Catalysis Letters, Vol. 118, Nos. 1–2, October 2007 (© 2007)
DOI: 10.1007/s10562-007-9140-7

Studies on coke formation and coke species of nickel-based catalysts in CO_2 reforming of CH_4

Li Xiancai,[a,*] Li Shuigen,[a] Yang Yifeng,[a] Wu Min,[a] and He Fei[b]

[a]*Department of Chemistry, Nanchang University, Nanchang, Jiangxi 330031, China*
[b]*State Key Laboratory. of C1 Chemistry and Technology, Tianjin University, Tianjin 300072, China*

Received 15 April 2007; accepted 7 May 2007

Three nickel-based catalyst systems, Ni/γ–Al_2O_3, Ni/$BaTiO_3$, and Ni–0.75wt%La–$BaTiO_3$, were investigated for the CO_2 reforming of CH_4. The temperature of CH_4 decomposition on catalyst Ni/γ–Al_2O_3 is the lowest and the relative content of H_2 is the highest; but the temperature of CH_4 decomposition on catalyst Ni–0.75 wt%La–$BaTiO_3$ is the highest and the relative content of H_2 is the lowest. The amount of carbon deposition via CH_4 decomposition decreases with the increase of rare earth La and the temperature of decomposition also declines gradually. Different active coke species were formed on different catalysts. The higher activity of coke species is, the easier the reaction with activated CO_2 is. The coke species were investigated by the XPS technique. Several surface coke species existed on catalysts after the reaction. The surface species with the binding energy near 282 and 286 ev are the main coke species. These species resulted in the catalyst deactivation. By analyzing the coke on catalyst, it was found the catalyst Ni–0.75wt% La–$BaTiO_3$ suppressed the formation of coke species whose binding energy is near 282 and 286 ev.

KEY WORDS: rare earths; impregnation; sol–gel; catalysts; XPS.

1. Introduction

The reaction of methane reforming with CO_2 has gained increasing attention due to the importance of synthesis gas as a major feedstock for fuel cells and Fischer–Tropsch reaction and both natural gas and CO_2 can affect the environment and energy resources [1–3]. Most VIII group metals, such as Fe, Co, Ni [4–6], are often used as active component for the reforming reaction. But the catalyst deactivation is the main hindrance for a catalyst to be considered for an industrial application. Several factors can contribute to catalyst deactivation in the synthesis gas process. These include coke formation [7–10], poisoning and transformation of active components, sintering and recombination of active components [11,12]. Among these, coke formation is the most detrimental factor because it can result in the poisoning of active centers, the clogging of the pores and even the pulverization of catalysts [13]. Because of the high carbon content in the feedstocks of the catalytic process, carbon dioxide reforming of methane is much more prone to carbon deposition.

Coke formation is a complicated physical and chemical process. The common coke types are whisker-like carbon, encapsulating carbon, and pyrolytic carbon. And the three carbons have different reactive activities. Different catalysts can produce different coke species. There are three main reactions of carbon deposition in syngas preparation:

$$2CO \rightarrow C + CO_2 \quad \Delta H_{298} = -171 \text{ KJ/mol} \qquad (1)$$

$$CH_4 \rightarrow C + 2H_2 \quad \Delta H_{298} = 75 \text{ KJ/mol} \qquad (2)$$

$$CO + H_2 \rightarrow C + H_2O \quad \Delta H_{298} = -175.3 \text{ KJ/mol} \qquad (3)$$

and some researchers [14–16] think the carbon deposition during the reforming of methane is due to either equation (1) or (2).

Based on the mechanism of the reforming reaction [17]: both CO_2 and CH_4 should be absorbed and activated before the relevant bonds are broken. Coke is formed via the surface carbon polymerization that occurs after the cleavage of C–H and C=O bonds, which requires many coordination numbers or big active groups on catalysts surface. It has been proven that active group needed for the reaction of carbon deposition is bigger than that of hydrogen conversion. As proposed by Rostrup–Nielsen [18], the number of the active ensemble size necessary for the conversion from hydrocarbon to carbon monoxide and hydrogen is 12, while for coke formation the number is 16. Therefore,

controlling the active ensemble size can enhance the ability of resistance to carbon deposition. Thus, any substance or method that can decrease CH_4 dehydrogenation activity and increase the activity of CO_2 for eliminating coke or improve and maintain dispersed degree of catalytic active component will achieve the ultimate objective of suppressing coke formation.

