Gas permeation properties of asymmetric carbon hollow fiber membranes prepared from asymmetric polyimide hollow fiber

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Abstract

Asymmetric carbon hollow fiber membranes were prepared by pyrolysis of an asymmetric polyimide hollow fiber membrane, and their mechanical and permeation properties were investigated. The carbon membrane had higher elastic modulus and lower breaking elongation than the polyimide membrane. Permeation experiments were performed for single gases such as H_2, CO_2, and CH_4, and for mixed gases such as H_2/CH_4 at high feed pressure ranging from 1 to 5 MPa with or without toluene vapor. The permeation properties of the carbon membranes and the polyimide membrane were compared. There was little change in the properties of the carbon membranes with a passage of time. The properties were hardly affected by the feed pressure, whether the feed was accompanied with the toluene vapor or not, because the carbon membranes were not affected by compaction and plasticization. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Gas and vapor permeation; Gas separations; Carbon; Polyimide; Hollow fiber membranes

1. Introduction

Most of commercial membranes for gas separation have been prepared from polymers such as polysulfone, polycarbonate, cellulose, polyimide [1]. These polymers have high gas permselectivities as membrane materials. Asymmetric membranes, consisting of thin skin layers supported on porous layers and consequently displaying high membrane performance, can be produced from these polymers. Furthermore, mass production of the asymmetric polymeric membranes and modules such as hollow fiber configuration and spiral-wound one have been industrialized. Recently, membrane separation systems using the polymeric membranes have been come into a market of gas separation. However, it is pointed out that the membrane performance declines with a passage of time, especially in the cases of their uses on severe environments like high pressure and like atmospheres having heavy hydrocarbons, aromatics, and polar solvents.

Inorganic membranes with excellent thermal and chemical stabilities have attracted much attention for their potential uses in gas and vapor separation. Particularly, carbon molecular sieve membranes prepared by pyrolysis of thermostable polymers have grown interesting [2–19], because it has been reported that

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the carbon membranes displayed higher permeabilities and higher selectivities than the polymeric ones. However, the carbon membranes are not almost on the market because what they are brittle and not flexible makes the continuous production difficult. Batchwise production has been used in many studies [2,3,9–19].

In our previous paper [8] and patents [4–7], we reported that asymmetric carbon hollow fiber membranes were continuously prepared by pyrolyzing an asymmetric polyimide hollow fiber membrane with a simple apparatus, and that they displayed high gas permeability and selectivity. In this study, we measured gas permeation properties of the carbon membranes and the polyimide membrane, i.e. the precursor of the carbon membranes, at high pressure of feed gases ranging from ca. 1 to 5 MPa (10–50 kgf/cm^{2}G) without or with toluene vapor. We will discuss characterization and the permeation properties in comparison between the carbon membranes and the polyimide one.

2. Experimental

2.1. Membrane preparation

The asymmetric polyimide hollow fiber membrane that has been produced by UBE Industries [20] was used as the precursor of the asymmetric carbon hollow fiber membranes. It was made from a polyimide prepared from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and aromatic diamines, as described previously [8], and was treated under nitrogen at 270°C before the use in this study. The outside and inside diameters were ca. 0.40 and 0.12 mm, respectively.

The polyimide membrane was treated thermally in atmospheric air at 400°C for 30 min before the pyrolysis. In this paper, the thermal treated hollow fiber is called thermostabilized hollow fiber. The asymmetric carbon hollow fiber membranes were prepared by pyrolyzing the thermostabilized hollow fiber at temperatures ranging from 600°C to 1000°C for 3.6 min, as described in detail previously [8]. The outside and inside diameters of the carbon membranes decreased with an increase in the temperatures of the pyrolysis, and were ca. 0.35–0.28 mm and 0.11–0.09 mm, respectively [8].

2.2. Gas permeation

Schemes of a membrane module and an apparatus for gas permeation measurement are shown in Figs. 1 and 2, respectively. Hollow fiber membrane modules were one-end-opened types and consisted of about 6–10 pieces of the fiber of ca. 8 cm active length. One end of the fiber bundle was sealed with an epoxy resin and the other was potted in a stainless steel pipe of 5 cm length and 6 mm diameter with the epoxy. The effective membrane areas of the modules were ca. 6–10 cm^2. The feed gas was introduced to the outside of the hollow fiber. The permeation experiments for single gases such as H_2, CO_2, and CH_4, and for mixed gases such as H_2/CH_4 were performed at feed pressure ranging from 1 to 5 MPa and at temperatures of 50°C and 80°C [8]. After the carbon membrane modules were made, the permeation properties were first measured for mixed gas of 50% H_2 in CH_4 at 1 MPa and 80°C. Maximum deviation of the permeation rates of H_2 was ±30% of the mean value.

