

Performances of different additives on NiO/ γ -Al₂O₃ catalyst in CO methanation

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Received: 27 January 2016 / Accepted: 24 May 2016 / Published online: 14 June 2016
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Abstract In this work, NiO/ γ -Al₂O₃ catalyst with different additives prepared by excessive dipping method, was investigated in CO methanation in an attempt to improve the reaction activity and enhance the anti-coking property. The influences of additives, such as Zr, Co, Ce, Zn and La, on catalysts in performance of CO methanation were studied in a fixed-bed reactor. The catalysts were characterized by XRD, H₂-TPR, H₂-TPD and CO-TPD. The results showed that the addition of the additives could promote the dispersion of nickel species on support and decrease the crystallite size of Nickel species. The reduction temperatures of catalysts were all reduced except the one with Mg. The catalytic results showed that additives improved the reaction activity of CO methanation. Especially, the addition of La gave the best catalytic performance of 100 % CO conversion and 99.61 % CH₄ selectivity, respectively. The space–time yield of CH₄ was achieved as high as 2134.5 g kg⁻¹ h⁻¹.

Keywords CO methanation · Nickel-based catalysts · Additives · Fixed-bed reactor

Introduction

Methanation is one of the core technologies of coal to synthetic natural gas (SNG) process [1]. This technology requires catalyst with high activity and high stability due to

the high exothermic of the methanation reaction [2–4]. Currently, commercial methanation technology was mastered by Lurgi (LURGI), Johnson Matthey (DAVY) and Topsoe (TOPSØE) [5]. All of these technologies are performed in adiabatic fixed-bed reactor. Ni-based catalyst is the most widely investigated system due to its high efficiency and low cost. NiO/ γ -Al₂O₃ catalyst has received renewed interests for the methanation of carbon monoxide.

It is known that the main reasons for Ni-based catalyst deactivation are the carbon deposition and sintering in methanation reaction process [6–8]. The addition of rare earth oxide can change the interaction between NiO and the support, as well as the pH of the catalyst surface to improve the Ni dispersion. They are beneficial for the catalyst activity, stability and resistance to carbon deposition [9]. The suitable content of MgO could increase the monolayer capacity of NiO on the surface of the supports. And the reduction of the nickel grain was become smaller due to the introduction of Mg additives. But MgO would enhance the chemical interaction between the NiO and the supports, resulting in a new formation of NiO–Al₂O₃–MgO catalyst, which was not easy to be reduced [10]. Jun et al. [11] developed a Ni–Co bimetallic aerogel catalyst prepared by a sol–gel method for the production of SNG via CO methanation. The catalyst exhibited higher conversion of CO, higher yield and selectivity of CH₄. Moreover, the NiCo catalyst showed no deactivation in 100 h reaction. This good stability was attributed to the superior property. However, the aerogel NiCo catalyst showed poor fluidization through the nanoparticle agglomerates. Guido et al. developed nickel doped with cobalt catalyst for hydrogen production by ethanol steam reforming. The structure characteristic of Ni–Co–Zn–Al catalyst was studied [12]. The calcination of the layered precursors performed a high surface area of mixed oxides. It was a

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well distributed mixture of a rock salt phase (NiO), a wurtzite phase (ZnO) and a spinel phase. But application of catalyst with Zn and Co in the process of methane had not been reported. In the last decade, many efforts have been made to improve the catalytic performance of the Ni/Al₂O₃ catalyst. The addition of small amount of second metal, such as Mg, Co, Zr, Ce, La and Zn has been attempted to enhance the stability and catalytic activity of the methanation of carbon monoxide [13].

Although the Ni/ γ -Al₂O₃ catalysts have been reported in some methanation reaction of H₂-rich syngas, there are few works reported on methanation catalysts promoted by different additives. Especially, the optimized amount of structural promoter, electronic promoter and lattice defects promoter in methanation reaction have not been reported. In this work, the effect of different additives metal oxides on the interactions of NiO and support, and carbon deposition resistance over such catalysts has been studied. The selection of different additives for Ni/ γ -Al₂O₃ catalysts with low Ni contents for syngas methanation was conducted. A series of NixMyAl (M = Mg, Co, Zr, Ce, La, Zn) catalysts were prepared using excessive dipping method and characterized using XRD, H₂-TPR, H₂-TPD and CO-TPD. The influences of different additives on the performances of NixMyAl catalysts were investigated.

