Journal of the Taiwan Institute of Chemical Engineers 000 (2018) 1–6

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Synthesis of mechanically robust epoxy cross-linked silica aerogel membranes for CO_2 capture

Yi-Feng Lin[a,*], Yen-Ju Lin[a], Chang-Chun Lee[b], Kun-Yi Andrew Lin[c,**], Tsair-Wang Chung[a], Kuo-Lun Tung[d]

[a] Department of Chemical Engineering and R&D Center for Membrane Technology, Chung Yuan Christian University, Chungli, Taoyuan 320, Taiwan, ROC
[b] Department of Power Mechanical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC
[c] Department of Environmental Engineering, National Chung Hsing University, Taichung 250, Taiwan, ROC
[d] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan, ROC

ARTICLE INFO

Article history:
Received 13 January 2018
Revised 5 March 2018
Accepted 7 March 2018
Available online xxx

Keywords:
Tri-epoxy cross-linked SiO_2 aerogel
Mechanical strength
Membrane contactor
CO_2 capture
Superhydrophobic

ABSTRACT

Mesoporous SiO_2 aerogels are multi-functional porous materials with diverse applications. However, the fragile characteristics and low mechanical strength of mesoporous SiO_2 aerogels limits their development for use in industrial applications. The mechanical strength of SiO_2 aerogels can be greatly enhanced by the addition of tri-epoxy cross-linkers. Tri-epoxy cross-linked SiO_2 aerogels with tri-epoxy concentrations of 7.5%, 15%, 30% and 45% were coated on macroporous Al_2O_3 membrane supports. The surface of the tri-epoxy cross-linked SiO_2 aerogel membranes became superhydrophobic after fluoroalkylsilane (FAS) modification. Compared to native SiO_2 aerogel membranes in the absence of tri-epoxy cross-linker, the pore size of the tri-epoxy cross-linked SiO_2 aerogel membranes with tri-epoxy concentrations of 15% and 30% increased to approximately 6 nm, resulting in an increase in the CO_2 absorption flux. The highest CO_2 absorption flux of 1.4 mmol/m^2s was reached for the tri-epoxy cross-linked SiO_2 aerogel membrane with a tri-epoxy concentration of 15%. The durability of the as-prepared SiO_2 aerogel membranes for CO_2 absorption is also demonstrated in this work. Consequently, the mechanically robust tri-epoxy cross-linked SiO_2 aerogel membranes have potential applications in membrane contactor systems for CO_2 capture.

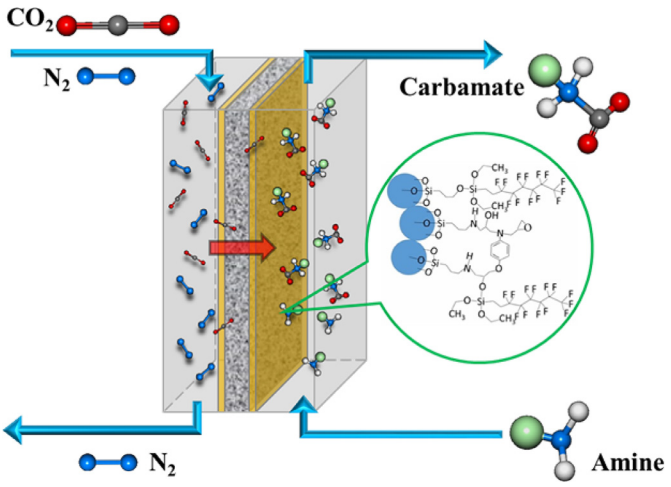
1. Introduction

SiO_2 aerogels [1] have attracted great research interests due to their high porosity (at least 90%), large specific surface area (400–1200 m^2/g), large pore volume and mesoporous structures (pore size between 2 and 50 nm). SiO_2 aerogels have been successfully prepared via sol–gel processes using a variety of precursors, such as tetraethyl orthosilicate (TEOS) [2], tetramethyl orthosilicate (TMOS) [3], and methyltrimethoxysilane (MTMS) [4]. Diverse applications of SiO_2 aerogels, such as thermal insulation [5], drug release [6], drug delivery [7], wavegiudes [8], catalysis [9], catalytic supports [10] and adsorption [11], have been studied in the previous literature. The SiO_2 aerogels [12] were also added in the chitosan (CS) polymers to form mixed-matrix membranes (MMMs), just like the zeolite/CS MMMs [13,14], for the ethanol/water separations. However, the SiO_2 aerogels suffer from low mechanical strength and fragile structural features, which limits their applications. To improve the mechanical strength and fragile structural features of SiO_2 aerogels, Meador et al. [15,16] successfully synthesized mechanically strong, lightweight SiO_2 aerogels via cross-linking of amine-modified SiO_2 aerogels with epoxides. The modulus of the epoxy cross-linked SiO_2 aerogels (10–100 MPa) [15] is 2 orders of magnitude higher than that of native SiO_2 aerogels (0.5–1.0 MPa) [15]. Consequently, the mechanical strength of SiO_2 aerogels can be effectively increased by the addition of epoxy cross-linkers.

