Development of hydrogen-selective triphenylmethoxysilane-derived silica membranes with tailored pore size by chemical vapor deposition

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Abstract

Amorphous silica membranes were developed, based on an *in silico* molecular design, to exhibit excellent hydrogen-selective performance for separating hydrogen from mixtures containing larger organic molecules, such as methylcyclohexane and toluene. Triphenylmethoxysilane (TPMS) was synthesized and used as a novel precursor to prepare membranes by the counter-diffusion chemical vapor deposition method. Under the optimized bubbler temperature and counter-diffusion chemical vapor deposition reaction time, the fresh membranes showed high reproducibility and high hydrogen permeance in the order of $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and high H_2/SF_6 ideal selectivity of over 12000 at 573 K. Moreover, the TPMS-derived membrane exhibited good stability after hydrogen regeneration, even after placement in a dehumidifier cabinet at room temperature for 90 days. Single gas permeation performance and normalized Knudsen-based permeance evaluation showed that the TPMS-derived membrane (three phenyl groups on the precursor) had a pore size of 0.486 nm, and exhibited looser structures with larger pore size than those of a diphenyldimethoxysilane (DPDMS)-derived membrane (two phenyl groups on the precursor). These results suggest that the pore size of silica membranes can be tailored with various structured silica precursors containing phenyl groups.

Keywords: Silica membrane; Triphenylmethoxysilane; Chemical vapor deposition; Quantum chemical calculation; Pore size control;

1. Introduction

Hydrogen-selective membranes have gained considerable attention as membrane materials with potential uses in a broad range of applications, from large-scale hydrogen production for power generation with CO₂ capture to small-scale integration with fuel cells [1–3]. Amorphous silica membranes, as one of the most promising hydrogen-selective membranes, may potentially be used over a large temperature range and under tough test conditions [1–21]. To date, two routes for the preparation of silica membranes, the sol-gel method [1, 4, 6, 8–10, 16–20] and the chemical vapor deposition (CVD) method [3, 7, 11–15, 21], have been reported. However, the pore size of most reported silica membranes appears too small to efficiently separate hydrogen from hydrogen-organic gas mixtures (e.g., the methylcyclohexane-toluene-hydrogen mixture system in the methylcyclohexane dehydrogenation reaction). If the membrane pore size is controlled to approximately 0.5 nm and higher hydrogen permeance and permselectivity could be obtained, then such silica membrane would be a viable choice for systems, such as a mixture containing methylcyclohexane (kinetic diameter: 0.60 nm) and toluene (0.59 nm). Therefore, it is important to develop a microporous membrane-structure controlled method, in particular, a method to tailor and enlarge the pores of the silica membranes.

There have been reports on the tailoring of the pore size of silica membranes by using the chemical structures of silica precursors via both the sol-gel route and CVD method. The precursors are various structured alkoxides: bridged alkoxides with $\equiv\text{Si-R-Si}\equiv$ structure (e.g., bis(triethoxysilyl) ethane) [19, 20], disiloxane alkoxides with $\equiv\text{Si-O-Si}\equiv$ structure (e.g., hexamethyldisiloxane, hexaethoxy disiloxane, tetraethoxydimethyl disiloxane) [16, 17, 21], and silanes consisting of organic functional groups (methyl, propyl, hexyl, phenyl), which are directly

attached to a single silicon atom [8, 11, 12, 22, 23]. For example, in our previous work, three series of silica membranes were prepared by the CVD method using tetramethoxysilane (TMOS), phenyltrimethoxysilane (PTMS), and diphenyldimethoxysilane (DPDMS, also called dimethoxydiphenylsilane (DMDPS) in the references [12, 14, 15]) as the silica precursors (the chemical structures of the precursors are provided in Figure 1) [12]. We found that membrane performance was successfully controlled by regulating the number of phenyl groups on the precursor. The order of gas permeance and the membrane pore size increased among the series in the same order, DPDMS>PTMS>TMOS. The DPDMS-derived membranes had larger pores of approximately 0.40 nm, looser structures, and a wider pore distribution than the other two precursors [12]. The DPDMS-derived membrane showed excellent hydrogen permeance of over 10^{-6} mol m⁻² s⁻¹ Pa⁻¹ and high H₂/SF₆ ideal selectivity of over 6800 at 573K. To explain the relation between the structure of the precursors and the membrane pore size, we previously focused on the bond dissociation enthalpies of the precursors. We hypothesized that the precursors formed silanone structures as important intermediates during CVD, and that these structures greatly affected the pore structures. The study indicated that the DPDMS-derived membrane was mainly prepared through the methoxyphenylsilanone intermediate, whereas the PTMS-derived and the TMOS-derived membranes were mainly prepared through the dimethoxysilanone intermediate. We proposed that the presence of phenyl groups in the intermediate has a large effect on the enlargement of the pore size [12].

