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열분해성 그룹이 도입된 폴리이미드로부터 유도된 탄소분자체막의 수소 분리 특성

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Hydrogen Separation of Carbon Molecular Sieve Membranes Derived from Polyimides Having Decomposable Side Groups

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요 약: 본 연구에서는 카르복시기를 갖는 폴리이미드 전구체로부터 탄소분자체막을 제조하였다. 카르복시기를 갖고 있는 고분자 막의 경우 카르복시기 사이의 수소 결합에 의해 다른 곁가지(-CH_3, -CF_3)와 비교하여 다른 입체 특성을 보여주고 있다. 하지만 폴리이미드 전구체에서의 카르복시기의 영향과 비교하여 탄소분자체막의 구조에 있어서는 다른 특성을 보여준다. 즉, 카르복시기의 열분해에 의해 제조된 탄소분자체막의 경우 wide angle X-ray diffraction, 질소 흡착 거동, 기체 투과 실험을 통해 탄소분자체막의 microporous한 탄소막 형성에 중요하게 작용하고 있음을 확인할 수 있었다. 또한 탄소분자체막의 기체 분리 특성에 있어 최종 열분해 온도가 투과도 및 선택도를 결정하는 중요한 인자로 작용함을 알 수 있었다. 본 연구를 통한 기체 투과 실험 결과 카르복시기를 갖는 폴리이미드 전구체를 700°C에서 열분해를 통해 제조된 탄소분자체막의 경우 수소 투과도 3,809 Barrer, 수소/질소 선택도 46, 수소/메탄 선택도 130을 보여 주었다. 반면 카르복시기를 포함하지 않는 폴리이미드 전구체로부터 유도된 탄소분자체막의 경우 수소 투과도 3,272 Barrer, 수소/질소 선택도 136, 수소/메탄 선택도 177을 보여 주었다.

Abstract: Carbon molecular sieve (CMS) membranes were prepared by pyrolysis of polyimides having carboxylic acid groups and applied to the hydrogen separation. The polymeric membranes having carboxylic acid groups showed different steric properties as compared with polymeric membranes having other side groups (-CH_3 and -CF_3) because of the hydrogen bond between the carboxylic acid groups. However, the microporous CMS membranes were significantly affected by the decomposable side groups evidenced from the wide angle X-ray diffraction, nitrogen adsorption isotherms, and single gas permeation measurement. Furthermore, the gas separation properties of the CMS membranes were essentially affected by the pyrolysis temperature. As a result, the CMS membranes prepared by pyrolysis of polyimide containing carboxylic acid groups at 700°C showed the H_2 permeability of 3,809 Barrer [1×10^{-10} cm^3 (STP)cm/$cm^2 \cdot s \cdot cmHg$], H_2/N_2 selectivity of 46 and H_2/CH_4 selectivity of 130 while the CMS membranes derived from polyimide showed the H_2 permeability of 3,272 Barrer, H_2/N_2 selectivity of 136 and H_2/CH_4 selectivity of 177.

Keywords:

ntroduction

The membrane-based gas separation industry is still growing and changing. As well known, they have been focused on the oxygen enrichment, refinery hydrogen recovery, acid gas treatment, and helium recovery[1,2]. Among the various applications of gas separation, the hydrogen separation from nitrogen in ammonia purge gas streams was commercially applied for the first time. In ammonia synthesis, ammonia is typically produced

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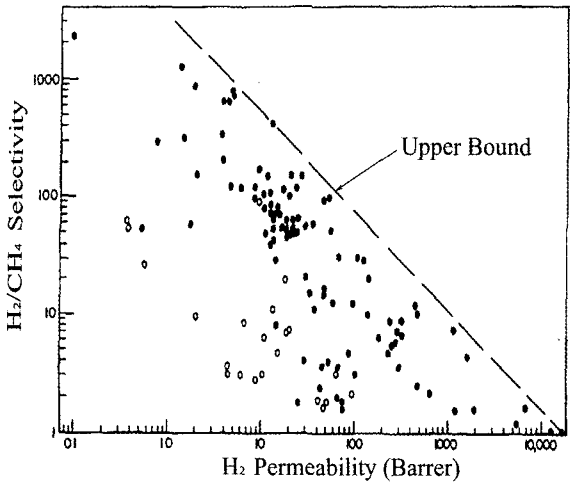


Fig. 1. Relationship between H_2 permeability and H_2/CH_4 selectivity for rubbery (○) and glassy (●) polymer membranes[4].

by reacting hydrogen and nitrogen at high pressure and temperature. Therefore, membranes provided the high-purity hydrogen that leads to energy savings and an effective capacity. In addition, the hydrogen/methane separation in refinery off-gases was launched by Monsanto in 1983[3]. This process is one of the most practical gas separations for membrane in refining operations.

