CeO$_2$ promoted the performance of Ni/Al$_2$O$_3$ catalyst for CRM reaction

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Abstract: The promoted effect of CeO$_2$ on the reaction of Ni/Al$_2$O$_3$ catalyst in the syngas of CO$_2$ reforming of methane (CRM) was studied. The results showed that the catalyst prepared with CeO$_2$ addition exhibited high activity and stability, and the conversions of CH$_4$ and CO$_2$ could reach 96% at 800 °C when the amount of Ce was 5 wt%. SEM, H$_2$-TPR, CH$_4$-TPSR and CO$_2$/O$_2$-TPO characterization indicated that addition CeO$_2$ could enhance the interaction between support and Ni species in preparation process, enabling the capacity of catalyst to resist carbon deposition and metal sintering.

1. Introduction

The CO$_2$ reforming of methane (CRM) reaction (CH$_4$+CO$_2$=2CO+2H$_2$ $\Delta H_{298} ^\circ$ = +247.3 kJ/mol) can not only consume CH$_4$ and CO$_2$, but also produce synthesis gas with low H$_2$/CO ratio, which is an ideal raw material for production of hydrocarbons via Fischer-Tropsch synthesis and oxygenated chemicals[1].

Because CRM is an extremely endothermic and complex reaction process, the development of catalysts with high activity is the focus of the study[2]. In the process of CRM reaction to generate syngas, it will be affected by competitive side reactions, which will increase the probability of carbon deposition, such as CH$_4$ decomposition reaction (CH$_4$=C+2H$_2$ $\Delta H_{298} ^\circ$ = +74.9 kJ/mol), RWGS reaction (CO$_2$+H$_2$=CO+H$_2$O $\Delta H_{298} ^\circ$ = +41.2 kJ/mol), and the boudouard reaction (2CO=CO$_2$+C $\Delta H_{298} ^\circ$ = -172.4 kJ/mol). Therefore, the preparation of catalyst with high activity, long-term stability and low cost is the focus of current research[3]. At present, the catalysts widely used in CRM reaction are mainly noble and non-noble metals, such as Ru, Rh, Pt, Ni, Co, Fe, perovskite oxide, and core-shell catalysts[4-5]. Although noble metal catalysts have higher activity and carbon deposition resistance than non-noble metal catalysts, the high cost and sacristy restrict its application in industry.

Several factors, such as active metals, supports, promoters, synthesis method, calcination temperatures, and particle size, affected the activity and carbon deposition of catalysts[6]. Different active metals such as Ni and supports such as Al$_2$O$_3$, MgO, and CeO$_2$ have been investigated as catalyst in CRM reaction[7]. It is necessary to select appropriate metal as catalyst promoter to enhance the physical and chemical properties of Ni based catalyst and to improve the inhibition of carbon
deposition. In this respect, considering that CeO$_2$ is a special oxide with good oxidation potential (Ce$^{4+}$/Ce$^{3+}$), high oxygen storage and high temperature resistance, this property can improve the dispersion of Ni species on the catalyst surface and the gasification performance of carbon deposition[8-9]. Daza et al.[10] investigated the performance of Ni-Ce/clay catalyst in CRM reaction, and found that the addition of Ce not only improved the catalytic activity, but also reduced the formation of carbon deposition[11]. Wang et al.[12] also found the higher reducibility and metal dispersion of Ce promoted Ni/Al$_2$O$_3$ catalysts than Ni/Al$_2$O$_3$ catalyst.

In this paper, Ni&Ce/Al$_2$O$_3$ catalysts were synthesized by impregnation method. The effect of different Ce contents on the performance of catalyst was investigated. The performance of catalysts at different reaction temperatures was compared, and the promotion effect of Ce on the Ni/Al$_2$O$_3$ catalyst was analyzed.

2. Experimental

2.1. Catalyst preparation

Al$_2$O$_3$ was obtained by calcination Al$_2$O$_3$-nH$_2$O (AR, 98%, Chalco Shandong Branch, China) at 550 °C for 2 h, after cooling, grinding and sieving to the desired particle size of between 250 ~ 550 μm Al$_2$O$_3$ supports. The catalyst 5Ni$_x$Ce/Al$_2$O$_3$ was prepared by impregnation method, Ni(NO$_3$)$_2$·6H$_2$O (AR, 98%, Sichuan Xilong Chemical Co., Ltd., China) and Ce(NO$_3$)$_3$·6H$_2$O (AR, 98%, Zhengzhou Paini Chemical Reagent Factory, China) as precursors. 1g Al$_2$O$_3$ was added to the prepared Ni&Ce metal mixed solution (Ni: 5 wt%; Ce: 0, 1, 3, 5, 10 wt%) and treated by ultrasonic (40 kHz) for 20 min, then laying 18 h and dried overnight at 110 °C. Subsequently, the samples were calcined at 500 °C for 2 h.

