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Fabrication of High Permeable Nanoporous Carbon-SiO_2 Membranes Derived from Siloxane-containing Polyimides

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Abstract: The silica containing carbon (C-SiO_2) membranes were fabricated using poly(imide siloxane) (PIS) having -CO- swivel group. The characteristics of porous C-SiO_2 structures prepared by the pyrolysis of poly(imide siloxane) were related with the micro-phase separation between the imide block and the siloxane block. Furthermore, the nitrogen adsorption isotherms of the CMS and the C-SiO_2 membranes were investigated to define the characteristics of porous structures. The C-SiO_2 membranes derived from PIS showed the type IV isotherm and possessed the hysteresis loop, which was associated with the mesoporous carbon structures, while the CMS membranes derived from PI showed the type I isotherm. For the molecular sieving probe, the C-SiO_2 membranes pyrolyzed at 550, 600, and 700°C showed the O_2 permeability of 924, 1076, and 367 Barrer (1×10^{-10} cm^3(STP)cm/cm^2·s·cmHg) and O_2/N_2 selectivity of 9, 8, and 12.

Keywords: *carbon-silica membrane, gas separation, carbon molecular sieve, poly(imide siloxane), micro-phase separation*

1. Introduction

Poly(imide siloxane) (PIS) copolymers are one of important materials for microelectronic and gas separation applications[1,2] due to their excellent adhesion and high gas permeability. The high gas permeability of PIS is due to the large distance between polymer segments and the low rotational energy of dimethyl groups around the siloxane bond of PDMS[3]. In addition, the gas separation properties of PIS membranes are highly depended upon the siloxane content and the micro-phase separated structures. With these characteristics of PIS membranes, we have previously prepared the carbon membranes containing silica (C-SiO_2) consisted of carbon phases and SiO_2 phases, and reported their high gas separation properties for small gas molecules, such as He/N_2, CO_2/N_2, and O_2/N_2. The high permeabilities and selectivities of C-SiO_2 membranes were essentially determined by silica-rich phases derived from siloxane blocks (dianhydride-PDMS) and carbon-rich phases derived from imide blocks (dianhydride-diamine) during the pyrolysis. That is, the carbon-rich phase provided the high gas selectivity, while the silica-rich phase was responsible for the high gas permeability.

Up to now, carbon molecular sieve (CMS) membranes were prepared by the pyrolysis of polymeric precursors, such as poly(furfuryl alcohol), phenolic resin, polyacrylonitrile, and polyimides[4-11] and polymer blends containing thermal labile polymer[12,13]. The gas separation properties of CMS membranes were generally determined by the properties of porous carbon structures developed during the pyrolysis. Furthermore, the porosity of CMS membrane was controlled by the introducing thermal labile side groups in polymer precursors, which affected the improved gas permeation performances[14-16].

In contrast to polymeric precursors, the phase sep-

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aration properties of imide- and siloxane-domain in poly(imide siloxane) were depended upon the content and the molecular weight (chain length) of siloxane block, which affected their pyrolytic porous C-SiO_2 structures as confirmed in our previous works. The present investigation is a continuation of our study of a series of C-SiO_2 membranes derived from poly(imide siloxane). The goal of this study was the development of the gas permeation performance through the C-SiO_2 membrane derived from poly(imide siloxane) precursor having the flexible swivel group. In the previous study[17], we confirmed that the swivel groups (-CO-) in polyimide affected the microstructures of CMS membranes, such as pore volume, pore size, and pore size distribution. As a result, the CMS membranes prepared from benzophenonetetracarboxylic dianhydride (BTDA)-based polyimide showed higher permeabilities as compared with those of CMS membranes derived from pyromellitic dianhydride (PMDA)-based polyimide precursor. Therefore, this paper discusses the effect of flexible swivel group in poly(imide siloxane) on the properties of porous C-SiO_2 membranes and their gas permeation performances using pure gases, such as He, CO_2, O_2, and N_2.

2. Experimental

2.1. Materials

The synthesis of poly(imide siloxane) (PIS) was proceeded with the employed dianhydride and diamine monomers. Benzophenonetetracarboxylic dianhydride (BTDA, Aldrich Chem. Co., Milwaukee, WI, USA) was used as a dianhydride. 4,4'-oxydianiline (ODA) was purchased from Tokyo Kasei Co., Inc., Tokyo, Japan and α,ω-aminopropyl poly(dimethyl siloxane) (PDMS, Shinetsu Co. Inc., Tokyo, Japan), which had M_n = 900 and n = 10 was used. Tetrahydrofuran (THF) and *N*-methylpyrrolidinone (NMP) were obtained from Aldrich Chem. Co., Milwaukee, WI, USA and used after drying in 4 Å molecular sieves.