Therefore, polymers are still essential materials for the membrane-based gas separations in spite of their tradeoff relation between permeability and selectivity. Robeson reported this conception by graphing the available data on the basis of an exhaustive literature survey as shown in Fig. 1[4]. To overcome the limitation of polymeric membranes, much research has focused on new membrane materials, such as carbon molecular sieves (CMS), silica and zeolites[5] and carbon-silica [6,7]. The CMS membrane materials were first applied as gas separation membranes, their excellent gas separation performances have been demonstrated with similar molecular size such as O_2/N_2, CO_2/CH_4, and CO_2/N_2[8]. Since Koresh and Soffer studied the preparation of carbon membrane in 1983[9], the various types of carbon membranes have been researched extensively. In general, carbon membranes can be divided by the configurations such as flat, hollow fiber, capillary, and tube[10-13]. Furthermore, the pyrolysis conditions (pyrolysis temperature, heating rate, soaking time, and pyrolysis atmosphere) and kinds of polymer precursors (polyimide, phenol resin, polyfurfuryl alcohol, polypyrrolone, and polyaromatic resin) are essentially considered[14-21].

In our previous study[22], we studied the effect of thermally decomposed pendent side groups such as carboxylic acid groups (-COOH), and we revealed that they typically affected the microporous carbon structures and their gas permeation properties. As a result, the CMS membranes derived from polyimide containing 50 mol% diamines having carboxylic acid groups showed the maximum gas permeability for O_2 of 707 Barrers [1×10^{-10} cm^3 (STP)cm/cm^2·s·cmHg] and an O_2/N_2 selectivity of 9 at 25°C. Above all, the carboxylic acid groups affected the packing density and chain mobility of polymeric membranes because of the hydrogen bond between them, but on the other hand, they affected the creation of microporous carbon structures in the CMS membranes by the decomposition during the pyrolysis. Therefore, they significantly corresponded to the gas permeation properties[23-25]. For the CMS membranes, their gas permeation properties mainly depend on the porous carbon structures, particularly related with the pore size, pore size distribution, pore volume, and compactness. Note that the characteristics of porous carbon are essentially influenced by the amount of evolvable gas molecules (e.g. CO, CO_2, CH_4, and H_2) during the pyrolysis.

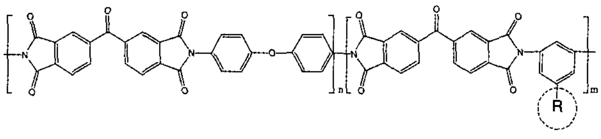
Up to now, the CMS membranes derived from polyimide have not been actively studied on the hydrogen separation. One of the research groups, Suda *et al.* [26] prepared CMS membranes derived from Kapton as a function of pyrolysis temperature. From the results, the CMS membranes pyrolyzed at 1,000°C showed H_2/N_2 selectivity of 1,450. This study is the continuation of our previous work[22], which studied the effect of removal side groups (-COOH) during the pyrolysis on the gas permeation properties using He, CO_2, O_2, and N_2, and we additionally prepared the CMS membranes as a function of pyrolysis temperature. In the hydrogen recovery and refinery systems, membranes compete with catalytic and pressure swing adsorption processes. Among the various membrane-based gas separation industries, hydrogen permeable and selective membranes have attracted the production of fuels, many chemical industries, and fuel cell applications[27-29]. Therefore, the CMS membranes having high permeabilities proved in our previous study were applied to the hydrogen separation, and we will report in this study on the separation of hydrogen from H_2/CH_4 and H_2/N_2 using CMS membranes prepared by pyrolysis of polyimide having carboxylic acid groups as a function of pyrolysis temperature.

Experimental

Preparation Polyimides and CMS Membranes

The polyimides were synthesized from dianhydride monomer (benzophenone tetracarboxylic dianhydride (BTDA)) and diamine monomers [4, 4'-oxydianiline (ODA), *m*-phenylene diamine (*m*PDA) and 3,5-diaminon benzoic acid (DBA)]. The BTDA, DBA, and *m*PDA were purchased from the Aldrich Chemical Co., (Milwaukee, WI, USA). ODA was purchased from the TCI Co. Ltd., (Tokyo, Japan). Dimethyl sulfoxide (DMSO, Aldrich Chemical Co., Milwaukee, WI, USA, minimum assay 99%) was used after drying in 4 molecular sieves. High purity hydrogen (H_2, 99,999%), nitrogen (N_2, 99.999%), and methane (CH_4, 99.999%) were used to investigate the gas permeation performance without further purification.

