



Permeation properties of BTESE–TEOS organosilica membranes and application to O₂/SO₂ gas separation



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ABSTRACT

In the present study, a BTESE–TEOS mixed precursor was proposed for control of the pore sizes of organosilica networks in organic–inorganic hybrid silica membranes. FT-IR spectrometry confirmed the formation of a partially cross-linked polysiloxane structure with hydrocarbon units in a BTESE–TEOS-derived silica network produced by the co-hydrolysis and condensation of BTESE with TEOS, which also showed an improved thermal stability. Single gas permeation measurements and normalized Knudsen-based permeance (NKP) established the order of the average membrane pore sizes as follows: BTESE > BTESE–TEOS > TEOS. The organosilica membranes derived from BTESE–TEOS exhibited a superior O₂ permeance that was higher than 10^{−8} mol m^{−2} s^{−1} Pa^{−1} with an O₂/SO₂ selectivity of 7.3, which indicated that the pore size control in organosilica networks using BTESE–TEOS as a precursor was effective for selective O₂/SO₂ separation. Moreover, the effective molecular size of SO₂ permeates through organosilica membranes was discussed.

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1. Introduction

One vital issue in recent years has been the development of effective approaches for the capture and separation of SO₂, which is an origin of air pollution and global warming [1,2]. As an alternative to solvent absorption, membrane separation has been considered an attractive method in systems including sour gas purification and concentration of SO₂ [3]. Thus far, polymer membranes have been extensively investigated to remove SO₂ and purify exhaust gases, and these have shown remarkable SO₂ solubility and selectivity, which favors SO₂ permeation [3]. A novel application is the O₂/SO₂ separation in the Iodine–Sulfur thermochemical water-splitting cycle (IS process) for hydrogen production [4]. The separation of O₂ and SO₂ could significantly increase the O₂ yield in SO₃ decomposition, as confirmed by theoretical studies [5]. Since the SO₃ decomposition reaction takes place at high temperatures under an oxygen atmosphere, polymeric membranes are not suitable for this application. Forsberg et al. [6] reported that ZrO₂ membranes with pore sizes on the order of 1 nm showed an O₂ permeance of 2.0 × 10^{−10} mol m^{−2} s^{−1} Pa^{−1} with an O₂/SO₂ permeation ratio of 1.05 at 130 °C. For dense inorganic membranes, He et al. [7] prepared oxygen ion conducting dense membranes and applied them to the separation of O₂ and SO₂ at high temperatures. Unfortunately, it was obvious that the

membrane performance was degraded once SO₂ was introduced into the feed stream. These results suggest that the main drawbacks of state-of-the-art inorganic membranes for O₂/SO₂ separation are low O₂ selectivity and low chemical stability to SO₂. Given the components involved in this system, O₂ ($d_{k,O_2} = 0.346$ nm) and SO₂ ($d_{k,SO_2} = 0.360$ nm) [8], membranes with a narrow pore size distribution are expected to enhance the separation efficiency. Moreover, for O₂/SO₂ separation, the thermal stability of membrane materials under an oxidizing atmosphere is required.

Organosilica membranes [9,10] composed of covalent bonds between both hydrocarbons and oxygen to silicon, have recently attracted considerable attention because of their tunable membrane pore sizes, and improved hydrothermal stability due to a decrease in silanols on the surface, compared with pure inorganic silica membranes. To date, organosilica membranes have performed well in a variety of applications, including gas separation [11], pervaporation [12], reverse osmosis [13] and membrane reactors [14].

The pore size of organosilica membranes is dependent on the size of the organic–inorganic hybrid silica network, which can be controlled either by the organic-template method [15] or by spacer technology using Si–C bridges [16,17]. In the organic-template method, organic ligands were used as micropore templates that were embedded in the inorganic matrix and were removed during the pyrolysis process, to create a larger average pore size for membranes which resulted in an increased CO₂ permeance [15]. The average pore size of a separation functional layer can be

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adjusted by varying the size of the minimum unit in organosilica networks [16]. A spacer technology [17] was proposed and confirmed using various types of bridged alkoxy silanes comprised of bridging units ($\text{Si}-\text{CH}_2-\text{Si}$, $\text{Si}-(\text{CH}_2)_2-\text{Si}$). As opposed to silica membranes prepared from tetraethoxysilane (TEOS), organosilica membranes derived from bridged bis-silyl precursors such as bis(triethoxysilyl)methane (BTESE) and bis(triethoxysilyl)ethane (BTESE) show a hybrid silica network with looser micro-structures, which facilitates gas permeation. In addition, membrane pore sizes can also be controlled by the size of the linking units, the larger the linking unit ($\text{Si}-(\text{CH}_2)_2-\text{Si} > \text{Si}-\text{CH}_2-\text{Si}$), the higher the gas permeance. For BTESE-derived silica membranes [17], the H_2 permeance was one order of magnitude higher ($\sim 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) than that of pure silica membranes, and a high H_2/SF_6 selectivity of 25,500 with a low H_2 to N_2 permeance ratio (~ 20) was recorded. In our recent work [18], the $\text{H}_2\text{O}/\text{BTESE}$ molar ratio for preparation of BTESE-derived silica sols was a key factor in controlling the membrane pore size. Less densification in organosilica networks was achieved by decreasing the $\text{H}_2\text{O}/\text{BTESE}$ molar ratio from 240 to 6, which resulted in an increase in the pore size of BTESE-derived membranes. Herein, we propose a novel strategy to control pore size by using a mixed precursor derived from different alkoxides. TEOS was mixed with BTESE for the possible tuning of pore sizes between TEOS and BTESE-derived silica membranes.

