

Preparation and gas separation performance of composite carbon molecular sieve membranes derived from NTDA-based polyimides

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Carbon molecular sieve(CMS) membranes were prepared by pyrolyzing composite precursor membranes at the temperatures ranging from 500 to 700 °C in a N₂ flow for 1 h. The precursor membranes were prepared by coating NTDA-based polyimides with CF₃ group and/or sulfonic acid triethylammonium salt on ceramic porous supports. The CF₃ group and the sulfonic acid salt decomposed in the range of 450 to 700 °C and 300 to 400 °C, respectively. With increasing pyrolysis temperature, gas permeances for the CMS membranes increased and then decreased, while ideal separation factors continued to increase. The optimal pyrolysis temperature was around 600 °C. The composite CMS membranes prepared here had defect-free top layer of 1.5 to 4 μm thick. Compared to the CMS membranes reported in literature, they displayed higher O₂ and CO₂ gas permeances with reasonably high ideal separation factors for O₂/N₂ and CO₂/N₂ separations.

Key words: NTDA-based polyimides, composite membranes, carbon molecular sieve membranes, trifluoromethyl group, sulfonic acid group, gas permeation and separation

1. INTRODUCTION

Carbon molecular sieve(CMS) membranes are promising as gas separation membranes because of their excellent permeation and separation properties and good thermal and chemical stability [1]. We have reported that flat pyrolytic membranes prepared by pyrolyzing 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA)-based polyimides with pendant sulfonic acid groups at 450 °C displayed higher performance for CO₂/N₂ and propylene/propane separations [2]. The sulfonic acid groups decomposed but the substantial cleavage of the polyimide backbone did not yet occur at 450 °C. Therefore, the membranes were more flexible than conventional CMS membranes. The higher permeability may be due to large amounts of microvoids caused by "template-like effect" of sulfonic acid groups.

CMS membranes are commonly prepared by pyrolyzing polymeric membranes at temperatures ranging from 500 to 800 °C. It is interesting to investigate gas separation performance of the membranes prepared by pyrolysis of the sulfonated polyimides(SPIs) at high temperatures. The flat membranes pyrolyzed at these temperatures, however, were not self-standing. A composite CMS membrane composed of a carbonized layer on an inorganic porous support has an advantage of good mechanical strength. In this study, we report on the composite CMS membranes derived from the polyimides prepared from NTDA and sulfonated or non-sulfonated diamines.

2. EXPERIMENTAL

2.1 Materials and synthesis of polyimides

NTDA, 2,2'-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (BAPHF) and 4,4'-bis(4-aminophenoxy)biphenyl (BAPB) were purchased from Tokyo Kasei Co.. 2,2'-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane disulfonic acid (BAPHFDS) and 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS) were prepared by direct sulfonation of BAPHF and BAPB, respectively, as previously reported [3,4].

Figure 1 shows the chemical structures of precursor polyimides. They were synthesized by a one-step method using triethylamine, benzoic acid and m-cresol. [3,4]