Fig. 2 shows the chemical structure of polyimide synthesized in this study. In the first stage, diamine monomers (ODA/*m*PDA=5/5 and ODA/DBA=5/5 by mmol) were dissolved in DMSO under a nitrogen atmosphere, and then, the purified BTDA powder was gradually added to each diamine solution. The prepared poly(amic acid) (PAA) solution was thermally imidized after casting onto glass plate in a vacuum oven. The total concentration of PAA solution used was 20 wt%. Hereafter, the polyimide precursors were denoted as PI-1 and PI-2 (sample PI-1: BTDA/ODA/*m*PDA and sample PI-2: BTDA/ODA/DBA).



Sample PI-1: R= -H

Sample PI-2: R= -COOH

Fig. 2. Chemical structures of polyimides synthesized in this study.

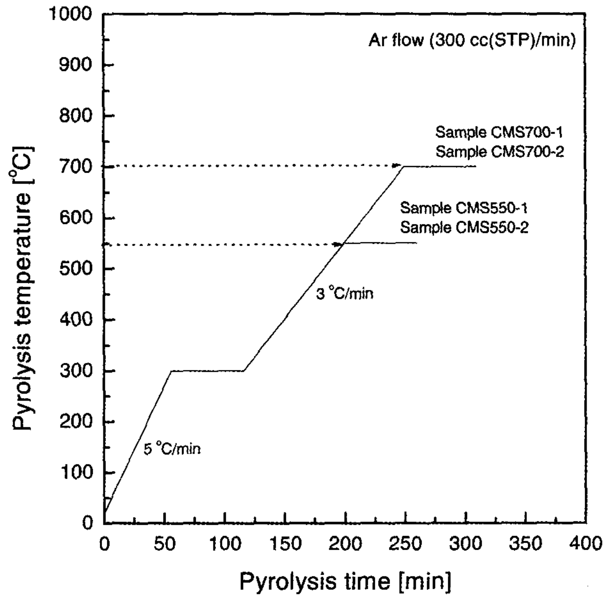


Fig. 3. Protocols for pyrolysis of polyimide precursors.

The pyrolytic CMS membranes used in this study were prepared by pyrolysis of polyimide precursors with final pyrolysis temperatures of 550°C and 700°C (samples CMS550 and CMS700). Before the pyrolysis experiments, the polyimides were treated at 100°C in a vacuum oven to remove any residual solvent, absorbed water vapor, and any dust. Fig. 3 shows the pyrolysis protocols used for an appropriate pyrolysis of the precursors. A detailed schematic diagram of the pyrolysis furnace used in this study has been given elsewhere [30]. The final CMS membranes were isolated from any source of moisture until use in analysis or in the gas separation experiments.

Characterization

Thermogravimetric analysis (TGA) was performed using a TA Instruments TGA2050 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) to study the thermal properties of the polyimide precursors. Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku Denki model RAD-C (Rigaku, Tokyo, Japan) with CuKα radiation of wavelength 1.54 Å to evaluate the average *d*-spacing values of the CMS membranes prepared by pyrolysis of polyimide precursors.

Gas Permeation Measurements

Hydrogen separation properties of CMS membranes derived from polyimide precursors were analyzed using single gases (H_2 and CH_4). Hydrogen permeabilities were measured using a single-gas permeation technique by the time-lag method at a feed pressure of 760 Torr and a feed temperature of 25°C. The permeability, P $[P=(R/A)/(\Delta P/l)]$, was obtained from the steady-state permeation rate, R, where A is the effective membrane area (cm^2) and l is the membrane thickness (cm). ΔP (cmHg) is the pressure difference between the feed side and permeate side.

The ideal separation factor $(\alpha=P_1/P_2)$ for components 1 (P_1) and 2 (P_2) is defined as the ratio of the pure gas permeabilities of each component. All the gas permeation experiments were repeated more than three times, and the error in the permeation measurements was less than 5%.

Results and Discussion

Thermal Stabilities of Polyimide Precursors

Fig. 4 shows the thermal properties of polyimide precursors. The thermal decomposition curves exhibited two major weight-losses at temperatures of 450-550 and 550-700°C. As can be seen, sample PI-1 was stable up to 550°C and then began to lose weight due to the decomposition of the main chains as observed generally in polyimide, while sample PI-2 having carboxylic acid groups showed a two-step weight loss at temperatures of 450-550 and 550-700°C. For the sample PI-2, the first weight loss was caused by the removal of the carboxylic acid groups, which were evolvable gas molecules such as CO and CO_2. The thermal decomposition profiles of polyimides showed significantly different weight-loss by the presence of carboxylic acid groups or not, as observed in the TGA results. In our previous study[22], we confirmed that the decomposed side groups affected the porous carbon structures such as pore volume and pore size in the carbon membranes. In addition, they will obviously influence on the gas permeabilities and selectivities.

