# Gas Permeation through Micropores of Carbon Molecular Sieve Membranes Derived from Kapton Polyimide

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The evolution of micropores and the gas permeation properties have been investigated on carbon molecular sieve dense membranes prepared by pyrolysis of Kapton polyimide films under several conditions. With decreasing the pore sizes upon pyrolization under vacuum, the gas permeability decreased, whereas the permselectivity increased. The change in the heating rate was found to affect the permeation properties to a lesser extent; however, the pyrolysis atmosphere (vacuum or inert purge pyrolysis) did not appreciably influence the properties within the experimental conditions studied. The highest permselectivities attained by a membrane were  $H_2/N_2 4700$ ,  $He/N_2 2800$ ,  $CO_2/N_2 122$ , and  $O_2/N_2 36$ , respectively, at 308 K. The permeabilities of the selected gases were shown to be in the order  $H_2 > He > CO_2 > O_2 > N_2$  for almost all the membranes, whose order was not exactly in accordance with the order of kinetic gas diameters. From the temperature dependencies of permeability, diffusivity, and sorptivity of the membrane, the anomalous behavior that  $H_2$ , with a larger kinetic diameter, permeated faster than the smaller He was explained to originate in the larger sorptivity of  $H_2$  than that of He.

## Introduction

A growing interest can be seen in the synthesis of novel inorganic membranes for gas separation mainly because of their chemical and thermal stability. One of the candidates is a carbon molecular sieve (CMS) membrane, which is obtained by pyrolysis of a polymeric precursor. The CMS membrane has extensively been studied and shown to exhibit excellent gas separation performance.<sup>1–11</sup> A distinctive feature is that the controlled pyrolysis of a precursor can yield a series of CMS membranes that possess micropores of desired dimension. Nevertheless, the factors determining the microstructure and gas permeation properties of CMS membranes are not completely open to control, because these properties are significantly affected by several factors and vary from sample to sample. These factors include (a) the choice of polymeric precursor, (b) the membrane formation method, and (c) the pyrolysis condition.

The choice of polymeric precursor (a) is the first important factor since pyrolysis of each precursor may bring about different CMS membranes, sometimes even leaky ones. Polyfurfuryl alcohol was used by Bird and Trimm<sup>1</sup> to prepare unsupported and supported CMS membranes, but it proved impossible to prepare a continuous membrane. Koresh and Soffer<sup>2,3</sup> carried out detailed studies on the gas separation performance of CMS hollow fiber membranes derived from thermosetting polymers. Rao and Sircar<sup>4</sup> prepared nanoporous carbon membranes by pyrolysis of a polyvinylidene chloride layer coated on a graphite disk support, in order to separate gas mixtures by selective surface flow. Shusen et al.5 proposed a one-step preparation method of asymmetric CMS membranes, consisting of the formation of phenol formaldehyde film followed by pyrolysis and unequal oxidation steps. In recent years, polyimides are considered to yield CMS membranes with better separation properties. Jones and Koros<sup>6</sup> reported gas separation properties of CMS asymmetric hollow fiber membranes prepared by pyrolysis of 6F-containing polyimide. The polyimide used was derived from a reaction of 2,4,6,-trimethyl-1,3-phenylene diamine, 3,3',4,4'-biphenyltetracarboxylic dian-

Whether the membrane formation (b) is carried out either by coating of the precursor on porous support or by phase inversion techniques, both followed by pyrolysis steps, or by one-step pyrolysis of precursor dense film is another factor. In some of the past studies<sup>5,6,11</sup> asymmetric membranes have been prepared, because the thinner skin layer formed on a porous support is desirable for practical use in providing higher fluxes. Our previous study,<sup>10</sup> however, revealed that the microstructure and gas permeation properties of asymmetric CMS membranes prepared on the basis of the phase inversion technique were difficult to control and were sensitively influenced by preparation conditions particularly at the gelation step. The formation method<sup>1,4,7</sup> of repeating the coating-pyrolysis cycle for several times until no pinholes are depicted also needs time and special care. The simplest method<sup>8,9</sup> of pyrolysis of commercially available Kapton film instead can produce dense CMS membranes with better reproducibility. These dense membranes are not practical from the viewpoint of industrial application; however, they are preferable to asymmetric ones in making clear the factors that determine the basic properties.

