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

Ayumi Ikeda, Ryuhei Ono and Mikihiro Nomura

Department of Applied Chemistry, Shibaura Institute of Technology, Japan

Abstract: H₂ 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 O₃ or O₂. 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/O₂ derived membrane deposited at 450°C showed the highest H₂ permselectivity. The H₂ permeance was 2.1×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with the H₂/ SF₆ permeance ratio of 5.9×10⁻⁶. H₂ permeances through the HTMOS derived membranes increased with increasing the deposition temperatures. While the H₂ permeance through the PhTMOS and DPhDMOS derived membranes decreased with increasing the deposition temperatures. The PhTMOS derived membrane prepared at 150°C showed the H₂ permeance of 1.7×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with the H₂/ SF₆ permeance ratio of 13. The PhTMOS membrane prepared at 320°C showed the highest H₂/ SF₆ permeance ratio of 1.8×10⁻⁶ among the PhTMOS derived membranes. However, the H₂/ SF₆ permeance ratio through the DPhDMOS membranes showed the different trend. Higher H₂/ SF₆ permeance ratio was found through the DPhDMOS derived membranes deposited at 180°C and 360°C. The maximum H₂/ SF₆ permeance ratio was 4.2×10⁻⁶ 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 O₃ stability after the high temperature treatment. Thus, high H₂ permselective membranes were prepared by the HTMOS at 450 °C.

Keywords: Silica hybrid membrane, counter diffusion CVD method, H₂ 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 hydrogen as 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 methycyclohexane are considered 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 (SiH₄) [4], silicon tetrachloride (SiCl₄) [6], tetratriethoxysilane (TMOS) [9,13] and tetraethylxosilane (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 H₂/N₂ 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/ O₃ at 150–200°C. This membrane was obtained the He permeance of 3×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with the He/N₂ permeance ratio of 950. Gapalakrishman et al. [11] reported that the H₂ permeance of 6.4×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ with a H₂/N₂ permeance ratio of 2,343 at 600°C through the membrane prepared by the counter diffusion CVD method of the TMOS/O₂ systems. They also obtained the three membranes module by using the counter diffusion CVD method [13]. Such a complex shape modules can be prepared by the CVD method that indicates a practical application of a membrane reactor.

Nomura et al. [14] used propyltrimethoxysilane (PrTMOS) as a silica precursor for the counter diffusion
CVD method. The H₂ permeance of $1.3 \times 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹ was obtained with an H₂/N₂ 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 $1.0 \times 10^{-8}$ mol m⁻² s⁻¹ Pa⁻¹) through the HTMOS/O₂ 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 H₂/SF₆ permeance ratio. The kinetic diameter of SF₆ 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 y-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 N₂ bubbler kept at 75–125°C and the vapor was introduced to the outside of the alumina substrate. O₃ was produced by using an O₃ generator (SOW-5000R, SYOKEN Co.). O₃ from the O₃ 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 H₂ (kinetic diameter: 0.29 nm), N₂ (0.36 nm), C₃H₆ (0.45nm), C₃H₈ (0.43nm) and SF₆ (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
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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: H₂O: NaOH= 1: 3.8: 42: 2.5, PhTMOS: EtOH: H₂O: NaOH= 1: 3.8: 30: 1.3 and DPhDMOS: EtOH: H₂O: 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 O₃ in O₂ 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 N₂ 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 (-OCH₃) 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 O₃ 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 O₃ treatments. The vertical axis shows the absorption ratio at 2,960 cm⁻¹ (C-CH₃) or 1,431 cm⁻¹ (Si-C₆H₅) of the O₃-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 O₃ treatment. The ratio at 2,930 cm⁻¹ decreased from 0.23 to 0.06 with increasing the O₃ 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 O₃ treatment at 180°C for the PhTMOS derived powder. The O₃ concentrations of the outlet of the reactor were measured by the O₃ concentration meter [14].

