

Carbon Molecular Sieve Membranes Dispersed with Nano Particles

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Nano particles-containing CMS membranes were prepared by pyrolysis of polyimides dispersed uniformly with precursors and their gas separation performances were examined, to elucidate the permeation mechanism and to further improve the gas separation performance. Consequently, it was suggested that the separation performance could be controlled by doping nano-particles in the CMS membranes, and that optimization of various factors, such as the size, content, and dispersion state of the nano particles would contribute for further improvement of the gas separation performance.

Key words: gas separation, carbon molecular sieve membrane, nano particles

1. INTRODUCTION

Carbon molecular sieve (CMS) membranes prepared by pyrolysis of polymeric precursors are known to exhibit outstanding gas separation performance based on diffusion selectivity and/or sorption selectivity [1]. 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 [2]. This implies that some influence may arise in the sorption, diffusion and permeation of gases by the incorporation of a selective permeation barrier like nano-sized particles near the permeation path (Fig. 1). Moreover, it is expected to contribute to an elucidation of permeation mechanism and improvement in the further separation performance, to investigate and control the selective permeation barrier effect.

The present study examined gas permeation

properties of CMS membranes dispersed with nano particles which are inert or active to gases permeated.

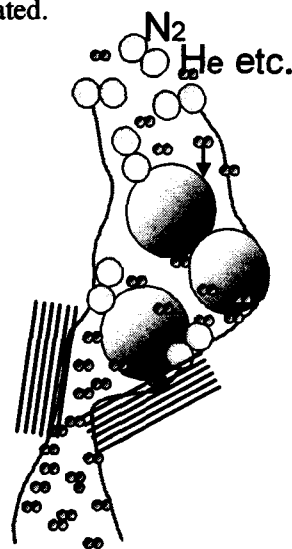


Fig.1 Concept on CMS membranes dispersed with nano particles.

2. EXPERIMENTAL

2.1. Preparation of CMS membranes dispersed with nano-particles

The PMDA-ODA type polyamic acid solution which was uniformly mixed with metal complex (Fe:ferrocene, Ag: Ag acetate, Pd: Pd(acac)₂ and others) of predetermined quantity was cast on a glass plate, followed by drying at ambient atmosphere, imidization under vacuum or nitrogen, and pyrolysis at 873-1273 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 dispersed with nano-particles inside the carbon matrix.

The CMS membranes containing Pd nano particles were also prepared via novel supercritical impregnation method. Batch-type high-pressure vessel in which PMDA-ODA type polyimide films and Pd(acac)₂ were sealed was pressurized by introduction of CO₂ followed by heating. The supercritical impregnation was performed at 313-473 K for 3-24 hrs. The pressure was 19.6 MPa for all impregnation runs. The pyrolysis protocol was the same as others.

2.2. Characterization

Microstructure of the CMS membranes dispersed with nano-particles 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 nano-particles were characterized by TG-MS apparatus (MAC Science, 2000S).

Micropore was analyzed by molecular probe method from analysis of adsorption isotherms at 298 K of probe gas molecules with different kinetic diameter [3] (CO₂, C₂H₆, n-C₄H₁₀, i-C₄H₁₀) by application of Dubinin-Astakhov equations [4],

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

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. The W_0 values were obtained from y-axis intersections in the plots of $\ln W$ against $(\ln(P_s/P))^2$. Samples were degassed at 473 K for 2 hours prior to each adsorption measurement.

Gas permeabilities of CMS membranes were measured at 308-373K with a high vacuum time-lag method [5] under the pressure difference of 1 atm (Fig.2). Permeability values were calculated by using the following equation:

$$P = \frac{dp}{dt} \left(\frac{V \cdot T_0 \cdot L}{p_0 \cdot T \cdot p_f \cdot A_m} \right), \quad (2)$$

where P is the permeability expressed in Barrer [1 Barrer = 1 x 10⁻¹⁰ {cm³(STP)•cm} / {cm²•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 N₂ (ideal separation factor). Apparent sorptivity, S was evaluated by the equation, $S=P/D$, since in the sorption-diffusion model [6], the permeability P is given as the product of the apparent diffusivity, D , and sorptivity, S ($P=DS$).

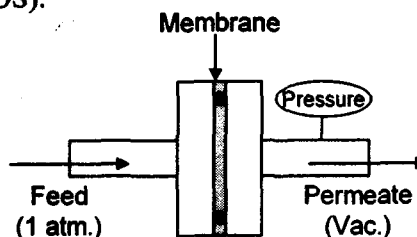


Fig.2 Schematic of high vacuum time-lag method.

