Stable Equilibrium Shift of Methane Steam Reforming in Membrane Reactors with Hydrogen-selective Silica Membranes

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Equilibrium shifts of methane steam reforming in membrane reactors consisting of either tetramethoxysilane-derived amorphous hydrogen-selective silica membrane and rhodium catalysts, or hexamethyldisiloxane-derived membrane and nickel catalysts is experimentally demonstrated. The hexamethyldisiloxane-derived silica membrane showed stable permeance as high as 8×10^{-8} *mol* m^{-2} s^{-1} Pa^{-1} *of* H_2 *after exposure to 76 kPa of vapor pressure at 773 K for 60 h, which was a much better performance than that from the tetramethoxysilane-derived silica membrane. Furthermore, the better silica membrane also maintained selectivity of* H_2/N_2 *as high as* 10^3 *under the above hydrothermal conditions. The degree of the equilibrium shifts under various feedrate and pressure conditions coincided with the order of* H_2 *permeance. In addition, the equilibrium shift of methane steam reforming was stable for 30 h with an S/C ratio of 2.5 at 773 K using a membrane reactor integrated with hexamethyldisiloxane-derived membrane and nickel catalyst.* © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 1882–1888, 2011

Keywords: membrane reactor, hydrogen, silica, steam reforming, methane

Introduction

Steam reforming of hydrocarbons is one of the best-established methods for industrial hydrogen production. The methane steam reforming reaction is generally used in large-scale hydrogen plants. The steam reforming reaction of methane is an endothermic equilibrium reaction, and its conversion is limited by the thermodynamic equilibrium. Thus, this steam reforming reaction must be conducted around at least 1100 K to enhance the conversion.

On the other hand, the application of membrane reactors with hydrogen-selective membranes to this steam reforming reaction of methane has been proposed. A membrane reactor is a system that integrates ‘‘reaction’’ with catalysts and ‘‘separation’’ with membranes. As the reaction and hydrogen separation occur simultaneously in a membrane reactor, this endothermic equilibrium reaction can be shifted forward beyond the thermodynamic equilibrium by extracting hydrogen from the reaction system using a hydrogen-selective membrane. In addition, this can make the hydrogen production system more compact and efficiently, compared with the conventional process which consists of reactors and separation unit such as PSA. In fact, there have been many ideas and

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trials on membrane reactors for methane steam reforming.[1–10] Furthermore, such membrane reactors have been proposed for other hydrogen production reaction systems, such as the decomposition of hydrogen sulfide,[11–13] or dehydrogenation reactions of organic chemical hydrides.[14,15] We have also developed a methodology for preparing hydrogen-selective amorphous silica membranes with control of their pore sizes,[16] which enables us to select a suitable silica membrane for each reaction system, and we successfully developed a membrane reactor for the decomposition of hydrogen sulfide[17] and for the dehydrogenation of cyclohexane.[18,19] In addition, the fluidized bed membrane reactor, which is very linked to the membrane reactor, has been proposed and developed recently by Grace and coworkers and Elnashaie and coworkers.[20–22] This type of reactor is similar in that the produced hydrogen is simultaneously extracted by using the membrane. And this reactor can take advantages of fluidized bed reactor in terms of effective utilization of catalysts and maintaining uniformity of reactor temperature. Furthermore, they have also tested comparatively larger, pilot-scale reactors using palladium-alloyed membranes with higher hydrogen permeance and higher hydrogen separation factor.[21] Anyway, the reactors where reaction and separation are occurred at the same time have gained much attention for applying to the steam reforming reactions.

