# Preparation of Composite Microporous Silica Membranes Using TEOS and 1, 2-Bis(triethoxysilyl)ethane as Precursors for Gas Separation[*]
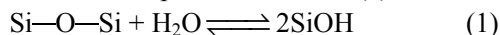
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**Abstract**    This paper reports on a new microporous composite silica membrane prepared *via* acid-catalyzed polymeric route of sol-gel method with tetraethylorthosilicate (TEOS) and a bridged silsesquioxane [1, 2-bis(triethoxysilyl)ethane, BTESE] as precursors. A stable nano-sized composite silica sol with a mean volume size of ~5 nm was synthesized. A 150 nm-thick defect-free composite silica membrane was deposited on disk support consisting of macroporous $\alpha$-Al$_2$O$_3$ and mesoporous $\gamma$-Al$_2$O$_3$ intermediate layer by using dip-coating approach, followed by calcination under pure nitrogen atmosphere. The composite silica membranes exhibit molecular sieve properties for small gases like H$_2$, CO$_2$, O$_2$, N$_2$, CH$_4$ and SF$_6$ with hydrogen permeances in the range of $(1-4) \times 10^{-7}$ mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$ (measured at 200 °C, $3.0 \times 10^5$ Pa). With respect to the membrane calcined at 500 °C, it is found that the permselectivities of H$_2$ (0.289 nm) with respect to N$_2$ (0.365 nm), CH$_4$ (0.384 nm) and SF$_6$ (0.55 nm) are 22.9, 42 and >1000，respectively, which are all much higher than the corresponding Knudsen values (H$_2$/N$_2$ = 3.7, H$_2$/CH$_4$ = 2.8, and H$_2$/SF$_6$ = 8.5).
**Keywords**    tetraethylorthosilicate, 1, 2-bis(triethoxysilyl)ethane, composite silica membranes, gas separation, molecular sieving

## 1    INTRODUCTION

Inorganic membrane technology for the separation of gases is foreseen to play an important role in reducing the environmental impact and costs of many industrial processes. Several materials have been proposed to be used as molecular sieving membranes, including zeolites, carbon, palladium and metal oxides, of which sol-gel derived silica membrane is one of the most promising materials [1]. In 1998, de Vos *et al.* [2] reported an important progress on sol-gel derived silica membrane for the separation of gases, which provided both high H$_2$ permeance ($2 \times 10^{-6}$ mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$) and sufficient H$_2$/CH$_4$ permselectivity (>500). However, the modest stability of amorphous silica under humid conditions severely restricts its broad industrial application, where water vapor environments are often encountered. Humidity can disrupt the —Si—O—Si— bonds in silica, inducing densification of the microporous silica network owing to the formation of mobile silica fragments [3], as depicted in reaction (1).

$$Si—O—Si + H_2O \rightleftharpoons 2SiOH \qquad (1)$$

Therefore, to prevent the interaction of siloxane bridges with water can improve the hydrothermal stability of silica membranes. Much work has been carried out to solve this problem, including modification of silica with metal oxide [4–9] and organotrialkoxysilanes [10, 11], or membranes fabricated from thermally and chemically more stable zirconia [12] and titania [13, 14], or composites thereof [15, 16]. However, further studies are still required to develop silica-based membranes exhibiting both high-enough separation performances and sufficient hydrothermal stabilities that

could be used industrially. Recently, a bridged silsesquioxane [1, 2-bis(triethoxysilyl)ethane, BTESE] was proposed as a precursor to fabricate hybrid organic-inorganic microporous membrane with excellent hydrothermal stability in the application of pervaporation [17] and gas separation [18] processes. Nevertheless, the properties of this membrane toward separation of gasses with small kinetic diameter, like H$_2$, CO$_2$, N$_2$ and CH$_4$, are still need to be improved.

As is well known that tetraethylorthosilicate (TEOS)-derived silica membranes provide with excellent gas separation properties, the composite silica membrane fabricated with TEOS and BTESE is foreseen to display sufficient hydrothermal stability while retains its separation performance. Herein we report on a new type of composite membrane developed by using TEOS and BTESE as precursors through sol-gel method. Considering that BTESE consists of hydrophobic backbone structures of —Si—CH$_2$—CH$_2$—Si— together with 6 —OEt groups (see Fig. 1), which will exhibits a much higher hydrolysis and condensation rate than that of TEOS. The polymeric sol size is controlled through adding BTESE precursor into the TEOS solution which has already been hydrolyzed and condensed for a certain period of time, instead of adding water directly into BTESE precursor to avoid formation of large particles. In this way, a much higher hydrolysis and condensation rate of BTESE precursor is under control and primarily linear polymers or low-branched polymers can be formed, as requested for the molecular sieving membranes fabrication. The composite silica membrane thus provides with structures consisting of both Si—CH$_2$—CH$_2$—Si— and Si—O—Si networks, as displayed in Fig. 2, which

