

CO₂ reforming of CH₄ over ceria-supported metal catalysts

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Abstract

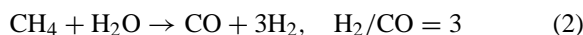
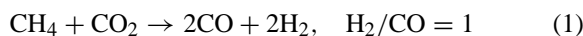
CO₂ reforming of CH₄ was studied over Fe, Co and Ni catalysts supported on cerium oxide at atmospheric pressure. Ni catalyst gave the highest activity; equilibrium conversion of methane was attained under the conditions of 1123 K, 1 g/h/mol, and CO₂/CH₄ = 1, and the composition of syngas formed was almost H₂/CO = 1. Carbon deposition was not observed, and the catalytic activity and the syngas selectivity were stable for 24 h over the catalyst. It was found that the high temperature treatment of the catalyst at 1123 K is important for such an excellent catalytic performance. Co catalyst exhibited an activity nearly equal to that of Ni catalyst when reduced sufficiently, whereas Fe catalyst showed a poor activity.

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Keywords: Ceria-supported; Activity; Catalyst

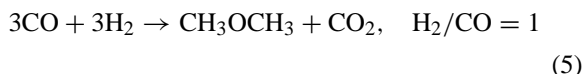
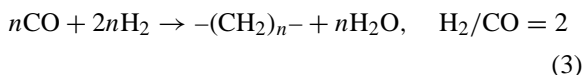
1. Introduction

As is well-known, the natural gas to liquid fuel process, so-called GTL process [1–3], is composed of two parts. One is the synthesis gas generation from natural gas (methane), and the other is synthesis gas conversion to liquid fuels. Synthesis gas with lower H₂/CO can be produced from methane by CO₂ reforming (Eq. (1)) compared with conventional steam reforming (Eq. (2))



The liquid fuel synthesis reactions from synthesis

gas, such as Fischer–Tropsch synthesis (Eq. (3)), methanol synthesis (Eq. (4)), and dimethyl ether synthesis (Eq. (5)), require lower H₂/CO ratio than that obtained by steam reforming



Therefore, CO₂ reforming can be important to control H₂/CO ratio. Another advantage is the effective use of CO₂, a known green house gas, as a carbon resource. In this process, novel catalysts with high performance are required, and thus, the development of catalysts

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with high activity and long life is a key research objective [4–6].

Noble metals such as Pt, Rh, and Pd are reported to be active and fairly stable for the CO₂ reforming of CH₄. However, they are too expensive to utilize practically. Inexpensive base metals such as Fe, Co, and Ni are also known to be active for the reaction to some extent, and of these Ni is the most promising. However, rapid deactivation is a serious problem when these metals are supported on common carrier materials such as silica and alumina. Several novel Ni catalysts with long life have been reported in the literature. These include Ni–MgO solid solution [7], Ni/perovskite [8], Ni/La₂O₃ [9], and CeO₂ modified Ni/Al₂O₃ [10] catalysts. It is noted that these catalysts contain basic supports or additives. It is known that carbon deposition is inhibited by basic materials. On the other hand, the authors reported that CeO₂ as such has a high activity for methane conversion, and gives CO and water at 1123 K [11]. In the present study, therefore, our aim was to obtain an excellent catalyst for CO₂ reforming of CH₄, and to examine the possibility of using CeO₂ as a catalyst support. Iron group metals were impregnated onto CeO₂ support, and the catalytic performance for the reaction was investigated.

2. Experimental

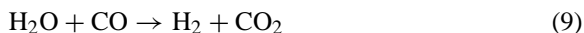
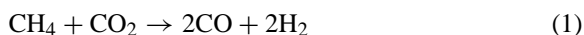
Ceria-supported Fe, Co, or Ni catalysts were prepared by the conventional impregnation method using aqueous solutions of those metal nitrates. The metal loading of each catalyst was 5 wt.%. After drying at 380 K and calcination at 673 K in air, the catalysts were ground down to 0.4–0.7 mm. 100–500 mg of the catalyst was charged into the reactor with 1.5 g of quartz sand as a diluent. Then, it was reduced in situ at 1123 K in H₂ flow for 0.5 h.

