High Hydrogen Permeance Silica Membranes Prepared by a Chemical Vapor Deposition Method

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Abstract: H_2 permselective silica hybrid membranes were successfully prepared by using a counter diffusion chemical vapor deposition (CVD) method. Hexyltrimethoxysilane (HTMOS), phenyltrimethoxysilane (PhTMOS) or diphenyldimethoxysilane (DPhDMOS) were used as silica precursors. The oxidants were O_3 or O_2. These reactants were provided at the opposite side of the γ-alumina substrates, and the deposition occurred in the pores of the substrates. The HTMOS/O_3 derived membrane deposited at 450°C showed the highest H_2 permselectivity. The H_2 permeace was 2.1×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with the H_2/SF_6 permeance ratio of 5.9×10^6. H_2 permeances through the HTMOS derived membranes increased with increasing the deposition temperatures. While the H_2 permeance through the PhTMOS and DPhDMOS derived membranes decreased with increasing the deposition temperatures. The PhTMOS derived membrane prepared at 150°C showed the H_2 permeance of 1.7×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with the H_2/SF_6 permeance ratio of 13. The PhTMOS membrane prepared at 320°C showed the highest H_2/SF_6 permeance ratio of 1.8×10^4 among the PhTMOS derived membranes. However, the H_2/SF_6 permeance ratio through the DPhDMOS membranes showed the different trend. Higher H_2/SF_6 permeance ratio was found through the DPhDMOS derived membranes deposited at 180°C and 360°C. The maximum H_2/SF_6 permeance ratio was 4.2×10^4 through the DPhDMOS membrane deposited at 180°C. The decomposition properties of organic groups on silica surface are investigated by using hydrolysis powders derived from the each silica precursor. The HTMOS powders showed O_3 stability after the high temperature treatment. Thus, high H_2 permselective membranes were prepared by the HTMOS at 450 °C.

Keywords: Silica hybrid membrane, counter diffusion CVD method, H_2 permselective membrane, pore size control, silica precursors.

1. Introduction

Recently, hydrogen is expected as a clean energy and as an energy carrier. Hydrogen takes gas state under ordinary pressure and temperature. To use liquefied hydrogenas transportation compounds, it is necessary to cool hydrogen until cryogenic temperature. The hydrogen transport materials are required safety, low cost and saving energy. Therefore, organic hydrides such as methylcyclohexane are concerned as can-didates to transport hydrogen. Separation to remove hydrogen from the organic hydrides should be operated efficiently. We have focused on a separation technique by using hydrogen permselective membranes for efficient hydrogen separation. The hydrogen permselective membranes require thermal stability due to the hydrogen decomposition temperature from the organic hydrides. Thus, many researches for hydrogen permselective ceramic membranes have been reported for the silica membranes.

The silica membranes have been prepared by using a sol-gel method [1-3] or a chemical vapor deposition (CVD) method [4-14]. In this paper, we discussed about the silica membranes prepared by using a CVD method. There were several kinds of the silica precursors used in the former reports such as silane (SiH_4) [4], silicon tetrachloride ($SiCl_4$) [6], tetratrimetho-xysilane (TMOS) [9,13] and tetratriethoxysilane (TEOS) [7-8]. The geometries of the CVD methods are important. The CVD methods are classified in two kinds by the direction to supply the reactants. All the reactants are provided from the one side of a porous substrate for the one-side CVD method, and two reactants are provided at the opposite side of the porous substrates for the counter diffusion CVD method. The H_2/N_2 permeance ratio of 880 through the membrane prepared by the one-side CVD method [7]. Nakao *et al.* [8] reported that the silica membrane was prepared by the counter diffusion CVD of TEOS/ O_3 at 150−200°C.This membrane was obtained the He permeance of 3×10^{-8} mol m^{-2} s^{-1} $Pa^{-1}$with the He/N_2 permeance ratio of 950. Gapalakrishman *et al.* [11] reported that the H_2 permeance of 6.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with a H_2/N_2 permeance ratio of 2,343 at 600°C through the membrane prepared by the counter diffusion CVD method of the TMOS/O_2 systems. They also obtained the three membranes module by usingthe counter diffusion CVD method [13]. Such a complex shape modules can be prepared by the CVD method that indicates apractical application of a membrane reactor.