2. Experimental

2.1. Preparation of the catalyst

Catalysts $Ni/BaTiO_3$ and $Ni–La/BaTiO_3$ were prepared according to a reference method [19], catalysts $Ni/\gamma–Al_2O_3$, $Ni–0.75wt\%La–BaTiO_3$ and $Ni – BaTiO_3$ were prepared according to a reference method [20]. Catalyst $Ni /La–BaTiO_3$(Ba/La = 1/0.002) was prepared by a sol–gel method. In brief, when a homogeneous and transparent solution was formed, measured volume solution of $Ba(Ac)_2$ and $La(Ac)_3$ were dropped into the prepared solution, then the homogeneous mixture was heated in a water bath to start the process of sol formation and transformation of sol into gel, the dried gel was calcined at 973 K for 3 h to yield the $La_2O_3–BaO–TiO_2$, $Ni /La–BaTiO_3$ was prepared by wet impregnation of aqueous solution of $Ni(Ac)_2$ onto $La_2O_3–BaO–TiO_2$ for 24 h. After drying, the sample was calcined in air at 923 K for 3 h.

The content of nickel was found to be 5.0wt%.

2.2. Temperature programmed hydrogenation (TPH) experiments of coke formation on the catalyst surface

Coke formation on a catalyst surface can be characterized by the TPH technique. In this study the TPH experiments were carried out by purging the catalyst with argon for a period of time after the catalyst was reduced by hydrogen, and then by coking on catalyst with pure methane. After that, the catalyst was purged with argon again to room temperature until the baseline became straight. The TPH experiments were performed with a heating rate of 10 k/min in pure hydrogen. Such experiments can determine the amount and activity of coke formation on catalyst surface.

2.3. X-ray photoelectron spectra

The XPS measurements were carried out to investigate the oxidation state variation of catalyst element and binding state of species. The XPS spectra were obtained with American PERKIN ELEMER PHI-1600 ESCA system: target, MgKα; voltage, 15 KV; power, 300 W; analysis area, 0.8 mm^2; vacuum room, 2×10^{-10} Torr; resolution, 0.7 eV; sensitivity, 80 Kcp; sample depth, 20–50 Å; electrify energy, 187.85 eV, 29.35 eV; calibration, (C1s = 284.6 eV).

3. Results and discussion

3.1. Characterization of coke formation on the catalyst surface

3.1.1. Coke formation from reaction of methane decomposition

Methane decomposition spectra of different catalysts are shown in figure 1. The profiles show that the temperature of methane decomposition is the lowest on catalyst $Ni/\gamma–Al_2O_3$ and the relative content of hydrogen is the highest. However, the temperature is the highest on catalyst $Ni–0.75wt\%La–BaTiO_3$ [20] and the relative content of hydrogen is the lowest. Based on the comparison of the two catalysts, $Ni/\gamma–Al_2O_3$ with $Ni/BaTiO_3$, it is clear that the structure and the characteristics of the supports are critical to carbon deposition resistance and stability. From curves 2 and 3 it is found that carbon deposition via further methane decomposition occurs readily on catalyst $Ni/BaTiO_3$. This observation indicates that the preparation methods, promoters present, and supports used are all linked to coke formation to a great extent.

3.1.2. TPH of coke formation of different La contents supported on catalysts

TPH experiments were performed to further investigate the influence of different promoter contents on catalytic activity and the resistance to carbon deposition. The findings are shown in figure 2. As can be seen in figure 2, the amount of carbon deposition reduces with the increase of rare earth La; the methane generation temperature is between 500 and 600 °C; the temperature decreases with the increase of rare earth La; the initial generation temperature is about 480 °C. The upper results (Figure 2) show that addition of the rare earth La will affect the activity of coke formation on catalyst surface, and thus affecting the amount of coke formation.

