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Influence of oxidation temperature on the gas permeation and separation properties in a microporous carbon membrane

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Abstract−Of thermosetting polymers, polyphenylene oxide (PPO) is considered as one of the promising alternative polymeric precursors for carbon membrane preparation. In this study, the PPO derived carbon membranes were prepared by carbonization and followed by air-oxidation as post-treatment method to modify the membrane pore structures. The characterization of the pore properties showed that air-oxidation enlarged the pore structure for the post-oxidized carbon materials. The permeation results for the post-oxidized carbon membranes showed that the extent of the permeation modification was strongly dependent on the oxidation temperature. In the binary mixture gas systems, the permeation performance of the adsorbing gas species increased due to the surface diffusion mechanism. It is considered in the oxidation effect on the permeation modification that the post-oxidation of the carbon membranes increased gas permeation and separation properties.

Key words: Carbon Membrane, Polyphenylene Oxide, Post-oxidation, Surface Diffusion

INTRODUCTION

The development of membrane processes has shown remarkable progress during the last two decades; consequently, they have become competitive with conventional separation methods in a wide variety of large-scale industrial applications. Of membrane processes, interest in inorganic membranes has increased for the potential use in gas separation technology due to good thermal and chemical stability [Hasegawa et al., 2002; Koros and Mahajan, 2000; Jung et al., 1999]. Attractive opportunities for gas separation are found in the various areas of natural gas processing, landfill gas recovery, olefin/paraffin separation, air separation and hydrogen recovery [Suda and Haraya, 1997; Kim and Sea, 2001; Kim et al., 2001]. Gas transport mechanisms in inorganic membranes are primarily varied depending on the pore size distribution and chemical interaction between the diffusing gas species and the membrane material [Lee and Hwang, 1986; Sircar et al., 1999; Moon et al., 2004]. Basically, the transport mechanism through inorganic membranes can be divided into four mechanisms: Knudsen diffusion, molecular sieving, surface diffusion, and capillary condensation mechanisms. When pore dimensions approach those of the diffusing gas species, gas separation occurs by the molecular sieving mechanism. Nearly infinite separation factors are theoretically attainable in the molecular sieving mechanism. In the presence of condensable gas species such as water vapor and butane, the capillary condensation occurs in the pores of the membranes having a mesoporous structure. In the surface diffusion mechanism, the transport of the adsorbing gas species increases because of the preferential adsorption onto the surface of the membrane pore structure. Therefore, the adsorbing gas species show a higher permeability than predicted from the Knudsen diffusion since the preferential adsorption reduces open porosity and limits the diffusion of the less adsorbing gases into the micropores [Moon et al., 2004; Fuertes and Menendez, 2002].

It is generally known that the gas permeation properties of a carbon membrane are affected by polymeric precursor, pyrolysis method, and post-treatment conditions [Suda and Haraya, 2000; Saufi and Ismail, 2004; Ismail and David, 2001]. So far, different polymeric materials have been considered such as polyimides, phenolic resins, polyfurfuryl alcohol, and phenol formaldehyde, polyacrylonitrile, cellulose and others for carbon membrane preparation. It is well known that polyimide polymer is one of the most important polymeric precursors for gas separation carbon membranes, which shows the closeness to the upper bound line in the correlation of the selectivity and the permeabililty [Kim et al., 2003, 2004]. Of polymers, polyphenylene oxide (PPO) is considered as one of the promising alternative polymeric precursors for carbon membrane preparation [Kruczek and Matsuura, 2000; Hamad et al., 2001; Story and Koros, 1992]. PPO has a linear structure assigned to the rotational motion of its phenyl ring, giving excellent mechanical properties. Also, the presence of ether linkages and the absence of polar groups inhibit chain packing and densification [Story and Koros, 1992]. The PPO polymer membrane has somewhat high gas permeability among aromatic polymers with high glass transition temperature, showing closeness to the upper bound line for polymeric membranes [Robeson, 1991].

