



Hybrid organosilica membrane with high CO₂ permselectivity fabricated by a two-step hot coating method



Xuyang Yang^{a,b}, Hongbin Du^b, Yichao Lin^b, Liping Song^a, Yajie Zhang^b, Xuechao Gao^b, Chunlong Kong^{b,*}, Liang Chen^{b,*}

^a School of Science, Department of Chemistry, Shanghai University, 200444 Shanghai, PR China

^b Institute of New Energy Technology, Ningbo Institute of Material Technology and Engineering, CAS, 1219 Zhongguan West Road, 315201 Ningbo, PR China

ARTICLE INFO

Article history:

Received 20 October 2015

Received in revised form

29 January 2016

Accepted 30 January 2016

Available online 2 February 2016

Keywords:

Hybrid organosilica

Sol–gel

Two-step

Carbon dioxide

Gas permeation

ABSTRACT

Using 1, 2-bis (triethoxysilyl) ethane as a precursor, a hybrid organosilica membrane with high CO₂ permselectivity, has been prepared by a two-step hot coating method. Here two sols with different sol particle sizes and microporous structures were prepared by tuning the dose of acid. By combining the two sols in the coating process using the two-step hot coating method, a thin and dense hybrid organosilica layer can be obtained. Single gas permeation experiments of the as-prepared membrane show a high permeance of $1.3 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for CO₂, with excellent CO₂/N₂ and CO₂/CH₄ separation factor of 23.5 and 31.5, respectively. Based on the mixture gas permeation experiments, the selectivities of CO₂/N₂ and CO₂/CH₄ at 20 °C were measured to be 10.5 and 17.5, respectively. The high perm-selectivity indicates that the as-prepared membrane contains only few defects. Furthermore, we demonstrate that the CO₂ separation performance of the as-prepared membrane is greatly controlled by its CO₂ adsorption properties.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Separation of CO₂ from natural gas and flue gas are of great importance for the energy and environmental perspective. Natural gas is one of the most widespread primary energy sources and shows many advantages, including high storage ability and high energy content [1]. However, the CO₂ contaminant, which commonly exists in the production of natural gas flow, is believed to reduce the conversion rate and energy content of natural gas. Thus, it should be removed before the natural gas flow is delivered to the pipeline. On the other hand, the accumulation of CO₂ in air is leading to severe global warming problem because it is a major greenhouse gas [2,3]. Therefore, developing efficient strategies to separate and capture CO₂ has attracted a great deal of attention in the past decades [4–9]. Toward this end, membrane separation technology is deemed as a promising solution because it is low energy cost and easy processing [10,11]. To date, a large variety of membrane materials with excellent CO₂-permselective performance have been designed and prepared [12–19].

Inorganic silica is one of the most important materials for fabricating membranes because of the remarkable thermal

stability and separation properties at elevated temperature. By using sol–gel and CVD methods, many silica precursors have been successfully applied in the fabrication of silica membranes [20]. The developed homogeneous membrane layer shows the selective permeation properties for gas molecules with different size, through which the smaller gas molecules (e.g., H₂ and He) can permeate rapidly while larger gas molecules (e.g., N₂ and CH₄) can hardly permeate [21]. Among the silica precursors, tetraethoxysilane (TEOS) is a commonly used monomer for the preparation of silica membranes. However, the resulting inorganic silica structure with a pore size of less than 0.25 nm shows a low permeation of smaller gas for practical applications [22]. Moreover, the low stability against water greatly limits its application in industrial processes involving hydrothermal conditions [23].

Organic–inorganic hybrid materials that could combine both advantages of organic and inorganic materials have attracted much attention for development of gas separation membranes to achieve both high permeance and selectivity [21,24]. To improve the gas permeation rate and hydrothermal stability of the silica membranes, organic–inorganic hybrid silica alkoxides have been applied as the precursors to fabricate silica membranes [25–27]. The resulting membranes show excellent performance in gas separation and pervaporation processes with a controllable pore size and hydrothermal stability [28–30]. For instance, bis (triethoxysilyl) ethane (BTESE) contains organic groups between two Si atoms, which can enable the design of pore size and control of gas

* Corresponding authors.

E-mail addresses: kongchl@nimte.ac.cn (C. Kong), chenliang@nimte.ac.cn (L. Chen).

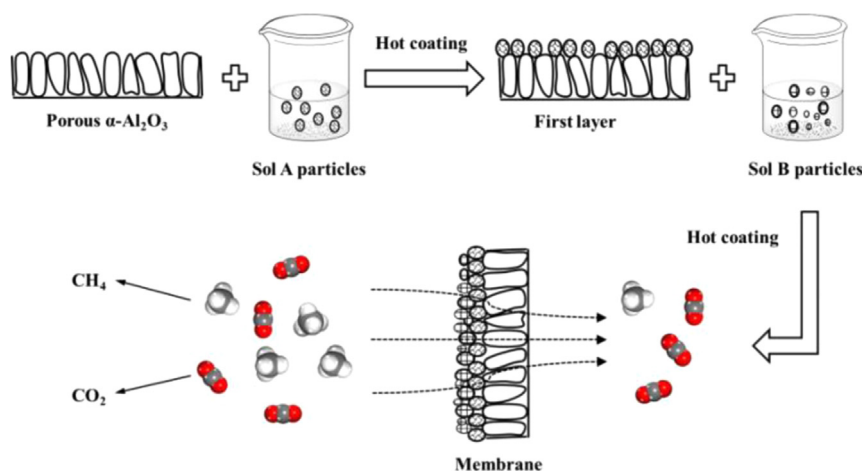


Fig. 1. Scheme for the preparation of hybrid organosilica membrane by the two-step hot coating method.

