Structure and Separation Performance of Carbon Membranes from Lignin-based Materials

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Carbon membranes were prepared by pyrolyzing lignocresol derived from wood using high frequency induction heating. The pore structure of the carbon membrane was studied by adsorption measurements and XPS. Gas adsorption measurements indicated that lignin carbon membrane has micropores in the range of 0.6-0.5 nm. C1s peak of XPS spectra of the lignin carbon membranes clearly showed that there are several hydrophilic functional groups, containing oxygen groups, on the surface of the membranes. Gas permeation rates through the membranes were also measured at 35°C. Carbon membranes from lignin-based materials have higher performance than conventional polymer membranes and provide a promising new class of separation membranes.

Key words: Lignin, Pyrolysis, Carbon membrane, Membrane separation, Adsorption

1. INTRODUCTION

In order to sustain the production of materials for human life under a sound ecological system, it is important to produce functional materials from renewable resources, and not from fossil resources. Among renewable resources the forest provides excellent raw materials, carbohydrates (cellulose and hemicellulose) and polyphenol (lignin) in both quantity and quality. Although the carbohydrates have been incorporated into human life for a long time, lignin has scarcely been utilized and now is the most abundant natural aromatic polymer. It serves as a cement between the cellulose fibers, a stiffening agent within the fibers and a barrier to the enzymatic degradation of the cell wall in plants [1]. In contrast to the importance and potential of lignin in nature, lignin-based products have scarcely been in human life, due to the fact that lignin molecules lack stereoregularity, and repeating units in its molecule are too heterogeneous and complex as shown in Figure 1 [2]. In addition, non-selective modifications during isolation from the cell wall make lignin molecules much more heterogeneous [3]. Recently one of us has developed a new process for separating lignocellulosics into lignin derivatives (lignocresol and lignophenol) and carbohydrates [4]. This process includes the phase separation reaction

Fig.1 Proposed structural model of spruce lignin [2].
system composed of cresol or phenol derivatives and concentrated acid. Such lignin derivatives having a linear structure offer greater versatility and are particularly suitable for the replacement of the phenolic products from fossil resources. Thus, in our recent reports [5-8], we chose lignocresol as novel precursor membrane materials for carbon molecular sieving membranes on the basis of high carbon yield and good film-forming properties without a pinhole during pyrolysis. Resulting membranes showed both higher permeability and higher selectivity than presently available polymers. In this report, the pore structure of the carbon membrane is studied by gas adsorption and XPS measurements.

2. EXPERIMENTAL

Lignocresol was synthesized from Hinoki cypress by the phase-separative treatment with cresol and sulfuric acid[4]. 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 in which the porous substrate was dipped into the 35 mass% lignocresol solution in tetrahydrofuran (THF) for 30 min at room temperature. The coated substrate was then pulled out at a rate of 1 cm/min. After air-drying at 70°C for 8 hours and then vacuum-drying at 100°C for 24 hours, the membrane was carbonized at 600 or 700°C under nitrogen atmosphere using high frequency induction heating system (Sekisuiomedical 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 two times. Membrane thickness was about 1 µm.

Thermogravimetry-mass spectrometry (TG-MS) was carried out on a Rigaku TG8120 - Shimadzu GCMS-QP5050. The average molecular weight was calculated from Gel permeation chromatogram (GPC) by calibrating with polystyrene standards in THF using TOSOH HLC-8121GPC/HT. Scanning electron microscopy (SEM) was measured using JEOL JSM6335F. X-ray photoelectron spectroscopy (XPS) was measured using ULVAC-PHI ESCA5700.

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.

Adsorption isotherms of N2 at 77K and CO2 at 273K on the carbon membrane, respectively. Adsorption isotherms were Type I according to IUPAC classification, which suggests the presence of a large amount of micropores in the membrane as a result of decomposition of lignocresol. It is well known that diffusion of nitrogen molecules into carbon micropores

3. RESULTS AND DISCUSSION

Figure 2 shows schematic structures of lignocresol[4]. The lignocresol separated from the carbohydrates by the phase-separative treatment is highly phenolic and highly stable. The weight-average molecular weight estimated by GPC was ca.7800.

The thermogravimetric analysis of the lignocresol [7] showed that the weight of lignocresol decreased by approximately 45% in the range of 350-450°C and then gradually decreased by 55% at 800°C. The gaseous products evolved from the lignocresol included methylphenol, dimethylphenol 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.

