

Studies of reforming natural gas with carbon dioxide to produce synthesis gas

X. The role of CeO₂ and MgO promoters

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Abstract

The behavior of carbon deposition on the Ni/Al₂O₃ catalysts promoted by CeO₂, MgO and CeO₂–MgO in CO₂ reforming methane to synthesis gas was investigated using TG, CO₂-TPD, TPSR, TPR and other techniques. The results indicate that the resistance to carbon deposition of catalysts promoted by CeO₂ and MgO is improved. It is found that the promoter MgO is the most effective one in the suppression of CH₄ dehydrogenation. The CeO₂ promoted catalysts can lower the temperature of the reforming reaction of CH₄ with CO₂ and improve the resistance to carbon deposition. The enlarged experiment result shows that the activity promoted by CeO₂ and MgO keeps well over 900 h. This indicates that the catalyst has not only high activity and selectivity, but also high stability and good resistance to carbon deposition. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: CeO₂; MgO; Promoter; Resistance to carbon deposition; Methane reforming with CO₂

1. Introduction

Renewed attention in both academic and industrial research has recently been focused on the CO₂ reforming with methane to syngas [1–3]. This pathway provides a high CO selectivity and produces synthesis gas with a high CO/H₂ ratio. Nickel-supported catalysts have a high catalytic activity for methane reforming with CO₂. But the reforming process is easily

interrupted due to carbon deposition and the shattering of catalyst [4]. In previous studies [5,6], we found that CeO₂ or MgO are the most effective promoters for the Ni/Al₂O₃ catalysts in the suppression of carbon deposition. These catalysts have high activity and stability [7–9]. The beneficial influence of the rare earth oxide is attributed to the existence of strong metal–support interactions effect [10]. In this paper, more detailed study in effect of CeO₂ and MgO promoters on activity of CH₄ dehydrogenation and CO₂ eliminating carbon was made. In addition, two kinds of catalysts promoted by CeO₂ and MgO are found having high stability and

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excellent property of resistance to carbon deposition.

2. Experimental

2.1. Catalyst preparation

The Ni/Al₂O₃ catalyst (Ni-5) was prepared by a conventional impregnation method using commercial γ -Al₂O₃ and Ni(NO₃)₂ · 6H₂O solutions. The Ni/Al₂O₃ catalyst were modified by CeO₂, MgO or CeO₂-MgO promoters, and the modified catalysts were called Ni-C, Ni-M or Ni/ACM, respectively. The contents of Ni, CeO₂ and MgO loadings are 9.17, 5.18, 3 (mass.%), respectively.

2.2. Catalytic activity

Temperature-programmed carbon depositions were carried out in the quartz gondola of thermal analysis balance with 25 mg of the catalyst. Before reaction, the catalysts were reduced (TPR) in 5.42 vol.% H₂ in Ar (purity-99.99%) at 700°C, then flushed the reactor with Ar cooled to room temperature and evacuated. The temperature surface reaction was performed in different feed ratio of CO₂/CH₄.

The catalytic activity of catalyst was examined in a fixed bed quartz micro-reactor and the reactants and products were analyzed on line

Table 1

The results of temperature programmed carbon deposition on catalysts

Catalyst	CO ₂ /CH ₄	T _B ^a (°C)	T _E ^b (°C)	C (%)
Ni-5	1:1	490	1200	11.5
Ni-5	1.34:1	500	1000	6.33
Ni-5	1.77:1	510	800	1.64
Ni-C	1:1	510	785	2.70
Ni-C	1.34:1	495	700	1.92
Ni-C	1.77:1	345	675	1.14

^aTemperature at the beginning of carbon deposition.

^bTemperature at the end of carbon deposition.

Table 2

Physico-chemical characterization of catalysts and the content of carbon deposited

Catalyst	Ni dispersion degree (%)	Ni crystal size (Å)	Amount of carbon deposited on catalyst (mass.%)
Ni-5	51.7 [4]	322	3.62 ^a 0.05 ^b
Ni-C	63.1	265	2.80 0.04
Ni-M	54.6	308	1.02 0.04
Ni/ACM	68.7	241	1.99 0.03

^aPure CH₄ (reaction for 1 h).

