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Gas Permeation Properties of Iron Containing Carbon Molecular Sieve Membranes

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Carbon molecular sieve (CMS) membranes containing iron were prepared by casting PMDA-ODA polyimide uniformly dispersed with iron compound, followed by drying and pyrolysis at 1123 K under vacuum. The gas permeation properties (permeability *P* and diffusivity *D* calculated from lag time) of the iron containing CMS membranes were evaluated by high vacuum time-lag method. Although the permeabilities for larger gases, such as, CO_2, O_2, N_2, CO, and CH_4, decreased greatly when the iron content increased, those for smaller gases such as H_2 and He seldom changed. Consequently, the ideal separation factors (permselectivities) for e.g. H_2/N_2, He/N_2 gas pairs increased. It was because the apparent sorptivity S ($=P/D$) for N_2 became small with the increase in iron content. This coincided with the results of gas adsorption measurement that the limiting pore volume for CO_2 probe gas adsorbed on the iron-containing CMS was smaller than that on CMS without iron. It was suggested that iron moiety is located near the micropore mouth within the CMS membrane, resulting in the novel function as a selective permeation barrier (sorption barrier and/or diffusion barrier).

Key words: carbon molecular sieve, membrane, gas separation, iron, permeation barrier

1. INTRODUCTION

Among inorganic membranes, a carbon molecular sieve (CMS) membrane is known to exhibit outstanding gas separation performance [1,2]. This is due to the presence of permeation path consisting of slit-like micropores with 0.3-0.5 nm in size, through which gases selectively permeate depending on their kinetic gas diameter [3]. This implies that some influence may arise in the sorption, diffusion and permeation of gases by the incorporation of a permeation barrier like hetero atoms near the permeation path. Moreover, it is expected to contribute to an elucidation of permeation mechanism and improvement in the further separation performance, to investigate and control the permeation barrier effect.

This study examined gas permeation properties of CMS membranes containing iron compound as what can affect the gas permeation behavior but without particular interaction with permanent gases used for the permeation tests.

2. EXPERIMENTAL

2.1. Preparation of iron-containing CMS membranes and characterization.

The PMDA-ODA type polyamic acid solution which was uniformly mixed with ferrocene of predetermined quantity (0, 5, 10 wt% as iron) was cast on a glass plate. The cast films were dried at ambient atmosphere, followed by imidization under vacuum or nitrogen, and pyrolysis at 1123 K with heating rate of 10 K/min under the vacuum of 10^{-5} torr for 2 hours. All the membranes were allowed to cool to room temperature under vacuum, resulting in the formation of CMS membranes containing iron compound inside the carbon matrix.

Microstructure of the iron-containing CMS membranes was investigated by X-ray diffractometer (MAC Science, MXP3), transmission electron microscopy (Jeol, JEM-2000FX), and gas adsorption apparatus (Nihon Bell, Belsorp 28). Thermal decomposition processes of polyimide membranes with and without iron were characterized by TG-MS apparatus (MAC Science, 2000S).

2.2. Micropore analysis

Micropore was analysed by molecular probe method from analysis of adsorption isotherms at 298 K of probe gas molecules with different kinetic diameter [4] (CO_2, C_2H_6, n-C_4H_{10}, i-C_4H_{10}) by application of Dubinin-Astakhov equations [5],

$$W = W_0 \bullet \exp\left\{-\left(\frac{A}{E}\right)^n\right\} , \quad (1)$$

where W is the pore volume, E is the characteristic energy of sorption, and W_0 is the limiting pore volume whose pore size is assumed to be larger than the kinetic diameter of each adsorbate. The adsorption potential A

[$=RT\ ln(P_s/P)$] is calculated from the saturated vapor pressure P_s, the equilibrium vapor pressure P, the gas constant R, and the measurement temperature T. The obtained adsorption data were well correlated when the parameter n is 2, in accord with those for microporous carbon [3]. The W_0 values were obtained from y-axis intersections in the plots of lnW against $(ln(Ps/P))^2$. Samples were degassed at 473 K for 2hours prior to each adsorption measurement.

2.3. Gas permeation measurements.

Gas permeabilities of CMS membranes containing iron compound were measured at 308-363K with a high vacuum time-lag method [6] under the pressure difference of 1 atm (Fig.1). Permeability values were calculated by using the following equation:

$$P = \frac{dp}{dt}\left(\frac{V \bullet To \bullet L}{po \bullet T \bullet pf \bullet A_m}\right), \quad (2)$$

where P is the permeability expressed in Barrer [1 Barrer = 1 x 10^{-10} {cm^3(STP)•cm} / {cm^2•sec•cmHg}], dp/dt is the rate of the pressure increase under the steady state, V is the volume, L is the membrane thickness, p_f is the feed pressure, T is the measurement temperature, A_m is the membrane area, and p_0 and T_0 are the standard pressure and temperature, respectively. Both the feed and permeate sides of the membrane cell were evacuated (< 10^{-5} torr) prior to each time-lag measurement. The rate of pressure rise on the permeate side was monitored by thermostated Baratron sensors. The temperature of the membrane cell set in a ventilated oven was kept at a desired value. Permselectivity is defined in the present study as the ratio of permeability of chosen gas over that of N_2 (ideal separation factor). Apparent sorptivity, S was evaluated by the equation, $S=P/D$, since in the sorption-diffusion model [7], the permeability P is given as a product of the apparent diffusivity, D, and the sorptivity, S, that is, $P=DS$.