2.2. Preparation of Poly(imide siloxane) and Carbon-SiO_2 Membranes

Poly(imide siloxane) (PIS) copolymer was synthesized as BTDA-ODA/PDMS system. The chemical composition of BTDA-ODA/PDMS was 10-8/2 by mmol. The PIS was synthesized as follows: (1) PDMS was dissolved in tetrahydrofuran (THF, Aldrich Chem. Co., Milwaukee, WI, USA) and then *N*-methylpyrrolidinone (NMP, Aldrich Chem. Co., Milwaukee, WI, USA) solution of ODA was added. (2) The powder of BTDA was added to THF/NMP solution of PDMS and ODA, and then the reaction mixture was stirred under a nitrogen atmosphere at room temperature for 6h to obtain homogeneous siloxane-containing poly(amic acid) (PAAS) solution. The solid concentration of PAAS was kept at 20% by weight. The PAAS solution was cast onto a glass plate and then thermally imidized at 250°C for 1 h.

To fabricate the carbon-SiO_2 (C-SiO_2) membranes, the PIS precursor was pyrolyzed at 550, 600, and 700°C under argon purge flow rate of 300 [cc(STP)/min] in a tube furnace supported on an alumina holding plate. The pyrolysis protocol used in this study was adjusted as follows: firstly, we employed an initial heating rate of 10°C/min from 25 to 400°C and then the heating rate was slowed to 3°C/min until the final pyrolysis temperature reached. Finally, the C-SiO_2 membrane was dwelt at the final pyrolysis temperature for 2 h and then the furnace was allowed to cool slowly to room temperature.

2.3. Characterization Methods

Thermal gravimetric analysis (TGA) was carried out in flowing nitrogen by use of TGA2050 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA) to investigate the thermal decomposition profiles of PI and PIS precursors. To avoid the influence of residual solvent or any absorbed vapors, the PI and PIS precursors were annealed at 300°C under vacuum condition.

Atomic force microscopy (AFM) was employed to observe the topology of the C-SiO_2 membranes using a Nanoscope II atomic microscope (Digital Instruments, Santa Barbara, CA). To define the characteristics of the phase separated SiO_2 domains, the poly(imide siloxane) precursor was treated with hydrogen fluoride (HF) acid etching to remove the SiO_2 phases for 24 h.

Nitrogen adsorption experiments using Brunauer-Emmett-Teller (BET) method were carried out to define the porosities of the CMS and the C-SiO_2 membranes derived from PI and PIS precursor using a Micrometrics model ASAP2010 (Micrometrics, GA, USA) at -196°C.

Gas permeabilities through the CMS and C-SiO_2 membranes were measured using a time-lag method at 25°C. To measure the gas permeability using high purity single gases (He [2.6 Å], CO_2 [3.3 Å], O_2 [3.46 Å], and N_2 [3.64 Å]), the permeate side pressure was kept below 1.33×10^{-3} Pa, while the feed side pressure was maintained at 1.01×10^{5} Pa. The selectivity of the C-SiO_2 membrane for a pair of gas components (Component 1 and Component 2) is expressed in terms of an ideal gas separation factor ($\alpha 1/2=P_1/P_2$). In particular, the pyrolyzed product (CMS and C-SiO_2 membrane) was masked using impermeable aluminum tape and then epoxy sealing was applied at the interface between the tape and the pyrolyzed product to inhibit any gas leak because the pyrolyzed product is too brittle to set on the gas permeation cell. The effective area and the thickness of the C-SiO_2 membrane were 2×2 cm^2 and 50 μm.