Figures 3 and 4 show the effect of carbonizing temperature for the adsorption amounts of N2 at 77K and CO2 at 273K on the carbon membrane, respectively. Adsorption isotherms were Type I according to IUPAC classification, which suggests the presence of a large amount of micropores in the membrane as a result of decomposition of lignocresol. It is well known that diffusion of nitrogen molecules into carbon micropores

![Fig.2 Schematic structure of lignocresol[4]](image)

![Fig.3 Adsorption isotherms of N2 at -196°C on carbon membrane prepared at 600°C and 700°C for 10 min under nitrogen atmosphere.](image)
is very slow at 77K and the diffusional limitations at this
temperature might influence adsorption in
ultramicropores (pore smaller than 0.7nm) [9].
Therefore, it has been recognized that problems of this
type can be eliminated by using CO₂ adsorption analysis
at 273K. At this temperature, CO₂ molecules can more
easily access ultramicropores than N₂ at 77K in spite of
the fact that critical molecular dimensions of both gases
are similar. Thus, CO₂ adsorption equilibrium data
were used for the calculation. The pore size
distribution of the membrane obtained from the NLDFT
analysis [10] of CO₂ isotherm is shown in Figure 5.
The membranes predominantly contain pores in the
range of 0.6-0.5 nm. The adsorption amounts of gases on
carbon membranes were in the order 600°C >700°C
>500°C. Large increase in adsorption amounts
occurred from 500°C to 600°C, which were due to
formation of a microporous structure as a result of
decomposition of lignocresol. Heating to higher
temperature such as 700°C caused the pores to shrink
and the resulting adsorption amounts decreased. At
above 600°C the weight loss was only 5%. MS spectra
showed only the evolution of small-size gas like H₂O,
CO and CO₂ in this range.

Figure 6 shows the gas permeation rates (R) at 35 °C
and 1 atm through lignocresol membranes
carbonized at 600°C and 700°C for 10 min in
nitrogen atmosphere. The membranes predominantly contain pores in the
range of 0.6-0.5 nm. The adsorption amounts of gases on
carbon membranes were in the order 600°C >700°C
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Figure 7 C1s peak of XPS spectra of lignocresol
membranes carbonized at 600°C for 10 min under
nitrogen atmosphere.

Figure 8 C1s peak of XPS spectra of lignocresol
membranes carbonized at 700°C for 10 min under
nitrogen atmosphere.
Carbon membranes derived from lignocresol with a high performance of gas permeation also showed a high water-selectivity in pervaporation of water/alcohol separation [8]. 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 water/ethanol and water/isopropanol mixtures. High permselectivity of the membrane can be attributed to the molecular sieving effect of the microporous membrane and the hydrophilic property of the membrane. The carbon surface is believed to be hydrophobic. 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. Figures 7 and 8 show the C1s peak of XPS spectra of the carbon membrane at 600°C and 700°C, respectively, which clearly shows that there are several hydrophilic functional groups containing oxygen on the surface of carbon membranes.

Curve fitting results for the main components of C1s spectrum are summarized in Figure 9. Compared with the precursor lignocresol (LC) membrane, the amount of functional groups on the surface of carbon membranes prepared at above 500 °C decreased, but trace of the peaks remained even at 800°C. These oxygen-containing functionalities may be assigned to oxidized carbon atoms at the surface of the membrane.

![Fig.9 C1s peak area of carbon membranes and precursor LC membrane](image)

4. CONCLUSION

Membrane separation appears to be a promising candidate because of low energy consumption, compact unit, simple operation and low environmental impact. Thus, there is growing interest in using microporous molecular sieving membranes to separate gas or liquid mixtures with very similar molecular dimensions. However, it is very difficult to prepare microporous membranes free of pinholes and with a molecular sieving effect. Lignocresol provide one of promising candidates as novel precursor materials for carbon molecular sieving membranes. Resulting membranes have micropores in the range of 0.6-0.5 nm judging from adsorption measurements and have several hydrophilic functional groups, containing oxygen groups, on the surface of the membranes from XPS analysis. Furthermore, the carbon membranes from lignocresol have higher performance than conventional polymer membranes.

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5. REFERENCES

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