



Mesoporous bis(trimethoxysilyl)hexane (BTMSH)/tetraethyl orthosilicate (TEOS)-based hybrid silica aerogel membranes for CO₂ capture

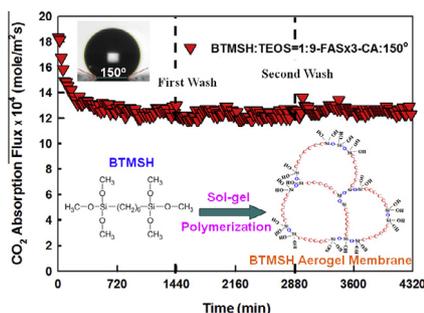
Yi-Feng Lin*, Jia-Wei Kuo

Department of Chemical Engineering, Chung Yuan Christian University, Chungli, Taoyuan 30023, Taiwan

HIGHLIGHTS

- The BTMSH/TEOS hybrid aerogels were coated onto Al₂O₃ tubular membrane supports.
- The BTMSH/TEOS aerogel membranes allow efficient carbon dioxide absorption into amines.
- The BTMSH/TEOS aerogel membranes are durable and reusable for CO₂ capture in power plants.
- The BTMSH/TEOS aerogel membranes show promise for large-scale CO₂ capture in power plants.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, bis(trimethoxysilyl)hexane (BTMSH) was successfully combined with tetraethyl orthosilicate (TEOS) to form hybrid silica aerogel membranes via a sol–gel process. Compared with the pore size of TEOS-based aerogels, that of the hybrid aerogels was efficiently enlarged because of the six-carbon chain that bridges the two silicon atoms of BTMSH. The as-prepared hybrid silica aerogels were further coated onto a macroporous alumina membrane support and used as a membrane contactor for CO₂ absorption. Among all of the examined membranes, the hybrid silica aerogel membrane with a BTMSH/TEOS molar ratio of 1/9 exhibited the highest CO₂ absorption flux, resulting from the corresponding decrease in the CO₂ mass transfer resistance. The same hybrid membrane was continuously operated for at least three days and was also reused for three one-day cycles of CO₂ absorption. As a result, the material is not only durable but also reusable as a membrane contactor for CO₂ absorption, which is a promising technology for large-scale post-combustion processing in power plants.

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1. Introduction

Microporous and mesoporous silica nanomaterials such as MCM-41 [1], SBA-15 [2], and silicate-1 [3] have been successfully prepared in the recent past using a variety of methods, including sol–gel, micelle and hydrothermal approaches. They have been

widely applied in numerous fields, such as catalysis [4], drug delivery [5], imaging [6], adsorption [7–9] and membrane technology [10]. For membrane applications involving gas separation, microporous silica membranes have commonly been prepared via a sol–gel reaction involving tetraethyl orthosilicate (TEOS) precursors [11]. Tsuru and co-workers have fabricated hybrid microporous silica membranes by adding bis(trimethoxysilyl)ethane (BTESE)—bisilane with a two-carbon chain between the two silicon atoms—to TEOS-based membranes [12–14]. Compared to the pore sizes of TEOS-based silica membranes, the pore sizes of these TEOS/

* Corresponding author.

E-mail address: yflin@cycu.edu.tw (Y.-F. Lin).

BTESE hybrid silica membranes are enlarged because of the alkyl-chain bridge of the BTESE precursors. The as-prepared TEOS/BTESE hybrid silica membranes have also been applied to gas separation and exhibited better gas permeation properties than TEOS-based silica membranes because of their larger pore size.

SiO₂ aerogels [15] are mesoporous materials (pore size of 2–50 nm) with a high porosity, a high specific surface area and a low density. Various precursors such as sodium silicate [16], tetramethyl orthosilicate (TMOS) [17], TEOS [18] and methyltrimethoxysilane (MTMS) [19,20] have been used to prepare SiO₂ aerogels via a sol–gel process. The Meador group [21,22] has incorporated epoxy, amine- and alkyl-linked bis-silanes such as bis(trimethoxysilyl)hexane (BTMSH) and BTESE into TEOS-based aerogels to promote flexibility in the silica networks. The mechanical strength of the as-prepared hybrid silica aerogels can be increased due to the incorporation of epoxy into TEOS-based silica aerogels. Furthermore, the pore sizes of these hybrid silica aerogels are typically increased by the alkyl-chain bridges of bis-silanes [22]. In our previous study, we generated SiO₂ aerogels [23,24] with a pore size of approximately 3–4 nm by a facile sol–gel reaction that used only TEOS precursors subsequently coated an Al₂O₃ membrane support with these aerogels. The as-prepared TEOS-based silica aerogel membranes were not only durable but also reusable for CO₂ absorption in membrane contactor applications, reaching a stable CO₂ absorption flux of approximately 1.1 mmol/m²s. The silica aerogel coating with a small pore size (approximately 3–4 nm) prevents membrane wetting by aqueous amine adsorbents and decreases the CO₂ mass transfer resistance, which results in an increase in the CO₂ absorption flux. However, if the pore size of the silica aerogel membrane is too small, then CO₂ gas cannot easily pass through and reach the amine solution; thus, the CO₂ mass transfer resistance is increased and the CO₂ absorption flux is decreased. We expect that the CO₂ absorption flux can be further increased without sacrificing the anti-wetting properties of the membrane if the pore size of the silica aerogel is enlarged.