Nomura *et al.* [14] used propyltrimethoxysilane (PrTMOS) as a silica precursor for the counter diffusion

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CVD method. The H_2 permeance of 1.3×10^{-7} mol m^{-2} s^{-1} Pa^{-1} was obtained with an H_2/N_2 permeance ratio of 30. The pore size of the silica hybrid membranes can be controlled by changing the deposition conditions due to the part of decomposition of the propyl groups in the silica precursor. HTMOS derived membranes have been developed for the propylene/propane separation [15]. The propylene/propane permeance ratio at 270°C was 414 (propylene permeance 1.0×10^{-8} mol m^{-2} s^{-1} Pa^{-1}) through the HTMOS/O_2 membrane deposited at 450°C. Ikeda *et al.* [16] reported silica reverse osmosis membrane prepared by PhTMOS as a silica precursor. However, the decomposition conditions for hydrogen permselective membrane were not clear. The organic groups of silica precursor can be changed such as hexyl group or phenyl group.

In this study, hydrogen permeabilities through three kinds of silica hybrid membranes by using the counter diffusion CVD method were discussed. The decomposition properties of organic groups on the silica surface were investigated by thermogravimetry (TG), the FT-IR measurements and temperature programmed desorption (TPD) with a mass spectrometry (MS). In order to develop the hydrogen permselective silica membranes for the dehydration of organic hydride, we have evaluated the H_2/SF_6 permeance ratio. The kinetic diameter of SF_6 is 0.55 nm that is similar to that of methylcyclohexane.

2. EXPERIMENTAL

2.1. Preparation of Membranes

Figure **1** shows the schematic diagram of an apparatus for a counter diffusion CVD method. Porous γ-alumina substrates (effective length: 40 mm, pore size: 4 nm) were provided by NOK Co. CVD was carried out at between 150–500°C for 5–90 min. Hexyltrimethoxysilane (HTMOS), phenyltrimethoxysilane (PhTMOS) or diphenyldimethoxysilane (DPhDMOS) was employed as a silica source (Shin-Etsu Chem. Co.). Figure **2** shows the structures of the silica precursors. HTMOS, PhTMOS or DPhDMOS were provided through the N_2 bubbler kept at 75–125°C and the vapor was introduced to the outside of the alumina substrate. O_3 was produced by using an O_3 generator (SOW-5000R, SYOKEN Co.). O_3 from the O_3 generator was introduced into the membrane module at 0.2 L min^{-1}. The CVD conditions of each silica precursors are shown in Table **1**.

2.2. Gas Permeation Test

Single gas permeances of H_2 (kinetic diameter: 0.29 nm), N_2 (0.36 nm), C_3H_6 (0.45nm), C_3H_8 (0.43nm) and SF_6 (0.55 nm) were performed at the deposited temperatures of the membranes below the 270°C deposition. If the membranes were deposited over 270°C, permeances were measured at 270°C. The permeance was measured through a pressure-change

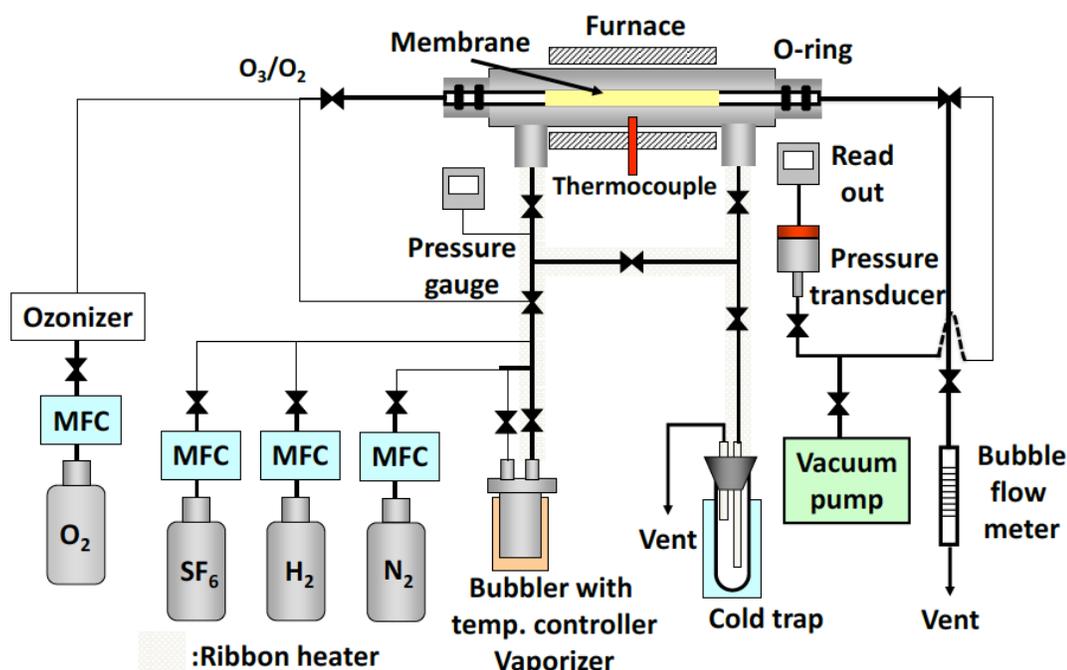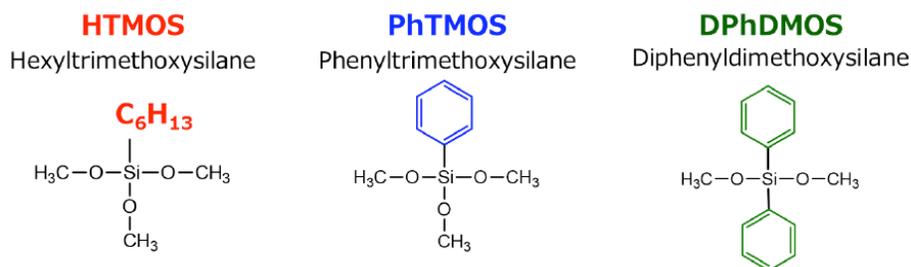**Figure 1:** Schematic diagram of the CVD/ permeation apparatus.