3. Results and Discussion

3.1. Thermal Stabilities of Polyimide and Poly(imide siloxane)

The thermal decomposition profiles of the PI and PIS precursors were investigated as shown in Figure 1. From the TGA result, the PIS precursor began to decompose drastically in the range of 400~500°C due to the poly(imide siloxane) segments (BTDA-PDMS), and then followed by second degradation occurring in the 550~650°C range because of the polyimide segments

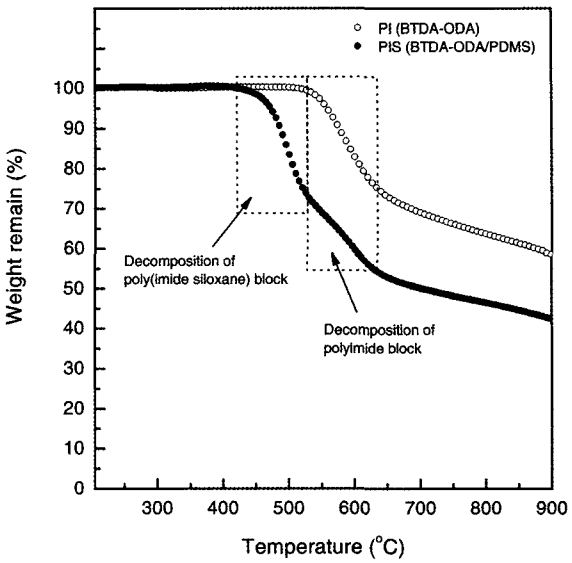
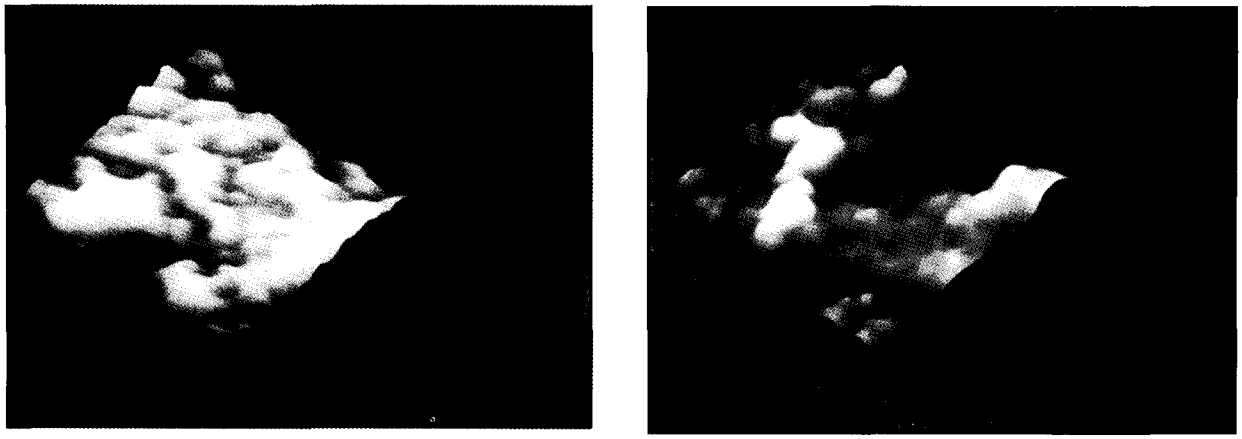


Fig. 1. Thermogravimetric analysis curves for polyimide and poly(imide siloxane).

(BTDA-ODA) as the PI (BTDA-ODA) precursor showed the one-step thermal decomposition profile in the range of 550~650°C. Even though TGA results did not provide enough information about the different microstructures of the CMS and the C-SiO_2 membrane, we can expect that the C-SiO_2 membranes (carbon phase and SiO_2 phase) might be formed the relative different structures at the identical pyrolysis temperature as compared with those of the CMS membranes (carbon phase).

