Desalination and Water Treatment
www.deswater.com

17 (2010) 120–126
May

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doi: 10.5004/dwt.2010.1707

Preparation of hydrogen separation membranes using disiloxane compounds

Hye Ryeon Lee, Masakoto Kanezashi, Tomohisa Yoshioka, Toshinori Tsuru*

Department of Chemical Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashihiroshima 739-8527, Japan
Tel. +81824247714; Fax +81824247714; email: tsuru@hiroshima-u.ac.jp

Received 31 July 2009; accepted 23 November 2009

ABSTRACT

Hybrid silica membranes were prepared using 1,1,3,3-tetraethoxy-1,3-dimethyldisiloxane (TEDMDS) as a silica precursor. Hybrid silica sol was synthesized by the acetic acid catalyzed hydrolysis and condensation of TEDMDS in ethanol as a solvent with different water molar ratio. Porous silica membranes were fabricated by coating the TEDMDS-derived hybrid silica sol, followed by drying and firing at 300°C or 450°C in nitrogen atmosphere. Single gas permeation characteristic of He, H_2, N_2, and SF_6 through TEDMDS-derived silica membranes were measured at 200°C. It was found that TEDMDS-derived silica membranes had loose amorphous structure than TEOS-derived silica membranes. TEDMDS-derived silica membrane fired at 300°C using TEDMDS/H_2O = 1/20 sol showed H_2 permeance of 2.05×10^{-6} m^3 m^{-2} s^{-1} kPa^{-1} with H_2/SF_6 selectivity of 260°C at 200°C. The water contact angles of TEDMDS-derived silica film were constant even after kept in humid atmosphere (60 RH%, 40°C) for about 35 d, suggesting a hydrophobic property due to the presence of CH_3 groups.

Keywords: 1,1,3,3-Tetraethoxy-1,3-dimethyldisiloxane; Structured silica network membrane; Hydrophobic property; Hydrothermal stability

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1. Introduction

Inorganic membranes have a great attention in the application field of gas separation and purification because of their excellent chemical and physical stabilities and low energy consumption. Silica membranes derived by chemical vapor deposition (CVD) and sol–gel method have been studied most extensively for gas separation [1,2]. In general, tetraethylorthosilicate (TEOS) or tetramethylorthosilicate (TMOS) was used as the silica precursor for the fabrication of microporous silica membranes. The CVD methods generally provide dense amorphous structures, resulting in lower H_2 permeance with high H_2 selectivity [3–5]. In order to increase flux and selectivity through silica membranes, appropriate control of micropore size is required. Sea et al. [6,7] prepared silica membranes by CVD using phenyltriethoxysilane (PTES) and diphenyldiethoxysilane (DPDES) as the Si source to control the pore size and compared the performance with TEOS-derived silica membrane. Gas permeation results suggested that the membrane prepared by PTES and DPDES had more open structures than TEOS-derived membrane, and the DPDES-derived membrane had lager than PTES-derived membrane. Ohta et al. [5] prepared silica membranes by CVD using TMOS, phenyltrimethoxysilane (PTMS), or dimethoxydiphenylsilane (DMDPS) as the silicon source. They also controlled pore sizes by changing the number of phenyl groups in the silicon precursor. The

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*Corresponding authors

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

permeation test of several gases revealed that larger pores could be formed upon increasing the number of phenyl groups in the source.

Similar attempts for the control of pore size have reported on sol–gel derived silica membranes. Methyltriethoxysilane (MTES) [8–12], octyltriethoxysilane (C8TES), dodecyltriethoxysilane (C12TES), octadecyltriethoxysilane (C18TES) [13], methacryloxypropyltrimethoxysilane (MOTMS) [14], etc. were used for the template to create a continuous network of micropores by removing of organic ligands embedded in a dense inorganic matrix. However, the inorganic networks prepared by organic template method (CVD, sol–gel method) using TEOS or TMOS and organic compounds might be densified in hydrothermal condition, since amorphous silica structures consist of ≡Si–O– unit, which are not stable, i.e., selectivities and permeances decreases in hydrothermal condition [6,15]. The replacement from siloxane group to organic group which has hydrophobic properties could be improved hydrothermal stability. The application of organically modified silica materials having hydrophobic property is one of attempts to increase hydrothermal stability. The methylated silica membrane [16–18] and fluorocarbon-modified silica membrane [19] were prepared for new hybrid membranes.

