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Hydrophobic fluorocarbon-modified silica aerogel tubular membranes with excellent CO_2 recovery ability in membrane contactors

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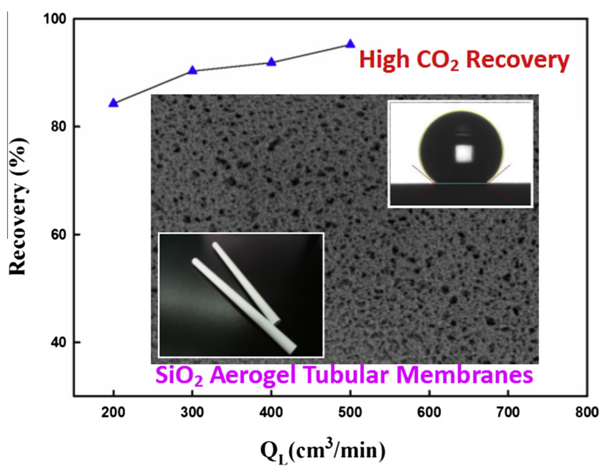
HIGHLIGHTS

- Silica aerogels were successfully coated onto Al_2O_3 tubular membrane supports.
- These as-prepared silica aerogel tubular membranes are not only durable but also reusable.
- CO_2 recovery using the silica aerogel tubular membranes is increased to almost 100%.
- These silica aerogel tubular membranes show promise for large-scale CO_2 capture in power plants.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, the pore size of macroporous Al_2O_3 tubular membranes were successfully shrunk by the coating of mesoporous silica aerogels on their surface. Fluoroalkylsilane (FAS) was successfully grafted on the surface of silica aerogel tubular membranes, resulting in a hydrophobic surface on the resulting membranes. The CO_2 absorption flux of the FAS-modified silica aerogel tubular membrane reaches a stable value of approximately 0.6 mmol/m^2 s in one day of operation. Furthermore, the as-prepared FAS-modified silica aerogel tubular membranes can be used continuously to absorb CO_2 for at least one day, and they can be reused in three consecutive cycles of CO_2 absorption. The results of this study demonstrated that these FAS-modified silica aerogel tubular membranes are not only durable but also reusable. The CO_2 gases are almost absorbed completely (97% CO_2 recovery) at liquid and gas flow rates of 500 and 200 sccm, respectively. Thus, these as-prepared silica aerogel tubular membranes with FAS modifications show promise for use in a large-scale CO_2 absorption in a power plant.

1. Introduction

The capture of CO_2 in a membrane contactor system is a technique that combines chemical absorption with a membrane process, resulting in a low cost method that is easily scaled up. A

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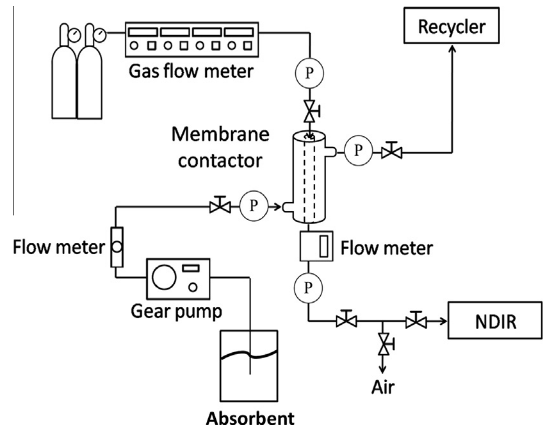
hydrophobic membrane serves as an interface between a CO_2/N_2 gaseous mixture and an aqueous amine solution to prevent membrane wetting by the aqueous amine solution. As a result, CO_2 gases pass through the membrane pore and are absorbed by the aqueous amine solution. As a result, a variety of hydrophobic polymeric membranes, such as polypropylene (PP) [1–4], polyphenylsulfone [5], polyvinylidene difluoride (PVDF) [6,7] and polytetrafluoroethylene (PTFE) [8,9], have been used in membrane contactors for CO_2 capture. However, these polymeric membranes are easily swelled by the aqueous amine solution to change their surface morphology and roughness, leading to a decrease in the CO_2 absorption capacity. To solve the swelling problem of the polymeric membranes, inorganic SiO_2 materials were successfully incorporated into PVDF nanofibrous membranes to form composite PVDF/SiO_2 nanofibrous membranes in our previous study [10]. The as-prepared PVDF/SiO_2 nanofibrous membranes can prevent the wetting of the membrane by aqueous amine solution and can continuously absorb CO_2 for at least four days; this finding indicates that the as-prepared composite PVDF/SiO_2 nanofibrous membranes are durable.