^bCO₂/CH₄ = 1.2 (reaction for 5 h).

using gas chromatograph. The catalysts are activated by reduction in H₂ at 700°C for 30 min, and then the reaction of natural gas reforming with carbon dioxide takes place at 700°C to produce synthesis gas. The catalytic activity is represented by the mole fraction of the synthesis gas in gaseous products.

The temperature-programmed surface reaction (TPSR) and other experiments were carried out under atmospheric pressure using a stainless reactor (4 mm inside diameter) with 50 mg of catalyst sample (30–60 mesh). The catalyst was first reduced in H₂ (25 ml/min) at 700°C for 30 min, then flushed the reactor with Ar for 45 min and cooled to 100°C. The CO₂-TPSR were performed in a flow of CO₂ + Ar (18 vol.% CO₂). Carbon dioxide temperature-programmed desorption (CO₂-TPD) in a flow of 24.5 ml/min of Ar was performed at a constant rate of 12.8°C/min. The temperature-programmed processes were recorded on line.

3. Results

3.1. Temperature-programmed carbon deposition in different ratio of CO₂/CH₄

The temperature-programmed carbon deposition was performed by thermo-gravimetric analysis (TG) from different feed ratio of CO₂/CH₄,

the contents of carbon deposition were obtained in Table 1.

The results of Table 1 show that T_B , T_E and the amounts of carbon deposition of Ni–C catalyst are lower than that of Ni-5 catalyst. Compared with Ni-5 catalyst, the results in Table 1 show that the resistance to carbon deposition of

Ni–C catalyst is superior to that of Ni-5 catalyst due to the addition of CeO_2 promoter.

3.2. Ni dispersion on catalysts

The Ni dispersion degree and the Ni crystal size were determined. According to results in