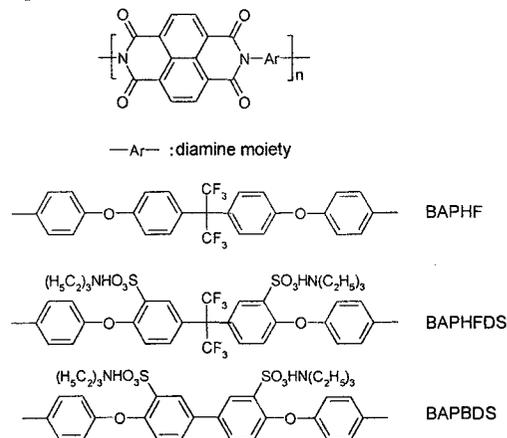


Fig.1 Chemical structures of NTDA-based polyimides

2.2 Membrane preparation

A dip-coating method was employed for preparation of composite CMS membranes. Porous α alumina tubes (average pore size: $0.14 \mu\text{m}$, outer diameter: 2.1mm , porosity: 40–48%) were used as membrane supports. The supports were coated with a *m*-cresol solution of polyimide by dipping and dried in vacuum at $150 \text{ }^\circ\text{C}$ for 5 h. In some cases, the coating was repeated three times, where the coated tubes were dried at $120 \text{ }^\circ\text{C}$ for 2h between the coatings. SPIs were used in triethylammonium salt form. The membranes were then pyrolyzed at a temperature ranging from 500 to $700 \text{ }^\circ\text{C}$ for 1 h at a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ and a nitrogen flow rate of $100 \text{ mL}/\text{min}$. This procedure is called the first C/P cycle in this work. Some membranes were prepared by repeating this C/P cycle one more time.

2.3 Measurements

Thermogravimetry-Mass Spectrometry (TG-MS) was carried out on a Rigaku TG-8120 connected to a Shimadzu GCMS-QP 5050 at a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ in helium (flow rate: $100 \text{ cm}^3/\text{min}$). Scanning Electron Microscopy (SEM) was performed using a Hitachi S2300. Gas permeation experiments were carried out at $35 \text{ }^\circ\text{C}$ and 1 atm using a vacuum time lag method [5] to determine the gas permeance R ($\text{GPU} = 1 \times 10^{-6} \text{ cm}^3(\text{STP}) / (\text{cm}^2 \text{ s cmHg})$), and the ideal separation factor as the R ratio.

3. RESULTS AND DISCUSSION

3.1 TG-MS analysis

Figure 2 shows TG-MS analysis result of the precursor NTDA-BAPHFDS polyimide (PI). Two stages of decomposition were observed. In the first stage, 30% weight loss occurred in the range of $300 \text{ }^\circ\text{C}$ to $400 \text{ }^\circ\text{C}$, accompanied by the evolution of SO_2 , H_2O , CO , CO_2 and other decomposed species with a mass-to-charged ratio (m/e) of 30. The species with m/e of 101 and 102, which corresponded to $\text{N}(\text{C}_2\text{H}_5)_3$ and $\text{NH}(\text{C}_2\text{H}_5)_3$, respectively, were also observed although their intensities were weak. The evolution of these species reached maxima around $380 \text{ }^\circ\text{C}$. After a short plateau of the TG curve, the second stage of decomposition began around $450 \text{ }^\circ\text{C}$. In this stage, H_2O , CO_2 , CO and HF evolved and reached their maxima around $580 \text{ }^\circ\text{C}$. SO_2 and the species with m/z of 30, 101 and 102 were not observed in this stage. These observations indicates that

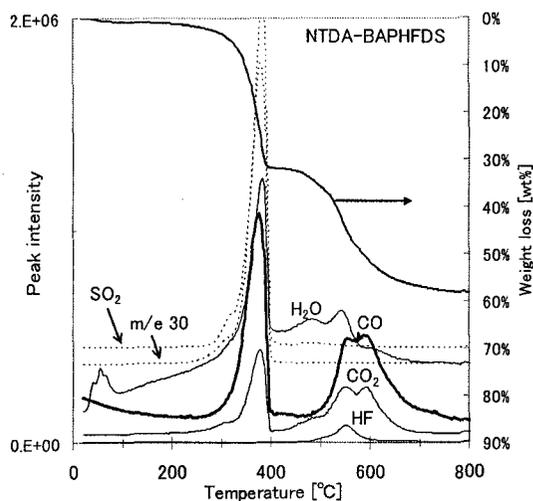


Fig.2 TG-MS spectra of evolved gases at pyrolysis of NTDA-BAPHFDS polyimide. The baseline of each mass spectrum is shifted a little for good view.

