**High-temperature stability of PECVD-derived organosilica membranes deposited on TiO₂
and SiO₂-ZrO₂ intermediate layers using HMDSO/Arplasma**

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Abstract

Organosilica membranes for gas separation were prepared on porous substrates by means of plasma-enhanced chemical vapor deposition (PECVD) using hexamethyldisiloxane as a precursor. Before the deposition of organosilica membranes, two types of intermediate layers with different pore sizes, a TiO_2 layer ($d_p \approx 5$ nm) and a SiO_2 - ZrO_2 layer (1 nm), were prepared on α -alumina porous supports via a sol-gel method. The stability at high temperatures was evaluated by measuring the gas permeation characteristics before and after heat treatment. PECVD membranes deposited on a SiO_2 - ZrO_2 intermediate layer were found to be more thermally stable than those deposited on a TiO_2 intermediate layer. After the treatment at 500°C , the membranes deposited on a SiO_2 - ZrO_2 intermediate layer had a selectivity of ~ 1040 for He against SF_6 with a He permeance of $1.41 \times 10^{-6} \text{ mol}/(\text{m}^2 \text{ s Pa})$ at 50°C , although the organosilica membranes were prepared at room temperature. On the other hand, the membrane deposited on a TiO_2 intermediate layer became non-selective after heat treatment at 400°C . The temperature dependence of single gas permeance for the membrane deposited on a SiO_2 - ZrO_2 intermediate layer was measured after the high-temperature stability test. The permeation of He, H_2 and N_2 for the 200°C -treated membrane showed an activated diffusion, while those for the 500°C -treated membrane followed a Knudsen permeation, suggesting that heat treatment at 500°C formed pores that allowed the permeation of molecules that were the size of N_2 (0.364 nm) and smaller. In addition, since the permeation of SF_6 for the 500°C -treated membrane showed an activated diffusion, the membrane should have a uniform structure with a small number of pinholes.

1. Introduction

Plasma-enhanced chemical vapor deposition (PECVD) has been recognized as a powerful method for depositing thin-films with uniform and pinhole-free structures [1, 2]. PECVD was first utilized in the semiconductor industry and now is being applied in various industrial fields, including optics, gas barrier, hard coating, and many other applications. The major advantage of PECVD over conventional thin-film formation methods, such as thermal CVD and sol-gel method, is that it allows the fabrication of highly cross-linked films at relatively low temperatures, even at room temperature [3]. Recently, several research groups have demonstrated that organosilicon thin-films deposited by PECVD are promising materials for the preparation of membranes used in gas separation [4-9], pervaporation [10, 11], and vapor permeation [12]. For example, Roualdes *et al.* studied the gas permeation properties of polysiloxane membranes deposited using organosilicon precursors such as hexamethyldisiloxane (HMDSO) onto cellulose ester substrates and found that plasma-deposited membranes had higher selectivity than conventional polysiloxane membranes [6]. Kafrouni *et al.* prepared silicon carbonitride membranes on γ -alumina substrates using hexamethyldisilazane and ammonia as precursors and reported a high He permeance of $10^{-7} \text{ mol}/(\text{m}^2 \text{ s Pa})$ with a He/N₂ selectivity of 50 at 150° [7].

In our previous study, we prepared organosilica membranes with molecular sieving properties by combining the use of the sol-gel-derived nanoporous intermediate layer with the subsequent plasma-deposition of the organosilica top layer [13, 14]. The organosilica membranes deposited using HMDSO as a precursor with argon as a carrier showed a He/N₂ selectivity of 10 at room temperature, which was higher than those reported in the literature for plasma-deposited membranes [7, 9]. In addition, we found that 2-step PECVD, which was the series of plasma-deposition with HMDSO/Ar plasma followed by HMDSO/O₂ plasma, could improve the selectivity of He/N₂ to 7,800. Moreover, although the membranes were prepared at

room temperature, we reported that the membranes prepared by PECVD showed high stability against the exposure to steam at 300°C [13]. However, at temperatures higher than 400°C, the membranes prepared using HMDSO/Ar plasma were found to be unstable [14]. Since the HMDSO/Ar plasma-deposited layer consists of a polysiloxane backbone with hydrocarbon side chains, degradation of the plasma-deposited layer was considered to be due to the same mechanism as in the case of polydimethylsiloxane (PDMS), which was thermally decomposed by depolymerization at temperature ranging from 400-650°C [15, 16].