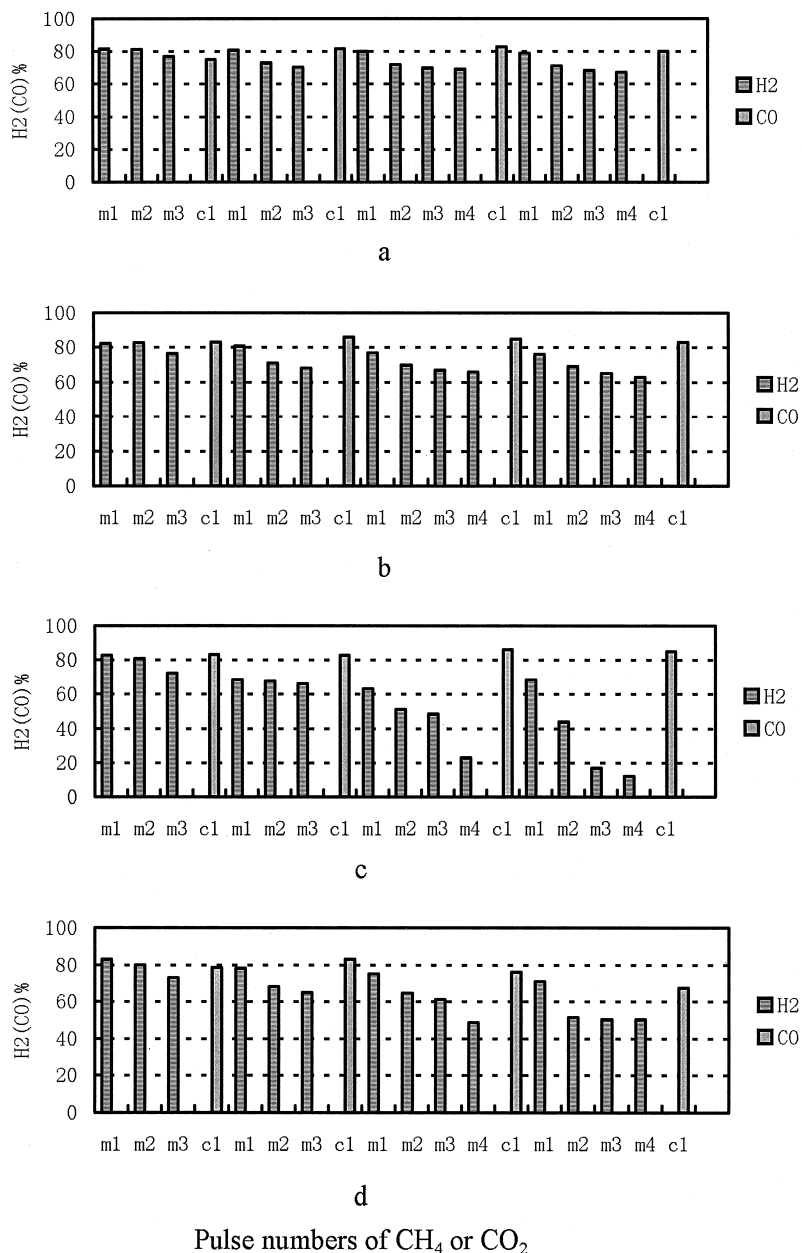


Fig. 1. Activity comparison of carbon deposition of CH_4 dehydrogenation and eliminating carbon by CO_2 . (a) Ni-5; (b) Ni-C; (c) Ni/ARM; (d) Ni-M ('m1, m2, m3, m4': pulse numbers of CH_4 ; 'c1': pulse numbers of CO_2).

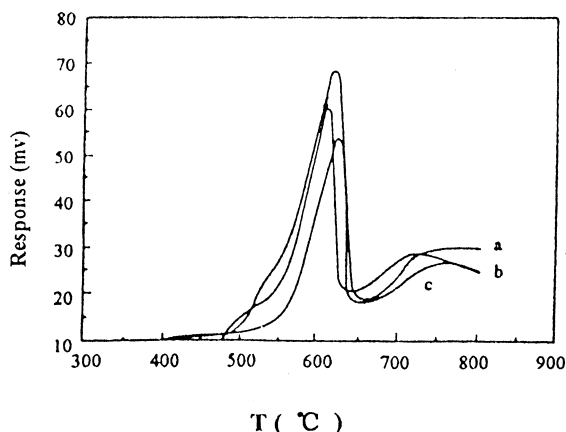


Fig. 2. CO_2 -TPSR spectra of deposited carbon on catalysts. (a) Ni-5; (b) Ni-C; (c) Ni/ARM.

Table 2, adding of CeO_2 and MgO can increase Ni dispersion degree and decrease the Ni crystal size. It can also inhibit CH_4 dehydrogenation and improve the resistance to carbon deposition.

3.3. Properties of CH_4 dehydrogenation and CO_2 eliminating carbon

In order to make comparison between the action CeO_2 and MgO promoters, CH_4 dehydrogenation and eliminating carbon by CO_2 was performed by using pulse chromatographic apparatus. The mole fraction of H_2 or CO was

used to represent the property of carbon deposition or the elimination of carbon.

During the process of pulse experiments, first, we pulsed CH_4 three times and then pulsed CO_2 one time, and then repeated again, secondly, we pulsed CH_4 four times and CO_2 one time, repeated again (Fig. 1). It is evident that the addition of single MgO promoter to Ni/ Al_2O_3 (Ni-M) can efficiently impress CH_4 dehydrogenation, and single CeO_2 promoter can improve the ability of CO_2 in eliminating carbon under similar circumstances. The results of Fig. 1 indicates that the addition of CeO_2 -MgO promoters to Ni/ Al_2O_3 (Ni/ACM) not only improves the ability of CO_2 in eliminating carbon, but also causes a decrease in the property of CH_4 dehydrogenation.

3.4. CO_2 -TPSR and CO_2 -TPD

The Ni-5, Ni-C and Ni/ACM catalysts were reduced by H_2 at 700°C for 30 min, and after flushing the reactor with Ar for 45 min, pulsing CH_4 five times, the ratio of accumulation of carbon deposition of catalysts is Ni-5:Ni-C:Ni/ACM = 1.5:1.25:1. Then, CO_2 -TPSR was performed, and the analysis results indicate that the tail gas contain much CO_2 and little CO. It