One of the most important issues in developing membrane reactors for methane steam reforming is the hydrogen-selective membrane; it is not an exaggeration to say that the membrane determines the performance of the membrane reactor. Palladium or its alloyed membranes are well-known as hydrogen-selective membranes with good performance because of their unique hydrogen separation mechanisms. On the other hand, microporous inorganic membranes are also attractive for such reactors. Among them, amorphous silica membranes have been studied by some groups. Silica is abundant compared with rare metals such as palladium, so it is desirable to prepare hydrogen-selective silica membranes that match palladium or its alloyed membranes in performance. However, it is well-known that the hydrogen-selective performance of silica membranes deteriorates under the severe hydrothermal conditions required for the methane steam reforming reaction system. This is why there are few reports on the development of membrane reactors for steam reforming reactions with hydrogen-selective amorphous silica membranes, even though many researchers have drawn attention to the efficiency of applying membrane reactors to steam reforming reactions.

Here we describe the successful development of membrane reactors for methane steam reforming with two hydrogen-selective amorphous silica membranes. The membranes were prepared by the counter-diffusion chemical vapor deposition (CVD) method with oxygen and tetramethoxysilane (TMOS) or hexamethyldisiloxane (HMDS) as silica precursors. We utilized the preparation method using TMOS previously established by our group. Yoshino et al. first reported preparation of HMDS-derived silica membranes,[23] and we carefully investigated the experimental conditions to improve the selectivity of hydrogen. We then studied the performances of the two membranes under the hydrothermal conditions appropriate for methane steam reforming. Finally, we operated the membrane reactors for methane steam reforming and demonstrated stable equilibrium shifts. It should be noted that a Ni catalyst was used with the HMDS membrane.

Experimental

Membrane preparation

Porous α-alumina tubes (outer diameter 6.3 mm, length 330 mm) with 70 nm pores were kindly supplied by Noritake, Japan and used as the substrate. Silica membranes were synthesized at the center of the substrate (100 mm) and the other parts were glazed with a sealant. Following Zahir et al.,[24] Ga-doped γ-alumina coating was applied to the substrate surface to reduce the pore size. The outer surface of the effective area of the substrate was dipped in a sol for 5 s, and then dried for 1 h in air and calcined at 873 K for 3 h. This coating process was repeated twice.

Both the TMOS and HMDS were purchased from Shin-Etsu Chemical, Japan, and both membranes were prepared using the counter-diffusion CVD method. The TMOS-derived membranes were prepared according to the optimized experimental conditions reported elsewhere.[25] Preparation conditions for the HMDS-derived membranes were investigated initially. Nitrogen was used for bubbling to carry the HMDS-saturated vapor to a membrane formation reactor. To determine the optimal experimental conditions, the temperature of the bubbler was changed from 295 to 303 K in 2 K steps. Oxygen was also supplied to the membrane formation reactor. HMDS was supplied from outside the substrate and oxygen was supplied from the inside. During the CVD reaction, the temperature of the substrate was maintained at 873 K, and the flow rates of both nitrogen and oxygen were controlled at 200 mL min^{-1} using a mass-flow controller. The effect of the CVD time was also investigated, in the range from 5 to 120 min.

Performance of the membranes under dry and hydrothermal conditions

The permeances of H_2, CO_2, N_2 and CH_4 were measured at 773, 673, and 573 K to assess the membranes' performance under dry conditions. A steam treatment test was also conducted to assess the membranes' performance under hydrothermal conditions. N_2 gas was bubbled through pure water kept at 365 K, at which temperature the vapor pressure was 76 kPa. In this way, a ratio of steam to N_2 of 3 was obtained, and the mixture was sent to the membranes. The permeances of H_2 and N_2 at 773 K were measured with time under these hydrothermal conditions.

Performance of the membrane reactors for methane steam reforming

Using the membrane reactor with the TMOS-derived membrane, 5 wt % Rh/Al_2O_3 granules were used as a catalyst, and for the membrane reactor with the HMDS-derived membrane, 15 wt % $Ni/Ce_{0.15}Zr_{0.85}O_2$ granules were used. For the Rh/Al_2O_3 catalyst, aqueous rhodium solution was prepared using pentaaminechloro rhodium(III) chloride at 353 K, and γ-alumina particles (reference catalyst ALO-6, kindly supplied by the Catalysis Society of Japan) were

