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Development and characterization of disk supported carbon membrane prepared by one-step coating-carbonization cycle

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ABSTRACT

Different dope solutions for the alumina disk supported carbon membrane preparation for CO_2/N_2 and CO_2/CH_4 separation was formulated in this study. The prepared polymeric membrane made of commercial co-polyimide BTDA-TDI/MDI (P84) was carbonized at 700 °C under N_2 gas flow. A defect-free membrane was obtained when high polymer composition was used. The disk supported carbon membrane with CO_2/N_2 and CO_2/CH_4 selectivity of 15 and 45, respectively, and CO_2 permeance of 400 Barrer were obtained by one-step spray coating technique. The polymer composition of 12 wt% was concluded to be the optimum composition for the alumina disk supported carbon membranes.

Introduction

The factor of impurity composition of acidic gas in natural gas as well as low quality gas up to 80% makes the natural gas purification crucial [1]. This situation had prompted researchers to study and enhance the performance of the available technologies towards gas separation application [2]. Gas separation membranes have been used in various applications, such as oxygen or nitrogen enrichment, hydrogen recovery, acid gas treatment, and natural gas dehydration [3–5]. Polymeric membranes have emerged as a potentially superior membrane for gas separation. However, it needs to be improved as it has limitations in its performance, such as poor thermal and chemical resistance [6,7]. Polymeric membrane that employs solution diffusion as its separation mechanism is not an effective mechanism to apply for gas separation. Carbon membrane is one of the promising membrane materials that proved to give high gas separation performance and can overcome the disadvantages of polymeric membranes [8]. There are four different types of separation mechanism such as Knudsen diffusion (>10 Å), surface diffusion (<50 Å), capillary condensation (>30 Å), and molecular sieving (<6 Å) [6]. Carbon membrane is fabricated by carbonizing polymeric membrane at high temperature (600–1000 °C) where most of the heteroatoms that present in the polymeric membrane will be released and replaced by carbon in the backbone of its molecular structure [9].

During the carbonization process, there is a possibility where the polymer precursor will melt due to the high temperature applied. To prevent this problem, thermosetting polymer is the best candidate to overcome this matter. The chosen polymer precursor must meet a number of criteria, such as high aromatic carbon content, high glass transition temperature (T_g), excellent thermal resistance, mechanical stability, and chemical stability, and provides high separation properties [10]. Polyimide has high possibility to fulfil those requirements and it has various classes which is determined by their different dianhydrides, which are pyromelliticdianhydride group (PMDA) such as Kapton [9], benzophenonetetracarboxylicdianhydride (BTDA) such as Matrimid and P84 [9–11], 3,30,4,40-biphenyltetracarboxylic dianhydride (BPDA) such as UIPR and UIP-S [11], and hexafluoroisopropylidene (6FDA) such as pyralin [12]. Among these classes, P84 that has superior gas separation performance [13–16] was chosen as the polymer precursor for this study. P84 is generally made by the polycondensation of aromatic acid dianhydrides and diamines. It was reported that its performance was influenced by the chemical structure of the constituent monomers as shown in Fig. 1. P84 co-polyimide (BTDA-TDI/MDI, co-polyimide of 3,3′,4,4′,-benzophenone tetracarboxylic dianhydride and 80% methyl phenylene- diamine + 20% methylene diamine) exhibits an excellent chemical and thermal resistance. This polymer is not only suitable for gas separation but also excellent in ultrafiltration and nanofiltration [10,17].

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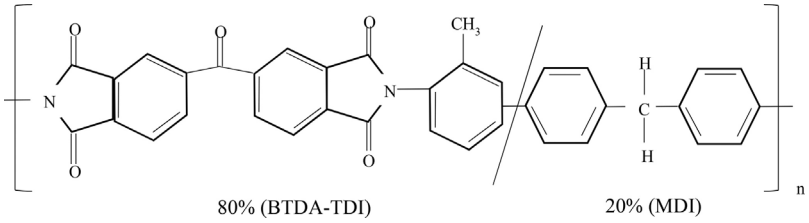

Fig. 1. Chemical structure of P84 (BTDA-TDI/MDI).