The feed gas was supplied from a compressed gas cylinder, and could be used as either dry or with
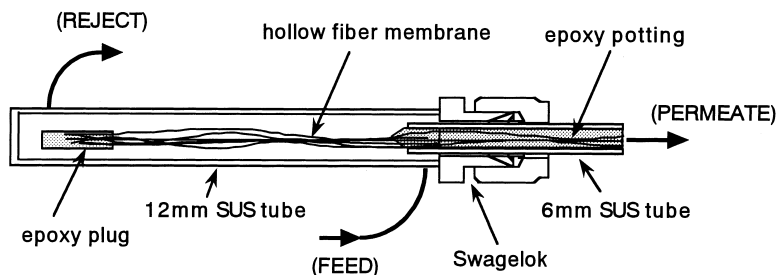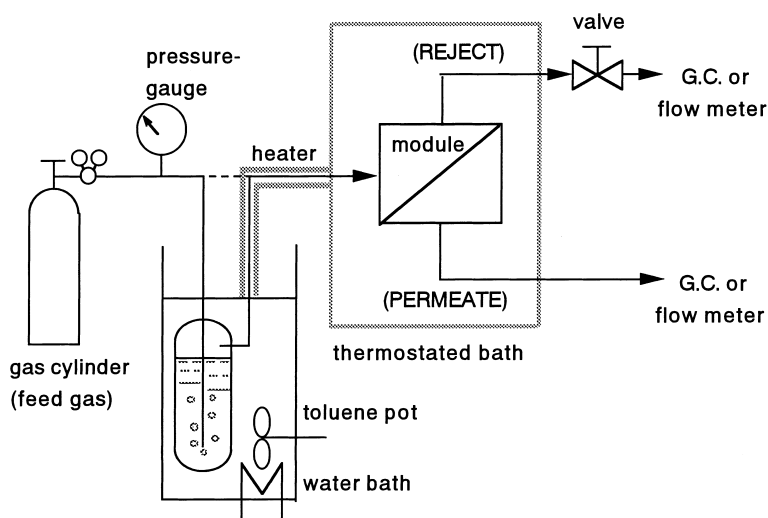

Fig. 1. Scheme of membrane module.

Fig. 2. Scheme of gas permeation apparatus.

toluene vapor. In case of the feed gas accompanied with toluene vapor, the gas from the cylinder was passed through a chamber of toluene prior to the membrane module. The chamber was a stainless steel bottle and was placed in a thermostated water bath.

2.3. Mechanical property

Tensile load-elongation curves for the hollow fibers were measured with an Orientic tensilon model UTM-II-20 at tensile rate of 10 mm/min and room temperature. A length of the specimen of the hollow fiber, l_0, was 20 mm. A breaking elongation, e, was calculated as $e = (l_f - l_0)/l_0$, where l_f is the length at a breaking point. A breaking strength, F, was calculated by dividing a breaking load by a cross-sectional area of the specimen. An initial modulus of elasticity, E, was estimated from an initial slope of the curve where the load increased linearly with an increase in the elongation. For five specimens, maximum deviation on the e, F, and E values was $\pm 1\%$ of each mean value of the readings.

3. Results and discussion

3.1. Mechanical properties

The tensile load-elongation curves for the polyimide hollow fiber and thermostabilized hollow fiber exhibited shapes that the load at first increased linearly but then increased more gently as the elongation increased. Those for the carbon hollow fibers exhibited almost linear. Fig. 3 shows the mechanical properties of the hollow fibers, e, F, and E, with the heat treatment temperature. With an increase in the heat treatment temperature, the E values significantly increased and the e values decreased. The E value of the carbon hollow fiber pyrolyzed at 800°C was 9
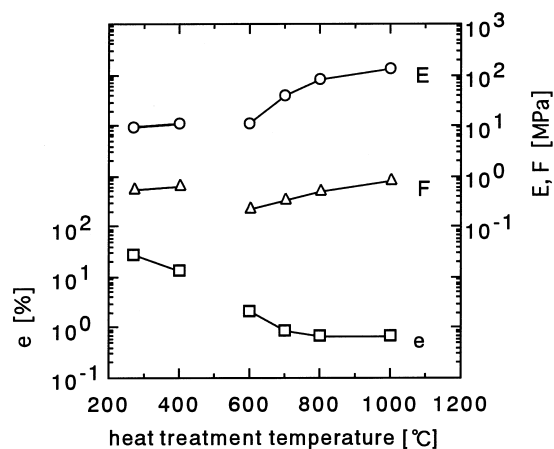

