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Pore Structure and Permeance of Amorphous Si-C-O Membranes with High Durability at Elevated Temperature

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ABSTRACT

A porous α-alumina tube of 2.4 mm o.d. with an average pore size of ca. 150 nm was coated with *p*-xylene solutions of polycarbosilane (PC) and polystyrene (PS). The weight fraction of PS to total solid mass (PC + PS) was varied as 0, 1, 3 and 5 wt% (denoted as PC-PS*x* for a solution of *x* wt%). Then the film was cured in air at 473 K and pyrolyzed in argon at 1223 K. The procedure of dipping, drying, and pyrolysis was repeated three or four times in total. An Si-C-O membrane that was prepared with the PC-PS1 solution exhibited an H_2 permeance of 4×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and an H_2/N_2 selectivity of 20 at 773 K. The PS was concentrated into ellipsoidal domains due to phase separation during the curing step, and it was depolymerized and dissipated during the pyrolysis step. All membranes were resistant to heat treatment at 1223 K in argon for 20 hours. Except for the PC-PS5 membrane, voids that were formed by the decomposition of PS did not perforate the top layer. When the PC-PS1 membrane was exposed to a mixture of steam and helium at 773 K, the permeance was decreased to half in the first day, but was not greatly changed during the next 2 days.

INTRODUCTION

To attain the preference of inorganic membranes over polymeric ones, we should synthesize inorganic membranes with high thermal and chemi-

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cal stability and excellent permeation. Gavalas et al. (1) first prepared a molecular-sieving silica membrane in macropores of a porous glass support tube by the chemical vapor deposition method. Yan et al. (2) and Morooka et al. (3) obtained a supported silica membrane by evacuating reactants through a porous α-alumina support tube. The evacuation method was very effective to plug macropores of the support. A silica membrane formed by this technique showed an H_2 permeance of 10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ and an H_2/N_2 permselectivity of the order of 1000 at 873 K. These inorganic membranes are applicable to membrane reactor systems for selective hydrogen withdrawal (4, 5). Catalytic dehydrogenation of hydrocarbons proceeds mostly at temperature below 800 K, and conventional inorganic membranes are usable. However, some reactions such as H_2S decomposition occur above 1000 K (6, 7). No molecular-sieving membranes reported in the literature are workable in this temperature range (4, 5). Tsapatsis et al. (8) indicated that permselectivity of a silica membrane was severely depreciated by exposure to a temperature higher than 873 K. Kameyama et al. (7) and Shelekhin et al. (9) reported that porous glass membranes lost permeability after heat treatment above 1000 K.

Glassy polymers like polyimides are promising as materials for membranes (10). Polyimide membranes formed with 2,2-bis(3,4-decarboxyphenyl)hexafluoropropane dianhydride (6FDA) possess especially high permeance and selectivity (10, 11), and they are usable below glass-transition temperature of 500–700 K. When polyimide is carbonized, pores smaller than 1 nm are formed as a result of gas evolution by thermal decomposition of functional groups. Koresh and Soffer (12) prepared crack-free carbon membranes by carbonizing polymeric hollow fibers at 1073–1223 K. Selectivities of helium to oxygen and nitrogen were 8 and 20, respectively, and permeance of helium was 3×10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ at ambient temperature. Hayashi et al. (13) carbonized a BPDA-ODA polyimide membrane coated on an α-alumina support tube. Carbonization at 873–1073 K increased the gas permeation rate by two to four orders compared with the initial polyimide membrane. Permeance of carbon dioxide was of the order of 10^{-7} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$, and selectivity of carbon dioxide to methane reached 100 at 303 K. However, carbonized membranes are not stable under an atmosphere containing steam, oxygen, or hydrogen at an elevated temperature.

Silicon-based organic–inorganic composite membranes were prepared by controlled pyrolysis of polymeric precursors at a temperature lower than that of carbonization. Li and Hwang (14, 15) polymerized silane compounds impregnated in a porous wall and pyrolyzed the polymer film. Shelekhin et al. (16) and Grosgogeat et al. (17) formed silicon-based mem-

branes by coating porous Vycor glass tubes with polysilastyrene solutions and by pyrolyzing the films at 743 K. Kusakabe et al. (18) pyrolyzed a polycarbosilane (PC) film at 623–823 K, coated on a γ-alumina-modified α-alumina support tube. The organic–inorganic membrane prepared showed an H_2 permeance of 5×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1} and an H_2/N_2 permselectivity of 7.2 at 673 K. The membrane was amorphous and stable in inert atmosphere at 773 K. Kusakabe et al. (19) characterized and improved the amorphous Si-C-O membranes. When a precursor film was pyrolyzed at 823 K, hydrogen permeance was quite high, but H_2/N_2 permselectivity was unsatisfactory. For an Si-C-O membrane coated three times and pyrolyzed at 1223 K, on the other hand, H_2 permeance was about (10^{-9} to 10^{-8}) mol·m^{-2}·s^{-1}·Pa^{-1}, and H_2/N_2 selectivity reached 18–63 at 773 K. When polystyrene (PS) was added by 5 wt% to polycarbosilane, H_2 permeance was increased to 10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}, whereas H_2/N_2 selectivity was decreased to 13 at the same permeation temperature. Thus the addition of PS changed the macropore structure of the pyrolyzed membrane, but details were not elucidated.

In the present study a PC-PS polymeric film was formed on a porous α-alumina support tube. The film was then cured in air at 473 K and pyrolyzed in argon at 1223 K. The effects of composition of starting solutions and cured time on permeation of the membranes were investigated. Stability of the membranes was also studied in inert and steam-containing atmospheres at elevated temperatures.

EXPERIMENTAL

Preparation of Membranes

A porous α-alumina tube (2.4 mm, o.d.; 1.8 mm, i.d.; average pore size, ca. 150 nm) supplied by NOK Corp., Japan was used as the support. Polycarbosilane was provided by Nippon Carbon Co., Japan. The number-average molecular weight was ca. 1300, and the melting point was 512 K. The approximate composition excluding oxygen was $SiC_{1.8}H_4$, and the oxygen content was below 1 wt%. Polystyrene (number-averaged degree of polymerization = 1600–1800) was purchased from Wako Pure Chemical Ind. The PC and PS powders were dissolved in *p*-xylene. The weight fraction of PS to the total solid mass (PC + PS) was fixed at 0, 1, 3, and 5 wt%. The solutions are hereafter denoted as PC-PS0, PC-PS1, PC-PS3, and PC-PS5. The total solid concentration in each solution was adjusted to 5 or 25 wt%. The α-alumina support tube was dipped in the 25 wt% solution for 1 minute and dried overnight at room temperature. The film was cured in air by heating at a rate of 25 K·h^{-1} and keeping at

473 K for 1 hour, or at a rate of 33 $K \cdot h^{-1}$ and keeping at 473 K for 2 hours. Then the film was heated in argon at a rate of 100 $K \cdot h^{-1}$ to 1223 K, where it was pyrolyzed for 1 hour. Next, the 5 wt% solution was applied, and the procedure of dipping, drying, and pyrolysis was repeated twice unless otherwise noted. The curing and pyrolysis conditions were selected from the literature (20–22). Top surfaces and fractured sections of membranes were observed with a field emission scanning electron microscope (SEM, Hitachi S-900).