2.2. Catalyst characterization

The surface morphology of catalysts were observed via the high resolution scanning electron microscope (HRSEM) using Zeiss EVO18. The operating parameters were 15.0 kV, 20 mbar of low vacuum and 3 nm of resolution, respectively. The temperature programmed reduction (TPR) analysis of the catalysts were carried out on Xianquan Industrial and Trading TP-5080 adsorption instrument. 50 mg catalyst sample was pretreated at 400 °C for 1 h under the condition of 30 mL/min N$_2$ flow. The experiment was performed from 100 to 900 °C under H$_2$/N$_2$ (5/30 mL/min) mixture gas. The contents of CH$_4$ and H$_2$ in the gas at the outlet of the reaction were monitored on-line by mass spectrometry. 0.1g catalyst was pretreated at 400 °C for 1h in Ar atmosphere. The experiment was performed from 100 to 900 °C (10 °C/min) under CH$_4$/Ar (5/30 mL/min) mixture gas. The types of carbon deposition were studied, after CH$_4$-TPSR analysis, the catalyst cooling down to room temperature in Ar, 5 mL/min CO$_2$/O$_2$ was introduced. The experiment was performed from 100 to 900 °C (10 °C/min), and the amount of CO/CO$_2$ in the reaction tail gas was monitored by mass spectrometry.

2.3. Activity evaluation

The catalyst activity in CRM process was evaluated in a quartz tube vertical fixed-bed reactor of 6 mm ID at atmospheric pressure. Before each run, 0.1 g of the catalyst was loaded in the quartz tube and 20 mL/min of Ar was introduced to replace the air in the reaction tube. The reaction temperature was controlled in the range of 600 ~ 900 °C (10 °C/min) under a flow of pure Ar. Before the reaction, the catalyst was reduced with flowing 5% H$_2$ diluted with Ar at 800 °C for 2 h. The CO$_2$ and CH$_4$ mixture with volume ratio of 1 and total flow rate of 40 mL/min were fed into the reactor once the temperature reached the desirable temperature, and the GHSV was 24 L/g/h. The reaction lasted for 4 h; the outlet gases were cooled and detected by an on-line mass spectrometer (Thermostar™ GSD320).

3. Results and discussion

Figure 1 (a) shows many pores and gullies on the surface of Al$_2$O$_3$ support prepared by Al$_2$O$_3$-nH$_2$O, so it is suitable to be used as catalyst support. In figure 1(b), it is found that the pore structures of Al$_2$O$_3$ are filled by NiO after the loading of active metal. However, the dispersion effect of active component
Ni species on the catalyst surface is not ideal, and the particles formed are large. Figure 1(d) shows the 5Ni5Ce/Al2O3 catalyst before reaction, the dispersion of Ni species on the surface of the catalyst containing Ce is relatively uniform. In addition, the catalysts after the reaction of Ni/Al2O3 and 5Ni5Ce/Al2O3 are shown in figure 1(c) and (e), respectively. Compared with that before the reaction, the surface of Ni/Al2O3-4h catalyst appears sintering phenomenon, while 5Ni5Ce/Al2O3-4h catalyst does not find obvious sintering. Therefore, this indicates that the dispersion of Ni in the catalyst can be improved by adding CeO2, which can also improve sintering resistance of catalyst.

The H2-TPR profiles of catalysts with different Ce contents are shown in figure 2. The TPR profiles could be divided three forms of Ni species on the surface of metal support[13], the temperature zone between 300 °C and 550 °C is related the free-state on the support surface. The temperature zone between 550 °C and 750 °C is attributed to the dispersed-state. The temperature zone between 750 °C and 900 °C is corresponding to the fixed-state. The main reduction peak of 5Ni0Ce catalyst is around 650 °C, which belongs to NiO in dispersed state. However, the catalysts with CeO2 promoter all showed a large H2 consumption peak around 800 °C, which should be attributed to NiO in a fixed-state. This indicated a stronger association between NiO and the support, which can inhabit the sintering and loss of Ni particles during the reaction.

