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CATALYTIC MEMBRANE REACTION FOR METHANE STEAM REFORMING USING POROUS SILICA MEMBRANES

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ABSTRACT

Catalytic membranes, which have hydrogen permselectivity over other gaseous molecules and catalytic activity for methane steam reforming, were prepared by 2 different procedures and applied to methane steam reforming at 450–500°C. Type A catalytic membranes were manufactured by the preparation of a hydrogen separation layer from silica-zirconia colloidal sols, followed by the application of a nickel catalyst coating. Type B catalytic membranes were prepared via the impregnation of a nickel catalyst inside the α-alumina porous substrates, followed by the application of a coating on the hydrogen separation layer. Hydrogen permselectivity over nitrogen was degraded by coating the catalyst layer, as in the Type A membranes, and in addition, methane conversion decreased with time probably because of catalyst sintering or carbon deposition. Type B catalytic membranes showed a steady conversion for a longer period than did Type A, and the permeability ra-

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tio of hydrogen to nitrogen was approximately 200; therefore, Type B was found to be the effective route to preparing catalytic membranes. Methane steam reforming through the use of catalytic membranes revealed that methane conversion beyond the equilibrium conversion levels could be achieved either by sweeping the permeate stream or by pressurizing the feed stream at 6 bar and not using sweeping gas.

INTRODUCTION

Inorganic membranes have received attention because of their potential application for high-temperature chemical processes, such as in heterogeneous or homogeneous reactions. Membrane reactors, which combine membrane separations and reactions in one system, have great potential for a variety of applications. Among the advantages of this technique are the removal of one of the reaction products, which shifts the reaction conversion limited by thermodynamic equilibrium; the removal of one of the products before it can further react to form undesirable products; and the controlled addition of reactants to the reaction system (1–3). In particular, hydrogen-permselective membranes have been investigated as a means to increase the conversion of thermodynamic equilibrium-limited reactions, such as methane steam reforming:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2$$
$$CO + H_2O \leftrightarrow CO_2 + H_2$$

By removing hydrogen from the reaction system, the conversion of methane can be higher than would be obtained in conventional catalytic reactors, and in addition, the operating temperature can be lowered.

Hydrogen separation membranes are either nonporous or porous. Nonporous membranes, which are typically prepared from palladium and an alloy of palladium and silver, show an infinite selectivity to hydrogen over other gases because the separation mechanism is based on the selective dissolution of hydrogen atoms into the metal matrix. In applications of this technology to methane steam reforming, researchers have reported that membrane reactors increase the conversion of methane beyond the equilibrium conversion levels (3,4). However, several disadvantages have been pointed out with respect to metal membranes, including high cost, carbon deposition, and poisoning by impurities such as sulfur and chloride (3). Porous membranes, which are typically prepared from chemical vapor deposition (5–7) and a sol-gel process, are also hydrogen permselective. We have reported the successful preparation of porous hydrogen-permselective membranes through the use of silica and silica-zirconia by a sol-gel process (8–10).

Several types of membrane reactor configurations have been proposed for use, including packed-bed membrane reactors (PBMR), fluidized-bed membrane reactors (FBMR), and catalytic membrane reactors (CMR) (3). PBMR and FBMR consist of permselective membranes and catalytic beds either as a packed or a fluidized bed. However, catalytic membranes have the functions of both catalysis and separation in one membrane and as a result can be applied in a more compact fashion than other types of membrane reactors. Some catalytic membranes are inherently catalytic, such as zeolitic membranes. In a second class of catalytic membranes, the catalysts are attached to the membrane surface or on the pore surfaces (1).

Methane steam reforming has been mainly investigated for use in PBMR and FBMR using metallic nonporous membranes (4), but very few researchers have reported on the possible use of a membrane reaction system that has porous membranes (11,12). Recently, highly hydrogen-selective silica membranes were prepared by chemical vapor deposition and employed for dry reforming of methane in PBMR (7). The purpose of our research was to investigate catalytic membranes that have not only hydrogen-permselectivity but also catalytic activity for methane steam reforming at 450–500°C. The catalytic membranes were prepared with silica-zirconia composite oxide as separation membranes, which had relatively large hydrogen permselectivity, and nickel catalysts, which were attached to the silica-zirconia layers.

