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Gas permeation properties of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) derived carbon membranes prepared on a tubular ceramic support

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Abstract

The carbon membranes were prepared by the pyrolyisis of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) polymer coated on the surface of the macroporous alumina tubular ceramic support. The permeation results showed that gas transport through the PPO derived carbon membranes was controlled by the molecular sieving effect. The influence of the pyrolysis temperature on the permeation performances indicates that the pore structure developed at a low temperature and then the pore characteristic values (pore volume, surface area, etc.) were increased with increasing pyrolysis temperatures, and decreased at further temperature. The correlation of the permeability versus the permselectivity for the PPO derived carbon membranes showed higher values than the upper bounds for polymeric membranes, and excellent performance comparable to polyimides derived carbon membranes.

Keywords: Carbon membrane; PPO; Gas permeation; Permeability; Pyrolysis

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1. Introduction

Interests on inorganic membranes have been increased for the potentials in gas separation technology due to good thermal and chemical stabilities [1,2]. Attractive opportunities for gas separation are found in the various application areas, such as natural gas processing, landfill gas recovery, olefin/paraffin separation, air separation and hydrogen recovery [3]. Gas transport mechanisms are primarily varied with pore size distribution and to some extent with chemical interaction between diffusing gas species and membrane materials [4–6]. In general, the transport mechanisms through inorganic membranes can be divided into the following four mechanisms, that is, the Knudsen diffusion, the molecular sieving, the surface diffusion, and the capillary condensation mechanism. When pore dimensions approach those of the diffusing gas species, gas separation can occur by the molecular sieving mechanism. Nearly infinite separation factors are theoretically attainable in the mechanism, even though the values of gas permeance are low compared with the other mechanisms.

Of inorganic membranes, carbon molecular sieving (CMS) membrane is considered to be one of the promising materials for membrane-based gas separation because of their excellent permeation and separation properties and thermal and chemical stability even under harsh conditions, such as high pressure and high temperature [7–9]. The preparation of carbon membranes having high permeation performances involves the following several steps: polymer precursor selection, polymeric membrane preparation, pretreatment, pyrolysis/carbonization, post-treatment, and module construction [9]. It is generally known that the gas permeation properties of CMS membranes are mainly affected by the polymeric precursor, pyrolysis method, and post-treatment conditions [10,11].

Among polymeric precursors, poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) having a high glass transition temperature is considered as one of the alternative promising polymeric materials for carbon membrane preparation [12–14]. PPO polymer membranes have a somewhat high gas permeability among aromatic polymeric membranes since the presence of ether linkages and the absence of polar groups inhibit chain packing and densification [15,16]. Furthermore, the methyl groups attached on both sides of phenyl ring hinder the free rotation of the phenyl ring, resulting in moderate selectivity of PPO membranes [17]. The correlation of the

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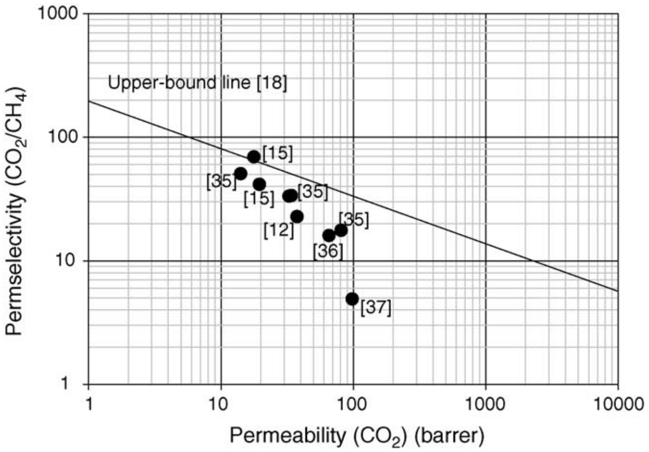

Fig. 1. Correlation of the permeability vs. the permselectivity of CO_2 in the PPO polymer membranes [12,15,18,35–37].

