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Pure hydrogen production by methane steam reforming with hydrogen-permeable membrane reactor

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Abstract

Low temperature steam reforming of methane mainly to hydrogen and carbon dioxide ($CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$) has been performed at 773 and 823 K over a commercial nickel catalyst in an equilibrium-shift reactor with an 11-μm thick palladium membrane (Mem-L) on a stainless steel porous metal filter. The methane conversion with the reactor is significantly higher than its equilibrium value without membrane due to the equilibrium-shift combined with separation of pure hydrogen through the membrane. The methane conversion in a reactor with an 8-μm membrane (Mem-H) is similar to that with Mem-L, although the hydrogen permeance through Mem-H is almost double of that through Mem-L. The amount of hydrogen separated in the reaction with Mem-H is significantly large, showing that the hydrogen separation overwhelms the hydrogen production because of the insufficient catalytic activity.

Keywords: Membrane reactor; Hydrogen separation; Palladium membrane; Methane steam reforming; Nickel catalyst

1. Introduction

Pure hydrogen is required as the desulfuration agent for petroleum, a raw material in chemical industries, an energy source for fuel cells, etc. Industrial hydrogen production is based on steam reforming of methane followed by a hydrogen separation process such as pressure swing adsorption [1]. Since the reforming reactions are highly endothermic and equilibrium limited, that is, ΔG and ΔH for $CH_4 + H_2O = 3H_2 + CO$ at 1000 K are −28 and 225 kJ mol^{-1}, respectively, and those for $CH_4 + 2H_2O = 4H_2 + CO_2$ are −30 and 191 kJ mol^{-1}, respectively, a high reaction temperature is required to achieve a sufficient methane conversion. The high temperature operation causes some demerits, e.g., the expensive tubular reformers made of high alloy nickel chromium steel with fire burners, irreversible carbon formation in the reactor, and large energy consumption. Hydrogen removal from the reaction mixture shifts the equilibrium to a higher methane conversion even at a low reaction temperature. In order to realize it, some reactors equipped with hydrogen-permeable membranes have been proposed [2–23]. Oertel et al. first reported significant increase in hydrogen production in a reactor with a palladium disk whose thickness was 100 μm, but the reaction temperatures were 973–1073 K probably because of the low hydrogen permeability of the disk [2]. Palladium membranes thinner than 20 μm often show a high performance in the membrane reaction at a temperature less than 900 K. Uemiya et al. developed thin palladium membranes supported on porous glass substrates and obtained a methane conversion of 88%, which highly exceeds the equilibrium under the reaction conditions, with their membrane reactor at 773 K [4]. However, their membrane support is fragile and difficult in connecting to metallic applications. These problems are inevitable when using porous ceramic materials as a membrane support, although thin palladium based membranes often fabricated on the materials [24–28]. Porous sintered metal, which is inexpensive and pertinent for industrial applications, is an alternative to porous ceramics, but the rough surface usually results in pinholes on the membrane [29–34]. To prevent the defect formation, our group modified the surface of the sintered metal with ceramic particles and prepared thin palladium membranes [35–37]. Since the resulting membranes were almost pinhole free, they were applied to membrane reactors for pure

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hydrogen production by methane steam reforming around 800 K [22,23]. In the tests, we confirmed that a high methane conversion close to 100% could be produced with low space velocities at around 800 K. However, the conversion decreases with an increase in the space velocity, while the reaction equilibrium can be easily attained even at significantly higher space velocities without the membrane. That is, the high space velocity causes production of an excessive amount of hydrogen to the hydrogen separation with the membrane and results in insufficient equilibrium-shift of the reaction. Hence, a reactor with a highly hydrogen permeable membrane should produce a high methane conversion even at a high space velocity. In the present paper, we have prepared two thin palladium membranes on metal supports and compared the performance in the membrane reaction. It was found that the difference in the hydrogen permeability does not affect the methane conversion as much as the separation rate of hydrogen because the catalytic activity is the other factor to promote the equilibrium-shift.