In the present work, a BTESE–TEOS mixed sol was proposed as the Si precursor for the fabrication of organic–inorganic hybrid silica membranes with tunable pore sizes. BTESE–TEOS-derived silica sols were prepared *via* co-hydrolysis and condensation of BTESE with TEOS, and were characterized by the Fourier transform infrared (FT-IR) spectrometry and thermogravimetric–mass spectrometric (TG–MS) analysis. Single gas permeation measurements were conducted to investigate the effect of a hybrid precursor on the average pore size of organosilica membranes, which was also quantitatively evaluated *via* normalized Knudsen-based permeance (NKP). As a preliminary study, a binary-component gas separation of O_2 and SO_2 was carried out to investigate the gas transport properties, thermal stability and chemical resistance of organosilica membranes.

2. Experimental

2.1. Preparation of organosilica sols and membranes

BTESE, BTESE–TEOS and TEOS were used as silica precursors. For the preparation of a BTESE or TEOS sol, BTESE or TEOS was

initially mixed with ethanol. Subsequently, H_2O and HCl were added and the mixture was stirred for 5 h at 50°C to achieve a final sol. In the case of a composite organosilica sol (BTESE–TEOS), BTESE, TEOS and ethanol were mixed and vigorously stirred, followed by the addition of H_2O and HCl with continuous stirring for 5 h at 50°C to produce a hybrid sol. The molar ratios of the added reagents were (BTESE or BTESE–TEOS or TEOS)/ $\text{H}_2\text{O}/\text{HCl}$ at 1/60/0.1, respectively, and the precursors were maintained at 5 wt%. For a BTESE–TEOS sol, the molar ratio of BTESE to TEOS was 1/1.

Porous $\alpha\text{-Al}_2\text{O}_3$ tubular substrates with a pore diameter of $1 \mu\text{m}$, an outside diameter of 10 mm and a length of 100 mm were supplied by Mitsui Grinding Wheel Co., Ltd. and were employed as supports. To develop a smooth mesoporous particle layer for an organosilica membrane, $\alpha\text{-Al}_2\text{O}_3$ powders (Sumitomo Chemical Co., Ltd.) with particle diameters of 1.9 and $0.2 \mu\text{m}$ were dispersed in a $\text{SiO}_2\text{-ZrO}_2$ colloidal sol. A fresh support was coated with the large-sized particle sols to eliminate the possibility of defects and relatively large pores on outer surface of support, followed by 0.5 h calcination at 550°C , and then the coating procedure was repeated using the small-sized particle sols. A $\text{SiO}_2\text{-ZrO}_2$ intermediate layer was deposited by coating a 0.5 wt% concentration of the $\text{SiO}_2\text{-ZrO}_2$ ($\text{Si}/\text{Zr}=1$) sol that was obtained from the hydrolysis of zirconium tetrabutoxide (ZrTB) and TEOS onto the particle layer [19]. After coating and drying, the $\alpha\text{-Al}_2\text{O}_3$ supported $\text{SiO}_2\text{-ZrO}_2$ membranes were calcined by heating to 550°C for 0.5 h. For membrane fabrication, organosilica sols (BTESE, BTESE–TEOS) were applied onto the $\text{SiO}_2\text{-ZrO}_2$ intermediate layer by coating, followed by subsequent drying at room temperature and calcination at 300°C for 0.5 h.

2.2. Characterization of organosilica gels

The Fourier transform infrared (FT-IR) spectra for BTESE-derived and BTESE–TEOS-derived silica films coated on KBr pellets were recorded with a FT-IR spectrometer (FT/IR-4100, Jasco Co., Japan). Powdered samples of the BTESE-derived and BTESE–TEOS-derived silica gels were obtained by drying organosilica sols at 40°C under air. Thermogravimetric–mass spectrometric analysis (TG–MS, TG-DTA-410S, Rigaku Co., Japan) was conducted on the BTESE-derived and BTESE–TEOS-derived silica powders to characterize the thermal decomposition behavior of the membranes under an air flow of $300 \text{ cm}^3 \text{ min}^{-1}$. The rate of temperature increase was $10^\circ\text{C min}^{-1}$ to 550°C .

2.3. Single and binary-component gas permeation measurement

Single gas permeation testing was performed using an

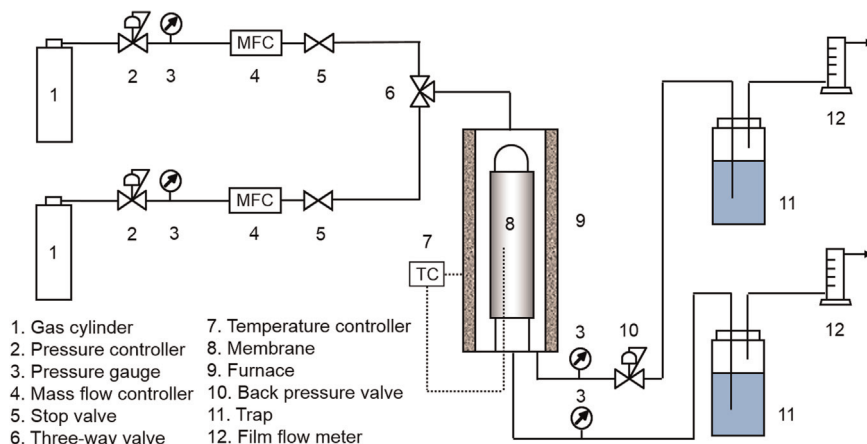


Fig. 1. Schematic diagram of the experimental setup for single and binary-component gas permeation measurement.

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