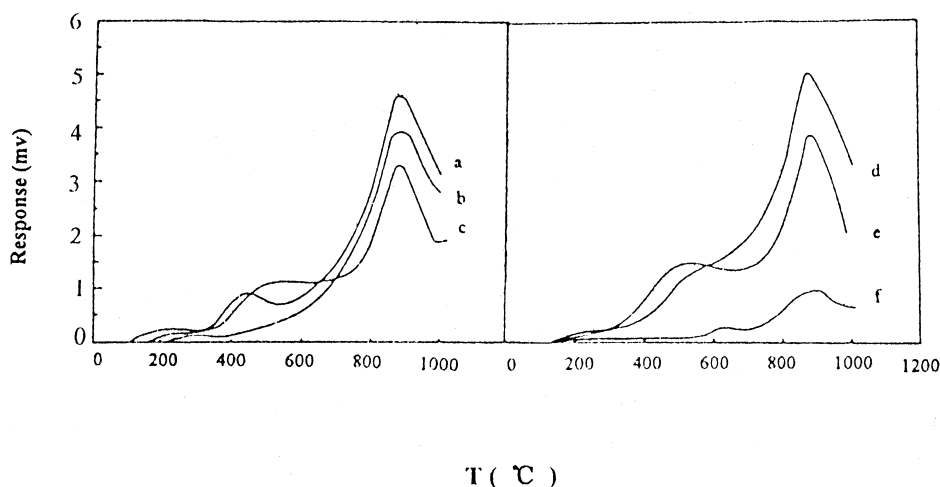


Fig. 3. TPD spectra of CO_2 adsorbed on catalysts. (a) Ni-C; (b) Ni-5; (c) Ni/ARM; (d) carrier of Al_2O_3 - CeO_2 ; (e) carrier of Al_2O_3 - CeO_2 -MgO; (f) carrier of Al_2O_3 .

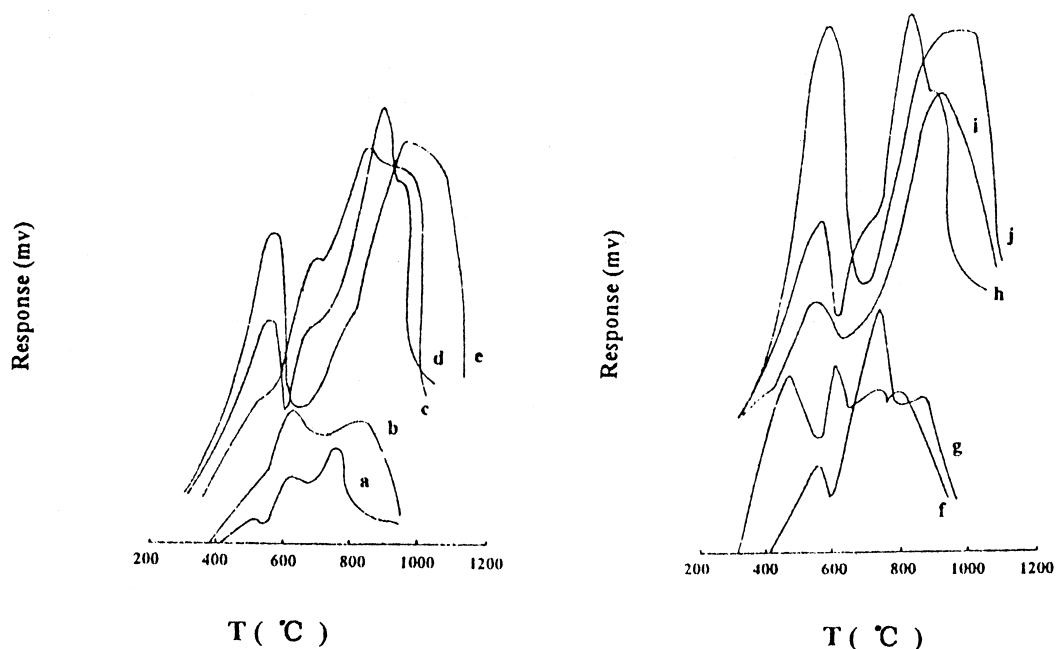


Fig. 4. TPR spectra of catalysts and carriers. (a) Carrier of $\text{Al}_2\text{O}_3\text{-CeO}_2$; (b) carrier of $\text{Al}_2\text{O}_3\text{-CeO}_2\text{-MgO}$; (c) Ni-C; (d) Ni-5; (e) Ni/ARM; (f) carrier of $\text{Al}_2\text{O}_3\text{-MgO}$ (MgO6%); (g) carrier of $\text{Al}_2\text{O}_3\text{-MgO}$ (MgO3%); (h) Ni-5; (i) Ni-M (MgO3%); (j) Ni-M (MgO6%).

can be seen (Fig. 2) that all the catalysts have maximum carbon eliminating peaks between 550–650°C. Analyzing the peak area of the catalysts, Ni-5:Ni-C:Ni/ACM is about 1.68:1.21:1. This is in accordance with the results of carbon deposition.

