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CO_2 reforming of CH_4 over ceria-supported metal catalysts

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Abstract

CO_2 reforming of CH_4 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 $CO_2/CH_4 = 1$, and the composition of syngas formed was almost $H_2/CO = 1$. 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.

Keywords: Ceria-supported; Activity; Catalyst

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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 H_2/CO can be produced from methane by CO_2 reforming (Eq. (1)) compared with conventional steam reforming (Eq. (2))

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2, \quad H_2/CO = 1 \tag{1}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad H_2/CO = 3 \tag{2}$$

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 H_2/CO ratio than that obtained by steam reforming

$$n CO + 2n H_2 \rightarrow -(CH_2)_n- + n H_2O, \quad H_2/CO = 2 \tag{3}$$

$$CO + 2H_2 \rightarrow CH_3OH, \quad H_2/CO = 2 \tag{4}$$

$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2, \quad H_2/CO = 1 \tag{5}$$

Therefore, CO_2 reforming can be important to control H_2/CO ratio. Another advantage is the effective use of CO_2, 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 CO_2 reforming of CH_4. 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 theses 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/La_2O_3 [9], and CeO_2 modified Ni/Al_2O_3 [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 CeO_2 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 CO_2 reforming of CH_4, and to examine the possibility of using CeO_2 as a catalyst support. Iron group metals were impregnated onto CeO_2 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 H_2 flow for 0.5 h.

CO_2 reforming runs were performed using a fixed bed quartz reactor with 8 mm ID under atmospheric pressure. After the catalyst reduction, H_2 gas was replaced with high purity N_2, followed by the introduction of the reaction gas mixture to the reactor. The composition of the reactor feed was $CH_4/CO_2 = 1/1$ (molar ratio). The standard conditions were as follows: temperature, 1123 K; catalyst charge, 500 mg; total flow rate, 100 ml/min (STP).

Reactants (CH_4 and CO_2) and reaction products such as H_2 and CO were analyzed with an on-line gas chromatograph.

3. Results and discussion

Fig. 1 shows the changes in CH_4 conversion and H_2/CO ratio for Ni/CeO_2 and Co/CeO_2 catalysts. Ni/CeO_2 catalyst showed stable activity; CH_4 conversion was almost constant for 20 h, and H_2/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 H_2/CO ratio is unity

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{1}$$

$$CH_4 \rightarrow C + 2H_2 \tag{6}$$

$$2CO \rightarrow C + CO_2 \tag{7}$$

$$CH_4 + 3CO_2 \rightarrow 4CO + 2H_2O \tag{8}$$

$$H_2O + CO \rightarrow H_2 + CO_2 \tag{9}$$

When carbon deposition occurs, even if it proceeds through either CH_4 decomposition (6) or disproportionation of CO formed ((1) and (7)), the H_2/CO ratio is more than 1. Water formation (8), on the other hand, results in a decrease in H_2/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

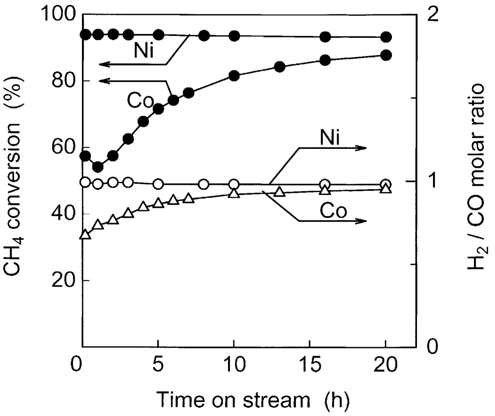

Fig. 1. Catalytic performance of CeO_2-supported Ni and Co catalysts. Temperature, 1123 K; *W/F*, 2 g h/mol; reduction, 0.5 h.

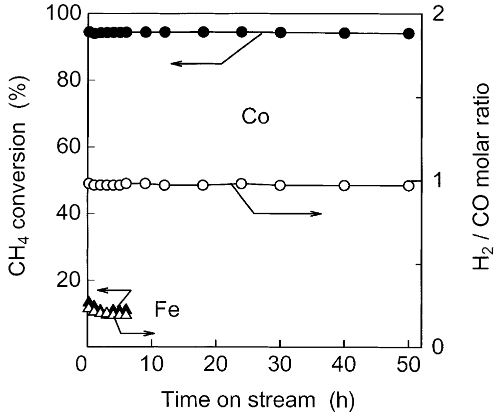

Fig. 2. Catalytic performance of CeO_2-supported Co and Fe catalysts. Temperature, 1123 K; *W/F*, 2 g h/mol; reduction, 4 h.