CO₂ reforming runs were performed using a fixed bed quartz reactor with 8 mm ID under atmospheric pressure. After the catalyst reduction, H₂ gas was replaced with high purity N₂, followed by the introduction of the reaction gas mixture to the reactor. The composition of the reactor feed was CH₄/CO₂ = 1/1 (molar ratio). The standard conditions were as follows: temperature, 1123 K; catalyst charge, 500 mg; total flow rate, 100 ml/min (STP).

Reactants (CH₄ and CO₂) and reaction products such as H₂ and CO were analyzed with an on-line gas chromatograph.

3. Results and discussion

Fig. 1 shows the changes in CH₄ conversion and H₂/CO ratio for Ni/CeO₂ and Co/CeO₂ catalysts. Ni/CeO₂ catalyst showed stable activity; CH₄ conversion was almost constant for 20 h, and H₂/CO ratio was also constant during the period with the value nearly equal to unity. If the reaction proceeds stoichiometrically only through reaction (1), the H₂/CO ratio is unity



When carbon deposition occurs, even if it proceeds through either CH₄ decomposition (6) or disproportionation of CO formed ((1) and (7)), the H₂/CO ratio is more than 1. Water formation (8), on the other hand, results in a decrease in H₂/CO ratio. If the water gas shift reaction (9) occurs successively to the water formation, the overall reaction comes to the dry reforming reaction (1). The results above suggest strongly

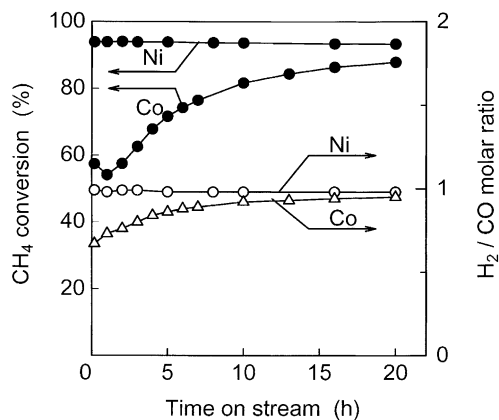


Fig. 1. Catalytic performance of CeO₂-supported Ni and Co catalysts. Temperature, 1123 K; W/F, 2 g h/mol; reduction, 0.5 h.

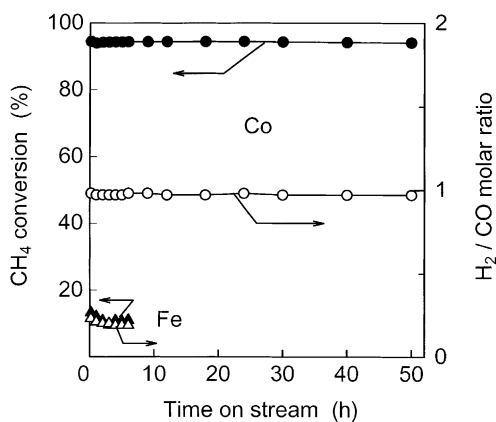


Fig. 2. Catalytic performance of CeO_2 -supported Co and Fe catalysts. Temperature, 1123 K; W/F , 2 g h/mol; reduction, 4 h.

that neither carbon deposition nor formation of water proceeds over Ni/CeO_2 catalyst. CH_4 conversion over Co/CeO_2 catalyst increased gradually as time passed to reach a steady state for about 20 h. It is inferred that the initial low conversion is due to an insufficient reduction of the catalyst.

Fig. 2 shows the catalytic performance of CeO_2 -supported Co and Fe catalysts with thorough reduction. When the Co/CeO_2 catalyst had been reduced fully for 4 h, CH_4 conversion of 94%, which is almost equal to the equilibrium conversion, was obtained, and the catalytic activity was stable for 50 h. The H_2/CO ratio was also constant and almost unity during the period. On the other hand, however, the activity of Fe/CeO_2 catalyst was very low even though it had been reduced thoroughly.