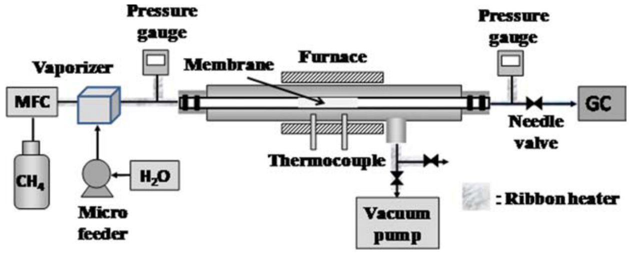

Figure 1. Schematic diagram of the membrane reactors for methane steam reforming.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

impregnated with the solution. Next, the particles were dried at 383 K for 12 h and calcined at 873 K for 3 h. The granular catalysts were reduced in hydrogen and then loaded inside the tube membrane. For the Ni/$Ce_{0.15}Zr_{0.85}O_2$ catalyst, aqueous nickel solution was prepared using nickel(II) chloride hexahydrate, and $Ce_{0.15}Zr_{0.85}O_2$ particles with the size range of 1.18–1.7 mm, which were kindly supplied by Daiichi Kigenso Kagaku Kogyo, Japan, were impregnated with the solution. Next, the particles were dried at 383 K for 12 h and calcined at 823 K for 3 h. The granular catalysts were also reduced in hydrogen and then loaded inside the tube membrane.

The experimental setup of the membrane reactor is illustrated in Figure 1. As a feed material, water was vaporized and carried to the membrane reactor, and methane was carried to the reactor by using a mass-flow controller. The flow rate of methane ranged from 5.0×10^{-7} mol s^{-1} to 1.0×10^{-5} mol s^{-1}, and the S/C ratio was controlled at 3 or 2.5. The temperature of the membrane reactor was fixed at 773 K. The pressure on the reaction side ranged from 0.1 to 0.3 MPa, and on the permeate side was 0.01 MPa. The concentrations of the gases (CO_2, CO, and unreacted CH_4) were measured using gas chromatography (GC-14B, Shimadzu Co., Japan), and using these data the conversion of methane was calculated.

Results and Discussion

Optimization of the HMDS-derived membrane preparation

First, the effect of the temperature of the bubbler on the performance of the HMDS-derived silica membrane was examined. The bubbler temperatures were 295, 297, 301, or 303 K, and the CVD time was fixed at 60 min. This bubbler temperature determines the amount of saturated vapor of HMDS carried to the membrane formation reactor, so this parameter seems crucial to the membrane formation reaction. Under these experimental conditions, all membranes had good H_2/N_2 selectivity around 100 to 1000. Next, the effect of the CVD time on the performance of the silica membrane was studied. The bubbler temperature in this experiment was 301 K. The relationships between the CVD time at 873 K and the membrane performance at 773 K are shown in Figure 2. The permeance of H_2 dropped drastically in the first 20 min, which indicates that the active layer for H_2 separation was fabricated successfully. The permeance decreased slightly with time. On the other hand, the permeance of N_2 decreased more with time, resulting in larger selectivity of H_2/N_2 with time. In 120 min, the permeance of H_2 remained over 1×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, and that of N_2 dropped below 1×10^{-10} mol m^{-2} s^{-1} Pa^{-1}. This performance prepared under these conditions was excellent, so we accepted the bubbler temperature as 301 K and the CVD time as 120 min in preparing the HMDS-derived membrane.

