Effect of CeO_2 Promoter on the Performance of Catalyst for CH_4, CO_2 with O_2 to Synthesis Gas

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Abstract: In the reaction of methane, carbon dioxide with oxygen to synthesis gas, conversion of CH_4 was increased, but CO selectivity was reduced when CeO_2 was added to Ni/CaO-Al_2O_3 catalyst. The characterization of TPR, XPS, XRD and H_2-TPD exhibited that, on one hand， the CeO_2 promoter decreased the reduction temperature of catalyst. On the other hand, addition of CeO_2 resulted in an increase in the electron density of active component Ni, and as a result, reduced the ability of CH_4 deep cracking and enhanced the resistance to carbon-deposition of catalyst. In addition, the existence of CeO_2 was beneficial to decrease the Ni crystal particle size.

Keywords: Methane, carbon dioxide, oxygen, synthesis gas.

In recent years, the reaction of methane, carbon dioxide with oxygen to synthesis gas has been receiving more attention from the viewpoint of preserving global environment, because CH_4 and CO_2 are of greenhouse gases and their contribution to global warming is very large owing to their huge amount released in the atmosphere[1]. In addition, there are two advantages in this process obviously, by changing the ratio of feed, it can achieve thermal neutralizing and the CO/H_2 ratio can be varied in the range of 0.5~1 to fit different industrial requirement. There are hardly any papers to explore the influence of CeO_2 promoter on the catalytic behavior for this reaction.

In this paper, Ni/CaO-Al2O3 catalyst was modified by CeO2 promoter. A series of methods including TPR, H2-TPD, XPS and XRD was applied in order to study the effect of promoter on reducibility, resistance to carbon deposition, Ni binding energy and Ni crystal particle size of the catalyst.

The catalyst was prepared by adding CeO_2 (15mol%) to Ni (10wt%) /CaO-Al_2O_3 catalyst. The evaluation of catalysts was carried out using a fixed-bed micro-reactor with a Gas chromatograph equipped with thermal conductivity detector. $CH_4/CO_2/O_2$=1/0.4/0.5 molar ratio, CH_4 space velocity of 25000h^{-1}. H_2-TPR, H_2-TPD were performed at the rate of 15℃/min. X-ray diffraction (XRD) was studied on D/max-B x-ray diffractormeter with CuKα radiation at 40KV × 30mA. XPS measurements were taken on a NP-1 instrument with MgKα source at 15KV×8mA.

Results and discussion

1 Effect of CeO_2 on activity and selectivity of catalyst

From the results of **table 1**, it is surprisingly found that addition of CeO_2 to Ni/CaO-Al_2O_3 affected the performance of catalyst remarkably. There was a greater increase in the conversion of CH_4, especially below 750℃. On the contrary, addition of CeO_2 resulted in a decrease in CO selectivity in a certain degree.

Table 1 Effect of CeO_2 on catalytic activity and selectivity

Reaction temperature (℃)		800	750	700	650
C (CH_4)	Ni/CaO-CeO_2-Al_2O_3	91.15	86.33	74.70	66.49
(%)	Ni/CaO-Al_2O_3	90.37	81.31	64.88	43.25
S (CO)	Ni/CaO-CeO_2-Al_2O_3	71.19	68.82	72.16	77.11
(%)	Ni/CaO-Al_2O_3	72.16	74.89	78.44	87.20

2 Effect of CeO_2 on reducibility of catalyst

TPR results listed in table 2 indicated that addition of CeO_2 decreased the reduction temperature of NiO crystal phase and $NiAl_2O_4$ spinel phase, namely, increased the reducibility of NiO crystal phase and $NiAl_2O_4$ spinel. In addition, existence of CeO_2 promoted the amount of reducible NiO as compared with that of NiO/CaO-Al_2O_3. It is easily explained that introduction of CeO_2 weakens the interaction between NiO and Al_2O_3 support.