The pyrolysis condition (c), such as the pyrolysis temperature, the heating rate, and the pyrolysis atmosphere, is the third factor. Although the pyrolysis temperature should be varied in accordance with the precursor polymer, all the temperatures in the past studies fall within the range 773-1273 K. The heating rate, typically in the range 1-13.3 K/min, may also affect the membrane performance. The choice of pyrolysis atmosphere has drawn increasing attention, especially because the atmosphere can change the pore size and geometry or even the nature

hydride (BPDA), and 5,5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-isobenzofurandione. Hayashi et al.<sup>7</sup> prepared CMS membranes by dip-coating of BPDA–4,4'-oxydianiline (ODA) solution on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> porous support tube followed by pyrolysis. We have reported that both the flat, dense<sup>8,9</sup> and asymmetric capillary<sup>10</sup> CMS membranes prepared by pyrolysis of a Kapton type polyimide under controlled conditions exhibited the highest gas permselectivities among those in the past. The Kapton type polyimide was derived from pyromellitic dianhydride (PMDA) and ODA.

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Figure 1. Pyrolization process of Kapton polyimide membranes.

of the surface by sintering (pore closure) or activation (pore opening by removal of surface groups or by burn-off) effects. The atmospheres of He,<sup>11</sup> Ar,<sup>8,11</sup> or N<sub>2</sub><sup>4,5,7</sup> were used for the inert purge pyrolysis, whereas the vacuum pyrolysis technique was employed by Koros et al.<sup>6,11</sup> and Suda et al.<sup>9,10</sup> Geiszler and Koros<sup>11</sup> compared the two pyrolysis techniques on asymmetric CMS membranes derived from 6F-containing polyimide and concluded that the vacuum pyrolysis produced more selective but less productive membranes than the inert purge pyrolized membranes. They also investigated the other variables and discussed effects of residual oxygen in inert gases. All of the above factors may diversify the resulting membrane properties, and thus should be controlled to yield better CMS membranes, but are not compared thoroughly.

Another significant problem is that few studies have investigated gas permeation properties in connection with the microstructure of a membrane and the diffusivity and the sorptivity of a penetrant. One of the interesting phenomena encountered is the anomalous behavior<sup>4,8–10</sup> that H<sub>2</sub>, with a larger kinetic diameter, permeates through CMS membranes faster than the smaller He. Considering that the permeability of a given membrane may be the product of the diffusivity (kinetic factor) and the sorptivity (thermodynamic factor),<sup>12</sup> studies on the two factors are indispensable for understanding the permeation behavior. Therefore a systematic study on both the microstructure and the gas permeation properties of wellcharacterized flat, dense CMS membranes may serve to explain all aspects of CMS membrane properties.

One of the objectives in the present study is a clarification of the factors that determine the microstructure and the permeation properties of CMS dense membranes derived from Kapton polyimide film. The other is to gain insight into the permeation mechanism through the study of permeability versus kinetic diameter in connection with diffusivity and sorptivity.

#### **Experimental Section**

1. Preparation of CMS Membranes and Characterization. The CMS membrane was fabricated by pyrolysis of Kapton polyimide film 100H (Toray, Dupont Inc., thickness 25  $\mu$ m) between graphite blocks at mainly 873–1273 K for 2 h with a heating rate of 10 K/min under a vacuum of 10<sup>-5</sup> Torr<sup>9</sup> (Figure 1). Films of 125  $\mu$ m thickness (500H) were also used



Figure 2. Illustration of the apparatus for gas permeation measurement by the time-lag method.

as precursor, in order to measure accurate time lags for the smaller penetrants such as He and H<sub>2</sub>. Heating rate (1.33-13.3 K/min) and pyrolysis atmosphere (under vacuum or Ar flow) were also controlled so as to study the effects of pyrolysis conditions on the CMS membrane properties. All the membranes were allowed to cool to room temperature under each atmosphere. The microstructure of the prepared CMS membranes was investigated by Fourier transform infrared spectroscopy (Nicolet, Magna 550), elemental analysis (Carlo Erba, 1106 & EA-1108), XPS (X-ray photoelectron spectroscopy) (Perkin Elmer, PHI 5600ci), X-ray diffractometry (Rigaku, RAX 12), high-resolution transmission electron microscopy (Jeol, JEM-2000FX), and gas sorption measurements (Nihon Bell, Belsorp 28).