Experiment

Catalyst preparation

The catalysts were prepared with excessive dipping method. First, Ni(NO₃)₂·6H₂O were mixed with Mg(NO₃)₂, Co(NO₃)₂·6H₂O, La(NO₃)₃·6H₂O, Ce(NO₃)₃·6H₂O, Zr(NO₃)₄·5H₂O and Zn(NO₃)₂·6H₂O, respectively. Then, the Al₂O₃ (surface area 246 m²/g, Shandong Aluminum Co. Ltd) were impregnated in the different solution for 24 h at room temperature, dried for 12 h at 120 °C then calcined for 4 h at 450 °C to give the oxide catalyst. The catalysts were noted as NixMyAl (M = Mg, Co, Zr, Ce, La, Zn) catalyst. The catalyst composes of 12 wt% of NiO and 4 wt% M₂O_w (M = Mg, Co, Zr, Ce, La, Zn).

Catalyst evaluation

Initially, the catalyst was loaded into a pressurized fixed-bed reactor and reduced with H₂/N₂ mixture gas at the ratio of 1:4 at 550 °C for 4 h. Then, the reactor was cooled to 200 °C. The pressure of the system was slowly increased with nitrogen gas. The feed gas was switched into the reactor gradually to the desired pressure. The activity of methanation catalyst was tested at 400 °C with the reaction

pressure of 1 MPa. The flow ratio of the H₂/CO was 3:1 at the space velocity of 12,000 h⁻¹.

Catalyst characterization

The crystalline structure of the catalyst was determined with X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Ka radiation source in the range of 10°–85°. H₂-TPR was carried out in a quartz-tube fixed-bed micro reactor system. The sample (20 mg) was pretreated with Ar at 300 °C for 1 h and then cooling to 50 °C. Afterwards, the flowing gas was switched to 10 vol% H₂/Ar and heated to 800 °C at a ramping rate of 10 °C/min. H₂-TPD and CO-TPD experiments were performed with similar procedure. The sample was pretreated in Ar flow (50 ml/min) at 300 °C for 1 h, then cooling to 50 °C and kept at this temperature for 40 min in 10 vol% H₂/Ar or 10 vol% CO/Ar. Afterward, the sample was swept with He for 60 min. Finally, the desorption step was performed from 50 to 800 °C at a heating rate of 10 °C/min with He flow of 50 ml/min. The desorbed products were all monitored using TCD.

Results and discussion

The influences of additives on the catalytic activity of the nickel-based catalyst for CO methanation

The catalytic results of the catalyst for CO methanation are shown in Table 1. The loading amount of additives and NiO were 4 and 12 % in weight, respectively. The results showed that the addition of La, Zn, Ce, Co and Zr into Ni/ γ -Al₂O₃ catalyst improved the catalytic performance of CO methanation. The most effective catalyst was the one with La promoter. The CO conversion was 100 %, and CH₄ selectivity was 99.6 % at CH₄ space-time yield of 2134.5 g/kg h. However, the Mg promoter decreased the catalytic activity. In summary, it was showed that they would change the chemical environment and the state, which would ultimately affect the catalytic activity for CO methanation.

X-ray diffraction (XRD) characterization

The XRD characterization of the catalyst was shown in Fig. 1. The diffraction peaks at the 2 θ peaks of 37.2°, 43.2° were the characteristic peaks of NiO. Compared with Ni₁₂Al catalyst, the introduction of Zr, Co, Ce, Zn and La additives decreases the intensity of diffraction peak of NiO. The diffraction peak tends to become broader due to high

Table 1 The influences of additives on the catalytic activity of the nickel-based catalyst for CO methanation