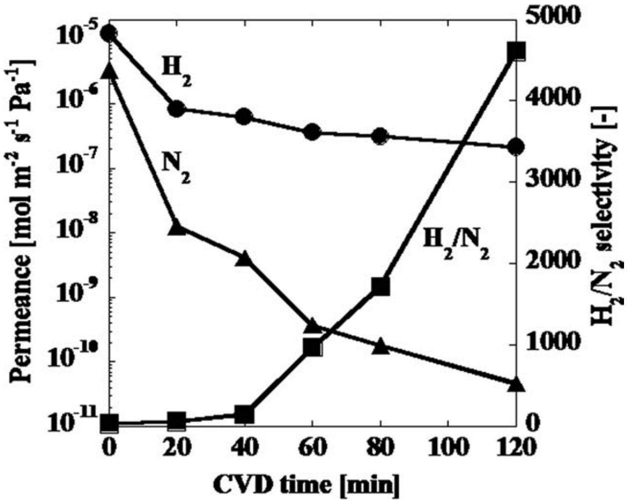

Figure 2. The relationships between the permeances of H_2, N_2 and selectivity at 773 K and the CVD time at 873 K through the HMDS-derived silica membrane prepared under the condition where the bubbler temperature was 301 K.

Comparison of the performances of the two membranes under dry conditions

Figure 3 shows the permeances of H_2, CO_2, N_2, and CH_4 through the TMOS- and HMDS-derived membranes at 773 K. With the TMOS-derived membrane, the H_2 permeance

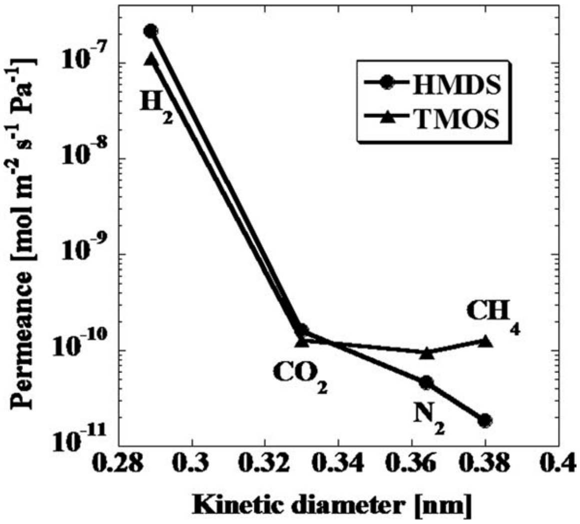

Figure 3. Permeances of H_2, CO_2, N_2, and CH_4 through the TMOS- and HMDS-derived membranes at 773 K.

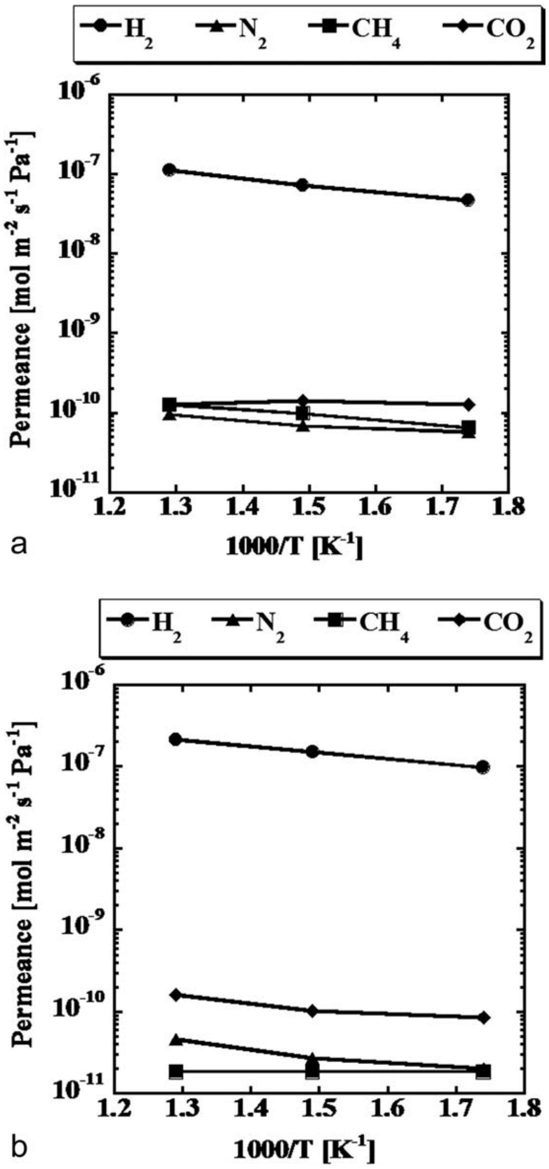

Figure 4. Arrhenius plots of H_2, CO_2, N_2, and CH_4 through (a) the TMOS- and (b) the HMDS-derived membranes.