3.1.3. TPH experiments of methane decomposition on different catalysts

The TPH spectra profiles are shown in figure 3. As shown in figure 3 the height of peak indicates the amount of coke formation. Obviously, the amount of coke formation on the promoted catalysts is less than

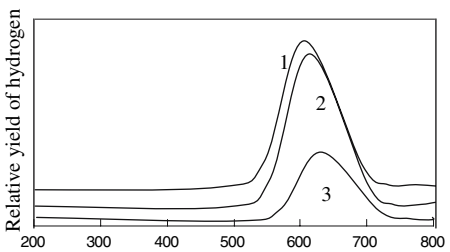


Figure 1. Amount of coke formation via methane decomposition on different catalysts (1) $Ni/\gamma–Al_2O_3$; (2) $Ni/ BaTiO_3$; (3) $Ni–0.75wt\%La–BaTiO_3$.

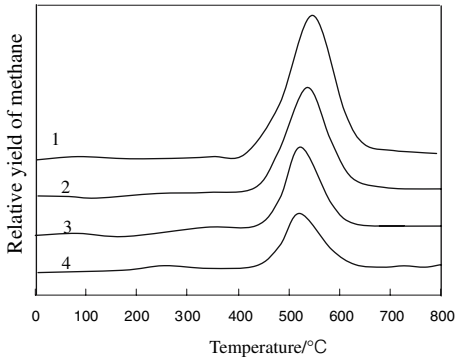


Figure 2. TPH of different rare earth La content (1) $Ni/BaTiO_3$; (2) $Ni–0.1wt\%La/BaTiO_3$; (3) $Ni–0.5wt\%La/BaTiO_3$; (4) $Ni–1.0wt\%La/BaTiO_3$.

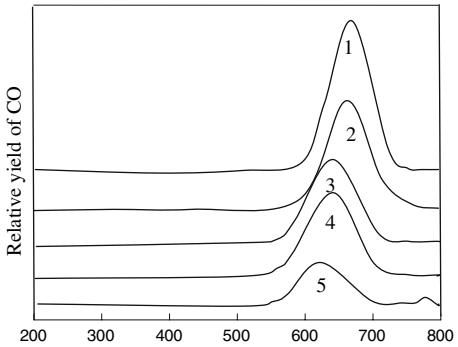


Figure 4. $TPRco_2$ of different catalysts (1) $Ni/\gamma–Al_2O_3$; (2) $Ni/BaTiO_3$; (3) $Ni–1.5\ wt\%La/BaTiO_3$ (4) $Ni/La–BaTiO_3$; (5) $Ni–0.75\ wt\%La–BaTiO_3$.

that on the unprompted catalysts, which proves the addition of rare earth promoter can suppress the coke formation from further methane decomposition. At the same time, the temperature indicates the activity of surface carbon, the lower temperature shows the higher activity of surface carbon, which further indicates that different supports can produce different active coke species.

As shown in figure 3, on different catalysts, the amount of coke formation via methane decomposition is not the same, and the formation temperature of methane on different catalysts is different, which is consistent with the assumption that different active coke species were formed on different surfaces of catalysts, the lower the formation temperature of methane is, the higher the activity of corresponding coke species is, which has been proven previously by the other researchers [21].

3.1.4. $TPRco_2$ experiments of coke formation on the catalyst surface

TPR experiments of using carbon dioxide to eliminate coke were performed to further study the activity of surface carbon. The results are shown in figure 4.The profiles show that the initial formation temperature of carbon monoxide is different, the order is $Ni–0.75La–BaTiO_3 < Ni/La–BaTiO_3 < Ni–1.5La/BaTiO_3 < Ni/BaTiO_3 < Ni/\gamma–Al_2O_3$, which shows different active coke species were formed on different catalysts, the higher the activity of coke species is, the easier the reaction with active CO_2 is. Therefore, eliminating coke reaction can occur at a lower temperature, thus the coke on catalyst surface was eliminated rapidly, which can prolong the life of catalysts.

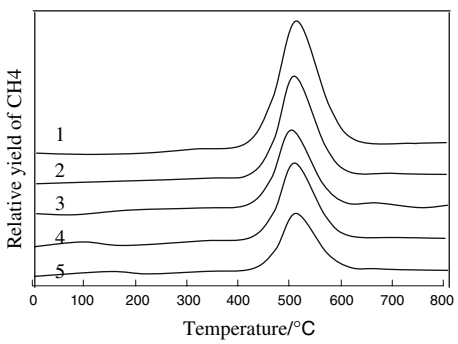


Figure 3. TPH of different catalysts (1) $Ni/\gamma–Al_2O_3$; (2) $Ni/BaTiO_3$; (3) $Ni–1.5\ wt\%La/BaTiO_3$; (4) $Ni/La–BaTiO_3$; (5) $Ni–0.75\ wt\%La–BaTiO_3$.