A few research groups have proposed the use of a new type of organic–inorganic hybrid alkoxide that contains the organic groups between two silicon atoms, such as bis(triethoxysilyl)ethane (BTESE, –Si–C–C–Si– unit). Castricum et al. [18, 20] successfully prepared various type of hybrid silica membranes using BTESE. However, hydrothermally stable BTESE-derived silica membranes were used for pervaporation, not for gas separation. Kanezashi et al. [21] prepared BTESE-derived silica membrane for gas separation. Gas permeation results suggested that BTESE-derived silica membranes had more loose structure than silica membranes prepared with single Si atom unit precursors such as TEOS.

In this work, 1,1,3,3-tetraethoxy-1,3-dimethyldisiloxane (TEDMDS, CH_3–Si–O–Si–CH_3 unit structure) was used for the design of a loose organic–inorganic hybrid silica networks with hydrothermal stability. The presence of disiloxane unit with CH_3 groups in TEDMDS alkoxide is expected to form loose amorphous silica networks with hydrothermal stability. We reported various processing for the preparation of TEDMDS polymeric sol and TEDMDS-derived silica membrane by sol–gel method. Gas permeation characteristics of TEDMDS-derived silica membranes were evaluated and hydrophobicity of TEDMDS-derived film was evaluated by measuring the time course of water contact angle in humid atmosphere.

2. Experimental

2.1. Preparation of TEDMDS-derived silica membrane

TEDMDS-derived silica sol were synthesized by hydrolysis and polymerization of TEDMDS. A specified amount of TEDMDS and water in ethanol under various catalysts, which were HCl, HNO_3 and CH_3COOH as acid catalyst and NH_3 as an alkaline catalyst, were stirred at 60°C for 24 h. The composition of the solution was TEDMDS: H_2O: CH_3COOH = 1: x: 0.2 in a molar ratio and total weight of the solution was 50.0 g. The water molar ratio in the solution was controlled at 4, 20, and 100, respectively.

A porous α-alumina support (NOK Corp., Japan, O.D. 3.0 mm, pore size 100–150 nm) was used as a support for the TEDMDS-derived silica membrane. Intermediate layer was formed on an alumina support by coating TiO_2 anatase sol, TiO_2 and SiO_2-ZrO_2 (Si/Zr=1) sol and drying at 80°C and firing at 550°C [22]. After formation of intermediate layer, the TEDMDS-derived silica membrane was fabricated by coating TEDMDS sol, followed by drying at 80°C and firing at 300°C or 450°C in N_2 atmosphere. A cross section of TEDMDS-derived membrane was observed by field emission scanning electron microscope (FE-SEM, S-5000, Hitachi Ltd., Japan).

2.2. Characterization of TEDMDS sol and membranes

Non-volatile weight was measured by thermo gravimetric (TGA-50, Shimadzu, Japan). Temperature was increased at ramping rate of $5°C \cdot min^{-1}$ and kept at 100°C for 30 min in N_2 flow 30 cm^3 min^{-1}. TEDMDS-derived gel powder was prepared by drying at 40°C in air and grinded using a mortar. TG analysis was conducted for TEDMDS-derived powder to evaluate gel characteristics with ramping rate of 5°C min^{-1} up to 1,000°C in nitrogen atmosphere. Before TG measurement, adsorbed water molecules and ethanol were completely removed at 100°C for 5 h. Dried TEDMDS powder and calcinated TEDMDS powder samples were characterized by FT-IR (FTIR-8300, Shimadzu, Japan).