2. Analysis of Pore Size Distribution. Pore size distributions were estimated by the molecular probe method from analysis of sorption isotherms at 298 K of probe gas molecules with different kinetic diameter  $\sigma^{13}$  (CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *i*-C<sub>4</sub>H<sub>10</sub>) by application of Dubinin–Astakhov equation:<sup>14</sup>

$$W = W_0 \exp\{-(A/E)^n\}$$
(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 sorbate. The sorption 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 sorption data were analyzed with the parameter n = 2, in accord with those for microporous carbon.<sup>7</sup> The  $W_0$  values were obtained from *y*-axis intersections in the plots of ln *W* against  $A^2 = (RT \ln(p_s/p))^2$ . Samples were degassed at 573 K for 2 h prior to each sorption measurement.

**3.** Gas Permeation Measurements. Gas permeabilities were measured at 308–373 K with a high-vacuum time-lag method<sup>15,16</sup> under the pressure difference of 1 atm (Figure 2). Permeability values were calculated by using the following equation:

$$P = \frac{\mathrm{d}p}{\mathrm{d}t} \left( \frac{VT_0 L}{p_0 T p_\mathrm{f} A_\mathrm{m}} \right) \tag{2}$$

where *P* is the permeability expressed in Barrer [1 Barrer =  $1 \times 10^{-10} \{\text{cm}^3(\text{STP})\cdot\text{cm}\}/\{\text{cm}^2\cdot\text{s}\cdot\text{cmHg}\}$ ], 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



Figure 3. Changes in the weight and film diameter as a function of pyrolysis temperature.



Figure 4. Infrared spectra of (a) original Kapton film and Kapton films pyrolized at (b) 873, (c) 1073, and (d) 1273 K under vacuum for 2 h.

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 within an accuracy of  $\pm 0.5$  K. Permselectivity is defined in the present study as the ratio of permeability of chosen gas over that of N<sub>2</sub>:ideal separation factor.

# **Results and Discussion**

**1.** Pyrolization Process of Kapton Polyimide Film under Vacuum. Upon heating, the color of the film changed from transparent yellow to dark brown, and then black due to pyrolization. The weight and the film diameter decreased abruptly at around 800-900 K and then gradually (Figure 3). The weight loss at a lower pyrolysis temperature of about 800-900 K is attributed to  $O_2^{17}$  or CO and  $CO_2$ ,<sup>18</sup> at an intermediate temperature of 900-1100 K to  $H_2$ ,<sup>18</sup> and at higher than 1100 K mainly to  $N_2^{17,18}$  released during thermal degradation of Kapton polyimide. The ATR infrared spectra shown in Figure 4 indicate that the peak intensities for the aliphatic or aromatic C-N (1100-1200 cm<sup>-1</sup>, 1300-1400 cm<sup>-1</sup>), C=O ( $\sim 1700$  cm<sup>-1</sup>, 1200-1300 cm<sup>-1</sup>), and C-H bonds (600-900 cm<sup>-1</sup>, 1000-1200 cm<sup>-1</sup>) were reduced at higher pyrolysis temperatures.

It is characteristic of the Kapton polyimide film that pyrolysis of the film yields CMS dense membranes without pinholes despite the rather large weight loss of about 40% and shrinkage of about 25% at 1273 K. The micropores of CMS membranes are considered to be developed by the evolved gases channeling out of the matrix during pyrolysis. Thus the pyrolysis condition is expected to strongly affect the pore structure, which will be described later.

The CMS membrane obtained at 1273 K under vacuum was revealed to consist of almost only carbon by the infrared spectrum (Figure 4 (d)). The elemental analysis revealed that the membrane KP1273 contains about 85% carbon, 7.6%



**Figure 5.** High-resolution transmission electron micrographs of the CMS membranes.

oxygen, 5.9% nitrogen, 1.0% hydrogen, and 0.5% other elements. The unexpected large amount of oxygen may be due to surface-sorbed oxygen, as was suggested by Jones and Koros,<sup>6</sup> where the oxygen was able to be etched away by Ar ablation. The O<sub>1s</sub> peak located at around the binding energy of 532.5 eV in XPS spectra of our 1273 K membrane indeed became negligibly small after Ar etching for only 30 s, while the peaks of C<sub>1s</sub> (284 eV) and N<sub>1s</sub> (399 eV) were almost unchanged even after the etching, resulting in a carbon content of about 95%.

