Carbon 113 (2017) 10–17

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Adjustable microstructure carbon molecular sieve membranes derived from thermally stable polyetherimide/polyimide blends for gas separation

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ARTICLE INFO

Article history:
Received 2 September 2016
Received in revised form
4 November 2016
Accepted 11 November 2016
Available online 14 November 2016

ABSTRACT

Carbon molecular sieve (CMS) membranes were prepared by controlled pyrolysis of polyetherimide (PEI) blended with polyimide (PI). The microstructure and gas separation properties of the precursor membranes and supported CMS membranes were characterized in terms of the different weight ratios of PI to PEI. The thermogravimetric analysis indicated that the co-pyrolysis in the PEI/PI appeared above 450 °C. Both permeability and selectivity of supported CMS membranes increased with increasing PI content in the precursors. The positron annihilation lifetime (PAL) results showed that the free volume size and the pore size were enhanced as the PI content is increased and that there is a close relationship between the microstructures of polymer blend precursors and CMS membranes. These results confirmed that the microstructure and gas separation performance of CMS membranes can be adjusted by blending two thermally stable polymers. For CMS membrane derived from a precursor containing 75 wt% PI and pyrolyzed at 700 °C, the gas permeance for CO_2 was 40 GPU and CO_2/N_2 selectivity was 39.

1. Introduction

Carbon dioxide produced as a result of fossil fuel combustion is a primary cause of human-induced climate change. In mitigating this global climate change, flue gas carbon dioxide capture and storage (CCS) is expected to play a key role [1,2]. Recently, developments in CCS include membrane separation, because membrane technology only requires lower energy consumption [3–5]. In addition, high-temperature CO_2 perm-selective membranes can be applied to pre- and post-combustion processes for CO_2 capture. Another application of membrane technology is O_2 enrichment of combustion air in industrial burning. Oxygen enrichment to achieve better fuel economy is one the most common and readily adaptable methods of saving fuel in industrial burning processes, along with partial substitution of a valuable fuel by a less valuable one [6]. The concept of oxygen enriched combustion, by the removal of nitrogen in air, has undergone theoretical and experimental investigations by several researchers and patents [7–10]. Since the presence of nitrogen in air can lead to incomplete combustion and increased energy losses, reducing its amount in the reactant mixture is an important topic of scientific researches and applications. Membranes can effectively separate nitrogen from air with a power draw that is reasonable for burner-based power generation applications. Therefore, it is imperative to develop high-performing gas separation membranes for both CO_2 capture and oxygen enriched combustion.

Carbon molecular sieve (CMS) membranes have received considerable attention for their high thermal and chemical stability and excellent gas separation performance that could be beyond the upper bound of the trade-off relationship between permeability and selectivity, in the case of polymeric membranes [11–14]. CMS membranes are very suitable for separating gas components with similar molecular sizes such as CO_2/N_2 and O_2/N_2 [15–17]. In addition, the gas separation performance of CMS membranes is not very much affected by the feed pressure [18,19]. However, CMS membranes are also characterized with their brittleness. To improve the mechanical strength while maintaining high

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http://dx.doi.org/10.1016/j.carbon.2016.11.026

selectivity, supported CMS membranes are one of the favored choices, since these can be fabricated by forming thin molecular sieving carbon layer on top of the support substrate.

CMS membranes are derived from the pyrolysis of polymeric precursors. As a result of the carbonization, CMS membranes become highly aromatic structures comprised of disordered sp^2 hybridized carbon sheets. A combination of ultramicropores and micropores is believed to provide the molecular sieving function and high permeability of CMS membranes [20]. So far, much of researches focus on identifying appropriate polymer precursors and pyrolysis conditions to attain optimum pore structure of CMS membranes [21–24]. The pore size and their distribution in CMS membranes are not only dependent on pyrolysis conditions, but also are greatly affected by its polymer precursor. The microstructure of precursor plays a key role in determining the performance of the resultant CMS membranes. Park et al. showed that an increase in fractional free volume increased the permeability coefficients of polyimides and their CMS membranes [22].

In literature, various polymers such as phenol formaldehyde (PF) [25], poly(furfuryl alcohol) (PFA) [26], cellulose [27], poly(phenylene oxide) (PPO) [28], and polyimide and derivatives [29,30] have been tested as homopolymer precursors for CMS membranes. To improve the permeation flux of CMS membranes from homopolymer, some researchers studied the gas separation behaviors of CMS membranes made from polymer blends, which consist of thermally stable and thermally labile polymers [31–35]. The pore structure of such CMS membranes combined two kinds of pores, which were derived from the pyrolysis of two different polymers: thermally stable polymer leads to micropores; thermally labile polymer creates mesopores. Mesoporous carbon membranes are not ideal for the separation of smaller gas molecules. In the present work, polyetherimide/polyimide (PEI/PI) blends were prepared to adjust the microstructure of CMS membranes. The decomposition of blends of two thermally stable polymers is quite different than that containing thermally labile component. The aim of this study is to prepare adjustable microporous CMS membranes using polymer blends containing both thermally stable polymers and to investigate the effects of pore constructing materials on the microstructure and gas separation properties. This study just changed the composition of PEI/PI blends but fixed the carbonization temperature for clearly survey the effect of precursor compositions.