In our previous study, for the first time, highly porous SiO_2 aerogels modified with hydrophobic fluorocarbon functional groups ($-CF_3$) by fluoroalkylsilane (FAS) were successfully coated onto a macroporous Al_2O_3 membrane [17–19]. The FAS-modified SiO_2 aerogel membranes were further applied in a membrane contactor for CO_2 absorption. The hydrophobic SiO_2 aerogel membrane served as an interface between an aqueous amine solution and a CO_2/N_2 gas mixture. CO_2 gases passed through the pores of the hydrophobic SiO_2 aerogel membranes and were absorbed by the aqueous amine solution. The hydrophobic SiO_2 aerogel membrane prevented the membrane from being wet by the aqueous amine solution in order to increase the CO_2 absorption flux. The CO_2

* Corresponding author.
** Corresponding author.
E-mail addresses: yflin@cycu.edu.tw (Y.-F. Lin), linky@nchu.edu.tw (K.-Y.A. Lin).

https://doi.org/10.1016/j.jtice.2018.03.019
1876-1070/



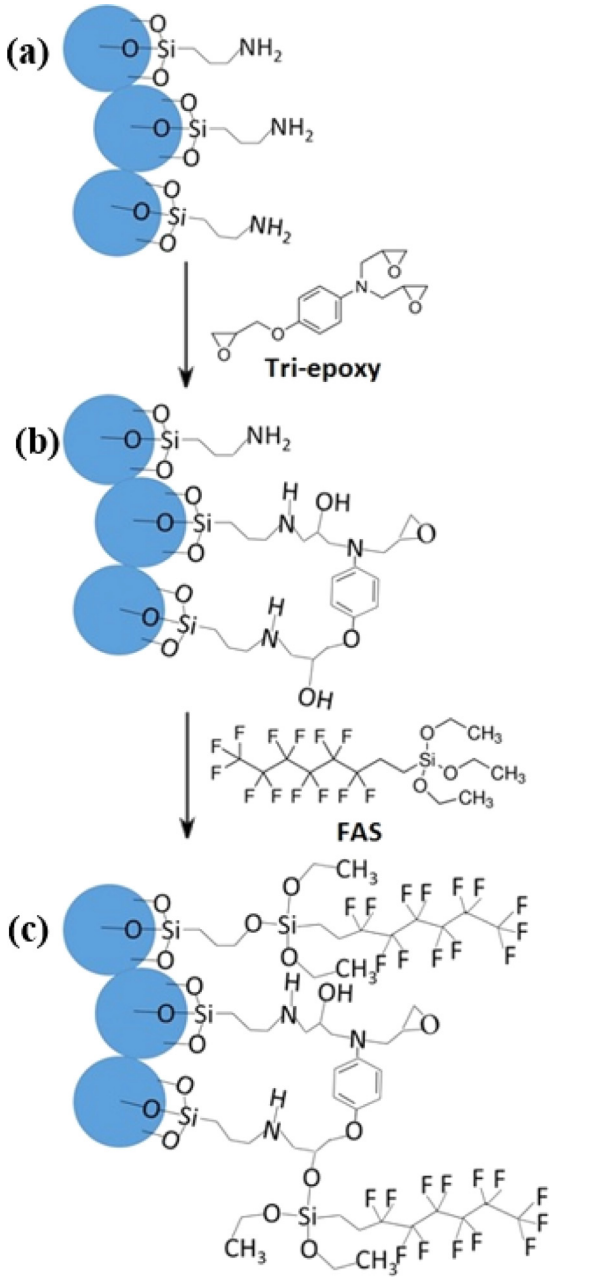
Scheme 1. Scheme of CO_2 absorption in a membrane contactor using the FAS-modified tri-epoxy cross-linked SiO_2 aerogel membrane.