HTMOS
Hexyltrimethoxysilane

PhTMOS
Phenyltrimethoxysilane

DPhDMOS
Diphenyldimethoxysilane

Figure 2: Chemical formulas of silica precursors.

Table 1:   The CVD Conditions of Each Silica Precursors

Silica precursor	Bubbler temp. (°C)	O_3 flow rate (L min^{-1})	CVD time (min)
HTMOS	125	0.2	5
PhTMOS	75	0.2	90
DPhDMOS	125	0.2	90

method. Three gases were provided independently to the outside of the membrane. The inner side of the membrane was evacuated, and the rate of the pressure change at the inside of the membrane was measured by turning off the valve between the module and the vacuum pump.

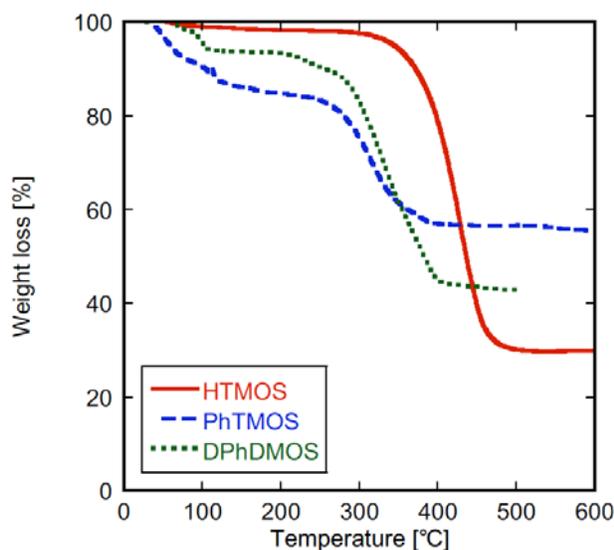## 2.3. The Thermal Decomposition Properties of the Silica Hydrolysis Powders

Powder samples were prepared in order to discuss the decomposition of the organic groups on the silica surface. HTMOS, PhTMOS or DPhDMOS was stirred at 80°C for 2 h in ethanol (Wako Pure Chem. Ind.). The molar compositions of the sol were HTMOS: EtOH: H_2O: NaOH= 1: 3.8: 42: 2.5, PhTMOS: EtOH: H_2O: NaOH= 1: 3.8: 30: 1.3 and DPhDMOS: EtOH: H_2O: NaOH= 1: 3.8: 30: 1.3 respectively. After the stirring, the obtained gel was dried at 100°C for 12 h. The dried powder samples were set in the center of the quartz tube (φ: 2 mm) and O_3 in O_2 was provided at 0.2 L min^{-1} (49.7 g m^{-3}). The treatments were conducted at 150–450°C for 90 min. The treated powder samples were evaluated by using TG (TGA 50, Shimadzu Co.) and FT-IR (FTIR-8400S, Shimadzu Co.). Thermal decomposition of phenyl groups (mass-to-charge:m/z=78) on the PhTMOS and the DPhDMOS derived powders were measured by the TPD (BELCAT, MicrotracBEL) with the MS (BELMass, MicrotracBEL).

