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Preparation and characterization of carbon and carbon/zeolite membranes from ODPA–ODA type polyetherimide

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ABSTRACT

A novel precursor, 3,3′,4,4′-oxydiphthalic dianhydride-4,4′-oxydianiline (ODPA–ODA) type polyetherimide (PEI), was synthesized and used to prepare carbon membranes by preoxidation and heat treatment. The thermal stability of the ODPA–ODA type PEI was evaluated by thermogravimetric analysis. The surface properties, elemental composition, microstructure, morphology and gas separation performance of the as-made carbon membranes were examined by the Fourier transform infrared spectroscopy, elemental analysis, X-ray diffraction, scanning electron microscopy and gas permeation techniques. The effects of the preoxidation temperature and zeolite incorporation on the microstructure and gas separation performance of carbon membranes were investigated. The results have shown that ODPA–ODA type PEI is a good precursor for producing carbon membranes. The preoxidation of the ODPA–ODA type PEI is essential to make defect-free carbon membranes, which also helps to improve the thermal stability and porosity during pyrolysis by forming crosslinking structure in precursor. The carbon membranes made after preoxidation at 480 °C and heat treatment at 650 °C have an oxygen permeability of 131.5 Barrer and an ideal O_2/N_2 selectivity of 9.7. The incorporation of ZSM-5 into the carbon membranes further helps to improve the separation performance of the carbon/zeolite membranes for H_2/N_2 gas mixture.

1. Introduction

Carbon molecular sieve membranes (CMSMs, or carbon membranes for short), a kind of porous inorganic membrane material with tuned pore structures, have drawn much attention since 1980s simply because they can efficiently separate gas mixtures via the molecular sieving mechanism [1]. The CMSMs have many unique properties such as chemical and thermal stability, and are of great potential in a variety of gas separation applications including the enrichment of nitrogen or oxygen from air, the separation of hydrogen from gasification gas, the purification of natural gas, the recovery of hydrogen from hydrocarbons, the separation of light alkenes/alkanes, the removal of organic vapor or sour gas from mixture, *etc.* [2]. Nevertheless, up to now, few CMSMs are available commercially though the Blue Membranes GmbH in Germany is producing plate-type CMSMs and the Carbon Membranes Ltd. in Israel is offering hollow fiber CMSMs on a pilot scale. The high production cost of the CMSMs is one of the key issues that has hindered their commercialization, and this is especially the case in comparison to the conventional polymeric membranes [3,4]. In general, the CMSMs can be made by the pyrolysis of polymeric membranes, and in this regard, considerable efforts have been made in terms of developing cheap precursors or optimizing preparation procedure with an aim of reducing the production cost of the CMSMs [2,5]. The precursor of the CMSMs plays a key role of governing both the production cost and the structure and gas separation performance of the CMSMs to a great degree [6]. Among the new precursors developed recently, the polyetherimide (PEI), a series of derivatives of polyimide with flexible C–O bonds in the molecular backbones, has attracted more attention. The PEI has aromatic imide units that result in stiffness and heat resistance, and the swivel groups such as –O– that function as flexible chains and result in good processability. These features endow the PEI with many advantages over the traditional polyimides, including good solubility and thermoplastics, low cost and easy processability. These make the PEI hold promise as a precursor for carbon membranes [6]. There are some reports about the preparation of

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PEI-based carbon membranes. Fuertes and Centeno [7] prepared plate-like CMSMs from the PEI by pyrolysis at 800 °C, showing a selectivity for gas pairs O_2/N_2 of 7.4, He/N_2 of 121, CO_2/CH_4 of 25 and CO_2/N_2 of 15. Sedigh et al. [8] made tubular CMSMs from 1,4-bis (3,4-dicarboxyphenoxy)-benzene dianhydride type PEI by pyrolysis at 600 °C, showing a separation factor of 145 for CO_2/CH_4 and 155 for H_2/CH_4. They also fabricated Ultem 1000 type CMSMs from the PEI, showing a CO_2/CH_4 permselectivity of 12.5 [9]. Favvas et al. [10] obtained hollow fiber CMSMs from a blend of 3,3′4,4′-benzophenone tetracarboxylic dianhydride, 80% methylphenylene-diamine and 20% methylene diamine co-polyetherimide (P84) by pyrolysis at 900 °C, showing a separation factor of 843 for H_2/CH_4 at 100 °C. Nevertheless, the CMSMs mentioned above are not defect-free, and cannot meet the requirements for the separation of permanent gas mixtures, which may be due to the thermoplastic property of the PEI that undergoes a melting stage in the heat treatment step. It has been partly demonstrated that the cross-linking structure formed in a temperature range between the glass transition temperature (T_g) and degradation temperature (T_d) of the PEI helps to eliminate the melting stage, and to improve the separation performance of the final CMSMs [11,12]. The crosslinking of the thermoplastic polymeric PEI has resulted in the formation of oxygen bridges between the aromatic molecules, which helps to tune the growth of aromatic crystallites during the pyrolysis step by forming amorphous carbon structures. As such, the CMSMs with a tuned pore structure can be fabricated [13]. Hosseini and Chung [14] and Salleh and Ismail [15,16] have made PEI-based CMSMs by making use of p-xylene diamine as cross-linker and by air preoxidation before the pyrolysis step. Wey et al. [17] have made composite membranes by coating the crosslinked PEI on Al_2O_3 support at 240 °C for 6 h.