Hydrophobicity of TEDMDS-derived films on the slide glass, which were prepared by firing at 450°C in N_2 atmosphere, was evaluated by measuring water contact angle (DM-300, Kyowa, Japan) before and after exposure to humid atmosphere (60 RH%, 40°C) for specified time intervals.

2.3. Gas permeation measurement

Fig. 1 shows a schematic diagram of gas permeation equipment. Before the measurement, membranes were

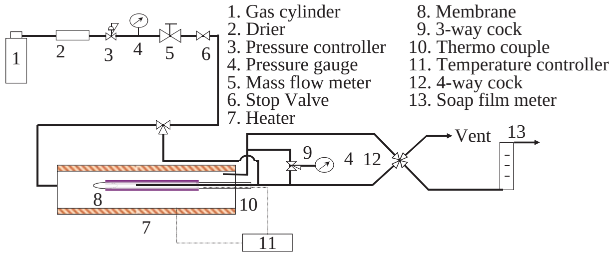

Fig. 1. A schematic diagram of gas permeation equipment.

pretreated with helium flow at 250°C in overnight. Single gas permeation characteristics (He, H_2, N_2, and SF_6) for TEDMDS-derived silica membranes were evaluated at 200°C. The permeation flow rate was measured by a soap film flow meter.

3. Result and discussions

3.1. Characterization of TEDMDS sol

The silica precursors were hydrolyzed and silica polymer was gradually formed by polymerization during the hydrolysis and polymerization reactions. Hydrolyzed TEDMDS is less volatile than unreacted TEDMDS (the boiling point of TEDMDS is 100°C at 20 mmHg [23]) and the silica polymer is a non-volatile substance. Therefore, the TG residual weight of the non-volatile at 100°C was used to evaluate the hydrolysis reaction rate. TEDMDS-derived sols were synthesized with acid and alkaline catalysts with different water molar ratio. Figs. 2a and b show non-volatile weight of TEDMDS sols as a function of reaction time with various catalysts at different water molar ratio of 1/4 and 1/20, respectively. When NH_3 was used as alkaline catalyst, the non-volatile weight of TEDMDS was less than 0.5 wt% even in high water molar ratio as shown in Fig 2b, suggesting no hydrolysis reaction in alkaline condition.

On the other hand, hydrolysis and condensation reaction occurred in acid systems. Non-volatile weights under strong acid systems (HCl, HNO_3) rapidly increased within 2 h and approached to constant even in low water molar ratio. However, insoluble precipitation appeared all of reaction under strong acid systems. When acetic acid was used as a catalyst, there was no insoluble precipitation, i.e., solution was clear at each TEDMDS/H_2O molar ratio (x = 4, 20 and 100). Table 1 summarizes the effect of catalysts with different water molar ratio on reaction behavior of TEDMDS alkoxide.

At the low water molar ratio ($x = 4$), the non-volatile weight of TEDMDS was less than 0.5 wt%, which was the same as alkaline system. With increasing the water molar ratio ($x = 20$ and 100), the reaction rate increased in acetic acid system. The concentration of non-volatile weight at $x = 100$ was almost the same as strong acid system (HCl, HNO_3). On the other hand, the concentration of non-volatile weight at $x = 20$ was slowly increased and it was almost same at 24 h in Fig. 2b. It indicates TEDMDS monomer was slowly hydrolyzed at low water molar ratio under acetic acid system, while at high water molar ratio, hydrolysis and polymerization reactions could occur in a fast reaction rate. From the hydrolysis reaction rate to high water molar ratio cases.