3. RESULTS AND DISCUSSIONS

In the preparation of the silica hybrid membranes contained organic groups by using a counter diffusion CVD method, the decomposition properties of organic groups on the silica surfaces were the important factor as controlling the pore size of the deposited membranes. Firstly, the HTMOS, the PhTMOS and the DPhDMOS derived powders were measured by TG in N_2 atmosphere. Figure **3** shows the TG curves of the hydrolysis powders. A weight loss of the HTMOS derived powder decreased sharply from 330°C to 450°C. The decomposition temperatures of the PhTMOS and the DPhDMOS derived powders were 50°C lower than that for the HTMOS derived powders. The hexyl groups on silica surface has higher thermal stability than the organic groups derived from PhTMOS and DPhDMOS. It indicates that this difference of the thermal stability must be related to the thermal decomposition of the organic groups during the CVD procedures. Thus, the deposition temperature for the CVD should be investigated. The decomposition temperature ranges of the PhTMOS and the DPhDMOS derived powders were from 280°C to 380°C, while a weight loss of the DPhDMOS derived powder was about 15% lower than that of the PhTMOS derived powder. It can be explained by the numbers of the phenyl groups in the silica precursors. Next, the difference of the number of phenyl groups in the silica precursors were studied by using the TPD with a MS. Figure **4** shows the intensity of m/z= 78 by changing the temperature from 100°C to 500°C. This intensity shows the amounts thermally decomposed phenyl groups. In comparison with Figure **3**, it seems that the difference between PhTMOS and DPhDMOS is larger. However, it is not the case because this vertical axis was log scale. From the result shown in this figure, the

decomposition of phenyl groups can be classified in two steps at 300°C. The intensity of the DPhDMOS derived powder were changed ten times the PhTMOS derived powders higher than 300°C. It indicates that thermal stability over 300°C for the DPhDMOS membrane might be lower than that for the PhTMOS membrane. PhTMOS has three methoxy groups (-OCH_3) in one molecule, while DPhDMOS has two methoxy groups (cf. Figure **2**). The silica network derived from PhTMOS must be a three-dimensional mesh shape, while that derived from DPhDMOS should
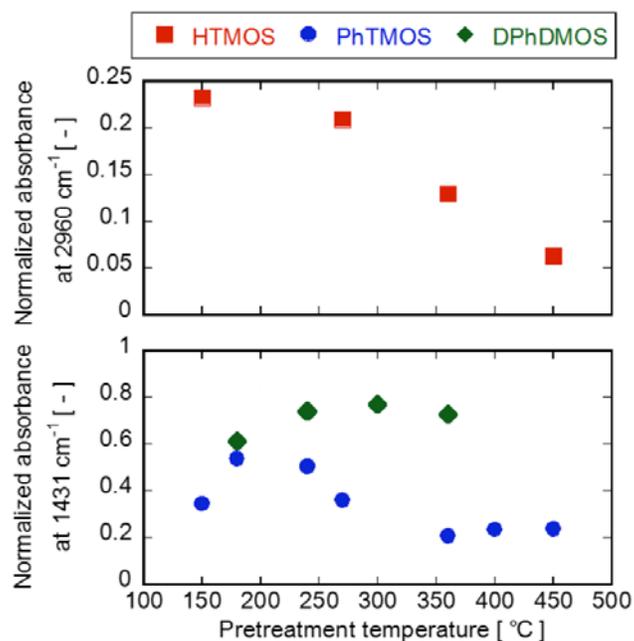
be linear structures. The thermal stability difference between PhTMOS and DPhDMOS can be explained by the silica structures based on the numbers of the methoxy groups in the silica precursor.

Next, the decomposition properties of the organic groups in high temperature O_3 atmosphere were investigated by using the FT-IR. Figure **5** shows the FT-IR results of the HTMOS, the PhTMOS and the DPhDMOS derived powders after 90min of the O_3 treatments. The vertical axis shows the absorption ratio at 2,960 cm^{-1} (C-CH_3) or 1,431 cm^{-1} (Si-C_6H_5) of the O_3-treated powders over those of the as-made powders. HTMOS was evaluated by the absorption ratio at 2,960 cm^{-1}. PhTMOS and DPhDMOS was evaluated by the absorption at 1,431 cm^{-1}. The absorption ratio of 1 shows all organic groups were remained in the silica hydrolysis powder, while the absorption ratio of 0 shows that no organic group remained on the silica hydrolysis powder by the O_3 treatment. The ratio at 2,930 cm^{-1} decreased from 0.23 to 0.06 with increasing the O_3 treatment temperatures for the HTMOS derived powders. This decrease is due to the thermal decomposition. Hexyl groups were remained after the 450°C treatment, indicating the high thermal stability for the HTMOS deposition. A maximum ratio of 1,431 cm^{-1} was 0.54 after O_3 treatment at 180°C for the PhTMOS derived powder. The O_3 concentrations of the outlet of the reactor were measured by the O_3 concentration meter [14]. At 300°C