exceeded 1×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, which was much higher than that of any of the other molecules, and the molecules larger than CO_2 permeated the membrane by the Knudsen diffusion mechanism. This performance was the same as in the previous report by our group.[22] On the other hand, the HMDS-derived membrane showed a higher permeance of H_2 of 2×10^{-7} mol m^{-2} s^{-1} Pa^{-1}. This was larger than that through the TMOS-derived membrane. The permeance of CO_2 was almost the same as that through the TMOS-derived membrane; however, it should be noted that the permeances of N_2 and CH_4 again decreased. This indicates that there are a few larger pores that can separate CO_2/N_2 or N_2/CH_4 by a molecular sieving mechanism. The selectivity of H_2/N_2 through the HMDS-derived membrane at 773 K was 4600, which is a large value. Figures 4a, b show the Arrhenius plots of H_2, CO_2, N_2, and CH_4 through the TMOS- and HMDS-derived membranes, respectively. The activation energy for H_2 permeation through the TMOS-derived membrane was 16 kJ mol^{-1}, while that through the HMDS-derived membrane was just 9.3 kJ mol^{-1}, and the permeance remained as high as 1×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, even at 573 K. These data also indicate that the HMDS-derived membrane has larger pores than the TMOS-derived membrane. Compared with the palladium or its alloyed membranes,[26,27] it is indeed that the permeance of H_2 and the selectivity were lower. However, as mentioned above, hydrogen is separated by the molecular sieving mechanism in the case of the silica membranes. For applying the silica membranes to the membrane reactors for methane steam reforming, the membranes are required to separate hydrogen from CO_2, CO, and methane. This means that the pore size of the membranes should be around 0.3 nm. Considering this and economic side, such hydrogen separation performances of the silica membranes shown here are comparatively excellent.

In membrane reactors for H_2 production, both higher permeance of H_2 and higher selectivity of H_2 are important factors. In particular, the higher selectivity is important to obtain H_2 with higher purity. Therefore, the HMDS-derived membrane is preferable for membrane reactors for steam reforming reactions.

Comparison of the performances of the two membranes under hydrothermal conditions

The time courses of H_2 permeance in the TMOS- and HMDS-derived membranes under hydrothermal conditions are shown in Figure 5. With the TMOS-derived membrane, the H_2 permeance decreased to 3×10^{-8} mol m^{-2} s^{-1} Pa^{-1}. This tendency was reported previously[28]; in that study the H_2 permeance decreased to $3-5 \times 10^{-8}$ mol m^{-2} s^{-1} Pa^{-1}. On the other hand, with the HMDS-derived membrane, while the H_2 permeance also decreased in the first 10–20 h after steam treatment, it became stable at no less than 8×10^{-8} mol m^{-2} s^{-1} Pa^{-1}. It is notable that this stable permeance is almost the same as or higher than that for a fresh TMOS-derived membrane. In addition, the selectivity of H_2/N_2 remained above 1000 for 58 h. These results mean that the HMDS-derived membrane has both sufficient selectivity of H_2/N_2 and a large permeance for H_2, and that these excellent performances can be maintained even under the hydrothermal conditions where steam reforming reactions occur. Therefore, the HMDS-derived membrane is suitable for membrane reactors for methane steam reforming.