2. Experimental

2.1. Materials and membrane preparation

Polyimide (PI, Matrimid®) was obtained from Aldrich Co., Polyetherimide (PEI, Ultem® 1010) was purchased from Alfa Aesar Co., *N*-Methyl pyrrolidone (NMP), employed as the solvent to prepare the polymer solution, was supplied by Tedia and used as received (reagent grade). Ceramic substrate, porous α-alumina disk with a diameter of 30 mm, an average pore size of 100 nm, and total thickness of 1 mm, was purchased from Fraunhofer Institute for Ceramic Technologies and Systems. CO_2, O_2, and N_2 of 99.95%, 99.60%, and 99.95% purity, respectively, were supplied by Ming-Yang Co., Taiwan.

The polymer blend solution of PEI/PI was prepared by adding PI and PEI to NMP to form a 12 wt% solution. The weight fractions of PI were controlled to 0.00, 0.25, 0.50, 0.75, and 1.00. The polymer blend solution was casted on a glass plate at a thickness of 300 μm and then dried at 80 °C for 24 h to get free-standing membranes. The primitive membranes were further dried under vacuum at 200 °C for another 24 h to remove trace residual solvent. On the other hand, the supported PEI/PI precursor with similar coating layer thickness was prepared by spin coating the NMP solution containing 15–17 wt% polymers on ceramic substrate surface. Polymer solutions with similar viscosity use to control the thickness of membranes. We varied the polymer concentration of polymer solutions to control the different solutions with similar viscosity. The viscosity of all solutions keeps about 1000 cP. The spin-coating rate on the porous α-alumina disk ceramic substrate was kept at 3000 rpm. The composite membrane was evaporated in an oven at 70 °C for 20 min to remove the solvent, then heated at 100 °C vacuum oven for 8 h to further remove residual solvent. The compositions of supported PEI/PI precursors were summarized in Table 1.

Carbonization of the supported precursor was done in a quartz tube set of a three-zone horizontal furnace (Thermo Fisher Scientific) to prepare supported CMS membranes. The supported precursor was placed at the central zone of the furnace where the temperature profile was uniform. Then, the system was evacuated overnight with an Edwards RV12 rotary pump to a pressure below 5×10^{-2} torr. The pyrolysis procedure for the supported precursors was divided into three parts. First, the temperature was raised from ambient to 100 °C at a rate of 10 °C/min and then maintained at 100 °C for 10 min. Second, the temperature was increased from 100 °C to 300 °C at a rate of 5 °C/min and then maintained at 300 °C for 1 h. Third, the carbonization temperature was set to 700 °C and kept at that temperature for 2 h. The heating rate of the third stage was kept low at 1 °C/min to avoid uncontrolled shrinkage of the membrane. Then, to avoid aging effects induced by oxygen chemisorption, supported CMS membranes were kept in a vacuum desiccator and characterized immediately. The notations of supported CMS membranes were shown in Table 1.

2.2. Characterization

The morphologies of CMS membranes were examined using scanning electron microscope (Hitachi Co., FE-SEM Model S-4800). Attenuated total reflectance-Fourier transform infrared (ATR-FT-IR) (Perkin-Elmer Spectrum One) spectroscopy was operated in the wavenumber range of 4000–650 cm^{-1} to qualitatively evaluate the degree of carbonization of precursors. Dynamic mechanical analysis, using Perkin-Elmer DMA-7e, was applied to determine the glass transition temperature of precursor membranes. Under a helium atmosphere, the samples were tested from −10 to 350 °C at a heating rate of 5 °C/min. A 2 × 0.5 cm membrane sample was tested under the dynamic testing mode with a dynamic force of 100 mN at frequency of 1 Hz. Thermogravimetric analysis (Perkin-Elmer TGA-7) was done at temperatures of 50–800 °C at a rate of 5 °C/min in helium atmosphere.

Free volume in polymers and cavity in inorganic materials can be calculated from the lifetime data obtained with positron annihilation lifetime spectroscopy (PALS) [36–39]. For precursor membranes, PALS was carried out with the use of a conventional fast-fast coincidence spectroscope with a time resolution of 260 ps The positron source ^{22}Na (10–20 μCi) was sandwiched between two Kapton foils (6-μm thick). Two million counts were collected with each PALS spectrum. On the other hand, for the supported CMS membrane, a variable monoenergy slow positron beam

Table 1
Notation of PEI/PI precursors and resulting supported CMS membranes.

Precursor	PI fraction	Pyrolysis temperature (°C)	CMS membrane
PI-000	0	700	CMS-000
PI-025	0.25	700	CMS-025
PI-050	0.50	700	CMS-050
PI-075	0.75	700	CMS-075
PI-100	1.00	700	CMS-100