Therefore, in this present study, we design and synthesize a new silica precursor, triphenylmethoxysilane (TPMS, shown in Figure 1). Quantum chemical calculations indicate that the membrane prepared with this new precursor would have larger pores than the DPDMS-derived

membrane. However, TPMS is solid at room temperature and, because almost all the previous reports on silica membranes via CVD employ precursors in the liquid state, it would not be easy to prepare silica membranes via CVD with TPMS. Although it is a challenge to prepare silica membranes using TPMS, such membranes will have a high hydrogen permeation performance owing to the larger pore size of approximately 0.5 nm. We first investigate the preparation parameters, such as bubbler temperature and CVD reaction time on gas permeation performance. We then present gas permeation properties, pore size evaluation and stability of the as-synthesized TPMS-derived silica membranes in this work.

Fig. 1. Chemical structures of tetramethoxysilane (TMOS), phenyltrimethoxysilane (PTMS), diphenyldimethoxysilane (DPDMS), and triphenylmethoxysilane (TPMS).

2. Experimental

2.1 Quantum chemical calculations for estimating bond energies

The sum of electronic and thermal enthalpies in the gas phase (H°) was calculated by the geometry optimization of each compound followed by a frequency analysis for thermal and zero point energy corrections. For this calculation, we employed the density functional theory (DFT) method at the B3LYP/6-311++G(d,p) level of theory and set the most stable conformation as determined by using molecular mechanics with the Merck molecular force field (MMFF) as the

initial geometry. Bond dissociation enthalpies or reaction enthalpies (ΔH°) were obtained from the calculated enthalpies of the reactants (H°_{rea}) and products ($\Sigma H^\circ_{\text{pro}}$) [12]. Calculations were performed using the Gaussian09 and Spartan'14 programs.

2.2 Preparation of TPMS monomer

In a dry argon atmosphere, 50 mL (1.2 mol) of methanol and 16.7 mL (120 mmol) of triethylamine were placed in a 300 mL two-necked flask and the flask was cooled at 273 K. To this, 29.5 g (100 mmol) of chlorotriphenylsilane was slowly added and the mixture was stirred at this temperature for 12 h. After the removal of excess methanol and triethylamine under reduced pressure, the residue was dissolved in 100 mL of diethyl ether and washed with water (100 mL $\times$ 3 times). The ethereal layer was dried over anhydrous magnesium sulfate and the solvent was evaporated to provide 28.4 g (9.69 mmol) of TPMS as a colorless solid: m.p.: 331.1 K; EI-MS: 290 (M^+); ^1H -NMR (400 MHz, in CDCl_3): δ = 3.65 (s, 3H, MeO), 7.36–7.48 (m, 9H, *m*- and *p*-Ph), 7.63 (dd, 6H, J = 1.6, 8.0 Hz, *o*-Ph). The NMR data, provided in the Supporting Information, agree with the data reported in the literature [24].

2.3 Preparation and performance of TPMS-derived silica membranes

Silica membranes were prepared by the counter-diffusion CVD method using oxygen and TPMS as the silica precursor on the modified ceramic substrates. A porous $\alpha\text{-Al}_2\text{O}_3$ symmetrical capillary with pore size of 150 nm (O.D. 6 mm; thickness 1.1 mm; supplied from Noritake Co. Ltd, Nagoya, Japan) was used as the substrate. As described in our previous work [12], the support was modified with a boehmite sol by a sol-gel procedure. After the dip-coating, drying, calcination processes were repeated three times, the pore size of the modified $\gamma\text{-Al}_2\text{O}_3/\alpha\text{-Al}_2\text{O}_3$ support was found to be approximately 4 nm by permoporometry measurements.

Figure 2 provides a schematic diagram of the CVD apparatus used for preparation of the silica membrane. The bubbler temperature of the silica precursor was kept constant in the range from 463 K to 528 K during the preparation of the silica membranes. The saturated vapor of TPMS was supplied with 200 mL min^{-1} of N_2 as the carrier gas from the outside of the modified support, while 200 mL min^{-1} of O_2 was supplied from the inside of the support. The CVD temperature was 873 K, and the reaction time ranged from 60 to 90 min. After the CVD procedure, the TPMS-derived silica layer was formed in the $\gamma\text{-Al}_2\text{O}_3$ pores and on the surface of the $\gamma\text{-Al}_2\text{O}_3$ layer.