Of post-treatment methods, the post-oxidation in the air circumstance is considered to increase the pore size and the pore volume for carbon membranes. It is known that permeation performance is affected by the post-oxidation conditions, such as oxidation temperature and oxidation time for the carbon membranes derived from phenolic resins and polyimides. In previous results, the permeating

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gas species was transported by the molecular sieving effect in the carbon membrane derived from a phenolic resin film. However, gas transport was affected by the surface diffusion mechanism for the post-oxidized carbon membranes prepared at temperatures between 100 and 450 °C due to the enlargement of the membrane pore structure [Fuertes, 2000, 2001]. Yamamoto et al. showed that the values of the permeability and the selectivity in the presence of the adsorbing gas species (e.g., C_2H_6, C_3H_6, C_3H_8) increased after carbonization of polyimide polymeric precursor, followed by air oxidation (300-400 °C) [Yamamoto et al., 1997]. As far as we know, the post-oxidation effect on the gas permeation performance for the PPO derived carbon membranes has not been reported. In this study, the carbon membranes were prepared by preparation of a PPO polymeric film on a macroporous tubular ceramic support and pyrolysis, followed by the post-oxidation of carbon membranes in the air condition. The main aim of this work was to analyze the effect of the extent of oxidation on the permeation properties of PPO derived carbon membranes. And, the separation properties for a post-oxidized carbon membrane were considered in the single and binary mixture gas systems in the presence of the adsorbing gas species.

EXPERIMENTAL

As polymeric precursor, 3 wt% of the PPO polymer (Aldrich, USA) solution in chloroform (Wako, Japan) was coated on the surface of the tubular macroporous α-alumina ceramic membranes (NOK, Japan) having an average pore size of 100 nm and porosity of 40%. Carbonization was performed by heating up to the pyrolysis temperature of 600 °C at a heating rate of 5 °C/min in Ar atmosphere (flow rate: 200 ml/min). For the oxidation of the PPO derived carbon membranes, the oxidation was conducted at different temperatures (between 100 and 400 °C). The heating rate for the oxidation was set to 5 °C/min at a flow rate of 200 ml/min in the air environment.

Weight change during heat treatment of the polymeric precursor and its carbonized material was measured by means of a thermogravimetric analyzer (TG-DTA 2000SA, Bruker AXS) in the same condition for the pyrolysis and the post-oxidation. The pore properties of carbon materials were characterized by nitrogen adsorption at −196 °C using an automatic adsorption apparatus (BELSORP-18, BEL-Japan) after pretreatment at 300 °C for 5 hours in vacuum condition. The surface morphology and the cross-section of a carbon membrane were examined by using a scanning electron microscope (SEM), S-2400, Hitachi, Japan.

Gas permeance of He (2.6 Å), CO_2 (3.3 Å), N_2 (3.64 Å), CH_4 (3.8 Å) and C_2H_6 (4.0 Å) was measured for the post-oxidized carbon membranes by using a permeation apparatus having a film flow meter (STEC, Japan) at a temperature range between 35 and 150 °C in order to investigate the influence of the oxidation temperature on the gas permeation performance. The permselectivity in the single gas system was estimated as the ratio of the permeance of each permeating gas species. In the gas transport and separation properties in the binary mixture gas systems, gas composition of permeate was analyzed by using a gas chromatograph (Ohkura 802, Japan) with a thermal conductivity detector. Helium was used as a carrier gas through 200 cm-long Poropak Q packed column (50/80 mesh). For the separation properties in the binary mixture gas system, the selectivity of gas pairs was estimated as the ratio of the mole fraction between the permeate and the feed streams.

