



Amine-containing polymer/zeolite Y composite membranes for CO₂/N₂ separation



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ARTICLE INFO

Article history:

Received 8 July 2015

Received in revised form

6 September 2015

Accepted 15 September 2015

Available online 18 September 2015

Keywords:

CO₂-selective membrane

Polymer/inorganic composite membrane

Polyvinylamine

Mobile carrier

Facilitated transport

ABSTRACT

New amine-containing polymer/zeolite Y composite membranes were successfully synthesized for CO₂/N₂ separation from flue gas. The polyvinylamine (PVAm) with a high molecular weight ($M_w = 719,000$) was synthesized and used as the fixed-site carrier for CO₂ facilitated transport. The PVAm was incorporated with different amino acid salts (mobile carriers), including potassium glycinate (KG), lithium glycinate (LiG) and piperazine glycinate (PG). The amine-containing polymer blend solution was coated onto a zeolite Y seed layer on top of a polyethersulfone (PES) substrate. The composite membrane with a selective amine layer thickness of more than 200 nm showed a better CO₂/N₂ separation performance compared to the membrane without the zeolite Y seed layer, which was due to the fact that the zeolite Y layer had a smaller interparticle pore size than the PES substrate, resulting in minimizing the penetration of amine-containing polymer solution into the pores underneath and thus reducing the mass transfer resistance of CO₂ molecules through the membrane. The effects of different kinds of mobile carriers and various compositions and thicknesses of the amine-containing polymer layer were investigated. The resultant amine-containing polymer/zeolite Y composite membrane exhibited a CO₂ permeance up to ~1100 GPU and a CO₂/N₂ mixed gas selectivity of at least 200 at the typical flue gas temperature of 57 °C. This high separation performance showed a great potential for the application of carbon capture from flue gas.

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1. Introduction

Carbon dioxide (CO₂) emission from the fossil fuel combustion is one of the main reasons for global warming, and therefore there is a significant need of developing technologies for CO₂ separation from flue gas. Membrane separation is an energy-efficient and cost-effective alternative [1–6] to the conventional technologies including absorption processes using amine-based solvents, adsorption processes employing solid adsorbents, and cryogenic distillation. The membrane transport performance for CO₂/N₂ separation from flue gas is mainly characterized by two parameters, the CO₂ permeance and the CO₂/N₂ selectivity [7]. The CO₂ permeance ($\frac{P_{CO_2}}{l}$) is defined as

$$\frac{P_{CO_2}}{l} = \frac{J_{CO_2}}{(p_{iCO_2} - p_{pCO_2})} \quad (1)$$

The common unit of permeance is the gas permeation unit (GPU), 1 GPU = 10⁻⁶ cm³(STP)/(s cm² cmHg). P is referred as the permeability, and its common unit is Barrer, 1 Barrer = 10⁻¹⁰ cm³(STP) cm/(s cm² cmHg). The CO₂/N₂ selectivity can be expressed as the ratio of permeabilities of CO₂ over N₂, as shown in Eq. (2). To achieve a high CO₂ recovery (> 90%) with a high CO₂ purity (> 95%) in a membrane-based process for carbon capture from flue gas, both a high CO₂ permeance and a high CO₂/N₂ selectivity are required [8–11].

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \quad (2)$$

Polymer and inorganic membranes are two major categories for CO₂ separation membranes, and they follow different transport mechanisms (Fig. 1). Solution–diffusion polymer membranes such as Polaris™ and Polyactive® have shown the potential to achieve

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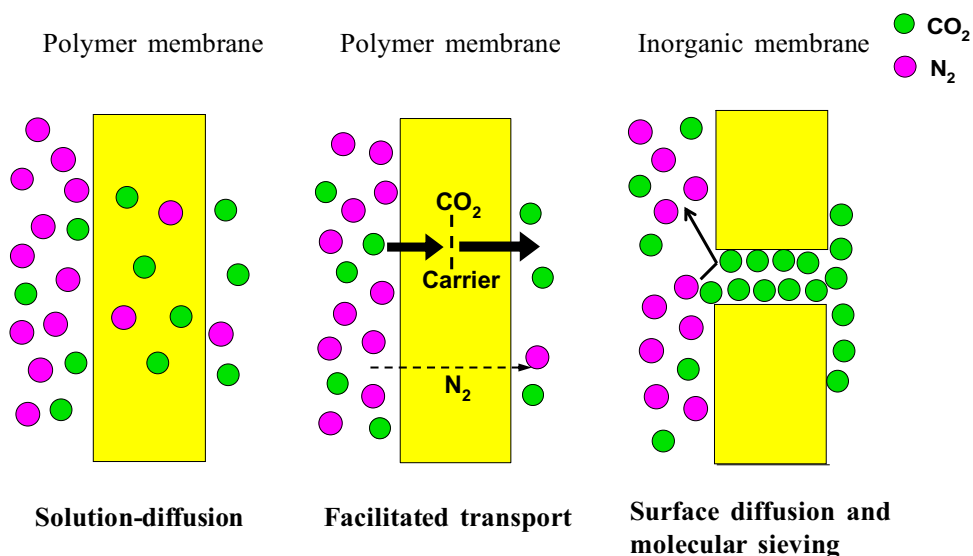


Fig. 1. Schematic of CO₂/N₂ transport mechanisms through polymer and inorganic membranes.

high CO₂ permeances up to ~2000 GPU [11–15], but they have shown low CO₂/N₂ selectivities (usually below 30 at 57 °C) governed by the Robeson upper bound [16,17].