Gas permeation performances through the as-synthesized silica membrane were measured using a single-component gas in temperatures ranging from 573 to 373K. As shown in Figure 2, the permeances of H_2 , O_2 , and N_2 gas were measured by a film flow meter (SF, Horiba Ltd., Kyoto, Japan), while those of CF_4 and SF_6 were determined with the pressure difference method [12]. The surface and cross-section of the silica membrane were observed using FE-SEM (Hitachi, S-4800).

Fig. 2. Schematic diagram of experimental apparatus for preparation and gas permeation measurements of silica membranes.

3. Results and discussion

3.1 Prediction of intermediate based on DFT calculations

Table 1 provides the bond dissociation enthalpies calculated at the B3LYP/6-311++G(d,p) level of theory. The calculated results suggest that the SiO-CH₃ bond is relatively weak when compared with the other bonds. Therefore, this bond will be the first to be broken for each precursor monomer in the CVD process. PTMS and DPDMS contain three and two SiO-CH₃ bonds, respectively, hence, a consecutive SiO-CH₃ bond breaking may occur to a certain extent. However, the most plausible pathway is the SiO-CH₃ bond breaking followed by Si-C₆H₅ bond dissociation, in which the formation of a Si=O double bond stabilizes the dissociation product.

The calculated enthalpies of reaction (1) are 131 kJ/mol and 110 kJ/mol for PTMS ($n = 1$) and DPDMS ($n = 2$), respectively. These values are significantly smaller than the enthalpies of other possible bond breakings such as SiO-CH₃ (ca. 350 kJ/mol). Consequently, silanone compounds, $\text{O}=\text{Si}(\text{OCH}_3)_{3-n}(\text{C}_6\text{H}_5)_{n-1}$, are expected to form as transient intermediates in the CVD process. These results for PTMS and DPDMS agree with the previous study [12].

The newly designed and synthesized silica precursor, TPMS, contains only one SiO-CH₃ bond. For this precursor, the exclusive dissociation of the Si-C₆H₅ bond is expected after triphenylsilane radical formation. The enthalpy of reaction (1) was calculated to be 118 kJ/mol for TPMS ($n = 3$). Thus, a major intermediate will be diphenylsilanone in the TPMS-CVD process, as shown in Table 1. The intermediate compound for TPMS, $\text{O}=\text{Si}(\text{C}_6\text{H}_5)_2$, may easily undergo the subsequent oligomerization (Eq. 2) and oxidation reactions to form silica networks [12, 25].

The bulky phenyl groups in the siloxane segments will be burned off and replaced by the atomic oxygen in the presence of O₂. So the silica membrane has a looser structure [12, 25]. Based on the hypothesis that the size of the intermediate affects the membrane structure, we predict that the pore size distribution of the TPMS-derived membrane shifts toward a larger pore size than that of PTMS and DPDMS.

Table 1 Bond dissociation enthalpies calculated at the B3LYP/6-311++G(d,p) level and the predicted intermediates.

Precursor	Bond	ΔH° (kJ/mol)	Intermediate
PTMS	SiO–CH ₃	357
	Si–C ₆ H ₅	396	
	Si–OCH ₃	453	
DPDMS	SiO–CH ₃	353
	Si–C ₆ H ₅	400	
	Si–OCH ₃	438	
TPMS	SiO–CH ₃	348
	Si–C ₆ H ₅	374	
	Si–OCH ₃	413	

3.2 The influence of bubbler temperature and CVD reaction time on gas permeation performance through TPMS-derived silica membranes