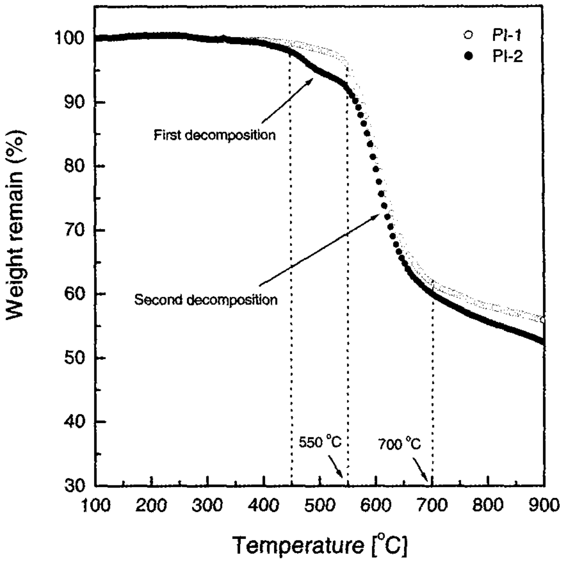


Fig. 4. Thermogravimetric analysis curves of polyimide precursors.

Gas Permeation Measurement of CMS Membranes

The gas permeabilities of CMS membranes derived from polyimide precursors were determined using H_2 (2.89 Å), N_2 (3.64 Å), and CH_4 (3.80 Å). Fig. 5 shows the H_2 and CH_4 permeabilities for the CMS membranes pyrolyzed at 550°C. From these results, the CMS membranes derived from sample PI-2 showed the higher H_2 and CH_4 gas permeabilities than those of CMS membranes derived from sample PI-1. For the CMS membranes pyrolyzed at 700°C, as shown in Fig. 6, their gas permeabilities were significantly influenced

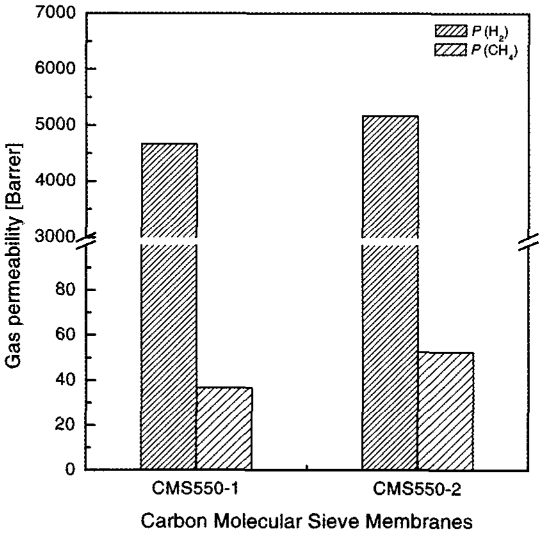


Fig. 5. Gas permeabilities of CMS membranes pyrolyzed at temperature of 550°C.

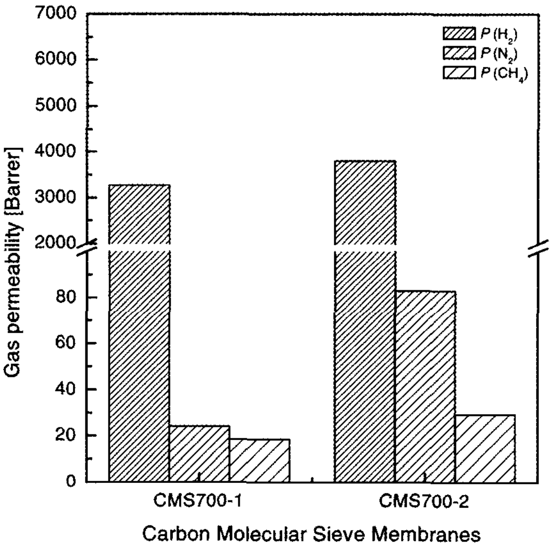


Fig. 6. Gas permeabilities of CMS membranes pyrolyzed at temperature of 700°C.

by the presence of decomposable carboxylic acid groups. The gas permeation results were reasonably explained because the larger micropores or more pore volume was built by the evolved gases produced by the decomposition of side groups (-COOH) and main chains during the pyrolysis, and also the created micropore size and volume were reduced with increasing the pyrolysis temperature. That is, the larger and more diffusional path-ways (micropores) to transport gas molecules were built in the CMS membranes at 550°C.