**Figure 1   Molecular structures of precursors for TEOS (a) and BTESE (b)**



(a) With TEOS                                        (b) With TEOS+BTESE
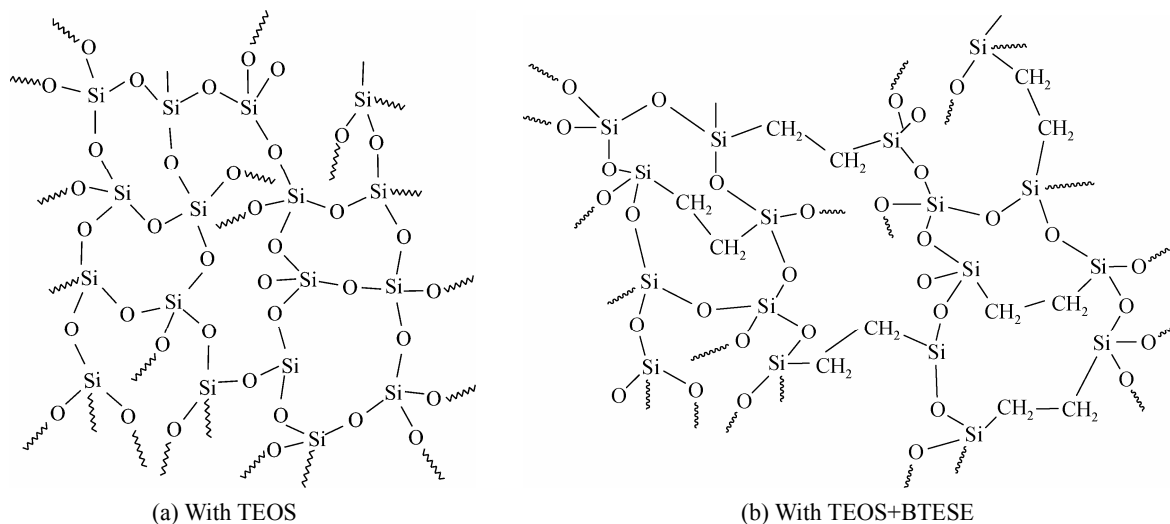
**Figure 2   Proposed structures for microporous silica membrane and composite silica membrane fabricated with TEOS and TEOS+BTESE as precursors**

will exhibit more hydrophobic properties than that of pure silica membranes.

## 2   EXPERIMENTAL

### 2.1   Supports preparation [19, 20]

Disk-shaped supports were prepared by using a colloidal filtration approach. High-purity $\alpha$-Al$_2$O$_3$ powder (AKP-30 Sumimoto, Japan) was dispersed in nitric acid followed by ultrasonic dispersing, after which the colloidal suspension was poured into a dedicated filter and vacuum sucking. The dried green supports were left overnight and sintered at 1100 °C afterwards. After polishing, supports were provided with a porosity of ~30% and a pore size of ~100 nm [20]. $\gamma$-Al$_2$O$_3$ intermediate layer was prepared by dip-coating the aforementioned disk $\alpha$-Al$_2$O$_3$ supports in a boehmite sol and subsequently calcined at 600 °C, which was illustrated in detail elsewhere [19]. The same procedure was reproduced for one more time in order to repair the defects in the supports.

### 2.2   Preparation of TEOS/BTESE sol and composite silica membranes

Composite silica sol was prepared through acid-catalyzed polymeric route of sol-gel method with TEOS and BTESE as precursors. TEOS (98%, Aldrich) and ethanol were mixed and then immediately placed in an ice bath to avoid premature hydrolysis. Water

and nitric acid were slowly introduced into the TEOS precursor under vigorous stirring followed by refluxing at 60 °C for 90 min. A mixture of BTESE (97%, ABCR) and absolute ethanol was drop-wise added into the aforementioned TEOS solution, which had already been hydrolyzed and condensed for 90 min. The refluxing was maintained at 60 °C for an additional 90 min, after which the sol was cooled down to the room temperature with a final mol ratio of 1 : 0.3 : 5.6 : 0.085 : 6.5 (TEOS : BTESE : Ethanol : H$_2$O : HNO$_3$). This sol was diluted for 6 times (hereafter referred to as T/B sol) before the final dip-coating step.