The saturated vapor concentration of the silica precursor, which is generally controlled by the bubbler temperature, and CVD reaction time are the most important parameters for the preparation

of amorphous silica membranes by the CVD method. Figure 3 shows the gas permeation results at 573 K through TPMS-derived silica membranes prepared with different bubbler temperatures for 60–90 min. There was no significant influence of bubbler temperature on the H₂ and N₂ permeances when the temperatures were varied from 463 to 528 K. However, the SF₆ permeance was seriously affected by bubbler temperature. Under the fixed oxygen flow of 200 mL min⁻¹ during the CVD process in this work, it is not appropriate to supply the TPMS with too large or too small vapor concentration to form a high-selectivity silica membrane under higher or lower bubbler temperatures. It means there should be an optimized bubbler temperature for preparing the membranes having higher H₂ permeance and H₂/SF₆ selectivity. Therefore, as shown in Figure 3, the membrane prepared with a bubbler temperature of 478 K (the vapor concentration of TPMS was 0.099 mol TPMS/m³ N₂) provided the highest H₂ permeance (1.2×10^{-6} mol m⁻² s⁻¹ Pa⁻¹) and lowest SF₆ permeance (6.9×10^{-11} mol m⁻² s⁻¹ Pa⁻¹) among the silica membranes investigated. It means that this membrane displayed a satisfactory ideal selectivity of H₂/SF₆ as high as 16800 (also presented in Table 2).

Fig. 3. Effect of bubbler temperature on gas permeation performance.

Three series of TPMS-derived silica membranes were prepared with different CVD reaction times from 60 to 90 min when the silica bubbler temperature was set at 478 K. Figure 4 shows the gas permeation performance of these three membranes over a temperature range from 573 to 373 K. Commonly, the single-gas permeance of H₂ and SF₆ or ideal selectivity of H₂/SF₆ are evaluation criteria for excellent silica membranes. As seen in Figure 4a–c, all the gas permeances were not sensitive to a temperature variation. The order of magnitude of H₂ permeance through these membranes was approximately 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ even after the CVD reaction time was increased to 90 min. However, the order of magnitude of SF₆ permeance decreased from 10⁻¹⁰ to 10⁻¹¹ mol m⁻² s⁻¹ Pa⁻¹ with an increasing CVD reaction time. Compared with the number of pores through which only hydrogen can permeate, the number of pores through which SF₆ can permeate should be lower. The trend shown in Figure 4 indicates that the small number of larger pores through which SF₆ can permeate would become even smaller with a prolonged CVD time. Thus, the ideal selectivity of H₂/SF₆ increased with CVD deposited time from approximately 3000 to over 16800 for these silica membranes. Meanwhile, as shown in Figure 4d, the extended CVD reaction time has almost no influence on the hydrogen and nitrogen permeances because the kinetic diameter of the hydrogen molecule (0.289 nm) and nitrogen molecule (0.364 nm) is far smaller than the pore size of these TPMS-derived membranes. Additionally, a DPDMS-derived silica membrane was also prepared at 873 K for 60 min using the same modified support as a comparison membrane, which is an optimized condition for DPDMS. The preparation procedure of the DPDMS (Shin-Etsu Chemical Co., Ltd., Tokyo, Japan) membrane has been described in previous work [12–15]. As shown in Figure 4d, H₂ and N₂ permeances of the TPMS-derived membrane reacted for 90 min were higher than those of the DPDMS-derived membrane, while SF₆ permeance was almost the

same at around $6.4\text{--}6.9 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. This suggests that the TPMS-derived membrane has much larger pores and looser structures than those of the DPDMS-derived membrane.

Fig. 4. Gas permeation performance through TPMS-derived silica membranes prepared with different CVD reaction times: (a) 60 min; (b) 75 min; (c) 90 min; and (d) comparison with DPDMS-derived silica membranes.

Fig. 5. The reproducibility of TPMS-derived silica membranes.

Fig. 6. SEM images of TPMS-derived silica membrane on the modified support: surface (a, b) and cross sections (c, d).

The high reproducibility of permselective membranes with high permeation properties is an important aspect for potential applications. Therefore, the reproducibility of the TPMS-derived membranes was investigated in this work. Three series of silica membranes were prepared under the same optimized conditions, that is, a bubbler temperature of 478 K and CVD reaction time of 90 min. As shown in Figure 5, these membranes exhibited high hydrogen permeance and H₂/SF₆ ideal selectivity at 573 K. The average values of H₂, N₂, and SF₆ permeance were $(1.07 \pm 0.07) \times 10^{-6}$ mol m⁻² s⁻¹ Pa⁻¹, $(1.13 \pm 0.37) \times 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹, and $(9.02 \pm 1.51) \times 10^{-11}$ mol m⁻² s⁻¹ Pa⁻¹, respectively, corresponding to an average H₂/SF₆ ideal selectivity of over 12000. These results exhibit the high reproducibility of the TPMS-derived membranes. As seen in Figure 6, the continuous compact γ -Al₂O₃ layer of around 5.5 μ m was uniformly formed on the support. Amorphous silica was deposited in the γ -Al₂O₃ pores and on the surface of the γ -Al₂O₃ layer, which was also reported in our previous work [12]. Although the thickness of the SiO₂ layer, which determines hydrogen permeance, is not clear at this stage, such a uniform layer (see Fig. 6b and Fig. 6d of high magnification images) results in the high hydrogen permeance in the order of 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and ideal selectivity of H₂/SF₆ over 12000.

