Effects of Promoters on the Structure, Performance, and Carbon Deposition of Ni-Al₂O₃ Catalysts for CO₂−CH₄ Reforming

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ABSTRACT: Modified Ni-Al₂O₃ catalysts with Ca, Co, and Ce species as promoters were prepared by the combustion method, and the structure, morphology, reduction characteristic, and CO₂−CH₄ reforming of the catalysts were discussed by X-ray diffraction (XRD), H₂-temperature-programmed reduction (H₂-TPR), energy-dispersive X-ray (EDX) mapping, NH₃-temperature-programmed desorption (NH₃-TPD), N₂ adsorption–desorption, thermogravimetric–differential thermal analysis (TG-DTG), and temperature-programmed hydrogenation (TPH) methods. The crystal size of Ni on Ca-Ni-Al₂O₃ was 16.97 nm, and the active component and additive were distributed well in the catalyst. Co-Ni-Al₂O₃ presented a surface area of 65.70 m²·g⁻¹ and a pore diameter of 161.60 nm. Ce-Ni-Al₂O₃ showed relatively stable nickel–aluminum spinel (NiAl₂O₄), which could not be easily reduced to the active component Ni. Evaluation results demonstrated that the performance of the catalysts followed the order Co-Ni-Al₂O₃ > Ca-Ni-Al₂O₃ > Ni-Al₂O₃ > Ce-Ni-Al₂O₃. Carbon deposition analysis showed that the carbon resistance of Ca-Ni-Al₂O₃ was poor and graphitic carbon was generated on the catalyst. However, Ce-Ni-Al₂O₃ showed less carbon deposition, which might have resulted from the lower activity of the catalyst.

1. INTRODUCTION

Emission of CO₂ and CH₄ gases is an important factor leading to global warming.¹⁻³ Clean and efficient utilization of CO₂ and CH₄ is urgent for improving our environment and for transforming the valuable carbon resources. CO₂−CH₄ reforming (CO₂ + CH₄ = 2H₂ + 2CO, DRM) discovered by Fischer and Tropsch is of great importance in industry and research. DRM can produce a kind of feed gas, syngas, for chemical production. Syngas can be used as a raw material for synthesis of carbonyl compounds and for Fischer–Tropsch synthesis.⁴⁻⁶

In the DRM process, cracking of methane (CH₄ = C + 2H₂) and the disproportionation reaction of carbon monoxide (2CO = CO₂ + C) are the main reasons for generation of carbon deposits, resulting in rapid deactivation of the used catalyst.⁷ Noble metal nanoparticles (such as Pd, Pt, Rh, etc.) presented better performance but their high cost restrains their large-scale application in industry.⁸⁻⁹ The Ni metal showed good catalytic performance comparable to noble metals, and the low price is beneficial for its wide use in DRM.¹⁰ However, sintering of Ni and carbon deposition are two reasons hindering the application of Ni-based catalysts for high-temperature reactions.¹¹,¹² Therefore, it has become the focus of researchers to improve the stability performance of catalysts by adjusting the preparation technology, adding promoters, and optimizing the reactive conditions.

Ji et al.¹³ prepared Ni-based catalysts by the solution combustion method. Results showed that the combustion flame was stable and lasted for a long time and that the prepared catalysts presented a small particle size, demonstrating good dispersion, resulting in high catalytic activity. Rezaei et al.¹⁴ found that the addition of CeO₂, ZrO₂, and La₂O₃ to MgO improved the specific surface area and that a 5 wt % Ni/5 wt % La₂O₃-95 wt % MgAl₂O₄ catalyst exhibited a higher area of 306 m²·g⁻¹. Mo et al.¹⁵ found that a 0.95 wt % La addition catalyst showed a Ni crystallite size of 7.71 nm and presented high performance. Alipour et al.¹⁶ reported that MgO, CaO, and BaO enhanced the activity of Ni-based catalysts, and the MgO-promoted catalyst showed higher activity due to the formation of a MgAl₂O₄ phase. Chawl et al.¹⁷ found that ZrO₂-, CeO₂-, K₂O-, and MgO-promoted Ni/Al₂O₃ catalysts exhibited good activity, stability, and long-term operation as compared to the unpromoted one. Wang et al.¹⁸ found that a Ca promoter could significantly reduce the grain size of Ni. And Ni-Ca-4, with Ca addition of 4 wt %, showed better
performance due to the small Ni size of 13.67 nm and high dispersibility of Ni and Ca elements. Al-Fatesh et al.\textsuperscript{15} studied the influence of Ca, Ce, and Zr promoters on Ni/γ-Al\textsubscript{2}O\textsubscript{3} stability, coke deposition, and H\textsubscript{2}/CO ratio for methane dry reforming. A 3\%Ni/γ-Al\textsubscript{2}O\textsubscript{3} catalyst promoted with 0.15\%Ce and 0.05\%Ca showed better performance. Zhu et al.\textsuperscript{20} reported that the initial oxidation state of CeO\textsubscript{2} (Ce\textsuperscript{3+}/Ce\textsuperscript{4+}) can be influenced by the calcination condition. Budiman et al.\textsuperscript{21} reported that the addition of cobalt to a nickel catalyst could suppress carbon deposition.