Facilitated transport membranes, on the other hand, can provide a high CO₂ permeance while maintaining a high CO₂/N₂ selectivity. In the facilitated transport membranes, there is a reversible reaction between CO₂ and a reactive carrier which usually contains an amino group. Fixed carriers (amine-containing polymers) and mobile carriers (amine-containing small molecules) are two major categories of carriers for CO₂ transport in facilitated transport membranes. The fixed carriers such as polyallylamine [18–22], polyethylenimine [18,23] and polyvinylamine (PVAm) [24–27] have been reported in the literature. The common mobile carriers that have been reported in the literature include ethylenediamine [27–29], amino acid salts [30,31], and alkanolamines [32,33]. In the facilitated transport membranes, CO₂ molecules react with amine carriers first, and then the reaction products transport across the membrane, releasing the CO₂ molecules to the permeate side of the membrane. By this mechanism, the solubility of CO₂ molecules in the membrane is greatly enhanced. On the other hand, the non-reactive N₂ molecules transport through the membrane only by the solution-diffusion mechanism. Therefore, CO₂ transport gets facilitated, and a high CO₂/N₂ selectivity can be achieved through the facilitated transport mechanism.

The gas transport in inorganic membranes such as zeolite Y (with a pore size of 7.4 Å and a Si/Al ratio of 1.5–3.8) follows both surface diffusion and molecular sieving mechanisms. CO₂ (with a molecular size of 3.3 Å) favorably adsorbs and diffuses along the interior zeolite surface wall, while N₂ (with a molecular size of 3.64 Å) is blocked and cannot go through the membrane. By the combination of these two mechanisms, both a high CO₂ permeance and a high CO₂/N₂ selectivity can be achieved from inorganic membranes [34–37].

In this work, an amine-containing polymer/zeolite Y composite membrane for CO₂/N₂ separation was designed. First, zeolite Y with an average particle size of around 40 nm was deposited onto the PES substrate. For the polymer layer, PVAm with a high molecular weight was synthesized and acted as the fixed carrier, while different kinds of amino acid salts were incorporated as the mobile carriers in the coating solution. The viscous PVAm/mobile carrier coating solution was knife-coated onto the zeolite Y layer to form a thin selective layer.

2. Experimental

2.1. Materials

Glycine (98.5%), potassium hydroxide (KOH, 85%), lithium hydroxide (LiOH, 98%), piperazine (99%), n-vinylformamide (NVF, 98%), α,α'-azodiisobutyramidine dihydrochloride (AIBA, 97%) and isopropanol (IPA, 99.9%) were purchased from Sigma-Aldrich. Hydrochloric acid (HCl, Certified ACS Plus) and ethanol (99.5%) were purchased from Fisher Scientific. Strong base anion-exchange resin (Purolite® A600OH) was kindly donated by Purolite Corporation (Bala Cynwyd, PA). All the chemicals were used as received without further purification.

Biomax polyethersulfone ultrafiltration flat-sheet membrane substrate with a molecular weight cut off of 300 kDa (PES300, with a pore size of ~72 nm and a porosity of ~15%) was purchased from EMD Millipore (Billerica, MA). The PES300 substrate was soaked in deionized water for overnight and then in IPA for 30 min to remove the glycerol in the pores before usage.

2.2. Synthesis of PVAm and amine-containing mobile carriers

High-molecular-weight PVAm was synthesized following the procedure in the literature [27,38]. First, the monomer NVF was distilled under vacuum and stored at –10 °C. Then, polymerization was carried out under nitrogen protection at 50 °C for 3 h. AIBA was used as the initiator of the polymerization, and water was used as the solvent. The initial monomer concentration was 30 wt%, and the initiator/monomer ratio was 0.5/100 (by weight). After the polymerization, 2 M HCl aqueous solution was added to carry out the acidic hydrolysis at 70 °C for 5 h. The molar ratio of HCl to monomer for hydrolysis was 2:1. After hydrolysis, the polymer solution was poured into a large amount of ethanol (ethanol/polymer solution volume ratio=4/1) for precipitation. The obtained polymer was dried in a vacuum oven at 60 °C for 48 h and then dissolved in water to form a 3 wt% solution. Strong base anion-exchange resin was added to the polymer solution to adjust the pH to 10, followed by vacuum filtration to remove the resin.

Mobile carriers of amino acid salts including potassium glycinate (KG), lithium glycinate (LiG) and piperazine glycinate (PG) were synthesized by the following procedure. First, glycine was dissolved in water to form a 17.5 wt% solution and stirred for 2 h at

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