Figure 3: Thermogravimetric curves of hydrolysis powders of silica precursors (Heating rate: 5°C min^{-1}, N_2 flow rate: 50 mL min^{-1}).
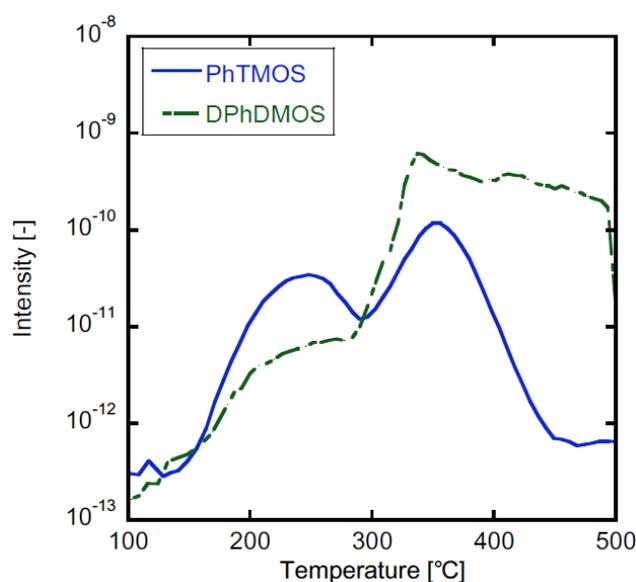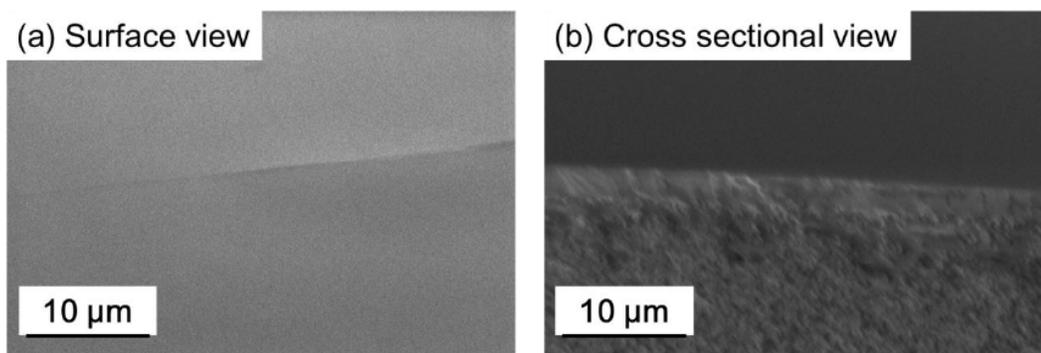

Figure 4: Temperature programmed desorption of the PhTMOS and the DPhDMOS derived hydrolysis powders (Heating rate: 5°C min^{-1}, He flow rate: 30 mL min^{-1}, m/z= 78).

Figure 5: FT-IR measurements for the HTMOS, the PhTMOS or the DPhDMOS derived hydrolysis powders (Pretreatment: O_3 flow rate 0.2 L min^{-1}, 90 min).

Figure 6: SEM images of the PhTMOS membrane deposited at 300°C (**a**) surface view, (**b**) cross sectional view.

of the reactor, the O_3 concentration was less than half of the feed O_3 concentration. Moreover, the O_3 concentrations were approximately 0 g m^{-3} at the 400°C of the reactor. Therefore, the decomposition of organic groups were due to O_3 at less than 300°C of the reactor, and O_3 must be thermally decomposed at higher than 300°C of the reactor. Phenyl groups on the surface of the PhTMOS derived powders remained by the O_3 treatments between 150°C and 270°C. This temperature range should be investigated by the CVD. The DPhDMOS derived powders show almost the constant ratio by all theO_3 treatment temperatures. These results indicate that the O_3 decomposition mechanism for phenyl groups are different from thermally decomposition shown the Figure **4**. However, the phenyl groups for the DPhDMOS derived powders were remained below 250°C, and the deposition conditions for the DPhDMOS derived membrane should be studied at the low deposition temperatures.

Figure **6** shows the SEM images of the PhTMOS derived membrane deposited at 300°C. The surface image of the membrane shows that the surface of the membrane is smooth with no deposited particles. The SEM image of the cross section shows the PhTMOS derived membrane had two layers. The bottom layer was α-alumina substrate. A porous alumina layer was thickness of 3.5 μm on the α-alumina substrate. The color of the top of the γ-alumina layer was slightly different. This part is thought the silica layer and shows the CVD layer was formed inside the pore of γ-alumina substrate. The layer thickness was almost constant regardless of different silica precursors and deposition temperatures. The silica layer thickness was difficult to evaluate because the border of layer was not clear.