Performance of the two membrane reactors

First, each of the membrane can go with both Rh and Ni catalysts. However, in general, Ni-catalysts tend to deactivate more easily than Rh-catalyst. In addition, the HMDS-derived membrane showed higher hydrogen permeance than the TMOS-derived membrane. It means that the atmosphere in the membrane reactor with the HMDS-derived membrane is assumed to be more crude for catalysts due to a large amount of extraction of the generated hydrogen. Therefore the membrane reactor with the HMDS-derived membrane and the Ni-catalyst was regarded to be a sever combination for applying to the steam reforming.

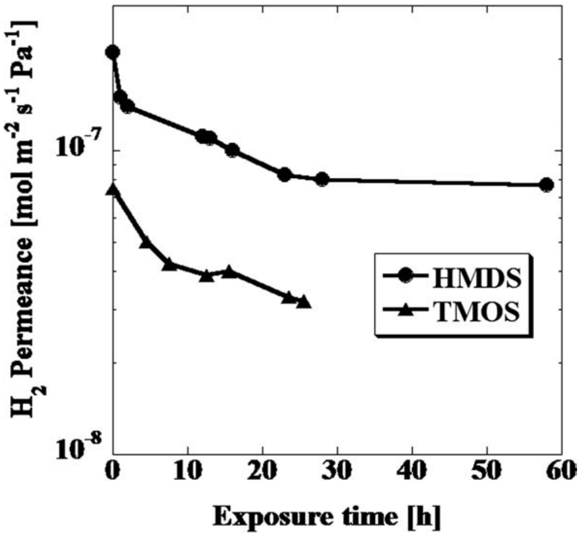

Figure 5. Time courses of H_2 permeances through the TMOS- and HMDS-derived membranes under 76 kPa of steam at 773 K.

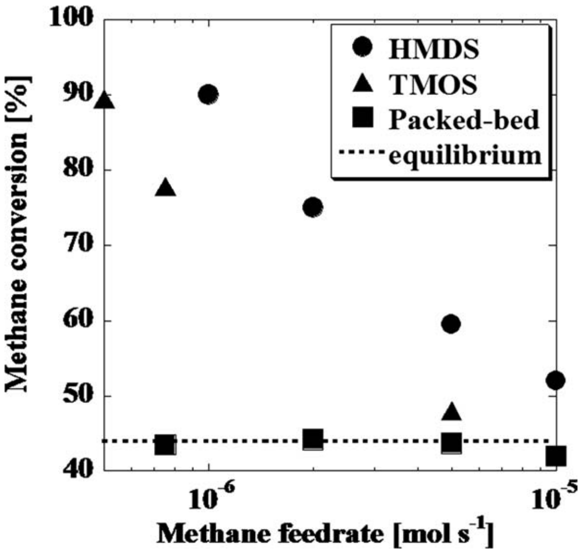

Figure 6. The relationship between the flow rate of methane and the conversion of the methane in the two membrane reactors with the TMOS- and HMDS-derived silica membranes.

The S/C ratio was 3, and the reaction temperature was 773 K.

Figure 6 shows the relationship between the flow rate of methane and the conversion of the methane in the two membrane reactors with the TMOS- and HMDS-derived silica membranes. In these experiments, the S/C ratio was 3. The equilibrium conversion under these conditions was 0.44. When a nonporous stainless tube was used instead of the silica membranes, the conversion of methane coincided-well with the equilibrium conversion predicted thermodynamically. This is because, this reactor acted as a packed-bed reactor with no H_2 extraction. On the other hand, in the membrane reactor with the TMOS-derived membrane, the conversion of methane exceeded the equilibrium conversion at every feedrate condition. In this case, the hydrogen product was selectively extracted from the reaction side to the permeate side, resulting in a shift in thermodynamic equilibrium and an enhancement of conversion. As the feedrate was reduced, the shift increased. For 5.0×10^{-7} mol s^{-1} of methane feedrate the conversion was as high as 0.9. This was because the longer residence time was better for equilibrium shift. In the membrane reactor with the HMDS-derived membrane, the conversion of methane again exceeded the equilibrium, and it was much greater at every feedrate condition than with the TMOS-derived membrane, as we had expected. The effect of the residence time was also the same as that in the case of the TMOS-derived membrane: for a methane feedrate of 1.0×10^{-6} mol s^{-1}, the conversion was as high as 0.9. These equilibrium shifts were, of course, caused by the high H_2 permeance through the TMOS- and HMDS-derived membranes. As shown in Figure 5, the TMOS-derived membrane showed 3×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, and the HMDS-derived membrane showed as large as 8×10^{-8} mol m^{-2} s^{-1} Pa^{-1} even under the hydrothermal condition where vapor pressure was 76 kPa. We should also note that the order of the degree of the equilibrium shift coincided with the order of hydrogen permeance.