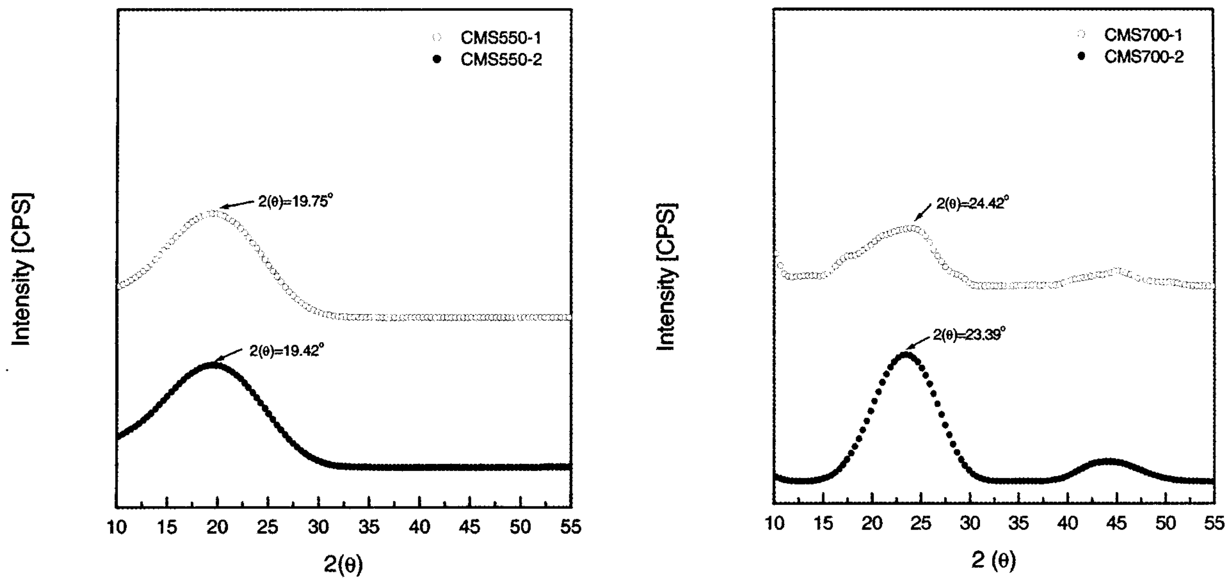
In general, the abrupt weight decrease was associated with the evolution of a large amount of CO_2, CH_4, and CO in the range of 550-650°C as illustrated in the literature[31]. Usually, the gas permeabilities through the microporous CMS membranes decreased with increasing the final pyrolysis temperature. In the literature[32], the higher final pyrolysis temperature tends to produce more compact microporous carbon membrane together with the higher selectivity, whereas relatively lower final temperature yields the carbon membranes with the higher permeability. Therefore, the relation between the pyrolysis temperature and the carbon structure well explained the gas permeation results of the CMS membranes fabricated in this study. Furthermore, as explained above, the micro pore size or pore volume could be controlled by the amount of evolvable gas molecules. Okamoto *et al.*[33] prepared the CMS membranes derived from phenolic resin with a pendant sulfonic acid group. They showed that the higher gas permeability of CMS membranes derived from phenolic resin having sulfonic acid groups than those of CMS membranes prepared by the pyrolysis of phenolic resin.

The permselectivities of the CMS membranes derived from samples PI-1 and PI-2 were listed in Table 1. The CMS membranes typically showed the tradeoff

Table 1. Gas Permeation Results for CMS Membranes at 25°C

Precursor	Pyrolysis temp. [°C]	Permeability [Barrer][a]			Selectivity	
		H_2	N_2	CH_4	H_2/N_2	H_2/CH_4
PI-1	550	4666	-	36.7	-	127
PI-1	700	3272	24	18.5	136	177
PI-2	550	5167	-	52.6	-	98
PI-2	700	3809	83	29.3	46	130