Fig. 3. Plots of mechanical properties, e, E, and F, against heat treatment temperature. Square, triangle, and circle plots show the e, E, and F values, respectively. Plots at 270°C and 400°C show the data of polyimide hollow fiber and thermostabilized hollow fiber, respectively.

times larger than that of the polyimide hollow fiber treated at 270°C. The carbon hollow fiber had higher E and lower e than the polyimide hollow fiber. The F values were same orders in the range of the heat treatment temperature, but increased with an increase in the temperature of the pyrolysis ranging from 600°C to 1000°C. The reasons why the E and F values increased with the increase in the temperature of the pyrolysis are considered that aromatic fragments grow and crosslink between the fragments progresses, and that the asymmetric structures of the membranes become dense, and so on. Results that the carbon contents of the carbon hollow fibers increased and the diameters of the ones decreased with the increase in the temperature of the pyrolysis have been reported in the previous paper [8]. The trends towards the increase in E and F of the carbon hollow fibers in this study were almost same as those of the carbon fiber prepared from polyacrylonitrile [21].

3.2. Effects of feed pressure on permeation properties

Fig. 4 shows effects of feed pressure, p_1, on permeation rates, P', to single H_2, CO_2, and CH_4 gases and ratios of the permeation rates for the carbon hollow fiber membrane pyrolyzed at 700°C and the polyimide hollow fiber membrane. The tests were performed firstly at p_1 from 1 to ca. 5 MPa in order, and further at p_1 from ca. 5 to 1 MPa. Fig. 5 shows effects of feed pressure on ratios of the P' values at arbitrary p_1 to those at p_1 of 1 MPa. With an increase in p_1, the P' values of the polyimide membrane largely decreased, on the other hand, those of the carbon membrane slightly changed. Okamoto et al. reported sorption and transport of CO_2 gas at upstream pressure up to about 28 atm (ca. 2.8 MPa) and temperatures ranging from 35°C to 80°C in some kinds of BPDA-based polyimide films prepared from 4,4'-oxydianiline (ODA), 4,4'-diaminodiphenyl sulfone (DDS), and dimethyl-3,7-diaminodibenzothiophene-5,5-dioxide (DDBT), and commercial Upilex-R film [22–24]. In these literatures, the dependence of permeability coefficients, P, to CO_2 gas on the upstream pressure was explained on the basis of the dual-mode transport model and the extended model. The permeability data of the polyimide hollow fiber membrane in this study were largely affected by p_1, as compared with those of
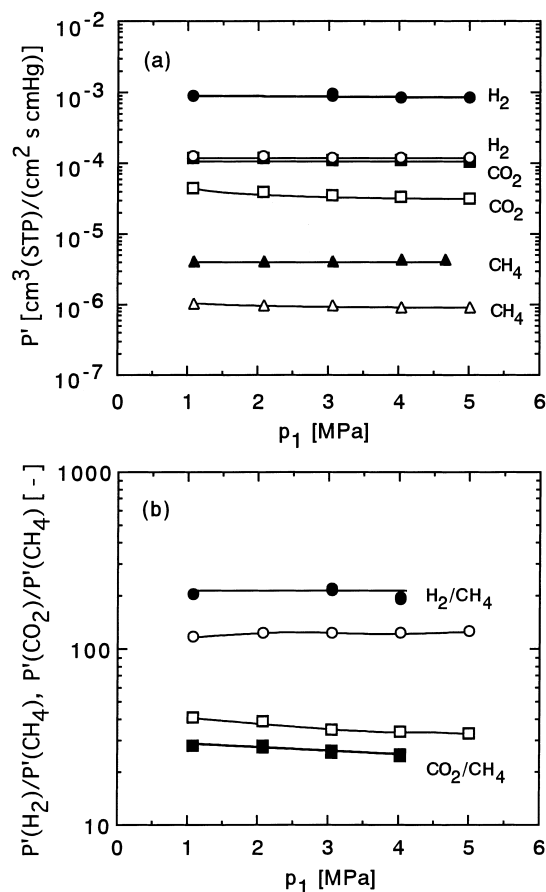