2. Experimental

Two palladium membranes were prepared by electroless plating on porous stainless steel tubes, as described elsewhere [35,37]. The support tubes were distributed from Mott Metrallugical Co. The filter length was 7.0 cm with 0.95-cm OD. After the tube with a nominal particle retention size of 0.2 μm was modified with cerium hydroxide, 11 μm of a palladium membrane (Mem-L) was deposited on the surface by electroless plating. This membrane was almost defect-free, while the ratio of hydrogen flux to argon flux was ca. 2000 at 773 K at a pressure difference of 0.10 MPa. The other 8-μm palladium membrane (Mem-H) was plated on the tube (retention size, 0.5 μm) modified with aluminum hydroxide, and the H_2/Ar ratio was also ca. 2000. The flux of pure hydrogen through Mem-H was almost double that for Mem-L at 773–823 K as shown in Fig. 1, where p_1 and p_2 were hydrogen pressures outside and inside the tube, respectively, while p_2 was always atmospheric pressure.

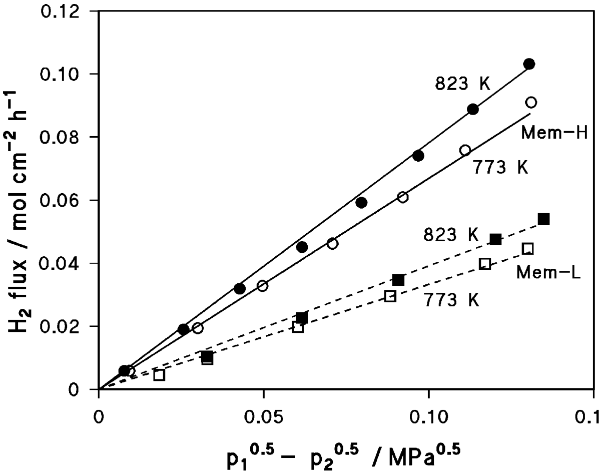

Fig. 1. Hydrogen permeation fluxes through palladium membranes at 773 and 823 K.

The membrane tube was installed in a reactor with 5.4 cm^3 of a commercial alumina-supported nickel catalyst whose nickel content was 47.2 wt.%, as described elsewhere [22,23]. In the reactor, the catalyst was preheated to 773 K in an argon stream, then, reduced in a stream of 50 vol.% hydrogen diluted with argon (12 dm^3 h^{-1}) at the same temperature. Steam reforming of methane was carried out at 773 or 823 K. A mixture of methane and steam with the S/C ratio of 3.0 was supplied quantitatively to the catalyst bed in down-flow. The reaction temperature was measured at the top of the catalyst bed. The effluent gas from the reactor (unpermeated gas) was dried with an ice trap and a silica-gel drier and analyzed with an on-stream Shimadzu GC-8A gas chromatograph (activated carbon, 1 m; Ar carrier) equipped with a thermal conductivity detector. No significant coke formation was observed in the experiment. Nitrogen (0.063 mol cm^{-2} h^{-1}) was concurrently led inside the membrane (permeation side) to sweep out the hydrogen permeated. The composition of the permeated gas was, also, analyzed with the same gas chromatograph using a flow-switch. Methane conversion and selectivities were calculated on the basis of carbon numbers. The mass balance was within the error of ±5%. Since the reaction data sometimes fluctuated due to instability of the steam feeder, the mean values of two samplings were employed here.

3. Results and discussion

3.1. Catalytic activity under equilibrium condition

The activities of catalysts were evaluated at 773 K without a membrane. The methane conversions at a space velocity (SV) up to 5600 h^{-1} were almost the same as the values calculated from the equilibrium of the reactions of $CH_4 + 2H_2O = 4H_2 + CO_2$ and $CH_4 + H_2O = 3H_2 + CO$ at 773 K (Fig. 2), while the data somewhat fluctuated at 0.1 MPa. The equilibrium conversions at 0.1, 0.2, and 0.3 MPa are 43.4, 34.0, and 29.3%, respectively, and the selectivities to carbon monoxide are calculated as 12.8, 10.1, and 8.6%, respectively. The selectivity to carbon monoxide increased discernibly with

