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Carbon Membranes from Wood Materials and their Separation Properties

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Carbon membranes were prepared by coating thin layers of lignocresol derived from Hinoki cypress by the phase-separation method and then carbonizing the lignocresol by high frequency induction heating at a heating rate of 500°C/min. The thickness of the membrane formed on the outer surface of a porous alumina substrate was about 1000 nm. Carbon membrane with a high performance of gas permeation showed a high water-selectivity in pervaporation of water/alcohol separation. The separation factor increased with increasing the heating temperature. The water concentration of the permeate was more than 99.5 wt% and the water flux was more than one or two order larger than the alcohol flux in the membrane prepared at 600 or 700°C. Carbon membranes derived from lignin-based materials provide one of the promising candidates for the separation of the liquid mixtures.

Key words: Lignocresol, Molecular sieve carbon membranes, Gas separation, Pervaporation, XPS

1. INTRODUCTION

Separation processes play critical roles in manufacturing and their proper application can significantly reduce costs and increase profits.[1] Alternative energy-saving and high efficiency separation process are strongly expected to be applied to many industries. Membrane separation appears to be a promising candidate because of low energy consumption, compact unit, simple operation and low environmental impact.[2] Strong interest, therefore, exists in the synthesis of membranes that exhibit both higher permeabilities and higher selectivities than presently available polymers. Recently[3-5] we have reported the preparation of microporous carbon membranes by pyrolyzing lignocresol which was a modified lignin recovered from wood by the phase-separative method.[6] Resulting membranes showed both higher permeability and higher selectivity than presently available polymers. Here we report the gas permeation and pervaporation results of the carbon membrane derived from lignocresol. The pore structure of the membrane studied by adsorption and XPS measurements is also described.

2. EXPERIMENTAL

Lignocresol was synthesized from Hinoki cypress by the phase-separative treatment with cresol and sulfuric acid.[6]

A porous cylindrical substrate of α-alumina was supplied by NOK Co. The substrate had a mean pore diameter of 150 nm with a porosity of about 40% and its dimensions were 2.25 mm outer diameter, 1.8 mm inner diameter and 20 mm length. The membranes of lignocresol were formed by a dip process as described previously.[5] The membrane was carbonized at 700°C under nitrogen atmosphere using high frequency induction heating system[5] (Sekisuimedical MU-1700) at 440 kHz with a heating rate of 500°C/min and then allowed to cool down to ambient temperature. The coating-carbonization cycle was repeated.

Gas permeation rates through the membrane were measured at 35°C and 1 atm using a vacuum time-lag method. The carbon membrane was sealed in the cell module with fluoro-rubber o-ring. Single component gas was fed to the outer side of the membrane in a permeation cell, which was placed in a thermostated air-bath.

Pervaporation experiments for water(10 wt%)/alcohol(90wt%) solution were carried out using the stainless-steel module which was placed in a thermostated air –bath. The carbon membrane was sealed in the cell module with fluoro-rubber o-ring. Liquid mixtures were fed by a liquid pump from a liquid reservoir to the outer side of the membrane in the module. Throughout the experiments, the flow rate of the feed was held at 30-37 cm^3min^{-1}. The permeated-side of the membrane was evacuated with a vacuum pump. The gaseous permeate was collected in a liquid nitrogen trap. The membrane performance of pervaporation was evaluated by measuring the permeation flux (Q in $kgm^{-2}h^{-1}$) and the separation factor (α). The permeation flux was calculated by weighing the liquid collected in the liquid nitrogen trap. The separation factor was determined as $\alpha_{A/B} = (Y_A/Y_B)/(X_A/X_B)$, where A is the preferentially permeating component, and

X_A, X_B, Y_A, and Y_B denote the weight fraction of component A and B in the feed and permeate, respectively. The compositions of feed and permeate were analyzed by gas chromatography (Shimadzu GC8A).

Vapor adsorption of water and alcohol at 303 K were measured volumetrically using the automated adsorption apparatus Bell-18SP. Each sample was degassed at 570 K for 24 h before performing a adsorption experiment. Therm mechanical analysis (TMA) of lignocresol was measured using Rigaku Thermoplus TMA 8310. Scanning electron microscopy (SEM) was measured using JEOL JSM6335F. X-ray photoelectron spectroscopy (XPS) was measured using ULVAC-PHI ESCA5700.

