Stable carbon dioxide reforming of methane over modified Ni/Al_2O_3 catalysts

Jae-Sung Choi [a], Kwang-Ik Moon [a], Young Gul Kim [a], Jae Sung Lee [a,*], Cheol-Hyun Kim [b] and David L. Trimm [b]

[a] *Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), San 31 Hyoja-dong, Pohang 790-330, South Korea*

[b] *Department of Chemical Engineering, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Kensington, 2052 Sydney, Australia*

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CO_2 reforming of methane was studied over modified Ni/Al_2O_3 catalysts. The metal modifiers were Co, Cu, Zr, Mn, Mo, Ti, Ag and Sn. Relative to unmodified Ni/Al_2O_3, catalysts modified with Co, Cu and Zr showed slightly improved activity, while other promoters reduced the activity of CO_2 reforming. Mn-promoted catalyst showed a remarkable reduction in coke deposition, while entailing only a small reduction in catalytic activity compared to unmodified catalyst. The catalysts prepared at high calcination temperatures showed higher activity than those prepared at low calcination temperature. The Mn-promoted catalyst showed very low coke deposition even in the absence of diluent gas and the activity changed only slightly during 100 h operation.

Keywords: coke deposition, Ni/Al_2O_3 catalysts, carbon dioxide reforming, Mn-modified Ni/Al_2O_3 catalyst

1. Introduction

Carbon dioxide has received the greatest attention as the most important “greenhouse gas” which may cause global warming. Various measures have been proposed to stabilize the atmospheric CO_2 concentration which include chemical fixation and recycling emitted CO_2 [1]. Besides CO_2, methane is also one of the major molecules contributing to global warming. The relative contribution of these molecules to global warming was estimated to be 47% for CO_2 and 14% for CH_4 [2]. Hence, it is natural that CO_2 reforming of CH_4 is attracting much interest:

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad (1)$$

However, the reverse water–gas shift reaction may take place which reduces the selectivity of CO:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad (2)$$

Compared to conventional steam-reforming of methane, CO_2 reforming provides a low H_2/CO product ratio which is suitable for the production of higher hydrocarbons and oxygenated derivatives. However, CO_2 reforming of methane has some limitations caused by catalyst deactivation due to the carbon deposition via methane dehydrogenation (reaction (3)) and the Boudouard reaction (reaction (4)) [3–8]:

$$CH_4 \rightleftharpoons C + 2H_2 \qquad (3)$$

$$2CO \rightleftharpoons C + 2CO_2 \qquad (4)$$

It has been reported by several authors that carbon deposition could be reduced by pretreatments such as sulfur passivation of Ni catalyst [3,4] or replacement of Ni catalyst with noble metal catalysts such as Rh [5,6] and Ru [7,8]. But sulfur passivation decreases the activity of catalysts, and the high cost and restricted availability limited the use of noble metals as catalysts. This situation is well summarized in recent reviews [9,10]. As a result, it is worthwhile to develop stable and effective nickel-based catalysts. Among the several ways of improving the performance of such catalysts, the addition of metal additives into nickel-based catalysts could be a relatively simple and effective method to increase their resistance to coking. Borowiecki and Golebiowski [11] have reported that the addition of molybdenum and tungsten into the nickel-based catalyst reduces carbon deposition while entailing no change in catalyst activity.

In this paper, we report the additive effects on the performance of a commercial nickel-based catalyst (ICI 46-1) in CO_2 reforming of methane with a particular attention to resistance to coking.