These CMS membranes were essentially X-ray amorphous, and the crystallinity became higher with increasing the pyrolysis temperature.<sup>9</sup> The carbon prepared by the pyrolysis of organic materials is known to have a turbostratic structure,<sup>19</sup> in which layer-planes of graphite-like microcrystallines are dispersed in a noncrystalline carbon. The high-resolution transmission electron micrographs (Figure 5) demonstrate that such a graphite-like structure starts to appear and develops at higher pyrolysis temperature. The abrupt evolution of gases in the early stage of pyrolization through either imide ring cleavage or C–N bond cleavage processes<sup>18</sup> changes the crystalline state of polyimide to an amorphous state, and the evolution of mainly N<sub>2</sub> gas in the further pyrolysis steps makes the layer-planes of graphite-like microcrystallines grow.

2. Pore Analysis of the Vacuum-Pyrolized CMS Membranes. To gain further insight into the structural change of the CMS membranes, we estimated pore size distribution. Sorption isotherms of probe molecules (Figure 6) imply how the pore size changes with increase in pyrolysis temperature. The membrane prepared at lower temperature (KP873) sorbed to some extent even *i*-C<sub>4</sub>H<sub>10</sub>, the largest sorbate ( $\sigma = 5.0$  Å),

100 A



Figure 6. Sorption isotherms of probe molecules for the CMS membranes (measured at 298 K).



Figure 7. Typical Dubinin–Astakhov plots for the CMS membrane KP1073.

whereas the membrane prepared at 1273 K (KP1273) sorbed only CO<sub>2</sub>, the smallest sorbate ( $\sigma = 3.3$  Å). All these isotherms were well fitted with the Dubinin-Astakhov equation<sup>14</sup> (Figure 7). The pore size distributions, plots of the limiting micropore volume  $W_0$  against the kinetic diameters of probe sorbate molecules, are shown in Figure 8a. It is clear from the distributions that with increasing the pyrolysis temperature, both the limiting pore volume and pore size decrease. The plots also indicate that pore size distributions become sharper when the pyrolysis temperatures rise. Figure 8b shows that pyrolysis at higher temperatures reduces the portion of larger pores. The  $W_0$  values for CO<sub>2</sub> increased from 0.15 (KP1273) to 0.22 cm<sup>3</sup>/g (KP873) with decreasing pyrolysis temperature, all of which were larger than that of the silica microporous membrane ( $W_0$ =  $0.11 \text{ cm}^3/\text{g}$ ).<sup>20</sup> Hayashi et al.<sup>7</sup> reported that the  $W_0$  increased from 0.16 to a maximum of about 0.36 cm<sup>3</sup>/g at a pyrolysis temperature of 1073 K for BPDA-ODA polyimide-derived CMS membranes. The results may indicate the possibility of larger micropore volume for CMS membranes derived from the other polymers than from Kapton. Assuming that the characteristic energy of sorption E obtained by CO<sub>2</sub> sorption is related to average pore size,<sup>7</sup> the values of 10.7, 11.4, and 11.5 kJ/ mol, for KP873, KP1073, and KP1273, respectively, were in accordance with the pore size reduction upon heating. The microstructure (pore size, pore volume, etc.) can therefore be tailored by controlling the pyrolysis temperature.

**3.** Gas Permeation Properties of the Vacuum-Pyrolized CMS Membranes. Figure 9 compares the permeation performance of the CMS membranes pyrolized under various conditions (pyrolysis temperature, heating rate, and pyrolysis atmosphere). The pyrolysis temperature was found to have the



**Figure 8.** (a, top) Pore size distributions of the CMS membranes; plots of limiting micropore volume  $W_0$  against kinetic diameters of probe sorbate molecules. (b, bottom) Change in volume of each pore size of the CMS membranes.

greatest effect on the microstructure and the gas permeation behavior for the vacuum-pyrolized CMS membranes; that is, the permeabilities of the selected gases measured at 373 K became lower, whereas the gas permselectivities became higher with increasing the pyrolysis temperature. For  $H_2/N_2$  and  $CO_2/$ N<sub>2</sub> gas pairs, the permselectivities reached up to 1450 and 101 at 308 K, respectively, for the membrane KP1273 (Table 1), whose values were much higher than those reported<sup>1-7</sup> by 1 or 2 orders of magnitude. Such extremely high gas permselectivities imply that the CMS membrane has a molecular sieving effect, by which the membrane can discriminate between the small and larger molecules. Thus the larger molecules such as N<sub>2</sub> are more restricted than the smaller ones to diffuse into the narrower pore whose size is close to or smaller than their kinetic gas diameters. In view of the turbostratic structure, gases are likely to permeate both through the cross-linked voids of the amorphous region and the interlayer spacing of the graphite-