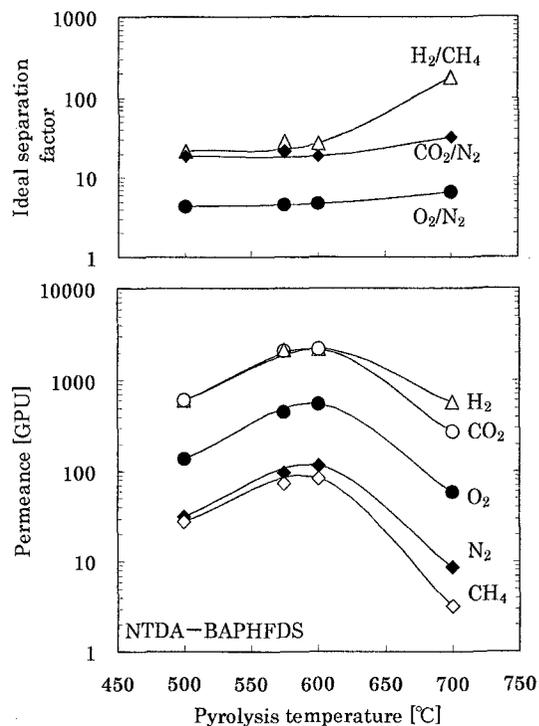


Fig.3 Influence of pyrolysis temperature on gas permeance at $35 \text{ }^\circ\text{C}$ and 1 atm for CMS membranes derived from NTDA-BAPHFDS polyimide.

Table 1 Gas permeation properties for CMS membranes prepared under different conditions.

Code	Precursor	1st C/P		2nd C/P		Permeance [GPU]					Ideal separation factor		
		<i>C</i>	<i>n</i>	<i>C</i>	<i>n</i>	H_2	CO_2	O_2	N_2	CH_4	H_2/CH_4	CO_2/N_2	O_2/N_2
M1	NTDA-BAPHF	5	1	—	—	2728	2094	449	90	91	30	23	5.0
M2	NTDA-BAPHF	5	1	3	1	1382	1171	250	56	53	26	21	4.5
M3	NTDA-BAPHF	4	1	—	—	977	394	94	17	14	71	23	5.5
M4	NTDA-BAPHF	4	1	3	1	450	130	31	4.2	2.5	182	31	7.4
M5	NTDA-BAPHFDS	10	3	—	—	2225	2202	542	116	82	27	19	4.7
M6	NTDA-BAPHFDS	10	3	10	1	682	674	139	27	15	46	25	5.1
M7	NTDA-BAPBDS	6	3	—	—	329	127	35	5.9	4.0	82	22	5.9

C and *n* refer to the polymer concentration of coating solution in wt% and the coating number. Pyrolysis temperature was $600 \text{ }^\circ\text{C}$.

Permeance and ideal separation factor were measured at $35 \text{ }^\circ\text{C}$ and 1 atm.

the sulfonic acid triethylammonium salt decomposed below 400 °C and the decomposition of the CF₃ group and cleavage of the polyimide backbone occurred at temperatures above 450 °C.

3.2 Gas permeation and separation properties

Figure 3 shows the influence of pyrolysis temperature on the gas permeance and the ideal separation factor for CMS membranes derived from NTDA-BAPHFDS PI. With increasing pyrolysis temperature from 500 to 700 °C, the gas permeances increased and reached at maxima around 600 °C, then rapidly decreased, whereas the ideal separation factors slowly increased. The increase in the selectivity was higher for the gas pair with a larger difference in molecular size such as H₂/CH₄ than for the gas pair with a smaller difference in molecular size such as CO₂/N₂ and O₂/N₂. The increase in the gas permeance and the slight increase in the ideal separation factor below 600 °C may be due to development of interpenetrating micropore structure [5]. The large decrease in the gas permeance and the increase in the ideal separation factor above 600 °C may be due to the shift of the size distribution of micropores to smaller size caused by shrinkage of membrane structure as a result of further decomposition. The pyrolysis temperature of 600 °C was optimal for the separation of these gas pairs.

Table 1 lists gas permeation properties for CMS membranes prepared using solutions with different concentrations and by different C/P cycles. The CMS membranes prepared using 4 wt% solution of NTDA-BAPHF PI displayed lower gas permeances than the membranes prepared using 5 % solution. SEM observation showed that in the case of former CMS membranes a pyrolytic layer was formed in the support down to a few μm depth in addition to a surface layer. The dipping solution penetrated into the pores of the support because of its lower viscosity. The concentration of the dipping solution must be higher than 5% for making a thin surface layer only on the support. Membranes M5 and M7 had a thin top layer without impregnation into the inner layer. Figure 4 shows SEM photograph of a cross-sectional view of the outer surface of the membrane M5. The thickness of pyrolytic layer on the support was about 4 μm. The pyrolytic layer thickness of M7 was 1.5 μm. Membranes M2, M4 and M6 were prepared by repeating the C/P cycle twice. The additional C/P cycle decreased gas permeance without improving the selectivity. One C/P cycle well gave a defect-free pyrolytic layer.