RESULTS AND DISCUSSION

1. Characterization of Carbonized Materials

An SEM microphotograph of the carbon membrane pyrolyzed at 600 °C showed that the PPO carbon layer has a dense film structure formed on the surface of the macroporous ceramic support and is well adhered to the surface of the support. It was observed in Fig. 1 that the PPO carbon layer has a thickness of about 1 mm on the support surface. Fig. 2 shows the thermogravimetric analysis results of the PPO polymeric precursor and the carbonized material. The thermal gravimetric plot for the polymeric precursor in the figure shows that the polymer structure started to degrade and develop a carbonized structure at around 450 °C. The weight loss was measured to 63% around 500 °C, and the remaining weight showed the values within 25 and 28% at higher temperature than 700 °C. In the thermal gravimetric plot in the figure, the total weight loss was meas-

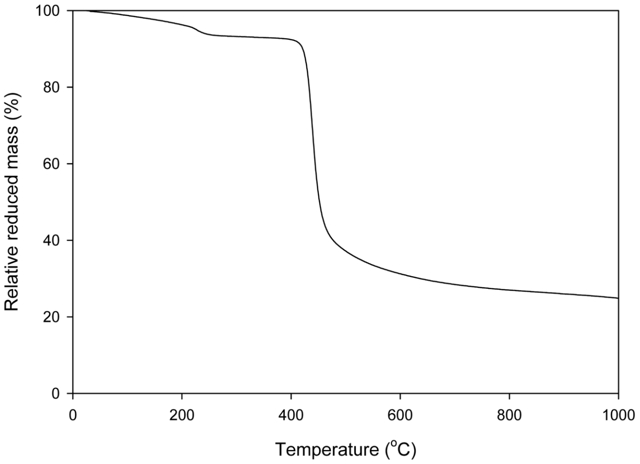

Fig. 1. Thermogravimetric analysis of the polymeric precursor.

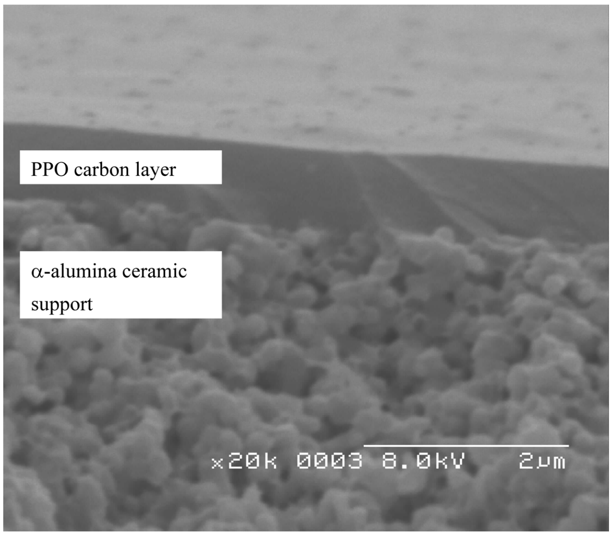

Fig. 2. SEM image of a cross-section of the carbon membrane pyrolyzed at 600 °C.

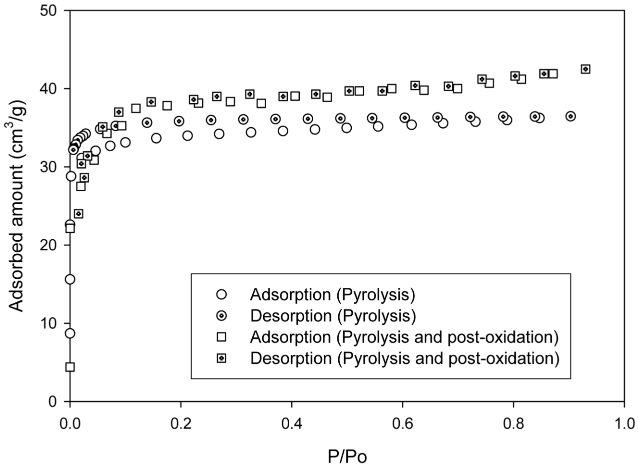

Fig. 3. Nitrogen adsorption isotherms for the pyrolyzed and post-oxidized carbon materials.