The TPD curves of CO_2 for the three catalysts and carriers are presented in Fig. 3. One can easily find out that the peaks of catalysts are similar to carriers' peaks except for $\gamma\text{-Al}_2\text{O}_3$. All the catalysts have high peak of about 900°C, and appear shoulder peaks at moderate temperature (300–650°C) except for the Ni-5 catalyst, and lower temperature peak between 150–300°C. It is clear that, the 900°C peaks are the strong base centers, the lower temperature peaks are the weak base centers, and the moderate temperature peaks indicate that the distribution areas of base sites in the Ni-C and Ni/ACM catalysts which contain CeO_2 and MgO are enlarged. This is in accordance with results of Zhang and Verykios [11] and Zhao et al. [12]. In general, the temperature of the reforming reaction is chosen under 800°C. It is supposed that

the moderate temperature peak will play an important role in the elimination of carbon by CO_2 . Therefore, the ability of CO_2 in eliminating carbon in Ni/ACM will be improved due to its absorption ability.

3.5. Catalyst characterization

Characterization of catalyst was carried out in order to study the influence of carbon deposition on the catalytic activity of methane reforming with carbon dioxide and the relationship between the size of nickel crystallites and the carbon deposition rate. XRD studies indicated that when the Ni loading is lower than 13.2%, no crystal phase of NiO would be formed obvi-

Table 3
The surface compositions of the catalysts

Catalyst	The surface concentration (at.%)			
	C	O	Ni	Al
Ni-5	0.154	1.71	0.054	1.00
Ni/ACM	0.177	1.80	0.068	1.00

ously. When Ni-3 catalyst is modified by CeO_2 and MgO, the dispersion of nickel on the surface of catalyst will be enhanced remarkably. One can easily find from Fig. 4 that nickel is reduced in the temperature range between 400 and 700°C. The nickel reduction peak for the modified catalyst is at the higher temperature. It is evident that with the addition of Ce_2O_3 and MgO to Ni/ Al_2O_3 catalyst, the interaction between active component Ni and the Al_2O_3 carrier increases.

Table 3 shows XPS results of the relative atom concentrations on catalyst surface, and the obtained results indicate that the $\text{Ni}^{+2}(2p_{3/2})$ electron binding energy of the Ni-5 catalyst is 855.2 eV, and the XPS results also show that with the addition of CeO_2 -MgO promoters to Ni-5, $\text{Ni}(2p_{3/2})$ binding energy of Ni^{2+} is lower (about 1.58 eV) than that of Ni-5 catalyst. It means that adding CeO_2 and MgO promoters to Ni-5 catalyst the electron density of surface Ni atoms increases.

The stability experiment results is shown in Fig. 5. It shows that the mole fraction of ($\text{H}_2 + \text{CO}$) is kept at around 94–96 mol% during 900 h test. After 900 h, there will be no carbon deposition on the surface of catalyst and no shattering phenomenon of catalyst. It means that, the Ni/ACM catalyst do not deactivate at

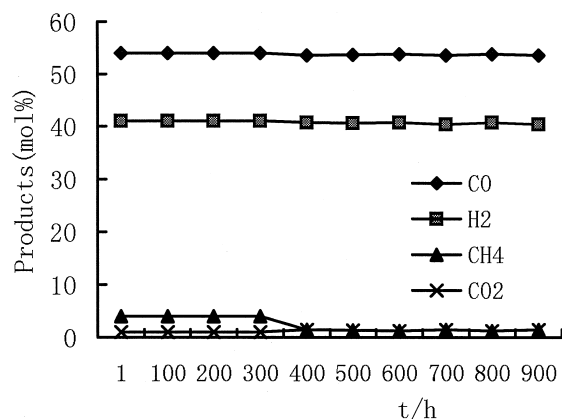


Fig. 5. The stability of the Ni/ACM catalyst. Temperature = 850°C, pressure = 0.1 MPa, $\text{CO}_2/\text{CH}_4 = 1.4/1$.

all during 800 h on stream with a CO_2/CH_4 ratio of 2.4/1 at 750 or 1.4/1 at 850°C.