EXPERIMENTAL

Preparation of Hydrogen Separation Membranes

Hydrogen separation membranes were prepared by a sol-gel process through the use of silica-zirconia composite sol solutions. Silica-zirconia composite sol solutions in a molar ratio of 9 to 1 were prepared by hydrolysis and condensation of tetraethoxysilane (TEOS) and zirconium-*n*-butoxide (ZTBO) with water and hydrochloric acid as a catalyst, as described in our previous papers (8–10,13,14). The colloidal sol solutions were coated on the outer surface of a cylindrical α-alumina porous substrate (pore size 1 μm, o.d. 1 cm, length 9 cm) after depositing α-alumina particles (average diameter 0.18 μm; Sumitomo Chemical Co. Ltd.) mixed with a colloidal sol solution, and then fired at 500°C. Details of this procedure are described elsewhere (8,13).

Preparation of Catalytic Membranes

A nickel nitrate solution of 40% (wt) was used in the preparation of catalytic membranes. As shown in Fig. 1, 2 different procedures for catalyst impregnation

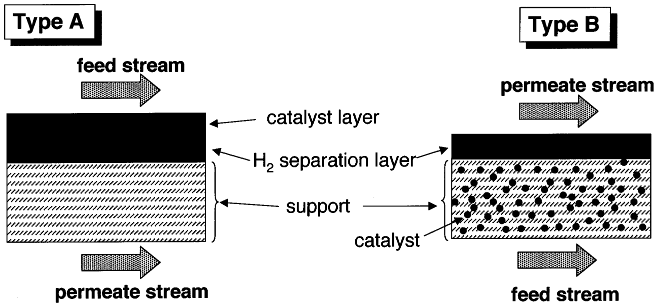

Figure 1. A schematic view of catalytic Type A and Type B membranes. Catalytic Type A membranes contain a catalyst layer on a hydrogen-separation membrane layer, while Type B membrane catalysts are impregnated inside the substrate.

were used. Type A (hydrogen separation) membranes were first prepared by the sol-gel process described under experimental procedures. After colloidal solutions of 100-nm diameter silica-zirconia particles were coated on the hydrogen separation membranes and fired at 500°C, the membranes were dip-coated with nickel nitrate solutions and then fired at 500°C. The nickel catalyst was impregnated onto Type B membranes by soaking an α-alumina substrate in the nickel nitrate solution and firing the substrate at 500°C in air. The hydrogen separation layer was then formed on the outer surface of the substrates. Catalytic membranes prepared by the described procedures were fired in air at 500°C and reduced to the metal state by treatment with hydrogen at 500°C prior to use.

Gas Permeation and Methane Steam Reforming

Permeances of pure gases (He, H_2, N_2, CO_2, CH_4, and SF_6) were measured in a continuous flow system as shown in Fig. 2 through the use of a soap film meter. The pressure of the feed stream, P_F, was maintained at 200 kPa, while that of the permeate stream, P_P, was maintained at atmospheric pressure. The temperature for permeance measurements was in 300–500°C. Permeances of H_2, N_2, H_2O mixtures (the partial pressure of each component was kept at 100 kPa) were also measured for periods up to 20 hours.

A mixture of methane and steam (H_2O-CH_4 = 5:1) was continuously supplied to the catalytic membranes at a methane flow rate of approximately 4×10^{-2} mL/s. The feed stream was pressurized at 110–600 kPa, while the permeate stream was maintained at atmospheric pressure. The reaction was carried out at

450–500°C. Reactant gaseous mixtures were fed to the outer and inner stream of the cylindrical Type A and Type B membranes, respectively.

Gas compositions were determined by an on-line gas chromatograph fitted with parallel packed columns of active carbon and Gaskuropack 54 at an operating temperature of 180°C. To investigate the effect of sweep gas, argon or nitrogen was introduced to sweep the permeate stream.