[a] 1 Barrer=10^{-10} $cm^3(STP)\cdot cm/cm^2\cdot s\cdot cmHg$

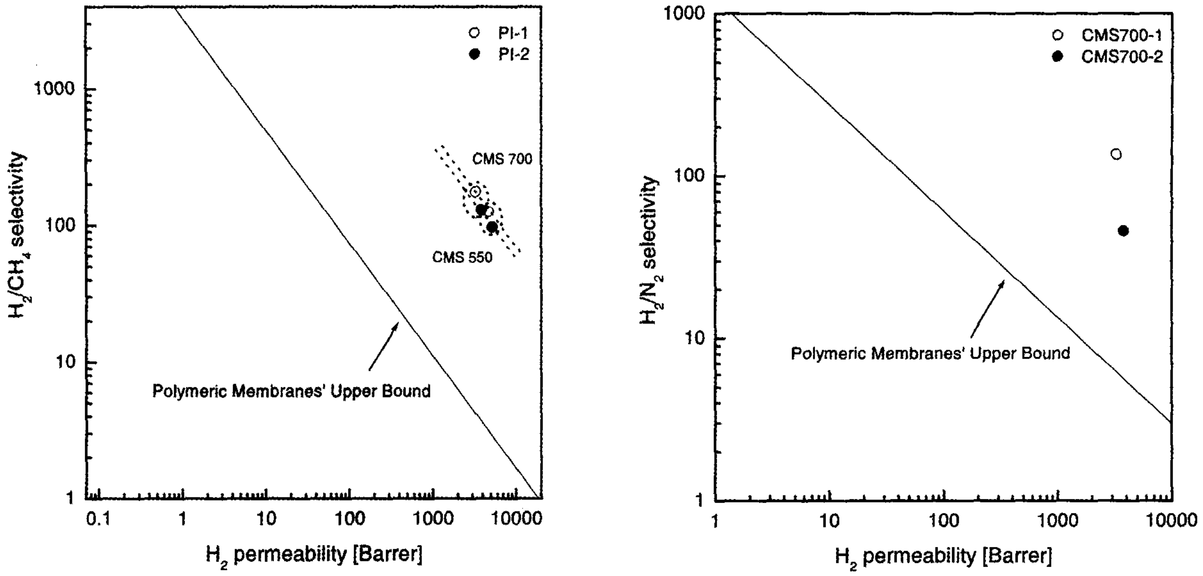


(a) (b)

Fig. 7. WAXD patterns of CMS membranes pyrolyzed at (a) 550°C and (b) 700°C.

relation between the permeabilities and selectivities. The samples CMS550-1 and CMS700-1 membranes showed the higher H_2/CH_4 selectivities than those of the samples CMS550-2 and CMS700-2 membranes. Furthermore, the selectivities of CMS membranes increased with the pyrolysis temperature. For the hydrogen/nitrogen separation, the CMS membranes pyrolyzed at 700°C were applied in this study. As a result, the CMS membranes derived from sample PI-1 showed the high H_2/N_2 selectivity as much as 136, while the CMS membranes derived from sample PI-2 showed the H_2/N_2 selectivity of 46. That is, the H_2/N_2 and H_2/CH_4 selectivities of microporous CMS membranes were essentially affected by the decomposed carboxylic acid groups and the pyrolysis temperatures. In general, the selectivity of a CMS membrane depended upon the density of the microporous carbon structures and micropore size, which considerably determined by the evolvable gas molecules and the pyrolysis temperature. As a result, the compact microporous carbon membranes showed the higher selectivities and the carbon membranes having the inclined micropore size created by the decomposed side groups led to the lower selectivities.

To confirm the structural difference of CMS membranes, their interlayer spacing (average *d*-spacing value) was measured using wide-angle X-ray diffraction (WAXD) patterns as functions of the pyrolysis temperature and the presence of carboxylic acid groups. WAXD is a useful technique for measuring the difference of regularity, ordered dimensions, and morphologies of carbon materials[5]. The average *d*-spacing value can be calculated from the Bragg equation ($n\lambda=2d\sin\theta$) where d is the *d*-spacing value, θ is the diffraction angle, λ is the X-ray wavelength, and n is an integral number. The average *d*-spacing value does not definitively indicate pore dimensions, but rather, relates with the distances between atoms in neighboring planes. Using X-ray diffraction results can provide qualitative and comparative evaluations of the degrees of packing of different carbon structures. As shown in Fig. 8, broad peaks of the CMS membranes pyrolyzed at 550°C and 700°C showed typical amorphous carbon structures. The diffraction angle (2θ) of CMS550-1 and CMS700-1 were observed at 19.75° and 24.42° [samples CMS550-1 (*d*-spacing=4.49 Å), CMS700-1 (*d*-spacing=3.65 Å)] while those of CMS550-2 and CMS700-2 were observed at



(a) (b)

Fig. 8. H_2 permeabilities *versus* (a) H_2/CH_4 and (b) H_2/N_2 selectivities of CMS membranes prepared in this study.

19.42° and 23.39° [samples CMS550-2 (*d*-spacing=4.57 Å), CMS700-2 (*d*-spacing = 3.80 Å)]. These results indicate that the average *d*-spacing values of the CMS membranes were affected by the pyrolysis temperature and the decomposition of carboxylic acid groups. As a result, the average *d*-spacing values decreased with increasing the pyrolysis temperature, and the CMS membrane derived from polyimide having carboxylic acid groups showed the higher average *d*- spacing values.