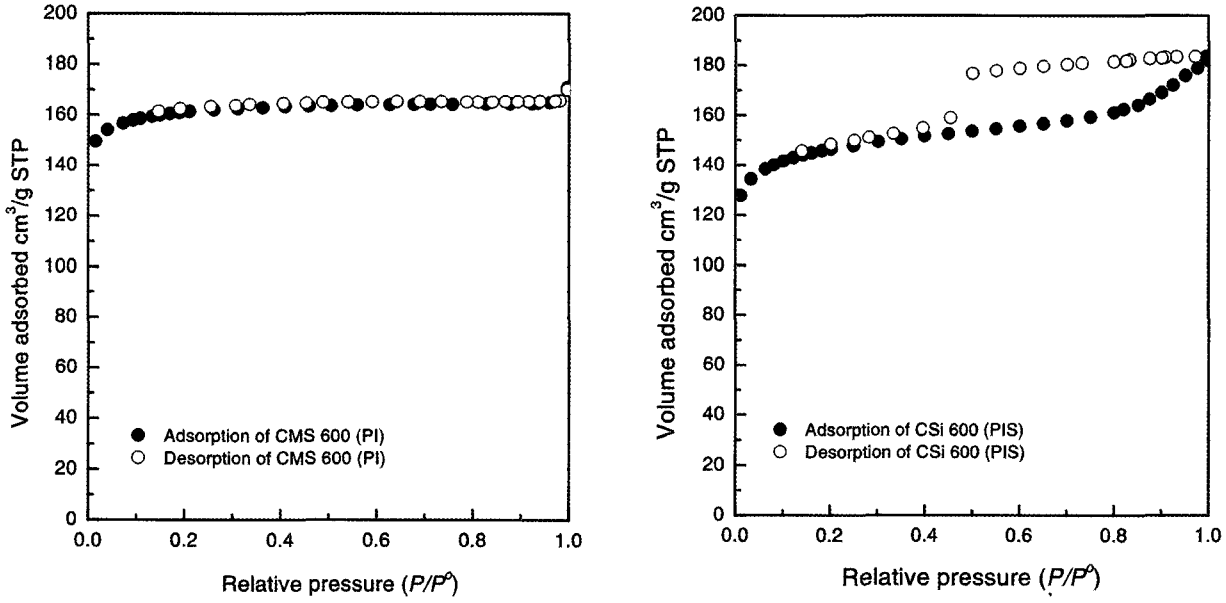
3.2. TM-AFM Image of Poly(imide siloxane)

Tapping-mode atomic force microscopy was used to study the surface morphology of the PIS precursor. In our previous studies[3,18], we confirmed that the surface of poly(imide siloxane) was consisted of two phases because of the difference in solubility of the two domains (polyimide: dianhydride-diamine and poly(imide siloxane): dianhydride-PMDS) during solvent evaporation. As shown in Figure 2, the characteristic of the surface morphology of PIS was in a good agreement with the result reported in the previous works. To confirm the SiO_2 phases, the poly(imide siloxane) precursor was treated with hydrogen fluoride (HF) acid. As shown in Figure 2 (b), the surface morphology



(a) (b)

Fig. 2. AFM images of (a) PIS and (b) HF treated PIS.



(a) (b)

Fig. 3. N_2 adsorption isotherms of (a) CMS membrane (CMS 600) derived from PI and (b) carbon-SiO_2 membrane (CSi 600) derived from poly(imide siloxane).

of PIS was consisted of the phase separated siloxane domains and the imide domains due to the solubility parameter difference of the two domains.

3.3. Properties of Porous CMS and C-SiO_2 Membranes

The porosities of the CMS and C-SiO_2 membranes prepared from the flexible PI and PIS precursors were studied by nitrogen adsorption/desorption analysis using a BET method. Figure 3 shows the nitrogen adsorption isotherms of the CMS and C-SiO_2 membranes pyrolyzed at 600°C. The CMS and C-SiO_2 membranes showed the accurately different nitrogen adsorption isotherms according to the introduction of PDMS. The CMS membrane showed the Type I isotherm, while the C-SiO_2 membrane showed the typical Type IV isotherm possessing a hysteresis loop associated with capillary condensation in mesopores. In general, Type I

isotherm is typical of microporous material, and Type IV isotherm possessing a hysteresis loop represents the mesoporous solids by the IUPAC classification[19]. Therefore, the CMS membrane basically obtained the microporous structures, while the C-SiO_2 membranes possessed the mesopores containing microporous structures. In particular, the adsorbed N_2 gases in the C-SiO_2 membrane was slightly desorbed to near P/P^o = 0.5, and then rapidly desorbed. This adsorption/desorption isotherm suggests that the formation of mesopores might be involved in the microporous structures such as ink-bottle like porous structures. In the literature[20], they reported that polysiloxanes $[RSiO_{1.5}]_n$ with R = CH_3 (PMS) and C_6H_5 (PPS) were transformed to Si-O-C ceramics of variable composition and structure upon pyrolysis in an inert atmosphere at 500 ~1500°C. They confirmed the formation of large transient open pores in the temperature range where thermal degradation occurred using a mercury intrusion measurement. This result is in a good agreement with the nitrogen adsorption isotherm results of the C-SiO_2 membranes.

To study the gas permeation performances of the nanoporous C-SiO_2 membranes, the gas permeabilities and selectivities of the C-SiO_2 membranes will be discussed in the following section.