Figure 5 shows relationship between gas permeances and kinetic diameters of gases for the CMS membranes. The thicknesses of the pyrolytic layers were 2, 4 and 1.5 μm for M1, M5 and M7, respectively. Taking the pyrolytic layer thickness into account, the diamine of precursor polyimide gave the higher gas permeance for the CMS membranes in the following order:

BAPHFDS > BAPHF > BAPBDS.

As mentioned above, the sulfonic acid groups

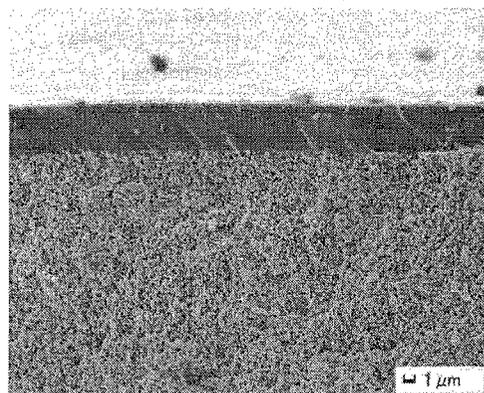


Fig.4 SEM photograph of a cross-sectional view of the composite CMS membrane M5.

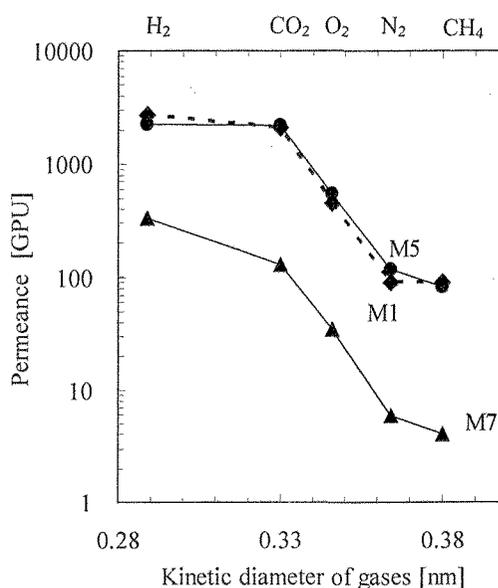


Fig.5 Relationship between gas permeances at 35 °C and 1 atm and kinetic diameters of gases for CMS membranes prepared from NTDA-based polyimides with different diamines.

decomposed at relatively lower temperatures of 300 to 400 °C accompanied by the evolution of relatively large decomposed species such as SO₂ and N(C₂H₅)₃, resulting in the enhanced gas permeances for the membranes pyrolyzed at 450 °C. This is probably because of formation of large amounts of microvoids, a kind of “template-like effect” of sulfonic acid groups [2]. If such a template-like effect were effectively held after the second stage of decomposition above 500 °C, the CMS membranes prepared from the SPI membranes would display higher gas permeances than those from the nonsulfonated polyimide membranes. This may be different from the present case. The CMS membrane (M7) derived from NTDA-BAPBDS PI displayed much lower gas permeances than that (M1) from the nonsulfonated PI, NTDA-BAPHF. In the case of NTDA-BAHF PI, the C(CF₃)₂ groups began to decompose at 450 °C slightly below the decomposition temperature of the polyimide backbone. This is

considered to induce another template-effect to enhance the CMS membrane. NTDA-BAHFDS PI has both sulfonic acid and $C(CF_3)_2$ groups and gave the higher gas permeances for the CMS membrane (M5) than for M1. This suggests the decomposition of sulfonic acid groups followed by the decomposition of $C(CF_3)_2$ groups just before the substantial decomposition of the polyimide backbone significantly enhanced the micro-pore structure of the resultant pyrolyzed membranes. Further study is in progress.

