Decomposition of Methane over Ni/SiO_2 Catalysts with Membrane Reactor for the Production of Hydrogen

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Decomposition of CH_4 to C and H_2 on Ni/SiO_2 catalyst was investigated with membrane reactor consisting of 90Pd10Ag alloy tube for the production of H_2. Application of membrane reactor was effective for increasing the yield of H_2 and consequently, CH_4 conversion far exceeded the equilibrium conversion of closed system by using the membrane reactor.

Hydrogen is expected as the new energy source without the emission of air pollutant. At present, hydrogen is mainly produced by the steam reforming of CH_4. However, this reaction is endothermic reaction and the large thermal energy is required for the production of hydrogen. Furthermore, hydrogen produced by steam reforming of CH_4 contains the large amount of CO_2 or CO as a by-product, consequently, separation process is also required for the production of H_2. In contrast, decomposition of methane to carbon and hydrogen has the following advantages for the production of H_2. Small thermal energy is enough for proceeding the reaction, since the reaction enthalpy is far smaller than that of steam reforming and the gaseous product is only hydrogen. In this study, decomposition of CH_4 over Ni/SiO_2 catalysts was investigated for the new production method of hydrogen by using membrane reactor where Pd-Ag alloy tube was used for the H_2 permeable films. The SiO_2-supported Ni catalyst exhibits high activity to the CH_4 decomposition,[1] however, the yield of H_2 becomes low in the temperature range lower than 773 K due to the chemical equilibrium. There have been some reports concerning on the application of membrane separation process with catalyst process[2,3] and it is suggested that the application of membrane separation process is effective for improving the overall conversion in various reactions.[4,5] However, application of these membrane reactor systems for the catalytic decomposition of hydrocarbon has not been reported.

The SiO_2-supported Ni catalyst with total metal loading of 10 wt % was prepared by the incipient wetness techniques. The catalysts were calcined at 573 K for 4h under air stream and were reduced at 673 K for 5 h under a hydrogen stream. Catalytic decomposition of CH_4 to C and H_2 was performed with a double-tubular type membrane reactor. Palladium-silver alloy (90Pd10Ag) tube (Tanaka Kikinzoku Co. Ltd.) with 250 μm in thickness and 10 mm in the outer diameter was used for the inner tube as the hydrogen permeable membrane. The SiO_2-supported Ni catalyst was placed between the inner Pd-Ag tube and the outer pyrex glass tube (23 mm in the outer diameter). The gaseous mixture of CH_4 and N_2 (CH_4:N_2=1:9) was fed to the catalyst bed at W/F=10 g-cat.h/mol under an atmospheric pressure, where W and F mean catalyst weight and flow rate, respectively. Argon gas was fed to the inside of Pd-Ag alloy tube at an atmospheric pressure for sweeping the permeated hydrogen. Conversion of CH_4 and yield of H_2 were determined by the analysis of CH_4 and H_2 in the reactor side and permeated side with TCD gas chromatography. The yield of carbon was estimated by the mass balance of carbon .

Figure 1 shows the comparison of overall CH_4 conversion in the membrane reactor and that in the fixed bed reactor. Comparing with the molar amount of converted CH_4, almost the equimolar amount of C and the twice molar amount of H_2 were formed in the both membrane reactor and fixed bed reactor. Therefore, only decomposition of CH_4 was proceeded in the both reactors. The SiO_2-supported Ni catalyst exhibited the high activity for the decomposition of CH_4 to C and H_2, however, the

