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Pervaporation dehydration performance of microporous carbon membranes prepared from resorcinol/formaldehyde polymer

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ABSTRACT

Microporous carbon membranes for pervaporation applications were prepared on a porous α-alumina support by a partially carbonization of a resorcinol/formaldehyde resin. The stability and dehydration performances of the carbon membranes were determined. The carbon membranes were used for the dehydration of several organic solvents (methanol, ethanol, *i*-propanol, and acetic acid) containing water; it was found that water was selectively permeated through the membrane and the separation factor increased with the molecular diameter of the organic solvents. The high selectivity to water can be explained by not only the hydrophilic nature of the pore surface but also the molecular sieving effect. Furthermore, the membranes showed high durability in the pervaporation of water/alcohol mixtures. On the other hand, the membranes were unstable in water/acetic acid mixture. However, the sulfonated carbon membranes were stable in pervaporation of water/acetic acid mixture and maintained their separation properties.

1. Introduction

The global focus on green technologies requires the development of separation processes, which account for about 40% of the total energy consumption in chemical and petrochemical industries worldwide. Currently, the alcohol dehydration processes become increasingly important because of the advancements in the development of renewable biomass and biofuel technologies. Additionally, acetic acid with low water content is also needed in various chemical processes, such as production of vinyl acetate monomer, terephthalic acid, and acetate esters. Pervaporation is a promising technique and practical alternative to facilitate alcohol and acetic acid dehydration [1,2]. This membrane-based separation technique permits the separation azeotrope, close-boiling mixtures, and thermally degradable organic mixtures. In addition, pervaporation possesses many advantages: easy process design, high selectivity, low energy consumption, and moderate cost-to-performance ratio.

Polymeric membranes are widely adopted as separation materials in the field of pervaporation for solvent dehydration and separation of organic mixtures. However, polymeric membranes are often unstable at high temperatures. The applications of polymeric membranes are further restricted by unfavorable swelling, which subsequently results in the decline of their separation properties with respect to time [3]. Moreover, they cannot be used in concentrated acetic acid mixtures due to the low acid tolerance. Inorganic microporous membranes such as silica [4–6] and zeolite [7–10] have been developed as promising materials to overcome the above chemical and thermal instabilities. In general, they possess stable separation performance at high feed or water concentrations and elevated temperatures. Therefore, the separation operation can be applied for a broad range of applications and over an extended time period. Nevertheless, there are drawbacks reported in the preparation and separation stability of the inorganic microporous membranes. In addition to the chemical instability of silica against water and alkaline solutions [11], membranes are thick to form defect-free zeolite membranes [12]. Although well-known zeolite LTA membranes possess a high separation performance for water/alcohol systems, they have a major drawback of acid-sensitivity.

Microporous carbon membranes offer the best candidates for the development of new membrane technologies, because of their advantages, such as excellent permeation selectivity, high hydrothermal stability, and high corrosion resistance [13]. Furthermore, their microstructure and surface properties can be altered by post-treatment. Due to their highly porous structures with a sharp distribution of pore sizes ranging from 0.3 to 0.6 nm, the

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carbon membranes are suitable for the gas separations such as H_2/N_2, O_2/N_2, CO_2/N_2, and CO_2/CH_4. Research efforts have been focused on the gas separation [13–20]. However, very few investigations have been reported on the application of the carbon membranes for pervaporation [20,21]. Furthermore, to the best of our knowledge, there are no investigations on the application of the carbon membranes for dehydration of acetic acid.

Suitable carbon precursors for molecular sieve membrane production must not cause any crack formation after a pyrolysis step. A thermosetting phenolic resin can withstand relatively high temperatures and possess surface-modifiable phenolic hydroxyl groups. In this study, microporous carbon membranes for pervaporation applications were prepared on a porous α-alumina support by a partially carbonization of a resorcinol/formaldehyde resin. In addition, we attempt to chemically modify the carbon surface by sulfonation treatment. The separation performances of the carbon membranes were investigated for the pervaporation separation of water/alcohol mixtures. Furthermore, we use the membranes for pervaporation separation of water/acetic acid mixture and investigate the effect of sulfonation on the stability and dehydration performance.

2. Experimental

2.1. Materials

Resorcinol, formaldehyde (36–38 wt%), 5 N NaOH, 2 N H_2SO_4 and ethanol were purchased from Wako Pure Chemical Industries and used as received. α-Alumina porous tubular supports (outer diameter: 10 mm; inner diameter: 7 mm; length: 450 mm; average porosity: 35%; average pore size: 0.1 μm) were purchased from Noritake Co. Ltd. and cut into 35 mm long pieces.

