



Alcohol dehydration by pervaporation using a carbon hollow fiber membrane derived from sulfonated poly(phenylene oxide)

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ABSTRACT

The performance of carbon hollow fiber membranes derived from sulfonated poly(phenylene oxide) (SPPO) was investigated with respect to the dehydration of aqueous alcohol solutions. SPPO carbon hollow fiber membranes were prepared by pyrolysis of precursor polymer membranes at 600 °C, which possess sufficient membrane flexibility and excellent gas separation performance. In pervaporation tests, SPPO carbon membranes exhibited high flux and high separation factors in the separation of water and larger alcohol molecules, indicating that the main permeation mechanism is molecular sieving. In addition, water permeance was much higher than that of H₂, which is similar in size to water, suggesting that surface diffusion occurred. Water adsorption measurements and surface analysis by ESCA indicate the presence of oxygen-containing functional groups on the surface of the carbon membrane as adsorption sites. Increasing the temperature resulted in lower water permeances for water/2-propanol systems, though flux exhibited opposite tendencies. The activation energy for water permeation was negative, supporting the likelihood of adsorption effects. Furthermore, water permeance gradually increased with water concentration. Temperature and concentration did not have much influence on ideal selectivity, and maintained a value over 10000 for the range of conditions investigated.

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1. Introduction

Pervaporation has quickly become an alternative to conventional separation processes such as distillation and adsorption. For separating azeotropic mixtures, such as alcohol/water, acetone/methanol, and ethanol/ethyl acetate, pervaporation is widely regarded as the most promising technology. Compared to the distillation process [1,2], pervaporation is more energy efficient and raises fewer environmental concerns. The pervaporation dehydration alcohols with low molecular weights, such as ethanol and 2-propanol, are most common, and a number of hydrophilic membranes, acting as water-selective membranes, have been investigated. Polymeric membranes such as poly(vinyl alcohol) and polyimides are studied for solvent dehydration by pervaporation. Various approaches, including cross-linking, introduction of charged groups, and hybridization with inorganic materials, have been examined to improve performance, usability and stability [3–5]. Simultaneously, microporous ceramic membranes, which offer higher chemical and thermal stability, have also been developed as prospective candidates. Microporous silica and zeolite membranes are often prepared for pervaporation separations. In certain cases they provide superior performance in both flux and separation factor for water/alcohol systems [6–8].

Recently, microporous carbon membranes have become more prevalent in pervaporation separations and gas separations due to their robust thermal and chemical resistances while retaining excellent shape selectivity [9–11]. Kita [10] studied the pervaporation of ethanol–water mixtures using tubular type carbon membranes prepared by coating thin layers of phenolic resin on porous alumina support and then carbonizing the polymer under a nitrogen atmosphere at 500–800 °C for 1 h. They reported that the carbon membrane selectively permeated water from water/ethanol mixtures, and both the separation factor and the flux of the membrane carbonized at 700 °C were larger than those of the membrane carbonized at 500 °C. Dong et al. [12] produced resorcinol/formaldehyde derived carbon membranes deposited on porous disks and performed the dehydration of aqueous ethanol and 2-propanol mixtures. They found that carbon membrane pyrolyzed at 800 °C showed a separation factor of 1155 for the 5 wt% water/2-propanol mixture at 30 °C, but decreased at 70 °C due to the pore blocking effect by the permeation of 2-propanol. Tin et al. [13] used polyimide synthesized on an α -alumina tube as a precursor for a carbon membrane to accomplish the dehydration of ethanol. Their studies indicate that a separation factor of 50 coupled with a high flux of about 4 kg m⁻² h⁻¹ is achieved at 60 °C for 50 wt% water/ethanol separation by the supported carbon membrane carbonized at 650 °C. Tanaka et al. [14] examined the dehydration of several organic solvents by pervaporation using tubular carbon membranes prepared on a porous α -alumina support by a partial carbonization of a resorcinol/formaldehyde resin. The membrane

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carbonized at 400 °C possessed a higher separation factor (4150, molar basis) for the separation of 10 wt% water/2-propanol at 70 °C and showed superior long-term stability (192 h).

These carbon membranes are most frequently prepared as composite tubular configurations similar to silica and zeolite membranes because carbon materials are brittle and thus not optimal for self-organized membranes [15]. However, self-supported hollow fiber configurations for pervaporation applications are considered more attractive because they offer greater area per specific module volume than flat or tubular membranes. Preparation of carbon hollow fiber membranes derived from polyimides [16–18], cellulose derivatives [19,20], polyetherimide [21], polyacrylonitrile [22] and poly(phenylene oxide) [23,24] have been reported.

We have successfully developed carbon hollow fiber membranes with good flexibility using sulfonated poly(phenylene oxide) (SPPO) as a precursor [25]. The SPPO-derived carbon membrane exhibits excellent performance for gas separation such as O₂/N₂ and CO₂/CH₄. In this study, dehydration of alcohols such as ethanol and 2-propanol was investigated by pervaporation with the SPPO carbon hollow fiber membrane.