3. RESULTS AND DISCUSSION

The separated lignin derivatives from the carbohydrates by the phase-separative treatment[6] have several structural characteristics, for example highly phenolic and highly stable. The weight of lignocresol decreased by approximately 45% in the range of 350-450°C and then gradually decreased by 55% at 800°C from the thermogravimetric results of the lignocresol.[5] The gaseous products evolved by pyrolyzing lignocresol included methylphenol, dimethyphenol and several compounds with higher molecular weight together with traces of carbon dioxide and methanol. These evolved pyrolysis fragments effectively contribute to micropore formation of carbonized lignocresol membranes.[5]

Figure 1 shows SEM photographs of the surface of the precursor lignocresol membrane and the membrane carbonized at 700°C for 10 min under nitrogen atmosphere and the cross section of the membrane. SEM observation of the membrane indicated that there were many cracks at the surface of the precursor membrane, however, there were no cracks at the carbonized membrane. The TMA analysis of lignocresol clearly shows it begins to melt at 120°C as shown in Fig. 2. Thus, the repair of cracks of the precursor membrane occurs by the melting of lignocresol at the beginning of carbonization. The thickness of the carbon layer was about 1000 nm judging from the cross sectional SEM view of the carbon membrane in Fig. 1(C).

Figure 3 shows the gas permeation rates through the lignocresol membrane carbonized using high frequency induction heating for 10 min in nitrogen atmosphere. Compared with permeation rates of small molecules such as He, H_2, CO_2, it should be noted that considerable decrease in permeation rates of larger molecules such as N_2 and CH_4, which indicates that the membrane behaved like molecular sieve. Figure 3 also shows an effect of heating temperature for the gas permeation rates through the membranes. When the pyrolysis temperature was raised from 400°C to 500°C, permeation rates through the membrane increased due to the formation of a microporous structure as a result of the decomposition of

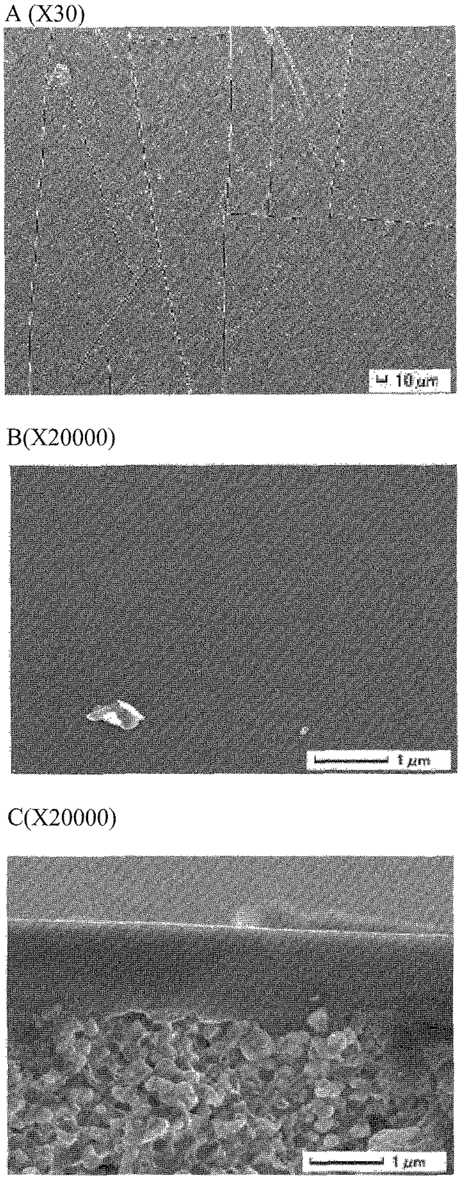

Fig. 1 SEM photographs of the precursor lignocresol membrane (A) and the carbonized membrane (B and C) prepared by 2-times coating using high frequency induction heating at 700°C for 10 min.