3.4. Gas Permeation Results of C-SiO_2 Membranes

The gas permeation data of the CMS and C-SiO_2 membranes pyrolyzed at 550°C are shown in Figure 4. For the CMS and C-SiO_2 membranes, the gas permeabilities of selected gases were in the order: He (2.6 Å) > CO_2 (3.3 Å) > O_2 (3.46 Å) > N_2 (3.64 Å). This result shows that the permeabilities of small gas molecules through the CMS and C-SiO_2 membranes derived from the PI and PIS precursors agree with the order of the kinetic diameter of the gases. Even though the C-SiO_2 membranes derived from poly(imide siloxane) possessed the mesopores, the gas permeabilities were essentially determined by the molecular sieving effect because of the ink-bottle-like porous structures. That is,

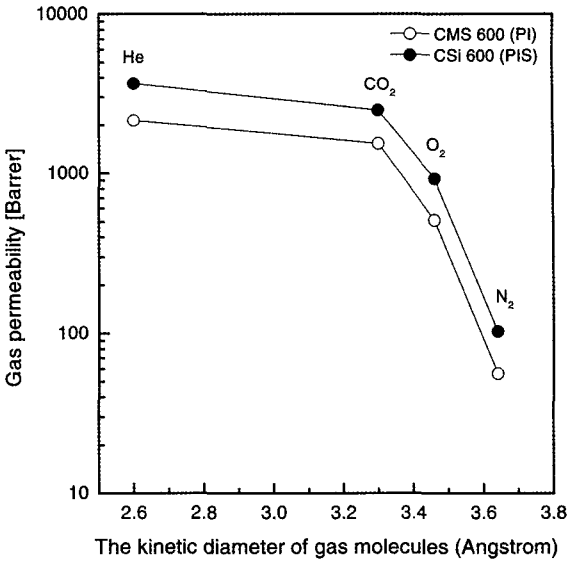


Fig. 4. Gas permeabilities of CMS membrane (CMS 600) derived from PI and carbon-SiO_2 membrane (CSi 600) derived from PIS.

the gas molecules could be transported fast through the large pores constructed in the microporous C-SiO_2 membranes. Therefore, the C-SiO_2 membrane showed the attractive permeation capacities as compared with the CMS membranes. For instance, Haraya *et al.*[21] prepared the CMS membranes pyrolyzed PMDA-ODA polyimide at 600~1000°C and reported their gas permeation performances (CMS membranes pyrolyzed at 600°C: $P(H_2)$ = 1600, $P(CO_2)$ = 1820, $P(O_2)$ = 383, and $P(N_2)$ = 82 barrer). On the other hand, the C-SiO_2 membrane pyrolyzed at 600°C showed much higher gas permeabilities as follows: P(He) = 4753, $P(CO_2)$ = 3115, $P(O_2)$ = 1076, and $P(N_2)$ = 135 barrer.

The gas separation properties of CMS membranes were depended upon the pyrolysis conditions, such as pyrolysis temperature, heating rate, isothermal time, and pyrolysis atmosphere[4,10,12,22,23]. In general, CMS membranes exhibited lower gas permeability and higher selectivity as the pyrolysis temperature increased. As shown in Table 1, the permeabilities and selectivities of the C-SiO_2 membranes pyrolyzed at 550, 600, and 700°C showed the reverse trends in the range of 550~600°C because more pores were developed in the C-SiO_2 membranes during the pyrolysis.

Table 1. Gas Permeation Results of Carbon and Carbon-SiO_2 Membranes Derived from Polyimide and Poly(imide siloxane) at 25°C

Precursors	Pyrolysis temperature [°C]	Permeability [Barrer]*				Selectivity to N_2		
		He	CO_2	O_2	N_2	He	CO_2	O_2
PI	550	2134	1535	509	56	38	27	9
PIS	550	3659	2491	924	103	36	24	9
	600	4753	3115	1076	135	35	23	8
	700	2899	908	367	31	94	29	12

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

As confirmed in Figure 1, the rapid weigh-loss of poly(imide siloxane) precursor was proceed to 600°C. That is, the formation of pores was primarily carried out until the pyrolysis temperature of 600°C, and then the produced initial pore sizes decreased with higher pyrolysis temperature. Therefore, the C-SiO_2 membranes pyrolyzed at 700°C showed lower gas permeabilities and higher selectivities. As a result, the C-SiO_2 membranes pyrolyzed at 550, 600, and 700°C showed O_2/N_2 selectivities of 9, 8, and 12, respectively.

