

Rapid Pyrolysis of Lignin-based Materials for the Synthesis of Molecular Sieve Carbon Membrane

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Carbon membranes were prepared by coating thin layers of lignocresol derived from lignin by the phase-separation method and then carbonizing the lignocresol by high frequency induction heating at a heating rate of 500°C/min or conventional tube reactors at a heating rate of 5 °C/min. The thickness of the membrane formed on the outer surface of a porous alumina substrate was about 400-1000 nm judging from SEM observation. Gas permeation rates through the membranes were measured at 35 °C and 1 atm using a vacuum time-lag method. Carbon membranes derived from lignin-based materials provide one of the promising candidates for high performance membrane. Especially, the carbon membrane prepared by rapid pyrolysis shows a high permeance, which can be attributed to a more open structure of the membrane.

Key words: Lignocresol, Molecular sieve carbon membranes, Gas separation, Microporous membranes, Rapid pyrolysis

1. INTRODUCTION

The development of membrane processes for the separation of gas mixtures has made remarkable progress during the last two decades and strong interest exists in the synthesis of membranes that exhibit both higher gas permeabilities and selectivities than presently available polymers.^{1,2}

On the other hand, 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. Recently one of us has developed a new process for separating lignocelluloses into lignin and carbohydrates.³ The separated lignin derivatives have several structural characteristics, for example highly phenolic and highly stable.

Here, we report the preparation of carbon membranes by pyrolyzing lignocresol using high frequency induction heating and the gas permeation properties. Lignocresol was selected on the basis of high carbon yield without deforming during heating and pyrolysis.

2. EXPERIMENTAL

Lignocresol was synthesized from native lignin (Hinoki) by the phase-separative treatment with cresol and sulfuric acid.³ Figure 1 shows schematic structures of lignocresol.

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 capped with Teflon tape was dipped

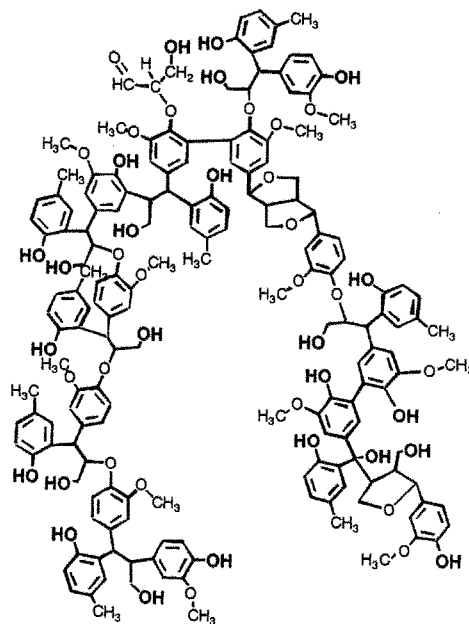


Fig. 1 Schematic structure of lignocresol

into the 35 mass% lignocresol solution in THF or MEK 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°C under nitrogen atmosphere or using high frequency induction heating system Sekisui Medical MU-1700 at 440 kHz with a heating rate of 500°C/min or conventional tube reactors with a heating rate of 5 °C/min and then allowed to cool down to ambient temperature. The coating-carbonization

cycle was repeated. Figure 2 shows a schematic diagram of high frequency induction device. The membrane was set in a carbon tube. The temperature controlled by a radiation thermometer.

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

Thermogravimetry-mass spectrometry (TG-MS) was carried out on a Rigaku TG8120-Shimadzu GCMS-QP5050.

Scanning electron microscopy (SEM) was measured using JEOL JSM6335F.