Dip-coating of membranes was performed in the clean room (class 1000) with a dedicated apparatus (Velterop BV, The Netherlands). After that, the composite silica membranes were calcined at 400 °C, 500 °C and 600 °C for 3 hours under pure N$_2$ atmosphere with heating and cooling rate of 0.5 °C·min$^{-1}$. The membranes were thus referred to as T/B 400, T/B 500 and T/B 600, respectively.

### 2.3   Characterization of composite silica powder and supported membranes

Particle size distribution (PSD) of the T/B sol and its stability were characterized by Dynamic Light Scattering (DLS) process using Zetasizer NanoZS apparatus (Malvern Instruments Ltd. UK.). Unsupported composite silica membranes (powder) were obtained by the evaporation of the corresponding T/B sol in a petri-dish overnight. Subsequently, part of the dried powder was subjected to the thermal gravimetric

analysis (TGA, Setsystem 16/18, Setaram, France), which was measured under $N_2$ atmosphere (flow rate: 20 ml·min$^{-1}$) with a heating rate of 1 °C·min$^{-1}$ up to 800 °C and dwelling for 3 h. The other part of the dried powder was further calcined under $N_2$ atmosphere at 400 °C for 3 h and subjected to $N_2$ sorption measurement afterwards. The pore characteristics of powder were determined by the $N_2$ adsorption method (Micromeritics, Tristar). Morphology of the composite silica membrane was observed by Field-Emission Scanning Electron Microscopy (FE-SEM, LEO Gemini 1550, UK.). Single gas permeances of the membrane were characterized through a gas permeation set up with dead-end mould placed in the furnace, as shown in Fig. 3. The membrane was placed in a stainless-steel mould with the top membrane layer at the feed side. Prior to testing, the membranes were dried at 200 °C overnight to eliminate the moisture in micropores. The feed pressure was controlled by the electronic pressure transducer and set at $3.0 \times 10^5$ Pa while the permeate side was vent to the atmosphere. The permselectivity ($F_\alpha$) of the composite silica membranes was determined by the ratio of various gas permeance measured at 200 °C and $3.0 \times 10^5$ Pa, as depicted with Eq. (2).

$$F_\alpha = F_x / F_y \tag{2}$$

where $F_\alpha$ is the permselectivity of membrane, $F_x$ and $F_y$ the permeances of membrane for two different gases measured at the same temperature and transmembrane pressure.
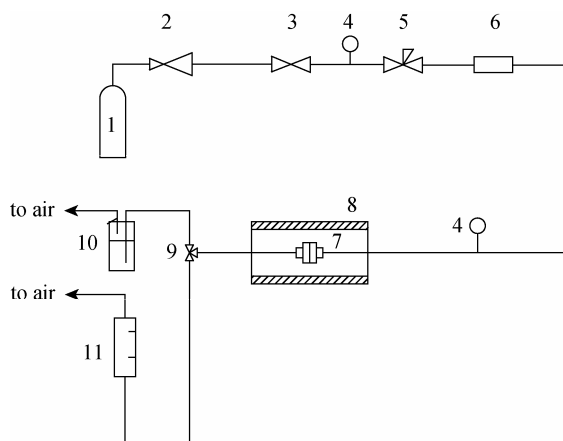


**Figure 3** Schematic diagram of the apparatus for the determination of single gas permeance of composite microporous silica membranes
1—gas cylinder; 2—pressure reducing valve; 3—stop valve; 4—pressure gauge; 5—pressure controller; 6—mass flow controller; 7—disk membrane module; 8—furnace; 9—three-way valve; 10—gas washing bottle; 11—soap-film flow meter

# 3 RESULTS AND DISCUSSION

## 3.1 T/B sol size and its stability

Particle size distribution (PSD) of freshly prepared T/B sol, together with PSD of the sol after stor-