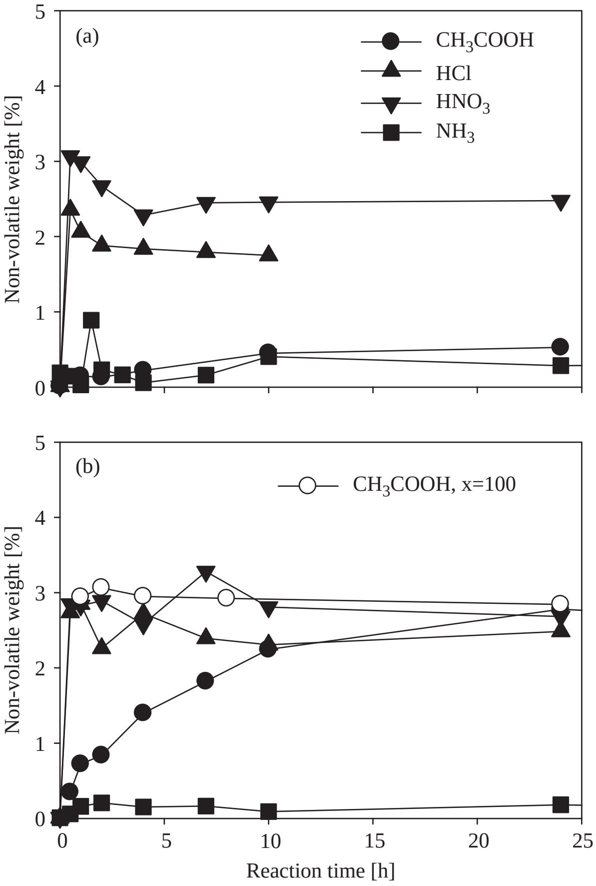

Fig. 2. Non-volatile weight by different catalyst and water molar ratio; (a) TEDMDS/H_2O=1/4, (b) TEDMDS/H_2O=1/20.

The hydrolysis reaction rate probably concerned with molecular weight of TEDMDS polymer. TEDMDS polymer size at low water molar ratio might be smaller than high water molar ratio cases.

There can be expected the two types of TEDMDS polymer structures; linear or cross-linked types as shown in Figs. 3a and b. When initial weight % of TEDMDS in the polymer is 5 wt%, theoretical non-volatile residual weight of linear polymer can be calculated at 2.70 wt% and cross-linked polymer at 2.38 wt%.

Table 1
The summary of catalyst effect by different water molar ratio.

TEDMDS/H_2O [–]	HCl	HNO_3	CH_3COOH	NH_3
1/4	Precipitation (7–10 h)	Precipitation (7–10 h)	Clear	No reaction
1/20	Precipitation (2–3 h)	Precipitation (2–3 h)	Clear	No reaction
pH	2–3	2–3	5–6	8–9

Non-volatile weight of polymer with high water molar ratio ($x = 20$, 100) under acetic acid catalyst was about 2.8 wt% in Fig. 2b. It is close to non-volatile weight value of linear polymer. Therefore, TEDMDS polymer probably had linear polymer structure than cross-linked structure in acetic acid system.

3.2. TEDMDS gel characterization

Fig. 4 shows TG curve of TEDMDS-derived silica gel powder with different water molar ratio as a function of temperature in nitrogen atmosphere. There were no clear difference for weight loss between T/W=1/20 (b) and T/W=1/100 (c). However, in the case of T/W=1/4 (a), the weight residual drastically decreased between 200°C and 450°C. The weight loss of (a), (b), and (c) between 200°C and 450°C was 30.8%, 6.3%, and 3.2 %, respectively. The weight loss probably can be attributed to dehydration and decomposition of un-reacted ethoxy compounds. The weight loss for TEDMDS gel with $x = 4$, 20, and 100 between 450°C and 1,000°C was 12.9%, 7.5%, and 7.7 %, respectively. This is due to decomposition of methyl groups [24]. When methyl group of TEDMDS burns out and turns to SiO_2 structure at high temperature in air atmosphere, theoretical non-volatile weight of linear TEDMDS polymer can be calculated at 77.6 wt%. Non-volatile weight with T/W=1/4 was less than theoretical value, while, that with T/W=1/20 and 1/100 were higher than theoretical one. These results suggest that high molecular weight of TEDMDS polymer, which was prepared with higher water molar ratio, was difficult to evaporate and decompose in nitrogen atmosphere compared to low molecular weight of TEDMDS polymer.