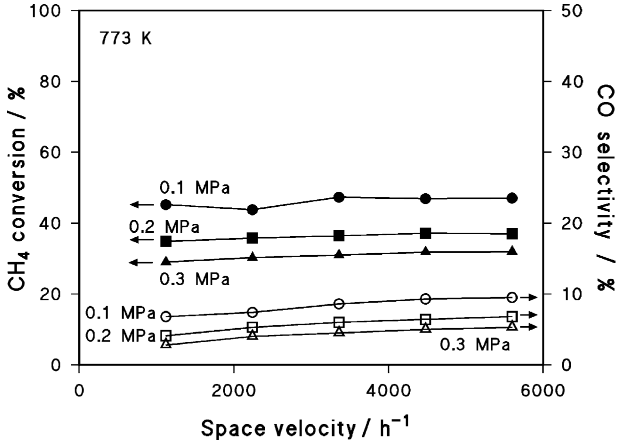

Fig. 2. Steam reforming of methane in an equilibrium reactor at 773 K.

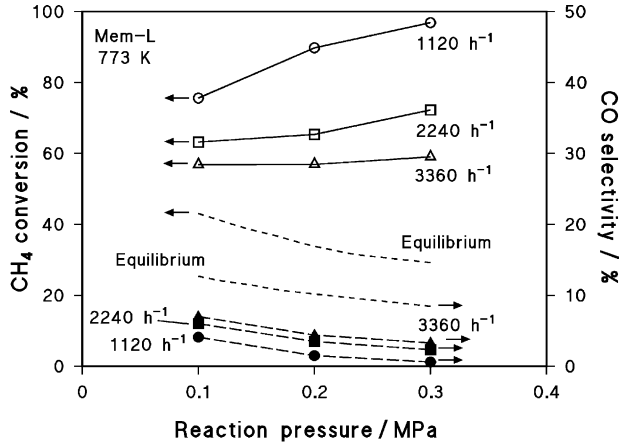

Fig. 3. Steam reforming of methane in a membrane reactor with Mem-L at 773 K.

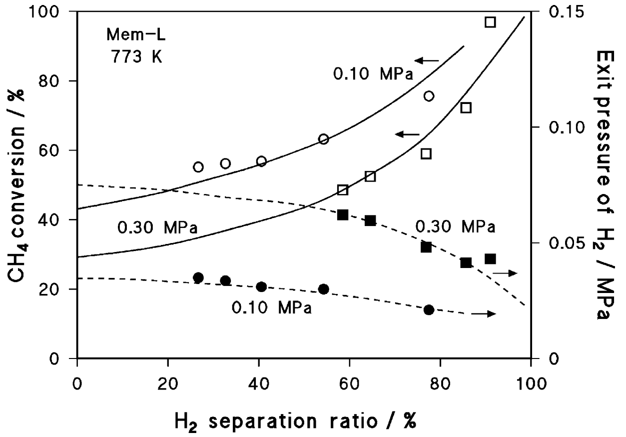

Fig. 5. Relationship between methane conversion and hydrogen separation ratio in a membrane reactor with Mem-L at 773 K. The curves are calculated from the reaction equilibrium. The space velocities of the data points are 1120, 2240, 3360, 4480, and 5600 h^{-1} from the right.

an increase in the space velocity, while it was always lower than the equilibrium value.

3.2. Hydrogen production in the reactor with Mem-L

Although the equilibrium conversion of methane decreases with an increase in the reaction pressure, the methane conversion increased in the reactor equipped with Mem-L at a low space velocity of 1120 h^{-1} and at 773 K (Fig. 3). The conversion decreased with an increase in the space velocity. The hydrogen flux through the membrane increased with an increase in the reaction pressure (Fig. 4), because the partial pressure of hydrogen in the catalyst side increased at a high reaction pressure. No impurity was detected in the separated hydrogen. The hydrogen separation ratio (the relative rate of hydrogen separation to the total production of hydrogen in the reaction), also, increased with an increase in the reaction pressure, and 91% of hydrogen was separated from the reactor at 1120 h^{-1} and at 0.3 MPa. The space velocity affected the hydrogen flux at 0.2 and 0.3 MPa, but the flux at 0.1 MPa did not greatly depend on the space velocity probably due to the small difference in hydrogen pressure between the two sides of the membrane. The hydrogen separation ratio decreased with an increase in the space velocity, because the rate of hydrogen separation does not increase as much as an increase in the total production rate of hydrogen, which relates to the multiplication of the space velocity and the methane conversion. The methane conversions measured under different space velocities (1120–5600 h^{-1}) were plotted against the hydrogen separation ratios (Fig. 5). The methane conversions increased with an increase in the hydrogen separation ratio and were close to the equilibrium (solid curves), showing that the equilibrium-shift of the reaction by the hydrogen separation takes place sufficiently.