	Con-CO (%)	Sel-CH ₄ (%) / standard deviations	STY-CH ₄ (g kg ⁻¹ h ⁻¹) / standard deviations
Ni ₁₂ La ₄ Al	100	99.61/0.28	2134.5/13.19
Ni ₁₂ Zn ₄ Al	100	98.64/0.29	2113.7/13.28
Ni ₁₂ Ce ₄ Al	100	96.28/0.26	2063.1/14.04
Ni ₁₂ Co ₄ Al	100	94.83/0.24	2032.1/13.22
Ni ₁₂ Zr ₄ Al	100	94.72/0.27	2029.7/12.88
Ni ₁₂ Mg ₄ Al	100	92.74/0.28	1987.3/12.76
Ni ₁₂ Al	100	95.10/0.29	2037.9/13.24

Reaction conditions: CO:H₂ = 1:3, 12,000 h⁻¹, 1 MPa, 400 °C

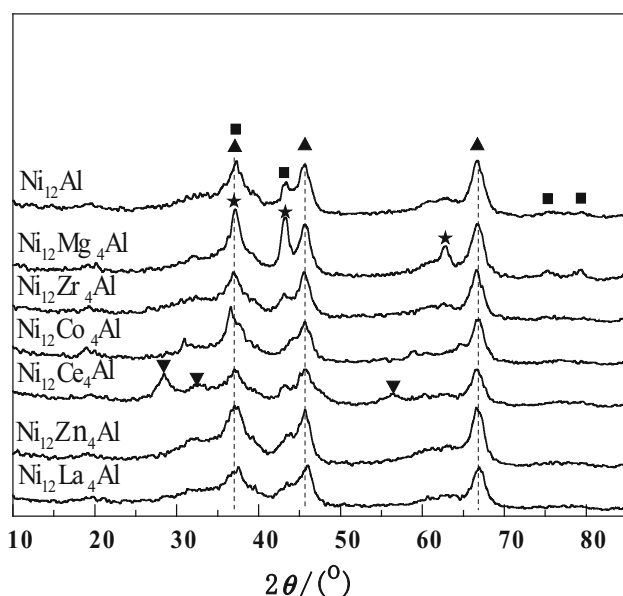


Fig. 1 The XRD patterns of nickel-based catalysts with different additives *star* MgNiO₂ *square* NiO *inverted triangle* CeO₂ *triangle* γ-Al₂O₃

dispersion of NiO. The dispersion of NiO decreased in the order La > Co > Ce >> Zr > Zn. It was reported that the rare earth metal of La can effectively improve the dispersion of NiO on the surface of the support and the particle size of NiO crystal descended after calcinations [14, 15]. The peaks of Ni₁₂Mg₄Al sample at the 2θ peaks of 37.1°, 43.1°, 62.6° are due to MgNiO₂. It showed that the MgNiO₂ formation was difficult to be reduced due to the strong interaction between MgO and NiO. The peaks of Ni₁₂Ce₄Al at the 2θ of 28.5°, 33°, 47.4° and 56.3° belong to CeO₂. The Ce³⁺ was oxidized to Ce⁴⁺ after Ce was introduced into the γ-Al₂O₃. The filling of Ce⁴⁺ in Al₂O₃ crystal lattice vacancies made the original lattice distorted because of different valence of Ce⁴⁺ and Al³⁺. Therefore, Ce⁴⁺ mainly located on the surface of the crystal phase with a lower energy state or precipitate to form crystal

[16, 17]. The characteristic diffraction peaks of Zr, Co, Zn and La oxides were not observed in XRD spectra. This indicated that Zr, Co, La and Zn were well dispersed on the surface of the support [18]. It suggests that the introduction of additives could improve the dispersion of NiO on the surface of γ-Al₂O₃.