Effects of Ca, Co, and Ce promoters on the crystal structure, morphology characteristics, and CO\textsubscript{2}—CH\textsubscript{4} reforming performance of Ni-Al\textsubscript{2}O\textsubscript{3} catalysts prepared by the solution combustion method are investigated in this paper. By means of X-ray diffraction (XRD), H\textsubscript{2}-temperature-programmed reduction (H\textsubscript{2}-TPR), and other characterization methods, the structure—performance—carbon deposition relationship for the prepared catalysts and the reforming reaction is discussed.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterizations (Structure). 2.1.1. X-ray Diffraction (XRD) Analysis. Figure 1 shows the XRD spectra of the catalyst samples after calcination and reduction. There are obvious diffraction peaks for Ni-Al\textsubscript{2}O\textsubscript{3}, Ca-Ni-Al\textsubscript{2}O\textsubscript{3}, and Co-Ni-Al\textsubscript{2}O\textsubscript{3} at 2\(\theta\) = 43.3, 63.1, and 75.1\(^\circ\), respectively, belonging to the characteristic diffraction peaks of NiO with a good peak effect, indicating that NiO in the three catalysts shows a certain crystal structure. Diffraction peaks of NiAl\textsubscript{2}O\textsubscript{4} spinel can be observed at 2\(\theta\) = 31.4, 36.9, 44.7, 59.5, 65.2, and 77.5\(^\circ\) for the Ce-Ni-Al\textsubscript{2}O\textsubscript{3} catalyst. Some researchers have pointed out that the spinel is ascribed to a strong metal—support interaction, which might cause the appearance of NiAl\textsubscript{2}O\textsubscript{4} species detected only in the Ce-Ni-Al\textsubscript{2}O\textsubscript{3} catalyst. Peaks of NiO (Figure 1a) can be obviously detected in the samples of Ca-Ni-Al\textsubscript{2}O\textsubscript{3}, Co-Ni-Al\textsubscript{2}O\textsubscript{3}, and Ni-Al\textsubscript{2}O\textsubscript{3} catalysts, and the NiO intensity in the former two catalysts is more diffuse, indicating that the existence of Ca and Co promoters can improve the dispersion of the catalyst, showing a good “confinement effect”.

Figure 1b shows the XRD diagram of the promoted catalysts after reduction. The characteristic diffraction peaks of Ni were detected at 2\(\theta\) = 44.3, 51.6, and 75.7\(^\circ\). The intensity of Ni diffraction peaks of Ce-Ni-Al\textsubscript{2}O\textsubscript{3} is weaker, which might be related to the strong interaction between Ni and the support after reduction of NiAl\textsubscript{2}O\textsubscript{4} resulting in the improvement of dispersion and stability of the Ni metal. According to Scherrer’s formula\textsuperscript{25,26} \((D = 0.89\lambda / (\beta \cos \theta))\), the Ni crystal size of each catalyst is calculated at 2\(\theta\) = 51.6\(^\circ\), and the results are shown in Table 1. The crystal size of Ni follows the order Ni-Al\textsubscript{2}O\textsubscript{3} < Ca-Ni-Al\textsubscript{2}O\textsubscript{3} < Co-Ni-Al\textsubscript{2}O\textsubscript{3} < Ce-Ni-Al\textsubscript{2}O\textsubscript{3}.