An improvement in the high-temperature stability of silicone rubber by adding inorganic nanomaterials as filler compounds has been reported. The effect of inorganic fillers such as silica [17], clay [18], and silicon carbide [19] on the thermal stability of silicone rubber has been investigated in detail. Zirconium compounds such as zirconia and zirconium carbide were also considered to be inorganic filler candidates for the improvement of the thermal stability of silicone rubber [20].

Since the chemical structure of the PECVD-derived organosilica membranes are similar to PDMS, such an effect of inorganic nanomaterials shows promise for improvement of the high-temperature stability of PECVD-derived organosilica membranes. Therefore, in the present study, we prepared organosilica membranes on two different porous substrates, which consisted of TiO₂ or SiO₂-ZrO₂ intermediate layers, at room temperature by means of PECVD using HMDSO as a precursor with argon gas as the carrier, and evaluated the high-temperature stability of the membranes. Heat treatment was conducted at temperatures of up to 500°C. The high-temperature stability of the membranes was evaluated based on single gas permeation measurements. Interestingly, in the present study, we found that the high-temperature stability of membranes depended upon which intermediate layers were used for PECVD. The change in the gas permeation properties of the PECVD-derived organosilica membranes after heat treatment at different temperatures was also discussed based on the temperature dependence of gas

87 permeances.

2. Experimental

2.1. Preparation and characterization of intermediate layers

Organosilica membranes were fabricated on porous α -alumina tubular supports (average pore size, 150 nm; outer diameter, 3 mm, length, 50 mm). Prior to the deposition of organosilica layers, intermediate layers were prepared on the porous α -alumina supports via the sol-gel method. In the present study, in order to determine the effect of an intermediate layer on the permeation properties of PECVD-derived organosilica membranes, we prepared two different intermediate layers with different pore sizes; one was a TiO_2 intermediate layer with a pore size of 5 nm and the other was a SiO_2 - ZrO_2 intermediate layer with a pore size of 1 nm which was smaller than that of the TiO_2 intermediate layer [21]. The procedure for the preparation of the intermediate layers was as follows: First, a TiO_2 sol solution was coated on the surface of a porous support, and the support was fired at 550°C for 15 min. These procedures were repeated several times to cover large pores that might have resulted in pinholes in the final membrane. Accordingly, a TiO_2 intermediate layer with pore sizes of several nanometers was obtained. Subsequently, a SiO_2 - ZrO_2 ($\text{Si}/\text{Zr} = 1/1$) sol was coated onto the TiO_2 intermediate layer and fired at 550°C to form a SiO_2 - ZrO_2 intermediate layer with a pore size of approximately 1 nm.

The pore size distributions of the intermediate layers were evaluated using the nanoporometry technique [22, 23]. The basic principle of nanoporometry is based on the capillary condensation of a vapor inside nanopores and on its blocking effect on the permeation of a non-condensable gas. In the present study, the permeance of nitrogen as a non-condensable gas was measured as a function of the vapor pressure of hexane in a mixture of nitrogen and hexane at 25°C. The pore size distribution was obtained by plotting the dimensionless permeances of nitrogen, which were normalized by the permeances under dry conditions, as a function of the Kelvin diameter calculated from the vapor pressure of

hexane. According to our previous study, the pore size, as estimated by nanoporometry, showed a good correlation with the separation performance of membranes having pore sizes as small as 0.6 nm [23].

2.2. Plasma-deposition of organosilica layers

Using the porous substrates consisting of TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers, organosilica layers were deposited onto the intermediate layers by means of PECVD. The schematic diagram of the experimental setup was shown in **Fig. 1**. A radio frequency (RF) plasma reactor (SAMCO Inc., Japan) consisted of a quartz tube surrounded by an 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. Hexamethyldisiloxane (HMDSO), the silica precursor, was introduced to the reactor using argon as the carrier. The feed-flow rate of argon was fixed at 10 sccm with a HMDSO mole fraction of 10%. Plasma was produced at room temperature using a 13.56 MHz RF generator (AX-300III, AD-TEC, Japan) with an RF power of 30 W. During the deposition, the pressure inside the reactor was maintained at around 150 Pa. The deposition rate of organosilica layers under these experimental conditions was determined to be 120 nm/min based on SEM measurement in our previous work [14]. The organosilica films were also deposited onto a silicon wafer. The chemical structure of the PECVD-derived films was characterized using FT-IR spectrometry (JASCO, Japan).