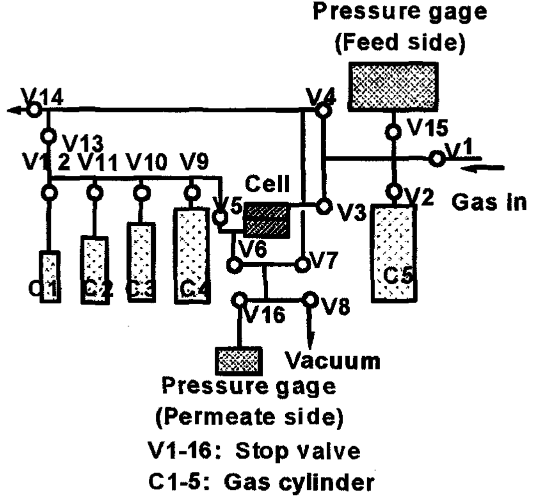

Fig.1 Schematic of high vacuum time-lag apparatus used for gas permeation test.

3. RESULTS AND DISCUSSION

3.1. Preparation and characterization

TG and chemical analyses implied that ferrocene is very volatile and it completely losts its weight at around 400 K. To make the content of iron in the membranes as nearly the same as the predetermined value, drying step was carried out slowly. The next imidization step started after the surface layer of the polymer matrix hardened, otherwise more than half of the ferrocene was removed away during the imidization step. This pretreatment results in nearly the expected amount of iron (4.9 and 7.7 wt%), compared to the predetermined contents of 5 and 10 wt%, respectively.

TG-MS measurements were conducted with heating rate of 10 K/min under argon. The PMDA-ODA type polyimide without iron started to decompose at around 800-900 K (ca. 34 wt% loss), followed by a continuous slight decrease of weight at higher temperatures. The total weight loss at 1123 K was 42 %. The polyimide containing 5 wt% of iron showed, on the other hand, three major steps for weight loss; first at 500-700 K (10 wt% loss), second at 800-900 K (26 wt%), and third (continuous weight loss: 10 wt%). The first weight loss may correspond to the decomposition of ferrocene inside the polyimide matrix or polyimide itself which was induced by the presence of ferrocene. The polyimide containing iron with a predetermined quantity of 10 wt% exhibited similar decomposition tendency.

3.2. Gas permeation and sorption properties

Figure 2 shows the gas permeation property of iron containing CMS membranes. Although the permeabilities for larger gases, such as, CO_2, O_2, N_2, CO, and CH_4, decreased greatly when the iron content increased to 5 wt%, those for smaller gases such as H_2 and He seldom changed. Consequently, the permselectivities for e.g. H_2/N_2, He/N_2 gas pairs increased.

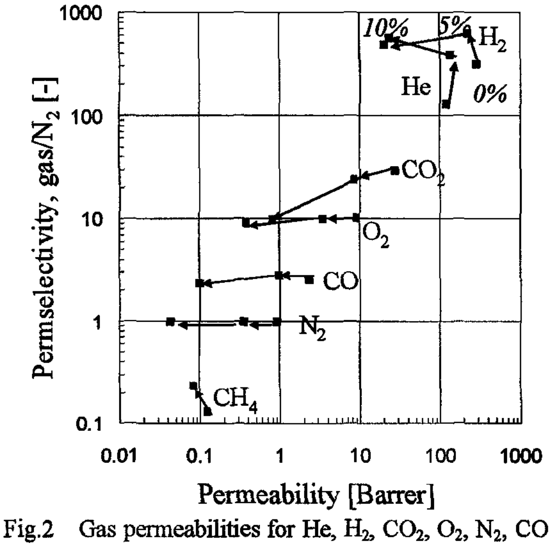

Fig.2 Gas permeabilities for He, H_2, CO_2, O_2, N_2, CO, and CH_4, and their permselectivities for each permeant against N_2 for CMS membranes containing 0, 5, and 10 wt % of iron (measurement temperature: 363 K).