Fig. 5 shows FT-IR spectra of TEDMDS gel powders with TEDMDS/H_2O=1/100 in nitrogen atmosphere. The wide band at 3,500 cm^{-1} present in the dried powder sample and fired at 300°C can be assigned to –OH stretching [24,25]. The OH peak was due to the presence of un-reacted silanol group on TEDMDS and adsorbed water. The OH peak drastically decreased between powder and fired sample at 300°C, suggesting that the weight loss until 300°C was dehydration and decomposition of un-reacted ethoxy group. The bands at 1,400 cm^{-1} and 2,900–3,000 cm^{-1} are due to the Si–CH_3 bands, suggesting that methyl groups still existed in the gel fired at 550°C in nitrogen atmosphere.

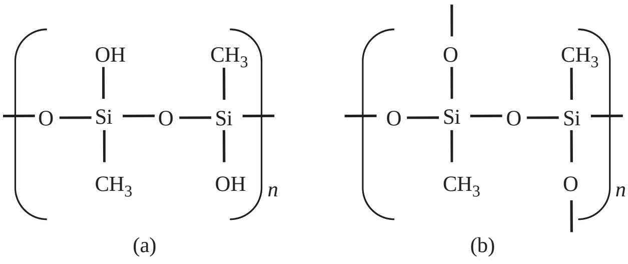

Fig. 3. Molecular structure of TEDMDS polymer; (a) linear polymer and (b) cross-linked polymer.

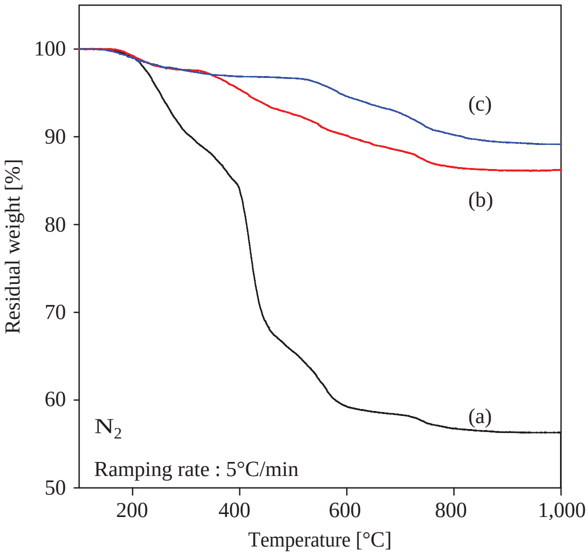

Fig. 4. TG curve of TEDMDS-derived silica gel powder with different water molar ratio (TEDMDS/H_2O=1/4; (a), 1/20; (b), 1/100; (c)) as a function of temperature.

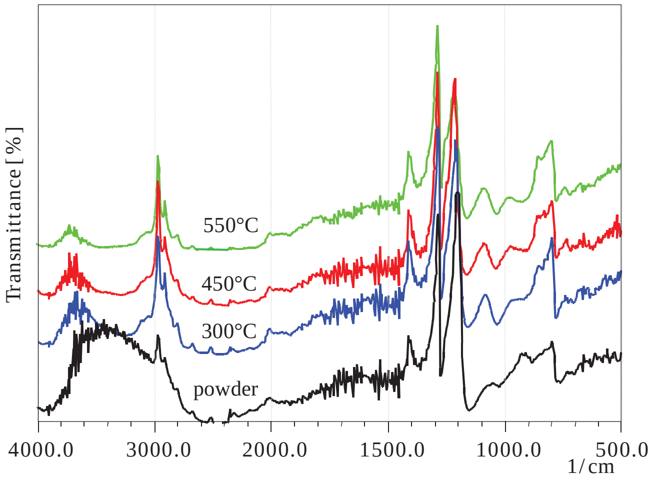

Fig. 5. FT-IR spectra of TEDMDS powders with TEDMDS/H_2O=1/100 in nitrogen atmosphere.