2. Experimental

All catalysts were prepared by the incipient wetness technique. Commercial ICI 46-1 catalyst was crushed and sieved to obtain 150–200 mesh size particles. ICI 46-1 catalysts have a macroporous structure and a composition of NiO (22 wt%), CaO (13 wt%), K_2O (6.5 wt%), SiO_2 (15 wt%), MgO (12 wt%) and Al_2O_3. Alkaline earth and alkali metal oxides are added to reduce the carbon deposition. The precursors of modifying elements were used in their nitrate form except tin, for which $SnCl_2$ was employed. The metal precursors were dissolved in water except Ti, which

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[*] To whom correspondence should be addressed.

was dissolved in ethanol. The amount of additive loading was 2 wt% as metal. The impregnated catalysts were dried at 120 °C for ca. 12 h and calcined at 500 °C for 6 h in air. The specific surface area of calcined samples was determined by the N_2 BET method on a Micromeritics constant-volume adsorption system (Accusorb 2100E).

The CO_2 reforming of methane was carried out using a conventional flow-type quartz reactor. A thermocouple which was connected to a PID temperature controller was placed on top of the catalyst bed. All catalysts were reduced *in situ* with H_2 for 2 h at 800 °C. After reduction, the temperature was lowered under He flow to the reaction temperature. The reaction mixture of $CH_4 : CO_2 : He = 1 : 1 : x$ ($x = 0$–4) was introduced into the reactor at a total flow rate of 81.7 μmol/s. In some cases, the flow rate is expressed in weight hourly space velocity (WHSV) which is defined as total flow rate (l/h) divided by the weight of catalyst (kg). The total pressure was kept at atmospheric pressure in all cases. The reaction products were analyzed using a gas chromatograph (Hewlett-Packard 5890) equipped with a Porapack Q and a thermal conductivity detector. The amount of carbon deposition was measured by using a LECO CHNS-932 analyzer after reaction. The XRD spectra were recorded on a Rigaku Dmax-B diffractometer with Cu Kα radiation.

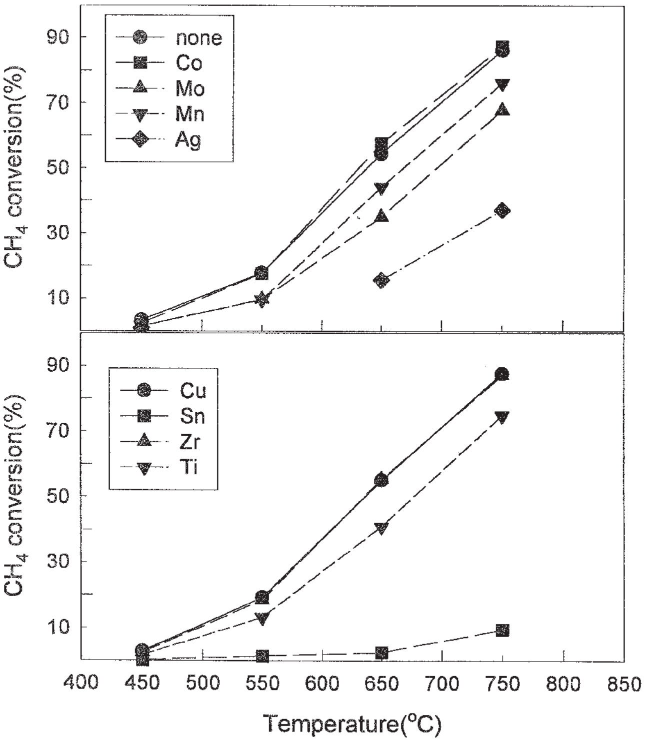

Figure 1. Effect of modifier on CH_4 conversion as a function of reaction temperature: $CH_4 : CO_2 : He = 1 : 1 : 4$; atmospheric pressure; WHSV = 72,000 l/(kg h).

Table 1
Specific surface area (S_{BET}) and particle size (d_p) of metal-impregnated Ni catalysts.

Modifier[a]	S_{BET} (m^2/g)	d_p[b] (nm) of Ni
none	22.8	28.6
Co	24.3	25.2
Mo	23.8	21.4
Mn	23.6	23.8
Ag	22.8	24.0
Cu	17.8	23.8
Sn	21.2	16.4
Zr	30.0	25.2
Ti	27.3	26.9

[a] 2 wt% as metal impregnated.
[b] Calculated from XRD line broadening.

