to be 0.91, which was higher than the Knudsen value (0.71). An increased permeance ratio for helium, the smallest molecule, to larger ones such as H₂ and N₂, suggests that the pore size of the plasma-deposited layer of the MTMOS membrane was very small, so that the molecular sieving effect became dominant even for the permeation of these small gases. However, the permeance ratio of He/SF₆ was diminished to less than 100, suggesting that defects such as pinholes still existed in the membrane.

---(Figure 7)---

Figure 7. Single gas permeances and permeance ratios at room temperature for the membranes prepared using HMDSO, TMMOS and MTMOS as a function of plasma-deposition time.

Figure 8 (a) shows the kinetic diameter dependency of the single gas permeances at room temperature for the membranes prepared using HMDSO, TMMOS, and MTMOS with plasma-deposition time of 20 min. The kinetic diameter dependencies of the relative permeances normalized by He permeance are also represented in Figure 8 (b). The HMDSO-derived membrane showed the highest He permeance, followed by the TMMOS-derived and MTMOS-derived membranes. The He/N₂ permeance ratio for the TMMOS-derived membrane was 7.7, and was nearly the same as that for the HMDSO-derived membrane. In contrast, the He/N₂ permeance ratio for MTMOS-derived membranes was 15, which was more than twice that of the HMDSO-derived membrane, suggesting that the MTMOS-derived membrane had smaller pore sizes than the HMDSO-derived membrane. These results suggest that the gas permeation characteristics of plasma-deposited membranes might be controlled by changing the species of the precursors.

---(Figure 8)---

Figure 8. Kinetic diameter dependence of single gas permeances for the membranes prepared using HMDSO, TMMOS, and MTMOS.

To understand the effect of the chemical structure of precursors on the gas permeation characteristics of PECVD-derived membranes, the permeance ratios of He/H₂, He/N₂ and He/SF₆ obtained from the gas permeation measurements were plotted against the oxygen-to-silicon atomic ratio (O/Si) of the precursors, as shown in Figure 9. It is noted that O/Si ratios of 0.5, 1 and 3 correspond to HMDSO, TMMOS, and MTMOS, respectively. The He/H₂ and He/N₂ permeance ratios increased with an increase in the O/Si atomic ratio of the precursors, suggesting that the size of those silica networks, which are effective for the permeation of small gas molecules, was decreased with an increase in the O/Si atomic ratio of the precursors. On the other hand, the He/SF₆ permeance ratio seemed independent of the O/Si ratio because the permeation of large gas molecules such as SF₆ took place through large pores such as pinholes. These results indicate that a precursor with a higher O/Si atomic ratio provides a separation active layer, which has an inorganic “silica-like” structure, with a higher permselectivity.

---(Figure 9)---

Figure 9. Effect of the O/Si atomic ratio of the precursor on the permeance ratios of plasma-deposited organosilica membranes.

Thermal annealing of the MTMOS membrane

According to the FTIR analysis, the plasma-deposited film prepared using MTMOS was found to be stable to at least 550°C. In this section, therefore, a heat-treatment of the plasma-deposited MTMOS membrane was conducted in order to determine the effects of heat-treatment on the gas permeation properties. The heat-treatment procedure was as follows. First, the single gas permeances of He, N₂ and SF₆ were measured at 50°C. The membrane was then heated at 200°C under a N₂ flow for 1 hour. The membrane was cooled to 50°C, and the single gas permeances at 50°C were measured again. Likewise, the membrane was heat-treated at 300, 400, and 500°C for 1 h followed by single gas permeances measurements at 50°C. The maximum treatment temperature was set to be 500°C in order to avoid the thermal transformation of SiO₂-ZrO₂ intermediated layer, whose firing temperature was 550°C.