Oxygen content in membranes was determined with an O N analyzer (Leco TC-436). Surface area was calculated from the adsorption–desorption isotherm of nitrogen determined with a BET unit (Micromeritics, ASAP 2000). Membranes were also characterized by x-ray diffraction analysis (XRD, Shimadzu XD-D1). To evaluate oxygen content, surface area, and crystallinity, the polymer solution was cast on a clean glass plate and dried. Then it was processed under the same conditions as used to prepare the membrane on the support tube.

Permeation and Stability

Permeance of membranes was determined with single component He, H_2, CO_2, N_2, C_3H_8, and i-C_4H_{10} in the temperature range of 283–973 K. The apparatus used was shown elsewhere (2). Each permeating gas was introduced into the shell side, and permeated gas was carried by argon in the tube side. The flow rate was measured with a soap-film flowmeter, and the gas composition was analyzed with a gas chromatograph equipped with a thermal conductivity detector (Shimadzu GC9A). Mean partial pressure of permeating gas in the permeate side was calculated by logarithmically averaging the partial pressures at the inlet and outlet of the membrane tube. The total pressure in the outer and inner sides of the membrane was kept atmospheric. Permeance of the i-component, P_i, is calculated from

$$P_i = Q_i/(A\Delta p_i) \tag{1}$$

where Q_i is the permeation rate, A is the surface area of the membrane, and Δp_i is the partial pressure difference of the i-component. The selectivity of i to j is defined by P_i/P_j.

Membranes were heated in argon at a rate of 50 $K \cdot h^{-1}$ to 1223 K, which was maintained for 5, 10, 15, and 20 hours in total. After the heat treatment, permeances to He, N_2, and CO_2 were determined. The PC–PS1 membrane was exposed to a mixture of He and H_2O (7.8 wt%) at 773 K for 12, 24, 48, and 72 hours, and permeances to H_2 and N_2 were measured.

RESULTS AND DISCUSSION

Structure of Membranes

To elucidate the decomposition mechanism of the polystyrene, it was heated in air at a rate of 25 $K \cdot h^{-1}$ and kept at 473 K for 2 hours. The atmosphere was then switched to deoxidized argon. The temperature was increased again at a rate of 50 $K \cdot h^{-1}$ to 623 K, which was maintained for 1 hour. The mass of the polymer was changed from 0.350 to 0.314 g after the curing at 473 K and to 0.070 g after the pyrolysis at 623 K. From the elemental analysis, the composition of the sample was H 7.60 wt%, C 91.38 wt%, and ash 0.42 wt% after the curing; and H 7.58 wt%, C 92.18 wt%, and ash 0.13 wt% after the pyrolysis at 623 K. The results mean that polystyrene remained unchanged during the curing period, and that it was depolymerized during the pyrolysis period. After the curing for 1 hour, the PC-PS0 and PC-PS5 samples contained oxygen at 12 and 10 wt%, respectively. After subsequent pyrolysis for 1 hour, the oxygen contents were 12 and 11 wt%. This suggests that oxygen was acquired mainly by polycarbosilane. After curing for 2 hours, the oxygen uptake was increased to 18 and 13 wt% for the PC-PS0 and PC-PS5 samples, respectively. Since polystyrene was decomposed in the pyrolysis step, oxygen was incorporated with the polycarbosilane moiety. These oxygen uptakes are in the range reported by Hasegawa et al. (20) and Bouillon et al. (22). XRD analysis revealed that the membranes were amorphous after the pyrolysis under the present conditions, as reported previously (19). This is in agreement with the result of Bouillon et al. (22) and Soraru et al. (23).

Figures 1(a)–(d) show top surfaces of the membranes formed by the 2-hours curing and 1-hour pyrolysis. The top surface of the PC-PS0 membrane was very smooth. Round holes seen on the top surfaces of the PC-PS1, PC-PS3, and PC-PS5 membranes were formed by depolymerization of polystyrene, which was concentrated in globular domains due to phase separation in the curing stage. Figures 2(a)–(d) show the fractured sections of these membranes. No voids penetrated the membranes.

Figures 3(a)–(d) and Figs. 4(a)–(d) show the top surfaces and fractured sections of the membranes which were heat-treated at 1223 K for 20 hours in argon. The membranes were formed by the 2-hours curing and 1-hour pyrolysis. The morphology of the PC-PS0 membrane was unchanged during the heat treatment, but voids of the PC-PS5 were enlarged. Figure 4(d) indicates a void penetrating the PC-PS5 membrane. Figures 5(a)–(d) and Figs. 6(a)–(d) show the top surfaces and fractured sections of the membranes which were exposed to the H_2O–He mixture at 773 K for 72