The selectivity to carbon monoxide was decreased with an increase in the reaction pressure (see Fig. 3), appearing that the water-gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) is, also, promoted by the hydrogen separation.

High methane conversions were produced at 823 K (Fig. 6), while the hydrogen separation ratios were similar to those at 773 K (cf. Figs. 4 and 7). The similar hydrogen fluxes at 0.1 MPa were probably due to the small difference in hydrogen pressure between the two sides of the membrane as observed at 773 K (see Fig. 4). The methane conversions at a space velocity of 2240–5600 h^{-1} were similar to the equilibrium values

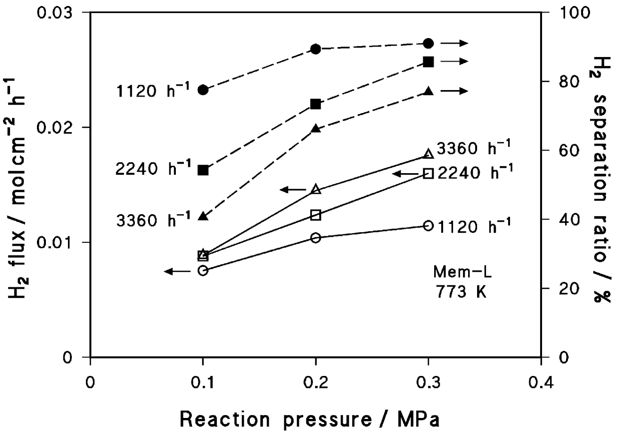

Fig. 4. Hydrogen permeation flux through Mem-L in a membrane reactor and the hydrogen separation ratio at 773 K.

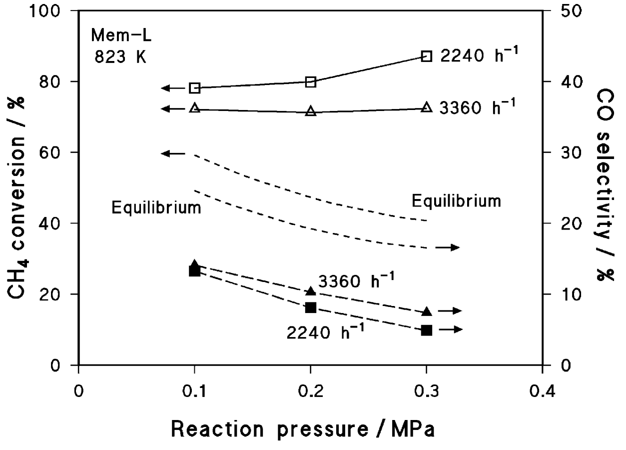

Fig. 6. Steam reforming of methane in a membrane reactor with Mem-L at 823 K.

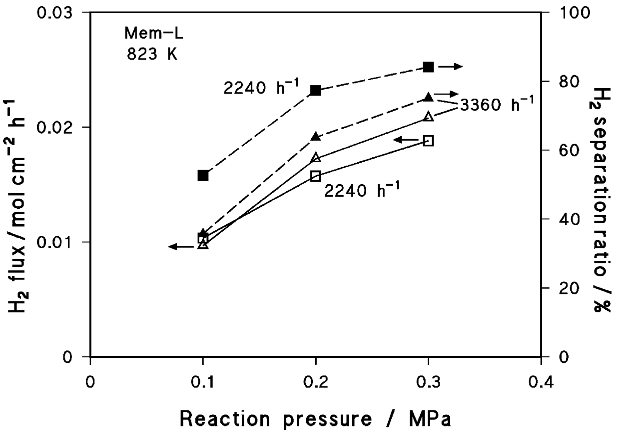

Fig. 7. Hydrogen permeation flux through Mem-L in a membrane reactor and the hydrogen separation ratio at 823 K.

calculated for the corresponding hydrogen separation ratios (Fig. 8). That is, the methane conversion higher than that at 773 K is due to the increase in the equilibrium conversion, which increases with an increase in the reaction temperature.