Figure 3: Thermogravimetric curves of hydrolysis powders of silica precursors (Heating rate: 5°C min⁻¹, N₂ 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: O₃ flow rate 0.2 L min⁻¹, 90 min).
of the reactor, the O₃ concentration was less than half of the feed O₃ concentration. Moreover, the O₃ concentrations were approximately 0 g m⁻³ at the 400°C of the reactor. Therefore, the decomposition of organic groups were due to O₃ at less than 300°C of the reactor, and O₃ 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 O₃ 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 the O₃ treatment temperatures. These results indicate that the O₃ 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 H₂ permeances and the H₂/SF₆ permeance ratios through the HTMOS derived membranes by changing the deposition temperatures. The HTMOS derived membrane deposited at 450°C showed the highest H₂ permeance of 2.1×10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with the highest H₂/SF₆ permeance ratio of 5.6×10⁶. The permeance of various gases measured at 270°C is shown in Table 2. The C₃H₆/C₃H₈ permeance ratio was 353. Then, the pore size were estimated around 0.45 nm based on the molecular size of C₃H₆ and C₃H₈. The H₂/SF₆ 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 O₃ treatments. Slightly remained hexyl groups must be the keys for the high H₂/SF₆ selectivity at the 450°C deposition of the HTMOS derived membrane.
Then, the effects of the deposition temperatures were investigated for the PhTMOS and the DPhDMOS derived membranes. Figure 8 shows the $\text{H}_2$ 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 $\text{H}_2$ permeance of $1.7 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ among the PhTMOS derived membranes. While the DPhDMOS derived membrane deposited at 240°C showed the highest $\text{H}_2$ permeance of $1.3 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ among the DPhDMOS derived membranes. Figure 9 shows the dependence of the $\text{H}_2$/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 $\text{H}_2$/SF$_6$ permeance ratio of $1.9 \times 10^4$, while the DPhDMOS derived membrane deposited at 180°C exhibited the highest $\text{H}_2$/SF$_6$ permeance ratio of $4.2 \times 10^4$.

![Figure 8](image1.png)

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

![Figure 9](image2.png)

**Figure 9:** The $\text{H}_2$/SF$_6$ permeance ratios through the PhTMOS and the DPhDMOS membranes 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 $\text{H}_2$/SF$_6$ selectivity was above 6,800 with the $\text{H}_2$ permeance of around $10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 300°C [17]. The hydrogen permeance was $1.0 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ and the selectivity of $\text{H}_2$/SF$_6$ was 10,000 through the organosilica membrane by a sol-gel method [18]. These membranes showed higher $\text{H}_2$ permeances at approximately $1.0 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$. Thus, the HTMOS derived membrane deposited at 450°C was obtained the maximum $\text{H}_2$/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 $\text{H}_2$/SF$_6$ permeance ratios were significantly different between the PhTMOS and the DPhDMOS derived membranes. The $\text{H}_2$/SF$_6$ permeance ratio through the DPhDMOS derived membrane was 3,000 times larger than that through the PhTMOS derived membrane. However, the $\text{H}_2$ permeances were the similar through those membranes. The intensity of mass number of 78
at 180°C for the DPhDMOS derived powder was $1 \times 10^{-12}$ 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 O₃ treatment was 0.53 and 0.61. Therefore, the decomposition of phenyl groups was greatly affected by O₃ 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 O₃ treatments for the PhTMOS derived powders were approximately half for the DPhDMOS derived powders. H₂, N₂ and SF₆ 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 SF₆ (0.55 nm). Therefore, the PhTMOS derived membrane deposited at 180°C showed the high H₂ permeance of 1.8 $\times$ 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with the low H₂/SF₆ 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 SF₆. Therefore, the maximum H₂/SF₆ permeance ratio of 4.2 $\times$ 10⁴ was found to phenyl groups. Amounts of organic groups in the deposited silica layer in the O₃ 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 H₂ permeances were 1–1.2 $\times$ 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ with the H₂/SF₆ permselective ratio of 8–9 $\times$ 10³. 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 membranes was stable at 360°C and the H₂/SF₆ permeance ratio of 302. The low H₂/SF₆ 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 H₂ permeances through the HTMOS, the PhTMOS and the DPhDMOS derived membranes with the H₂/SF₆ permselective membrane >1000. These membranes have the excellent H₂/SF₆ selectivity. The big difference between the HTMOS derived membranes and the DPhDMOS derived membranes was the deposition temperature range to obtain the higher H₂ 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 H₂ permselective membrane. The excellent H₂/SF₆ permeance ratio of 5.6 $\times$ 10⁸ 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 H₂ permeances for high H₂ permselective membrane (H₂/SF₆ permeance ratio >1000).

4. CONCLUSIONS

The maximum H₂/SF₆ permeance ratio of 560,000 was obtained with the H₂ permeance of 2.1 $\times$ 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ through the HTMOS derived membrane deposited at 450°C. The H₂ permeance was higher
than those reported in the former reports. The DPhDMOS derived membrane deposited at 180°C showed a $H_2$ permeance of $7.7 \times 10^{-7}$ 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.

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