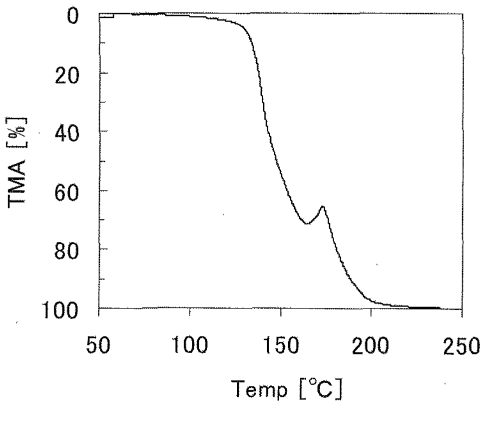

Fig. 2 TMA curves of lignocresol.

Table I Gas and Pervaporation performance of the carbon membrane prepared from lignocresol by pylolyzing in N_2 for 10 min

Pyrolysis Temp.	Gas[1)]						Pervaporation[2)]		
	Permeation rates(GPU)[3)]			Selectivity			Permeate	Flux	$\alpha_{H2O/EtOH}$
°C	H_2	CO_2	O_2	H_2/CH_4	CO_2/CH_4	O_2/N_2	H_2O wt%	kg/(m^2h)	-
400	110	130	24	22	27	3.4	10.0	-	leak
500	490	600	130	20	24	4.0	57.0	0.88	12
600	440	190	39	150	65	6.8	99.5	0.47	1800
700	290	57	17	1300	260	12	99.6	0.41	2000
800	220	110	25	55	29	4.9	10.0	-	leak

1) 35°C, 1 atm
2) 75°C, Feed: H2O/EtOH (10/90 wt%)
3) GPU= $10^{-6}cm^3(STP)/(cm^2 s cmHg)$

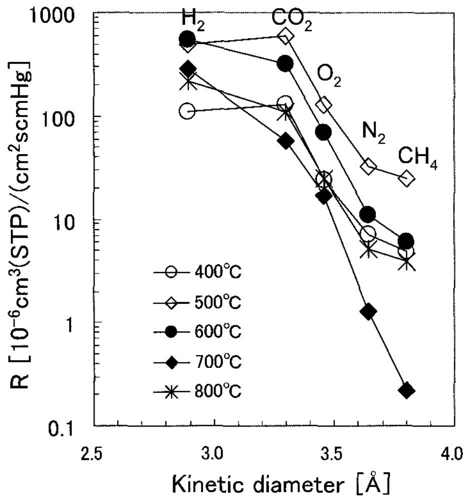

Fig. 3 Gas permeation rates (R) at 35°C and 1 atm through lignocresol membranes carbonized using high frequency induction heating for 10 min in N_2.

lignocresol. With increasing the heating temperature upto 700 °C permeation rates of larger molecules such as O_2, N_2, CH_4 decreased drastically. Heating to higher temperatures up to 800°C caused the pore shrink and the resulting carbon membranes seems to have some defects acting as pinholes, which is often observed for carbon membranes prepared by high temperature or long time pyrolysis.[7] Furthermore, it should be noted that the permeation rate of CO_2 is in the same order as that of H_2. The faster permeation of CO_2 seems to be caused by adsorption and surface flow of CO_2 as reported previously.[5]

Table I shows the gas permeation and pervaporation performance through the carbonized membrane. Carbon membrane with a high performance of gas permeation showed a high water-selectivity in pervaporation of water/alcohol separation. The separation factor increased with increasing the heating temperature. The water concentration of the permeate was more than 99.5 wt% and the water flux was more than one or two order larger than the alcohol flux in the membrane prepared at 600 or 700°C.

Table II shows pervaporation performance through the carbon membrane prepared at 700°C. The separation factor increased with increasing the size of alcohol. The membrane behaves like a molecular sieve in water/ethanol and water/isopropanol separation. The water flux was more than one or two order larger than the alcohol flux in water/ethanol and water/isopropanol mixtures. Water molecules with smaller size (0.28 nm) can pass through the membrane pore, but ethanol (0.43 nm) and isopropanol (0.50 nm) having a larger molecular size can hardly pass through the membrane. On the other hand, the separation factor in water/methanol was two order smaller than those in water/ethanol and water/isopropanol and the flux in water/methanol mixture was only about half as large as those in water/ethanol and water/isopropanol system due to the small difference of molecular size between water (0.28 nm) and methanol (0.38 nm). Methanol molecules can pass through the membrane pore and obstruct transport of water molecules.