3.3. Hydrogen production in the reactor with Mem-H

Since the methane conversion increases with an increase in the hydrogen separation ratio, the higher conversion should be produced when using a membrane with high hydrogen permeability. Hence, we installed Mem-H, whose hydrogen permeation was almost double of that for Mem-L (see Fig. 1), to the reactor and tested its performance in the membrane reaction. However, the methane conversions produced at 773 K and at 0.10 MPa were almost the same as those with Mem-L (cf. Figs. 3 and 9), even though the hydrogen fluxes through Mem-H in the reaction were significantly greater than those for Mem-L at 2240 and 3360 h^{-1} (cf. Figs. 4 and 10). The hydrogen fluxes at 1120 h^{-1} were not significantly larger than those with Mem-L, suggesting that hydrogen production on the catalyst limits the hydrogen flux when the methane conversion is high [23].

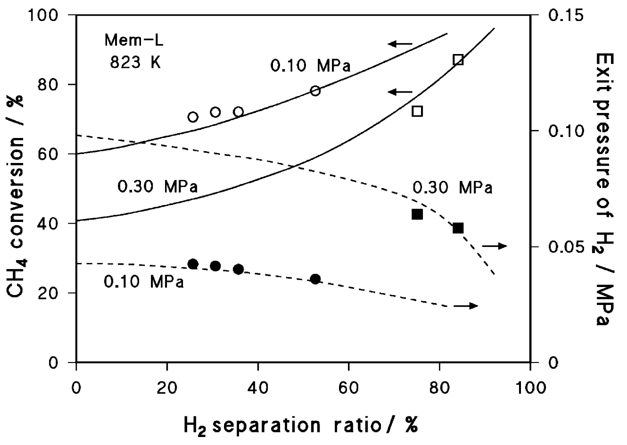

Fig. 8. Relationship between methane conversion and hydrogen separation ratio in a membrane reactor with Mem-L at 823 K. The curves are calculated from the reaction equilibrium. The space velocities of the data points are 2240, 3360, 4480, and 5600 h^{-1} from the right.

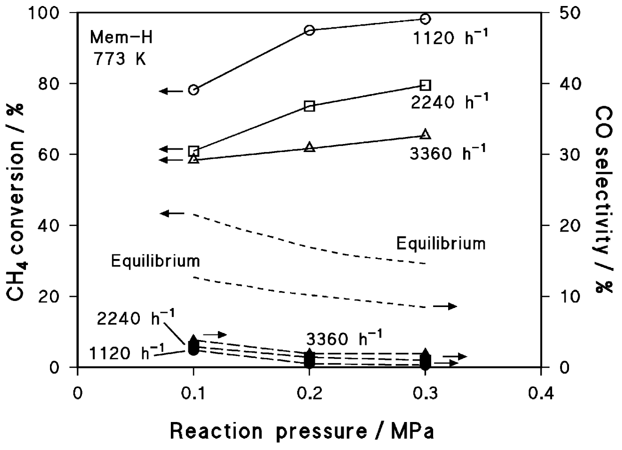

Fig. 9. Steam reforming of methane in a membrane reactor with Mem-H at 773 K.

The conversions with Mem-H at the higher pressures were discernibly higher than those with Mem-L. The insufficient methane conversion is not due to the limitation of reaction heat supply, because the maximum hydrogen formation rate of the equilibrium reaction in Fig. 2 was 115 mol h^{-1} dm^{-3} (0.1 MPa and 5600 h^{-1}) and larger than that of 97 mol h^{-1} dm^{-3} in Fig. 9 (0.3 MPa and 3360 h^{-1}). As can be seen in Fig. 11, the methane conversion at 1120 h^{-1} (the far right symbols) was almost the same as the equilibrium values, but those at the higher space velocities to 5600 h^{-1} were significantly lower. Since the membrane reactor promotes the reaction by the equilibrium-shift combined with the hydrogen separation, the reaction equilibrium should be attained in the whole part of the reactor for the efficient promotion. On the other hand, the attainment of the equilibrium is not necessary in the usual equilibrium reactor except for the exit. Hence, the catalytic activity is very important in the membrane reactor, and Fig. 11 shows that the activity is insufficient at the space velocity of 2240 h^{-1} or above. This suggests that the larger amount of the catalyst is necessary to produce the methane conversion close to the equilibrium in the case of the reactor with Mem-H at a high feed