The XRD characterization of the reduced catalyst for CO methanation as shown in Fig. 2. The 2θ peaks of 44.4°, 51.8°, 76.3° were the characteristic diffraction peaks of nickel. The characteristic diffraction peaks of nickel were decreased compared with the catalyst Ni₁₂Al, when Zr, Co, Ce, Zn, La, Mg additives is introduced. Considering the particle size data of nickel in Table 2, the catalyst of nickel particle size had been decreased. The Ni₁₂Ce₄Al and Ni₁₂La₄Al catalysts showed the weakest peak intensity of nickel. This indicated that the addition of La and Ce additives in the process of catalyst preparation could effectively reduce the particle size of nickel. The 2θ peaks

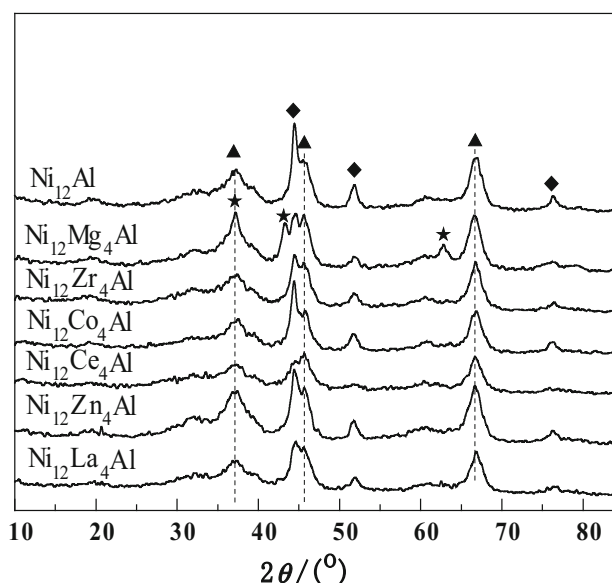


Fig. 2 The XRD patterns of different additives of reduced nickel-based catalysts. *star* MgNiO₂, *diamond* Ni *triangle* γ-Al₂O₃

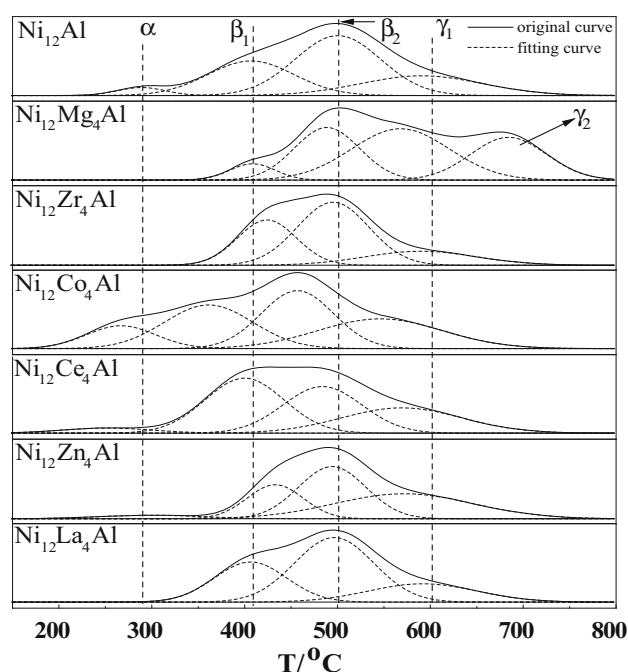
Table 2 Analytic results of the reduced Ni crystallites

Catalyst	2θ (°)	FWHM (°)	Average diameter (nm)
Ni ₁₂ Al	44.41	0.72	15.08
Ni ₁₂ Mg ₄ Al	44.47	1.06	10.34
Ni ₁₂ Zr ₄ Al	44.39	1.02	10.76
Ni ₁₂ Co ₄ Al	44.37	0.88	12.48
Ni ₁₂ Ce ₄ Al	44.38	0.15	7.22
Ni ₁₂ Zn ₄ Al	44.41	1.13	9.70
Ni ₁₂ La ₄ Al	44.54	1.23	8.91

of 37.1°, 43.1°, 62.6° belong to MgNiO₂ formation of characteristic diffraction peaks. It indicated that the MgNiO₂ formation could not be reduced completely in the reduction condition of 550 °C [19]. Therefore the quantity of nickel in the surface of active center could be reduced and the activity of CO methanation was not enhanced. In addition, all the catalysts do not have characteristic diffraction peaks of oxide of Zr, Co, Ce, Zn, La, maybe due to the formation of amorphous phases. Another reason for this is probably that Zr, Co, Ce, Zn, La metal or oxide grain is too small to be detected by XRD. In summary, the introduction of additives changed the chemical environment of the catalyst surface as well as the particle size of the nickel [20].