Fig. 4. Effects of feed pressure on permeation rates and ratios of permeation rates for single gases at 50°C. Closed and open plots show the data of carbon membrane pyrolyzed at 700°C and polyimide membrane, respectively.

the BPDA-DDS and BPDA-DDBT films reported by Okamoto. In case of the polyimide hollow fiber membrane having the asymmetric structure consisted of nodules [8], ''compaction effect'' is considered as the reason that P' largely decreased with the increase in p_1. Force owing to the feed pressure works on the outside, i.e. the skin layer side, of the hollow fiber membrane in this study because the feed gas is introduced to the outside. The compaction effect is considered to attribute to how a transition area between the skin layer and the porous layer becomes dense by the force. Furthermore, it is considered that what the nodules' selves and interfaces between the nodules on the skin layer grow dense simultaneously may participate in the effect. On the other hand, the
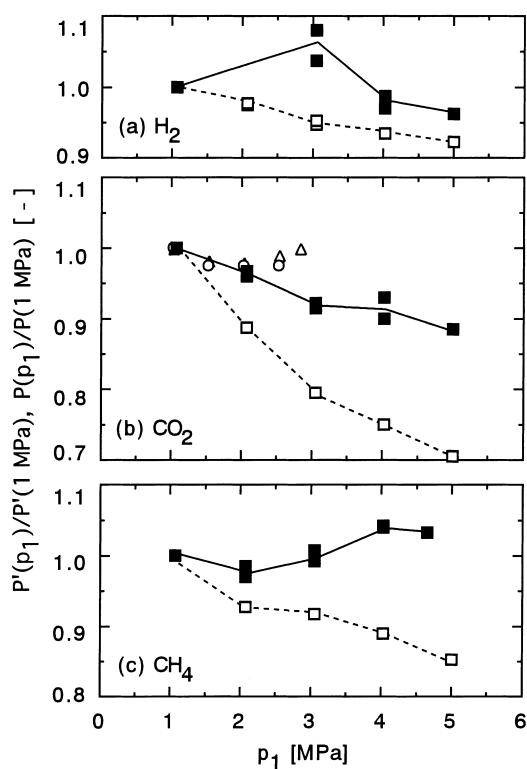
Fig. 5. Effects of feed pressure, p_1, on ratios of permeability data at arbitrary p_1 to those at p_1 of 1 MPa and 50°C. Closed and open square-plots show data of carbon membrane pyrolyzed at 700°C and polyimide membrane, respectively. Circle and triangle plots show data for BPDA-DDS film [22] and BPDA-DDBT one [23], respectively.

Fig. 6. Effects of concentration of toluene vapor in feed of mixed gas of 50% H_2 in CH_4 on $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ at feed pressure of 1 MPa and 50°C. Closed and open plots show the data of carbon membrane pyrolyzed at 700°C and polyimide membrane, respectively.

permeation rates of the carbon hollow fiber membrane were hardly dependent on p_1. It is considered that the carbon membranes are not affected by the compaction.