----(Fig. 1)----

Fig. 1. Schematic diagram of the PECVD and gas permeation experimental setup.

2.3. Gas permeation measurement

The gas permeation properties of the PECVD-derived organosilica membranes were evaluated using the same apparatus that was used for the plasma-deposition. The gas permeances were measured using the constant-volume variable-pressure method at room temperature with a constant feed pressure, p_1 , of 105 kPa. The permeate was vacuumed to 10 Pa prior to the measurement, and the pressure in the permeate, p_2 , was measured using a pressure transducer (MKS Baratron). The fixed volume of the permeate side, V_2 , including the glass balloon, was $5.05 \times 10^{-4} \text{ m}^3$. By measuring the time course of the pressure in the permeate, the single gas permeance, P , was determined by using 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.

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.

2.4. High-temperature stability test

The stability of the PECVD-derived organosilica membranes at high temperatures was evaluated by measuring gas permeances at 50°C after heat treatment. First, the gas permeances of He, N₂, and SF₆ were measured at 50°C, and then the membrane was heat-treated at 100°C under an N₂ flow for 1 h. The membrane was cooled to 50°C, and gas permeances of He, N₂, and SF₆ at 50°C were measured again. Likewise, the membrane was heat-treated at 200, 300, 400, and 500°C for 1 h, and then gas permeances were measured at 50°C after heat treatment. It should be noted that we confirmed that gas permeance reached a plateau within less than 20 min of heat-treatment.

3. Results and discussion

3.1. Gas permeance of as-deposited PECVD-derived organosilica membranes

The pore size distributions of TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers were determined by nanoporometry. Fig. 2 shows the typical curves for the dimensionless permeances of nitrogen for TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers, which were normalized by the permeances under dry conditions, as a function of the Kelvin diameter. The average pore sizes of the TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers, defined as the Kelvin diameter at which the dimensionless permeances became 50%, were 5.2 ± 0.3 and 0.9 ± 0.1 nm, respectively. As shown in Fig. 2, the $\text{SiO}_2\text{-ZrO}_2$ intermediate layer had a small average pore size and a narrow pore size distribution compared to the TiO_2 intermediate layer.

---- (Fig. 2) ----

Fig. 2. Dimensionless permeance of nitrogen for TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers as a function of the Kelvin diameter.

Organosilica membranes were deposited onto porous TiO_2 and $\text{SiO}_2\text{-ZrO}_2$

intermediate layers by means of PECVD and were subjected to gas permeation measurement. Hereafter, the PECVD-derived organosilica membranes deposited on TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers will be referred to as “ SiOCH/TiO_2 ” and “ $\text{SiOCH/SiO}_2\text{-ZrO}_2$ ” membranes, respectively. To verify the reproducibility of the membrane preparation, multiple experiments were conducted on multiple samples of both types of membranes: four SiOCH/TiO_2 membranes (denoted as T-1, T-2, T-3, and T-4) and three $\text{SiOCH/SiO}_2\text{-ZrO}_2$ membranes (SZ-1, SZ-2, and SZ-3).

Fig. 3 shows the single gas permeances of He , N_2 and SF_6 at room temperature for PECVD-derived organosilica membranes deposited on either TiO_2 or $\text{SiO}_2\text{-ZrO}_2$ intermediate layers as a function of the plasma-deposition time. As shown in Fig. 3 (a), the He permeances for both SiOCH/TiO_2 and $\text{SiOCH/SiO}_2\text{-ZrO}_2$ membranes greatly decreased by about 2 orders of magnitude within the first 10 min of plasma-deposition, and then reached a steady value on the order of $10^{-8} \text{ mol}/(\text{m}^2 \text{ s Pa})$. The N_2 permeances, as shown in Fig. 3 (b), followed a trend that was similar to those of He permeances, and the steady value for both SiOCH/TiO_2 and $\text{SiOCH/SiO}_2\text{-ZrO}_2$ membranes was found to be approximately $10^{-9} \text{ mol}/(\text{m}^2 \text{ s Pa})$. In contrast, as shown in Fig. 3 (c), the permeances of SF_6 for $\text{SiOCH/SiO}_2\text{-ZrO}_2$ membranes reached a relatively lower steady value compared to those for SiOCH/TiO_2 membranes. The results suggest that the difference in the pore size of the intermediate layer had little impact on the He and N_2 permeances, but had considerable impact on the permeances of large gas molecules such as SF_6 .