H₂-TPR characterization

The H₂-TPR characterization of the catalyst for CO methanation was shown in Fig. 3. The Gauss fitting analysis of H₂-TPR spectrum was given in Table 3. It was observed that H₂ consumption started at about 300 °C for all the Ni-based catalysts. The reducible NiO species are usually classified to three types, including low temperature peak α (200–350 °C), middle temperature peak β (300–600 °C), high temperature peak γ 1 (500–700 °C) [21]. Each peak corresponded to different states of NiO species. The peaks located in the temperature region (200–350 °C) were assigned to α -type NiO species, which was attributed to free nickel oxides possessing a weak interaction with alumina support. The middle temperature peaks (300–600 °C) represent β -type NiO species, which has a stronger interaction with alumina than the α -type NiO. It could be further classified into β 1-type (300–500 °C) and β 2-type (400–600 °C). The former peak located at 300–500 °C was attributed to the more reducible NiO in Ni-rich mixed oxide phase. While the latter at 400–600 °C was attributed to the less reducible one in Al-rich phase. The high temperature peaks (500–700 °C) were assigned to γ 1-type NiO species, which was stable nickel

**Fig. 3** H₂-TPR profiles of nickel-based catalysts

aluminum phase with the spinel structure. The new high temperature reduction peak γ 2-type at 680 °C was assigned to the reduction peak of MgNiO₂, when the Mg promoter was employed. This showed that addition of Mg promoter increased the reduction temperature of the catalyst. The reduction peak of NiO at the low temperature region shifted to lower temperature direction, and the peak area was increased. The high temperature reduction peak also shifted to low temperature direction, and the area of reduction peak was reduced when the promoter of Ce, Zr, La was introduced. It was suggested that the introduction of Ce, Zr, La make the NiO easier to be reduced, while inhibiting the strong interaction between NiO and γ -Al₂O₃ [22]. The low temperature reduction peaks of Ni-based catalysts with Ce promoter and CeO₂ were overlapped.

Table 3 Gaussian fitting analysis of H₂-TPR patterns

Catalyst	Reduction temperature/°C					Relative content/%				
	α	β_1	β_2	γ_1	γ_2	α	β_1	β_2	γ_1	γ_2
Ni ₁₂ Al	288.76	406.74	500.42	590.68	/	3.51	27.41	47.09	21.99	/
Ni ₁₂ Mg ₄ Al	/	408.49	488.53	567.86	684.22	/	5.97	27.61	40.44	25.98
Ni ₁₂ Zr ₄ Al	/	424.08	495.31	589.96	/	/	30.47	51.67	17.85	/
Ni ₁₂ Co ₄ Al	266.91	361.21	456.79	545.86	/	11.88	28.93	31.43	27.75	/
Ni ₁₂ Ce ₄ Al	252.10	399.80	483.78	569.24	/	3.95	37.71	31.96	26.38	/
Ni ₁₂ Zn ₄ Al	298.77	432.84	494.28	571.37	/	3.88	20.66	38.03	37.43	/
Ni ₁₂ La ₄ Al	/	404.48	496.43	601.18	/	/	28.33	55.59	16.07	/