**Figure 9.** Gas permeabilities (measured at 373 K) of the CMS membranes prepared at 873, 1073, and 1273 K under vacuum and at 1223 K under Ar flow. Permeabilities are given in Barrer, where 1 Barrer equals  $1 \times 10^{-10}$  cm<sup>3</sup>(STP)·cm / cm<sup>2</sup>·s·cmHg.

like microcrystallines. The question is which path mainly contributes to the molecular sieving effect, and it is the subject of further investigation.

The reasons that we obtained the highest permselectivity for the selected gases are having pyrolized the film at appropriate temperature and selecting the polymer film suitable for the pyrolysis. The membrane pyrolized at lower temperatures (KP873) exhibited higher permeability (for instance,  $PH_2 =$ 1600 Barrer at 308 K) with relatively much loss in permselectivity ( $H_2/N_2 = 19.6$ ). This is because of a large amount of micropore volume whose size is large enough for N<sub>2</sub> molecules  $(\sigma = 3.64 \text{ Å})$  to permeate through. This means that the pyrolysis temperature should be varied in accordance with target gases to be separated. Pyrolysis of the films other than Kapton polyimide might bring about the presence of a large amount of an amorphous portion or larger pores or even cracks,<sup>1</sup> resulting in the preference for permeation of larger gases through these voids. Rao's nanoporous carbon membranes<sup>4</sup> prepared by pyrolysis of polyvinylidene chloride layer coated on a graphite disk support may be one of the cases, although the membranes could efficiently separate hydrocarbons from H<sub>2</sub> by competitive adsorption and surface diffusion of the more strongly adsorbed components.

4. Effects of the Other Pyrolysis Conditions on Gas Permeation Properties. Figure 9 also shows that the permeability decreases with decreasing the heating rate from 13.3 to 1.33 K/min. The reason for this trend may be that with decreasing the heating rate the pyrolization proceeds very slowly, which may make the pore smaller. The longer total time for pyrolysis may also contribute to the pore size reduction due to a sintering effect. The membrane pyrolized at the slowest heating rate of 1.33 K/min under Ar flow exhibited the highest permselectivity of all the membranes studied (H<sub>2</sub>/N<sub>2</sub> 4700 and O<sub>2</sub>/N<sub>2</sub> 36 at 308 K), indicating the possibility of their use in the processes of hydrogen recovery, oxygen enrichment of air, etc.

It is worthwhile mentioning the effects of pyrolysis atmosphere, because from a study on several factors of an inert purge pyrolysis technique Geiszler and Koros<sup>11</sup> concluded that even the residual trace levels of oxygen (0.3 ppm) in the inert gases affected the membrane properties. They also mentioned that the trace of oxygen made the pore larger, but the reduction in the purge flow rate from 200 to 20 cm<sup>3</sup>(STP)/min had the opposite effect of reduction of pore size presumably due to deposition of carbon. To investigate the inert gas effect, the pyrolization was carried out also in the present study under high purity Ar flow (purity >99.9995%, flow rate 500 cm<sup>3</sup>(STP)/ min). According to the supplier Nihon-sanso. Co. Ltd., the Ar contained at most 0.2 ppm of oxygen. The trace of oxygen was thus reduced by passing the Ar through heated graphite blocks at the inlet side of a furnace. Comparing the difference in the pyrolysis atmosphere from the two curves for KP1273 (10 K/min, vac) and KP1223 (13.3 K/min, Ar) (also in Table 1), the trace of oxidative gases was shown not to exhibit a severe effect on the permeation performance owing to the reduction of the trace level and to the higher flow rate.