In this study, supported carbon membrane was prepared by introducing porous disk alumina as a support material to overcome the brittleness of the carbon membrane. Obtaining a defect-free thin layer film of carbon membrane is crucial as several parameters need to be considered, such as composition of the polymer precursor, coating method, and parameters during the heat treatment process, which includes temperature, heating rate, gas flow rate, environment gas, and soaking time [16]. Spin, spray, slip, and dip coating are the common methods applied to fabricate the supported carbon membrane. Past studies would suggested to implement several time of coating-carbonization cycle in order to obtain a defect-free carbon membrane layer that reflect in the gas separation performance [18,19]. However, these repeating methods are time and cost consuming. The one-step spray coating technique was proposed in this study by investigating the effect of polymer composition on gas permeation performance. The polymer precursor was distributed uniformly on the porous alumina support material. Until now, there are no studies reported on supported carbon membrane derived from P84 via spray coating technique. In 1999, Archarya and Foley applied spray coating method to form a fine mist of PFA on the porous support using airbrush that took less than 15 s to complete for one sample [20]. Most of the previous literatures were reported on dip and spin coating techniques, and recently, slip coating technique with several time of coating-carbonization cycles was also reported to reduce defect on the supported carbon membrane [9].

Air spray method can produce ultra-thin selective layer which can provide high selectivity without deteriorating the gas permeability [21]. The distribution of the polymer solution on the support is significantly affected by the polymer solution composition. Generally, dilute solution (2–5 wt% of polymer) is used when applying spray coating method to form uniform and thin layer. Furthermore, it is convinced that the spray coating method has a high potential for reproducibility of the thin and uniform carbon membrane layer [22]. Thus, the objective of this research was to investigate the effect of polymer compositions on the gas separation performance of the supported carbon membrane. The membrane was characterized by means of TGA, FTIR, BET, XRD, SEM images, and single gas permeation measurement.

Experimental

Materials

Commercial co-polyimide BTDA-TDI/MDI (P84) powder purchased from Sigma–Aldrich (CAS#: 58698-66-1) was used as polymer precursor. *N*-Methyl-2-pyrrolidone (NMP) procured from Merck (Germany) was chosen as the solvent. Commercial symmetric porous alumina disk was utilized as supporting material with diameter of 47.0 mm, thickness of 1.0 ± 0.05 mm, and mean pore size of 0.14 μm was bought from Shanghai Gongtao Ceramics Co., Ltd.

Carbon membrane preparation

P84 polyimide powder was dried in an oven at 60 °C for one day to remove water vapour. The polymeric solution was prepared by dissolving four different compositions of P84 at 6, 9, 12, and 15 wt% in NMP. The polymeric solution was stirred and heated at 70 °C until homogenous solution was formed. It was sonicated for 3–4 h to eliminate bubble formed during stirring process. The supporting material was polished using fine silicon carbide (SiC) paper of grit P2000 before dry it in an oven for 3 h prior coating process. Porous alumina was coated by homogeneous solution via spray coating method at 1 bar at room temperature. The dope solution was sprayed directly towards the supporting material using air spray with distance of the spray nozzle and the alumina support at 20 cm. The coated alumina support was dried in an oven at 60 °C overnight. The coated porous alumina disk with polymer precursor membrane was placed in the centre of the Carbolite horizontal tubular furnace for heat treatment process. It was carbonized at 700 °C with heating rate of 3 °C/min under nitrogen, then it was left to cool down to room temperature. This process took almost 4 h to achieve the final carbonization temperature and another 4 h to reach room temperature after the carbonization process. The nomenclature of the resultant disk supported carbon membranes was given in the form of P-polymer composition for polymeric membrane (P-6, P-9, P-12, P-15) and CM-polymer composition for carbon membrane (CM-6, CM-9, CM-12, CM-15).

Membrane characterization

Thermal behaviour of the membrane was obtained from thermogravimetric analysis (TGA 2050), carried out at temperatures between 50 °C and 1000 °C at a rate of 10 °C/min under nitrogen gas at 50 ml/min. Elemental analysis was carried out using elemental analyzer model Vario Micro Cube indicate the percentage of the present elements in the membrane sample. While the functional groups that influence the gas performance were evaluated via Fourier transform infrared spectroscopy (FTIR), using single reflection diamond for Spectrum Two spectrometer (PerkinElmer, L1600107). The X'Pert PRO X-ray different diffractometer (XRD) from PANalytical with the 2θ diffraction angle of 10–90° was performed using Cu Kα radiation of 1.54 Å wavelength. Bragg's Law ($n\lambda = 2d \sin \theta$) was adapted to determine inter planar distance (*d*-spacing) between the individual layers of the carbon. Brunauer–Emmett–Teller (BET) were obtained by utilizing equipment model Micromeritics 3 Flex Surface Characterization Analyzer. This nitrogen (N_2) adsorption method was applied to obtain surface area and pore volume of porous materials from polymeric and carbon membrane. Surface and cross sectional morphologies of the carbon membrane was observed by scanning electron microscopy (SEM) model EOL JSM-5610LV. The prepared samples were coated with gold by sputter coating under vacuum to create neutral charge during SEM characterization. The viscosity of the polymeric solution was measured using a viscometer (Brookfield).