3.2. XPS analysis of coke species

To further probe the essential mechanism of coke formation on catalysts, besides the origin of coke formation, we were interested in the structure and characteristics of the coke formed on the catalyst surface. Therefore, we studied the catalyst with coke formation at molecular level. XPS experiments were performed to investigate the coke species. All binding energy values are referenced to C_{1s}, as shown in figures 5–8.

Lu *et al.* [22] studied the catalyst system of $Co/\gamma–Al_2O_3$ by the XPS technique. The results showed that there existed three coke species on the surface of catalyst: carbonization, polluted carbon, and surface carbonate, respectively.

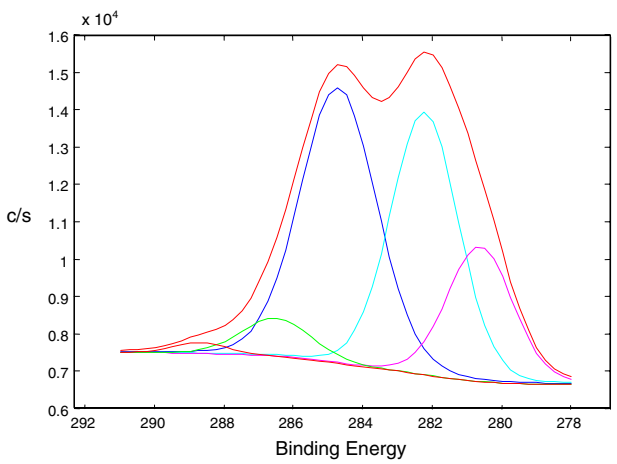


Figure 5. C1s binding energy on catalyst $Ni/\gamma–Al_2O_3$ after reaction.

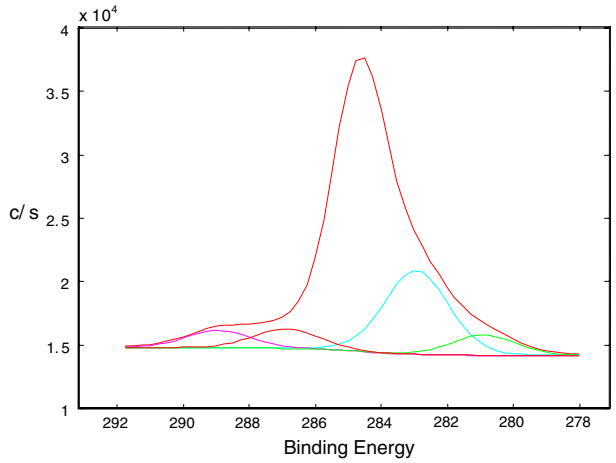


Figure 6. C1s binding energy on catalyst Ni–0.75wt%La–$BaTiO_3$ after reaction.

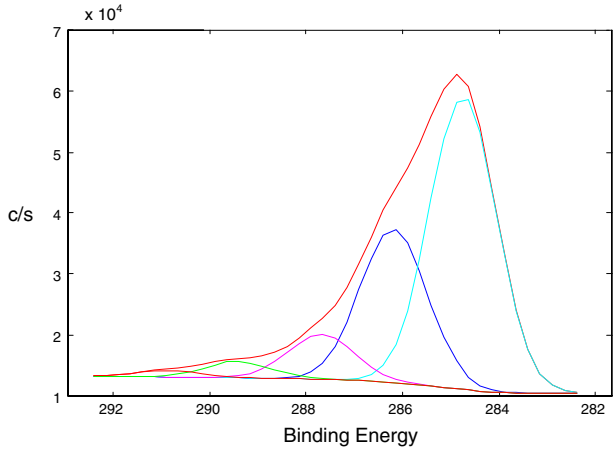


Figure 7. C1s binding energy on catalyst Ni/$BaTiO_3$ after reaction.