5. Order of Gas Permeabilities against Kinetic Diameters of Gas Molecules. The permeabilities of the selected gases measured at 373 K (Figure 9) and at 308 K (Table 1) were shown to be in the order  $H_2 > He > CO_2 > O_2 > N_2$  for all the CMS membranes except for KP873. The order was not exactly in accordance with the order of kinetic gas diameter,<sup>13</sup> since the kinetic diameter sequence is  $He < H_2 < CO_2 < O_2 < N_2$ . Similar results have been obtained for our asymmetric CMS membranes<sup>10</sup> and for Rao's nanoporous carbon membranes,<sup>4</sup> while the silica microporous membrane with a pore size of less than 20 Å used by Shelekhin et al.<sup>21</sup> exhibited an "expected" ordinary trend; that is, the permeabilities followed the order of kinetic diameter. It is valuable to give an interpretation for the order of gas permeabilities against kinetic diameter, since this kind of correlation is related to the estimation of molecular

TABLE 1: Gas Permeabilities and Permselectivities Measured at 308 K for the CMS Membranes Prepared At 873, 1073, and 1273 K under Vacuum, and at 1223 K under Ar Flow; The Data for the Thicker Membrane (Thickness 113  $\mu$ m) Are Shown within Parentheses

	KP873 (10 K/min, vac)	KP1073 (10 K/min, vac)	KP1273 (10 K/min, vac)	KP1223 (13.3 K/min, Ar)	KP1223 (4.5 K/min, Ar)	KP1223 (1.33 K/min, Ar)
$PH_e^a$	534	248	27.9	26.4	21.1	11.6 (4.97)
$H_e/N_2^b$	6.54	81.4	680	618	739	2810
$PH_2$	1600	669	59.4	53.1	41.3	19.4 (6.89)
$H_2/N_2$	19.6	220	1450	1240	1450	4700
$PCO_2$	1820	128	4.15	3.54	2.51	0.50
$CO_2/N_2$	22.2	42.2	101	82.7	87.7	122
$PO_2$	383	34.8	0.96	0.92	0.66	0.15
$O_2/N_2$	4.70	11.5	23.4	21.6	23.0	36.0
$PN_2$	81.6	3.04	0.04	0.04	0.03	0.004
$N_2/N_2$	1	1	1	1	1	1

<sup>*a*</sup> Permeability [in Barrer] measured at 308 K; 1 Barrer =  $1 \times 10^{-10} \{\text{cm}^3(\text{STP})\cdot\text{cm}\}/\{\text{cm}^2\cdot\text{s}\cdot\text{cmHg}\}$ . <sup>*b*</sup> Permselectivity for A and B gases:  $P_A/P_B$ .

TABLE 2: Properties of Penetrants and Gas Permeation Data (Permeability *P*, Diffusivity *D*, and Sorptivity *S*) for the Membrane KP1223 (1.33 K/min, Ar, thickness 22  $\mu$ m) Obtained at 373 K, and the Corresponding Pre-exponential Factors *P*<sub>0</sub>, *D*<sub>0</sub>, *S*<sub>0</sub>, Apparent Activation Energies for Permeation *E*<sub>P</sub>, for Diffusion *E*<sub>D</sub>, and Heat of Sorption *H*<sub>S</sub>; The Latter Values Were Determined through Temperature Dependencies of Permeability, Diffusivity, and Sorptivity within the Temperature Range 308–373 K; The Data for the Thicker Membrane (Thickness 113  $\mu$ m) Are Shown within Parentheses (1 Barrer = 1 × 10<sup>-10</sup> {cm<sup>3</sup>(STP)·cm}/{em<sup>2</sup>·s·cmHg})

penetrant	kinetic diameter $\sigma$ [Å] <sup>13</sup>	L-J potential $\epsilon/k [K]^{25}$	P [Barrer]	D [cm <sup>2</sup> /s]	S [cmHg <sup>-1</sup> ]	P <sub>0</sub> [Barrer]	<i>D</i> <sub>0</sub> [cm <sup>2</sup> /s]	$S_0$ [cmHg <sup>-1</sup> ]	E <sub>P</sub> [kJ/mol]	E <sub>D</sub> [kJ/mol]	<i>H</i> s [kJ/mol]
He	2.60	10.2	18.1			152			6.61		
			(8.90)	$(3.90 \times 10^{-7})$	$(2.28 \times 10^{-3})$	(143)	$(1.83 \times 10^{-5})$	$(7.82 \times 10^{-4})$	(8.62)	(11.9)	(-3.32)
$H_2$	2.89	59.7	28.1			151			5.27		
			(11.4)	$(1.57 \times 10^{-7})$	$(7.25 \times 10^{-3})$	(124)	$(1.91 \times 10^{-5})$	$(6.50 \times 10^{-4})$	(7.42)	(14.9)	(-7.47)
$CO_2$	3.30	195	0.47	$1.13 \times 10^{-10}$	$4.18 \times 10^{-1}$	0.35	$1.88 \times 10^{-8}$	$1.87 \times 10^{-3}$	-0.95	15.9	-16.9
$O_2$	3.46	107	0.26	$5.01 \times 10^{-10}$	$5.11 \times 10^{-2}$	3.05	$5.85 \times 10^{-7}$	$5.22 \times 10^{-4}$	7.74	21.9	-14.2
$N_2$	3.64	71.4	0.013	$2.75 \times 10^{-11}$	$4.84 \times 10^{-2}$	2.86	$7.31 \times 10^{-7}$	$3.93 \times 10^{-4}$	16.7	31.8	-15.1