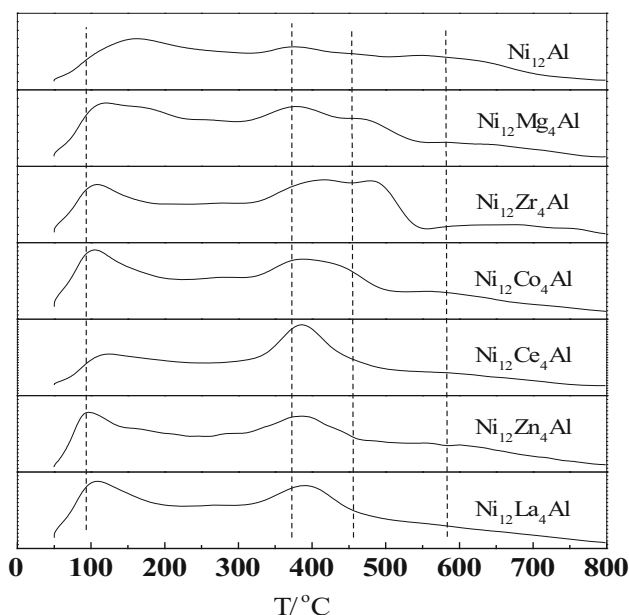
Combined with the catalyst hydrogen consumption data in Table 4, it could be noticed that the catalyst consumption of La promoter was larger compared with Ce, Zr additives. The number of active center nickel was also the largest in all the reduced catalyst. The Co promoter was introduced to greatly decrease the reduction temperature of the catalyst. The reduced Co was also an important catalytic active center in the process of methanation [23]. The reduction peak shifted to the lower temperature, and the peak area decreased after the introduction of the Zn promoter. This shows that Zn has an inhibitory effect on the Ni-based catalyst [24].

CO-TPD characterization

The CO-TPD characterization results of the catalysts are showed in Fig. 4. All of the catalysts had a low temperature desorption peak near 100 °C, which is attributed to the desorption of CO adsorbed on nickel on the surface of the catalyst. The low temperature peak of CO desorption of the catalyst with promoter shifted to a even lower temperature compared to the results of Ni₁₂Al catalyst. This showed that nickel surface was reduced when the additives were introduced. At the same time, there were three other chemical desorption peaks named α , β and γ , ranging from 400 to 600 °C, corresponding to three different states of the

Table 4 H₂-consumption analysis of nickel-based catalysts

Catalyst	H ₂ -consumption/mmol g ⁻¹
Ni ₁₂ Al	1.64
Ni ₁₂ Mg ₄ Al	1.36
Ni ₁₂ Zr ₄ Al	1.63
Ni ₁₂ Co ₄ Al	2.20
Ni ₁₂ Ce ₄ Al	1.66
Ni ₁₂ Zn ₄ Al	1.84
Ni ₁₂ La ₄ Al	2.03

**Fig. 4** CO-TPD profiles of nickel-based catalysts

Ni species [25]. CO desorption temperature of the catalyst is related to desorption activation energy [26]. The adsorbed component with lower activation energy was easily desorbed from the catalyst, which leads to the decrease of desorption temperature. The adsorption component with high desorption activation energy was more conducive to the adsorption on the catalyst, which leads to the increase of desorption temperature [27]. The γ -desorption peak disappeared when Mg promoter was added. The α -desorption peak was attributed to NiO of loading on the surface of the support. The β -desorption peak was attributed to the MgNiO₂ formation. CO desorption peak area was relatively small due to a large number of MgNiO₂ formation, which is difficult to be reduced. The CO desorption peak area of catalyst Ni₁₂Co₄Al was slightly increased. This indicated that the introduction of Co promoter improved

the dispersion of Ni species on the catalyst surface and enhanced the adsorption of CO. The γ -desorption peak disappeared in $\text{Ni}_{12}\text{Zr}_4\text{Al}$, but α -desorption peak area and β -desorption peak area were greatly increased. Thus, the introduction of Zr promoter improved the dispersion of Ni to a great extent and enhanced the adsorption of CO. The β -desorption peak and the γ -desorption peak of CO desorption were disappeared on $\text{Ni}_{12}\text{Ce}_4\text{Al}$ and $\text{Ni}_{12}\text{La}_4\text{Al}$ catalyst. The α -desorption peak area was increased. Therefore, the introduction of rare earth elements Ce, La can improve the dispersion of nickel on the surface, as well as reduce the CO desorption peak temperature and the desorption activation energy, which was more beneficial for the adsorption of CO form the activated site.

H_2 -TPD characterization

The H_2 -TPD profiles of the supported Ni-based catalysts usually contain two or more desorption peaks. The number of desorption peaks reveals the types of catalyst surface active sites. The H_2 -TPD results of the catalyst for CO methanation are given in Fig. 5. All the H_2 -TPD profiles of the catalysts showed a low temperature desorption peak (nearby 150 °C) and a high temperature desorption peak (nearby 400 °C). The low temperature peak was attributed to desorption of hydrogen adsorbed on the metal surface, and the high temperature peak was attributed to desorption of the hydrogen spillover hydrogen adsorbed on the surface of the oxide [28].