Table 2 Effect of CeO_2 on reducibility of catalyst

Catalyst	Reduction temperature (℃)		Peak area of NiO (cm^2)	Peak area of $NiAl_2O_4$ (cm^2)
	NiO	$NiAl_2O_4$		
Ni/CaO-Al_2O_3	420	870	13.5	7.7
Ni/CaO-CeO_2-Al_2O_3	350	830	15.2	6.0

3 Effect of CeO_2 on resistance to Ni-Al composite oxides

After the catalysts with and without CeO_2 were calcined at 900℃ for 2 h, as compared with both TPR results in **Table 3**, one could observe plainly that the intensity of NiO crystal phase reduction peak was weakened due to the formation of $NiAl_2O_4$ spinel for the latter catalyst. But by adding CeO_2, it prevented the formation of $NiAl_2O_4$ spinel effectively, namely, promoted the ability of resistance to Ni-Al composite oxides.

Table 3 Influence of CeO_2 on resistance to Ni-Al composite oxides

Catalyst	Treatment condition	Peak area of NiO(cm^2)	Peak area of $NiAl_2O_4$ (cm^2)
NiO/CaO-CeO_2-Al_2O_3	Fresh	15.2	6.0
	Calcined	8.0	13.3
NiO/CaO-Al_2O_3	Fresh	13.5	7.7
	Calcined	3.6	17.6

4 Effect of CeO_2 on resistance to carbon deposition

Table 4 showed the amount of carbon deposited on Ni/CaO-Al_2O_3 and Ni/CaO-CeO_2-Al_2O_3 catalysts for reaction of 3 h. After addition of CeO_2, the amount of carbon deposition reduced from 0.8×10^{-3}g/g to 0.5×10^{-3}g/g, therefore, it is evident that existence of CeO_2 enhances the resistance to carbon deposition of the catalyst.

Table 4 The amount of carbon deposition on catalysts*

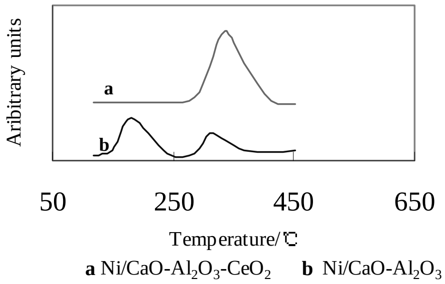
catalyst	C_{CH4}(%)	S_{CO}(%)	Amount of carbon deposition (g/g)
NiO/CaO-Al_2O_3-CeO_2	86.3	68.82	0.5×10^{-3}
NiO/CaO-Al_2O_3	81.3	74.89	0.8×10^{-3}

* Reaction conditions: CH_4:CO_2:O_2=1:0.4:0.5, CH_4 GHSV 2500h^{-1}, 750℃.

5 H_2-TPD

Figure 1 presented the H_2-TPD profiles of Ni/CaO-Al_2O_3 and Ni/CaO-CeO_2-Al_2O_3 catalysts. TPD results demonstrated that addition of CeO_2 changed the shape and intensity of desorption peaks, Ni/CaO-Al_2O_3 catalyst had two desorption peaks, in contrast, Ni/CaO-CeO_2-Al_2O_3 catalyst had only one, but the total peak area was 1.33 times that of Ni/CaO-Al_2O_3 catalyst, which implied that it raised the dispersion of Ni on catalyst.

Figure. 1 H2-TPD profiles of catalysts



6 XPS and XRD investigations

From the results of XPS, it was found that, adding CeO_2 altered the Ni(2p1/2) binding energy from 852.72 eV to 852.47 eV, that is to say, increased the d-orbital electron density of active component Ni, and as a result, suppressed CH_4 deep cracking and CO disproportion to form carbon, therefore, enhanced the resistance to carbon deposition, it is in agreement with the results of **Table 4**.

XRD results displayed that addition of CeO_2 weakened the Ni diffraction intensity of catalyst, and the Ni crystal particle size was reduced from 45 nm to 31.3 nm, which was also responsible for the higher resistance to carbon deposition of Ni/CaO-CeO_2-Al_2O_3 catalyst. It is obvious that addition of CeO_2 favor the dispersion of active component Ni, which is in accordance with the results of H_2-TPD.

Reference

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Received 11 June 1999