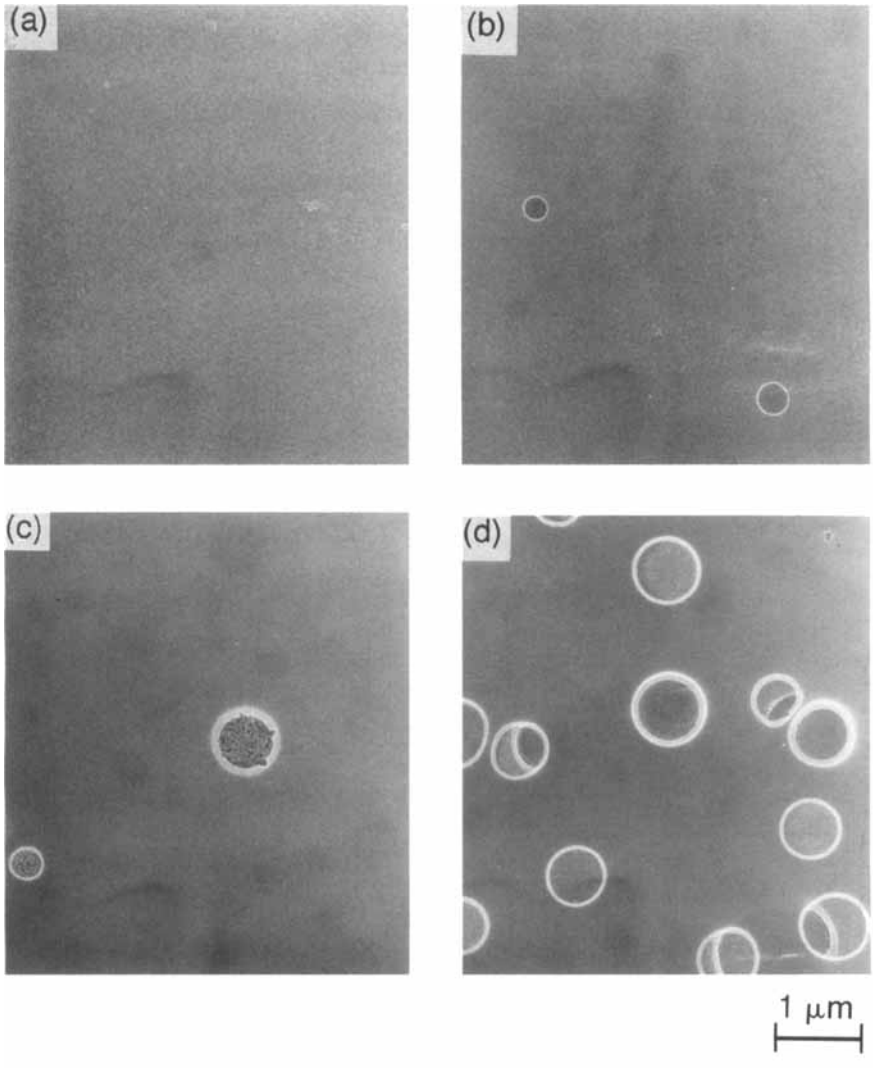

FIG. 1 Top surfaces of membranes prepared by curing for 2 hours and pyrolysis for 1 hour: (a) PC-PS0, (b) PC-PS1, (c) PC-PS3, (d) PC-PS5.

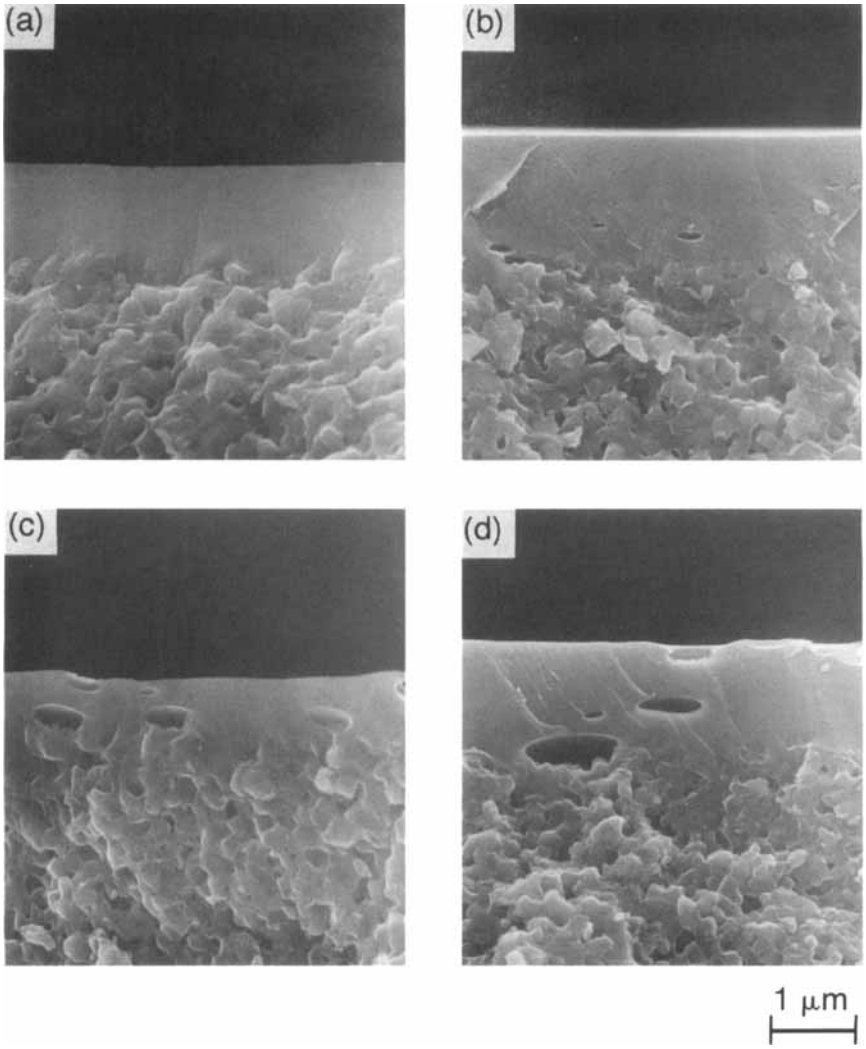

FIG. 2 Fractured surfaces of the membranes shown in Fig. 1.