2. Experimental

2.1. Materials

PPO [poly (2,6-dimethyl-1,4-phenylene oxide)] supplied by SABIC Innovative Plastics Co. Ltd. (reagent grade) was used. SPPO was synthesized in one step using chlorosulfonic acid according to previous studies [26,27]. The degree of substitution was adjusted to 0.35 in this study. Chlorosulfonic acid, chloroform, dimethylacetamide (DMAC), methanol, ethanol, 2-propanol and 1-butanol were purchased from Wako Pure Chemical Industries Ltd. (reagent grade).

2.2. Membrane preparation

The carbon hollow fiber membranes were prepared by the pyrolysis of SPPO polymeric hollow fibers as a precursor membrane. The methods of membrane preparation are based on our own previous work [25,28] but some experimental conditions were changed for optimization of the membrane properties. SPPO polymeric hollow fibers were fabricated through a dry/wet spinning process using a 28 wt% H-form SPPO solution in DMAC/methanol (36/36 wt%). The as-spun hollow fibers were stored in ion-exchanged water overnight, then dried in air at room temperature. After being preoxidized in air at 290 °C for 1 h, the hollow fibers were carbonized at 600 °C with a heating rate of 10 °C min⁻¹ for 1 h using a quartz tube furnace under vacuum conditions. A pyrolysis temperature of 600 °C provides the best gas separation performance with sufficient membrane flexibility, as reported in our previous study [25].

2.3. Characterization

Cross-section morphologies of the membranes were observed with a scanning electron microscope (SEM, S-3400N, Hitachi). The samples were coated with gold in a sputter coater (E-1010, Hitachi) before SEM observation.

Electron spectroscopy for chemical analysis (ESCA) is an effective technique for characterizing surface elemental compositions of carbon membranes. A quantum 2000 spectrometer (ULVAC-PHI Inc.) with AlK α radiation was used for the ESCA experiment.

Water adsorption isotherms at 25 °C were measured using an automatic volumetric adsorption apparatus (BELSORP-max; Bel Japan, Inc.). Prior to the adsorption measurements, the sample was outgassed under vacuum at 200 °C for 3 h.

2.4. Gas permeation

The single gas permeances for H₂, CO₂, O₂, N₂, CH₄, C₂H₆, C₃H₈ and *i*-C₄H₁₀ were measured at 30 °C by the time-lag method under a pressure difference of 0.1 MPa. In addition, the effects of temperature on permeation properties for H₂, CO₂, O₂, N₂, CH₄ were investigated at 30, 75 and 120 °C. The permeance (Q_i) of gas *i* is expressed in SI units as mol m⁻² s⁻¹ Pa⁻¹, where 1 mol m⁻² s⁻¹ Pa⁻¹ = 2.99 × 10³ cm³ (STP) cm⁻² s⁻¹ cm Hg⁻¹; it is given as

$$Q_i = \frac{P_i}{l} = \frac{j_i}{(p_{hi} - p_{li})} \quad (1)$$

where P_i is the permeability coefficient, l is the membrane thickness, j_i is the molar flux with units of mol m⁻² s⁻¹, and p_{hi} and p_{li} are the partial pressures of gas *i* on the feed and permeate sides, respectively. The ideal selectivity (α_{ij}) is determined by considering the ratio of permeances for selected gas pairs.

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{Q_i}{Q_j} \quad (2)$$

2.5. Pervaporation

Pervaporation experiments were carried out using several aqueous alcohol solutions (methanol, ethanol, 2-propanol and 1-butanol) with different concentrations at 50–80 °C. The permeate was collected in a liquid N₂ trap with a controlled pressure of about 1 kPa. Both the feed and the permeate concentrations were analyzed by gas chromatography with TCD (GC323, GL Sciences).

The permeation flux of component *i* in pervaporation is usually given as mass flux (J_i), with typical units kg m⁻² h⁻¹. Mass flux is converted into molar flux (j_i) using the molecular weight of component *i* (M_i):

$$j_i = \frac{1000 \times J_i}{3600 \times M_i} \quad (3)$$

As Wijmans et al. advocate, pervaporation data should be expressed in a driving force normalized form, such as permeability (P_i), permeance (Q_i), and ideal selectivity (α_{ij}), in order to understand the real trend of the membrane intrinsic properties [29,30]. The permeance (Q_i) of component *i* in pervaporation can be recalculated as follows:

$$Q_i = \frac{P_i}{l} = \frac{j_i}{(x_i \gamma_i p_{hi}^{sat} - p_{li})} \quad (4)$$

where x_i is the molar fraction of component *i*, γ_i is the liquid phase activity coefficient, and p_{hi}^{sat} is the vapor pressure for the pure component *i*. The activity coefficient was obtained using a computer simulation program (ChemCad) and the vapor pressure was calculated by Antoine's equation.

In this study, β_{ij} is used to identify separation factor to avoid confusion with ideal selectivity (α_{ij}). We have:

$$\beta_{i/j} = \frac{Y_i/Y_j}{X_i/X_j} \quad (5)$$

where Y_i , Y_j , X_i and X_j are the weight fractions of the components *i* and *j* in permeate and feed solutions, respectively.

3. Results and discussion

3.1. Membrane characterization

SEM images of the cross sections of the prepared carbon hollow fiber membrane are shown in Fig. 1. The membrane is dense and defect-free even when observed under large magnifications, as

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