4. Discussion

4.1. The MgO promoter

The results of XRD indicated that no clear MgO phase peak is found except for CeO_2 and Ni peaks. The results of TPR show that with addition of CeO_2 -MgO to Ni/ Al_2O_3 , the reduction peaks shift to high temperature (Fig. 4, curves c, e, h and j). This means there is interaction happened between the promoter and the carrier. According to Ref. [1], a solid solution or partial solid solution is formed on supported Ni catalyst.

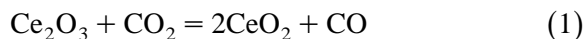
From Table 2, the Ni dispersion of Ni-M catalyst is higher than that of Ni-C and is similar to that of Ni/ACM, and the amount of carbon deposition for CH_4 dehydrogenation is the least among the catalysts.

4.2. The CeO_2 promoter

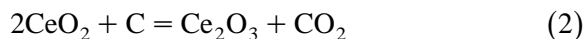
According to Table 2, the CeO_2 promoter may have two effects: first, the addition of CeO_2 to Ni/ Al_2O_3 can shift the reforming reaction of CH_4 and CO_2 to lower temperature and improve Ni dispersion (Table 1); second, CeO_2 plays a role of transferring electrons.

While the Ni-5 and Ni-C catalysts were reduced by H_2 at 700°C for 30 min, and flushed by Ar for 45 min, it was found that a little amount of H_2 is replaced by pulsing CO. When the third pulse of CO was carried out, the H_2 area disappeared. The results show that the H_2 area replaced by CO on Ni-C catalyst is smaller than that of Ni-5 catalyst. The existence of Ni-H has been proven by Ref. [13]. The studies of Zhang and Verykios [14] of the results of H_2 -TPD revealed that the Ni-H bond on Ni/ La_2O_3 catalyst is fewer and weaker than that of Ni/ Al_2O_3 catalyst. Momteiro and Noronha's studies [15] also demonstrated that the addition of CeO_2 to Pd/ Al_2O_3 catalyst

would decrease H₂ uptake and diminish the H/Pd ratio. The partial or total inhibition of hydrogen on the metals was attributed to an electronic effect [16]. As mentioned above, there is electron interaction between CeO₂ and Ni. It is known that Ce is rich in d electrons, and Ni has unfilled d orbitals, and the unfilled d orbitals of Ni atom can accept d electrons of Ce. So the Ni–H bond will be weakened and diminished. According to Shyu et al. [17], below 1000°C, CeO₂ can be reduced by H₂ only to Ce₂O₃. Monteiro and Noronha's studies [15] also showed that the reduction of CeO₂ supported on Al₂O₃ depends on the loading: with lower contents (3% CeO₂), the reduction is incomplete, while with higher contents (20% CeO₂), it will be reduced completely. Hence, when the CeO₂ promoter in Ni/ACM catalyst was reduced by H₂ at 700°C for 30 min, oxides Ce₂O₃ and CeO₂ might exist. During the reforming process, the reactant CO₂ first absorbs base centers, and then dissociates on Ce₂O₃ by transferring electrons to CO₂, and forms CO and CeO₂. Then, CeO₂ reacts with carbon deposited by CH₄ dehydrogenation, and CeO₂ changes to Ce₂O₃ again. The reaction process is:



[18]



[19].

In fact, the above reactions imply a process of transferring oxygen. As CO₂ dissociates and forms CO, and absorb oxygen (Oa) or oxygen-containing species [18], the affinity of the adsorbed oxygen (Oa) for the carbon atom of CH₄ is responsible for the inhibition of carbon formation of the reaction. Therefore, the presence of CeO₂ and Ce₂O₃ in catalyst will improve the inhibition of the surface carbon formation.

In addition, the ability of resistance to carbon deposition of the Ni/ACM catalyst might be related to the property of CO₂ adsorption from macroscopic point of view. Fig. 3 shows that the surface carbon on catalysts is removed from

most part before the temperature reaches 700°C. So, we hold that a moderate temperature of CO₂ adsorption would play an implant role in eliminating carbon.

It is known that when the reforming reaction was carried out, surface carbon would be formed by the dehydrogenation of CH₄ on the one hand, and CO₂ can eliminate the surface carbon on the other hand. So, whether the carbon deposition exists or not on surface of catalyst, it is decided by the two competition reactions. With the addition of CeO₂ and MgO to Ni/Al₂O₃ catalyst, the area of moderate temperature increased, which will lead to the increase in the CO₂/CH₄ ratio on the surface of Ni/ACM catalyst compared with the other catalysts at the same feed ratio of CO₂/CH₄.