permeation. Kanezashi et al. [25] have reported that the membranes prepared with a BTESE precursor exhibit a high permeance of $10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for H_2 and high separation selectivity for of 1000 H_2/SF_6 . In particular, the presence of Si–C–Si bonds in the silica networks results in enhanced hydrophobicity and a decreased possibility of formation of Si–OH groups in the hydrothermal atmosphere, which can greatly improve the hydrothermal stability [31, 32]. However, the BTESE-derived membrane usually shows a moderate performance for CO_2/CH_4 and CO_2/N_2 separation, compared with traditional inorganic silica membrane [21].

Very recently, it is shown that the dose of acid catalyst can influence the pore size of the BTESE-derived hybrid silica network [33]. Inspired by this work, we propose a two-step hot coating method to tune the pore structure of BTESE-derived membrane to achieve a high CO_2 -permselective performance. Herein, two types of BTESE polymer sols were prepared by tuning the dose of acid catalyst, and then they were coated on porous substrates to fabricate hybrid silica membranes, as depicted in Fig. 1. First, the sol A was prepared with large dose of acid so that the obtained large sol particles could modify the large pores of the substrate. In addition, the resulting sol particles with large pore size could reduce the diffusion resistance. Subsequently, the sol B prepared with small dose of acid is beneficial for the formation of thin and dense separation layer because the particles of sol B are rather small. As a result, the as-prepared hybrid silica membranes are expected to display excellent gas separation performance.

2. Experimental

2.1. Preparation of organosilica sols and membranes

The organosilica sols were prepared by hydrolysis and polymerization of BTESE (J&K Scientific Ltd) and catalyst HCl in ethanol. In this work, two types of sols A and B were prepared for hybrid silica layer coating. The sol A was prepared with molar ratios of BTESE/ethanol/ H_2O /HCl (37 wt%) = 1/38/60/10 and was used for the first layer coating. The mixtures of BTESE, HCl and ethanol were stirred vigorously for 2 h in ice bath, and then the solution was moved into a 40°C water-bath for 1 h. The sol B was prepared with molar ratios of BTESE/ethanol/ H_2O /HCl (37 wt%) = 1/46/60/0.1. The mixtures were stirred at 30°C for 5 h. Finally, both of the prepared sol A and sol B were stored in the icebox.

Porous α -alumina tubes (average pore size: $1.5 \mu\text{m}$, outside diameter: 12 mm) were used as the substrates for preparation of hybrid organosilica membranes. In order to remove the large pores

that might result in pinholes in the membrane, the tubes were coated with colloidal silica (Sigma-Aldrich Co. LLC) and then calcined at 550°C for 20 min. Subsequently, the tube was heated at 130°C for 15 min, and then coated with the sol A and dried at 80°C for 15 min. Immediately, the tube was calcined at 300°C for 20 min. This step was repeated several times. Finally, the sol B was repeatedly coated on the tubes to form dense separation layer. The coated process was similar to that of sol A.

2.2. Characterization

The sol particle sizes of as-prepared sols were measured by dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS at 25°C . The powders of sol A and sol B prepared by calcination at 300°C were characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet 6700, Thermo Company) and N_2 adsorption/desorption isotherms at 77 K on Accelerated Surface Area and Porosimetry System (ASAP 2020M, Micromeritics Company), and then the adsorption isotherms of CO_2 , CH_4 and N_2 were measured at 20°C . Thermogravimetric analysis (Pyris Diamond TG/DTA, Perkin-Elmer) of the powders were performed in air. The flow rate of air was set at 120 mL min^{-1} and the temperature was increased from 25 to 850°C at a rate of $10^\circ\text{C min}^{-1}$. The morphology of as-prepared membranes was acquired by SEM (the Quanta FEG 250, FEI Company).

2.3. Gas permeation test of the hybrid membrane

The gas separation performance of the as-prepared hybrid membranes was measured on a home-made permeance apparatus. The single gas permeation of H_2 , CO_2 , N_2 and CH_4 was measured at a temperature range of 20 – 80°C and the averaged results of three runs were obtained from at least two membranes. Subsequently, binary gas mixture (CO_2/N_2 and CO_2/CH_4) were measured at 20 and 80°C , respectively. Before we evaluated the permeation properties, the membranes were dried at 120°C in vacuum oven for 12 h, and then sealed in a module with silicone O-rings. The test gas was fed to the outside of the cylindrical membranes, while the permeate stream was kept at atmospheric pressure. The pressure drop through the membranes was maintained at 0.1 MPa. The gas permeance (P) was calculated by the formula:

$$P = \frac{F}{A} \times \frac{1}{\Delta P}$$

F (mol/s) is the molar flow rate of the examined gas.

Download English Version:

<https://daneshyari.com/en/article/632478>

Download Persian Version:

<https://daneshyari.com/article/632478>

[Daneshyari.com](https://daneshyari.com)