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TECHNICAL NOTE

Carbon Membranes for Gas Separation

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ABSTRACT

Two kinds of pyrolysis carbon membranes for gas separation were prepared by control of preparation conditions. One was characterized by higher selectivity and another by higher permeability. The preparation process of the carbon membranes consists of pyrolysis and activation steps. The first step was conducted under inert gas and the second step in an oxidation environment. A thermosetting phenol formaldehyde resin membrane was chosen as the precursor. Preparation conditions were important factors for the structures and properties of the resulting carbon membranes. Pore size distribution was measured and morphology was observed. Effects of membrane structure on characteristics were discussed.

Key Words. Membrane; Gas separation; Carbon; Selectivity; Permeability.

INTRODUCTION

The development of inorganic membranes paved the way for the application of membranes in high temperature gas separation. As opposed to polymeric membranes, inorganic membranes are characterized by high thermal and chemical resistances. Typical inorganic membranes are Vycor glass, silica, alumina, and porous ceramic membranes. However, the application of these materials is often limited to lower selectivities due to their relatively larger average pore size. Generally, the pore sizes of the typical inorganic membranes are larger than 2.0 nm, and selectivities for oxygen/nitrogen are lower than 1.0 (1). For this reason, membranes with higher selectivities and permeabilities have been of great interest in the field of industrial gas separations.

The idea of preparing molecular sieve carbon membranes by pyrolysis of organic polymers was developed by Koresh and Sofer (2). Preparation of the carbon membrane consisted of pyrolysis and oxidation steps. Micropores were achieved as a result of small gaseous molecules channeling their way out of the solid matrix of the polymer during pyrolysis. The micropore structure was further widened by oxidation which removed carbon chains in the pores. The pore structure was made narrower by high temperature sintering which shrinks the pore size. The molecular sieve carbon membranes were supposed to have greater permselectivities.

Obviously, all of the preparation conditions which shrink the pore size of the carbon membrane would be beneficial for improvement of selectivities, while the conditions for widening pore size should be favorable for increasing permeabilities. With this background in mind, membranes with various characteristics could be obtained by means of different preparation conditions. Preliminary results on research concerning the characteristics and structures of the membranes are reported in this paper.

EXPERIMENTAL

Preparation of Pyrolysis Carbon Membrane

A thermosetting phenol formaldehyde resin was synthesized by a conventional method. Some suitable additives were added to it for improvement in the resulting membrane toughness. A mold pressing process was chosen for shaping the precursor, and a phenol formaldehyde resin film of 0.05 to 0.10 mm thickness was obtained.

A pyrolysis carbon membrane was prepared in two steps: pyrolysis and activation. Figure 1 is a schematic view of the pyrolysis experimental setup. The pyrolysis reactor is a quartz tube with a diameter of 10 cm and a length of 100 cm. Both the source of the inert gas and the source of the activated gas were connected to the pyrolysis tube. The pyrolysis tube was positioned within a high temperature tubular furnace equipped with a temperature controller. Several pieces of precursors were positioned in the center of the pyrolysis tube. The pyrolysis process was performed under an inert gas environment at 800 to 950°C. After the pyrolysis step, the source of inert gas was closed and the valve for the activated gas was opened. The activation step was conducted for 20 to 60 minutes at the same temperature as the first step. Finally, the pyrolysis samples were cooled to room temperature in an inert gas environment, and pyrolysis carbon membranes were obtained.

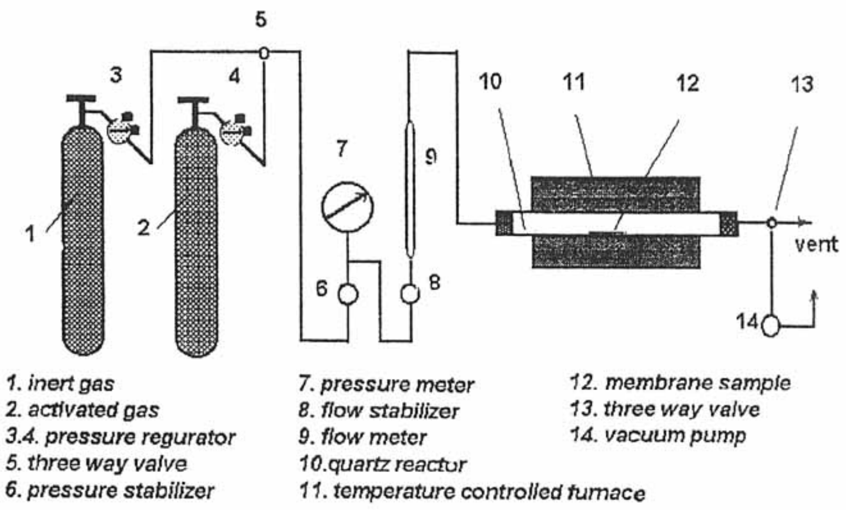

FIG. 1 Experimental setup for pyrolysis.