Herein, we report on the synthesis of a novel precursor, 3,3′, 4,4′-oxydiphthalic dianhydride-4,4′-oxydianiline (ODPA–ODA) type PEI, for the preparation of CMSMs. Fig. 1 shows the chemical structure and the schematic stereo-structure of the repeated basic unit in ODPA–ODA PEI molecules. Compared with the traditional PEI molecules, the ODPA–ODA PEI has a simple molecular structure, in which the flexible oxygen bridging units between the diphenyl linkages have changed the rigidity of the chain segments resulted from the bulky groups. This chemical structure helps to prevent the tight packing of the polymeric chains, and finally result in membrane materials with improved gas permeation properties [18,19]. Because of this unique chemical structure, the ODPA–ODA PEI has been tested for making separation membranes, and the insulator of microelectronic devices [20–23]. However, to our best knowledge, little has been done on the production of CMSMs from the ODPA–ODA PEI. In the present work, the ODPA–ODA PEI was used to make high performance CMSMs for gas separation. The variation of the structure and property of the PEI precursor and the as-made CMSMs have been investigated in terms of the influence of the preoxidation and pyrolysis conditions. Our previous work has demonstrated that the gas separation performance of the CMSMs can be efficiently tailored, to some degree, by incorporating porous inorganic additives such as zeolites into the membrane matrix [24,25]. With this in mind, here we also studied the influence of the added ZSM-5 on the separation performance of the carbon/zeolite membranes.

2. Experimental

2.1. Preparation of carbon membranes

A poly(amic acid) (PAA) solution of ODPA–ODA type PEI was first synthesized by a typical condensation polymerization reaction of two monomers, 3,3′,4, 4′-oxydiphthalic dianhydride and 4, 4′-oxydianiline in N-methyl-2-pyrrolidone (NMP). Before polymerization, the commercial monomers, ODPA and ODA, were purified by recrystallization in acetic anhydride and tetrahydrofuran, respectively. Then, they were dried at 140 °C under vacuum. The NMP was distilled over CaH_2 before use. The polymerization reaction was conducted at room temperature with an equimolar amount of ODPA and ODA in an appropriate amount of NMP under constant stirring and in flowing N_2 for 6 h. Finally, a transparent homogeneous PAA solution was obtained with a solid content of *ca.* 15 wt%.

Free-standing polymeric membranes were fabricated by a casting method in a dust-free environment. First, the pre-polymer PAA solution was directly casted onto clean glass plates to make polymeric membranes, which were dried at 40, 60, 100 and 200 °C for 24 h, in order to completely remove the remaining solvent and to make stable imidization moieties with tuned molecular structure. The as-made PEI membranes were cut into coin-like sheets with a diameter of *ca.* 3.2 cm before the subsequent heat treatment. In order to avoid or eliminate the melting stage in the pyrolysis step, the PEI membranes were preoxidized in air at a rate of 2 °C/min from room temperature to a pre-set temperature for 30 min. Then, the preoxidized membranes were heated in a horizontal tubular furnace, first at a heating rate of 2 °C/min from room temperature to 200 °C for 30 min, then to 300 °C for 30 min, and 400 °C for 30 min, and during this period, the imidization of molecules was fully completed. Then, the membranes were further

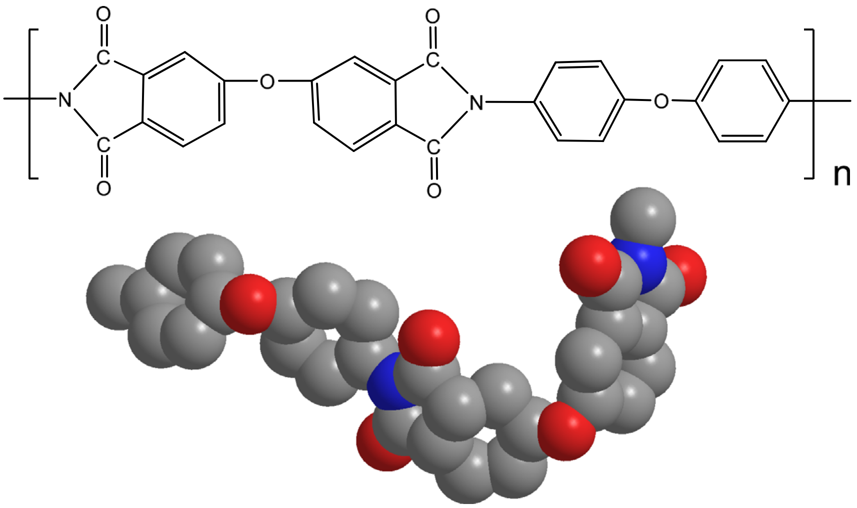

Fig. 1. Chemical structure of repeated unit in ODPA–ODA type Polyetherimide.