This difference in the permeation properties of SiOCH/TiO_2 and $\text{SiOCH/SiO}_2\text{-ZrO}_2$ membranes can be more clearly seen in the permeance/selectivity trade-off relationship. In **Fig. 4**, the He/SF_6 permeance ratios for SiOCH/TiO_2 and $\text{SiOCH/SiO}_2\text{-ZrO}_2$ membranes, with a plasma-deposition time of more than 20 min, were plotted as a function of He permeances. For comparison, the data for TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers were also plotted in the same

figure. In general, gas separation properties of membranes follow the trade-off between permeance and selectivity. The solid line in Fig. 4 shows the trade-off upper bounds for SiOCH/TiO₂ membranes: a maximum He/SF₆ permeance ratio of 95 was obtained at a He permeance of $1.9 \times 10^{-8} \text{ mol}/(\text{m}^2 \text{ s Pa})$ at room temperature. On the other hand, the SiOCH/SiO₂-ZrO₂ membranes showed a significantly higher permselectivity than the SiOCH/TiO₂ membranes. The maximum He/SF₆ permeance ratio for SiOCH/SiO₂-ZrO₂ membranes was 590 with a He permeance of $1.4 \times 10^{-8} \text{ mol}/(\text{m}^2 \text{ s Pa})$. The limitation of He/SF₆ selectivity for SiOCH/TiO₂ membranes can be ascribed to the few remaining defects or uncovered pores. Thus, it is likely that a continuous layer of organosilica was formed in the SiOCH/SiO₂-ZrO₂ membranes, but some uncovered pores, which limits the selectivity, must have remained in the SiOCH/TiO₂ membranes due to a larger pore size and a broader pore size distribution of the TiO₂ intermediate layer.

---- (Fig. 3) ----

Fig. 3. Time courses for gas permeances of (a) He, (b) N₂ and (c) SF₆ at room temperature for PECVD-derived organosilica membranes deposited onto TiO₂(closed symbols) and SiO₂-ZrO₂ intermediate layers (open symbols) as a function of plasma-deposition time.

---- (Fig. 4) ----

Fig. 4. He/SF₆ permeance ratios for PECVD-derived organosilica membranes (SiOCH/TiO₂ and SiOCH/SiO₂-ZrO₂) and intermediate layers as a function of He permeances. The solid line in this figure shows the trade-off line for SiOCH/TiO₂ membranes.

3.2. High-temperature stability of PECVD organosilica membranes

The membrane performance at 50°C for PECVD-derived organosilica membranes before the high-temperature stability test are listed in **Table 1**. A SiOCH/TiO₂ membrane, which is referred to as “T-1” in Table 1, was the same membrane as the T-1 described in Fig. 3, and had a total deposition time of 10 min. Similarly, in the case of SiOCH/SiO₂-ZrO₂ membranes, those corresponding to the SZ-1 and SZ-2 described in Fig. 3 were subjected to a high-temperature stability test. The total deposition times for SZ-1 and SZ-2 were 30 and 40 min, respectively.

---- (Table 1) ----

Table 1. Membrane performance at 50°C for plasma-deposited organosilica membranes before the high-temperature stability test.