In Figure 10, the single gas permeances of He, N₂ and SF₆ at 50°C before and after heat-treatment are plotted as a function of the heat-treatment temperatures. The permeances of He and N₂ increased gradually with heat-treatment temperatures of up to 300°C. In contrast, the permeance of SF₆ was unchanged in this temperature range. The permeance ratio for He/N₂ decreased from 17.4 to 8.2, while the permeance ratios for He/SF₆ and N₂/SF₆ increased from 93 to 200 and 5.3 to 24.5, respectively, after a heat-treatment temperature at 300°C. Those results suggested that micropores in which both He and N₂ could permeate but SF₆ could not, were formed during the heat-treatment in this temperature range. Since the permeation of SF₆ takes place via large pores such as pinholes, the unchanged SF₆ permeance suggests that no additional pinholes were formed, and that the plasma-deposited layer itself was not affected by the heat-treatment at this temperature range. The increases in He and N₂ permeances should, therefore, probably be ascribed to the desorption of small molecules such as unreacted monomers, and/or their oligomers, that were adsorbed onto the plasma-deposited layer.^[21] Subsequently, when the membranes were heat-treated at 400 and 500°C, the permeances for all types of gases increased more rapidly than during 200 and 300°C-treatments. These increases in permeance were due to the thermal decomposition of the plasma-deposited layer, which led to a decrease in the thickness of the top layer. However, although the heat-treatment temperature was substantially high compared with the plasma-deposition temperature, the membrane after heat-treatment still exhibited the gas permeation selectivity. While the permeance ratio for He/N₂ decreased to 3.3, the permeance ratio for He/SF₆ remained above 200 even after the treatment at 500°C. More surprisingly, the permeance ratio for N₂/SF₆ increased to 60 after the treatment at 500°C, suggesting that silica networks with larger pore sizes were formed during the heat-treatment at 400-500°C. Those networks are suitable for the separation of large molecules, such as SF₆, from smaller molecules. The change in the silica network structure in this temperature range was probably due to the thermal degradation of methyl groups in the plasma-deposited layer. These results demonstrate the superior thermal stability of room-temperature-fabricated MTMOS-derived membranes. It is also noteworthy that heat-treatment at high temperature could be a way to modify the porous structure of plasma-deposited organosilica membranes.

---(Figure 10)---

Figure 10. Effect of heat-treatment temperature on the permeances at 50°C of the MTMOS-derived membrane.

Temperature dependency of gas permeances

Figure 11 (a) shows the temperature dependency of single gas permeance for the MTMOS-derived membrane heat-treated at 200°C. The permeances of He, H_2 and N_2 increased with temperature, while the permeance of SF_6 was independent of temperature. The activation energies, $E_{P,i}$, of permeation were obtained by fitting the experimental permeance, P_i , to a modified gas translation model^[32-34]

$$P_i = \frac{k_{0,i}}{\sqrt{M_i RT}} \exp\left(-\frac{E_{P,i}}{RT}\right)$$

where $k_{0,i}$ is the pre-exponential factor, M_i is the molecular weight, R is the gas constant, and T is the absolute temperature. The observed activation energies of permeation for He, H₂, N₂, and SF₆ were 11.4, 10.3, 9.9, and 2.1 kJ/mol, respectively. The permeation mechanism for He, H₂, and N₂ can be classified as an activated diffusion, and that for SF₆ can be characterized as Knudsen diffusion. In microporous membranes, the activated diffusion occurs when the pore size becomes as small as the size of the permeating molecules. The permeating molecules are restricted in their movement due to the effect of the pore wall, and must overcome certain energy barriers in order to permeate through the pores. In contrast, Knudsen diffusion takes place in larger pores where the pore sizes are comparable to, or smaller than, the mean free path of the permeating molecules. Therefore, considering the size of the molecules tested, these results indicate that the permeation of small molecules occurred mainly through the plasma-deposited MTMOS-derived organosilica networks where the pore sizes were as small as the sizes of the permeating molecules, and that of large molecules such as SF₆ took place through the large pores such as pinholes.

---(Figure 11)---

Figure 11. Temperature dependency of permeances for the MTMOS membrane heat-treated at (a) 200°C, and (b) 500°C.