The conversion of methane in the retentate and permeate streams was defined based on the flow rate of each component, which contained a carbon atom, q_i.

$$X = \frac{q_{CO} + q_{CO_2}}{q_{CH_4} + q_{CO} + q_{CO_2}}$$

The overall conversion was defined using a flow rate of retentate (q_r) and permeate stream (q_p) as follows:

$$X_{total} = \frac{q_r X_r + q_p X_p}{q_r + q_p}$$

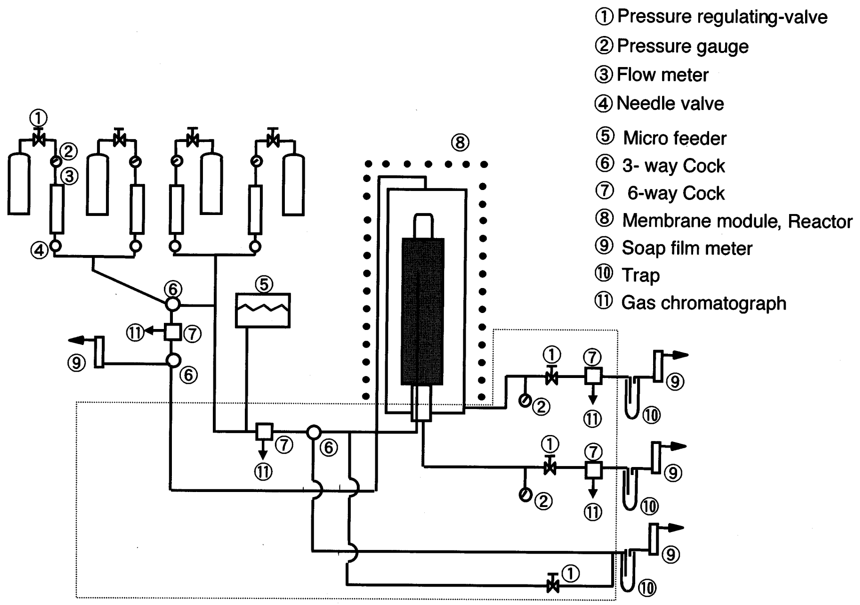

Figure 2. Experimental apparatus for measurements of gas permeance and membrane reactions of methane steam reforming.

RESULTS AND DISCUSSION

Effect of Steam on Gas Permeability

The methane steam-reforming reaction was carried out in the presence of a large amount of water vapor at high temperature. Therefore, the effect of steam on membrane performances was an important investigation (5). Figure 3 shows a time course for the permeabilities of H_2, H_2O, and N_2 in mixtures in which the partial pressures of the 3 components were maintained at 100 kPa at 500°C. Permeances of hydrogen decreased gradually and approached a constant value, while that of nitrogen decreased drastically during the initial 10 hours. Therefore, the ratio of the permeance of hydrogen to nitrogen increased with time from approximately 50 to 450. As described in previous papers (8,10), the pores through which nitrogen could permeate were decreased by a hydrothermal treatment that accelerated the densification of the silica matrix. In other words, the generation and the condensation of silanol functional groups reduced the effective pore size for nitrogen permeation. Water vapor was found to be less permeable than hydrogen and much more permeable than nitrogen. The separation factor of hydrogen to water was approximately 3. Figure 4 shows Arrhenius

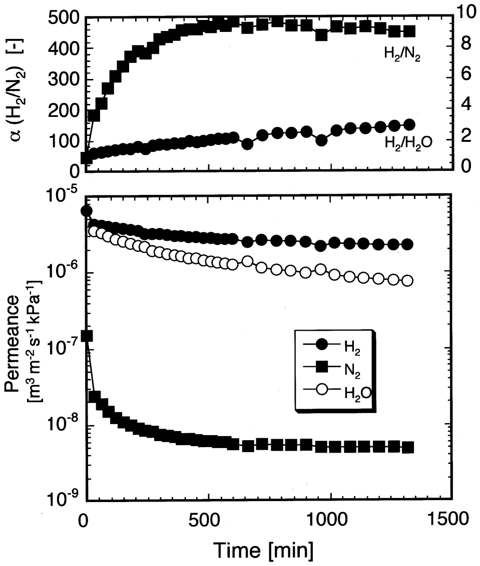

Figure 3. Permeances of hydrogen, nitrogen, and water vapor mixtures as functions of elapsed time. Partial pressure of each component was kept at 100 kPa.