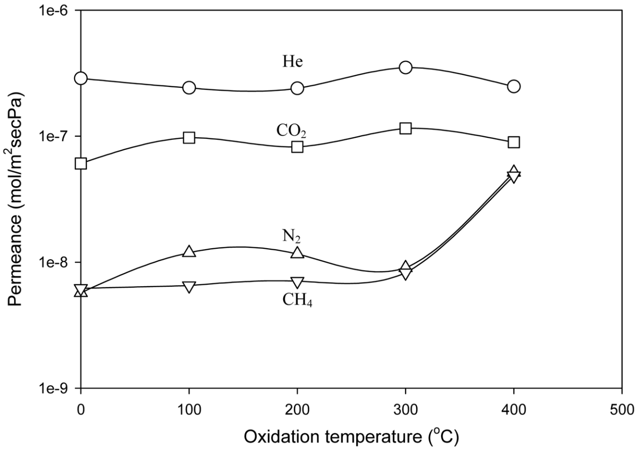

Fig. 4. Influence of oxidation temperature on the permeance (Permeation temperature: 150 °C).

ured to 75% up to 1,000 °C. The weight loss was measured to 0.5% even when the temperature increased up to 400 °C for the post-oxidized carbonized material. At higher temperature than 450 °C, a notable decrease was observed in the weight loss, showing 7% of the weight loss at around 500 °C. The thermal properties of the post-oxidized carbon material indicate that the pyrolyzed carbon material has thermal stability even in air-oxidation.

Fig. 3 shows the nitrogen adsorption-desorption isotherm for the pyrolyzed and post-oxidized carbon materials. The adsorption-desorption for both carbon materials in the figure represent the Type I adsorption isotherm according to the BDDT (Brunauner, Deming, Deming, and Teller) classification, indicating that they have microporous structures [Kim et al., 2004; Sing et al., 1985]. Based on the nitrogen adsorption measurements, the pore size and its distribution of the post-oxidized carbon material were estimated by the HK (Horvath and Kawazoe) method, and the results were compared with those of the pyrolyzed carbon material. The representative peak diameter of the post-oxidized carbon material was estimated as 0.68 nm (6.8 Å), higher value than that of the carbon material (See Table 1). In the analysis result of the BET adsorption isotherm based on the nitrogen adsorption, the pore volume and the surface area for the post-oxidized carbon material were estimated to be 31.92 cm^3/g and 138.93 m^2/g, respectively, higher than those of the pyrolyzed carbon material at 600 °C. It is assumed that the pore structure enlarged due to air-oxidation of the remaining carbons in the pyrolyzed structure. The pore characterization results based on the nitrogen adsorption showed that the pyrolyzed and post-oxidized carbon materials have a microporous structure and that the pore characteristic properties increased due to the post-oxidation.

2. Permeation Properties for the Carbon Membranes

The extent of the modification of gas permeance by the oxidation of the carbon membrane was investigated and the permeation results at a temperature of 150 °C are shown in Fig. 4. In the figure, the oxidation temperature of 0 °C represents the pyrolyzed carbon membrane at 600 °C (P 600). Similar values of the gas permeance were measured for the carbon membranes prepared at oxidation temperatures between 100 and 300 °C when the results were compared with those of the carbon membrane of P 600. Considering the permeation results of post-oxidized carbon membrane at 400 °C (POx 400), the permeation results of He and CO$_2$ showed similar permeation modification effect with those for the other post-oxidized carbon membranes. However, the permeance of the gas species having a larger molecular size (N$_2$ and CH$_4$) notably increased for the post-oxidized membrane of POx 400, indicating that the air-oxidation increased the pore volume [Fuertes, 2001]. The permeance of N$_2$ and CH$_4$ was measured to 5.16×10^{-8} and 4.85×10^{-8} mol m^{-2}sec^{-1} Pa^{-1}, respectively, which is about 9 and 7 times higher than that of P 600.