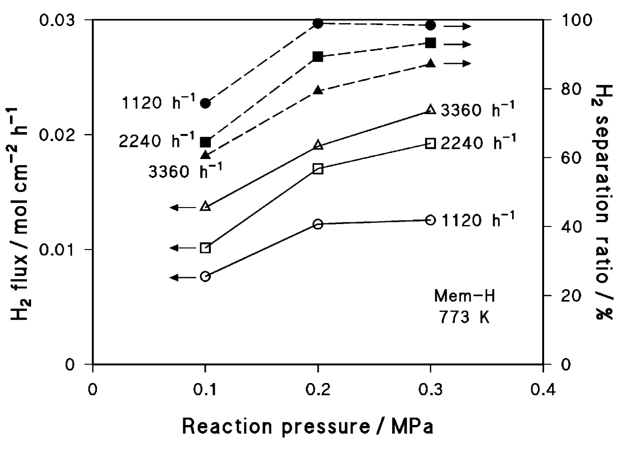

Fig. 10. Hydrogen permeation flux through Mem-H in a membrane reactor and the hydrogen separation ratio at 773 K.

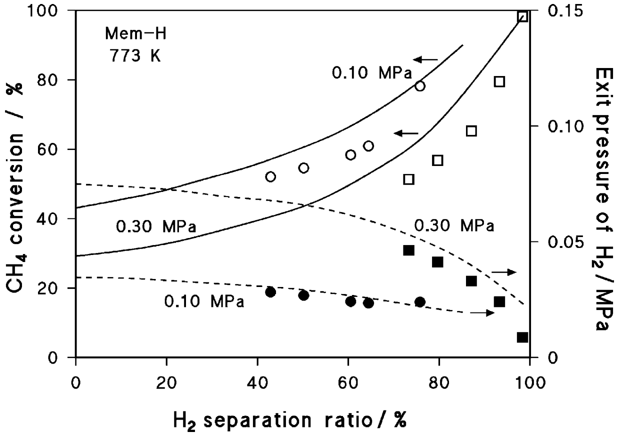

Fig. 11. Relationship between methane conversion and hydrogen separation ratio in a membrane reactor with Mem-H at 773 K. The curves are calculated from the reaction equilibrium. The space velocities of the data points are 1120, 2240, 3360, 4480, and 5600 h^{-1} from the right.

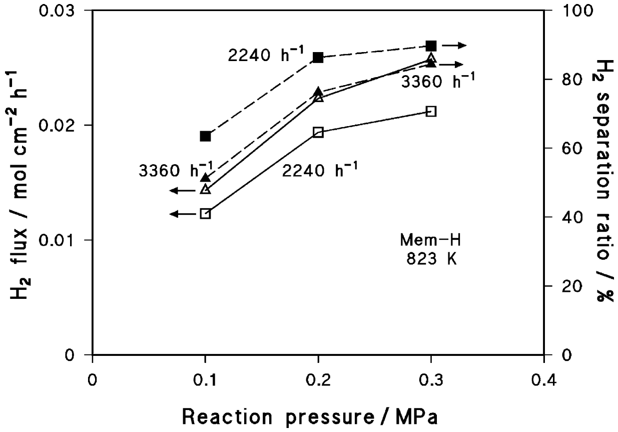

Fig. 13. Hydrogen permeation flux through Mem-H in a membrane reactor and the hydrogen separation ratio at 823 K.

rate of the reaction gas. As a result, the space velocity becomes low and it increases the reactor size. The hydrogen pressure at the reactor exit was lower than that expected from the equilibrium (broken curve), appearing that the hydrogen separation overwhelms the hydrogen production by the reforming because of the insufficient catalytic activity.

It is noteworthy that the selectivity to carbon monoxide was significantly lower than that for Mem-L, showing that the water-gas shift reaction is sensitively affected by the hydrogen separation. Since carbon monoxide is more reactive than methane, the shift reaction should take place in preference to the methane reforming. The contribution of the shift reaction will be great at a low reaction pressure because of the high selectivity to carbon monoxide. This accounts for the similar methane conversion with Mem-H to that with Mem-L at 0.1 MPa despite the higher hydrogen separation ratio of Mem-H.