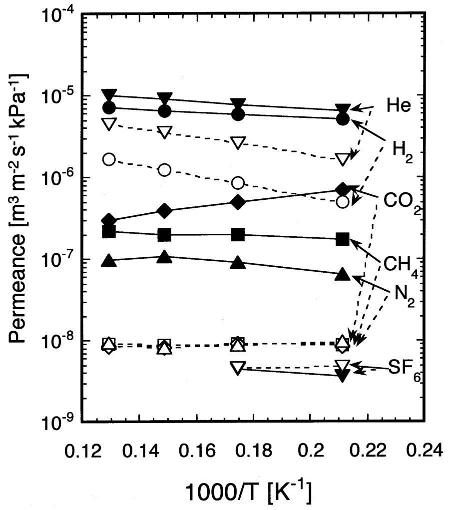

Figure 4. Arrhenius plots of permeances of pure gases (He, H_2, CO_2, CH_4, N_2, SF_6) before (closed) and after (open) hydrothermal treatment.

plots for permeances of pure He, H_2, CO_2, CH_4, N_2, and SF_6 before and after the hydrothermal treatments. Prior to hydrothermal treatment, He, H_2, CH_4, and N_2 show activated diffusion where a permeance increases with temperature. After hydrothermal treatment, the permeability ratio of He to H_2 increased from 1.1 to 2; that is, helium, which has a smaller molecular size (kinetic diameter 0.26 nm), became more permeable relative to hydrogen (0.29 nm). Moreover, the activation energies of He and H_2 permeation increased. The activation energy corresponds to the energy barrier, which serves as a repulsive force between the permeating molecules and the pore walls, and the repulsive force increases within short distances from the pore walls. However, CO_2, CH_4, and N_2 decreased approximately to the same level of permeance and showed a temperature dependency similar to that described by Knudsen diffusion where the permeance decreases with the square root of the absolute temperature. SF_6 (kinetic diameter 0.5 nm) shows a similar permeance, irrespective of the hydrothermal treatment. These results suggest that the hydrothermal treatment densified the small pores through which H_2 and He were able to permeate and molecules of larger size could not, and the large pores that allowed SF_6 permeation and possibly corresponds to pinholes of the hydrogen separation layer, were not affected by the treatment. Intermediate size pores, which allowed nitrogen permeation but not SF_6 permeation and were probably formed as interparticle pores, were diminished by the hydrothermal treatment (10).

Type A Catalytic Membrane

Type A catalytic membranes require several processing steps before membrane reaction experiments. Figure 5 shows the permeability ratios of hydrogen to nitrogen, α(H_2/N_2), at each processing stage during the preparation of 5 catalytic Type A membranes. After the preparation of the hydrogen separation membranes, α(H_2/N_2) values, which were in a range of 50–80, decreased drastically to less than 40 after the preparation of the catalyst layer, while no detectable change was observed after the H_2-reduction process. Because catalysts were coated on the hydrogen separation layer by dip-coating them in nickel nitrate aqueous solutions, the porous hydrogen separation membranes were possibly negatively affected by breakage of the porous structure because of capillary force and/or the densification of the silica-zirconia matrix in a way similar to that caused by the hydrothermal treatment shown in Fig. 3. α(H_2/N_2) attained by the method of Type A membrane preparation had a maximum value of 35. Figure 6 shows the methane conversion in the retentate stream as a function of elapsed time for the system in which the reaction was carried out at steam-methane ratio of 5:1 at 450°C. The feed stream was slightly pressurized at an absolute pressure of 1.1 bar. The conversion at 450°C was approximately 0.5 and appears to decrease slightly with time. By applying sweeping nitrogen in the permeate stream at a flow rate of 0.4 mol/s, we saw the conversion increase to more than 0.7, which is beyond the equilibrium conversion based on the feed composition. α(H_2/N_2) of a catalytic membrane was approximately 20 before and after the reaction at 450°C. After the reaction, the temperature was increased to 500°C, and the methane conversion decreased drastically without the nitrogen sweep. No significant increase in conversion was observed even after sweeping the permeate stream. The catalytic activity has been postulated to decrease by either sintering or coking (1).