Membrane no.	Intermediate layer	Deposition time [min]	He permeance [mol/(m ² s Pa)]	Permeance ratio	
				He/N ₂	He/SF ₆
T-1	TiO ₂	10	9.26×10^{-9}	6.8	25.7
SZ-1	SiO ₂ -ZrO ₂	30	1.72×10^{-8}	25.9	635
SZ-2	SiO ₂ -ZrO ₂	40	3.02×10^{-9}	10.8	88.8

In **Fig. 5**, He permeances and permeance ratios for He/N₂ and He/SF₆ at 50°C after heat treatment at the specified temperatures were plotted as a function of the heat treatment temperatures. For the membrane deposited onto a TiO₂ intermediate layer (T-1), the membrane before heat treatment had a He permeance of 9.26×10^{-9} mol/(m² s Pa) with He/N₂ and He/SF₆ permeance ratios of 6.8 and 25.7, respectively. With an increase in the heat treatment temperature up to 300°C, the He permeances gradually increased by 3-4 times, whereas the permeance ratios of He/N₂ and He/SF₆ were slightly decreased to 4.8 and 13.8, respectively. The permeance ratios for the T-1 membrane decreased after the heat treatment at 300°C, but still remained higher than the Knudsen selectivity. The increases in permeance were thought to be due to an evaporation of small molecules such as unreacted precursors and its oligomers that were present in the organosilica layer. After the T-1 membrane was further heat-treated at 400°C for 1 h under a nitrogen flow, the He permeances increased by 2 orders of magnitude, as compared with those before heat treatment, and the membrane became non-selective. He permeance after heat treatment at 400°C was 1.57×10^{-6} with He/N₂ and He/SF₆ permeance

ratios of 1.7 and 3.6, respectively. This can be explained by the thermal decomposition of the PECVD-derived organosilica layer, which resulted in either the formation of defects or a loss of the separation layer.

Fig. 6 shows the FT-IR spectra of the PECVD-derived film deposited onto a silicon wafer. The spectra showed the absorption bands that characteristically correspond to siloxanes (Si-O-Si, at 1,100-1,000 cm^{-1}) [24-26] and methylsiloxanes (Si-CH₃, at 1,275-1,245 cm^{-1}) [26, 27]. The result indicates that the PECVD-derived film had a polysiloxane structure. The absorption bands that appeared at 2,970 and 2,935 cm^{-1} could be ascribed to the presence of methyl (-CH₃) and methylene (-CH₂-) groups, respectively [28]. The presence of a methylene group, together with the molecular structure of the silicon precursor HMDSO suggested the formation of a partially cross-linked polysiloxane structure with hydrocarbon units. In general, it is well known that the thermal decomposition of polysiloxanes such as PDMS in an inert atmosphere occurs by depolymerization over a temperature range of 400-650°C to form cyclic oligomers [15, 16]. Since the chemical structure of the PECVD-derived organosilica membranes was similar to that of polysiloxanes, it is reasonable to conclude that the thermal decomposition of the PECVD-derived organosilica membranes followed the same mechanism as PDMS.

The membranes with a SiO₂-ZrO₂ intermediate layer were heat-treated at temperatures up to as high as 500°C. The SZ-1 membrane before the heat treatment had a He permeance of $1.72 \times 10^{-8} \text{ mol}/(\text{m}^2 \text{ s Pa})$ with He/N₂ and He/SF₆ permeance ratios of 25.9 and 635, respectively. With an increase in the heat treatment temperature to 400°C, He permeances increased 3-fold, but the permeance ratios changed little. The permeance ratios after heat treatment at 400°C were 12.1 for He/N₂ and 1,040 for He/SF₆. After further heat treatment at 500°C, He permeance for the SZ-1 membrane was increased by 2 orders of magnitude to $1.41 \times 10^{-6} \text{ mol}/(\text{m}^2 \text{ s Pa})$. Although the SZ-1 membrane lost its selectivity for He/N₂, the permeance ratio for He/SF₆ remained as high as 1,040. As for the SZ-2 membrane, the permeance of He

increased from 3.02×10^{-9} to 1.30×10^{-7} after heat treatment at 500°C, while the permeance ratios for He/N₂ and He/SF₆ were unaffected by the heat treatment and maintained at 6.29 and 96.6, respectively, which was considerably higher than the values for Knudsen permeation.

