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Cyclic tertiary amino group containing fixed carrier membranes for CO_2 separation

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ABSTRACT

Fixed carrier membranes containing amino groups show attractive performance in CO_2 separation for clean energy supply and greenhouse gas reduction. However, the separation performance of fixed carrier membranes at high feed pressure is limited by the facilitated transport ability of membranes as well as the CO_2-induced plasticization. In this work, the tertiary amino group containing fixed carrier membranes were prepared by interfacial polymerization (IP) with hexane-soluble trimesoyl chloride (TMC) and aqueous-soluble 1,4-bis (3-aminopropyl) piperazine (DAPP), *N*-aminoethylpiperazine (EAP) and 3,3′-diamino-*N*-methyldipropylamine (DNMDAm). The results show that the membrane prepared with TMC and DAPP exhibits the highest CO_2 separation performance due to efficient CO_2 facilitated transport and high plasticization resistance. Efficient facilitated transport of CO_2 in the membrane is due to the high content of cyclic tertiary amino groups which possess high stoichiometric CO_2 loading and high rate constant of amine-CO_2 reaction. Moreover, high plasticization resistance of the membrane is attributed to the appropriate stiffness of polymer chains provided by IP. The membrane prepared with TMC and DAPP shows promising applications in high-pressure fuel gas purification.

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1. Introduction

Environmental and energy concerns have motivated intensive research on novel materials for efficient CO_2 separation processes for greenhouse gas reduction and clean energy supply [1–4]. Membrane technology for CO_2 separation has attracted increasing attention due to its high energy efficiency, simplicity in design, environmental compatibility and a small footprint [4,5]. Considerable polymeric membrane materials with high CO_2 separation performance, *i.e.* CO_2 permeance and selectivity, have been developed in recent years [6–9]. However, the separation performance at high feed pressure still has to be improved to increase industrial applications of polymeric membranes for high-pressure gas purification such as natural gas and syngas purification [7,10–12].

Membranes with fixed carriers, *i.e.* covalently bonded alkaline groups such as amino groups [13–23] and carboxylate groups [24], exhibit attractive performance. The carriers could reversibly react with CO_2 in the membrane and facilitate CO_2 transport. But the separation performance of fixed carrier membranes at high feed pressure is limited by the facilitated transport ability of membranes as well as the CO_2-induced plasticization that is a common problem for other polymeric membranes [25,26].

Enhancing the CO_2 facilitated transport is an effective way to improve the separation performance of fixed carrier membranes at high pressure. The CO_2 separation performance of fixed carrier membranes decreases with increasing feed pressure due to the fact that more and more carriers are saturated with CO_2 molecules and the rest of the CO_2 molecules transport across the membrane relying only on solution-diffusion mechanism [18–23]. The “carrier saturation” phenomenon hinders the application of fixed carrier membranes at high pressure. The enhancement of CO_2 facilitated transport could improve the separation performance of fixed carrier membranes, which may alleviate the low performance at high pressure. It could be achieved through increasing the carrier content [19,20], the stoichiometric CO_2 loading of carriers [13], the reaction rate constant between CO_2 and carriers [13] as well as decreasing the crystallinity of polymer chains containing carriers [27]. Tertiary amines have higher stoichiometric CO_2 loading [28,29] (Eq. (1)) than primary and secondary amines [28,30], and

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polymer chains containing tertiary amino groups generally have lower crystallinity [18,21] than polymer chains containing primary and secondary amino groups. However, tertiary amines generally have a lower reaction rate constant than primary and secondary amines [28–32]. The rate constant of amine-CO_2 reaction could be improved through increasing electronegativity of amines [29–32] and accessibility of amines to CO_2 [29,32]. The electronegativity of the nitrogen atoms of amino groups could be increased by the electron-donor substituent, such as alkyl groups. The accessibility of carriers with CO_2 could be improved by the cyclic and rigid structures [32] and the structure with well separated amino groups [29].

$$R_3N+CO_2+H_2O \leftrightarrows R_3NH^+ + HCO_3^- \quad (1)$$

Increasing the plasticization resistance is an effective way to improve the selectivity of membranes at high feed pressure. CO_2 typically acts as a plasticizer, swelling the polymer and causing the increase of the permeation of other gases at high CO_2 partial pressure, which may result in a significant loss in CO_2/gases selectivity of membranes [25]. It is a substantial barrier for polymeric membranes to be used for practical CO_2 separations at high CO_2 partial pressure. The plasticization resistance of membranes is mainly enhanced by covalent crosslinking structure and rigid polymer chains [33,34]. However, the CO_2 permeance generally decreases due to the densification of polymer chains [34]. Our research group proposed that the introduction of the crosslinked sections containing functional groups into the membrane could overcome these limitations, and the resulting membrane shows high CO_2 permeance and high plasticization resistance simultaneously [19,20]. Interfacial polymerization (IP) has been demonstrated to be an effective method to fabricate gas separation membranes with crosslinked sections containing functional groups [18, 21–23].