3. Results and discussion

The influence of the additives on the catalytic performance is compared in figure 1, which shows the dependence of CH_4 conversion on reaction temperature for each catalyst. The observed order of methane conversions over doped nickel catalysts is Co, Cu, Zr $\geqslant$ none $>$ Mn $>$ Ti $>$ Mo $>$ Ag $>$ Sn. The carbon dioxide conversions also showed the same trend. Nitrate-form metal precursors were used except for Sn, for which $SnCl_2$ was employed, so the low activity of Sn-promoted catalysts might have been the influence of metal precursor rather than that of the metal itself. The surface area of modified catalysts and reference Ni catalysts are shown in table 1. The specific surface area of modified catalysts did not change significantly by addition of metal additives. The particle size of nickel, d_p, determined by XRD line broadening showed a slight decrease after modification. Even after the second calcination step at 500 °C, there was no remarkable reduction in surface area. Yet, we could not observe any relationship between catalyst performance and specific surface area and/or the particle size of nickel.

Besides the conversion of CH_4 and CO_2, the CO selectivity (moles of CO produced/(moles of CO_2 reacted $\times$ 2)) and amounts of coke formation are also important factors to compare the performance of catalysts. Table 2 summarises comparison of effects of modification relative to reference Ni catalyst on catalytic performance, expressed as CH_4 conversion, CO selectivity, and amount of coke deposition at 650 °C, atmospheric pressure and WHSV of 72,000 l/(kg h). While Co-, Cu-, Zr-promoted catalysts showed slightly improved activity compared to the reference Ni catalyst, these catalysts showed very poor resistance to coke deposition. On the other hand, Mn- and Mo-promoted catalysts retained the majority of the catalytic activity of the reference catalyst and showed remarkable reduction of coke deposition. With respect to activity and resistance to coke formation, Mn-promoted catalyst was found to show the most desired properties and was superior to Mo-promoted catalyst. As mentioned, Borowiecki and Golebiowski [11] reported that an introduction of small amounts of molybdenum and tungsten compounds into Ni/α-Al_2O_3 catalyst considerably reduced the carbon deposition in steam-reforming of methane. An increase in the coking resistance was also obtained af-

Table 2
The effect of modification of nickel catalyst for CO_2 reforming of methane.[a]

Modifer	CH_4 conversion (%)	CO selectivity (%)	Coke[b] (wt%)
none	54.5	91.7	25.4
Co	57.5	92.9	47.4
Mo	35.0	89.4	0.4
Mn	44.2	80.7	0.2
Ag	15.7	83.4	0.2
Cu	55.1	92.6	21.8
Sn	2.6	82.4	0.1
Ti	41.6	90.4	14.4
Zr	55.4	92.7	24.8

[a] Reaction: 650 °C, atmospheric pressure, WHSV $= 72{,}000$ l/(kg h).
[b] Taken after 2 h reaction.

ter the introduction of metal oxides (3–15 wt%) such as uranium [12], lanthanum [13], and cerium [14] into nickel catalyst. However, the steam reforming of methane over unmodified Ni catalyst in our laboratory did not show any coke deposition after 5 h reaction for $H_2O/CH_4 = 1$ [15]. For carbon dioxide reforming of methane, Yamazaki et al. [16] and Horiuchi et al. [17] found that the addition of basic metal oxides to Ni/Al_2O_3 or Ni–CaO–MgO catalysts suppressed the carbon deposition markedly. Horiuchi et al. [17] attributed the suppression of carbon deposition to the decrease in the ability of Ni catalyst for CH_4 decomposition. The commercial catalyst (ICI 46-1) used in the present work contains 13 wt% CaO, 6.5 wt% K_2O, and 12 wt% MgO. Hence, any beneficial effects of alkali and alkaline earth metal oxides have already been reflected in our reference unmodified catalyst which showed 25.4 wt% (defined as g of coke formed/total g of catalyst) carbon deposition, as shown in table 2. The drastic reduction of coke deposition while maintaining high reforming activity of Mn-promoted Ni/Al_2O_3, thus, appears unprecedented among modified nickel catalysts for CO_2 reforming of methane. For Ag-promoted catalyst, the coke deposition was very low but the catalytic activity was much lower than the Mn-promoted catalyst. Based on this result, Mn-promoted catalysts were selected as the best modified Ni catalysts for carbon dioxide reforming of methane.