Furthermore, air-oxidation temperature also affected the permselectivity of gas pairs. The permeation performance observed in the post-oxidized membranes at temperatures between 100 and 300 °C was higher than that of P 600, as shown in Table 2. It is noted that the permselectivity of CO$_2$/CH$_4$ showed a somewhat increased value between 12 and 15, higher values than P 600. The permselectivity of CO$_2$/CH$_4$ was significantly decreased (CO$_2$/CH$_4$=1.6) in the permeation results for POx 400. Also, the permselectivity of CO$_2$/N$_2$ was decreased from 10.6 (P 600) to 1.7 (POx 400) in the table. It is thought that the CO$_2$ permeance increased for the carbon membranes post-oxidized at a temperature between 100 and 300 °C due to a higher adsorption capacity than CH$_4$ and N$_2$ [Kim et al., 2003]. The permeation results indicate that the air-oxidation of carbon membranes increased the pore volume, the pore size and its distribution, due to the oxidation of the carbon in the pore structure.

Table 1. Characteristic values for the pyrolyzed and post-oxidized carbon materials based on the nitrogen adsorption measurements

Carbon material	Description	Representative pore size (Å)	BET pore volume (cm^3/g)	BET surface area (m^2/g)
P 600	Pyrolysis (600 °C)	5.3	23.83	108.12
POx 400	Pyrolysis (600 °C) and then post-oxidation (400 °C)	6.8	31.92	138.93

Table 2. Permselectivity of gas pairs (Permeation temperature: 150 °C)

		CO_2/CH_4	CO_2/N_2	He/CH_4	He/N_2
P 600		9.8	10.6	46.4	50.3
Oxidation temperature	100 °C	14.9	8.2	37.1	20.4
	200 °C	11.6	10.1	33.9	20.6
	300 °C	14.0	12.8	42.5	25.9
	400 °C	1.6	1.7	4.3	4.8

Table 3. Estimated activation energy of permeating gas species for carbon membranes (Unit: KJ/mol)

	P 600	POx 400
He	6.07	4.20
CO_2	10.24	−1.17
N_2	20.89	−1.57
CH_4	30.73	−1.51

The permselectivity value of He/CH_4 exists between 34 and 43 for the carbon membranes post-oxidized at a temperature between 100 and 300 °C , which is a lower value compared with that of P 600. Also, the permselectivity of He/N_2 showed decreased values (between 20 and 26) due to the enlargement of the pore structure. In permeation results of the post-oxidized membrane of POx 400, the permselectivity showed 4.3 and 4.8 for He/CH_4 and He/N_2, respectively. It is noted that the permeance significantly increased and the permselectivity decreased even though POx 400 has a microporous structure, as observed in Fig. 2. It is suggested that the post-oxidized carbon membrane has a diffusional path for gas transport in the structure [Kim et al., 2005].

The influence of the permeation temperature on the permeability can be estimated by the activation energy for each gas species. The estimated activation energies of He, CO_2 were 6.07 and 10.24 KJ/mol for the P 600, as shown in Table 3. For gas species having larger molecular size (N_2 and CH_4), the activation energy values were estimated to 20.9 and 30.7 KJ/mol, respectively, much higher than those of He and CO_2. The higher values of N_2 and CH_4 imply that there exists a greater barrier for the diffusion of those gas species [Suda and Haraya, 2000]. The estimated activation energy of each gas species in the table shows the positive values for all gas species for P 600, implying that the transport of examined gas species is controlled by the molecular sieving mechanism. The estimated activation energy of He was positive (4.2 KJ/mol) for the carbon membrane of POx 400. However, the activation energies of CO_2, N_2 and CH_4 were negative within −1.2 and −1.6 KJ/mol. The negative values indicate that the gas transport was more affected by the surface diffusion even though the post-oxidized carbon material has a microporous structure. It is thought that the permeation result of He showed a positive activation energy because of a small kinetic diameter and a low adsorption capacity. The relationship between permeation temperature and the permeability indicates that the gas transport was affected by surface diffusion mechanism. In addition, it is thought that the diffusional transport pathway was due to air-oxidation, thus decreasing the barrier for the gas transport.