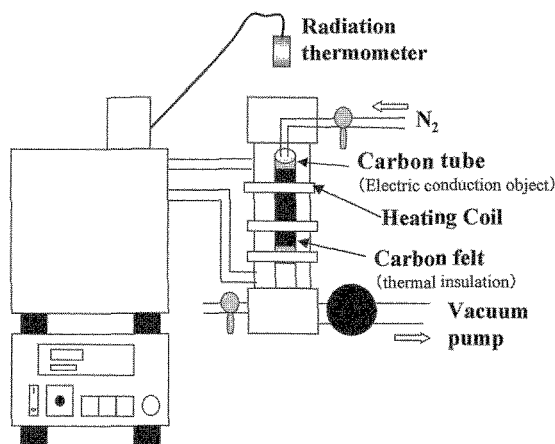
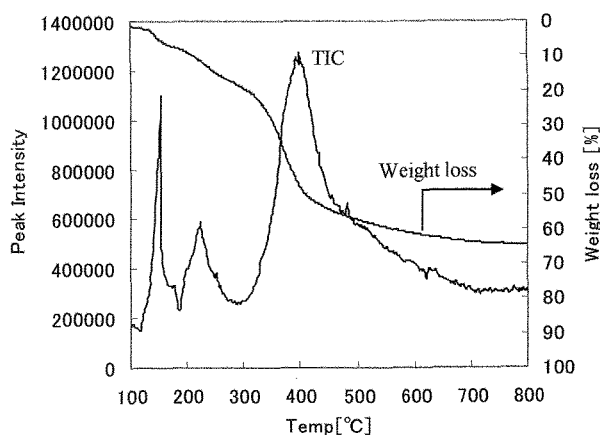


Fig.2 High frequency induction device

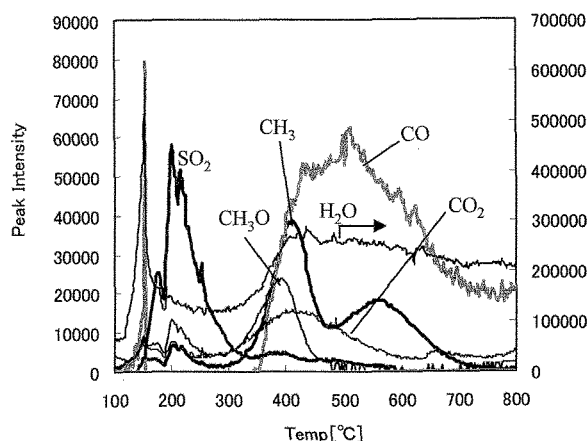
3. RESULTS AND DISCUSSION

Figure 3 shows TG-MS results of the pyrolysis of lignocresol in He. At the initial stage H₂O and residual solvent, p-cresol, and SO₂ from residual sulfuric acid were evolved, followed by the vigorous decomposition of lignocresol between 300-500°C. The weight of lignocresol rapidly decreased by approximately 60% in the range of 300-500°C and then gradually decreased by 65% at 800°C. The large weight loss occurring in the range 300-500°C was attributed to the evolving of gases as shown in Figure 3. The gaseous products evolved various pyrolysis fragments such as cresol, xylenol, guaiacol and creosol etc. together with CO, CO₂ from lignin-based materials between 300-600°C. These evolved pyrolysis fragments effectively contribute to micropore formation of lignocresol membranes. In previous studies,^{4,5} it has been reported that the pyrolysis temperature of 600°C gave the best membrane performance in the case of lignocresol. Thus, in this study carbon membranes derived from lignocresol were mainly prepared at 600°C. At above 600°C the weight loss was only 5% in the range 600-800°C. MS spectra showed the evolution of small-size gas like H₂O, CO and CO₂ in this range.

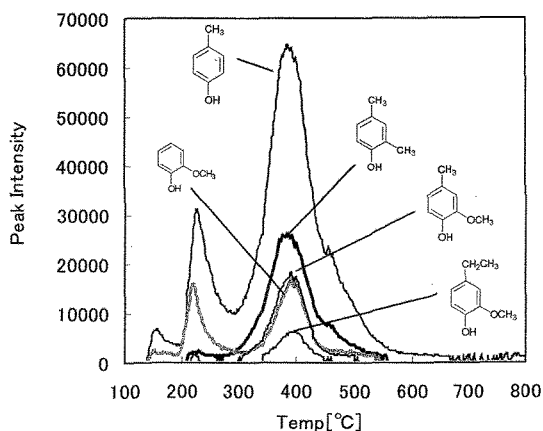
An example of SEM photographs of 2-coat membrane prepared by rapid pyrolysis at 600°C is shown in Figure 4. SEM observation of the carbon membrane indicated that there were no cracks but pinholes at the surface of



(a)