Figure 11 (b) shows the temperature dependency of single gas permeance for the MTMOS-derived membrane, which had been further heat-treated at 500°C. The permeance of He showed a slight increase with temperature, while those of H₂, N₂ and SF₆ were almost independent of temperature. The observed activation energies of permeation for He, H₂, N₂, and SF₆ were 5.5, 3.4, 1.5, and 0.8 kJ/mol, respectively. The activation energy of permeation for all gases decreased compared with those in the membrane treated at 200°C, suggesting that the network structure was loosened. Again, this was due to the thermal decomposition methyl groups in the plasma-deposited layer during the heat treatment at 400-500°C, which resulted in the formation of silica networks with larger pore size compared with as-deposited or the 200°C-treated membranes. This allowed the molecules to permeate the membrane more easily, and thus the activation energy of permeation became smaller. It was noteworthy that the MTMOS-derived membrane that was treated at 500°C showed a high permeability for H₂. The H₂ permeance was 6.5×10^{-7} mol/(m² s Pa) with a H₂/SF₆ selectivity of 410 at 200°C, and at 50°C, the permeance was 5.6×10^{-7} mol/(m² s Pa) with a H₂/SF₆ selectivity of 360. Thus, it can be concluded that thermal-annealing was effective in improving the gas permeation properties of the plasma-deposited organosilica membranes.

Conclusions

Organosilica membranes for gas separation were prepared by plasma-enhanced chemical vapor deposition (PECVD) using three different silicon precursors with different O/Si atomic ratios: hexamethyldisiloxane (HMDSO), trimethylmethoxysilane (TMMOS), and methyltrimethoxysilane (MTMOS). FTIR analysis revealed that the chemical structure of plasma-deposited films was changed from organic to inorganic when the O/Si atomic ratio was increased. The He/N₂ permeance ratio was highest for the MTMOS-derived membrane. The He/N₂ permeance ratio increased with an increase in the O/Si atomic ratio of the precursors, suggesting that the gas permeation characteristics were dependent on the molecular structure of the precursors. The results showed that the gas permeation characteristics of plasma-deposited organosilica membranes could be controlled by the O/Si atomic ratio of the silicon precursors. The thermal annealing of as-deposited membranes improved the gas permeation properties due to the partial decomposition of organic components. After heat-treatment at 500°C, the MTMOS-derived membrane showed a high H₂ permeance of 6.5×10^{-7} mol/(m² s Pa) with H₂/SF₆ selectivity of 410 at 200°C, and an H₂ permeance of 5.6×10^{-7} mol/(m² s Pa) with H₂/SF₆ selectivity of 360 at 50°C.

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Figure Captions

Figure 1. Schematic diagram of the PECVD experimental setup.

Figure 2. Molecular structures of hexamethyldisiloxane (HMDSO), trimethylmethoxysilane (TMMOS), and methyltrimethoxysilane (MTMOS).

Figure 3. FTIR spectrum of plasma-deposited films prepared using (a) HMDSO, (b) TMMOS, and (c) MTMOS. The spectra are normalized to the maximum absorption peak height and shifted vertically.

Figure 4. Deconvolution of the Si-O-Si asymmetric stretching band of the film prepared using (a) HMDSO, (b) TMMOS, and (c) MTMOS.

Figure 5. The peak height ratio of Si-CH₃ and Si-O-Si cage/Si-O-Si peak height ratio for plasma-deposited films as a function of the O/Si atomic ratio of the precursor molecules.

Figure 6. Effect of thermal annealing at 550°C on the FTIR spectrum of plasma-deposited films prepared using (a) HMDSO and (b) MTMOS. The spectra are normalized to the maximum absorption peak height of as-deposited films and shifted vertically.

Figure 7. Single gas permeances and permeance ratios at room temperature for the membranes prepared using HMDSO, TMMOS and MTMOS as a function of plasma-deposition time.

Figure 8. Kinetic diameter dependence of single gas permeances for the membranes prepared using HMDSO, TMMOS, and MTMOS.

Figure 9. Effect of the O/Si atomic ratio of the precursor on the permeance ratios of plasma-deposited organosilica membranes.

Figure 10. Effect of heat-treatment temperature on the permeances at 50°C of the MTMOS-derived membrane.

Figure 11. Temperature dependency of permeances for the MTMOS membrane heat-treated at (a) 200°C, and (b) 500°C.

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