dimensions from sorption kinetics<sup>22</sup> and the theoretical calculation of critical pore dimensions.<sup>23</sup>

A detailed study was thus conducted for the membrane KP1223 (1.33 K/min, Ar) in order to understand the permeability order. As is well-known, a CMS membrane produced by pyrolysis of a polymeric precursor is essentially a microporous material (the pore size is a few angstroms) with a turbostratic structure.<sup>19</sup> There seems no complete theory that is applicable to totally explain the gas permeation behavior through such a small micropore with a size comparable to the dimensions of the penetrant molecules. However considering the rather high sorptivity of gases in CMS than in the polymer and the fact that the so-called sorption time-lag<sup>16</sup> is observed on our membranes, it seems acceptable to apply a sorption—diffusion theory<sup>12</sup> of the polymer membrane to the gas permeation in CMS membranes in an analogous way.

Phenomenologically in the sorption—diffusion model, the permeation process of gas molecules through a membrane under a pressure difference is explained to consist of three steps: (I) sorption of gas molecules at the membrane surface of a higher pressure side, (II) diffusion of the sorbed gas molecules through the membrane under a pressure gradient, and (III) desorption of gas molecules at the membrane surface of a lower pressure side. In an ideal case where the diffusivity D and the sorptivity S are constant, applications of Fick's law of diffusion to step II and a linear relationship of the external gas pressure and the corresponding equilibrium concentration to the steps I and III give a simple expression:

$$P = DS \tag{3}$$

where the permeability P equals by definition the steady state flux divided by the driving pressure across the membrane normalized by the membrane thickness. The expression (3) means that the product of the diffusivity (kinetic factor) and the sorptivity (thermodynamic factor) determines the permeability of a penetrant through the membrane. The apparent diffusivity D was calculated by the equation<sup>24</sup>

$$D = L^2/6\theta \tag{4}$$

where  $\theta$  is the sorption time-lag observed in the early stage of permeation. Accordingly the apparent sorptivity *S* can be estimated from the expression (3) by using the obtained *P* and *D* values, while in the case where the diffusivity and the sorptivity are concentration dependent, they are given as

$$D = \int_{C_1}^{C_h} D(C) \, \mathrm{d}C / \int_{C_1}^{C_h} \mathrm{d}C$$
 (5)

$$S = (C_{\rm h} - C_1)/(p_{\rm h} - p_1)$$
 (6)

where D(C) is the local concentration-dependent diffusivity at a local point of concentration *C*, and *C*<sub>h</sub> and *C*<sub>l</sub> are the sorbed penetrant concentrations at the feed and permeate sides, respectively. As shown in the sorption isotherms (Figure 6), a straight line tangent to the isotherms at each point of pressure that corresponds to each sorptivity is not constant. Consequently the values of *D* and *S* reported in the present study are apparent ones expressed respectively by the eqs 5 and 6. Recalling the permeability being given as the product of the diffusivity and the sorptivity, the permeability may be expressed as follows:

$$P = P_0 \exp(\overline{E_P}/RT) = DS$$
  
=  $D_0 \exp(\overline{E_D}/RT)S_0 \exp(-H_S/RT)$  (7)  
=  $D_0S_0 \exp(-(E_D + H_S)/RT)$ 

Therefore in the present study, the apparent activation energy for permeation  $E_P$  was assumed to be the sum of the apparent activation energy for diffusion  $E_D$  and the apparent heat of sorption  $H_S$ .