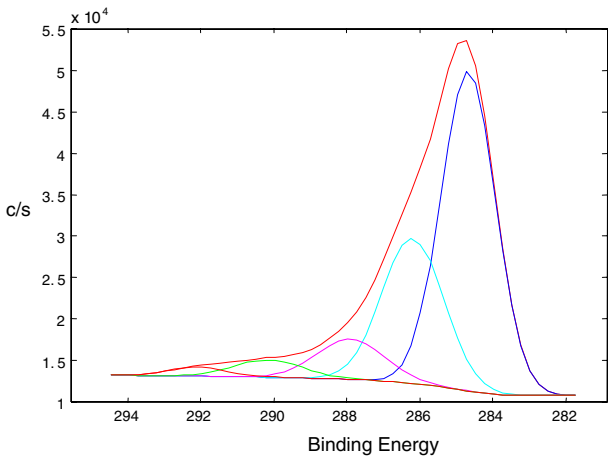


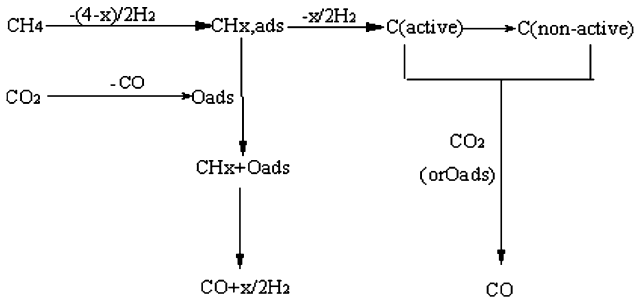
Figure 8. C1s binding energy on catalyst Ni–$BaTiO_3$ after reaction.

Table 1
C1s binding energy of coke species on catalysts surface

Catalysts	C_{1s} binding eEnergy (ev)	Contents (%)
Ni/γ–Al_2O_3	282.21 (34.85%)	284.69 (41.34%)
	286.48 (5.24%)	288.63 (1.18%)
Ni–0.75wt%La–$BaTiO_3$	282.91 (22.41%)	284.66 (61.97%)
	286.87 (5.42%)	288.92 (4.74%)
Ni/$BaTiO_3$	284.75 (57.08%)	286.18 (29.98%)
	287.67 (8.59%)	289.40 (3.09%)
Ni–$BaTiO_3$	284.67 (56.80%)	286.19 (28.87%)
	287.88 (8.92%)	290.15 (3.80%)

The results from table 1 show that several main coke species exist on the surfaces of catalysts, i.e., carbonization, polluted carbon, non-activated charcoal, and surface carbonate which binding energy is about 282, 284, 286, and 288 ev, respectively. The surface coke adjoining 282 and 286 ev is the main coke species, which can result in the deactivation of catalysts. Compared to the other two catalysts with the same support, catalyst Ni–0.75wt%La–$BaTiO_3$ exhibits better resistance to carbon deposition, (the total amount of deactivating coke on Ni–0.75wt%La–$BaTiO_3$, Ni/$BaTiO_3$ and Ni–$BaTiO_3$ is 0.67, 5.96, and 7.20 [20], respectively.) because it has strong anti-production ability of non-activated charcoal and carbonization. Therefore, it has better stability. By analyzing the surface coke species of the three catalysts, it is found that catalyst Ni–0.75wt%La–$BaTiO_3$ suppressed the production of the non-activated coke species which has a binding energy in the vicinity of 286ev. By comparing catalyst Ni–0.75wt%La–$BaTiO_3$ with Ni/γ–Al_2O_3, it shows that the coke species with a binding energy near 282ev was suppressed over catalyst Ni–0.75wt%La–$BaTiO_3$.

The coking-eliminating mechanism of CO_2 reforming of CH_4:



During the process, CO_2 will dissociate and produce absorbed oxygen and gaseous CO, while CH_4 will be activated and produces H_2 and CH_x. The latter will further react with oxygen coming from the dissociation of CO_2 to produce CO. The oxygen vacancies in $BaTi_{1-x}Ni_xO_{3-\delta}$ can speed up this process and the transfer of surface absorbed oxygen, thus speeding up CO_2 activation and dissociation. Compared with other catalysts,

catalyst Ni–0.75La–$BaTiO_3$ has more oxygen vacancies to speed up CO_2 activation and dissociation, thus before CH_4 further decomposing to surface coke species, $CH_{x,ads}$ has reacted with O_{ads} coming from CO_2 dissociation and produced CH_xO_{ads}, and further can react to produce $CO + x/2H_2$. Compared with catalyst Ni–0.75La–$BaTiO_3$, on catalysts Ni–1.5La/$BaTiO_3$ and Ni/La–$BaTiO_3$, CO_2 has lower active degree, so the amount of carbon deposition is higher.