Fig. 3 shows the influence of reaction temperature on CH_4 conversion and H_2/CO ratio at steady state over Ni and Co catalysts. Ni catalyst showed higher activity than Co catalyst; equilibrium conversion of CH_4 was attained above 1073 K. Although the H_2/CO ratio was less than unity at below 1073 K, and water formation was observed, it was almost unity above that temperature without formation of water or carbon. These findings show that the sequence of catalytic performance, in terms of the CH_4 conversion activity, selectivity to synthesis gas, and durability, could be expressed in the following order $\text{Ni} > \text{Co} \gg \text{Fe}$.

Effect of the time factor (W/F) on performance was examined over the most active Ni/CeO_2 catalyst by changing both catalyst charge and flow rate of the feed

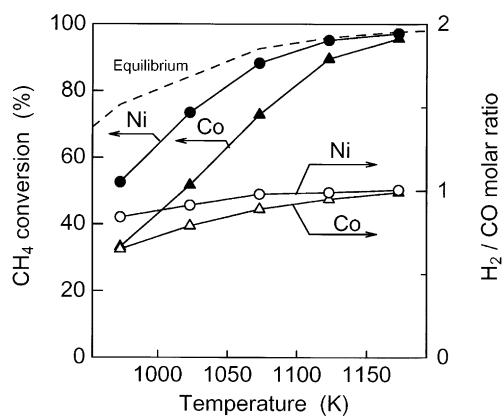


Fig. 3. Temperature dependence of Ni and Co catalysts at steady state. W/F , 2 g h/mol.

gas. Fig. 4 shows the CH_4 conversion and H_2/CO ratio as a function of W/F . Equilibrium conversion of CH_4 was attained above about 1 g h/mol, and the H_2/CO ratio was also near the stoichiometric value. Such high performance of the Ni/CeO_2 catalyst are comparable with those reported before [7,8].

Fig. 5 illustrates the durability of the Ni/CeO_2 catalyst at a high space velocity of 1 g h/mol. As can be seen in the figure, the catalyst maintained the high activity and selectivity for the synthesis gas formation for 50 h, only slight deactivation was observed.

Fig. 6 indicates the response of the CH_4 conversion when the reaction temperature was changed. Wang and Lu [6] reported that a rapid deactivation occurred

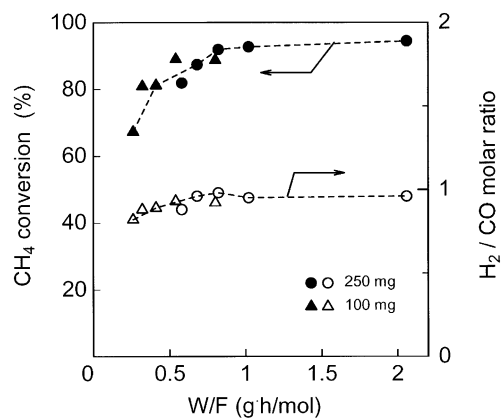


Fig. 4. Effect of time factor (W/F) for Ni/CeO_2 catalyst. Temperature, 1123 K.

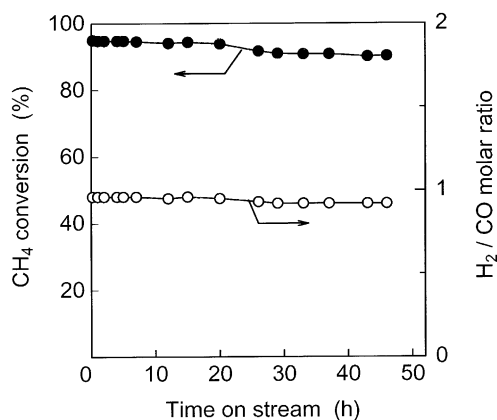


Fig. 5. Durability of Ni/CeO₂ catalyst. Temperature, 1123 K; W/F, 1 g h/mol.