To estimate the performance of the C-SiO_2 membranes derived from the poly(imide siloxane), the tradeoff relationship between O_2 permeability and O_2/N_2 selectivity was investigated as shown in Figure 5. Basically, the performances of the C-SiO_2 membranes were placed at the upper position of polymeric membranes' upper-bound. In addition, the C-SiO_2 membranes showed higher permeation capacities than those of other CMS membranes derived from polyimide precursors ((O) PMDA-ODA [21], (Δ) 6FDA-BPDA/TMPD[7]). Therefore, the nanoporous C-SiO_2 membranes showed the improved gas permeabilities due to lower diffusion resistance of the gas molecules through the large diffusional path-ways. The permeability of component A ($P_A = D_A \times S_A$) can be expressed as the diffusion coefficient (D_A) and the sorption coefficient (S_A), and the permselectivity of component A and B can be factored into terms for diffusion selectivity and sorption selectivity ($\alpha_{A/B} = (D_A/D_B) \times (S_A/S_B)$). Generally, the permeabilities of molecular sieving materials, such as zeolites and CMS membranes are determined by the sorption selectivity in the range of 0.7~2. In the case of the C-SiO_2 membranes pyrolyzed at 550, 600, and 700°C, O_2 diffusion coefficients were 3.2937×10^{-7}, 5.6952×10^{-7}, and 0.5181×10^{-7}, and O_2/N_2 sorption selectivities were in the range of 0.97~1.45. That is, the separation properties of the nanoporous C-SiO_2 membranes derived from poly(imide siloxane) were essentially determined by the diffusion selectivities. In addition, the C-SiO_2 membrane derived from BTDA-based PIS showed higher gas permeation performance than that of the C-SiO_2 membrane prepared from PMDA-based PIS. That is, the only difference in chemical structure between BTDA and PMDA is the ketone swivel group that is removed during pyrolysis. Therefore, the porosities of the C-SiO_2 membrane structures and their gas separation properties could be developed by the design of the chemical structure as well as the content and the molecular weight of siloxane block.

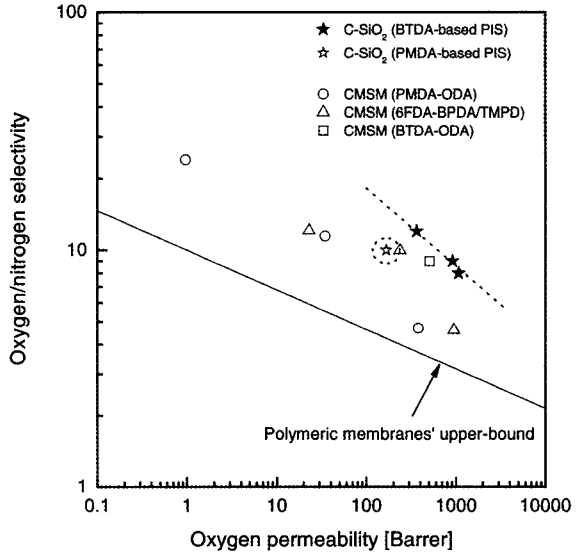


Fig. 5. O_2 permeabilities vs O_2/N_2 selectivities of carbon-SiO_2 membranes pyrolyzed at 550, 600, and 700°C.

4. Conclusions

C-SiO_2 membranes derived from the pyrolysis of poly(imide siloxane) were prepared at the final pyrolysis temperature of 550, 600, and 700°C. In the poly (imide siloxane) precursors, the properties, such as morphology and micro-phase separated poly(imide siloxane) were depended upon the solubility parameter difference between the imide block and the siloxane block. According to the nitrogen adsorption isotherms, the C-SiO_2 membranes derived from PIS showed type IV isotherms possessing a hysteresis loop, while the CMS membrane prepared from PI showed type I isotherms. From the gas permeation results of the C-SiO_2 membranes, their gas permeabilities were essentially determined by the molecular sieving effect, and the C-SiO_2 membranes showed higher gas permeation performances than those of the CMS membranes. Even though the C-SiO_2 membranes obtained the mesopores, the permeabilities and selectivities were placed at higher position as compared with the permeation performances of other CMS membranes due to the formation of high permeable SiO_2-rich phases and selective carbon-rich phases.

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