



# 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  $\text{H}_2/\text{SF}_6$  ideal selectivity of over 12,000 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.

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## 1. Introduction

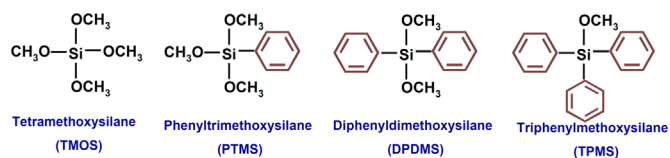
Hydrogen-selective membranes have gained considerable attention as membrane materials with potential uses in a broad range of applications, from large-scale hydrogen production for power generation with  $\text{CO}_2$  capture to small-scale integration with fuel cells [1–3]. Amorphous silica membranes, 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

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

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 Fig. 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  $10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and high  $\text{H}_2/\text{SF}_6$  ideal selectivity of over 6800 at 573 K. 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 Fig. 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.

## 2. Experimental

### 2.1. Quantum chemical calculations for estimating bond energies

The sum of electronic and thermal enthalpies in the gas phase ( $H^\circ$ ) 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 ( $\Delta H^\circ$ ) were obtained from the calculated enthalpies of the reactants ( $H_{\text{rea}}^\circ$ ) and products ( $\sum H_{\text{pro}}^\circ$ ) [12].

Calculations were performed using the Gaussian09 and Spartan'14 programs.

### 2.2. Preparation of TPMS monomer

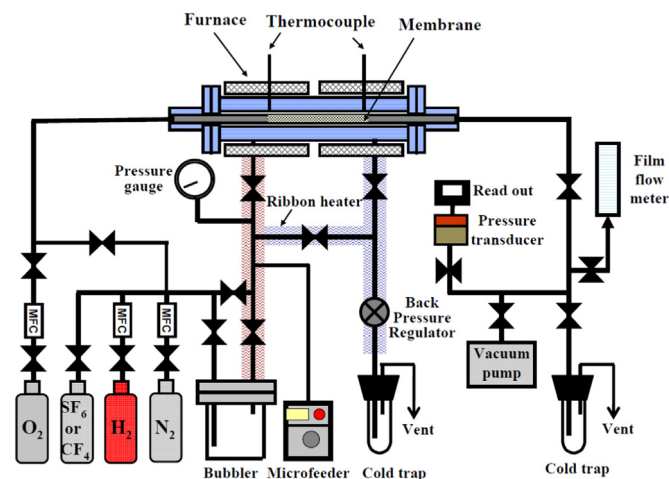
In a dry argon atmosphere, 50 mL (1.2 mol) of methanol and 16.7 mL (120 mmol) of triethylamine were placed in a 300 mL two-necked flask and the flask was cooled at 273 K. To this, 29.5 g (100 mmol) of chlorotriphenylsilane was slowly added and the mixture was stirred at this temperature for 12 h. After 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 ( $\text{M}^+$ );  $^1\text{H NMR}$  (400 MHz, in  $\text{CDCl}_3$ ):  $\delta$  = 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 permporometry measurements.

Fig. 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  $\text{min}^{-1}$  of  $\text{N}_2$  as the carrier gas from the outside of the modified support, while 200 mL  $\text{min}^{-1}$  of  $\text{O}_2$  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



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

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