Hydrophobic properties of the TEDMDS were evaluated by measurement of the water contact angle before and after kept in humid atmosphere. Fig. 6 shows a photograph of water contact angle of TEDMDS film ($x = 20$) fired at 450°C in nitrogen. A water contact angle of hydrophilic silica was about 30° [19] but water contact angle of TEDMDS film was 100.3° and independent of T/W molar ratio ($x = 4$, 20, and 100) as shown in Fig. 7. This suggests that TEDMDS film fired at 450°C in nitrogen atmosphere had hydrophobic property due to introduction of CH_3 groups. The water contact angles of TEDMDS-derived silica film were constant even after kept in humid atmosphere (60 RH%, 40°C) for about 35 days, suggesting an improvement of hydrothermal stability.

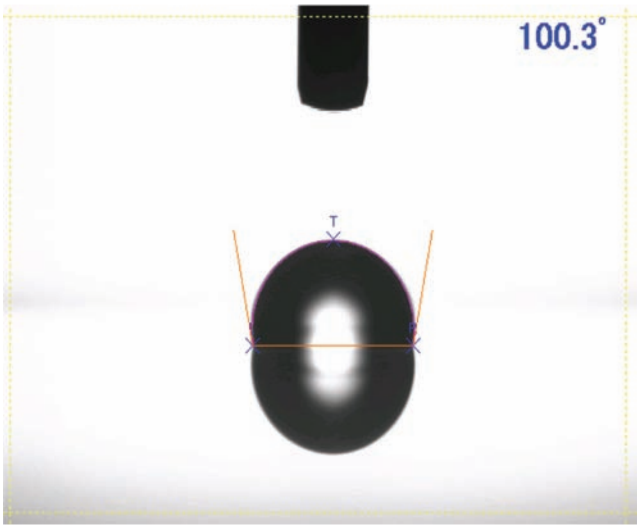

Fig. 6. A photograph of water contact angle of TEDMDS film calcinated at 450°C in nitrogen using TEDMDS/H_2O=1/20 sol.

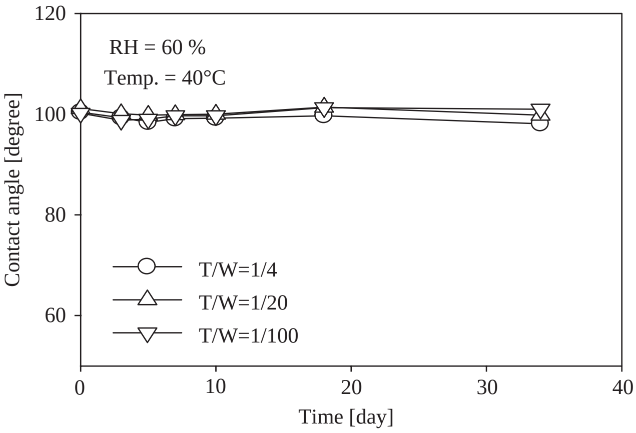

Fig. 7. Time course of water contact angle for TEDMDS-derived silica film fried at 450°C in nitrogen atmosphere with different water molar ratio (4, 20, 100) before and after exposure to humid atmosphere (RH 60%, 40°C).

3.3. *Gas permeation characteristics of TEDMDS-derived membrane*

Fig. 8 shows the FE-SEM image of cross section of TEDMDS-derived silica membrane. The two layers are the α-alumina layer and intermediate layer with separation layer. There was no obvious TEDMDS-derived silica layer on the surface of intermediate layer. The intermediate layer with separation layer was approximately 200 nm thickness on the top of the porous α-alumina layer.