3. Separation Properties in the Binary Mixture Gas Systems

Table 4. Transport data of the binary mixture gas systems for the carbon membrane of POx 400 (Permeation temperature: 35 °C)

A/B	Composition in the binary mixture (A : B)	Selectivity	
		Mixture	Single
CO_2/CH_4	45 : 55	1.47	0.70
CO_2/N_2	50 : 50	1.87	0.82
C_2H_6/CH_4	55 : 45	1.46	0.96
C_2H_6/N_2	33 : 67	2.11	1.11

In the surface diffusion mechanism, the permeance of an adsorbing gas species increases due to its preferential adsorption on the surface of the membrane pore structure, as mentioned before. Gas species with a high adsorption capacity preferentially adsorbs on the surface of the membrane pores, and then limiting the diffusion of the less adsorbing gas species into the pores, resulting in a higher permeance than the weakly adsorbing gas species. It is expected that the permeance in a binary mixture gas system is affected by different adsorption capacity of gas species [Rao and Sircar, 1996; Centeno and Fuertes, 2001; Shusen et al., 1996].

In this study, permeation experiments for the post-oxidized carbon membrane (POx 400) were separately carried out in order to investigate the influence of the adsorption on the permeation performance in the binary mixture gas systems. The permeances of the adsorbing gas species (C_2H_6 and CO_2) and the less adsorbing gas species (N_2 and CH_4) were measured at 35 °C and the selectivity in the binary mixture gas system was estimated. The permeance of CO_2 and C_2H_6 was measured to 3.88×10^{-8} and 5.30×10^{-8} mol $m^{-2}sec^{-1}Pa^{-1}$, respectively. For the less adsorbing gas species (CH_4 and N_2), their permeation results showed 5.53×10^{-8} mol $m^{-2}sec^{-1}Pa^{-1}$ for CH_4 and 5.53×10^{-8} mol $m^{-2}sec^{-1}Pa^{-1}$ for N_2, respectively. Table 4 shows the transport data for the binary mixture systems of CO_2/CH_4, CO_2/N_2, C_2H_6/CH_4 and C_2H_6/N_2 through the post-oxidized carbon membrane, and the result was compared with that of the single gas systems obtained from the separate permeation experiments. The binary mixture gas systems in the presence of the adsorbing gas species represent higher selectivity than their single gas systems, assuming that the preferential adsorption increased the adsorbing gas species due to the surface diffusion mechanism [Centeno and Fuertes, 2001; Fuertes, 2000]. In the permeation results for the system of CO_2 (CO_2/CH_4 and CO_2/N_2), the selectivity of CO_2/N_2 was higher than that of CO_2/CH_4 due to the lower permeance of N_2. Also, the system of C_2H_6/N_2 showed higher performance in the systems of C_2H_6/CH_4. The result implies that the extent of the gas transport inhibition in the binary mixture gas system increases more when the slowly permeating gas species has a lower adsorption capacity. Through the permeation performances in the single and binary mixture gas systems, it was shown that the permeation performances were affected by the permeation properties of the weakly adsorbing gas species as well as by the adsorption of the strongly adsorbing gas species.