The SEM images of several modified Ni catalysts after 5 h reaction are shown in figure 2. Filamentous carbon was

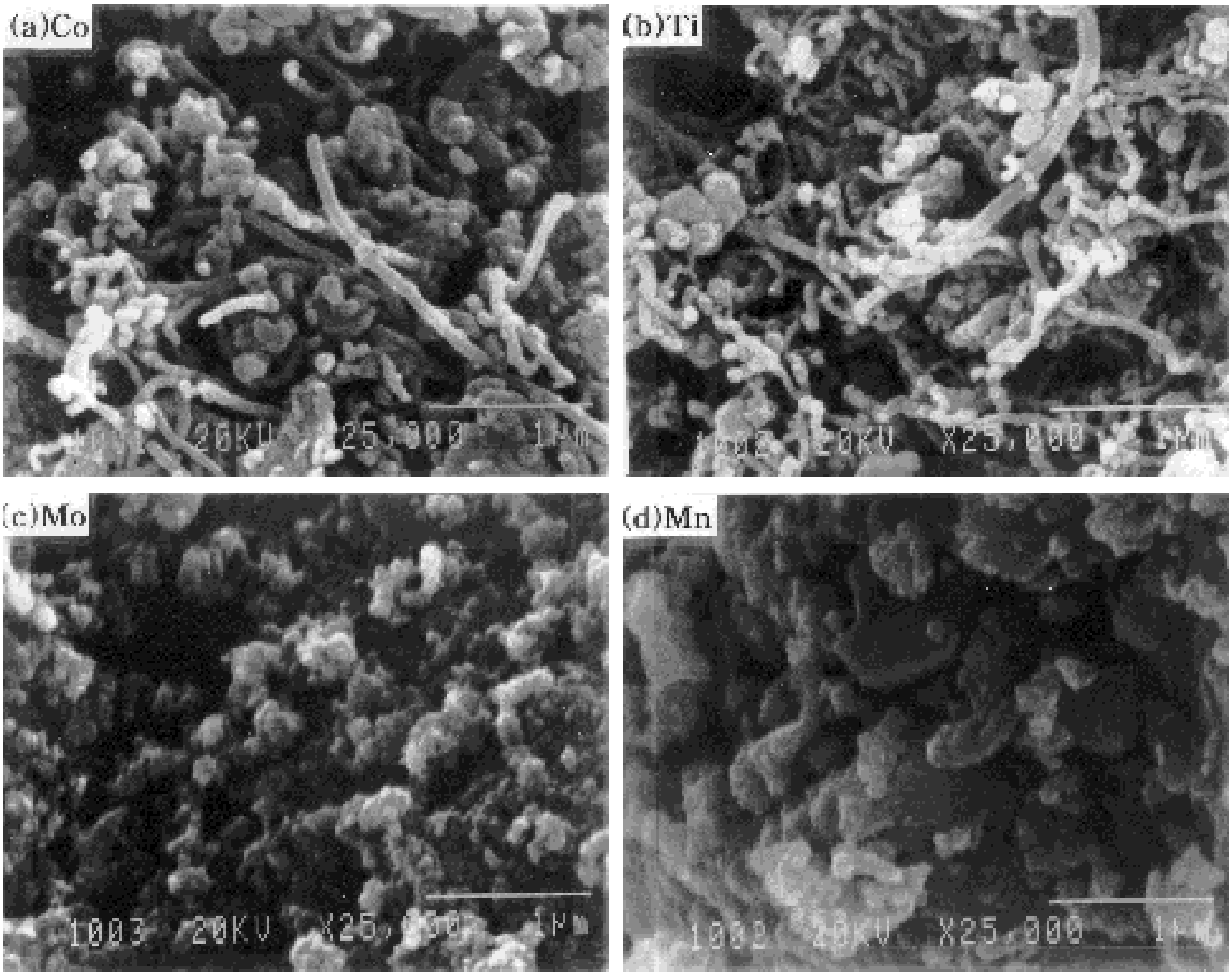

Figure 2. SEM images of modified nickel catalysts after CO_2 reforming for 5 h at 650 °C.

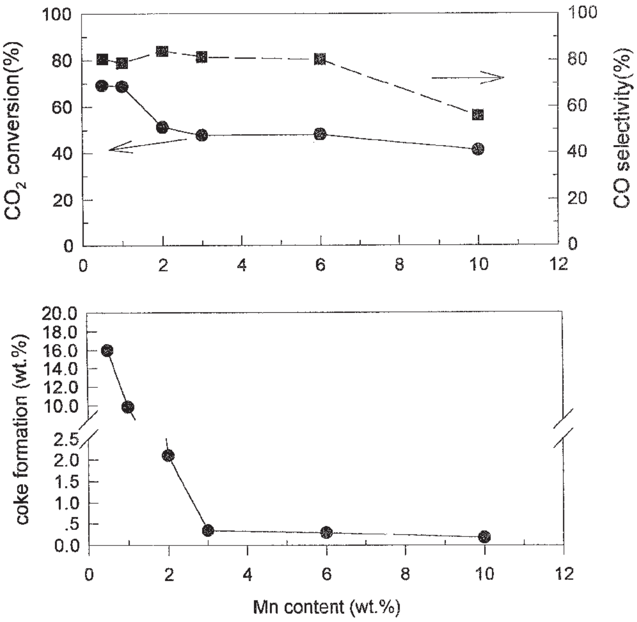

Figure 3. Effect of Mn content on the catalyst performance of Ni/Al_2O_3 in the CO_2 reforming of methane after 5 h of reaction: reaction temperature = 650 °C; atmospheric pressure; WHSV = 72,000 l/(kg h); $CH_4 : CO_2 : He = 1 : 1 : 4$.

formed on Co- and Ti-promoted catalysts, but for Mo- and Mn-promoted catalysts, there was no observable coke deposition. As reported by several authors [18–21], the reaction of hydrocarbons as well as carbon oxides over Ni catalyst can lead to the formation of the filamentous carbons and the carbon grows in a whiskerlike structure associated with nickel particles.

Figure 3 shows the effect of Mn content on catalytic activity and coke formation for CO_2 reforming of methane at 650 °C. As the Mn content increased, catalytic activity slightly decreased, yet resistance to coke formation increased significantly. The addition of more than 3 wt% of Mn dropped the coke formation to less than 0.2 wt%. Considering CH_4 conversion and CO selectivity, the optimal loading of Mn appears to be 3–6 wt%.

The influence of calcination temperature for 3 wt% Mn-promoted catalyst on conversions of CH_4 and CO_2 and CO selectivity at 650 °C is shown in figure 4. In contrast to the result of Chen and Ren [22], the activity increased with increasing calcination temperature. Regardless of the difference in catalytic activity, all the catalysts showed very small amount of coke formation (<0.2 wt%), as shown in table 3. The catalysts calcined at different temperatures were characterized by XRD and BET surface area measurements. The obtained BET surface areas are shown in table 3. The decrease in surface area with increasing calcination temperature is observed as expected. Yet, the phase of nickel observed by XRD spectra did not show any noticeable difference.