Figure 7 shows the relationship between the pressure on the reaction side and the conversion of the methane in the two membrane reactors with the TMOS- and HMDS-derived silica membranes. In these experiments, the S/C ratio was also fixed to 3, and feedrate of methane was 5.0×10^{-6} mol/s. In this equilibrium reaction, higher pressures are unfavorable for producing hydrogen from a thermodynamic point of view. However, the permeate flux of H_2 becomes larger at higher pressures because of the larger driving force for permeation, which results in a larger shift of the

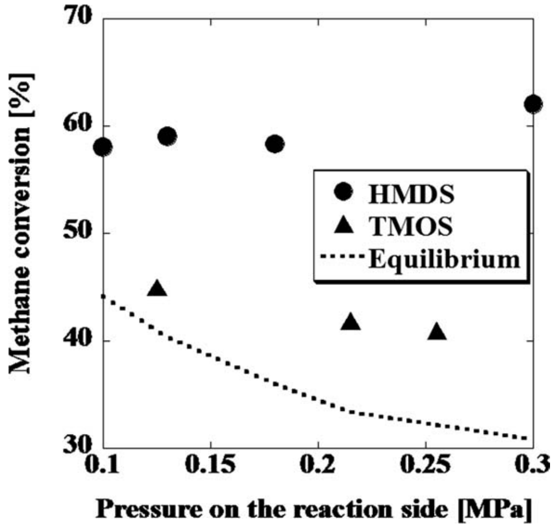

Figure 7. The relationship between the pressure in the reaction side and the conversion of the methane in the two membrane reactors with the TMOS- and HMDS-derived silica membranes.

The S/C ratio was 3, the feedrate of methane was 5.0×10^{-6} mol s^{-1} and the reaction temperature was 773 K.

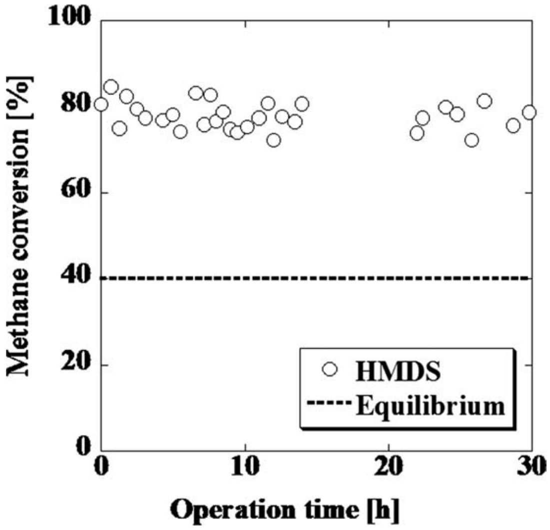

Figure 8. Continuous production of H_2 in the membrane reactor with the HMDS-derived silica membrane and Ni catalyst.