permeability and the permselectivity for PPO polymer membranes approaches the Robeson line, the upper bound line for polymer membranes [18]. As shown in Fig. 1, the permeability of CO_2 for PPO polymer membranes exists between 14 and 100 barrers (1 barrer = 10^{-10} cm^3 (STP) cm/cm^2 s cmHg) and the permselectivity of CO_2/CH_4 between 16 and 70. The permeation performance is somewhat lower than other promising polymers (e.g. polyimides) even though the permeation results of PPO polymer membranes showed the closeness to the upper bound line in the selectivity and the permeabililty. In the previous studies, the sulfonated PPO and metal substituted sulfonated PPO were prepared as a form of composite ceramic membranes in order to improve the permselective property of PPO polymer [12,13]. Still, the permeation performance of the PPO polymer membranes was affected by the chemical and thermal instability, showing the trade-off of the permeability and the permselectivity. Therefore, it is necessary to prepare carbon membranes which are more chemically and thermally stable than polymer membranes for the gas separation applications.

As far as we know, the preparation of PPO derived carbon membrane and the permeation results have been rarely reported [19–21]. In this study, the carbon membranes derived from PPO polymer were prepared by the consecutive steps, such as polymeric membrane preparation on the alumina support, pretreatment, and pyrolysis. The influences of the preparation conditions (PPO polymer concentration and pyrolysis temperature) on the permeation performances were investigated for the PPO derived carbon membranes. And, pore properties were characterized in order to investigate the influence of different pyrolysis temperature on the pore structures.

2. Experimental

The polymeric membranes were prepared on the surface of a tubular macroporous ceramic support (NOK, Japan) having the average pore size of 100 nm and the porosity of 41.0%. Concentrations of the PPO polymer (#18,178-1, Aldrich, USA) in $CHCl_3$ (Wako, Japan) were increased between 1 and 7 wt.%. The carbon membranes were prepared by the preoxidation of the dip-coated PPO polymer on the alumina ceramic support in the stagnant air condition, followed by the pyrolysis. The carbonization was performed by heating up to the maximum pyrolysis temperatures and cooling (rate of heating and cooling: 5 K/min) in the Ar atmosphere (flow rate: 200 ml/min). The maximum pyrolysis temperatures were changed between 773 and 1073 K and the duration time of each temperature was set to 1 h. The preparation steps (dip-coating of polymer film, preoxidation and pyrolysis) were repeated twice for making carbon membranes without defects.

The surface morphology and cross-section of the carbon membrane were examined using a scanning electron microscope (SEM), S-900 (Hitachi, Japan). Weight change during heat treatment of PPO polymer was evaluated under the Ar atmosphere (heating rate: 5 K/min and flow rate: 200 ml/min) by means of a thermogravimetric analyzer (TG-DTA2000SA, Bruker AXS). The pore properties of pyrolyzed carbon materials were characterized by the nitrogen adsorption at 77 K using an automatic adsorption apparatus (BELSORP-18, BEL Japan, Inc.) after the pyrolyzed carbon materials were pretreated at 573 K during 5 h in the vacuum condition. Also, the adsorption amount of CO_2 was measured for the pyrolyzed carbon materials at 298 K.

Gas permeances of selected gas species, He (0.26 nm), CO_2 (0.33 nm), N_2 (0.364 nm) and CH_4 (0.38 nm), were measured using a permeation apparatus having a film flow meter (STEC, Japan) at the permeation temperature range between 308 and 423 K. The influences of the PPO concentration and the pyrolysis temperatures on the gas permeation performances were investigated. And the permselectivity in the gas permeation experiments was estimated as the ratio of the permeance of each gas species.

3. Results and discussion

3.1. Characterization of the PPO derived carbon materials and membranes

The thermal stability of the preoxidized PPO polymer was observed during the carbonization and Fig. 2 shows the weight loss of the polymeric precursor with increasing temperature. Total weight loss was measured to 70% during the heat treatment, which is considered to be a somewhat higher value compared with the results for different polymeric precursors. In the previous results, the weight loss of the polyimide was reported to be 40% [3] and the phenolic resin 35% [22]. It is assumed that the methyl groups attached on both sides of phenyl ring were mostly degraded during heating in the Ar condition. The thermal gravimetric plot shows that the polymer structure started to degrade and develop the carbonized structure at around 673 K [12]. The thickness of the PPO derived carbon layer on the macroporous α-alumina ceramic support was measured as 3.1 ± 0.2 μm with the SEM analysis of the carbon membrane pyrolyzed at 973 K (Fig. 3). Also, it was shown in the figure that the PPO carbon layer has a dense film structure on the surface of the macroporous alumina ceramic support.