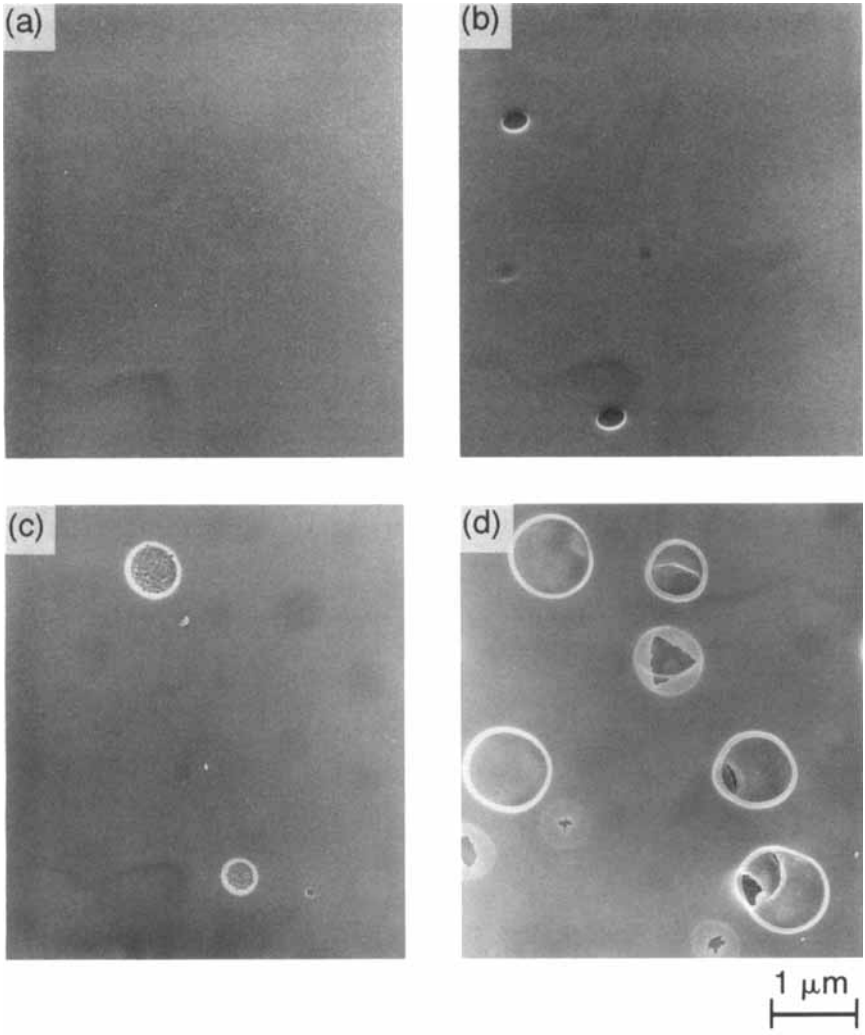

FIG. 3 Top surfaces of membranes prepared by curing for 2 hours, pyrolysis for 1 hour, and heat-treated at 1223 K for 20 hours: (a) PC-PS0, (b) PC-PS1, (c) PC-PS3, (d) PC-PS5.

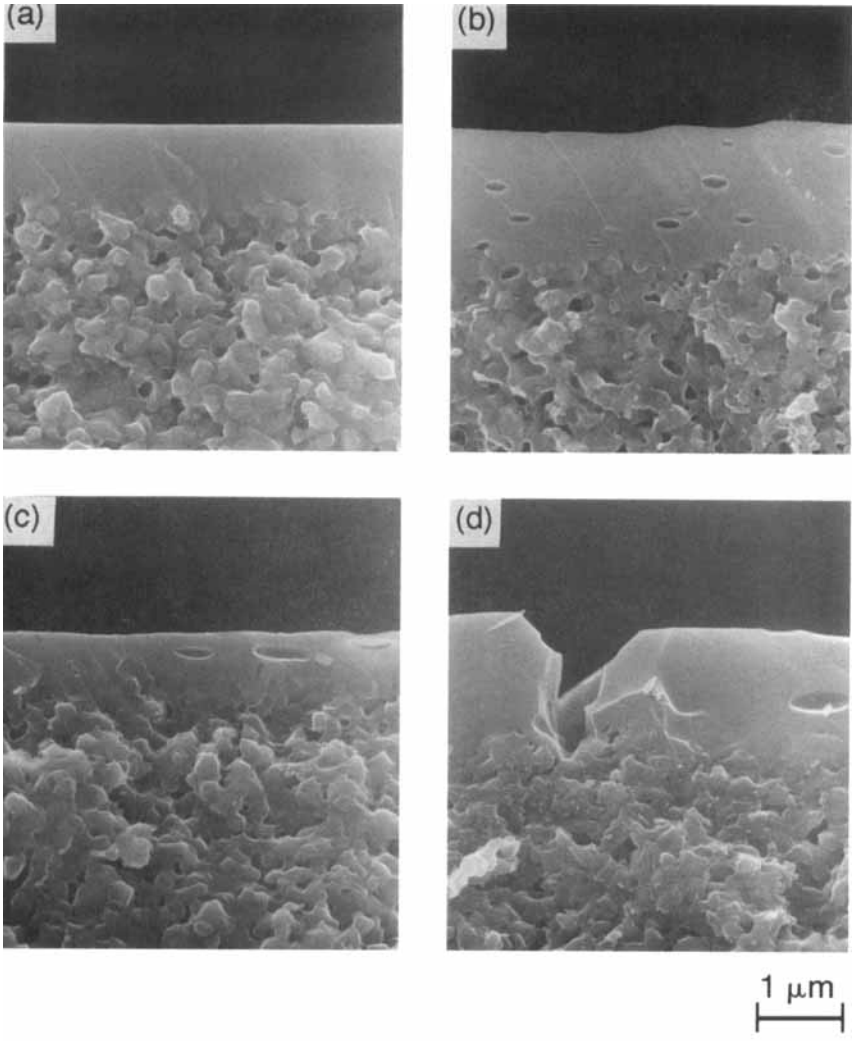

FIG. 4 Fractured surfaces of the membranes shown in Fig. 3.

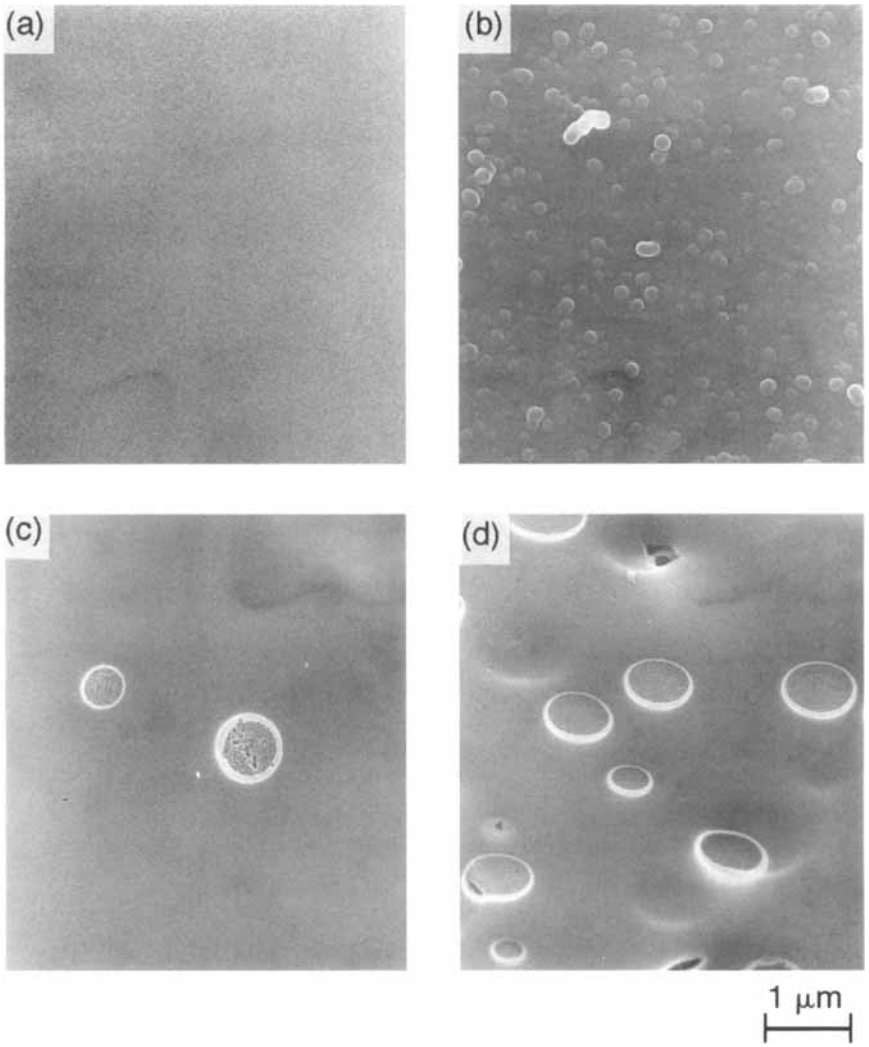

FIG. 5 Top surfaces of membranes prepared by curing for 2 hours, pyrolysis for 1 hour, and treated in H_2O–He mixture at 773 K for 72 hours: (a) PC-PS0, (b) PC-PS1, (c) PC-PS3, (d) PC-PS5.