age at −28 °C for various time intervals, is given in Fig. 4. It can be seen that the PSD of freshly prepared sol exhibits a uni-modal distribution with polymer size in the range of 1−30 nm with a mean volume size of 5.5 nm. The stability of the T/B sol stored at −28 °C is characterized by its PSD variation, as also shown in Fig. 4. It is worthwhile to note that the PSD of T/B sol shifts a little to a larger size as the storage time extended. Meanwhile, there is no larger size polymers formed in the sol, as evidenced by that the mean volume size is still stabled at ~5 nm even after 14 days storage. The results indicate a stable T/B sol, which is very important for the microporous membranes preparation.
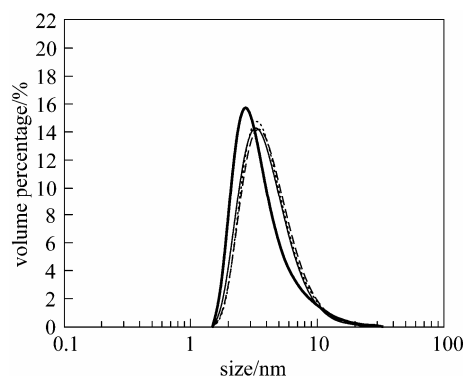


**Figure 4** Volume size distribution and stability of the composite silica sol
—— freshly prepared; —— after storage under −28 °C for 1day; --- after storage under −28 °C for 7days; ······ after storage under −28 °C for 14days

## 3.2 Characterization of unsupported composite silica membrane (powder)

### 3.2.1 *TG/DTA analysis*

Figure 5 shows the thermogravimetric (TG) and differential thermal analysis (DTA) curves of uncalcined unsupported membrane (T/B powder). A sharp initial weight decrease prior to 200 °C in TG curve is attributed to the removal of the physical absorbed water and solvent in the powder. A weight loss in the second stage starting from 200 °C and ending around 450 °C
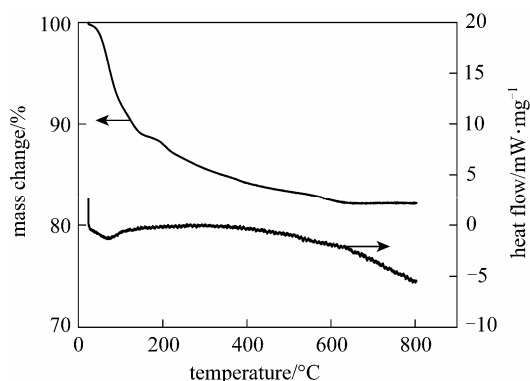


**Figure 5** TG and DTA curves of unsupported composite silica membranes (T/B powder) (Test condition: from room temperature to 800 °C with a heating rate of 1 °C·min$^{-1}$)

is corresponding to the removal of the organic substances. Pyrolysis of poly-1, 2-bis(triethoxysilyl)ethane induced by the thermal treatment should be responsible for the small amount of mass loss during the temperature range of 470 to 600 °C, as evidenced by that the T/B powder turns from white to black after heat treatment.

### 3.2.2  BET characterization

Figure 6 shows the $N_2$ adsorption/desorption isotherm of T/B powder as well as pure silica powder that both calcined at 400 °C under $N_2$ and air atmosphere, respectively. Both adsorption/desorption curves display a type I of microporous materials characteristic. However, if compared with the silica powder made from pure TEOS precursor [21], a lower BET surface area for T/B powder is apparent.
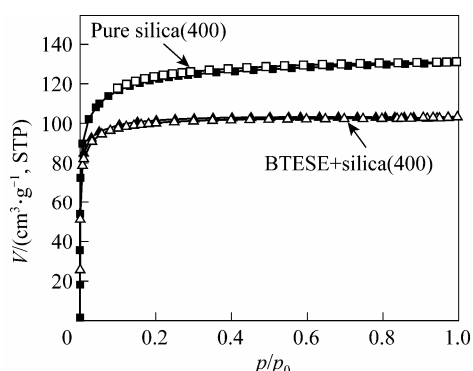
**Figure 7**  Single gas ($H_2$, $CO_2$, $O_2$, $N_2$, $CH_4$ and $SF_6$) permeances of microporous composite silica membranes (T/B 400, T/B 500 and T/B 600) calcined at 400 °C, 500 °C and 600 °C, respectively
■ T/B 400;  ● T/B 500;  ▲ T/B 600

