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Modifying the molecular structure and gas separation performance of thermally labile polyimide-based membranes for enhanced natural gas purification

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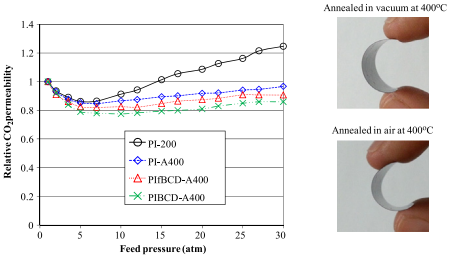
HIGHLIGHTS

- Annealing thermally labile polyimide membranes in air is investigated.
- Cyclodextrin and ferrocene are incorporated.
- Structural changes to the membranes are elucidated.
- More than 55% increment in CO_2/CH_4 selectivity is attained.
- Improved resistance to CO_2 plasticization and good mechanical strength.

GRAPHICAL ABSTRACT



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ABSTRACT

Thermal annealing is one of the feasible approaches to alter the molecular structure and enhance the gas separation performance of polyimide membranes for natural gas purification. In this study, annealing in air and incorporating β-CD and β-CD–ferrocene are employed to change the molecular structure and improve the CO_2/CH_4 gas-pair separation and stability of polyimide membranes. A 55% increment in CO_2/CH_4 selectivity at the expense of permeability are observed for the PI membrane annealed under air at 400 °C compared to the as-cast membrane. A further twofold improvement in the permeability of the β-CD containing membrane annealed under air at 400 °C is achieved. The CO_2/CH_4 selectivity also increases by 20%. With the inclusion of ferrocene, the membrane exhibits a decline in permeability with an improvement of CO_2/CH_4 selectivity to 47.3 when annealed in air at 400 °C. The structural changes are elucidated by characterization techniques (TGA, XPS and gel content). The annealed membranes in air have shown improved resistance to CO_2 plasticization and exhibit good mechanical strength. When subjected to a binary CO_2/CH_4 gas mixture, the gas separation performance remains almost unchanged compared to the pure gas tests. Membranes with high stability under binary gas tests, resistance to CO_2 plasticization and strong mechanical strength are developed.

1. Introduction

Natural gas, a cleaner and more efficient fuel compared to coal and crude oil, is in rising demand in energy sector and also in chemical sector as petrochemical feedstock. Besides constituting methane (CH_4) as the key component, natural gas contains some undesirable impurities like other hydrocarbons, carbon dioxide, water, nitrogen and hydrogen sulfide. Thus, natural gas has to be purified to increase its fuel heating value, reduce transportation costs, pipeline corrosion and atmospheric pollution (Baker and Lokhandwala, 2008; Xiao et al., 2009). One of the separation processes in natural gas purification is the removal of carbon dioxide (CO_2) from natural gas.

Membrane separation offers a promising alternative to conventional separation technologies such as amine absorption for

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CO_2 separation from light gases (He and Hägg, 2012; Peng et al., 2012; Shao et al., 2009). It possesses a higher energy efficiency and smaller footprint. It is easy to scale-up and is environmental friendly. Polymers are a suitable group of materials for fabricating membranes for gas separation due to their low costs and ease of processing into various configurations. A commonly used polymer is aromatic polyimide – a rigid glassy polymer with exceptional high chemical, thermal and mechanical properties and excellent gas separation properties (Ohya et al., 1996). For efficient and effective gas separation, membranes with a high permeability and selectivity are desirable. However, there exist well-known tradeoff curves between permeability and selectivity (Freeman, 1999; Robeson et al., 1994; Robeson, 2008). Besides that, other factors like CO_2-induced plasticization and mechanical strength need to be considered.

The gas transport in polyimide membranes is governed by (1) the penetrate size, (2) polymer chain mobility and (3) size and distribution of free volume (Xiao et al., 2009). The selective permeation of CO_2 over CH_4 for most polyimide membranes is attributed to the smaller kinetic diameter and higher condensability of CO_2. The chain mobility and the free volume of the membranes are affected by the molecular structure and the interactions between polymer chains and gas molecules. Some approaches undertaken to improve polyimide membranes include molecularly tailoring the structure to obtain new materials and modifying existing polyimide materials by heat treatment, grafting side groups on polymer backbone and cross-linking (Xiao et al., 2009). Numerous polyimide structures have been developed in literatures by varying the monomer structures (Álvarez-Gallego et al., 2007; Ayala et al., 2003; Cheng et al., 2003; Coleman and Koros, 1990; Stern et al., 1989; Xiao et al., 2007). Among various polyimides, aromatic polyimides containing 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) are of great interest. The bulky CF_3 group in 6FDA reduces chain packing and also increases chain stiffness due to steric hindrance. As a result, 6FDA-based polyimide membranes display good gas permeability and selectivity.