At 823 K, the methane conversions with Mem-H at 0.1 MPa were also similar to those produced with Mem-L, while the conversions at the higher pressures were appreciably higher than those with Mem-L (cf. Figs. 6 and 12). Although the hydrogen flux increased at 823 K in comparison with that at 773 K, the hydrogen separation ratio decreased (cf. Figs. 10 and 13), showing the production rate of hydrogen, also, increased. The selectivities to carbon monoxide decreased greatly in comparison with these for Mem-L at 823 K, appearing that the water-gas shift reaction takes place preferentially. The plots of the methane conversion versus the separation ratio (SV, 2240–5600 h^{-1}) show that the conversions were close to the equilibrium values in comparison with the cases at 773 K (Fig. 14). The activity of a nickel catalyst increases with an increase in the reaction temperature. Since the activation energy of nickel supported on alumina was reported to be 152 kJ mol^{-1} [1], the activity at 823 K will be ca. four times of that at 773 K. Hence, the increase in the methane conversion is due to the increase in the activity at the higher temperature.

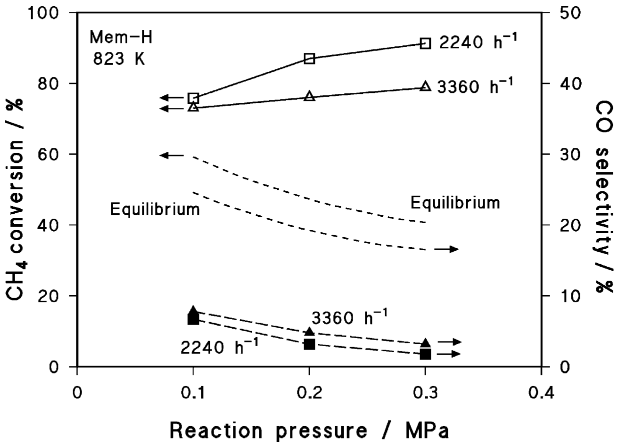

Fig. 12. Steam reforming of methane in a membrane reactor with Mem-H at 823 K.

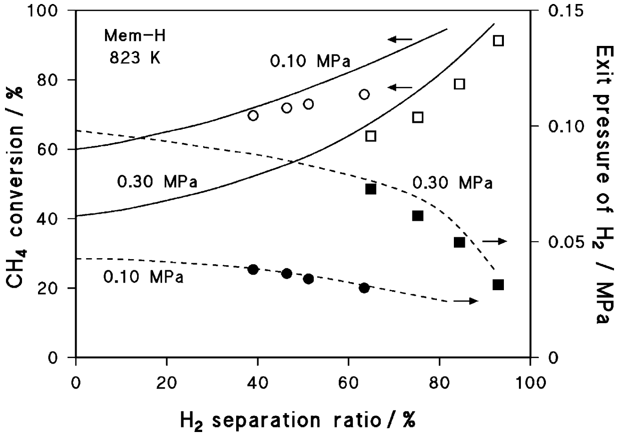

Fig. 14. Relationship between methane conversion and hydrogen separation ratio in a membrane reactor with Mem-H at 823 K. The curves are calculated from the reaction equilibrium. The space velocities of the data points are 2240, 3360, 4480, and 5600 h^{-1} from the right.

4. Conclusions

Separation of hydrogen through the palladium membrane shifts the equilibrium to the larger conversion of methane at 773 and 823 K. The conversion in a reactor with an 11-μm palladium membrane supported on a porous stainless steel filter is almost the same as the values expected from the equilibrium-shift produced by the hydrogen separation, appearing that the activity of the nickel catalyst is sufficient. In the cases of a low space velocity of 1120 h^{-1}, the methane conversion exceeds 70% due to the high hydrogen separation ratio. However, the ratio decreases with an increase in the space velocity, and as a result, the conversion decreases. The ratio is significantly increased using a reactor with an 8-μm palladium membrane whose hydrogen permeance is almost double of that of the 11-μm palladium membrane. However, the methane conversion is similar to that with the 11-μm membrane because the catalytic hydrogen production cannot catch up the equilibrium-shift produced with the highly permeable membrane. Thus, both a highly active catalyst and a highly permeable membrane will be required to produce a high methane conversion at a high space velocity in a membrane reactor.

Acknowledgement

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