In terms of selectivity, the membrane performance for T-1 was obviously diminished following the heat-treatment at 400°C. However, for the SZ-1 and SZ-2 membranes, the membrane performance changed little after the heat treatment at 400°C. Even after heat treatment at 500°C, both the SZ-1 and SZ-2 membranes continued to possess high He/SF₆ selectivity. Based on these results, the PECVD-derived organosilica membranes with a SiO₂-ZrO₂ intermediate layer were concluded to be thermally more stable than the membrane with a TiO₂ intermediate layer, and the separation layer in the membranes with a SiO₂-ZrO₂ intermediate layer was thermally stable at temperatures at least as high as 400°C. The improved thermal stability of organosilica membranes with a SiO₂-ZrO₂ intermediate layer can be explained by the incorporation of a SiO₂-ZrO₂ intermediate layer into the PECVD-derived organosilica layer. A number of studies have reported that the addition of inorganic nanomaterials to form hybrid structures improved the thermal stability of polymer materials including PDMS [17-20].

---- (Fig. 5) ----

Fig. 5. (a) He permeance and (b) He/N₂ and (c) He/SF₆ permeance ratios at 50°C for PECVD-derived organosilica membranes after heat-treatments ranging from 50 to 500°C.

----(Fig. 6)----

Fig. 6. FT-IR spectra of PECVD-derived organosilica film at a deposition time of 30 min.

3.3. Temperature dependence of gas permeance for a PECVD-derived organosilica membrane deposited on a $\text{SiO}_2\text{-ZrO}_2$ intermediate layer

The temperature dependence of gas permeances for $\text{SiOCH/SiO}_2\text{-ZrO}_2$ membrane(SZ-1) were measured after heat treatments at 200 and 500°C. For the 200°C-treated membrane, as shown in **Fig. 7 (a)**, the permeances of He, H_2 and N_2 increased with increasing temperature, showing an activated diffusion behavior. The permeance of CO_2 also increased with increasing temperature, suggesting that the primary mechanism of permeation was activated diffusion. However, the dependence on temperature for the permeance of CO_2 was weaker than it was for the other gases. This might be explained by the additional contribution of the surface or solution diffusion of CO_2 due to its strong affinity for the membrane. The activation energy of gas permeation, E_p , was obtained from the following equation [29] using the experimental single gas permeance data:

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right) \quad (3)$$

where P_0 is a pre-exponential factor that reflects the structure of a membrane, R is the gas constant and T is the temperature. The activation energies of gas permeation for He, H₂, CO₂, and N₂ were calculated to be 13.5, 12.5, 4.8, and 15.4 kJ/mol, respectively. The activation energies of gas permeation for the 200°C-treated membrane were in good agreement with those for the PDMS membranes [30-33], as summarized in **Table 2**. This indicates that the 200°C-treated membrane remained a PDMS-like structure. Therefore, the activated diffusion of gas molecules through the 200°C-treated membrane can be attributed to the free volumes between polymer chains that were formed by the thermal motion.

---- (Fig. 7) ----

Fig. 7. Temperature dependence of single gas permeances for the SZ-1 membrane after heat treatment at different temperatures: (a) 200 and (b) 500°C.

---- (Table 2) ----

Table 2. Activation energies of gas permeation for a PECVD-organosilica membrane (SZ-1) and PDMS membranes.

	He	H ₂	CO ₂	N ₂	SF ₆	Ref.
PDMS/PES	-	13.26	2.67	-	-	[30]
PDMS	-	10.72	-	8.56	-	[31]
PDMS	-	13.4	-	10.9	-	[32]
PDMS	15.20	-	2.70	14.30	-	[33]
PECVD, 200°C-treated	13.5	12.5	4.8	15.4	-	This study
PECVD, 500°C-treated	3.1	1.4	-	0.4	7.7	This study

For the 500°C-treated membrane, as shown in **Fig. 7 (b)**, the permeances of He, H₂, and N₂ were little affected by temperature, showing a Knudsen permeation behavior. The activation energies of gas permeation for He, H₂, and N₂ were 3.2, 1.4, and 0.5 kJ/mol, respectively, all of which were much smaller than those for the 200°C-treated membrane. It was also interesting to note that the permeation of SF₆ showed an activated diffusion behavior ($E_p = 7.7$ kJ/mol), which suggested the absence of pinhole even after heat treatment. Together with the gas permeation ratios, it is suggested that the structure of the SZ-1 membrane changed from a PDMS-like structure to a microporous structure with a narrow pore size distribution after heat treatment at 500°C. This structure change might be due to the pore formation by the release of hydrocarbon fragments, which was similar to results reported in the literature [34, 35].