Figure 6 shows the comparison of gas separation performance for the present CMS membranes with that for the CMS membranes reported in literature [1,5-13]. There seems to be a trade-off relationship between the gas selectivity and permeance for every separation system. The each solid line in Figure 6 is the upper bound line indicating the upper limit of separation performance for each separation system of CMS membranes developed up to now. The present CMS membranes displayed relatively high permeances to H_2 , O_2 and CO_2 . The plots for M1 and M5 are on the upper bound lines at the highest permeances for O_2/N_2 and CO_2/N_2 separation systems.

4. CONCLUSION

The CMS membranes prepared by the pyrolysis of composite membranes from NTDA-BAPHFDS polyimide at 600 °C for 1h displayed higher gas permeances and reasonably high ideal separation factors for O_2/N_2 and CO_2/N_2 separation systems compared to the other CMS membranes reported in the literature. The decomposition of sulfonic acid groups followed by the decomposition of $C(CF_3)_2$ groups just before the substantial decomposition of the polyimide backbone seemed to significantly enhance the micro-pore structure of the resultant pyrolyzed membranes.

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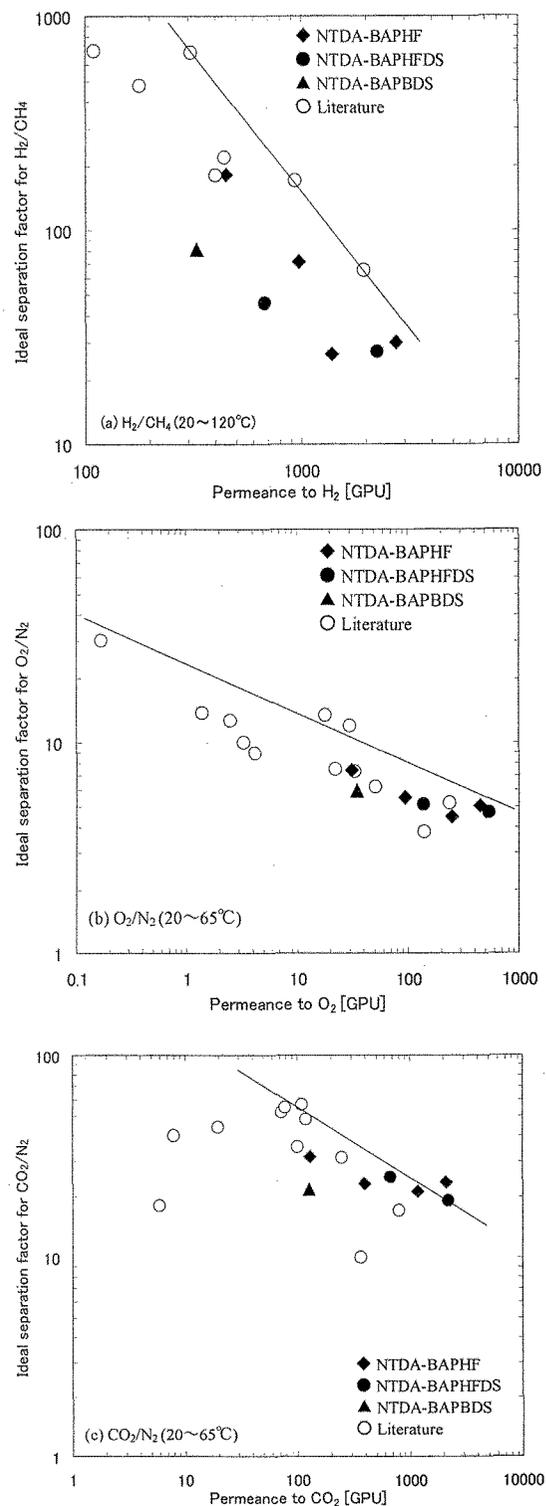


Fig.6 Comparison of separation performance between CMS membranes prepared in this study and reported in literatures. Each solid line is an upper bound line.

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