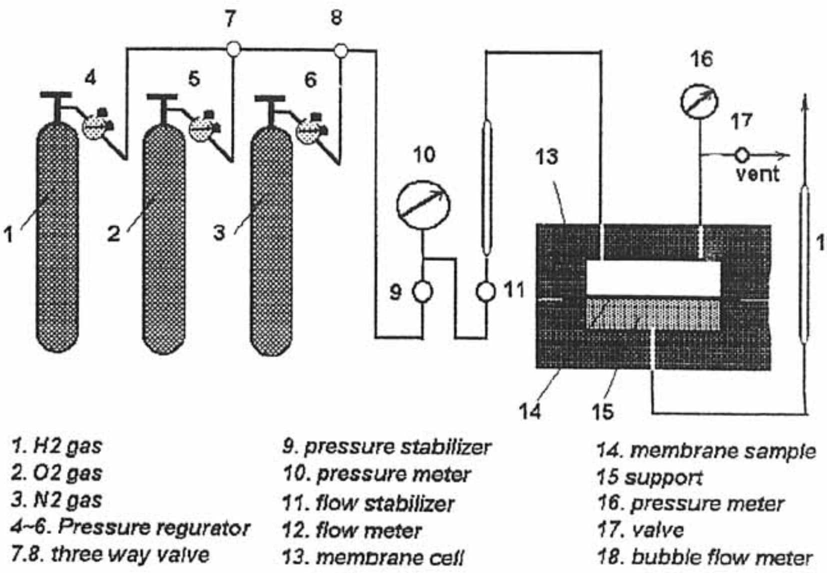

FIG. 2 Experimental setup for permeability measurement.

Measurement of Gas Permeabilities

The schemetic diagram of the gas permeation experimental set-up is shown in Fig. 2. The test gas was flowed through a pressure stabilizer, a flow stabilizer, and fed into the membrane cell. The rate of permeated gas was measured by a soup bubble meter. The permeabilities of the membranes were determined from steady-state permeation rates at constant temperature and pressure.

RESULTS AND DISCUSSION

Permeable Characteristics of Pyrolysis Carbon Membranes

At room temperature the permeabilities of hydrogen, oxygen, and nitrogen through the pyrolysis carbon membranes were measured and given by

$$Q(i) = [q(i)t]/(FP) \tag{1}$$

where $Q(i)$ = permeability of gas i through the membrane, $\mathrm{cm^3 \cdot cm/cm^2 \cdot s \cdot MPa}$

$q(i)$ = volumetric flow rate of permeate gas, $\mathrm{cm^3/s}$

t = thickness of the membrane, cm

F = effective area of the membrane, $\mathrm{cm^2}$

P = pressure difference across the membrane, MPa

The selectivity R was calculated based on the permeabilities of the pure gases:

$$R(i/j) = Q(i)/Q(j) \tag{2}$$

Using suitable preparation conditions, two kinds of pyrolysis carbon membranes were obtained. The first one was characterized by higher selectivity. For this kind of membrane, the selectivity of H_2/N_2 reached to 20–60, and that of O_2/N_2 was larger than 8.0. Selectivities of some typical pyrolysis carbon membranes are shown in Table 1. The second kind of membrane had high permeability. The permeabilities of the example membranes are shown in Table 2. For comparison, the permselectivities of a representative inorganic membrane (Vycor glass) and a polymeric membrane (silicon rubber) are shown in Table 3. By comparison of the data in Tables 1 and 3, we can see that the selectivities of the selective carbon membranes are not only much larger than those of the inorganic membrane, but also larger than those of the polymeric membrane. The selectivities of the pyrolysis carbon membranes in Table 1 are 10 to 20 times

TABLE 1
Permselectivities of High Selective Pyrolysis Carbon Membranes

Membrane	Permeability Q, 10^2 Barrer[a]			Selectivity	
	H_2	O_2	N_2	H_2/N_2	O_2/N_2
C 078	12.1	2.56	0.31	39.0	8.53
C 098	60.8	9.20	1.03	58.9	8.92
S 431	51.4	23.30	2.15	23.9	10.84

[a] 1 Barrer = 10^{-10} $cm^3 \cdot cm/s \cdot cm^2 \cdot cmHg$.

greater than those of the Vycor glass and silicon rubber membranes. A obvious contrast with the membranes in Table 1, the carbon membranes in Table 2 show much higher permeabilities. The average permeabilities are one order of magnitude higher than that of Vycor glass, even though their selectivities are closer.