3.3 Gas permeation properties through TPMS-derived silica membranes

Fig. 7. Gas permeation properties of the TPMS-derived silica membrane: the pressure difference effect on gas permeation performance at (a) 573 K; (b) 473 K; and (c) 373 K; and (d) Arrhenius plots of the gas permeances through the membrane at a pressure difference of 0.2 MPa.

The performances of the silica membrane prepared under the optimized conditions were investigated by determining the gas permeation properties under different temperatures from 573 to 373 K and pressure differences ranging from 0.1 to 0.5 MPa. As shown in Figure 7a–c, the permeances of H₂, O₂, N₂, CF₄, and SF₆ hardly showed any dependency on the pressure differences at the temperature region investigated in this work. Moreover, the order of magnitude of H₂ permeance was approximately 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ while that of SF₆ was below 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹. This shows that this TPMS-derived membrane displays high H₂/SF₆ ideal selectivity over 10000 under the different temperatures and pressure differences.

Generally, the gas permeance through the silica membranes is activated, and increases with increasing temperatures. Thus, the activation energies (E_a) of the gas permeation are obtained by fitting the experimental data to the Arrhenius law, using the following:

$$Q = Q_0 \exp(-E_a/RT), \quad (3)$$

where Q and Q_0 are the i th component gas permeance and permeation coefficient, respectively.

Figure 7d shows the Arrhenius plots of all the gas permeances through the TPMS-derived membrane under the pressure difference of 0.2 MPa according to the permeation results in Figure 7a–c. The permeances of H₂ and O₂ rarely showed any dependency on the permeation temperature. Their activation energies for permeation through the membrane were only 0.08 and 0.5 kJ mol^{−1} for H₂ and O₂, respectively. It should be noted that the activation energy of hydrogen through the TPMS-derived membrane is very lower than that of TMOS-, PTMS-, and DPDMS-derived membranes that were reported in our previous work, which were 19, 11, and 0.8 kJ mol^{−1}, respectively [12], and that of silica membranes summarized in Ref. [3] where E_a was reported to be in the range of 2.2–25 kJ mol^{−1} (see the Table 2 in Ref. [3]). Only the permeance of CF₄ exhibited a higher activation energy of 11.8 kJ mol^{−1}, while that of SF₆ was 4.1 kJ mol^{−1}. This indicates that the TPMS-derived membrane has large micropores from approximately 0.47 to 0.55 nm estimated on the basis of the molecular kinetic diameter of CF₄ and SF₆. The lower activation energies indicate that the TPMS (containing three phenyl groups)-derived membrane has a looser silica network and much larger pores than the TMOS-, PTMS-, and DPDMS-derived membranes investigated in our previous work owing to the different chemical structures for these silica precursors, which greatly influence the enlargement of pore size of the silica membranes [12]. This is also consistent with the results for pore size prediction by DFT calculations in the preceding Section 3.1 and the pore size evaluation in Section 3.5.

3.4 Membrane regeneration

Table 2 Gas permeation performance of the silica membrane at 573 K before and after membrane regeneration.

	H ₂ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)	N ₂ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)	SF ₆ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)	H ₂ /N ₂ ideal selectivity	H ₂ /SF ₆ ideal selectivity
Fresh membrane	1.2×10 ⁻⁶	1.6×10 ⁻⁷	6.9×10 ⁻¹¹	7.5	16800
Exposure at R.T. for 90 days	3.7×10 ⁻⁹	2.7×10 ⁻¹⁰	4.9×10 ⁻¹¹	13.7	76
After regeneration	1.1×10 ⁻⁶	8.3×10 ⁻⁸	9.6×10 ⁻¹¹	13.2	11000

As shown in Table 2 and the above discussion, the fresh membrane prepared under the optimized conditions displayed high hydrogen permeance and H₂/SF₆ ideal selectivity. However, after placement in a dehumidifier cabinet (the humidity lower than 1% RH) at room temperature for 90 days, the H₂ permeance of the membrane at 573 K drastically decreased from 1.2×10⁻⁶ to 3.7×10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹, as did the N₂ permeance, from 1.6×10⁻⁷ to 2.7×10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹. SF₆ permeance displayed less of a change, from 6.9×10⁻¹¹ to 4.9×10⁻¹¹ mol m⁻² s⁻¹ Pa⁻¹. This may be attributed to the small amount of physically adsorbed water molecules on the membrane surface or on the inside of the pore, thus decreasing the effective pore size for gas permeation [14].