Figures 3 and 4 show the dependencies of the apparent diffusivity and sorptivity on the iron content for the larger gases such as CO_2, O_2, N_2, CO, and CH_4. When the iron content increased to 5 wt%, the sorptivity drastically decreased, whereas the diffusivity seldom changed. Therefore the main cause for the improved permselectivity for the gas pair like H_2/N_2 is that the apparent sorptivity for N_2 becomes small with the increase in iron content. This coincides with the results of gas adsorption measurement that the amount of CO_2 probe adsorbed on the iron-containing CMS became small as the iron content increased (Fig. 5).

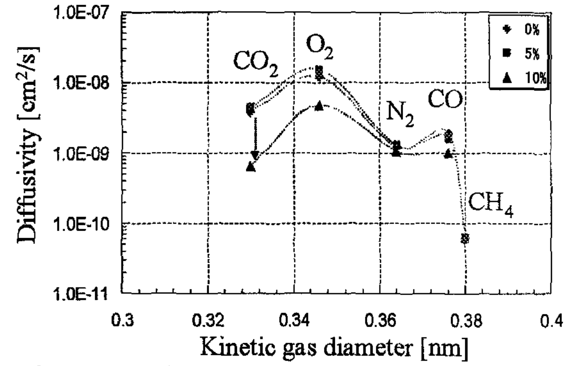

Fig.3 Dependencies of the apparent diffusivity *D* on the iron content for the larger gases such as CO_2, O_2, N_2, CO, and CH_4 as a function of kinetic gas diameter.

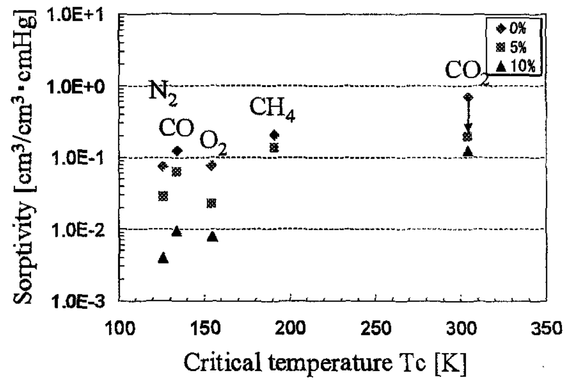

Fig.4 Dependencies of the apparent sorptivity *S* on the iron content for the larger gases such as CO_2, O_2, N_2, CO, and CH_4 as a function of critical temperature Tc.

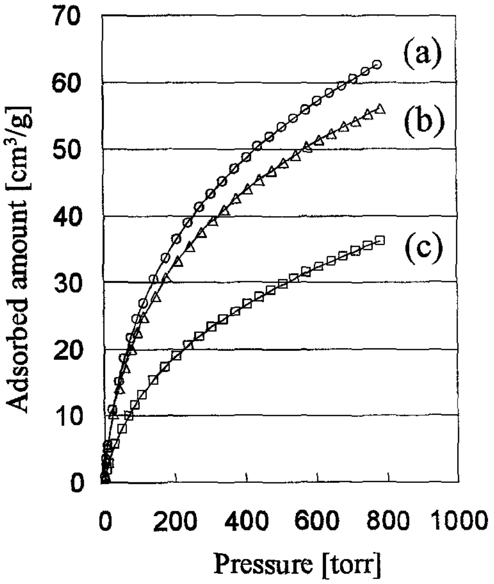

Fig.5 CO_2 adsorption isotherms for the CMS membranes containing (a) 0 wt%, (b) 5 wt%, and (c) 10 wt% of iron.

The limiting pore volume W_0 for CO_2 probe molecule also decreased from 0.25, 0.22 to 0.15 cm^3/g, as the iron content increased from 0, 5 to 10 wt%. Further increase of the iron content to 10 wt% results in almost no change in the permselectivity for H_2/N_2, He/N_2 gas pairs (Fig. 2), because the permeabilities for smaller gases also decreased in a similar manner as larger gases. In the case of this iron content, for larger gases, the decrease in diffusivities mainly contributes to the permeability change (Fig. 3). On the other for smaller gases, further decrease in the diffusivities with the increase in the iron content may contribute to the permeability change.

3.3. Plausible mechanism for selective permeation barrier effect

The present results suggest that iron compound is located near the slit-like micropore mouth within the CMS membrane, resulting in the change in the permselectivity. This can be suggested to be a plausible mechanism for the selective permeation barrier effect. Whether it functions as a sorption barrier or diffusion barrier depends on factors such as the content, the gases permeated, etc. The other possible cause such as a structural change of the carbon matrix induced by a high-temperature interaction with catalytic iron moiety can be undeniable.

4. CONCLUSION

To investigate the effect of permeation barrier on the sorptivity, diffusivity, and permeability of gases, CMS membranes containing iron compound were prepared and characterized. The iron moiety in the CMS matrix is shown to function as a selective permeation barrier (sorption barrier and/or diffusion barrier). The results also suggest that although it is possible to improve the gas separation performance by the introduction of hetero atoms in the carbon matrix, it is necessary to optimize structural factors such as hetero atom content.

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