In figure 5, the change of CO_2 conversion and CO selectivity with time on stream at different feed ratio for 3 wt% Mn-doped catalyst is shown. The CO_2 conversion decreased with decreasing the He feed. Since the total flow rate of feed gas was fixed, addition of He reduces the partial pressure of CH_4 in the feed. Hence, the three sets of conversion data for Mn-doped catalysts represent similar reaction rates. For the reference Ni catalyst, the reactor plugging due to the heavy coke deposition occurred after ca. 3 h. On the other hand, Mn-promoted nickel catalyst did not show deactivation with time on stream for ca. 10 h even in the absence of He feed. The coke formation in each case was less than 0.3 wt% (measured after finishing the reaction) but slightly increased with decreasing He feed ratio (from 0.18 to 0.28 wt%).

The stability of catalytic activity was examined at 650 °C for Mn-promoted catalysts (3 wt% of Mn) for an extended period of 100 h. A high space velocity of 18,000 l/(kg h) and reaction mixture of $CH_4 : CO_2 : He = 1 : 1 : 1$ were employed. As shown in figure 6, CO_2 conversion slightly de-

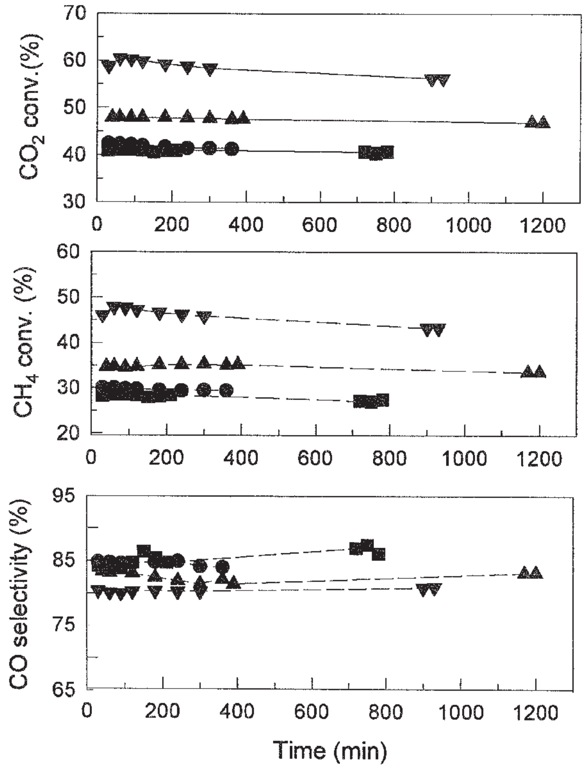

Figure 4. Effect of calcination temperature on CO_2 reforming of methane over Mn-promoted (3 wt%) Ni/Al_2O_3 catalysts: reaction temperature = 650 °C; atmospheric pressure; WHSV = 72,000 l/(kg h); $CH_4 : CO_2 : He = 1 : 1 : 4$; calcination temperature = 300 °C (■), 400 °C (●), 550 °C (▲), 700 °C (▼).

Table 3
Characterization of 3 wt% Mn-impregnated catalysts, prepared at different calcination temperatures.

Calcination temperature (°C)	S_{BET} (m^2/g)	Coke[a] (wt%)
300	26.5	0.17
400	24.8	0.18
550	21.2	0.16
700	17.1	0.15

[a] Taken after 4 h reaction.