The S/C ratio was 2.5, the feedrate of methane was 1.0×10^{-6} mol s^{-1} and the reaction temperature was 773 K.

equilibrium. Thus, higher pressures are favorable for producing hydrogen from an extraction point of view. Therefore, the conversion of methane is determined by the balance between these two effects. However, there have been few reports on successful operation under higher pressures of membrane reactors using silica membranes with higher permselectivity, except for our earlier articles.[18,19] In the membrane reactor with the TMOS-derived membrane, the conversion of methane exceeded the equilibrium conversion at every pressure higher than 0.1 MPa. With the HMDS-derived membrane, the conversion of methane was much higher than with the TMOS-derived membrane at every pressure, and it exceeded 0.6 with a pressure of 0.3 MPa on the reaction side, where the equilibrium conversion is only 0.3. The order of the equilibrium shifts also coincided with the order of hydrogen permeance. Here, we can observe an interesting tendency: with the membrane reactor with the TMOS-derived membrane the conversion slightly decreased with pressure, while with the HMDS-derived membrane, the conversion slightly increased with pressure. This difference can probably be attributed to the difference in the H_2 permeances. As mentioned above, the reaction pressure has two opposing effects on the conversion of methane: the thermodynamic effect and the extraction effect. Compared with the TMOS-derived membrane, the HMDS-derived membrane had a higher permeance of H_2 of 8×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, and when using a membrane with such high H_2 permeance the extraction effect would be dominant, which results in a positive effect of pressure on the conversion, as shown in Figure 7. In contrast, with a membrane with low H_2 permeance, such as the TMOS-derived membrane, the thermodynamic effect would be dominant, which results in a negative effect of pressure on the conversion.

Finally, to study the stability of the membrane reactor with the HMDS-derived membrane, which showed better performance, it was operated continuously to produce H_2 for 30 h. The pressure on the reaction side was just 0.1 MPa, the S/C ratio was only 2.5 and the feedrate of methane was 1.0×10^{-6} mol s^{-1}. In this case, the equilibrium conversion was calculated as 0.4. The time course of the conversion of methane is shown in Figure 8. Even with this low S/C ratio and using a Ni catalyst, as much as 0.8 of methane conversion was obtained and this equilibrium shift was stable for 30 h. No sudden decrement in the performance of the membrane reactor was observed. This result indicates that the HMDS-derived membrane stably extracted the produced H_2 and at the same time the catalyst also worked stably for this period of time. We can say that we successfully operated the membrane reactor for methane steam reforming stably when using the HMDS-derived H_2-selective silica membrane. It is indeed that there are some reports on the operation of membrane reactors or fluidized bed membrane reactors in much longer time. However, their studies utilized palladium or its alloyed membranes. It should be noted that this membrane reactor employed silica membranes. It is significant that stable equilibrium shift of methane steam reforming was successfully achieved using silica membranes for the first time.

Conclusions

In this study, we have successfully developed membrane reactors for the methane steam reforming reaction with H_2-selective amorphous silica membranes. Two different silica membranes were prepared with TMOS or HMDS for applying to the membrane reactors. The HMDS-derived membrane had much higher H_2 permeance, even under hydrothermal conditions where the vapor pressure was 76 kPa, and its stable value was 8×10^{-8} mol m^{-2} s^{-1} Pa^{-1}. This was almost the same as or higher than that of fresh TMOS-derived membrane. At the same time, the HMDS-derived membrane also maintained higher H_2 selectivity for the same hydrothermal conditions. Membrane reactors consisting of the TMOS-derived membrane and Rh catalyst or the HMDS-derived membrane and Ni catalyst were used for methane steam reforming, and exhibited equilibrium shifts for various feedrate and pressure conditions at 773 K with an S/C ratio of 3. The equilibrium shift was larger with the HMDS-derived membrane than with the TMOS-derived membrane. This order coincided with the order of hydrogen permeance. Finally, the membrane reactor with the HMDS-derived membrane was operated at 773 K with an S/C ratio of 2.5, and stable equilibrium shift was demonstrated for 30 h. This result means that the HMDS-derived membrane and Ni catalyst worked stably for this period of time.

It is notable that we developed membrane reactors for methane steam reforming with amorphous silica membranes, which are in general considered to be weak and to deteriorate in performance under hydrothermal conditions, even though there have been many proposals for the efficiency of using membrane reactors for steam reforming. For practical use, we should operate the membrane reactor in a larger scale, and we are now studying this approach.

Acknowledgments

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