In this work, we proposed an idea that the CO_2 facilitated transport and the plasticization resistance of membranes should be enhanced simultaneously to increase the CO_2 permeance and selectivity of membranes at high feed pressure. A crosslinked rigid structure containing tertiary amino groups was developed in the fixed carrier membrane by IP. The enhanced facilitated transport ability could be achieved through optimizing the carrier-CO_2 reaction and increasing the content of carriers. The high plasticization resistance could be achieved through the crosslinked rigid structure formed by IP. Trimesoyl chloride (TMC) was used as the monomer of organic phase. 1,4-bis (3-aminopropyl) piperazine (DAPP), *N*-aminoethylpiperazine (EAP) and 3,3′-diamino-*N*-methyldipropylamine (DNMDAm) were used as the monomer of aqueous phase, respectively. The flat sheet polysulfone (PS) membranes coated with crosslinked polydimethylsiloxane (PDMS) was the support layer. The membranes prepared with DAPP, EAP and DNMDAm were named DAPP-TMC-2 (the number represents the amount of tertiary amino groups per repeat unit), EAP-TMC-1 and DNMDAm-TMC-1 membranes, respectively. The reaction between DAPP and TMC is shown in Scheme 1, and the chemical structures of EAP and DNMDAm are shown in Scheme 2. The structural properties of the membranes were investigated by attenuated total reflectance infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Furthermore, the facilitated transport of CO_2 in the membrane was confirmed by obtaining the evidence for amine-CO_2 reaction through ATR-FTIR and zeta potential test. Moreover, to investigate the effects of the facilitated transport ability and the plasticization resistance on the membrane performance, the fixed carrier membranes were tested by CO_2/CH_4 mixture (10/90 by volume) and CO_2/N_2 mixture (15/85 by volume). The results indicated that DAPP-TMC-2 membrane shows high separation performance and plasticization resistance. After that, to investigate the membrane performance for high-pressure fuel gas purification, DAPP-TMC-2 membrane was tested by pure CO_2, CH_4 and H_2 gases, CO_2/CH_4 mixtures (10/90 by volume, 40/60 by volume) and CO_2/H_2 mixture (40/60 by volume). Finally, the permselectivity of DAPP-TMC-2 membrane was compared with that of other membranes at high CO_2 partial pressure.

2. Experimental

2.1. Material

The PS flat ultrafiltration membranes (Vontron Technology, China) with an average cut-off molecular weight of 6000 were used as supports. The PS membrane consists of the PS layer with thickness of about 60 μm and the polyester backing fabric with thickness of about 90 μm. PDMS (ShinEtsu, Japan), tetraethoxysilane (TEOS) (AR; Aladdin, China) and ditin butyl dilautate (DBD) (95%; Aladdin, China) were used to modify PS membranes. *N*-heptane (AR; Guangfu, Tianjin, China) was the solvent of PDMS coating solution. DAPP (98%; J&K, China), EAP (99%; Aladdin, China), DNMDAm (98%; Aladdin, China) and ethylenediamine (EDA) (99%; Aladdin, China) were used as monomers in aqueous phase. Na_2CO_3 (AR; Guangfu, Tianjin, China) was the acid acceptor in aqueous phase. For the preparation of the aqueous solution, reverse osmosis (RO) deionized water was used. TMC (99.5%; Sanli, Qingdao, China) was used as a monomer in organic phase and n-hexane (AR; Guangfu, Tianjin, China) was the organic phase solvent. All chemicals were used without any further purification.

2.2. Membrane preparation

The PDMS/PS membrane was prepared by casting crosslinked PDMS solution on PS membrane with a pre-set wet coating thickness (the gap between substrate and coating knife) by a homemade coating applicator with an accuracy of ± 10 μm. The highly permeable PDMS intermediate layer prevented the penetration of the IP formed layer into the porous structure of PS [18]. Crosslinked PDMS solution was prepared by dissolving PDMS, TEOS and DBD in *n*-heptane with a mass proportion of 2: 1: 1: 96, followed by stirring for 5 min and standing for 30 min at room temperature. TEOS was the crosslinker and DBD acted as the catalyst. The resulted membrane was dried at 30 °C and 40% relative humidity in an artificial climate chamber (Climacell 222R, Germany) for at least 12 h.

DAPP-TMC-2, EAP-TMC-1, DNMDAm-TMC-1 and EDA-TMC membranes were prepared by IP on the PDMS/PS support membrane. The concentrations of aqueous monomer and organic monomer were 0.0044 mol L^{-1} and 0.0038 mol L^{-1}, respectively. The concentration of Na_2CO_3 was 0.0377 mol L^{-1}. The flat sheet support membrane was initially immersed into the organic phase for 10 min. Afterwards, the excess solution was poured off from the soaked membrane surface. Then the membrane was air-dried at room temperature for about 1 min, until no visible remaining liquids. Subsequently, the impregnated membrane was placed into the aqueous phase for 3 min at 22 °C. After IP, the membrane was washed to eliminate excess monomers and byproducts. If the excess monomers and byproducts have not been eliminated, the surface of the dried membrane would turn yellow due to oxidization of monomers and byproducts. The membrane was washed with 200 mL deionized water for 1 min each time, and the process was repeated for 4 times. After washing, the surface of the dried membrane would not turn yellow.

2.3. Membrane characterization

The chemical characterization of the membrane surface was accomplished by ATR-FTIR spectroscopy (FTS-6000, Bio-Rad of

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