2.2. Preparation of carbon membranes and sulfonation treatment

A resorcinol/formaldehyde resin layer was coated on the α-alumina layer as follows. A coating solution was prepared from resorcinol, formaldehyde, ethanol, and NaOH. In a typical synthesis, resorcinol was completely dissolved in formaldehyde solution. The above resorcinol/formaldehyde solution was added to ethanol, NaOH solution was added, and the solution was heated at 80 °C for 5 min. The solution was sonicated at room temperature for 3 min before coating. The final molar composition of the coating solution was 1 resorcinol:2 formaldehyde:2×10^{-3} NaOH:6.4 ethanol:5.1 water. Membranes were prepared by dip-coating the alumina supports in the coating solutions at a withdrawal rate of 1.6 mm s^{-1} using a DIPCOATER DC4200 (Aiden Co., Ltd.). The coating procedure was repeated two times. For polymerization of the resorcinol with formaldehyde, the as-deposited samples were pre-heated at 100 °C for 30 min in air. The resultant brown deposition was carbonized under a nitrogen atmosphere at 400–800 °C for 1 h at a heating rate of 1 °C min^{-1}.

The sulfonated carbon membranes were as follows: 2 N H_2SO_4 was used as a sulfonation reagent. The carbonized carbon membranes were immersed in H_2SO_4 at room temperature for 1 h. After sulfonation, the membranes were rinsed with deionized water and dried at 200 °C.

2.3. Characterization

Fourier-transform infrared spectroscopy (FTIR) spectra of the samples were recorded in the 500–3500 cm^{-1} range using a IRAffinity-1 spectrometer (Shimadzu) at 4 cm^{-1} resolution. Thermogravimetric analysis (TGA) was performed on a DTG-60H apparatus (Shimadzu) at a heating rate of 2 °C min^{-1}. FTIR and TGA measurements were performed with a powdery sample. The composition and thickness of the membranes were measured by scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) analysis on a VE-8800 microscope (Keyence). The field emission scanning electron microscope (FESEM) images were recorded on an S-5000L Hitachi microscope at an acceleration voltage of 22 kV. No coating was carried out for the samples before the SEM and FESEM measurements. Raman spectra were recorded with a NRS-3100 spectrometer (JASCO) using a 532 nm laser as an excitation source. The amount of CO_2 adsorption on carbon powdery samples was measured at 298 K using a BELSORP 28 instrument (Bel Japan, Inc.). The carbon powdery samples were prepared on a non-porous silicon substrate and scratched from the substrate.

2.4. Pervaporation

Pervaporation experiments were performed using several organic solvents (methanol, ethanol, *i*-propanol, and acetic acid) containing water. The carbon membrane side faced the feed side. In the experimental apparatus, the downstream compartment was evacuated, and the permeate was collected in a vacuum trap condenser cooled using liquid nitrogen. The permeation flux, J, is defined by

$$J_{\text{mass}} = \frac{Q}{At}, \tag{1}$$

where Q is the weight of the collected permeate during the experimental time interval, t, and A is the effective membrane surface area (11 cm^2). The permeation fluxes on the mass basis can be converted to the molar permeation fluxes as follows

$$J_{\text{mole}} = \frac{J_{\text{mass}}}{3600\ M}, \tag{2}$$

where M is the molecular weight of component. The feed and permeate concentrations were determined by Karl Fisher titration. The separation factor of component i with respect to component j, $\alpha_{(i/j)}$, is defined by

$$\alpha_{(i/j)} = \frac{y_i/y_j}{x_i/x_j}, \tag{3}$$

where y_i and y_j are the mole fractions of component i and j in the permeate, respectively, and x_i and x_j are their corresponding mole fractions in the feed.

3. Results and discussion

3.1. FESEM and SEM/EDX observations

SEM and FESEM images of the cross-sectional views of the carbon membrane carbonized at 400 °C on the alumina support are given in Fig. 1. The carbon membrane had a smooth surface. There existed no defect from the top view of the membrane (data not shown). From the FESEM image, the membrane had a carbon dense layer approximately 1 μm thick. On the other hand, as can be seen from the photograph image shown as an inset in Fig. 1, the carbon was deposited deep into the alumina pores. The molar ratios of carbon and aluminum at the positions indicated by *a–f* in Fig. 1 are shown in Table 1. The SEM/EDX results suggest that the resorcinol/formaldehyde resin penetrated into the pores of the porous alumina support. An effective thickness of the carbon membrane is estimated to be about 2 μm.

3.2. FTIR and CO_2 adsorption measurements

The pyrolysis was performed in a nitrogen atmosphere at 400–800 °C for 1 h at a heating rate of 1 °C min^{-1}. The chemical