4. Conclusions

In summary, we have investigated methane decomposition and coke formation on several catalyst surfaces using the TPH, TPRco_2, and XPS techniques.The important physical and chemical characteristics of the catalysts were characterized, and the results were correlated with the carbon deposition resistance and stability of the catalysts. To sum up the experimental results and testing analysis, conclusions are as follow:

1. Characteristics of the support materials play an important role in catalytic reaction although the support itself has no catalytic activity. The existence of perovskite structure results in many oxygen defects. According to the mechanism of coke formation, the oxygen defects are beneficial to the activation of CO_2 and to some extent necessary for the eliminated with CO_2. Different supports can produce surface carbon of different activities.

2. The addition of a rare earth promoter on catalysts Ni–1.5wt%La/$BaTiO_3$, Ni/La–$BaTiO_3$ (Ba/La = 1/0.002) and Ni–0.75wt%La–$BaTiO_3$ can reduce the numbers of active groups that are responsible for coke formation, and thus increasing electron density of active component nickel atoms, which avails the absorption and activity of CO_2, thus strengthening the eliminating coke activity of CO_2, weakening carbon deposition coming from methane further decomposition, thus improving resistance to coke formation.

Acknowledgment

This work was supported by the Provincial Natural Science Foundation of Jiangxi.

References

[1] C.E. Quincoces, S.P. de Vargas, P. Grange and M.G. González, Mater. Lett. 56 (2002) 698.
[2] A. Valentini, N.L.V. Carreño, L.F.D. Probst, P.N. Lisboa-Filho, W.H. Schreiner, E.R. Leite and E. Longo, Appl. Catal. A Gen. 255 (2003) 211.
[3] C.E. Quincoces, E.I. Basaldella, S.P. de Vargas and M.G. González, Mater. Lett. 58 (2004) 272.
[4] B.S. Liu and C.T. Au, Appl. Catal. A: Gen 244 (2003) 181.
[5] J.S.B. Wang, S.Z. Hsiao and T.J. Huang, Appl. Catal. A 246 (2003) 197.
[6] R. Takahashi, S. Sato, T. Sodesawa and S. Tomiyama, Appl. Catal. A 286 (2005) 142.
[7] V.C.H. Kroll, H.M. Swaan and C. Mirodatos, J. Catal. 164 (1997) 387.
[8] Z.L. Zhang and X.E. Verykios, J. Catal. Today 21 (1994) 589.
[9] J.R. Rostrup-Nielsen and J.H.B. Hansen, J.Catal. 144 (1993) 38.
[10] S.M. Stagg, E.R. Salazar and D.E. Resasco, J. Catal. 168 (1997) 75.
[11] A.M. Gadalla and M.E. Sommer, J. Chem. Eng. Sci 44 (1989) 12.
[12] A. Erdohelyi, J. Cserenyi and F. Solymosi, J. Catal. 141 (1993) 287.
[13] I. Alstrup and M. Teresa Tavares, J. Catal. 135 (1992) 147.
[14] N. Laosiripojana and S. Assabumrungrat, Appl. Catal. B 60 (2005) 107.
[15] K. Takanabe, K. Nagaoka and K. Aika, Catal. Lett. 102 (2005) 153.
[16] N. Laosiripojana, W. Sutthisripok and S. Assabumrungrat, Chem. Eng. J 112 (2005) 13.
[17] W. Li, J. Coal Conver. 20 (1997) 1.
[18] J.R. Rostrup-Nielsen, J. Catal 5 (1984) 1.
[19] X. Li, L. Luo and K. Liu, J. Inorg. Mater 18 (2003) 686 in Chinese.
[20] X. Li, M. Wu, Z. Lai and F. He, Appl. Catal. A: Gen 290(1–2) (2005) 81.
[21] A. Erdohelyi, J Csernyi and F Solymosi, J. Catal. 141 (1993) 287.
[22] Y. Lu, C. Yu and Y. Liu, J. Nat. Gas Chem. Indus. 23(1) (1998) 4.