From the microcosmic point of view, it is known that CH₄ or CO₂ has stable molecular structure. If CH₄ and CO₂ are simultaneously activated, the catalyst should have Ni unfilled d orbitals to accept s electron pairs of C–CH bond of CH₄, or have high d-electron density of the surface Ni atoms to fill the unfilled anti-bonding π* orbitals of CO₂.

The XPS results of literature indicated that the addition of CeO₂ to Ni/Al₂O₃ catalyst, Ni(2p3/2) binding energy of Ni²⁺ caused negative displacement of 0.4 eV. But with the addition of CeO₂–MgO promoters to Ni/Al₂O₃, Ni(2p3/2) binding energy of Ni²⁺ was lower (1.6 eV) than that of the unmodified catalyst, and a strong electron interaction is found in the coexistence of promoter CeO₂ and MgO. It implies that, the CeO₂–MgO promoters will improve d-electron density of the surface Ni atoms, and the d-electron emigration ability to anti-bonding π* orbitals of CO₂ will increase, the CO₂ dissociation is promoted, and the ability of CO₂ elimination and resistance to carbon deposition of catalyst is also improved. At the same time, the property of CH₄ dehydrogenation is impressed due to the decrease of Ni unfilled d orbitals.

The enlarged experiment results have demonstrated that the activity of Ni/ACM catalyst

does not diminish at all during 900 h on stream of CO₂/CH₄ ratio of 2.4/1 (v/v) at 750°C or CO₂/CH₄ ratio of 1.4/1 (v/v) at 850°C. This fact indicates that the Ni/ACM catalyst has high catalytic activity, selectivity, excellent resistance to carbon deposition and high stability in reforming methane with carbon dioxide to produce synthesis gas.

Acknowledgements

Financial support of the Outstanding Youth Science Foundation of Heilongjiang province was gratefully acknowledged.

References

- [1] Y.H. Hu, E. Ruckenstein, *Catal. Lett.* 43 (1997) 71.
- [2] J.R. Rostrup-Nielsen, J.-H.B. Hansen, *J. Catal.* 144 (1993) 38.
- [3] O. Yamazaki, T. Nozaki, K. Fujimota, *Chem. Lett.* (1992) 1953.
- [4] A.M. Gadalla et al., *Chem. Eng. Sci.* 43 (11) (1988) 3049.
- [5] K. Shi, H. Xu, G. Xu, *Fenzi Cuihua (China)* 10 (1) (1996) 41.
- [6] H. Xu, Y. Fan, G. Xu, *Tianranqi Huagong (China)* 20 (1995) 1.
- [7] H.C. Yao, Y.F. Yu Yao, *J. Catal.* 86 (1984) 254.
- [8] Y. Qin, S. Yan, Z. Liang, *Huagong Xuebao (China)* 4 (1990) 436.
- [9] Z. Xu, Y. Li, J. Zhang, *Fenzi Cuihua (China)* 18 (5) (1997) 364.
- [10] M. Xin, M. Hao, Y. Yao, *Fenzi Cuihua (China)* 4 (4) (1990) 321.
- [11] Z.L. Zhang, X.E. Verykios, *Catal. Today* 21 (1994) 598.
- [12] L.h. Zhao, X. Zheng, J. Fei, *Cuihua Xuebao* 17 (3) (1996) 227.
- [13] E.G.M. Kuijpers, A.K. Bredijk, W.J.J. Wan derwal et al., *J. Catal.* 72 (1981) 210.
- [14] Z. Zhang, X.E. Verykios, *Appl. Catal. A: General* 138 (1996) 109.
- [15] R. de Souza Momteiro, F.B. Noronha, *Appl. Catal. A: General* 131 (1995) 89.
- [16] J.M. Herrmann, *J. Catal.* 89 (1984) 404.
- [17] J.Z. Shyu, W.H. Webor, H.S. Oandhi, *J. Phys. Chem.* 92 (17) (1988) 4964.
- [18] K. Otsuka, T. Ushiyama, I. Yamanaka, et al., *Chem. Lett.* (1993) 1517.
- [19] Y. Song, D. Fujian, *XiTu Jinshu Huaxue, Liao Ning Univ. Press*, 1989, p. 5.