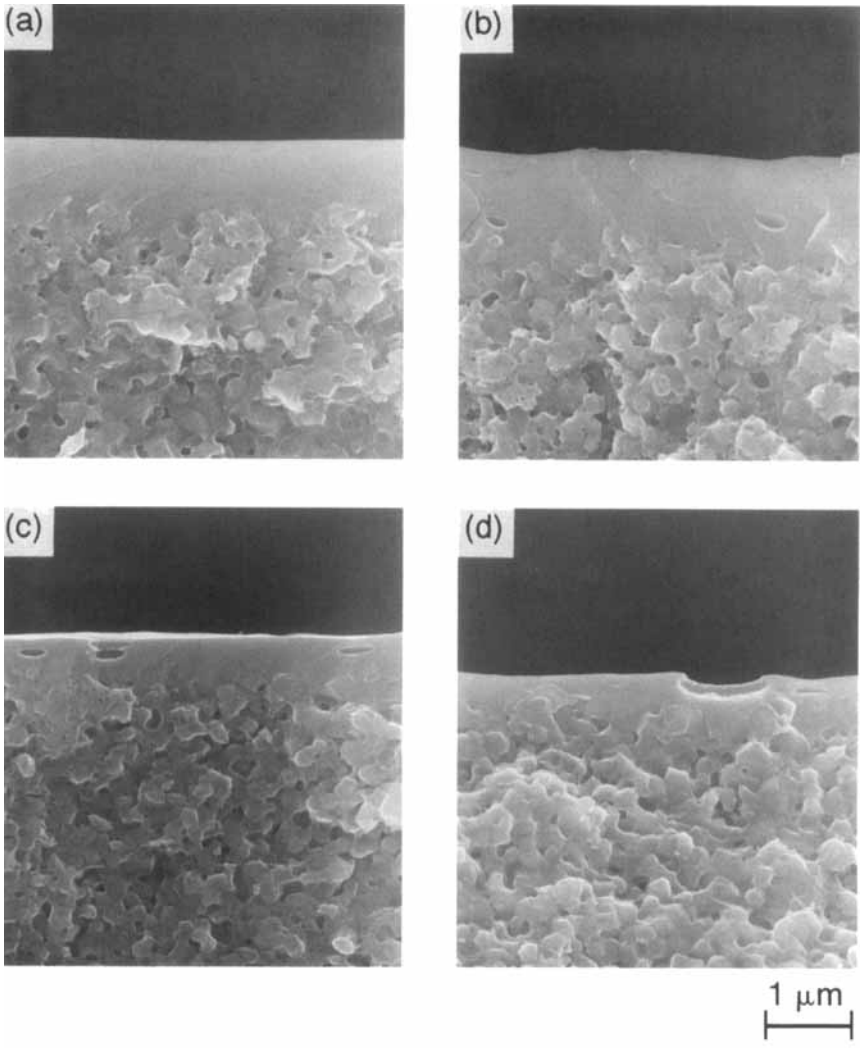

FIG. 6 Fractured surfaces of the membranes shown in Fig. 5.

hours. It was observed that few voids perforated the PC-PS5 membrane. No penetrating voids were found for the other membranes.

Permeation Rate

Figure 7 reveals permeances to hydrogen, helium, nitrogen, and carbon dioxide as a function of permeation temperature. The membranes were cured at 473 K for 1 or 2 hours and pyrolyzed at 1223 K for 1 hour. Permeances of the PC-PS0 membranes were dependent on the curing time. When the membrane was cured for 1 hour, permeances of hydrogen and nitrogen at a permeation temperature of 773 K were 6.6×10^{-9} and 1.8×10^{-10} mol·m^{-2}·s^{-1}·Pa^{-1}, respectively. When the PC-PS0 membrane was cured for 2 hours, H_2 and N_2 permeances were increased respectively to 1.1×10^{-8} and 2.5×10^{-10} mol·m^{-2}·s^{-1}·Pa^{-1}. In the case of PC-PS5 membranes, however, permeances were not greatly changed by the curing time. This is in accord with the result that the increment of oxygen content in the PC-PS0 membrane by the increase in curing time was much larger than the increment in the PC-PS5 membrane. Oxygen content in cured films is related to micropore volume after pyrolysis.

Figure 8 shows the effect of permeation temperature on permeances of the PC-PS0, PC-PS1, PC-PS3, and PC-PS5 membranes cured for 2 hours and pyrolyzed for 1 hour. The addition of PS increased the permeances of the membranes. The permeances of the PC-PS5 membrane were the highest, and those of the PC-PS0 membrane were the lowest. The BET surface areas of the membranes pyrolyzed at 1223 K were smaller than 3 m^2·g^{-1}. The membranes were also subjected to a sorption test using a constant-volume sorption unit (13). We tried to obtain a sorption isotherm of CO_2 at 298 K after degasing samples at 323 K for 6 hours. However, the amount of adsorbed CO_2 was too small to calculate parameters of the Dubinin–Astakhov equation (24). The pore volumes, and the permeances as well, of the membranes prepared in this study were smaller than those of carbonized membranes prepared by Hayashi et al. (13). This may be ascribed to the difference in properties of the precursors, polycarbosilane and polyimide.