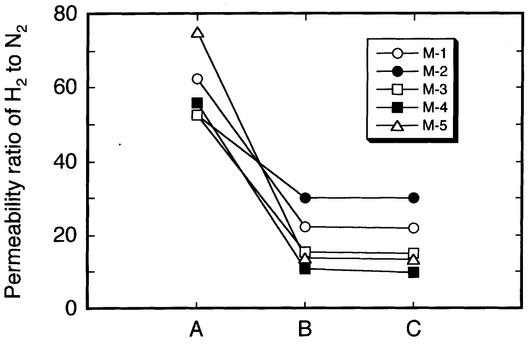

Figure 5. Permeability ratio of H_2 to N_2 at different stages in the preparation of a catalytic membrane (Type A): A) after membrane preparation, B) after loading catalyst, and C) after H_2 reduction.

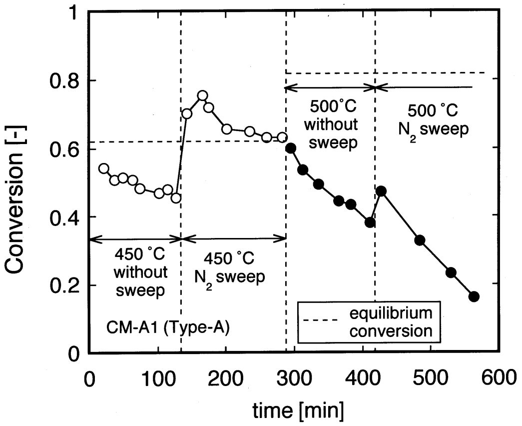

Figure 6. Conversion in the retentate as a function of the elapsed time at a temperature of 450 and 500°C (Type A with and without sweep gas; S/C= 10; $P_F \approx 1.1$ bar).

Calcium and potassium ions were introduced onto the silica surface to decrease the acidity of the silica surface, which is covered with silanol groups and is possibly a factor in carbon deposition (coking). Before being dipped into a nickel nitrate solution, the substrate was coated with calcium chloride or potassium chloride solutions and subsequent firing at 500°C to convert the silanol functional groups to alkali metal oxides. However, this resulted in a decrease in the conversion, as shown in Fig. 7, and the effect of alkali metals on conversion was not

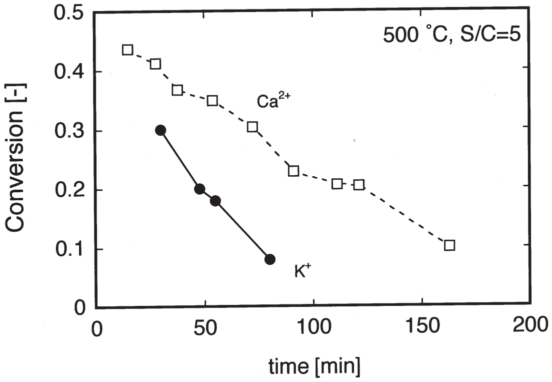

Figure 7. Conversion in retentate as a function of the elapsed time (Type A without sweep gas; S/C = 10; Ca and K were coated before Ni loading).

clearly observed. Regeneration of the deactivated catalytic membranes was carried out by feeding steam and hydrogen at 500°C to remove the deposited carbon, but the increase in conversion was at most 5%. Therefore, we concluded that the sintering of nickel is a likely cause for the decrease in catalytic activity. Sintering is postulated to occur readily because the nickel catalyst at a high temperature could be more mobile on the hydrogen separation membranes, the surface of which should be smooth enough to separate hydrogen from other gasses, than it is on ordinary porous supporting materials.