Silica aerogels [11] are a type of mesoporous materials (pore diameter between 2 and 50 nm) with large specific surface areas and high porosities (at least 90%). As a result, they have been widely investigated for applications in drug release [12], thermal insulation [13,14], catalysis [15] and adsorption [16]. In our previous work, mesoporous silica aerogels were successfully coated on a macroporous Al_2O_3 plate membrane support for CO_2 absorption in membrane contactor applications for the first time [17–19]. The as-prepared silica aerogel plate membranes can effectively prevent wetting of the membrane by aqueous amine solution and can continuously absorb CO_2 for at least four days. The reusability of the silica aerogel plate membranes was also demonstrated in three consecutive cycles. These results indicate that the silica aerogel plate membrane is not only durable but also reusable. However, the CO_2 recovery using the as-prepared silica aerogel plate membrane is quite low (~30%) due to the smaller surface areas of the plate membranes.

In this study, silica aerogels were successfully coated on the macroporous Al_2O_3 tubular membrane support via a sol–gel reaction. Hydrophobic silica aerogel tubular membranes were achieved after FAS surface modifications. FAS-modified silica aerogel tubular membranes were used for the continuous operation in CO_2 absorption for one day and were reused in three consecutive cycles. The results of this study demonstrate that these as-prepared silica aerogel tubular membranes are not only durable but also reusable. Most importantly, the CO_2 recovery using the silica aerogel tubular membranes was increased to almost 100% compared to the silica aerogel plate membranes (~30%). Thus, these silica aerogel tubular membranes show promise for applications in membrane contactors that are used for large-scale CO_2 capture in power plants.

2. Experimental methods

Silica aerogels with a pore diameter of approximately 3 nm were successfully prepared with a sol–gel reaction following our previous method [17]. Briefly, mixtures of tetraethyl orthosiliate (TEOS), ethanol and aqueous HCl were stirred for 90 min. The aqueous NH_4OH was then added to the resulting solution and stirred for 30 min. Subsequently, the macroporous Al_2O_3 tubular membrane support with a pore size of approximately 0.8 μm was immersed in the as-prepared sol solution for several hours. The inner and outer diameter of the tubular membranes is 0.8 and 1.2 cm, respectively. Furthermore, the module length of the tubular membrane is 24 cm. After gelation, the silica aerogel tubular membranes were aged in ethanol at 25 °C for two days, and the ethanol was refreshed each day. Then, the as-prepared silica aerogel tubular membranes were soaked in a 0.02M FAS/*n*-hexane solution at 40 °C, and the FAS solution was refreshed every 24 h (1, 2, 3 and 4 times).



Scheme 1. Scheme of CO_2 absorption experiment using silica aerogel tubular membranes.

For the CO_2 absorption experiment, one side of the silica aerogel tubular membrane was exposed to 2-amino-2-methyl-1-propanal (AMP)/piperazine (PZ) amine absorbents at various flow rates (200–500 sccm), while the other side of the membrane was exposed to 9 vol% CO_2/N_2 gas mixtures at different flow rates from 200 to 500 sccm, as shown in Scheme 1. The reusability of the silica aerogel tubular membrane that was modified by three FAS modifications was evaluated over three consecutive cycles. For the washing procedure in each cycle, pure N_2 gas was allowed to flow through the original gas side of the silica aerogel tubular membranes at 200 sccm for 2 h while the liquid side of the membranes remained exposed to stagnant amine absorbents. Surface contact angles and surface morphologies of silica aerogel tubular membranes were studied using an automatic interfacial tensiometer (Kypwa Interface Science, Face PD-VP) and a scanning electron microscope (Hitachi, S-4800). Young equation is commonly used for the calculation of contact angle in the form of $\cos\theta = \frac{\gamma_{SG}-\gamma_{SL}}{\gamma_{LG}}$. Where θ is the contact angle, γ_{SG}, γ_{SL}, and γ_{LG} are the surface tensions between three phases: solid (S), gas (G) and liquid (L). Pore size calculations are usually made with the aid of the Kelvin equation in the form of $r = \frac{2V_m\gamma}{RT\ln\frac{p}{p_0}}$. Here, r is the pore radius, p is the actual vapor pressure, p_0 is the saturated vapor pressure, γ is the surface tension, V_m is the molar volume, R is gas constant and T is temperature. The CO_2 output concentration was measured using a nondispersive infrared sensor (NDIR, Jusun AGM 400) to calculate the amount of CO_2 absorbed and the CO_2 absorption flux.

3. Results and discussion

Before studying the CO_2 absorption capacity of the silica aerogel coated Al_2O_3 tubular membranes, we investigated the CO_2 absorption flux of macroporous Al_2O_3 tubular membrane supports with one FAS modification, as shown in Fig. 1. The CO_2 absorption flux of the FAS-modified Al_2O_3 tubular membrane support decreased very rapidly in the initial 250 min due to the membrane wetting by the aqueous amine solution. The Al_2O_3 tubular membrane support with a large pore size of approximately 0.8 μm did not effectively prevent membrane wetting by the aqueous amine solution. To solve the membrane wetting problem, mesoporous silica aerogels with a pore size of approximately 3 nm were coated onto the macroporous Al_2O_3 tubular membrane support to shrink the