3. RESULTS AND DISCUSSION

3.1. CMS membranes dispersed with iron compounds

Figure 3 shows the gas permeation property of iron containing CMS membranes. Although the permeabilities for larger gases, such as, CO₂, O₂, N₂, CO, and CH₄, decreased greatly when the iron content increased, those for smaller gases such as H₂ and He seldom changed. Consequently, the ideal separation factors (permselectivities) for e.g. H₂/N₂, He/N₂ gas pairs increased. It was because the apparent sorptivity $S (=P/D)$ for N₂ became small with the increase in iron content. This coincided with the results of gas adsorption measurement that the limiting pore volume for CO₂ probe gas adsorbed on the iron-containing CMS was smaller than that on CMS without iron. It was suggested that iron is located near the micropore mouth within the CMS membrane, resulting in the novel function as a selective permeation barrier (selective sorption barrier and/or diffusion barrier).

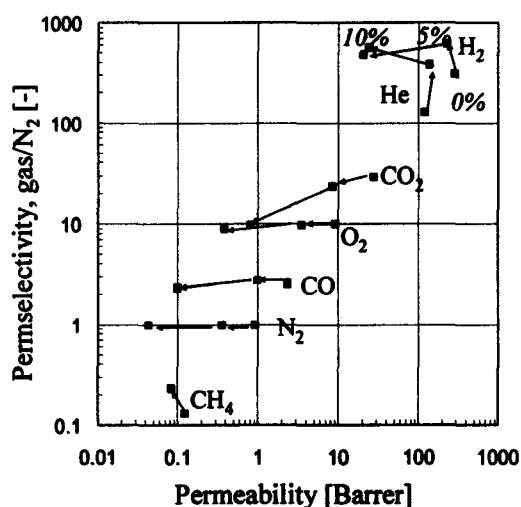


Fig.3 Gas permeabilities for He, H₂, CO₂, O₂, N₂, CO, and CH₄, and their permselectivities for each permeant against N₂ for CMS membranes containing 0, 5, and 10 wt % of iron (measurement temperature: 363 K).

3.2. CMS membranes dispersed with Ag nano particles

It was implied from TEM, XPS and XRD measurements that silver moiety existed as nano-sized Ag metal particle in the CMS matrix. Interesting phenomenon was observed

that O₂/N₂ permselectivity was improved by the incorporation of Ag nano particles and that O₂ diffusion was selectively enhanced compared with that of N₂.

3.3. CMS membranes dispersed with Pd nano particles

TEM photograph revealed that Pd nano particles with average diameter of c.a. 5 nm were uniformly dispersed within the CMS matrix (Fig. 4). The H₂/N₂ permselectivity was greatly improved by the incorporation of Pd nano particles (Fig. 5). Selective H₂ sorption selectivity was also observed in addition to the normal permeation barrier effect.



Fig.4 TEM photograph of CMS membrane dispersed with Pd nano particles with average diameter of c.a.5 nm.

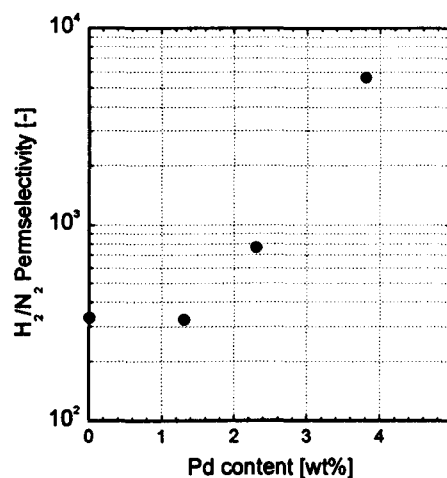


Fig.5 Dependence of H₂/N₂ permselectivity as a function of Pd content.

4. CONCLUSION

To investigate the effect of permeation barrier on the sorptivity, diffusivity, and permeability of gases, CMS membranes containing nano particles were prepared and characterized. The nano particles located near the slit-like micropore mouth in the CMS matrix were shown to function as a selective permeation barrier (sorption barrier and/or diffusion barrier). Whether the nano particles function as selective sorption barrier or diffusion barrier depends on the combination of types of nano particles, gases permeated and matrices. The present results also suggest that although it is possible to improve the gas separation performance by the introduction of nano particles in the CMS matrix, it is necessary to optimize structural factors.

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