over Ni/CeO₂ catalyst at 973 K. We also observed such deactivation at that temperature. CH₄ conversion was high and stable at 1123 K (solid line with open circles) as described above, whereas the initial conversion at 973 K was only 30%, and the conversion decreased quickly to only several percentage points for 2–3 h (dashed line). However, when the catalyst temperature was raised to 1123 K after the deactivation, the activity recovered to the same level as the solid line. Moreover, after the temperature was reduced to 973 K again, CH₄ conversion changed to about 60%, but no decline in conversion was observed. It is possible that the rapid deactivation observed at 973 K was caused

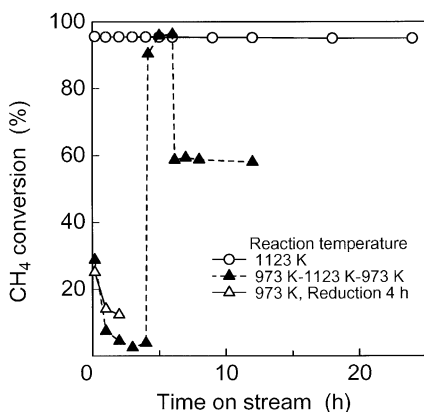


Fig. 6. Effect of initial reaction temperature for Ni/CeO₂ catalyst. W/F, 2 g h/mol.

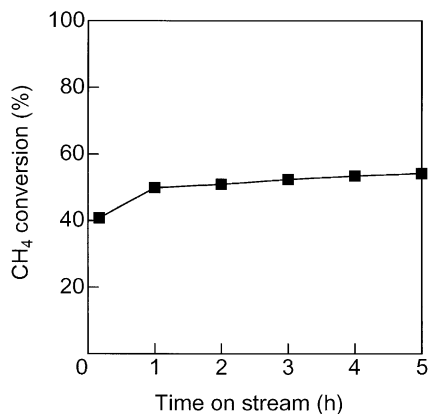


Fig. 7. Effect of heat treatment in N₂ flow at 1123 K for 0.5 h. Reaction temperature, 973 K; W/F, 2 g h/mol.

by insufficient reduction with the low temperature (973 K) and short reduction time (0.5 h). Therefore, reduction time was increased to 4 h. However, the performance of the catalyst was substantially the same as that of the catalyst which was reduced for only 0.5 h. This suggests that the high temperature plays a key role in achieving a high activity. It is interesting that heat treatment at 1123 K in N₂ flow without H₂ reduction prior to the reaction results in a stable catalyst at 973 K (Fig. 7). Thus, it is found that the Ni/CeO₂ catalyst shows an excellent performance when it is exposed to a high temperature around 1123 K. Although the effect of the high temperature treatment is not yet clear, it is suggested that the intimate interaction between Ni and CeO₂ support or the change in the number of the active sites should result in the high activity. Further characterization is in progress.

4. Summary

Reforming of methane with carbon dioxide was examined over Ni, Co, and Fe catalysts supported on cerium oxide, and the following results were obtained. The most effective catalyst among the three was Ni/CeO₂ catalyst, where 95% CH₄ conversion was achieved, H₂/CO ratio in the product gas was about unity, and the activity and selectivity were stable for 50 h at 1123 K and 1 g h/mol. Co catalyst, next to Ni catalyst, showed high activity, selectivity, and

durability when reduced fully. Fe catalyst showed poor activity and selectivity.

Although Ni/CeO₂ catalyst deactivates very quickly at low temperature of 973 K, the deactivated catalyst becomes active and stable when exposed to a high temperature (1123 K) reaction gas mixture. The excellent performance can be also obtained by treating the catalyst in an inactive atmosphere at a high temperature of 1123 K. It seems that the high activity and stability is due to the strong metal support interaction.

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