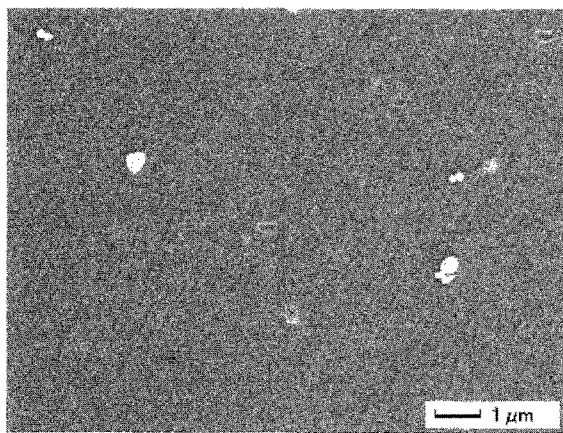


(b)

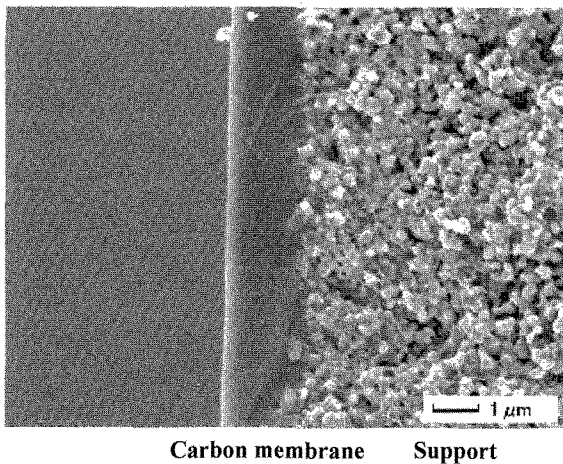


(c)

Fig. 3 TG-MS spectra and evolved gases during pyrolysis of lignocresol in He



(a) Surface (X10000)



(b) Cross section (X10000)

Fig. 4 SEM photo of surface and cross section of carbonized lignocresol membrane prepared by 2-times coating using high frequency induction heating at 600°C for 10 min

single-coated layer, however, multiple coated samples indicated a non-porous carbon layer. The surface of the membrane was very smooth and the thickness of the carbon layer was about 1000 nm judging from the cross-sectional view of the membrane.

Figure 5 shows the gas permeation rates through the lignocresol membranes carbonized using high frequency induction heating at 600°C in nitrogen atmosphere. Permeation rates through the membranes decreased with increasing kinetic diameter of the penetrant gas, which indicates that the membrane behaved like molecular sieve. Figure 5 also shows an effect of heating time for the gas permeation rates through the membranes. Permeation rates through the membrane increased with increasing of the heating time until 60 min and then decreased at 120 min. The values of permeation rates after 120-min heating were almost the same as those of the membranes prepared by conventional tube reactors with a heating rate of 5°C/min. Large increase in

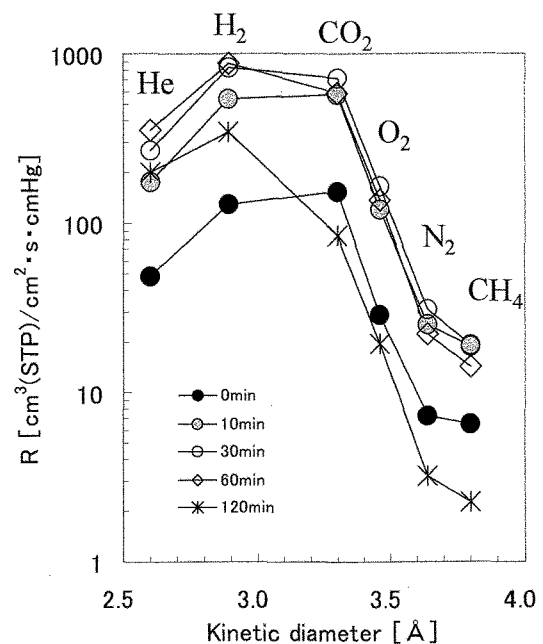


Fig. 5 Gas permeation rates at 35 °C and 1 atm through lignocresol membranes carbonized using high frequency induction heating at 600 °C in N₂

permeation rates in 10-60 min is due to the formation of a microporous structure without the decrease in the pore size and/or reduction in the fraction of the micropore (or porosity), although they are often observed for carbon membranes prepared by high-temperature or long-time pyrolysis.⁶ Furthermore, compared with permeation rates of larger molecules such as N₂ and CH₄, it should be noted that considerable increase in permeation rates of small molecules such as H₂, CO₂ and O₂ was observed, which suggests the formation of small pore in the early stage of the pyrolysis. Permeation rates of these gases enhanced by nearly 1 order of magnitude, while permeation rates of methane enhanced only three times as shown in Figure 5. Thus, the membrane prepared by rapid pyrolysis appears to have a more open structure in the early stage of the pyrolysis.