To further confirm the effect of carboxylic acid groups, N_2 adsorption isotherms [BET (Brunauer-Emmett-Teller) method] were observed at -196°C on the gas adsorption characteristics of the CMS membranes pyrolyzed at 700°C. The sample CMS700-2 showed the pore volume of 0.303 cm^3/g while the sample CMS700-1 measured the pore volume of 0.235 cm^3/g. In addition, the volume of adsorbed nitrogen was 150 cm^3/g for sample CMS700-1 while that of sample CMS700-2 was 200 cm^3/g at P/P_0=0.2. These results clearly indicate that the volume of micropores was influenced by the removal of the carboxylic acid groups during pyrolysis. By the analysis of CMS membranes using WAXD patterns and BET method, the gas permeation results of CMS membranes prepared by varying the pyrolysis temperature and the amount of decomposed carboxylic acid groups were reasonably confirmed in this study.

The H_2 permeabilities and selectivities (H_2/N_2 and H_2/CH_4) of the CMS membranes prepared in this study were plotted to understand the improvement of the performance of the CMS membranes when compared with other polymeric membranes first graphed by Robeson[4]. As shown in Fig. 8(a), The H_2 permeabilities and H_2/CH_4 selectivities of CMS membranes pyrolyzed at 550 and 700°C result in a significant improvement in the high H_2 gas permeabilities. Interestingly, the slope of the CMS membranes prepared by the different pyrolysis temperature is very similar to the slope of the upper bound of conventional polymeric membranes. That is, the higher pyrolysis temperature generally leads to the low gas permeabilities and the high gas selectivities in the CMS membranes. From the results, the sample CMS550-2 membranes showed the H_2 permeability of 5,167 Barrers and the H_2/CH_4 selectivity of 98. At high pyrolysis temperature, however, the sample CMS700-2 membranes showed the H_2 permeability of 3,809 Barrers and the H_2/CH_4 selectivity of 130. For the H_2/N_2 selectivities of CMS membranes pyrolyzed at 700°C, they showed the high H_2 permeabilities and H_2/N_2 selectivities when compared with other polymeric membranes as shown in Fig. 8(b). The CMS membrane derived from sample PI-1 showed the H_2/N_2 selectivity of 136, but on the other hand, the CMS membrane prepared by pyrolysis of polyimide having the carboxylic acid groups showed the H_2/N_2 selectivity of 46. Consequently, the presence of decomposable side group such as carboxylic acid group was surely considerable factor on the gas permeation performances of CMS membranes as much as the pyrolysis conditions considered in numerous studies.

Conclusions

The CMS membranes derived from polyimides having decomposable side group (-COOH) were prepared by pyrolysis at temperature of 550 and 700°C and applied to the hydrogen/methane separation. Their microporous carbon structures and their gas permeation properties were essentially affected by the amount of evolved gas molecules, which was characterized using wide-angle X-ray diffractometry, nitrogen gas adsorption isotherms, and single gas permeation measurements. From the results, the CMS membranes showed definitely enhanced gas permeation performance with the introduction of decomposable side groups. In addition, the hydrogen/methane selectivities of CMS membranes are well followed the final pyrolysis temperature.

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References

1. R. W. Baker, Membrane technology and applications, McGraw-Hill, New York (2000).
2. R. E. Kesting and A. K. Fritzsche, Polymeric gas separation membranes, John Wiley & Sons, Inc., New York (1993).
3. N. N. Li and J. M. Calo, Recent developments in separation science, CRC Press, FL (1986).
4. L. M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J Membrane Sci.*, **62**, 165 (1991).
5. D. Q. Vu, W. J. Koros, and S. J. Miller, Mixed matrix membranes using carbon molecular sieves I. Preparation and experimental results, *J. Membrane Sci.*, **211**, 311 (2003).
6. H. B. Park, I. Y. Suh, and Y. M. Lee, Novel pyrolytic carbon membranes containing silica: Preparation and characterization, *Chem. Mater.*, **14**, 3034 (2002).
7. H. B. Park and Y. M. Lee, Pyrolytic carbon-silica membrane: a promising membrane materials for improved gas separation, *J. Membrane Sci.*, **213**, 263 (2003).
8. H. B. Park, Y. K. Kim, J. M. Lee, S. Y. Lee, and Y. M. Lee, Relationship between chemical structure of aromatic polyimides and gas permeation properties of their carbon molecular sieve membranes, *J. Membrane Sci.*, in press (2004).
9. J. E. Koresh and A. Soffer, The carbon molecular sieve membranes. General properties and the permeability of methane/hydrogen mixture, *Sep. Sci. Tech.*, **22**, 973 (1987).
10. H. Hatori, Y. Yamada, and M. Shiraishi, Preparation of macroporous carbon films from polyimide by phase inversion method, *Carbon*, **30**, 303 (1992).
11. J. Hayashi, M. Yamamoto, K. Kusakabe, and S. Morooka, Simultaneous improvement of permeance and permselectivity of 3,3'4,4'-biphenyltetracarboxylic dianhydride-4,4'-oxydianiline polyimide membrane by carbonization, *Ind. Eng. Chem. Res.*, **34**, 4364 (1995).
12. J. Petersen, M. Matsuda, and K. Haraya, Capillary carbon molecular sieve membranes derived from Kapton for high temperature gas separation, *J.*

Membrane Sci., **131**, 85 (1997).