3.3. Effects of toluene vapor on permeation properties

The tests for the feed gas with or without toluene vapor were performed at feed gas composition of 50% H_2 in CH_4, at p_1 of 1 MPa, and at 50°C on the carbon hollow fiber membrane pyrolyzed at 750°C and the polyimide hollow fiber membrane. Fig. 6 shows effects of concentration of toluene vapor in the feed gas on $P'(H_2)$ and $P'(H_2)/P'(CH_4)$. It also shows the data for dry feed gas before and after the exposure of toluene vapor, that is, the data correspond to virgin membranes and regenerated ones, respectively. The
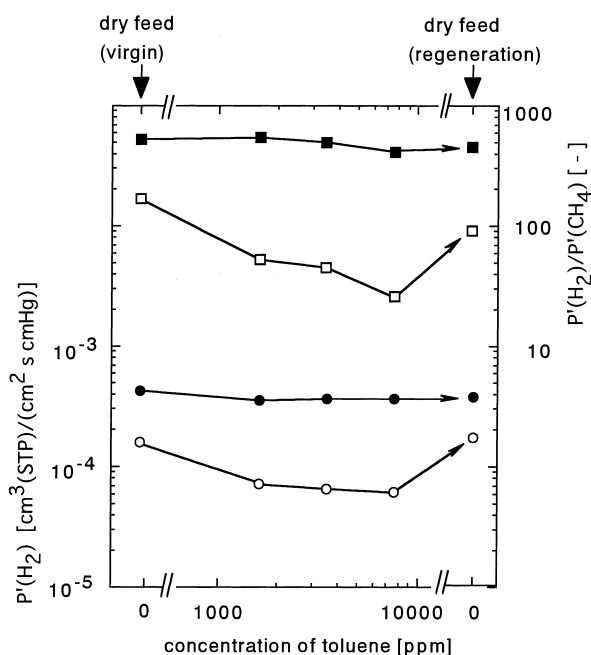
regeneration was carried out by only exchanging the feed gas with toluene vapor for the dry gas. The $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ values of the polyimide membrane decreased with an increase in the concentration of toluene vapor. The $P'(H_2)$ values on concentration of toluene vapor ranging from 1600 to 7600 ppm were 0.45–0.39 times those for virgin, and the $P'(H_2)/P'(CH_4)$ values were 0.31–0.16 times. It is considered that toluene sorbed causes plasticization of the active skin layer on the polyimide membrane and results in the loss of the selectivity. The loss of the permeability is considered because the sorbed toluene fills in domains of the gas permeation and the plasticization also promotes the compaction of the asymmetric structure. On the other hand, in case of the carbon membrane, the $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ values hardly changed with the increase in the concentration of toluene vapor. The $P'(H_2)$ values in case with toluene vapor were about 0.85 times those for virgin, and the $P'(H_2)/P'(CH_4)$ values were 1–0.78 times. The permeation properties of the carbon membrane were not affected by toluene.

For dry feed gas after the exposure of toluene vapor, on the polyimide membrane, the $P'(H_2)$ value for the regenerated sample was 1.08 times that of the virgin one, but $P'(H_2)/P'(CH_4)$ value for the regenerated one was a half that of the virgin one. The regeneration effect for the $P'(H_2)/P'(CH_4)$ value was small. In case of the polyimide membrane, the structure of the skin layer was damaged by sorbed toluene and was difficult to be regenerated. On the other hand, the $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ values of the carbon membrane were 0.88 and 0.86 times those of the virgin one, respectively. There was little difference in the permeation properties between for dry feed gas before and after exposure.

It is considered that the carbon membrane is composed of networks of the aromatic fragments having less molecular mobility, and consequently, it has higher E value and is not affected by the plasticization and the compaction. On the other hand, the polyimide hollow fiber membrane is apt to be affected by those. This is because the polyimide membrane is composed of chains having more molecular mobility.

3.4. Time courses of permeation properties with toluene vapor

The tests for the feed gas with toluene vapor were performed at feed gas composition at 65% H_2 in CH_4 with concentration of toluene vapor of 7500 ppm, at p_1 of 1 MPa, and at 50°C on the carbon hollow fiber membrane pyrolyzed at 750°C. The tests with toluene vapor were run to 240 h, but the dry gas was fed from 120 to 170 h. Fig. 7 shows the time courses of the $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ values for the run. These values were constant for the run. There was little change in the permeation properties of the carbon membrane with the passage of time.

The carbon membrane displayed the high permeation properties whether the feed gas was accompanied with toluene vapor or not. The carbon membrane was undamageable to the exposure of the gases and the vapor.

3.5. Comparison of membrane performance among carbon membranes

It is interesting to compare performance among carbon membranes reported in the literature. The
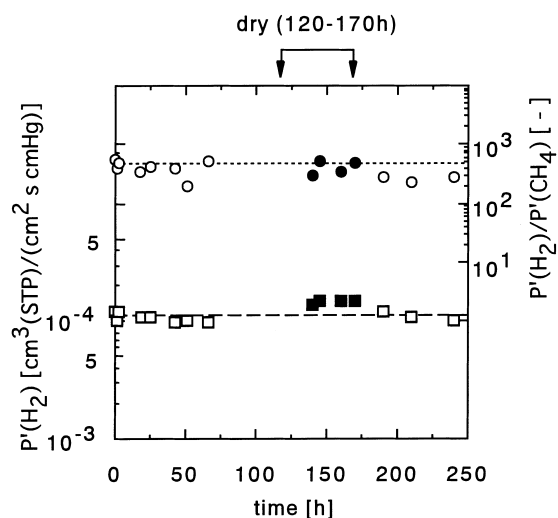