Figure 6 shows plots of permeability ratio of CO₂/CH₄ versus CO₂ permeability of carbon membranes together with the data of precursor polyimides and zeolite membranes. Microporous carbon membranes have much higher performance than other membranes, although the membrane performance significantly depended on the pyrolysis conditions such as temperature and time. Especially, carbon membrane prepared by high frequency induction heating shows a high permeance, which can be attributed to a more open structure of the membrane. Furthermore, it should be noted that the permeation rate of CO₂ is in the same order as that of H₂. The faster permeation of CO₂ seems to be caused by adsorption and surface flow of CO₂ as reported previously.⁶ Thus, the carbon membrane derived from lignocresol does offer good selectivity for CO₂/CH₄ or CO₂/N₂ and provides one of the promising candidates for the separation of CO₂.

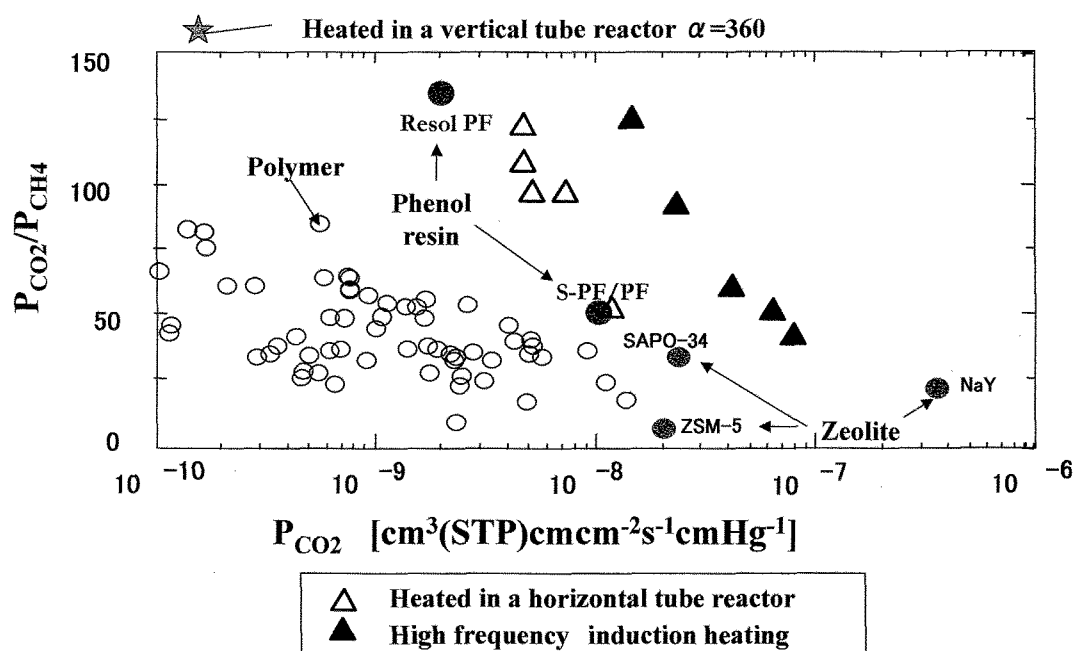


Fig. 6 Membrane performance of CO_2/CH_4 separation through carbon membranes derived from lignin (Δ ; carbonized by conventional horizontal tube reactor, \blacktriangle ; by high frequency induction heating) and phenolic resin (conventional heating), zeolite membranes and polyimides at 35 °C

4. SUMMARY

Carbon membranes were prepared by coating thin layers of lignocresol derived from lignin by the phase-separation method and then carbonizing the lignocresol by high frequency induction heating at a heating rate of 500°C/min or conventional tube reactors at a heating rate of 5 °C/min. Gas permeation rates through the membranes were measured at 35 °C and 1 atm using a vacuum time-lag method. Carbon membranes derived from lignin-based materials provide one of the promising candidates for high performance membrane. Especially, the carbon membrane prepared by rapid pyrolysis shows a high permeance, which can be attributed to a more open structure of the membrane.

The present work was supported by SORST of JST (Japan Science and Technology).

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(Received January 15, 2006; Accepted March 30, 2006)