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High pressure pure- and mixed-gas separation of CO_2/CH_4 by thermally-rearranged and carbon molecular sieve membranes derived from a polyimide of intrinsic microporosity

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ABSTRACT

Natural gas sweetening, one of the most promising venues for the growth of the membrane gas separation industry, is dominated by polymeric materials with relatively low permeabilities and moderate selectivities. One strategy towards improving the gas transport properties of a polymer is enhancement of microporosity either by design of polymers of intrinsic microporosity (PIMs) or by thermal treatment of polymeric precursors. For the first time, the mixed-gas CO_2/CH_4 transport properties are investigated for a complete series of thermally-rearranged (TR) (440 °C) and carbon molecular sieve (CMS) membranes (600, 630 and 800 °C) derived from a polyimide of intrinsic microporosity (PIM-6FDA-OH). The pressure dependence of permeability and selectivity is reported up to 30 bar for 1:1, CO_2:CH_4 mixed-gas feeds at 35 °C. The TR membrane exhibited ~15% higher CO_2/CH_4 selectivity relative to pure-gas feeds due to reductions in mixed-gas CH_4 permeability reaching 27% at 30 bar. This is attributed to increased hindrance of CH_4 transport by co-permeation of CO_2. Interestingly, unusual increases in mixed-gas CH_4 permeabilities relative to pure-gas values were observed for the CMS membranes, resulting in up to 50% losses in mixed-gas selectivity over the applied pressure range.

1. Introduction

Membrane gas separation is an emerging technology demonstrating strong commercial potential in diverse industrial applications including air and hydrogen separations, carbon capture/separation, and natural gas upgrading [1,2]. Today, natural gas is the world's fastest growing primary energy source with a two-fold increase in worldwide production from 1980 to 2010 [3]. Accordingly, membrane-based natural gas processing, particularly sweetening by CO_2 removal, has been among the fastest growing segments of the business [4,5]. This application often involves remote or offshore locations, where minimal operator attention, simple and continuous operation, low weight, and small footprint are significant advantages of membrane technology, besides the potential for energy efficiency [6]. In fact, among the largest industrial gas separation plants is the UGS Castor offshore platform being built by UOP near the coast of Spain to sweeten 980 million scfd of crude natural gas [7].

The state-of-the-art in industrially employed membrane gas separation technology is defined by polymeric materials with moderate selectivities and relatively low permeabilities [1]. Standard modules based on cellulose acetate membranes introduced from the early beginnings in the 1980s are still being used despite many promising materials developments on the laboratory scale [1,4,5]. In 2002, only nine polymeric materials made up 90% of the total membrane gas separation market despite the plethora of novel materials reported with better combinations of permeability and selectivity [1]. The transfer of a novel material from the laboratory scale to industrial use is complicated by several reasons, including (i) formation of defect-free asymmetric or thin-film composite membranes and (ii) unrealistic measurements and evaluations of performance. That is, most gas permeation studies are carried out with pure-gas feeds. Pure-gas testing cannot reveal the detrimental effects of one permeating component on the transport of the other observed in gas mixtures including competitive sorption and plasticization, which can lead to significant reduction in mixed-gas selectivity [8–16]. Besides the widely ranging concentrations of CO_2 in natural gas wells (0–20%), high delivery pressures (40–80 bar) necessary to meet pipeline requirements further challenge a membrane's integration into the process [17,18]. Moreover, the pure-gas permeability/selectivity trade-off performance assessments typically used for novel membrane materials [19] can be misleading when gas mixtures containing highly sorbing feed components are involved.

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One strategy actively pursued to generate gas separation materials with better combination of permeability and selectivity is the introduction of microporosity, entailing pores <20 Å. This can be achieved with solution-processable polymers of intrinsic microporosity (PIMs) [20–31] and also via thermal treatment of polymeric precursors, where the latter can yield more selective materials like carbon molecular sieves (CMS) [32–37] and thermally-rearranged (TR) polymers [38–42]. High-temperature pyrolysis to a CMS membrane generates ultramicroporous (<7 Å) constrictions that approach the molecular dimensions of the diffusing molecules leading to molecular-sieving and, hence, very high selectivity [34,43–45]. Thus, CMS membranes can achieve separation performance far beyond polymeric pure-gas upper-bounds. Until now, most investigations on gas transport in CMS membranes have focused on the effects of the preparation protocol including (i) oxidation conditions, (ii) heating temperature and rate and (iii) sweep gas atmosphere as evaluated by pure-gas measurements [43,44,46,47]. There are very few studies addressing the performance of CMS membranes in high-pressure and mixed-gas CO_2/CH_4 separations where mechanical stability, tolerance to feed impurities, and potentially detrimental non-idealities like plasticization and competitive sorption can compromise the promising results obtained through pure-gas testing [18,48,49]. The few other studies involving mixed-gas studies are typically limited to low feed pressures (<2 bar) or single-point pressure experiments [50–52]. Moreover, no reports are available for the mixed-gas performance of CMS membranes derived from intrinsically microporous precursors.