The permeation of H_2 and He in the PC-PS0 membrane was controlled by an activation diffusion mechanism, and the activation energies for those gases were in the range of 8–9 kJ·mol^{-1}. The activation energy for N_2 permeance in the same membrane was smaller than 1 kJ·mol^{-1}. Nitrogen permeated through macropores and mesopores rather than micropores of the amorphous Si-C-O layer. This reduced the activation energy. The activation energies for H_2 and He permeances of the PC-PS5 membrane were smaller than those of the PC-PS0 membrane. The permeance of CO_2 in all membranes prepared in the present study was controlled by a surface

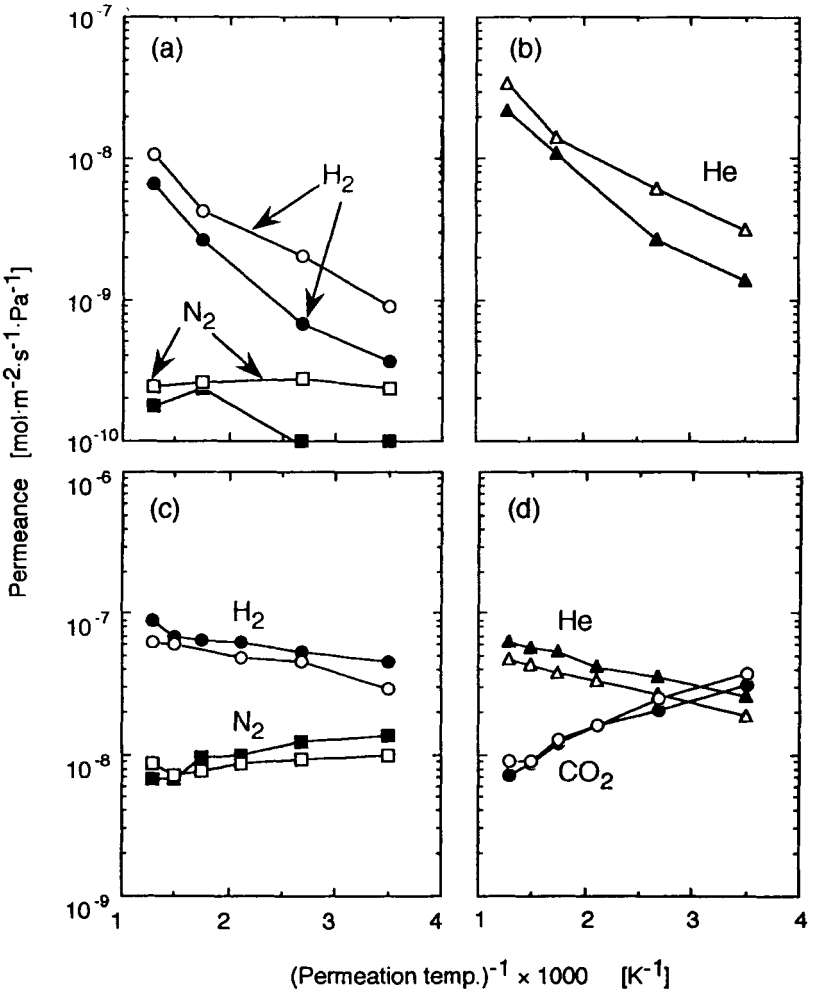

FIG. 7 Effect of curing time at 473 K on permeances: Filled keys, cured for 1 hour; open keys, cured for 2 hours. (a) and (b), pyrolyzed PC-PS0 membrane; (c) and (d), pyrolyzed PC-PS5 membrane.

diffusion mechanism, and was lower at higher permeation temperature. These results are in agreement with permeation properties generally observed with molecular-sieving inorganic membranes.

Figure 9 indicates selectivities of H_2, He, and CO_2 to N_2 for the membranes shown in Fig. 8. The lower the permeances, the higher the selectivi-

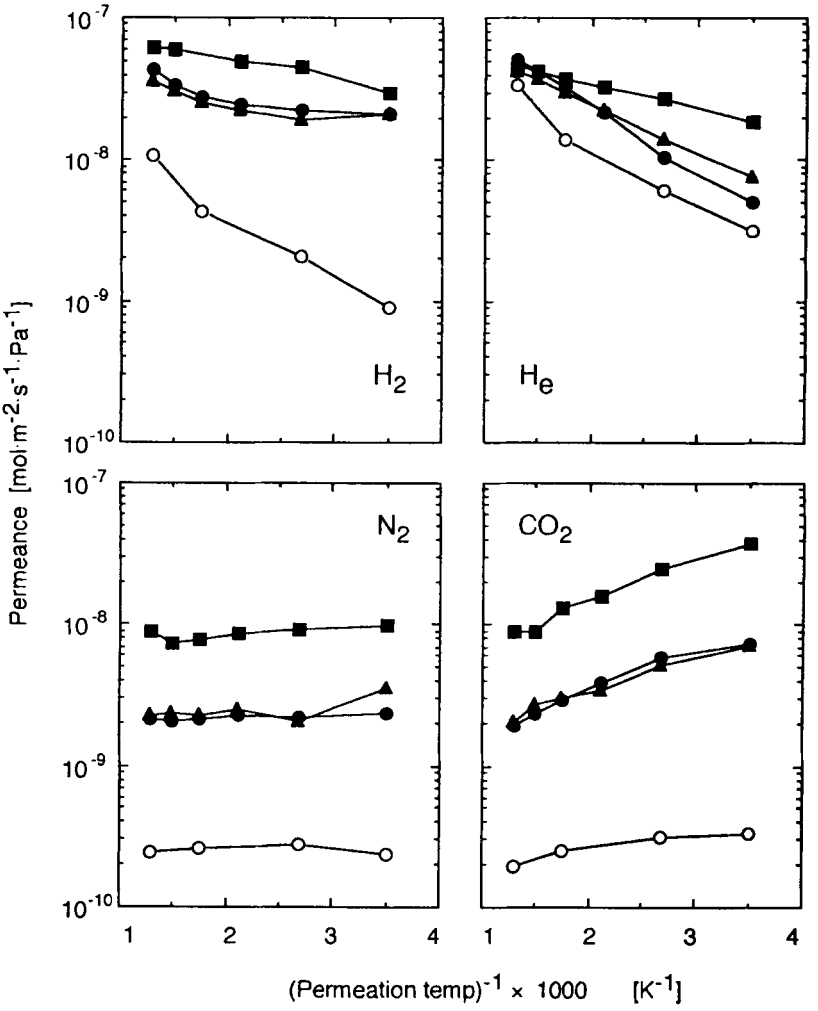

FIG. 8 Effect of PS content in precursor solution on permeance: Curing time, 2 hours: (○) PC-PS0; (●) PC-PS1; (▲) PC-PS3; (■) PC-PS5.

ties. The H_2/N_2 and He/N_2 selectivities increased with increasing temperature, whereas the CO_2/N_2 selectivity decreased with increasing temperature. All selectivities at permeation temperatures over 373 K were higher than the theoretical values calculated from Knudsen diffusion mechanism. Figure 10 shows permeances at 773 K as a function of gas