The influence of feed composition on the permeation performances was investigated in the binary mixture gas system of C_2H_6 and N_2. As shown in Fig. 5, the composition of C_2H_6 in feed was changed between 0.2 and 0.8. As the composition of C_2H_6 increased, a small increase was observed for the total permeance from 5.42×10^{-8} mol

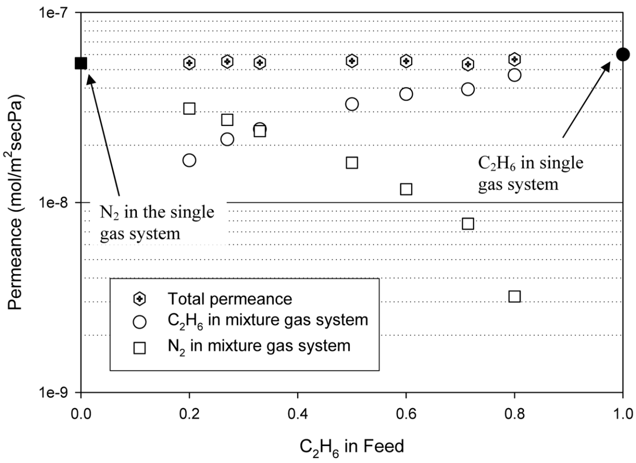

Fig. 5. Influence of C_2H_6 composition on permeance in the binary mixture gas system.

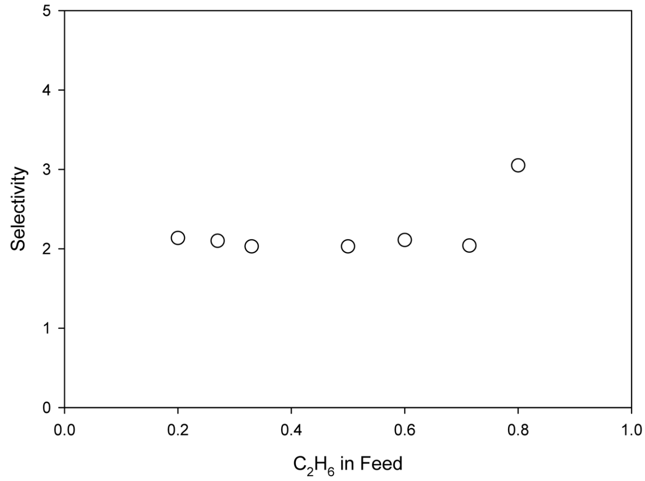

Fig. 6. Influence of C_2H_6 composition on the selectivity in the binary mixture gas system.

$m^{-2}sec^{-1}Pa^{-1}$ to 5.66×10^{-8} mol $m^{-2}sec^{-1}Pa^{-1}$. The N_2 permeance was notably decreased with increasing C_2H_6 composition, indicating that the permeation of the less adsorbing gas species was inhibited due to the preferential of the adsorbing gas species. Considering the selectivity in the binary mixture gas system in Fig. 6, the selectivity was higher than the single gas system (C_2H_6/N_2=1.1). In the permeation results with increasing the composition of C_2H_6 up to 0.71, the selectivity showed similar values between 2.0 and 2.1. The selectivity was estimated to 3.7 at 0.8 of the C_2H_6 composition in the feed stream. It is considered that the permeation performance in the presence of the adsorbing gas species was increased by the inhibition effect on the permeation of the less adsorbing gas species.

CONCLUSIONS

In this study, the PPO-derived carbon membranes were prepared by carbonization, followed by air-oxidation at different oxidation temperatures (between 100 and 400 °C) as post-treatment method. Characterization of the pore properties showed that the pore size, its distribution, and surface area were increased by the post-oxidation. Also, it is considered in the permeation results for the post-oxidized carbon membranes that the extent of the permeation modification showed a strong dependency on the oxidation temperature. Also, about 8-9 times increase was measured in the permeation results of the gas species with large molecular size (e.g. N_2 and CH_4). In the binary mixture gas systems, the permeation performance of the adsorbing gas species increased due to its preferential adsorption. Through the investigation of the post-oxidation effect on the permeation performance of the PPO derived carbon membrane, it was shown that the gas permeation and separation properties could be improved by the post-treatment of carbon membranes. In addition, the permeation performance was increased in the presence of the adsorbing gas species due to the surface diffusion mechanism.

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