Morphology and Pore Size Distribution

Generally speaking, a relatively high pyrolysis temperature is favorable for increasing carbon membrane selectivity, which is thought to be responsible for pore shrinkage. However, a relatively strong activation condition will help improve the permeability of a membrane, which is mainly due to opening and widening of the carbon membrane pores. The pore size and its distribution was measured by using a transient nitrogen adsorption technique. The results of the above-mentioned two kinds of typical carbon membranes are shown in Figs. 3 and 4, respectively. As shown in Fig. 3, the most probable pore size is 0.9 nm for the high selective carbon mem-

TABLE 2
Permselectivities of High Permeable Pyrolysis Carbon Membranes

Membrane	Permeabilities Q, 10^5 Barrer			Selectivity	
	H_2	O_2	N_2	H_2/N_2	O_2/N_2
C 108	11.0	9.93	5.85	1.70	1.88
C 148	12.5	3.95	3.23	3.87	1.22
C 130	26.8	5.35	5.51	4.86	0.99

TABLE 3
Permselectivities of Typical Inorganic and Polymer Membranes

Membrane type	Permeability *Q*, Barrer			Selectivity		Reference
	H_2	O_2	N_2	H_2/N_2	O_2/N_2	
Vycor glass	2.02×10^5	5.52×10^4	5.92×10^4	3.41	0.93	3
Silicon rubber	5.20×10^2	3.96×10^2	1.84×10^2	2.83	1.31	2

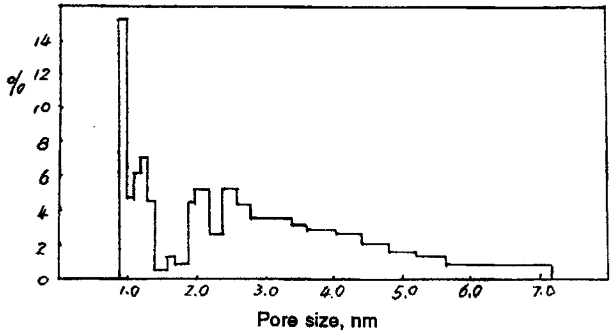

FIG. 3 Pore-size distribution of highly selective pyrolysis carbon membrane.

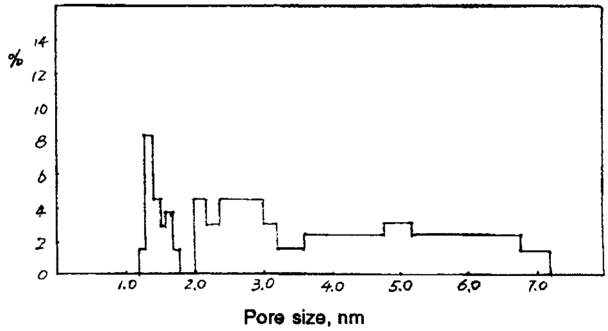

FIG. 4 Pore-size distribution of highly permeable pyrolysis carbon membrane.

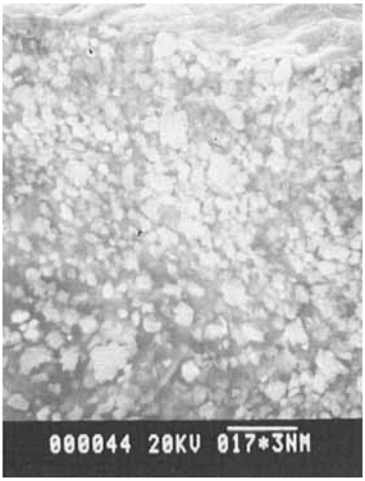

FIG. 5 Scanning electron microscope image of the cross-section of highly selective pyrolysis carbon membrane under a magnification of 800.

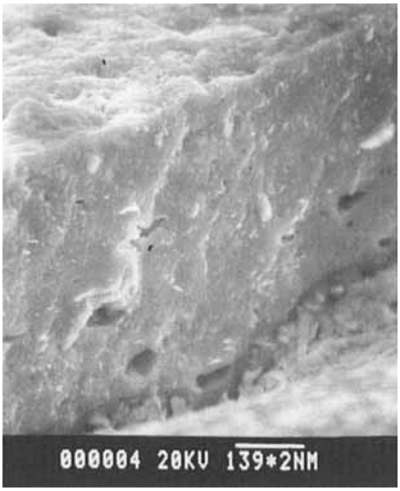

FIG. 6 Scanning electron microscope image of the cross-section of highly permeable pyrolysis carbon membrane under a magnification of 1000.

brane, while in Fig. 4 the corresponding pore size is 1.4 nm for the high permeable membrane.

Different preparation conditions on two sides of a carbon membrane, for example, a relatively strong activation condition on one side, and a relatively weak activation condition on the opposite side, would lead to formation of an asymmetric structure of the carbon membrane. The cross section of pyrolysis carbon membranes were visually observed with a scanning electron microscope (S-450, Hitachi Co.). At a magnification of 800, the highly selective carbon membrane showed an asymmetric structure (Fig. 5) while the highly permeable membrane showed a symmetric structure (Fig. 6).

CONCLUSION

Based on controlled preparation conditions, the selectivities or permeabilities of pyrolysis carbon membranes can be improved significantly. The selectivities of typical highly selective pyrolysis carbon membranes are 10 to 20 times greater than those of Vycor glass and silicon rubber membranes. The average permeabilities of typical highly permeable carbon membranes are one order of magnitude higher than that of Vycor glass. Thus the membranes have good potential for gas separation applications.

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