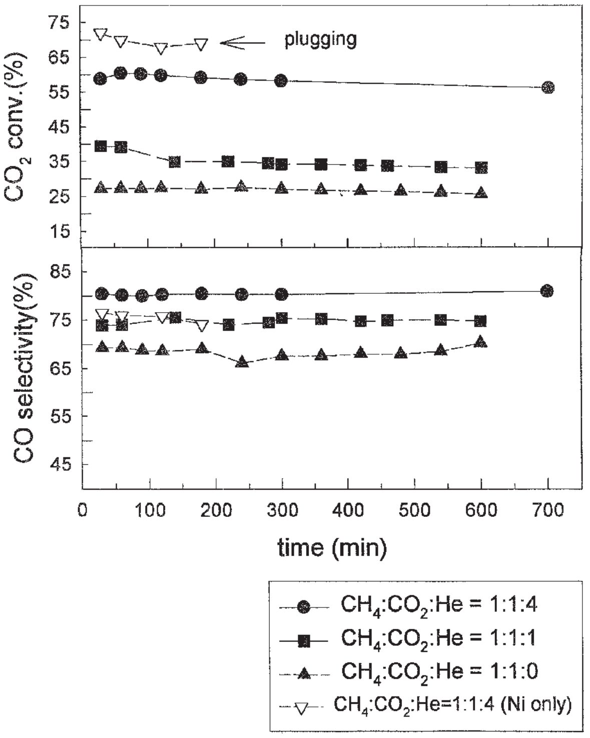

Figure 5. Effect of feed ratio on CO_2 reforming of methane over Mn-promoted (3 wt%) Ni/Al_2O_3 catalysts: reaction temperature = 650 °C; atmospheric pressure; WHSV = 72,000 l/(kg h).

creased from 53 to 44% during this period, but the amount of coke deposition, determined from analysis of used catalysts, was just 0.23 wt%. This implies that there was no severe coke deposition on these catalysts. In the case of Mo-promoted catalysts (3 wt% of Mo), which was the second best among modified catalysts, the activity of the catalyst decreased much more rapidly than that of Mn-promoted catalyst. According to the thermodynamic calculation done by Gadalla and Bower [23], high temperature operation above 870 °C is needed to prevent carbon deposition when the feed gas ratio of CH_4/CO_2 is 1 and the total pressure is 1 atm. Hence, the reaction conditions employed for experiments shown in figure 6 are rather severe in terms of carbon deposition. Further, other methods to reduce carbon deposition by sulfur passivation or replacement of Ni catalyst with noble metal catalysts have several restrictions as mentioned before. Hence, Mn-modified nickel catalyst looks promising as a coke-resistant nickel catalyst in CO_2 reforming of methane.

4. Conclusion

Mn-modified Ni catalyst is an excellent catalyst for CO_2 reforming of methane. It exhibits high stability and high catalytic activity. It shows no severe coke deposition even after 100 h operation, which is a much better result than those reported previously in the literature.

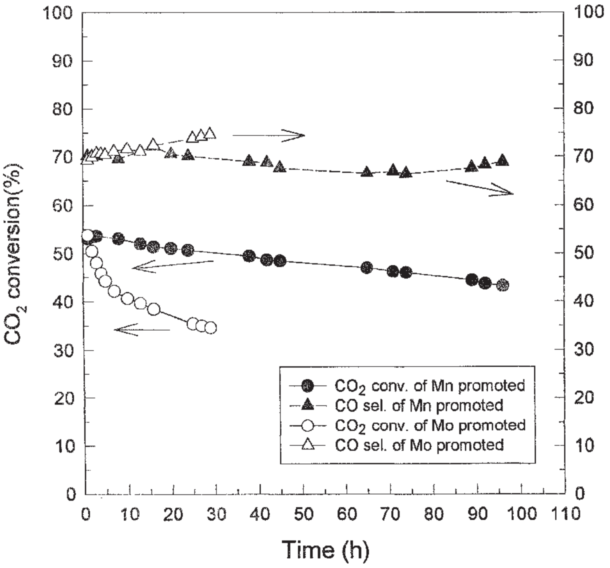

Figure 6. CO_2 conversion and CO selectivity with time on stream: atmospheric pressure; reaction temperature = 650 °C; WHSV = 18,000 l/(kg h); $CH_4 : CO_2 : He = 1 : 1 : 1$.

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