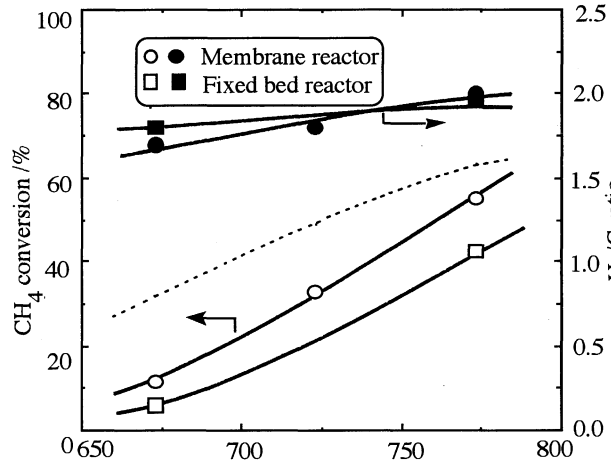

Figure 1. Temperature dependences of the CH_4 conversion and H_2/C ratio over Ni/SiO_2 with fixed bed reactor and membrane reactor. (··············) Equilibrium conversion
(W/F=10 g-cat.h mol^{-1}, Sweep Ar; 20 mlmin^{-1})

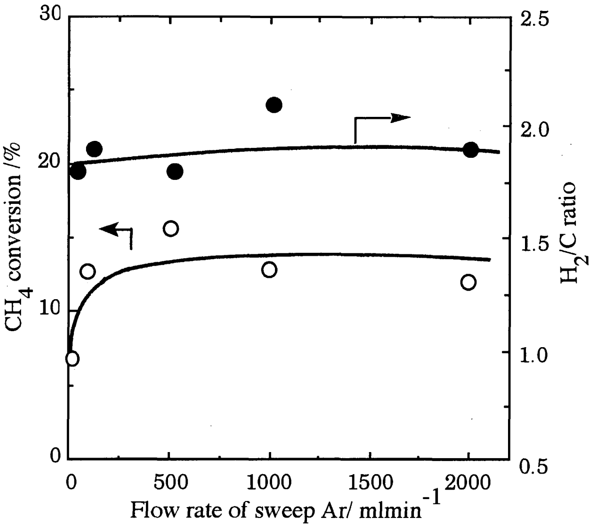

Figure 2. Effects of flow rate of sweep Ar on the activity of CH_4 decomposition. (673 K, W/F=10 g-cat.hmol^{-1})
(○)CH_4conv. (●)H_2/C ratio

CH_4 conversion was as low as 40 % at 773 K in case of the fixed bed reactor. Removing the formed hydrogen with Pd-Ag tubes was effective in enhancing the overall CH_4 conversion as shown in Figure 1. In particular, the positive effects of CH_4 conversion with membrane reactor became significant with increasing the reaction temperature, since the H_2 permeability became larger with elevating temperature. However, yield of H_2 is still low in the low temperature range even by using the membrane reactor. This may result from the low permeability of hydrogen of the used Pd-Ag alloy tube and the low reaction rate of CH_4 decomposition. Therefore, there is a possibility for the further increase in the CH_4 conversion by optimizing the reaction condition.

Figure 2 shows the effects of flow rate of sweep Ar on the overall conversion of CH_4 at 673 K. Since the increasing rate of sweep Ar enhances the permeability of H_2 through Pd-Ag tubes, the conversion of CH_4 increased with increasing the flow rate of sweep Ar and attained a value of 16 % when the flow rate of sweep Ar was 500 ml min^{-1}. However, conversion of CH_4 was almost independent of the flow rate of sweep Ar in the range above 200 ml min^{-1}. This suggested that the rate of CH_4 decomposition upon Ni/SiO_2 catalyst became smaller than that of hydrogen permeation by increasing the flow rate of sweep Ar.

The overall conversion of CH_4 was plotted in Figure 3 against the contact time, W/F, at 673 K. The conversion of CH_4 was increased with increasing the contact time and attained a value of 15 % when W/F was 60 g-cat.h mol^{-1}. Therefore, longer contact time was more preferable for the high yield of hydrogen. However, the dependence of CH_4 conversion upon contact time was small in the range longer than W/F=60 g-cat. h mol^{-1}. Consequently, the contact time higher than 50 g-cat.h mol^{-1} and the flow rate of sweep Ar higher than 200 ml min^{-1} were preferable for the high conversion for CH_4 decomposition, respectively.