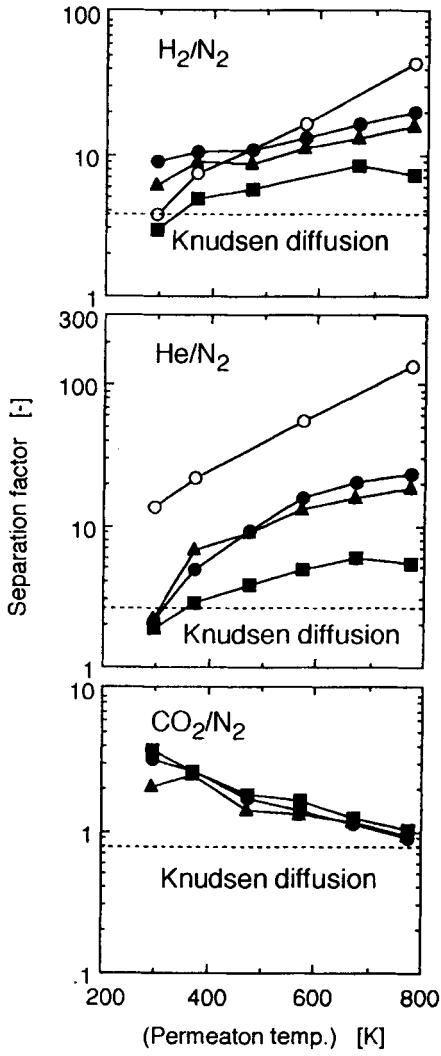

FIG. 9 Effect of PS content in precursor solution on permselectivity: Curing time, 2 hours. Keys are the same as in Fig. 8.

kinetic diameters, which are cited from the literature (25). For the PC-PS1 membrane, the selectivity of H_2 to i-C_4H_{10} was 95 at 773 K. Shelekhin et al. (16) reported that a polymer/inorganic composite membrane which was supported on a porous Vycor glass tube separated H_2 from SF_6 at a

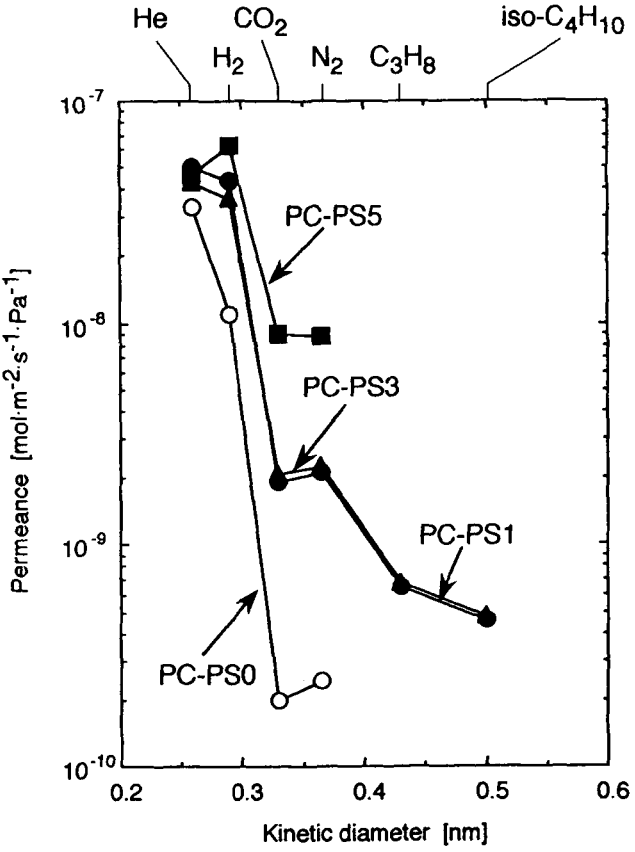

FIG. 10 Relationship between permeance and kinetic diameter of permeating gas: Curing time, 2 hours; permeation temperature, 773 K. Keys are the same as in Fig. 8.

selectivity of 328. They estimated that the pore size of the membrane was smaller than 0.45 nm. When the permeate was changed from C_3H_8 to i-C_4H_{10}, the permeances of the PC-PS1 and PC-PS3 membranes were not greatly decreased. This suggests that the membranes prepared in the present study possessed pores larger than i-C_4H_{10}, but the contribution of those pores to H_2 permeance was smaller than 0.01.

Stability of Membranes

The membranes used for the stability test in this section were prepared by repeating the coating and pyrolysis four times in total. Figure 11 shows

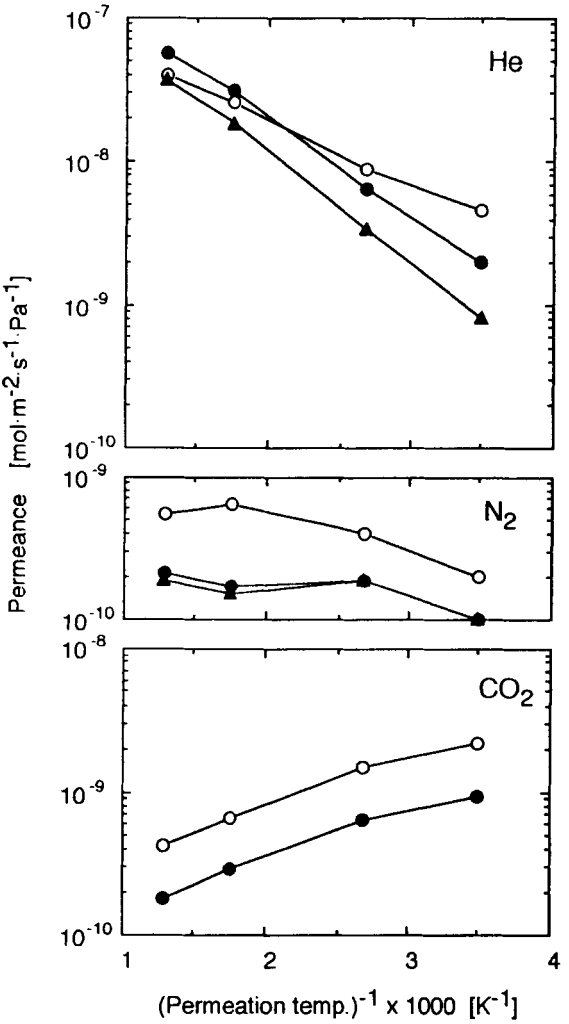

FIG. 11 Effect of heat-treatment time at 1223 K on permeance of PC-PS1 membrane: Curing time, 2 hours; coating, four times in total; heat-treatment time in total: (○) 1 hour; (●) 5 hours; (▲) 20 hours.

changes in permeances of the PC-PS1 membrane to helium, carbon dioxide, and nitrogen during thermal treatment at 1223 K. The permeances decreased with increasing treatment time. The He/N_2 selectivity at 773 K was 195 after heat treatment for 20 hours. As shown in Fig. 12, on the