of gas permeance with the increment of kinetic diameter of gases. It is reasonable that the permeance of hydrogen decreases from $3.59 \times 10^{-7}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ to $1.27 \times 10^{-7}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ as the calcination temperature elevated from 400 °C to 500 °C. The result indicates that a higher temperature densifies the membrane and leads to a smaller pore size. Meanwhile, a similar decrease tendency for $CO_2$, $O_2$, $N_2$ and $CH_4$ can also be observed in Table 1. However, if compared with the T/B 500 membrane, T/B membrane calcined at 600 °C shows higher gas permeances, especially for gases with comparatively large kinetic diameter (i.e. $CO_2$, $O_2$, $N_2$, $CH_4$ and $SF_6$). A higher calcination temperature of 600 °C leads to a sharp decrease of permselectivity of $H_2$ with respect to $N_2$, $CH_4$ and $SF_6$. For example, the permselectivity of $H_2/CH_4$ decreases from 42 to 5.5 as the calcination temperature increases from 500 °C to 600 °C. This phenomenon can be explained by the variation of the composite membrane structures in the calcination temperature range of 500−600 °C, as evidenced by TG curve shown in Fig. 5. There exists ~1% weight loss in the temperature range between 530 °C and 630 °C, which leads to pyrolysis of the poly-BTESE structure and therefore enlarges the pore size of the composite silica membrane. The pore size of the composite silica membrane is a little larger than that of the pure silica membrane, which has a permselectivity of >135 for $H_2/N_2$ and >4000 for $H_2/CH_4$ measured at 200 °C ($3.0 \times 10^5$ Pa) [1]. Nevertheless, the composite silica

**Figure 6**  $N_2$ sorption isotherm curves of T/B powder and pure silica powder

### 3.3  Single gas permeation properties

Single gas permeation properties of composite silica membranes are given in Table 1 and Fig. 7, respectively. Hydrogen permeances of the composite silica membranes are in the range of $(1−4) \times 10^{-7}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$, which are comparable with the $H_2$ permeances of pure silica membranes reported in literatures [10, 21]. Permselectivities of hydrogen with respect to $N_2$, $CH_4$ and $SF_6$ for T/B membranes calcined in the range of 400−600 °C are all much higher than the corresponding Knudsen values, which are 3.7($H_2/N_2$), 2.8 ($H_2/CH_4$) and 8.5($H_2/SF_6$), respectively. It is demonstrated that those membranes exhibit molecular sieving characteristic due to a sharp decrease
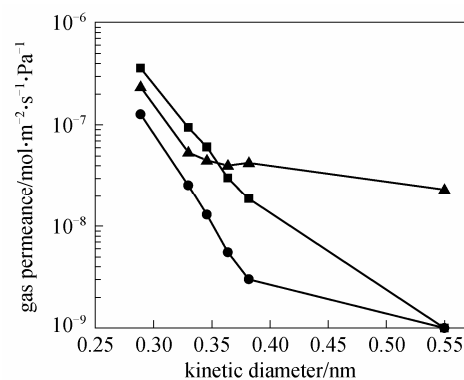
**Table 1**  Single gas permeances (measured at 200 °C and $3.0 \times 10^5$ Pa) of composite silica membranes calcined at various temperatures

| Microporous membranes | Single gas permeance $\times 10^7$/$mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ | | | | | | Permselectivity | | |
|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $CO_2$ | $O_2$ | $N_2$ | $CH_4$ | $SF_6$ | $H_2/N_2$ | $H_2/CH_4$ | $H_2/SF_6$ |
| T/B 400 | 3.59 | 0.941 | 0.608 | 0.302 | 0.187 | — | 12 | 19.2 | |
| T/B 500 | 1.27 | 0.256 | 0.13 | 0.0554 | 0.0301 | — | 22.9 | 42 | |
| T/B 600 | 2.35 | 0.54 | 0.45 | 0.401 | 0.426 | 0.232 | 5.9 | 5.5 | 10.1 |

Note: "—" shown in Table 1 indicates $SF_6$ permeance below the detection limit ($<1 \times 10^{-10}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$) of soap film flow meter.
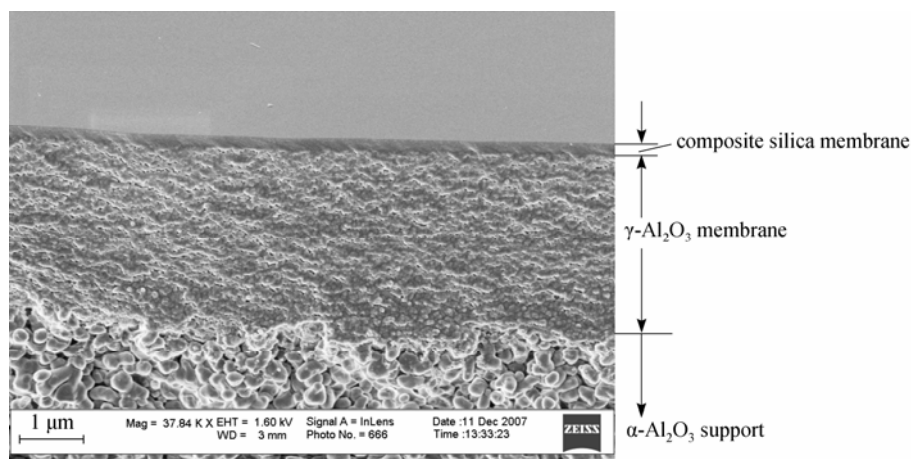
**Figure 8    HRSEM image of three-layer asymmetric composite silica membrane with a magnification of ×37000**