Thermally-rearranged (TR) polymers are achieved using milder thermal treatment conditions (typically 400–450 °C) that precede formation of the graphitic domains characteristic of CMS membranes. They can offer excellent performance for CO_2/CH_4 separation [38] with the added benefit of better mechanical properties than CMS membranes, which tend to be plagued by brittleness [53,54]. However, the separation performance of TR membranes in various gas separation applications has been predominantly evaluated with pure-gas measurements. To date, only one study thoroughly investigated the mixed-gas performance of a TR polymer with regards to feed composition and pressure, demonstrating very promising behavior for the CO_2/CH_4 gas pair [38]. In addition, as for CMS membranes, no reports have been made regarding mixed-gas CO_2/CH_4 transport of TR polymers derived from intrinsically microporous polyimides.

Recently, detailed pure-gas permeation, sorption, and diffusion data [55] for a series of step-wise, thermally-treated TR and CMS membranes (440, 600, 630 and 800 °C) derived from an intrinsically microporous polyimide (PIM-6FDA-OH) were reported [28]. Here, we provide the first report on mixed-gas CO_2/CH_4 transport properties of TR and CMS membranes derived from a polyimide of intrinsic microporosity. Permeability and selectivity isotherms are presented at 35 °C up to feed pressures of 30 bar to evaluate the transport properties of thermally treated membranes in environments where non-ideal effects like competitive sorption and plasticization normally degrade the performance of polymeric membrane materials.

2. Experimental

2.1. Polymer synthesis

The pristine polyimide PIM-6FDA-OH (Fig. 1) was synthesized according to our previously reported method [28]. In a 50 mL three-neck round bottle flask equipped with a magnetic stirrer, 4,4′-(hexafluoroisopropylidene)-dipthalic anhydride (1.0 mmol) was added in portions to a solution of 3,3,3′,3′-tetramethyl-1,1′-spirobisindane-5,5′-diamino-6,6′-diol (1.0 mmol in 5 mL of absolute NMP). After stirring at room temperature for 4 h, 1.0 mL of pyridine and 4.0 mL of toluene were added, and the mixture was heated to 160 °C under N_2. During the reaction, water was removed with a Dean-Stark trap. By repeated precipitation in methanol/water (1/1, v/v) and then drying under vacuum at 120 °C for 12 h, a light yellow powder (yield 91%) was collected. The number- and weight-average molecular weights were 8.54×10^4 and 1.65×10^5 g/mol, respectively, as determined by gel permeation chromatography (Agilent GPC 1200).

2.2. Polymer film preparation

The polymer was dissolved in a solution of THF (2–3% w/v) and then filtered with 1.0-μm PTFE cartridges. Isotropic films of PIM-6FDA-OH were obtained by slow evaporation of the solvent at 45 °C from a stainless steel ring supported by a leveled glass plate. After 2 days, the dry membranes (80–100 μm) were soaked in a mixture of *n*-hexane/dichloromethane (90/10) for 24 h, air-dried, and then heated at 120 °C for 24 h under high vacuum to remove any THF trapped in the micropores.

2.3. TR and CMS membrane preparation

Dry PIM-6FDA-OH films were cut into pieces 1-in. in diameter, placed into a glass plate and loaded into a Carbolite furnace where they were thoroughly purged under a N_2 flow of 50 mL/min. The heating procedures for the different membrane types are shown in Fig. 2.

For the 440 °C TR membrane, the pristine PIM-6FDA-OH was heated at a rate of 3 °C/min from room temperature to 80 °C and then held isothermally for 1 h to ensure removal of any O_2 in the atmosphere. Thereafter, it was heated to 440 °C at 3 °C/min and kept for 2 h before cooling to room temperature. The thermal rearrangement of the precursor polyimide results in the formation of a spirobisindane-containing polybenzoxazole [55,56], as shown in Fig. 3.

For the CMS membranes pyrolyzed at 600 and 630 °C, the heat treatment started from the 440 °C thermally-treated membrane protocol. The membranes were then further heated at a rate of 3 °C/min to the target temperature, at which a 30 min soak time was allowed before cooling to room temperature. The 800 °C treatment involved heating the pristine polymer membrane at a rate of 3 °C/min from room temperature directly to 800 °C, soaking for 30 min, and then cooling to room temperature. Each procedure

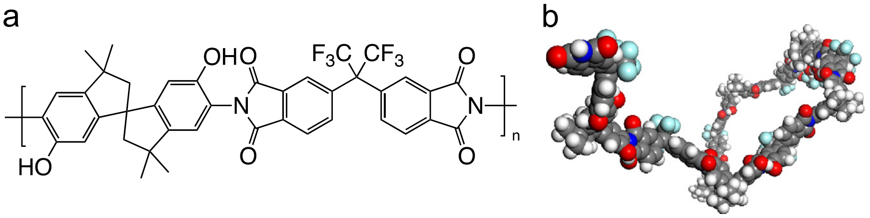

Fig. 1. (a) Structure of PIM-6FDA-OH; (b) energy-minimized structure obtained with Forcite module in Materials Studio 6.0 (Accelrys).