Thermal annealing is also employed to improve the performance of polyimides. Pyrolysis of polyimides at elevated temperatures (550–900 °C) has been studied to attain carbon molecular sieve membranes with superior permeability and selectivity (Bersema et al., 2004; Hägg et al., 2003; Saufi and Ismail, 2004; Shao et al., 2005; Tin et al., 2006). Despite the outstanding separation performance, the polyimide structure was not sustained. The resultant carbon membranes often show weak mechanical strength and high processing costs that limited their industrial applications. Another recent area of interest is the thermal rearrangement of polyimides to polybenzoxazoles. The single imide bond linkages are thermally rearranged to a stiff and rigid benzoxazole with formation of additional free volume. Higher permeability and selectivity of thermally rearranged polyimides are achieved (Park et al., 2010; Sanders et al., 2012; Wang et al., 2013; Yeong et al., 2012).

A low temperature pyrolysis method involving polyimides containing thermally labile groups has also been developed in various studies (Askari et al., 2012; Chua et al., 2012; Islam et al., 2005; Kratochvil and Koros, 2008; Maya et al., 2010; Qiu et al., 2011; Xiao and Chung, 2011). In a similar manner, microvoids were formed during thermal annealing. The decomposition of thermally labile groups such as sulfonated groups, carboxylic acid groups, cyclodextrin and saccharide units on the side group of the polyimide backbone creates microvoids that result in a higher free volume for gas transport. Hence, enhancements in membrane permeability were achieved. In addition, increases in gas-pair selectivity and CO_2 plasticization resistance due to thermal induced cross-linking were observed in the studies by Chung and his coworkers. The polymer used was a 6FDA-based polyimide containing 3,5-diaminobenzoic acid (DABA), which was cross-linkable upon annealing. By decomposing the grafted thermally labile units, they produced highly permeable membranes with improved selectivity and plasticization resistance. Furthermore, the toughness and flexibility of the membranes were retained after annealing at 425 °C. One of the thermally labile units used is β-cyclodextrin (β-CD). β-CD is an oligomer consisting seven α-D-glucose units bound together in a ring. The geometry of β-CD is of a hollow, toroidal and truncated cone with hydrophilic surface and hydrophobic cavity (Singh et al., 2010). It decomposes to smaller molecules at temperatures from 300 °C to 400 °C. Its unique structure can be altered by forming inclusion with guest molecules, such as metallocene.

Several factors affect the thermal annealing process as well as membrane properties. In our previous studies, an increase in thermal treatment temperature on thermally labile membranes resulted in the enhancement of gas separation performance. Membranes thermally treated from different thermally labile groups such as α, β, γ-cyclodextrin and saccharides also exhibited different resistance against CO_2 induced plasticization. Heat treatment environments also play an important role on separation performance. Meier-Haack et al. showed that the asymmetric polyamide-6 membrane dried in air had a lower flux but a higher water/2-propanol selectivity compared to that dried in vacuum as the removal rate of the entrapped water in the polymer matrix was slower (Meier-Haack et al., 2000). Wang et al. observed interference of oxygen in air to the thermal rearrangement of polyimides (Wang et al., 2013). The O_2 induced degradation led to structural changes of polybenzoxazole that resulted in enhancements in both gas permeability and selectivity at the expense of mechanical properties. Chen et al. found that the presence of trace oxidizer in the purge gas and varying the soaking time had a negligible effect on the thermal cross-linking of 6FDA-based polyimide hollow fibers consisting of carboxylic acid (Chen et al., 2013). On the other hand, cross-linking under open air conditions resulted in decrease in both permeance and selectivity. Densification of the skin and transition layer was observed.

From the above-mentioned studies, it would be interesting to study the change in molecular structure and gas separation performance of thermally labile polyimides annealed in air. β-CD and β-CD with a guest molecule will also be incorporated. Ferrocene, one type of metallocene, is chosen as the guest molecule in this study. It consists of two cyclopentadienyl rings bound on opposite sides of a central iron atom and is available commercially at a reasonable cost. Fig. 1 shows the proposed evolution of structural changes of the thermally labile polyimide in this study before and after annealed in air. The 6FDA-polyimide containing 3,5-diaminobenzoic acid (DABA) will be synthesized and then grafted with β-CD and β-CD–ferrocene (fBCD). Membranes will be fabricated and annealed under air environment. Material characterizations will be performed and gas separation performance of the membranes will be tested.

2. Experimental

2.1. Materials

The monomers for synthesizing the polyimide used in this study were 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,3,5,6-tetramethyl-1,4-phenylenediamine (durene diamine) and 3,5-diaminobenzoic acid (DABA). 6FDA (99% purity) and DABA (99% purity) were purchased from Clariant and Merck respectively and further purified via vacuum sublimation before use. Durene diamine (99% purity) was purchased from Sigma-Aldrich and purified by recrystallization from methanol. The