Table 2 lists the data of the permeability P, diffusivity D, sorptivity S at 373 K, and the apparent activation energies for permeation  $E_{\rm P}$ , for diffusion  $E_{\rm D}$ , and the heat of sorption  $H_{\rm S}$ , those parameters being estimated from the temperature dependencies of permeability, diffusivity, and sorptivity. The diffusivities decreased from  $10^{-7}$  to  $10^{-11}$  [cm<sup>2</sup>/s] in order with the kinetic diameters  $\sigma$  of penetrants, whereas the sorptivities increased from  $10^{-3}$  to  $10^{-1}$  [cmHg<sup>-1</sup>] in order with the Lennard-Jones potential  $\epsilon/\kappa$ .<sup>25</sup> This greater change in the diffusivity compared to that in the sorptivity implies that the excellent permselectivity of the CMS membranes is attributed to the molecular sieving effect that comes mainly from the dependence of diffusivity on the pore size. Rao's comment<sup>4</sup> that "a very small change ( $\sim 0.5$  Å) in the pore diameter in the 3-10 Å range reduces the diffusivity by an order of magnitude" is instructive in this respect. Comparison of the calculated diffusivity of N<sub>2</sub> as a function of pore diameter at 296 K<sup>4</sup> with the measured N<sub>2</sub> diffusivity (order of  $10^{-8}$  to  $10^{-11}$  [cm<sup>2</sup>/s]) on our CMS membranes suggests that the average pore sizes of the membranes are around 4 Å, consistent with those estimated from the molecular probe method (Figure 8). The  $E_{\rm D}$  data and  $-H_{\rm S}$  data were correlated linearly at a positive slope with the square of kinetic diameter and with  $\epsilon/\kappa$ , respectively. It was thus also implied that gases with larger cross-sectional area need greater activation energies for diffusion and that the more condensable gases are more easily sorbed.

The anomalous behavior that the larger H<sub>2</sub> gas ( $\sigma = 2.89$  Å) permeates faster than the smaller He gas ( $\sigma = 2.60$  Å) through our membranes including the previous ones<sup>8–10</sup> and Rao's

nanoporous membranes<sup>4</sup> may be connected with the sorptivity difference. The present study revealed that at 373 K the diffusivity of He is about 2 times larger than that of  $H_2$ , while the sorptivity of He is about one-third of that of  $H_2$  (Table 2). The above mentioned results imply that the larger sorptivity of  $H_2$  than that of He contributes the higher  $H_2$  permeability. The phenomenon that CO<sub>2</sub> ( $\sigma = 3.30$  Å) permeates faster than the smaller He ( $\sigma = 2.60$  Å) observed for the membrane KP873 (Figure 9, Table 1) and for Hayashi's CMS membrane pyrolized at 873 K<sup>7</sup> may be explained in a similar manner. It should be born in mind, however, that the present study reports only the ideal separation factors and not the mixed gas separation factors. Considering that the heavier hydrocarbons permeated faster than the smaller H<sub>2</sub> or CH<sub>4</sub> by selective surface flow through Rao's nanoporous carbon membranes,<sup>4</sup> the present CMS membranes are also expected to exhibit different behavior on mixed gas separations. Mixed gas permeation measurements now undertaken may give further insight into the permeation mechanism.

### Conclusions

It was proven in the present study that a series of CMS dense membranes with tailored microstructure (pore size, pore volume, etc.) can be obtained by controlling pyrolysis conditions (pyrolysis temperature, heating rate, and pyrolysis atmosphere). Of the pyrolysis conditions, the heating temperature had the greatest effect on microstructure and gas permeation properties. The trace of oxygen in Ar purge gas was shown within the present study not to exhibit a severe effect, presumably due to the reduction of the trace level and higher flow rate. The membrane pyrolized with the slowest heating rate of 1.33 K/min under Ar flow exhibited the highest permselectivity of all the membranes studied (H<sub>2</sub>/N<sub>2</sub> 4700 and  $O_2/N_2$  36 at 308 K). The excellent permselectivity of the CMS membranes was attributed to the molecular sieving effect that comes mainly from the dependence of diffusivity of penetrants on the size of the micropore. Furthermore, the higher permeabilities of H<sub>2</sub> and/ or CO2 gases compared with that of the smaller He gas were ascribed to the larger sorptivities of the former two gases.

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## **References and Notes**

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