Next, the deposition temperature dependency of the gas permeation performance through the HTMOS derived membranes was investigated. Figure **7** shows the H_2 permeances and the H_2/SF_6 permeance ratios

through the HTMOS derived membranes by changing the deposition temperatures. The HTMOS derived membrane deposited at 450°C showed the highest H_2 permeance of 2.1×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with the highest H_2/SF_6 permeance ratio of 5.6×10^6. The permeance of various gases measured at 270°C is shown in Table **2**. The C_3H_6/C_3H_8 permeance ratio was 353. Then, the pore size were estimated around 0.45 nm based on the molecular size of C_3H_6 and C_3H_8. The H_2/SF_6 permeances of more than ten thousand were obtained deposited at the temperature between 400°C to 500°C. This was the same trend to the TG result. The FT-IR measurements of the HTMOS derived powders showed the stability for the high temperature O_3 treatments. Slightly remained hexyl groups must be the keys for the high H_2/SF_6 selectivity at the 450°C deposition of the HTMOS derived membrane.
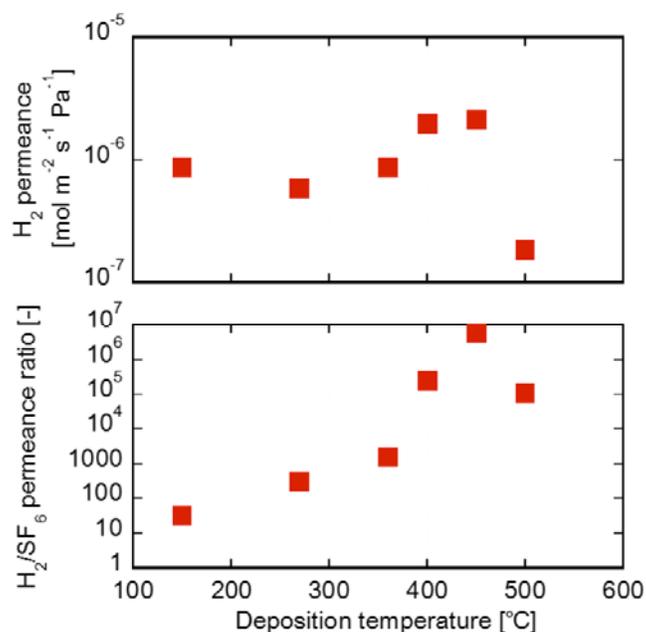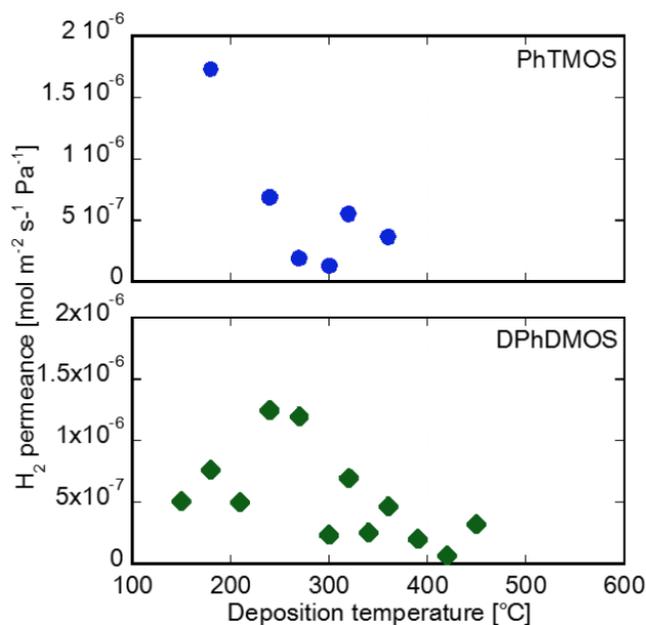

Figure 7: The H_2 permeances and the H_2/SF_6 permeance ratios through the HTMOS membranes deposited by changing the deposition temperatures.

Table 2: Single Gas Permeances at 270°C through the HTMOS Membrane Deposited at 450°C

Membrane	Single permeance (mol m^{-2} s^{-1} Pa^{-1})					H$_2$/SF$_6$ permeance ratio [-]
	H$_2$	N$_2$	C$_3$H$_6$	C$_3$H$_8$	SF$_6$	
HTMOS 450°C	2.1×10^{-6}	7.9×10^{-8}	1.2×10^{-9}	3.4×10^{-12}	3.6×10^{-13}	5.9×10^6

Then, the effects of the deposition temperatures were investigated for the PhTMOS and the DPhDMOS derived membranes. Figure **8** shows the H$_2$ permeances depending on the deposition temperature through the PhTMOS and the DPhDMOS derived membranes. The PhTMOS derived membrane deposited at 180°C showed the highest H$_2$ permeance of 1.7×10^{-6} mol m^{-2} s^{-1} Pa^{-1} among the PhTMOS derived membranes. While the DPhDMOS derived membrane deposited at 240°C showed the highest H$_2$ permeance of 1.3×10^{-6} mol m^{-2} s^{-1} Pa^{-1} among the DPhDMOS derived membranes. Figure **9** shows the dependence of the H$_2$/SF$_6$ permeance ratios through the same PhTMOS and the same DPhDMOS derived membranes shown in Figure **8**. The PhTMOS derived membrane deposited at 320°C showed the highest H$_2$/SF$_6$ permeance ratio of 1.9×10^4, while the DPhDMOS derived membrane deposited at 180°C exhibited the highest H$_2$/SF$_6$ permeance ratio of 4.2×10^4.