Temperature dependence of CH_4 conversion under thus estimated optimum reaction condition was shown in Figure 4. Comparing the temperature dependence of CH_4 conversion in Figure 1, the conversion of CH_4 increased drastically by increasing the flow rate of sweep Ar and the contact time. In particular, the increase in the CH_4 conversion in the temperature range above 723 K was significant. Consequently, the overall conversion of CH_4 in membrane reactor exceeded the equilibrium conversion in the temperature range higher than 700 K and methane was completely decomposed above 823K. On the other hand, carbon, by-product of H_2, was formed on the catalysts and it is expected that catalyst was deactivated by the coverage of formed carbon. However, the CH_4 conversion at about 70 % was stably sustained over examined 60 h at 773 K, W/F=10 g-cat.h^{-1}. The weight of Ni/SiO_2 catalyst was increased from 0.40 to 2.04 g after CH_4 decomposition for 60 h. The molar amount of carbon deposited on catalysts was 200 times larger than that of the supported Ni. TEM and SEM observations suggest that the formed carbon was a graphite filament with tublar shape and the Ni particle existed at the tip of filament. Therefore, it is expected that the activity of Ni/SiO_2 catalyst to CH_4 decomposition was stably maintained over a long period, because the carbon mainly deposited under the Ni particle and the Ni surface was exposed to the reactant even after the large amount of carbon deposited. It is also noted that the decrease in the H_2 parmeation rate of used Pd-Ag tube could not be observed. This study revealed that the decomposition of CH_4 to C and H_2 with membrane reactor is one of the promising methods for the production of hydrogen.

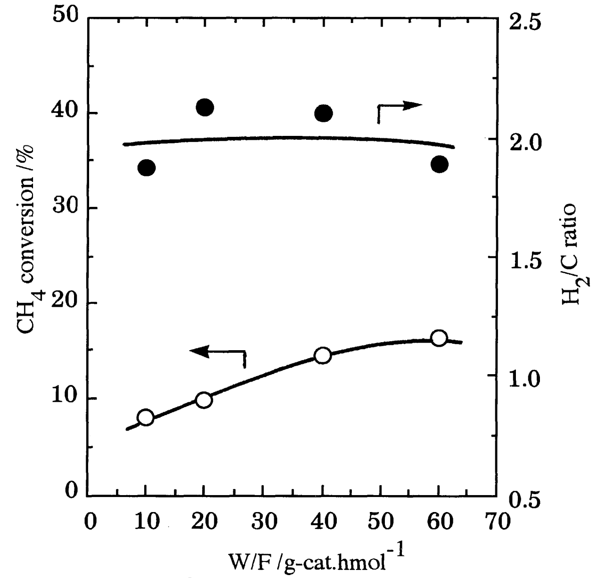

Figure 3. Effects of contact time on the activity to CH_4 decomposition. (673 K, Sweep Ar; 20 mlmin^{-1})
(○)CH_4 conv. (●)H_2/C ratio

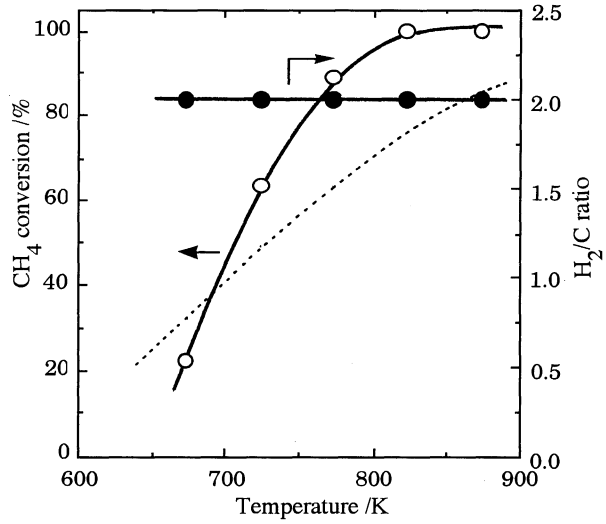

Figure 4. Temperature dependence of CH_4 decomposition over Ni/SiO_2 with the membrane reactor under optimized condition. (W/F=50 g-cat.h mol^{-1}, Sweep Ar; 200 ml min^{-1})

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References and Notes

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