Fig. 9 shows gas permeances for TEDMDS-derived silica membranes with different water molar ratio as a function of kinetic diameter. In the case of Knudsen permeation, the permeance ratios of H_2/N_2 and H_2/SF_6 are calculated at 3.73 and 8.51, respectively [5]. The permeance ratios of H_2/N_2 and H_2/SF_6 in TEDMDS-derived silica membrane with T/W=1/4 were 5.45 and 17.70, respectively, and those were close to Knudsen ratio. Because low molecular weight polymer is likely

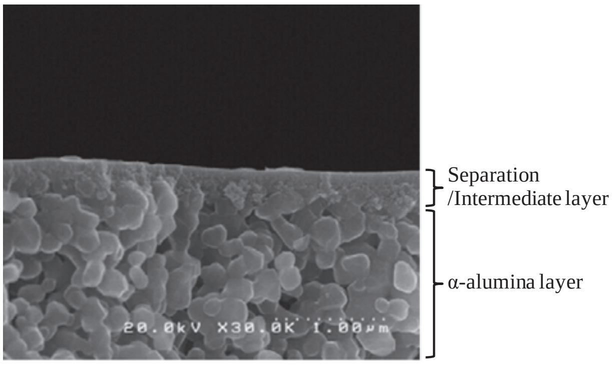

Fig. 8. FE-SEM image of cross section of TEDMDS-derived silica membrane on α-alumina tube.

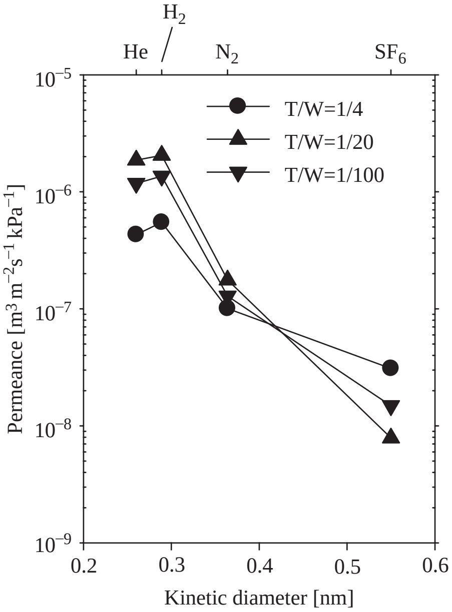

Fig. 9. Effect of water molar ratio on pore size distribution of TEDMDS-derived silica membranes fired at 300°C.

to penetrate into the support, the penetrated polymer might have blocked small pore sizes. However, low molecular weight polymer was not large enough to plug pinholes, resulting in low hydrogen permeance with high SF_6 permeance. On the other hand, in the case of coating polymer with T/W=1/100 on intermediate layer, active separation layer with less pinhole could be formed, giving relatively high H_2 permeance of 1.36×10^{-6} m^3 m^{-2} s^{-1} kPa^{-1} with H_2/SF_6 permeance ratio of 100. Probably because of no large difference between polymer molecular weight with water molar ratio at 20 and 100, similar pore size distribution could be observed in these TEDMDS-derived silica membranes (T/W=1/20, 1/100). This result suggests that high molecular weight of TEDMDS polymer is preferable for the formation of pinhole-free active separation layer.