Fig. 8 shows the kinetic diameter dependence of dimensionless gas permeances at 50°C, which were normalized by the permeances of He, for the SZ-1 membrane after heat treatments at 200, 400, and 500°C. Although the dimensionless permeances for H₂ and SF₆ were

not changed much, a change in the dimensionless permeance for N_2 was clearly observed after heat treatment at 500°C.

Therefore, it is strongly suggested that the heat treatment at 500°C formed network pores that allowed the permeation of molecules that were the size of N_2 (0.364 nm) and smaller, but not of larger molecules such as SF_6 (0.55 nm). In conclusion, we found it possible to control the pore size of PECVD-derived organosilica membranes via annealing at high temperatures.

---- (Fig. 8) ----

Fig. 8. Kinetic diameter dependence of dimensionless gas permeances at 50°C for an SZ-1 membrane before and after heat treatment at different temperatures.

4. Conclusions

Organosilica membranes for gas separation were prepared at room temperature on porous substrates using two types of intermediate layers with different pore sizes: a TiO_2 layer ($d_p \approx 5$ nm) and a SiO_2 - ZrO_2 layer (1 nm). The stability of PECVD-derived organosilica membranes at high-temperature was evaluated by measuring the gas permeation characteristics after heat treatment.

1. The SiOCH/SiO_2 - ZrO_2 membrane showed higher thermal stability compared with the SiOCH/TiO_2 membrane. After heat treatment at 500°C , the SiOCH/SiO_2 - ZrO_2 membrane possessed a selectivity as high as 1040 for He against SF_6 with a He permeance of $1.41 \times 10^{-6} \text{ mol}/(\text{m}^2 \text{ s Pa})$ at 50°C , while the SiOCH/TiO_2 membrane became non-selective after heat treatment at 400°C .

2. When the SiOCH/SiO_2 - ZrO_2 membrane was heat-treated at 200°C , gas permeation was dominated by an activated diffusion mechanism. The activation energies of gas permeation showed good agreement with those for polydimethylsiloxane membranes, suggesting that the activated diffusion of gas molecules through the 200°C -treated membrane can be attributed to free volumes between the polymer chains that were formed by thermal motion.

3. When the SiOCH/SiO_2 - ZrO_2 membrane was heat-treated at 500°C , the gas permeations of He, H_2 , and N_2 followed a Knudsen permeation mechanism, whereas that of SF_6 followed an activated diffusion mechanism. This result suggested that the heat treatment at 500°C led to the formation of a microporous structure that allowed the permeation of N_2 and smaller molecules.

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Tables

Table 1. Membrane performance at 50°C for plasma-deposited organosilica membranes before the high-temperature stability test.

Table 2. Activation energies of gas permeation for a PECVD-organosilica membrane (SZ-1) and

PDMS membranes.

Figures

Fig. 1. Schematic diagram of the PECVD and gas permeation experimental setup.

Fig. 2. Dimensionless permeance of nitrogen for TiO_2 and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers as a function of the Kelvin diameter.

Fig. 3. Time courses for gas permeances of (a) He, (b) N_2 and (c) SF_6 at room temperature for PECVD-derived organosilica membranes deposited onto TiO_2 (closed symbols) and $\text{SiO}_2\text{-ZrO}_2$ intermediate layers (open symbols) as a function of plasma-deposition time.

Fig. 4. He/ SF_6 permeance ratios for PECVD-derived organosilica membranes (SiOCH/TiO_2 and $\text{SiOCH/SiO}_2\text{-ZrO}_2$) and intermediate layers as a function of He permeances. The solid line in this figure shows the trade-off line for SiOCH/TiO_2 membranes.

Fig. 5. (a) He permeance and (b) He/ N_2 and (c) He/ SF_6 permeance ratios at 50°C for PECVD-derived organosilica membranes after heat-treatments ranging from 50 to 500°C .

Fig. 6. FT-IR spectra of PECVD-derived organosilica film at a deposition time of 30 min.

Fig. 7. Temperature dependence of single gas permeances for the **SZ-1** membrane after heat treatment at different temperatures: (a) 200°C and (b) 500°C .

Fig. 8. Kinetic diameter dependence of dimensionless gas permeances at 50°C for an **SZ-1** membrane before and after heat treatment at different temperatures.-