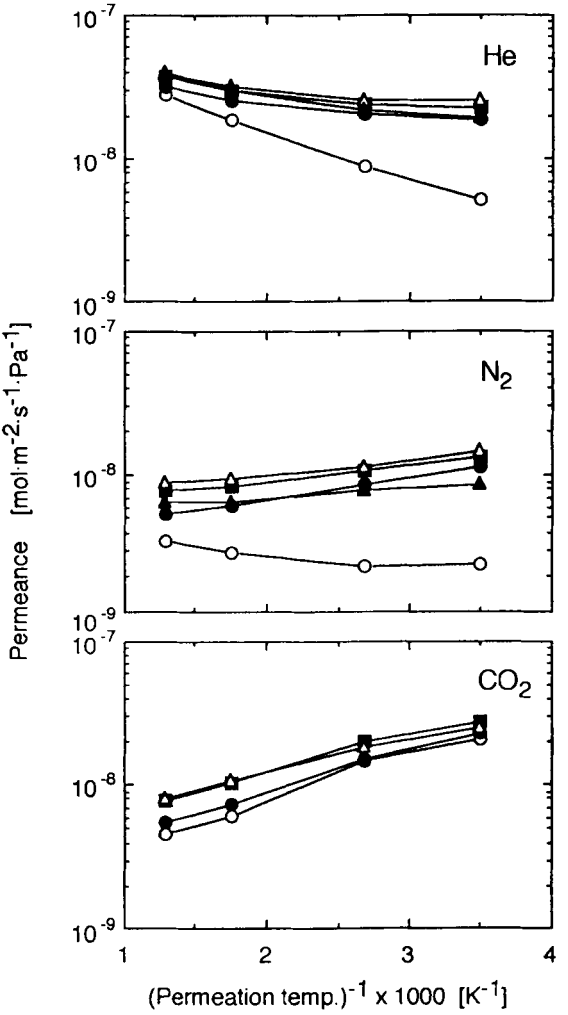

FIG. 12 Effect of heat-treatment time at 1223 K on permeance of PC-PS5 membrane: Curing time, 2 hours; coating, four times in total; heat-treatment time in total: (○) 1 hour; (●) 5 hours; (■) 10 hours; (△) 15 hours; (▲) 20 hours.

other hand, the permeances of the PC-PS5 membrane increased rapidly in the first 5 hours and remained nearly unchanged afterward. The PC-PS5 membrane was less permselective and less sensitive to the treatment time than was the PC-PS1 membrane. The initial increase in permeances

of the PC-PS5 membrane may be explained by the formation of pores due to decomposition of carbonaceous inclusions. Lin et al. (26) used a boehmite sol doped with lanthanum nitrate and prepared a membrane on an α-alumina support by dip-coating. Chai et al. (27) used a mixed sol of $BaO-Al_2O_3$ or $La_2O_3-Al_2O_3$ and prepared membranes consisting of a hexaaluminate phase. These membranes were stable at high temperature, but their H_2/N_2 permselectivities were 2–3 and were dominated by the Knudsen diffusion mechanism.

Figure 13 shows changes in H_2 and N_2 permeances of the PC-PS0 and PC-PS1 membranes during exposure to the mixture of H_2O and He at 773 K. The H_2 and N_2 permeances of the PC-PS0 membrane decreased gradually, and the H_2 permeance was 8.4×10^{-9} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ initially and 5.2×10^{-9} $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ after exposure for 72 hours. The

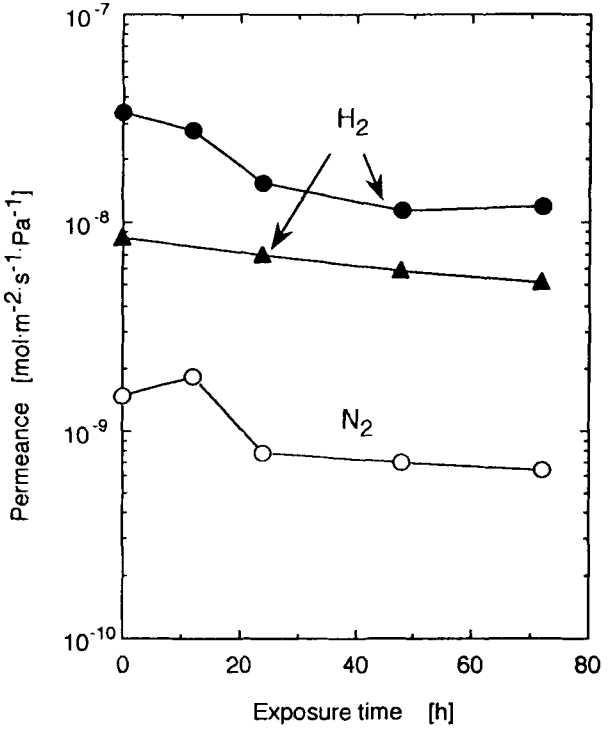

FIG. 13 Effect of exposure to H_2O–He mixture at 773 K on permeance: Curing time, 2 hours; permeation temperature, 973 K: (▲) H_2 of PC-PS0 membrane; (●) H_2 of PC-PS1 membrane; (○) N_2 of PC-PS1 membrane.

N_2 permeance was less than 10^{-10} mol·m^{-2}·s^{-1}·Pa^{-1}. For the PC-PS1 membrane, the H_2 and N_2 permeances decreased rapidly in the first 24 hours and then stabilized. The H_2 permeance and H_2/N_2 selectivity at 973 K were 1.2×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and 19, respectively, after 72 hours.

The above results indicate that the Si-C-O membranes prepared are quite stable at elevated temperature and possess high permselectivities. A silica membrane formed by Wu et al. (28) lost its hydrogen and nitrogen permeances by 66 and 74%, respectively, after a hydrothermal treatment at 873 K for 72 hours. As mentioned in the Introduction Section, no membranes based on porous glass and γ-alumina are usable at temperature above 1000 K. Normally, membranes having crystalline structures such as γ-alumina and perovskite compounds are not molecular-sieving. The amorphous Si-C-O membranes developed in the present study attained both molecular-sieving property and durability at temperature above 1000 K.

CONCLUSION

Polycarbosilane was coated on a porous support tube, cured at 473 K in air, and pyrolyzed in argon at 1223 K. An amorphous Si-C-O membrane was obtained by repeating this procedure. To increase the permeance of the membrane, polystyrene was added to the PC solution. The membrane formed from the PC-PS1 solution showed an H_2 permeance of 4×10^{-8} mol·m^{-2}·s^{-1}·Pa^{-1} and an H_2/N_2 selectivity of 20 at 773 K. During the curing and pyrolysis steps, PS was concentrated into ellipsoidal domains due to phase separation. The PS in the domains was depolymerized in the subsequent pyrolysis step and was dissipated. For the PC-PS1 and PC-PS3 membranes, no voids perforated the membrane. For the PC-PS5 membrane, however, some voids penetrated the membrane and reduced permselectivities after a heat treatment for 20 hours. All membranes were resistant to a heat treatment at 1223 K in argon. When the PC-PS1 membrane was exposed to a mixture of steam and helium at 773 K, the permeance was decreased to half in the first day, but was not greatly changed over the next two days.

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