Fig. 10 shows gas permeance for TEDMDS-derived (TEDMDS/H_2O=1/20) and TEOS-derived silica membrane [26] at 200°C as a function of kinetic diameter. It should be noted that TEOS-derived silica membranes were fired at 550°C in air atmosphere. TEDMDS-derived silica membranes fired at 300°C showed H_2/N_2 permeance ratio of 11.6 with H_2/SF_6 permeance ratio of 260, while that fired at 450°C showed H_2/N_2 permeance ratio of 8.3 with H_2/SF_6 of 335. All gas permeances for TEDMDS-derived silica membrane fired at 450°C were higher than those fired at 300°C, however, similar pore size distributions were observed despite the different calcination temperatures. This is because decomposition of un-reacted ethoxy group

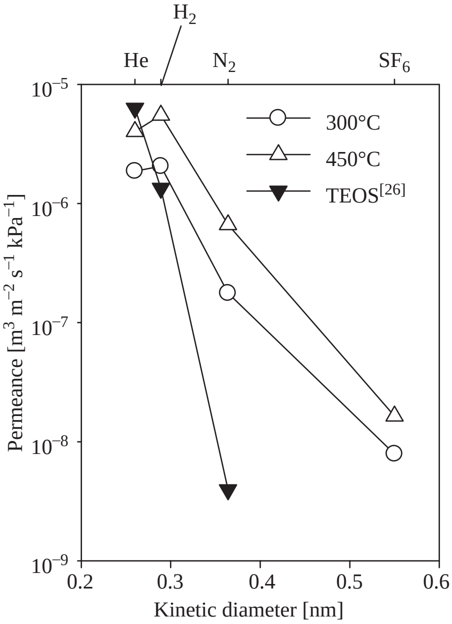

Fig. 10. Gas permeances for TEDMDS-derived (TEDMDS/H_2O=1/20) and TEOS-derived silica membrane at 200°C as a function of kinetic diameter.

was less than 6% between 300°C and 450°C as mentioned in Section 3.2. Both TEDMDS-derived silica membranes showed slightly high H_2 permeance than He, which is governed by Knudsen permeance through the loose amorphous networks. On the other hand, TEOS-derived membrane showed high selectivity of H_2/N_2 of 340 with H_2/SF_6 permeance ratio above 1,000 since SF_6 was less than 10^{-9} m^3 m^{-2} s^{-1} kPa^{-1}. TEOS-drived silica membrane showed high He permeance than H_2 due to molecular sieving mechanism, which is different permeation characteristic from TEDMDS-derived membranes.

Judging from the H_2/N_2 and H_2/SF_6 permeance ratio for TEDMDS-derived and TEOS-derived membranes, the average pore size can be estimated to be approximately in the range of 0.4–0.5 nm for TEDMDS-derived membrane and approximately 0.3 nm for TEOS-derived membrane. The difference in these pore size distributions is probably because amorphous silica structures created by TEDMDS, which consists of disiloxane unit (–Si–O–Si–) are expected to be much looser than those created by TEOS with mono silicon.

4. Conclusions

Hybrid silica membranes were prepared using TEDMDS as a silica precursor by sol-gel method. Gas permeation characteristics of TEDMDS-derived silica membranes were evaluated and hydrophobicity of TEDMDS-drived film was evaluated by measuring the time course of water contact angle in humid atmosphere.

The TEDMDS polymeric sols were prepared under the acetic acid system. In the case of water to TEDMDS molar ratio of 100, fully hydrolyzed monomer might be formed high molecular weight of TEDMDS polymer. A water contact angle of TEDMDS-derived films with different water molar ratio (T/W=1/4, 1/20, 1/100) fired at 450°C in nitrogen atmosphere was approximately 100° and it was constant before and after kept in humid atmosphere (60 RH%, 40°C) for about 35 d, suggesting a hydrophobic property due to the presence of CH_3 group.

TEDMDS-derived membranes fired at 300°C showed H_2/N_2 permeance ratio of 11.6 with H_2/SF_6 permeance ratio of 260. On the other hand, TEOS-derived membrane showed high selectivity of H_2/N_2 of 340 with H_2/SF_6 permeance ratio above 1,000. This is because amorphous silica structures created by TEDMDS, which consists of disiloxane unit (–Si–O–Si–), are much looser than those created by TEOS with mono silicon.

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