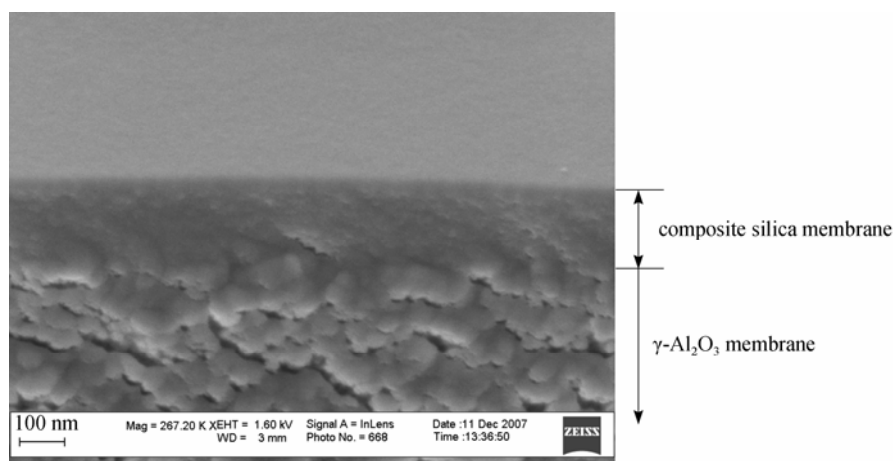**Figure 9    HRSEM image of top composite silica membrane with a magnification of ×260000**

membrane has a better gas separation properties than that of the hydrophobic membranes prepared using TEOS/MTES or MTES/BTESE as precursors, which have permselectivities of ~8 [21] or ~4 [22] for both $H_2/N_2$ and $H_2/CH_4$, respectively.

### 3.4    Microstructure of composite silica membranes

Figures 8 and 9 show the cross sectional micrographs of composite silica membrane. An asymmetric structure consists of α-alumina, γ-alumina and top composite silica layer with thicknesses of 2 mm, 3 μm and ~150 nm, respectively, as can be distinguished in Fig. 8. Although a little amount of composite silica sol penetrates into the γ-alumina layer beneath, the surface of the top layer retains smooth and defect-free, which can be demonstrated by a higher magnification micrograph as shown in Fig. 9.

### 4    CONCLUSIONS

A composite silica membrane with high permse-

lectivity of 42 for $H_2$ with respect to $CH_4$ was prepared by sol-gel method using TEOS and BTESE as precursors. A stable composite silica sol with mean volume size of ~5 nm was obtained using a two-step acid addition approach with the final molar ratio of 1 : 0.3 : 5.6 : 0.085 : 6.5 (TEOS : BTESE : Ethanol : $H_2O$ : $HNO_3$). The composite silica membrane with a thickness of ca. 150 nm was deposited on the γ-$Al_2O_3$ intermediate layer supported by the disk α-$Al_2O_3$ support. The membranes calcined in the temperature range of 400−600 °C exhibit comparatively high hydrogen permeances of $(1-4)\times10^{-7}$ mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$ (measured at 200 °C, $3.0\times10^5$ Pa) with the permselectivities of $H_2$ with respect to the gases (*e.g.* $N_2$, $CH_4$), which are all higher than the corresponding Knudsen values. The membrane calcined at 500 °C under pure $N_2$ atmosphere has optimal gas permeation properties as follows. The permselectivities for $H_2/CO_2$, $H_2/O_2$, $H_2/N_2$, $H_2/CH_4$ and $H_2/SF_6$ are 5, 9.8, 22.9, 42 and >1000, respectively, with $H_2$ permeance of $1.27\times10^{-7}$ mol·m$^{-2}$·s$^{-1}$·Pa$^{-1}$ (measured at 200 °C, $3.0\times10^5$ Pa). A

higher calcination temperature of 600 °C will impairs the gas separation properties of the composite silica membrane because of the pyrolysis of poly-BTESE structures. This composite silica membrane holds great promise in gas separation application field.

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