Liquid and gas separation abilities of carbon membranes synthesized using hydrothermal method

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Carbon membranes comprising micropores were successfully synthesized for the first time on ceramic supports using a hydrothermal method, and their liquid and gas separation abilities were evaluated. The activation temperature was observed to affect both the microstructure and chemical composition of the membranes. The membrane activated at the optimum activation temperature of 1173 K exhibited good ethanol/water separation ability, with a separation factor of approximately 8.1 for a 5 mol % ethanol aqueous solution. Finally, the excellent water resistance of this optimal membrane was confirmed.

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1. Introduction

Separation and purification of gas or liquid mixtures by membranes have become major operations in the chemical industry and the field of environmental sciences.

Water-ethanol separation is one of the important studies because it is used to produce biomass energy.¹,² Some separations using porous ceramics have been reported. Zeolite membranes are widely used inorganic membranes for H₂, CO₂ etc. because of their excellent properties, including high separation ability, thermal stability, and chemical resistance.³,⁴ On the other hand, zeolite membranes are sensitive to water and have restrictions on their use. Membranes having high water-resistant ability are needed. Carbon membranes have also been studied because of their hydrophobicity in addition to thermal stability and chemical resistance.⁵-⁸ Hydrophobicity realize water resistance. Therefore, many preparation methods for carbon membranes have been introduced. These include chemical vapor deposition and related technologies⁹-¹² and the carbonization of polymer films.¹³,¹⁴ These membrane shows excellent separation properties and permeability. And, new preparation methods of carbon membranes will be required from the viewpoint of film formation costs and environmental impact.

Recently, activated carbon particles were prepared using hydrothermal treatment of a sugar solution,¹⁵-¹⁸ which is a simple, low-cost, and eco-friendly process. Some attempts to control the morphology of carbon have been made, which is expected to further expand the possible applications.¹⁹ However, to date, this hydrothermal process has only been used to synthesize carbon particles even though the hydrothermal method is widely used for the preparation of zeolite membranes. In this study, we present the first successful synthesis of carbon membranes using the hydrothermal method and report on their liquid and gas separation abilities.

2. Materials and methods

First, 0.5 mol/L glucose solution was prepared from glucose powder (Wako Pure Chemical Industries, Osaka, Japan) and ion-exchanged purified water. Ceramic supports were prepared using a previously employed process²⁰-²² and the 0.5 mol/L glucose solution were loaded into a Teflon-lined autoclave and subsequently heated to 473 K for 5 h. Black membranes were formed on the ceramic supports. Precipitates were also formed at the bottom of the autoclave and were used for the N₂ adsorption-desorption tests. The obtained membranes and precipitates were heated at 873–1273 K for 1 h in a N₂ atmosphere.

The ethanol/water separation ability was evaluated using the self-made equipment, which is depicted in Fig. 1. The membrane was placed in a membrane holder, and vapors evolved from 5 mol % ethanol aqueous solution in a feed vessel held in a 313 K water bath. The feed liquid was stirred by natural convection due to heating. The vapor passed through the membrane and was trapped in a cold trap cooled by liquid N₂. The pressure was monitored downstream between the membrane and cold trap and
rapidly reached approximately 50 kPa before remaining constant. After operation for 30 min, the ethanol concentration of the trapped liquid was analyzed via gas chromatography using a thermal conductivity detector (GC-2014, Shimadzu Co., Kyoto, Japan), and the separation factor, $\alpha$, was calculated using Eq. (1):

$$\alpha = \frac{Y_{\text{EtOH}} / Y_{\text{water}}}{X_{\text{EtOH}} / X_{\text{water}}}.$$  

(1)

It was confirmed that the change in the concentration of the feed liquid has almost no effect on the experiment.

Here, $X$ and $Y$ are the mass fractions of ethanol and water on the feed and permeate sides, respectively. The flow was calculated from the weight of the obtained liquid.

$\text{H}_2$, He, $\text{CH}_4$, $\text{N}_2$, Ar, and $\text{CO}_2$ gas transmission measurements were conducted using a previously described system.\(^{23,24}\) The gas transmission rate ($\text{GTR}$) was calculated using Eq. (2):

$$\text{GTR} = \frac{Q}{A \Delta P},$$  

(2)

where $\Delta P$ is the pressure drop between the inlet and outlet of the gas flow as measured by a digital pressure gauge (GC61, Nagano Keiko Co. Ltd., Tokyo, Japan); $Q$ is the gas flow rate measured by a mass flow meter (Model 8500, Kojima Instruments Inc., Japan) or a soap film flow meter (GL Science, Tokyo, Japan); and $A$ corresponds to the cross-sectional area of the prepared filter. All the samples were placed under a constant gas flow with a pressure of 0.2 MPa for over 1 h before the gas flow measurements. During the gas flow measurements, all the samples remained at the measured pressure for approximately 30 min to allow the gas flow to stabilize. This procedure was repeated twice for each sample, and consequently, only small fluctuations in the gas permeability were observed. The $\text{N}_2$ adsorption–desorption isotherms were measured at −77 K using a surface area and pore size analyzer (Belsorp-mini II, Bel Japan Inc., Osaka, Japan). The microstructures of the membranes were examined using scanning electron microscopy (SEM; JSM-5310, JEOL, Tokyo, Japan). The chemical compositions were analyzed using X-ray photo-