In this study, a BTMSH precursor, an alkyl bis-silane with a six-carbon-atom chain bridging two silicon atoms (Scheme 1), was added to the TEOS reactant during the sol–gel reaction to form a hybrid BTMSH/TEOS silica aerogel membrane. The pore size of the as-prepared hybrid BTMSH/TEOS silica aerogel membrane was increased compared with that of the pure TEOS-based silica aerogel membrane because of the extended alkyl-chain bridge of the BTMSH precursor, as shown in Scheme 1. CO₂ gas easily passes through the larger pores of the hybrid BTMSH/TEOS silica aerogel membrane, thereby indicating a decrease in the mass transfer resistance for CO₂ absorption. As a result, the CO₂ absorption flux in the membrane contactor process of the hybrid BTMSH/TEOS silica aerogel membrane is effectively increased over that of the TEOS-based silica aerogel membrane. The resulting hybrid BTMSH/TEOS silica aerogel membranes are a promising technology for large-scale CO₂ absorption in the post-combustion processing of power plants.

2. Experimental

A macroporous Al₂O₃ membrane support (Kinik Company, Taiwan) with a diameter, thickness and pore size of approximately 47 mm, 2.4 mm and 1 μm, respectively, was used. TEOS (99.7%, SHOWA Company), BTMSH (96%, Uni-Onward Company), hydrochloric acid (HCl, 35%, SHOWA Company), ammonium hydroxide (NH₄OH, 28–30%, Fisher Scientific Company), and ethanol (EtOH, 99.5%, ECHO Chemical Company) were used for the preparation of the TEOS-based silica aerogel and the BTMSH/TEOS-based hybrid silica aerogel membranes. 2-amino-2-methyl-

1-propanol (AMP, 99.9%, Sigma–Aldrich Company), piperazine (PZ, 99%, Acros Company) and deionized water were used for CO₂ absorption experiments.

For the sol–gel preparation of the BTMSH/TEOS-based silica aerogel membranes, two different solutions (solution A and solution B) were stirred for 60 min. A mixture of TEOS (0.01, 0.0085 and 0.009 mol, respectively), HCl (0.01 mol) and EtOH (0.03 mol) were stirred for 60 min to form solution A, whereas solution B contained BTMSH (0.00, 0.0017 and 0.001 mol, respectively) and EtOH (0.03 mol) and was also stirred for 60 min. Solutions A and B were subsequently mixed together and stirred for an additional 30 min. Next, an NH₄OH solution (0.01 mol) was added to the combined solution (A + B) and stirred for 30 min. BTMSH and TEOS reactants with total 0.01 mol were used with three different molar ratios of precursors (BTMSH/TEOS = 0/1 (TEOS-based aerogel), 1/9 and 1/5). Subsequently, the Al₂O₃ membrane supports were immersed in the sol solutions for several hours. After gelation, the as-prepared hybrid silica aerogel membranes were aged in EtOH at room temperature for two days; the ethanol was refreshed each day. Prior to the hydrophobic modification with fluoroalkylsilane (FAS, 97%, Alfa Aesar Company), the resulting composite silica aerogel membranes were washed with *n*-hexane to remove residual EtOH from the membrane pores. For the one-time FAS modification, the hybrid BTMSH/TEOS silica aerogel membranes were soaked in an FAS/*n*-hexane solution (0.02 M) at 40 °C for 24 h. The FAS solution was refreshed 1–3 times every 24 h, depending upon the FAS modification times.

For CO₂ absorption experiments (shown in Scheme 2), one side of the FAS-modified composite BTMSH/TEOS silica aerogel membrane was exposed to the AMP (1 M)/PZ (0.2 M) amine adsorbents with a liquid flow rate of 100 sccm (standard cubic centimeters per minute) while the other side of the membrane was exposed to CO₂/N₂ gas mixtures (9 vol%) with a gas flow rate of 200 sccm. The inlet and outlet CO₂ concentration were measured using a non-dispersive infrared sensor (NDIR, Jusun AGM 4000) to calculate the CO₂ absorption flux. The CO₂ absorption flux (N, mole/m²s) was approximately estimated using ideal gas equation from the difference between the inlet and outlet CO₂ concentrations on the gas-phase side of the membrane as follows: $N = \frac{P(Q_{in}C_{in} - Q_{out}C_{out})}{ART}$. Where N is CO₂ molar flux (mole/m²s), A is contact area of the membrane (m²), R is ideal gas constant, T is temperature (K), P is pressure (atm), Q_{in} and Q_{out} are inlet and outlet gas flow rate (m³/s), respectively, C_{in} and C_{out} are the inlet and outlet CO₂ concentrations, which are expressed in terms of percent in volume (vol%). The increased CO₂ absorption flux was entirely attributed to the CO₂ absorption. After CO₂ absorption, the used hybrid BTMSH/TEOS silica aerogel membrane was washed with pure nitrogen at a flow rate of 200 sccm for 2 h in the gas phase side, whereas the liquid phase side of the membrane was exposed to stagnant amine adsorbents to prepare the membrane for regeneration studies. The operated temperature and humidity during the CO₂ absorption experiments is approximately at 25 °C and 50–60 RH, respectively.

The surface morphologies of the as-prepared TEOS-based and BTMSH/TEOS-based silica aerogel membranes were examined by field emission scanning electron microscopy (FESEM, Hitachi, S-4800). The specific surface areas and pore size distribution of the as-prepared TEOS-based and BTMSH/TEOS-based silica aerogels were measured using nitrogen adsorption/desorption isotherms (BET, Micromeritics, ASAP 2020). The specific surface areas of the as-prepared TEOS-based silica and BTMSH/TEOS-based silica aerogels are calculated by the Brunauer–Emmett–Teller (BET) theory. Furthermore, pore size calculations of the as-prepared TEOS-based and BTMSH/TEOS-based silica aerogels are made using the Kelvin equation in the form of $r = \frac{2\gamma}{RT \ln \frac{p}{p_0}}$ [24]. Here, r is the pore

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