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 Ni > Co ≫ 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 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

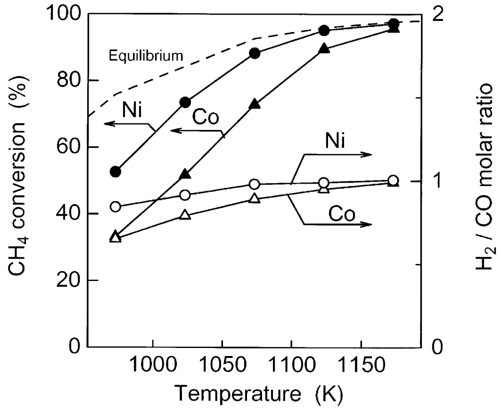

Fig. 3. Temperature dependence of Ni and Co catalysts at steady state. *W/F*, 2 g h/mol.

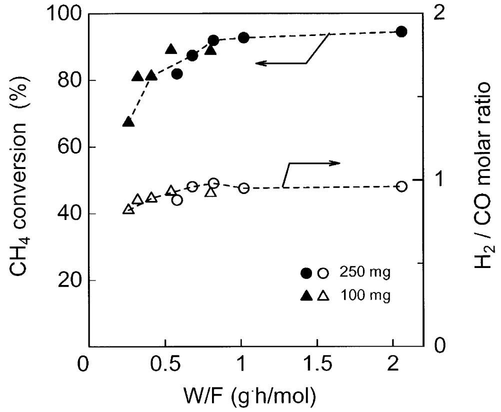

Fig. 4. Effect of time factor (*W/F*) for Ni/CeO_2 catalyst. Temperature, 1123 K.

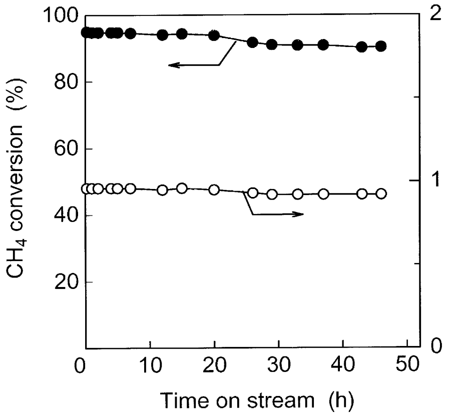

Fig. 5. Durability of Ni/CeO_2 catalyst. Temperature, 1123 K; *W/F*, 1 g h/mol.

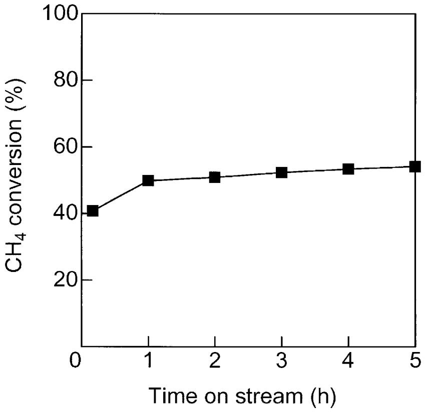

Fig. 7. Effect of heat treatment in N_2 flow at 1123 K for 0.5 h. Reaction temperature, 973 K; *W/F*, 2 g h/mol.

over Ni/CeO_2 catalyst at 973 K. We also observed such deactivation at that temperature. CH_4 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, CH_4 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 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 N_2 flow without H_2 reduction prior to the reaction results in a stable catalyst at 973 K (Fig. 7). Thus, it is found that the Ni/CeO_2 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 CeO_2 support or the change in the number of the active sites should result in the high activity. Further characterization is in progress.

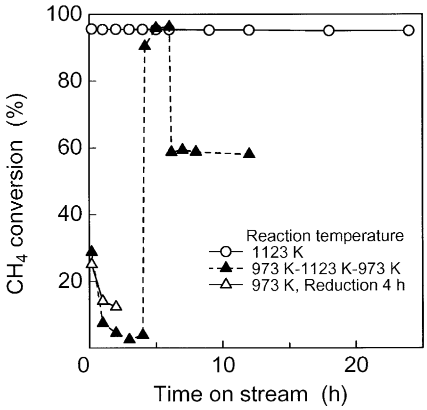

Fig. 6. Effect of initial reaction temperature for Ni/CeO_2 catalyst. *W/F*, 2 g h/mol.

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/CeO_2 catalyst, where 95% CH_4 conversion was achieved, H_2/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/CeO_2 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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