In order to study the catalytic effect of CeO2 on methane decomposition and the mechanism of CRM reaction, figure 3 shows the curves of CH4 and H2 current values detected by mass spectrometry during methane temperature programmed surface reaction (TPSR). It can be observed from figure 3 that the current value of H2 detected on 5Ni0Ce catalyst began to increase around 450 °C, while the current value of CH4 began to decrease, and the production of H2 and the consumption of CH4 reached the maximum at 585 °C. Compared with Ce-containing catalyst, the values of H2 and consumption of methane increase, and the values are the largest when the amount of Ce is 3%. In figure 3(b), there are three generation peaks of H2, the main H2 generation peak is at 600 °C, and the amount of H2 generation tends to increase again at 850 °C. According to the reaction mechanism of CRM, the three peaks are attributed to H2 released by CH4 the stepwise decomposition to CH3(= 1, 2, 3). This is because the higher the degree of dissociation, the more demanding the reaction conditions. In addition, from the H2 generation peaks and the CH4 consumption peak positions of 5NixCe catalysts, the temperature corresponding to the maximum peaks of H2 generation and CH4 consumption moved to the low temperature zone as the amount of CeO2 added increased. Therefore, the CeO2 helps keep methane decomposition required temperature down. But the amount of H2 and the consumption of methane begin to decrease when the amount of CeO2 is more than 3 wt%. This may be due to the excessive CeO2 covering the active metal Ni, reducing the number of active sites.
The carbon deposition in the CRM can be divided into amorphous carbon and graphite carbon. The amorphous carbon can react with CO$_2$ to produce CO; graphite carbon is relatively stable and has strong interaction with Ni, which makes it difficult to be gasified. In order to study the type of carbon deposition on the catalyst surface, figure 4(a) shows the CO$_2$-TPO test of the catalysts after the analysis of CH$_4$-TPRS. The gasification temperature of carbon on 5Ni0Ce surface area is about 617 $^\circ$C, the CO formation temperature corresponding to 5Ni1Ce, 5Ni3Ce, 5Ni5Ce, and 5Ni10Ce is 625 $^\circ$C, 615 $^\circ$C, 610 $^\circ$C, 570 $^\circ$C, respectively. The results show that the gasification temperature of carbon on the surface of the catalyst decreases with the increase of Ce contents. During the CRM reaction, the oxygen vacancies contained in CeO$_2$ release a large amount of free electrons and transfer to the center of Ni atom, increasing the density of Ni atom electron cloud, so that the catalyst can absorb more CO$_2$ and promote the CO$_2$ to eliminate carbon deposition[14].

Figure 4(b) shows the O$_2$-TPO test of the catalyst after the analysis of CH$_4$-TPRS, 5Ni0Ce has a CO$_2$ formation peak at about 500 $^\circ$C, which is attributed to carbon with weak binding to Ni, and the second CO$_2$ formation peak appears at 675 $^\circ$C, which should be graphite carbon with stable catalyst surface. With the increase of CeO$_2$ contents, the formation peak of CO$_2$ gradually moves to the low temperature zone, which indicates that the gasification temperature of graphite carbon decreases and the addition of CeO$_2$ can weaken the interaction between graphite carbon and Ni.

Figure 5 shows the performance of 5NixCe/Al$_2$O$_3$ catalysts in CRM reaction at different temperatures. The conversions of CH$_4$ and CO$_2$ could reach 96% at 800 $^\circ$C when the amount of Ce is 5 wt%. It can be seen from the conversions that the catalytic performance of catalyst with CeO$_2$ is significantly improved, especially under 800 $^\circ$C. This indicates that CeO$_2$ can significantly improve
the catalytic activity of nickel based catalysts. The H₂/CO ratio decreases with the increase of Ce contents, but the H₂/CO ratio corresponding to the catalyst increases when the Ce addition amount is 10%. It is indicated that the optimal addition amount of Ce is 3~5 wt%.

Figure 5. The catalytic performance of 5NixCe/Al₂O₃: GHSV=24 L⋅g⁻¹⋅h⁻¹, CH₄/CO₂=1.

4. Conclusions
The effect of different amounts of CeO₂ on the catalytic performance of 5NixCe/Al₂O₃ in CRM reforming was investigated. The addition of CeO₂ significantly enhanced the catalytic performance of the Ni/Al₂O₃ catalyst. TPR profiles showed Ce strengthen the interaction between Ni species and support, and improved the sintering resistance of the catalyst. The analysis of CH₄-TPRS and TPO showed that the addition of Ce not only reduced the energy required for CH₄ craking, but also promoted the carbon deposition on the catalyst to be easily eliminated, which improved the carbon deposition resistance of the catalyst.

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