Type B Catalytic Membrane

Figures 8a and 8b show scanning electron micrographs (SEM) of a cross-section and an inner surface of Type B catalytic membranes, respectively. A 1–2 μm intermediate layer was prepared by coating α-alumina particles to provide a sufficiently flat surface for the further coating of colloidal solutions on the outer surface of the substrate. A top layer, which functioned for hydrogen separation, was prepared by coating colloidal sol solutions, and the thickness appears to be less than 1 μm. Nickel particles of approximately 1 μm were clearly observed on the inner

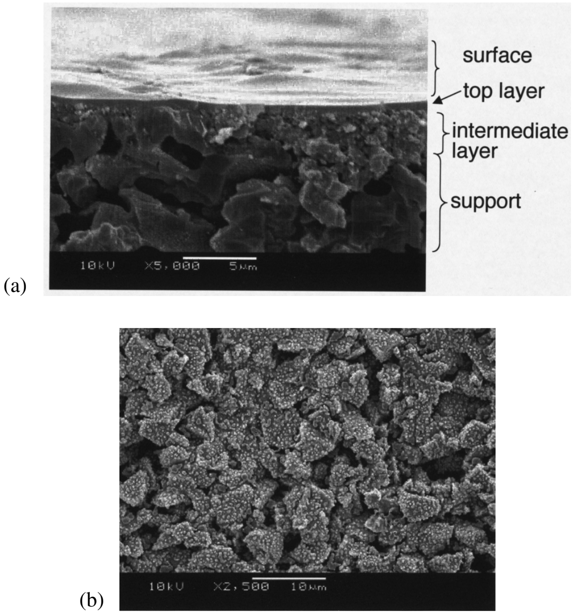

Figure 8. SEM images of catalytic Type B membranes: (a) cross-section (X2500) and (b) cross-section (X2500).

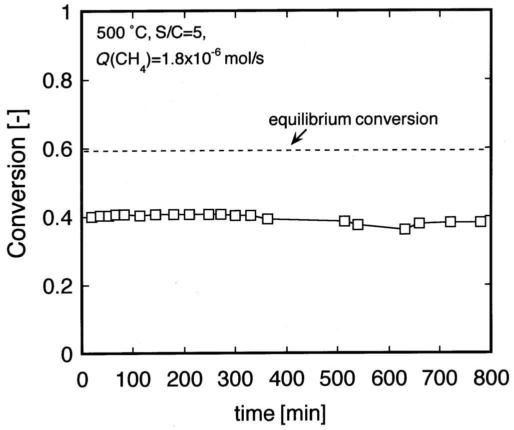

Figure 9. Conversion in retentate as a function of elapsed time in a single-pass flow through a catalyst-impregnated support (S/C = 5; approximate $P_F = 1.0$ bar).

surface of the catalytic membrane, and the amount of Ni impregnation was approximately 0.25 g. Figure 9 shows methane conversion as a function of elapsed time using a support membrane after the impregnation of a nickel catalyst. All the reactant feed gases were forced to permeate through the porous membrane. The conversion showed an approximate steady value of 0.4 for periods as long as 800 minutes, which is much longer than the case for Type A catalytic membranes. This result might be due to the ability of Type B membranes to load more catalysts than can Type A membranes. As shown in Table 1, a Type B catalytic membrane had a

Table 1. Permeance of Hydrogen and Permeability Ratio (H_2/N_2) at Each Stage for a Catalytic Membrane of Type B

	After Preparation of Hydrogen-Separation Membrane	After Hydrothermal Pretreatment*	After Reaction 1**	After Reaction 2***
H_2 permeance [m^3(STP)/$m^2 s \cdot kPa$]	3.4×10^{-6}	2.8×10^{-6}	0.62×10^{-6}	0.25×10^{-6}
Permeability Ratio α (H_2/N_2)	193	176	95.5	18

* Hydrothermal condition: 500°C; H_2O-N_2 = 50:50 kPa, 1800 minutes.
** Reaction 1 (membrane reaction with sweep gas shown in Fig. 10): 500°C; partial pressure of H_2O in feed is approximately 80 kPa; 1700 minutes.
*** Reaction 2 (membrane reaction without sweep gas shown in Figs. 11 and 12): 500°C; partial pressure of H_2O in feed is approximately 80–540 kPa; 1800 minutes.