Fig. 7. Time courses of $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ for mixed gas of 65% H_2 in CH_4 with toluene vapor of concentration of 7500 ppm at feed pressure of 1 MPa and 50°C. Square and circle plots show $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ of carbon membrane pyrolyzed at 750°C, respectively. Closed plots show data for the dry gas fed from 120 to 170 h. Broken and dotted lines show $P'(H_2)$ and $P'(H_2)/P'(CH_4)$ for dry gas before start of the run, respectively.

membrane performance of carbon membranes towards H_2 and He separation being at a relatively high level is listed in Table 1. Our carbon membranes reported in this study and previous one [8] were preferentially permeable to H_2 over N_2 and hydrocarbons. The order of magnitude of the permeation rates was corresponded with that of the kinetic diameters. This phenomenon was almost same as that on other carbon membranes, except for the nanoporous carbon membranes prepared from a poly(vinylidene chloride)-acrylate terpolymer (PVC-AC) [26]. Our carbon membranes had much higher permeation rates than others and had similar separation factor of others.

4. Conclusions

Asymmetric carbon hollow fiber membranes were prepared by pyrolysis of an asymmetric polyimide hollow fiber membrane. The permeation experiments were performed on these membranes for single and mixed gases at high feed pressure ranging from 1 to 5 MPa with or without toluene vapor. In comparison

Table 1
Membrane performance on carbon membranes

Pyrolysis methods			Permeation conditions		Membrane performance [c]			Reference
Materials [d]	Atmosphere	Temperature (°C)	System [e]	Temperature (°C)	P'	P	SF	
BP-based PI	N_2	700	M H_2/CH_4	50	420		540	[a]
			S H_2/CH_4	120	1500		100	[8] [b]
			S H_2/C_2H_6	120	1500		250	[8] [b]
		850	S H_2/N_2	50	80		380	[8] [b]
			S H_2/CH_4	120	310		680	[8] [b]
			S H_2/C_2H_6	120	310		3100	[8] [b]
PM-ODA PI	Vacuum	950	S H_2/N_2	35	0.7		1080	[9]
			S H_2/N_2	250	83		140	[11]
			S H_2/N_2	0	0.7		720	[11]
6F/BP-3MPD PI	Vacuum	500	M H_2/CH_4	rt	98		520	[15]
			M H_2/CH_4	rt	110		210	[15]
		550	M H_2/CH_4	rt	220		500	[12]
BP-ODA PI	N_2	700	S He/CH_4	65	250		110	[18]
			S He/C_2H_6	65	250		430	[18]
		800	S He/CH_4	65	36		240	[18]
Phenolic resin	N_2	600	S H_2/CH_4	35	52		37	[19]
COPNA resin	N_2	700	S H_2/C_2H_6	100	150		1600	[25]
Cellulose		950, 800	S He/N_2	rt		5200	22	[2]
PVC-AC	N_2	1000	S CH_4/H_2	22		660	5.1	[26]
			S C_2H_6/H_2	22		850	6.6	[26]

[a] This study.

[b] Our previous study. Ref. [8].

[c] P' is permeation rate in 10^{-6} cm³(STP)/(cm² s cmHg), P is permeability coefficient in 10^{-10} cm³(STP)cm/(cm² s cmHg), and SF is separation factor.

[d] PI, polyimide; BP, 3,3′,4,4′-biphenyltetracarboxylic dianhydride; 6F, hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride); 3MPD, 2,4,6-trimethyl-1,3-phenylenediamine; PM, pyromellic dianhydride; ODA, 4,4′-oxydianiline; COPNA resin, condensed polynuclear aromatic resin; PVC-AC, poly(vinylidene chloride)-acrylate terpolymer.

[e] M, mixed gas; S, single gas.

with the polyimide hollow fiber membrane, the carbon hollow fiber membranes had the following characteristics:

1. the permeation properties were hardly dependent on the feed pressure;
2. the properties for the feed gas with toluene vapor were about the same as that for the dry gas;
3. there was little change in the properties with the passage of time.

5. Nomenclature

E	initial modulus of elasticity (MPa)
e	breaking elongation (dimensionless)
F	breaking strength (MPa)
l_0	length of specimen (mm)
l_f	length at breaking point (mm)
P	permeability coefficient (cm³(STP)cm/ (cm² s cmHg))
P'	permeation rate (cm³(STP)/(cm² s cmHg))
p_1	feed pressure or upstream pressure (MPa)

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