Table II Pervaporation results (75°C) for water (10wt%)/alcohol(90wt%) mixtures through lignocresol membrane carbonized using high frequency induction heating at 700°C for 10 min in N_2

Alcohol	Permeate (H_2Owt%)	Flux (kg/(m^2h))	$\alpha_{H2O/EtOH}$
MeOH	86.64	0.24	58
EtOH	99.53	0.41	2000
i-PrOH	99.79	0.47	4400

High permselectivity of the membrane can be attributed to the molecular sieving effect of the microporous membrane and the hydrophilic property of the membrane. Figure 4 shows adsorption isotherms of water, ethanol and isopropanol at 50°C on the carbon membrane prepared at 700°C. The carbon surface is believed to be hydrophobic. Water molecules are slightly adsorbed at low relative pressure, indicating this hydrophobicity. The predominant water adsorption begins at the high relative pressure range as shown in Figure 4. This steep adsorption uptake has been believed to be associated with the cluster formation of water molecules.[8] Water molecules will initially adsorb onto hydrophilic groups, existing in the form of functional surface groups. Concentration of such functional groups can be estimated by XPS as mentioned below. Thus, the adsorbed amounts of water on the carbon membrane is two times larger than that of ethanol at the relative pressure of 1. Furthermore, with increasing the molecular size, the adsorbed amounts on the membrane decreased, indicating the molecular sieving effect of the microporous carbon membrane.

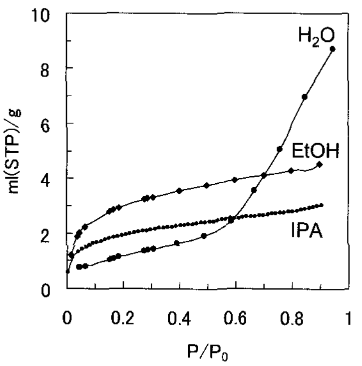

Fig. 4 Adsorption isotherms of water, ethanol and isopropanol at 50°C on the carbon membrane prepared at 700°C for 10 min under nitrogen atmosphere.

Figure 5 shows the C1s peak of XPS spectra of the lignocresol membrane and their carbonized membrane at 700 °C, which clearly shows that there are several hydrophilic functional groups containing oxygen, such as carboxyl, carboxylic, and carbonyl, on the surface of carbon membranes. The amount of these groups decreased with increasing the heating temperature.

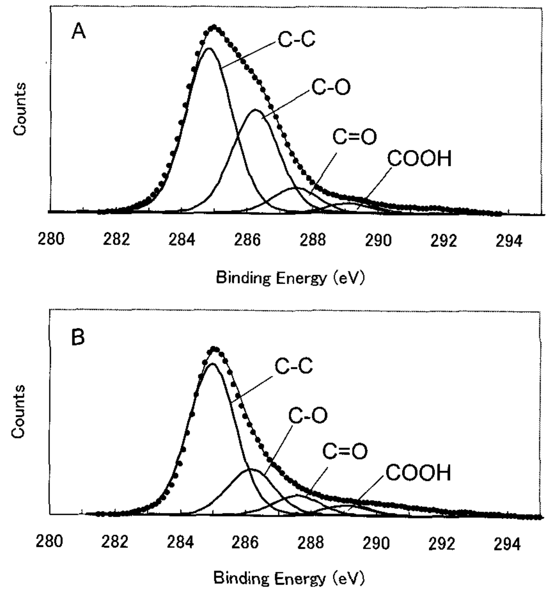

Fig. 5 C1s peak of XPS spectra of the precursor lignocresol membrane (A) and the carbonized membrane prepared at 700°C for 10 min under nitrogen atmosphere (B).

Furthermore, the membrane is stable after the long-term permeation experiment. The performance of the microporous membranes is far superior to any other membrane previously reported in both of pervaporation and vapor permeation.[9] Separation of these systems is difficult by a conventional distillation process because these components form azeotropic mixtures. Although azeotropic distillation and extractive distillation are used presently, these processes suffer from complexity and high energy consumption. It may, therefore, be concluded that carbon membrane provide one of promising candidates for the separation of the liquid mixtures.

Acknowledgment

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