13. C. W. Jones and W. J. Koros, Carbon molecular sieve gas separation membranes. Part II. Regeneration following organic exposure, *Carbon*, **32**, 1427 (1994).
14. Y. D. Cheng and R. T. Yang, Preparation of carbon molecular sieve membrane and diffusion of binary mixtures in the membrane, *Ind. Eng. Chem. Res.*, **33**, 3146 (1994).
15. M. B. Rao and S. Sircar, Performance and pore characterization of nanoporous carbon membranes for gas separation, *J. Membrane Sci.*, **110**, 109 (1996).
16. S. Wang, M. Zeng, and Z. Wang, Asymmetric molecular sieve carbon membranes, *Sep. Sci. Technol.*, **31**, 2299 (1996).
17. F. K. Katsaros, T. A. Steriotis, A. K. Stubos, A. Mitropoulos, N. K. Kanellopoulos, and S. Tennison, *Microporous Mater*, **8**, 171 (1997).
18. V. M. Linkov, R. D. Sanderson, and E. P. Jacobs, Highly asymmetrical carbon membrane, *J. Membrane Sci.*, **95**, 93 (1994).
19. H. Hatori, Y. Yamada, M. Shiraishi, H. Nakata, and S. Yoshitomi, Carbon molecular sieve films from polyimide, *Carbon*, **30**, 305 (1992).
20. H. Suda and K. Haraya, Molecular sieving effect of carbonized Kapton polyimide membrane, *J. Chem. Soc. Chem. Commun.*, **11**, 1179 (1995).
21. C. W. Jones and W. J. Koros, Carbon molecular sieve gas separation membranes. Part I. Preparation and characterization based on polyimide precursors, *Carbon*, **32**, 1419 (1994).
22. Y. K. Kim, J. M. Lee, H. B. Park, and Y. M. Lee, The gas separation properties of carbon molecular sieve membranes derived from polyimides having carboxylic acid groups, *J. Membrane Sci.*, 2003, submitted
23. R. E. Kesting and A. K. Fritzsche, Polymeric gas separation membrane, John Wiley & Sons Inc., New York (1993).
24. K. Tananka, M. Okano, H. Toshino, H. Kita, and K. Okamoto, Effect of methyl substituents on permeability and permselectivity of gases in polyimides prepared from methyl substituted phenylenediamines, *J. Polymer Sci.*, **B 30**, 907 (1992).
25. M. R. Coleman, R. Kohn, and W. J. Koros, Gas-separation applications of miscible blends of isomeric polyimides, *J. Membrane Sci.*, **50**, 285 (1990).
26. H. Suda and K. Haraya, Gas permeation through microporous of carbon molecular sieve membranes derived from Kapton polyimide, *J. Phys. Chem.*, **B101**, 3988 (1997).
27. R. Ramachandran and R. K. Menon, An overview of industrial uses of hydrogen, *Int. J. Hydrogen Energy*, **23**, 593 (1998).
28. T. N. Veziroglu, Hydrogen energy system as a permanent solution to global energy-environmental problems, *Chem. Ind.*, **53**, 383 (1999).
29. D. Lee, L. Zhang, S. T. Oyama, S. Niu, and R. F. Saraf, Synthesis, characterization, and gas permeation properties of a hydrogen permeable silica membrane supported on porous alumina, *J. Membrane Sci.*, 2004, In press.
30. Y. K. Kim, J. M. Lee, H. B. Park, and Y. M. Lee, Carbon molecular sieve membranes derived from thermally labile polymer containing polyimide and their gas separation properties, *Membrane J.* **13**, 182 (2003).
31. M. Inagaki, New Carbons: Control of structure and functions, Elsevier, New York (2000).
32. C. G. Vincent and W. J. Koros, Effect of polyimide pyrolysis conditions on carbon molecular sieve membrane properties, *Ind. Eng. Chem. Res.*, **35**, 2999 (1996).
33. W. Zhou, M. Yoshino, H. Kita, and K. I. Okamoto, Carbon molecular sieve membranes derived from phenolic resin with a pendant sulfonic acid group, *Ind. Eng. Chem. Res.*, **40**, 4801 (2001).