H_2/N_2 permeability ratio of 190, and therefore, one can expect better conversions by using a Type B catalytic membrane instead of a Type A catalytic membrane. Because the catalyst was impregnated before the preparation of the hydrogen separation layer, permselective membranes toward hydrogen might be prepared without being affected by the catalyst impregnation process. After consideration of catalytic activity and the ease of membrane processing, we found Type B catalytic membranes to be superior to Type A membranes in terms of configuration.

Figure 10 shows methane conversions in the retentate stream as a function of the flow rate of argon in the permeate stream. The conversion of methane increased with the sweep-gas flow rate. The sweep gas decreased the partial pressure of hydrogen in the permeate stream, resulting in the enhancement of hydrogen permeation and an increase in the conversion of methane. Argon can permeate through the porous catalytic membrane from the permeate stream to the feed stream as a function of the pressure gradient. Therefore, the permeated argon could dilute the feed stream and decrease the partial pressure of methane and water vapor in the feed, resulting in an increase in methane conversion. Argon permeance measured after the reaction experiments was 6.4×10^{-9} $m^3(STP)/m^2 s \cdot kPa$, by which the argon flow rate from the inner to the outer stream of the cylindrical membrane was estimated to be less than 1% of the feed-gas flow rate; therefore, the effect of dilution by the sweeping gas was confirmed to be negligible.

Figure 11 shows the conversion in the retentate and permeate stream and the overall conversion as a function of elapsed time for the case in which the feed stream was pressurized from 1.1 to 6 bar and the permeate stream was maintained at an atmospheric pressure at 500°C. Because no sweeping gas was introduced,

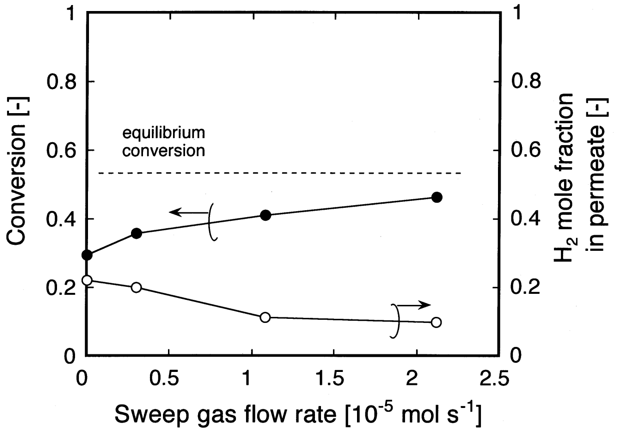

Figure 10. Conversion in the retentate and the H_2 mole fraction in the permeate stream as a function of the sweep-gas flow rate (Type B; sweep gas: Ar, 500°C; S/C = 5; approximate $P_F = 1.4$ bar; approximate $P_P = 1.0$ bar).

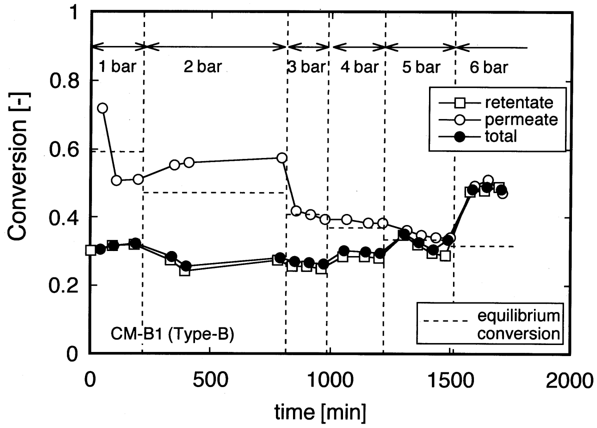

Figure 11. Conversion as a function of elapsed time (Type B; 500°C; S/C = 5; approximate $P_P = 1.0$ bar).

methane conversion was not increased by dilution. Because the flow rate of permeate stream was much less than that of the retentate stream, the overall conversions were nearly the same as those in the retentate stream. The material balance of carbon, hydrogen, and oxygen atoms was approximately less than 10%, irrespective of the applied pressure.