Pure hydrogen gas was fed at 300 mL min⁻¹ from the outside of the tubular membrane keeping the pressure difference at 0.2 MPa in order to evaluate membrane regeneration at 573 K. After regeneration for about 12 h, the permeance of H₂ and SF₆ was recovered, and the recovery of N₂ permeance was not as significant, which is similar to a previous report [14]. Good stability and high hydrogen permeation performance was observed for this membrane after regeneration as shown in Table 2. Based on the above results, the TPMS-derived membrane demonstrated good stability even after being placed in the dehumidifier cabinet at room temperature for as long as three months.

3.5 Pore size evaluation of the TPMS-derived silica membrane

Fig. 8. Pore size evaluation of the TPMS-derived silica membrane compared with the DPDMS-derived silica membrane.

The normalized Knudsen-based permeance (NKP) method is an effective mathematic model to evaluate the pore size of microporous membranes, such as zeolite membranes and silica membranes whose pore sizes are less than 1 nm [18, 19]. As shown in Figure 4d, the permeation resistances through the modified support were not as small as those through the silica membranes overall. According to the support resistance model [26–28], we exclude the permeation resistance of the support based on the gas permeation data in Figure 4d and Figure 7. The membrane layers are treated as analogous to electrical resistors in series, and the membrane resistance for gas permeation is assumed as a series process of the supports and top-layer resistance, where the permeation is the reciprocal of the resistance (Eq. 4) [26–28]:

$$1/Q_{total} = 1/Q_{top-layer} + 1/Q_{support} \quad (4)$$

Hydrogen is the smallest molecule in this work, which is thus taken as a reference (j th component).

The NKP value is the permeance ratio of the i th component (P_i) to that predicted from H_2

permeation based on the Knudsen diffusion mechanism ($P_{H_2} (M_j/M_i)^{1/2}$) [18, 19]. The pore size evaluation of TPMS-derived silica membrane by the NKP method is shown in Figure 8. The NKP simulated curve was in agreement with the membrane permeation data. The pore size of TPMS-derived membrane was evaluated as approximately 0.486 nm, which is between the kinetic diameters of CF_4 (0.47 nm) and SF_6 (0.55 nm). This also was in agreement with the discussion of the membrane activation energy provided in Section 3.3. For comparison, the DPDMS-derived membrane shown in Figure 4 indicates a pore size of around 0.420 nm with the NKP method (Figure 8). These results also suggest that the TPMS-derived membrane had looser structures and larger pore size than those of the DPDMS-derived membrane.

4 Conclusions

With the aid of quantum chemical calculations employing the DFT method at the B3LYP/6-311++G(d,p) level of theory, we designed and synthesized TPMS as a new silica precursor for preparation of the silica membrane with high permeation performance and with a larger pore size than those of PTMS- and DPDMS-derived membranes.

A uniform silica membrane was prepared by the counter-diffusion CVD method using oxygen and TPMS on the modified alumina substrates. The TPMS-derived silica membranes, which were prepared under the optimized bubbler temperature and CVD reaction time, showed excellent hydrogen permeance in the order of $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and high ideal selectivity of H_2/SF_6 over 12000 at 573 K. The silica membranes showed high reproducibility and good stability. High recovery of hydrogen permeation after membrane regeneration was observed even with exposure to room temperature for three months.

The TPMS-derived membrane was successfully tuned to have a pore size of approximately 0.50 nm according to the NKP evaluation method. It had looser structures and larger pore size than those of the DPDMS-derived membrane. Based on the results of the DFT calculations, we demonstrated that the pore size of silica membranes can be controlled by tuning the bond energies and substituent size of the silica precursor. The large groups, such as phenyl groups, in silica precursors exert a large influence on the augmentation of the pore size of amorphous silica membranes.

In summary, the development of such TPMS-derived membranes with high hydrogen permeation performance should provide more opportunities for high-purity hydrogen production from organic chemical hydrides.

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Graphical Abstract