absorption flux of the FAS-modified SiO_2 aerogel membranes reached a stable value of approximately 1.1 mmol/m^{2}s. The durability of the FAS-modified SiO_2 aerogel membranes was also demonstrated by their continuous operation for at least 4 days. To avoid the FAS hydrophobic post-modification, water-proof SiO_2 aerogel membranes were directly coated onto the macroporous Al_2O_3 membranes using hydrophobic MTMS precursors [20,21]. The MTMS-derived SiO_2 aerogel membranes were also utilized in membrane contactor for CO_2 absorption. The CO_2 absorption flux remained at a stable value of approximately 1.2 mmol/m^2 s with continuous operation for 4 days. Even though the utilization of SiO_2 aerogel membranes in membrane contactors for CO_2 absorption was well established, the mechanical strength of the SiO_2 aerogel membranes was not investigated in the previous literatures.

In this work, the addition of tri-epoxy cross-linkers to the SiO_2 aerogels successfully improved the mechanical strength of the SiO_2 aerogel membranes to overcome the fragility of the aerogels. The tri-epoxy cross-linked SiO_2 aerogel membranes were further used for CO_2 absorption in membrane contactor systems, as shown in Scheme 1. The effects on the CO_2 absorption flux and durability of the tri-epoxy cross-linked SiO_2 aerogel membranes with different tri-epoxy concentrations (7.5%, 15%, 30% and 45%) were also investigated in this study. This work indicates that the tri-epoxy cross-linked SiO_2 aerogel membrane with a tri-epoxy cross-linker concentration of 15% has the highest CO_2 absorption flux of approximately 1.4 mmol/m^{2}s and shows durability over continuous CO_2 absorption for at least 4000 min. The CO_2 absorption flux of approximately 1.4 mmol/m^2 s using the tri-epoxy cross-linked SiO_2 aerogel membranes is higher than that using TEOS-derived (1.1 mmol/m^2 s) and MTMS-derived (1.2 mmol/m^2 s) SiO_2 aerogel membranes. Consequently, the mechanically robust tri-epoxy cross-linked SiO_2 aerogel membranes have potential applications in membrane contactor systems for CO_2 capture.

2. Experimental

For the preparation of silica aerogel membranes via the sol–gel method, a mixture of TEOS (99.7%, SHOWA Company, 0.01 mol), ethanol (EtOH, 99.5%, ECHO Chemical Company, 0.03 mol), and 0.14 wt% hydrochloric acid (HCl, 35%, SHOWA Company) was stirred for 90 min. EtOH (0.05 mol) and 0.15 wt% ammonium hydroxide (NH_4OH, 28–30%, Fisher Scientific Company) were added to the above solution and stirred for 30 min. Subsequently, the Al_2O_3 membrane supports (Kinik Company, Taiwan) with a



Scheme 2. Scheme of the synthesis of the FAS-modified tri-epoxy cross-linked SiO_2 aerogels.

diameter, thickness and pore size of approximately 47 mm, 2.4 mm and 1 μm, respectively, were immersed in the sol solution for several hours. After gelation, the as-prepared SiO_2 aerogel membrane was aged in EtOH at room temperature for 2 days, where the ethanol was refreshed each day. Then, the SiO_2 aerogel membrane was immersed in (3-aminopropyl)trimethoxysilane (APTMS)/EtOH solution (25 wt%) for 1 day. THF was added to the resulting solution to remove the residual APTMS and EtOH over 2 days, where the THF was refreshed each day (Scheme 2(a)). Afterward, the APTMS-modified SiO_2 aerogel membranes were immersed in a solution of tri-epoxy cross-linker (*N*,*N*′-diglycidyl-4-glycidyloxyaniline) at 50 °C for 24 h (Scheme 2(b)). The resulting membranes were further immersed in THF for 24 h to remove the residual tri-epoxy cross-linker. The tri-epoxy cross-linked SiO_2 aerogel membrane was then transferred into n-hexane to remove the THF before the subsequent surface modification. The

Please cite this article as: Y.-F. Lin et al., Synthesis of mechanically robust epoxy cross-linked silica aerogel membranes for CO_2 capture, Journal of the Taiwan Institute of Chemical Engineers (2018), https://doi.org/10.1016/j.jtice.2018.03.019