Figure 12 summarizes the conversion of methane and the mole fraction of H_2 in the permeate stream as a function of applied pressure. As shown in the figure, the

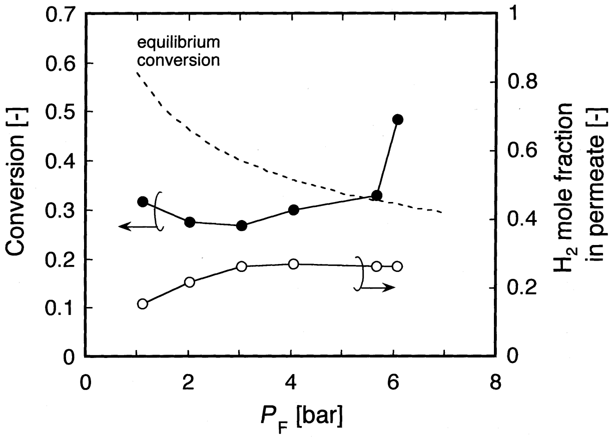

Figure 12. Overall conversion and H_2 mole fraction in permeate stream as a function of feed pressure (Type B; 500°C; S/C = 5; approximate $P_P = 1.0$ bar).

equilibrium conversion decreases with an increase in pressure. However, by increasing the applied pressure in a catalytic membrane, methane conversion increased because the produced hydrogen was selectively removed from the feed stream to the permeate stream. This selective hydrogen removal resulted in a shift in the conversion of methane (15). This tendency was clearly observed at high pressure, and the conversion at 6 bar was beyond the equilibrium conversion predicted by thermodynamic calculations. One can expect a better performance of membrane reactors in an appropriate range of the permeation rate-reaction rate ratio values, and an optimal operating condition would be possible after model calculations were completed for this membrane reactor. As shown in Table 1, the permselectivity was decreased mainly because of a decrease in hydrogen permeability. The probable cause of this decrease is more likely related to the exposure to steam at a relatively high partial pressure (500 kPa for the case of a 6-bar total pressure) than to the hydrothermal pretreatment of 50 kPa. However, the methane steam reforming reaction might affect the permeance of hydrogen by plugging the fine pores that are effective for hydrogen permeation. Further investigation will be required to clarify these causes of decreased hydrogen permeability.

CONCLUSIONS

Catalytic membranes, which have hydrogen permselectivity over other gaseous molecules and the catalytic activity for methane steam reforming, were prepared by 2 different procedures and applied for methane steam reforming at 450–500°C. The permeance of hydrogen decreased with time under hydrothermal conditions because of the densification of the silica matrix, which had permitted hydrogen permeation. Type A catalytic membranes were manufactured through the preparation of a hydrogen separation layer from silica-zirconia colloidal sols and the subsequent coating of a nickel catalyst on the hydrogen separation layer, while Type B catalytic membranes were prepared by the impregnation of a nickel catalyst inside an α-alumina porous substrate and the subsequent coating of the hydrogen separation layer. In Type A membranes, hydrogen permselectivity over nitrogen was degraded by the catalyst coating. In addition, the methane conversion decreased with time probably because of the catalyst sintering or carbon deposition. However, Type B catalytic membranes showed a steady methane conversion for a longer period than did Type A membranes. In addition, the permselectivity showed relatively large values; that is, the permeability ratio of hydrogen to nitrogen was approximately 200. Therefore, Type B membranes were considered more effective in the preparation of catalytic membranes than were type A membranes. Our study of methane steam reforming through the use of catalytic membranes revealed that the conversion of methane beyond the equilibrium conversion could be attained either by sweeping the permeate stream or by pressurizing the feed stream at 6 bar without the sweeping gas.

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