Figure 8: The H$_2$ permeances through the PhTMOS and the DPhDMOS membranes deposited by changing the deposition temperatures.

The performances of the membranes are compared those of the other groups. According to the former

report of the silica membrane prepared by the one-side diffusion CVD method, the H$_2$/SF$_6$ selectivity was above 6,800 with the H$_2$ permeance of around 10^{-6} mol m^{-2} s^{-1} Pa^{-1} at 300°C [17]. The hydrogen permeance was 1.0×10^{-6} mol m^{-2} s^{-1} Pa^{-1} and the selectivity of H$_2$/SF$_6$ was 10,000 through the organosilica membrane by a sol-gel method [18]. These membranes showed higher H$_2$ permeances at approximately 1.0×10^{-6} mol m^{-2} s^{-1} Pa^{-1}. Thus, the HTMOS derived membrane deposited at 450°C was obtained the maximum H$_2$/SF$_6$ permeance ratio. To investigate an effect of number of phenyl group, the PhTMOS and the DPhDMOS derived membranes of the three deposition temperature of 180°C, 300°C and 360°C were studied. Firstly, the membranes deposited at 180°C were discussed. The H$_2$/SF$_6$ permeance ratios were significantly different between the PhTMOS and the DPhDMOS derived membranes. The H$_2$/SF$_6$ permeance ratio through the DPhDMOS derived membrane was 3,000 times larger than that through the PhTMOS derived membrane. However, the H$_2$ permeances were the similar through those membranes. The intensity of mass number of 78
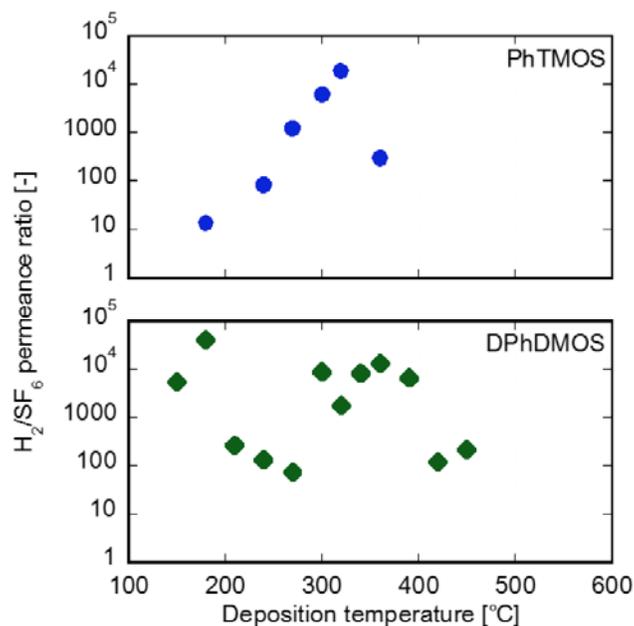
Figure 9: The H$_2$/SF$_6$ permeance ratios through the PhTMOS and the DPhDMOS membranes by changing the deposition temperatures.