The Ni_{12}Al catalyst H_2 -TPD profiles have desorption peak (90 °C) and a satellite peak (150 °C) at low temperature. This can be attributed to the weak and strong adsorption of hydrogen on the nickel surface. The desorption peak at high temperature (400 °C) was attributed to the desorption peak of spillover hydrogen [29]. The low temperature desorption peak disappeared when the Mg promoter was introduced. This showed that the amount of adsorbed hydrogen on the surface of nickel metal was very low. It is likely that the MgNiO_2 formation occurred during the calcination process. It was hard to be reduced, and directly affected the quantity of active center of nickel. The two desorption peaks (400 and 460 °C) with larger area at high temperature were also showed. This indicated that there was a large number of spillover hydrogen [30]. It was possible that a small amount of MgNiO_2 formation was reduced for high dispersion of nickel with strong ability to activate hydrogen. There were a desorption peak (100 °C) and a satellite peak (130 °C) in the low temperature range, when the Zr, Co, Ce, Zn and La promoter were introduced into the catalyst. These two desorption peaks could be attributed to weak adsorption and strong adsorption of hydrogen on the surface of nickel. The high temperature desorption

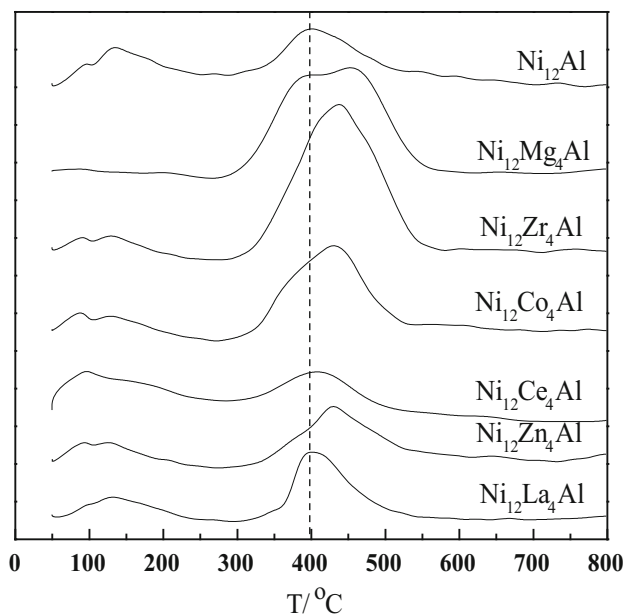


Fig. 5 H_2 -TPD profiles of nickel-based catalysts

peak (400 °C) shifted to the low temperature direction. The area of high temperature desorption peak was significantly increased when the catalyst was added with La, Co and Zr. This indicated that the spillover hydrogen and the quantity of activate hydrogen on the catalyst surface were increased. The Co has also an important catalytic activity in Fischer–Tropsch synthesis, but the ability to stick to its metallic cobalt is weak in harsh environment. There is a strong interaction between Ni and Zr, which makes it easy to form Ni-ZrO_2 and reduces the dispersion of nickel. The introduction of La promoter not only increased the number of spillover hydrogen on the catalyst surface, but also reduced the activation temperature of the spillover hydrogen.

Conclusion

To develop a high reaction activity and anti-coking coal to natural gas CO methanation catalyst, La, Zn, Ce, Co, Zr and Mg additives were introduced to the $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ during catalyst preparation. The rare earth metal La, Zr and Ce can effectively improve the dispersion of NiO on the surface of the support. This makes the nickel grains become easier reduced and gives higher catalytic activity. The La promoter introduced into the catalyst could effectively increase the amount of easily reduced NiO and provide more active centers. It was beneficial to generate active carbon species, which increased the number of spillover hydrogen on the catalyst surface and reduced the activation energy of hydrogen in CO methanation reaction.

Acknowledgments We would like to thank Beijing Municipal Science and Technology Commission for the support of the project. Professor Shuren Hao is also appreciated for his constructive advice.

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