electron spectroscopy (XPS; model 5500 MT, PerkinElmer Inc.) with monochromated Al $K\alpha$ radiation having a pass energy of 23.5 eV. The liquid contact angle of the membrane activated at 1173 K was measured by using a commercial contact angle meter (Dropmaster DM-500; Kyowa Interface Science Co., Japan). 3.0 $\mu$L droplets was used to measure the contact angles.

3. Results and discussion

Figure 2 shows a typical microstructure of a membrane obtained using this hydrothermal process. The ceramic support was covered with the membrane, and carbon
spheres were observed on the membrane. These spheres were obtained by the hydrothermal treatment of the aqueous glucose solution. The thickness of the membrane estimated from the cross section of the membrane in Fig. 2(b) was approximately 2 μm. Carbon also precipitated into the pores of the ceramic supports.

In Fig. 3, the ethanol/water separation factor (α) and the flow are plotted as functions of the activation temperature. First, a separation test (distillation of the 5 mol% ethanol aqueous solution at 313 K) was performed without the membrane, and α was approximately 4.8. This is the separation factor corresponding to vapor-liquid equilibrium. Then, the carbon membranes were evaluated. α of the membranes activated at 873 and 973 K were approximately 5.2. The value increased with increasing activation temperature, reaching approximately 8.1 at 1173 K. The flow gradually increased with increasing activation temperature. However, the membrane activated at 1273 K exhibited low α and a high flow value without repeatability. This finding is attributed to a possible pinhole opening in the carbon membrane. Incidentally, the samples activated at 1173 K exhibited the same α values and flow after holding in water for 200 h as an acceleration test. This finding indicates that the carbon membrane prepared using this method exhibits high water resistance.

To understand the pore formation in the membranes, N2 adsorption–desorption isotherms of the samples were obtained before and after heating in a N2 atmosphere [Fig. 4(a)]. The sample before heating shows low adsorption ability with type III N2 isotherms, according to the IUPAC classification.25) After being activated at 873–1173 K or higher, the isotherm transformed to type I. Major N2 adsorption was observed below 0.05 of relative pressure, with an almost horizontal plateau at higher relative pressures. This result indicates that the obtained carbon had a narrow pore size distribution. The pore size calculated by BJH method was approximately 0.7 nm. The N2 adsorption of the sample activated at 1273 K was significant not only at low relative pressures but also throughout the entire pressure range. The isotherm of this sample was characterized as a combination of types I and II, suggesting that the sample activated at 1273 K contains macropores. Thus, activation at 1173 K and below resulted in the formation of micropores in the membrane, which is preferable for gas separation, whereas at 1273 K, macropores (membrane pinholes) may form in the membrane. It is considered that these macropores lead to the low separation factor and the low reproducibility.

To evaluate the chemical compositions of the membranes, the O/C atomic ratios were determined using XPS, and the results are presented in Fig. 4(b). The O/C atomic ratio of the sample activated by 973 K was approximately 0.118 and decreased with increasing activation temperature, reaching approximately 0.05 at 1173 K. This decrease originates from the decrease of the desorption of the OH group. In order to estimate the affinity between surface and liquid, the contact angle measurement was carried out. The average water contact angle of 5 times measurement was approximately 107° (Fig. S1). The ethanol contact angle of this membrane could not be measured because the
ethanol droplet absorbed into the membrane. It indicates the ethanol affinity is higher than water affinity for the obtained carbon membrane. And the membrane was considered hydrophobic and acted as a water vapor barrier after activation.

Finally, the GTR of H₂, He, CH₄, and Ar gases was estimated. The results for the sample activated at 1173 K are presented in Fig. 5, where the horizontal axis represents the temperature, $T$, and molecular weight, $M$, and the vertical axis represents the GTR. \( (T/M)^{1/2} \) and GTR exhibited a proportional relation for all the gases. This finding indicates that the diffusion of all the gases followed the Knudsen model because the pore size was smaller than the mean free path of these gases (approximately 50–80 nm).

4. Conclusions

Carbon membranes were synthesized on ceramic supports using a hydrothermal method, and micropores were formed in the membranes by thermal activation. The activation temperature affected the microstructure and chemical composition of the membranes. The membrane activated at the optimum temperature of 1173 K exhibited good ethanol/water separation ability, with a separation factor of approximately 8.1 for a 5 mol% ethanol aqueous solution. This membrane also showed high water resistance and good gas separation ability.

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