at 180°C for the DPhDMOS derived powder was 1×10^{-12} that was the similar to that for the PhTMOS derived powder (Figure **4**). This shows that the influence of the precursor difference at 180°C decomposition is negligible because of the TPD performed under the He atmosphere. From the FT-IR measurement (Figure **5**), the absorption ratio of PhTMOS and DPhDMOS after O_3 treatment was 0.53 and 0.61. Therefore, the decomposition of phenyl groups was greatly affected by O_3 at 180°C. The amounts of phenyl groups for the as-made PhTMOS derived powders are half fartheras-made DPhDMOS derived powder. Thus, the remaining phenyl groups on the silica surface after the O_3 treatments for the PhTMOS derived powders were approximately half for the DPhDMOS derived powders. H_2, N_2 and SF_6 gas passes easily through the pore formed by the decomposition of phenyl groups because the size of phenyl group is about 0.6 nm that is larger than SF_6 (0.55 nm). Therefore, the PhTMOS derived membrane deposited at 180°C showed the high H_2 permeance of 1.8×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with the low H_2/SF_6 permselective membrane of 30. While the DPhDMOS derived membrane deposited at 180°C contained many phenyl groups and the small hole formed among phenyl groups must be smaller than SF_6. Therefore the maximum H_2/SF_6 permeance ratio of 4.2×10^4 was found to phenyl groups. Amounts of organic groups in the deposited silica layer in the O_3 atmosphere was important for the deposition at 180°C. Secondly, the deposition temperature of 300°C was discussed. This temperature was the key point from the TG and the TPD result. Phenyl groups of the PhTMOS and the DPhDMOS derived powders was remaining at 300°C. The H_2 permeances were $1–1.2 \times 10^{-6}$ mol m^{-2} s^{-1} Pa^{-1} with the H_2/SF_6 permeance ratios of $8–9 \times 10^3$. Finally, the PhTMOS and the DPhDMOS derived membrane deposited at 360°C were investigated. According to the result of TPD, DPhDMOS was easy to decompose at the high temperatures over 300°C. The silica network of the DPhDMOS derived is considered to be the linear structure as described in the former section. The linear structures are flexible not to be thermally stable. Then, it might be created the pinholes which SF_6 can pass through. The DPhDMOS derived membrane deposited at 360°C showed the H_2 permeance of 4.5×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with the high H_2/SF_6 permeance ratio of 1.3×10^4. The amount of phenyl groups of the DPhDMOS derived powders at 360°C was higher than that of the PhTMOS powders (cf. Figure **3**). Hence, the H_2/SF_6 selectivity was due to the effects of the remained phenyl groups. However, the PhTMOS

derived membranes should be the mesh shape. The silica network of the PhTMOS derived membranes was stable at 360°C and the H_2/SF_6 permeance ratio of 302. The low H_2/SF_6 selectivity was due to the low amounts of the remained phenyl groups. Thus, the thermal stability of phenyl group is affected by the structures of the deposited silica networks at the high deposition temperatures. Figure **10** shows the H_2 permeances through the HTMOS, the PhTMOS and the DPhDMOS derived membranes withthe H_2/SF_6 permeance ratios >1000. These membranes have the excellent H_2/SF_6 selectivity. The big difference between the HTMOS derived membranes and the DPhDMOS derived membranes was the deposition temperature range to obtain the higher H_2 permeances. The temperature range for the HTMOS derived membranes was between 360°C and 450°C, and that for the DPhDMOS derived membranes was between 150°C and 320°C.The HTMOS derived membranes deposited at 450°C showed the high thermal stability that can be the best H_2 permselective membrane. The excellent H_2/SF_6 permeance ratio of 5.6×10^6 was obtained because a pore size of the HTMOS derived membranes might be smaller than the pore size of the DPhDMOS derived membranes.
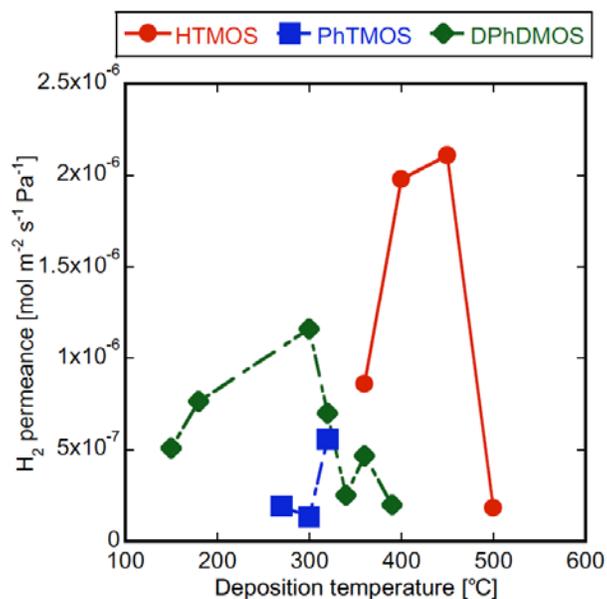
Figure 10: The trend of the H_2 permeances for high H_2 permselective membrane (H_2/SF_6 permeance ratio＞1000).

4. CONCLUSIONS

The maximum H_2/SF_6 permeance ratio of 560,000 was obtained with the H_2 permeance of 2.1×10^{-6} mol m^{-2} s^{-1} Pa^{-1} through the HTMOS derived membrane deposited at 450°C. The H_2 permeance was higher

than those reported in the former reports. The DPhDMOS derived membrane deposited at 180°C showed a H_2 permeance of 7.7×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with a H_2/SF_6 permeance ratio of 42,000. These excellent membrane can be apply to the module for the dehydration of organic hydrides. The deposition mechanisms for these membranes were discussed by using the analysis for the hydrolysis powders of HTMOS and DPhDMOS.

ACKNOWLEDGEMENT

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