Table 1. Size of Ni Metal of the Reduced and Spent Catalysts

| Catalyst          | Ni-crystal size (nm) | after reduction | after reaction | increasing rate (%) |
|-------------------|----------------------|----------------|---------------|---------------------|
| Ni-Al\textsubscript{2}O\textsubscript{3}     | 26.53                | 45.36          | 41.51         |
| Ca-Ni-Al\textsubscript{2}O\textsubscript{3} | 16.97                | 29.25          | 41.99         |
| Co-Ni-Al\textsubscript{2}O\textsubscript{3} | 11.61                | 34.03          | 65.88         |
| Ce-Ni-Al\textsubscript{2}O\textsubscript{3} | 34.63                | 32.28          | -7.29         |

2.1.2. Temperature-Programmed Reduction (H\textsubscript{2}-TPR). The reduction peaks of each catalyst are relatively dispersed from the H\textsubscript{2}-TPR profiles (Figure 2), and the reduction process mainly occurs between 400 and 900 °C. The H\textsubscript{2}-TPR profile can be divided into three regions according to the interaction between NiO and Al\textsubscript{2}O\textsubscript{3} reflected by the reduction temperature.\textsuperscript{27–29} The temperature of the reduction peak less than 500 °C belongs to free NiO, i.e., \(\alpha\)-NiO, implying a weak interaction between NiO and Al\textsubscript{2}O\textsubscript{3}. The peak around 500–
Table 2. Gaussian Fitting Results from H2-TPR Profiles of the Catalysts

| catalyst          | peak areas (au) | peak area proportion (%) |
|-------------------|-----------------|--------------------------|
|                   | \(\alpha\) (<500 °C) | \(\beta\) (500–700 °C) | \(\gamma\) (700–900 °C) | \(\alpha\) (<500 °C) | \(\beta\) (500–700 °C) | \(\gamma\) (700–900 °C) |
| Ni-Al2O3          | 11 059.72       | 53 724.81                | 29 258.74                | 11.76                  | 57.13                  | 31.11                  |
| Ca-Ni-Al2O3       | 25 770.94       | 51 594.41                | 33.31                    | 66.69                  |                        |                        |
| Ce-Ni-Al2O3       | 41 095.77       | 32 363.59                | 55.94                    | 44.06                  |                        |                        |
| Co-Ni-Al2O3       | 41 813.47       | 23 254.27                | 64.26                    | 35.74                  |                        |                        |

Figure 3. N2 adsorption—desorption profiles of the catalysts after reduction: (a) N2 adsorption—desorption isotherms; (b) pore size distributions; and (c) mesopore distributions.

700 °C is attributed to \(\beta\)-NiO, presenting a strong interaction with the support. And the high-temperature peak (more than 700 °C) is ascribed to \(\gamma\)-NiO, indicating a very strong interaction or the formation of spinel, for example, NiAl2O4. Gaussian fitting results from H2-TPR profiles are shown in Table 2. The promoted catalyst did not show \(\alpha\)-type NiO and the proportion of \(\gamma\)-type NiO was increasing, which may be due to the fact that the addition of the promoter strengthened the interaction between NiO and the carrier.30

According to Figure 2, it can also be seen that there is a small reduction peak around 445 °C for the Ni-Al2O3 catalyst, which can be attributed to \(\alpha\)-NiO peak. And there is no \(\alpha\)-NiO peak in the promoted catalysts. Peakfit software was used to treat the Ca-Ni-Al2O3 reduction profile. The result indicates that the reduction peaks of Ca-Ni-Al2O3 can be fitted as two peaks with the peak temperatures of 613 and 770 °C, demonstrating that Ca-Ni-Al2O3 shows a strong interaction. The positions and peak areas of Co-Ni-Al2O3 and Ce-Ni-Al2O3 are similar, and there are two reduction peaks at about 590 and 780 °C. According to XRD (Figure 1a) characterization, there is NiAl2O4 spinel in Co-Ni-Al2O3, which can be reduced only at a higher temperature. The spinel is undetected in Co-Ni-Al2O3, implying that some very small spinel particles might permeate into the lattice of the support.

2.1.3. N2 Physical Adsorption. 2.1.3.1. N2 Adsorption—Desorption Profiles. N2 adsorption—desorption isotherms (a) and pore size distributions (b) of all of the catalysts are shown in Figure 3. The isotherm adsorptionlines of different catalysts with Al2O3 as the support might be ascribed to type III.31 A feature of this type is that the adsorption heat of the adsorbate is less than its liquefying heat as the adsorption goes on, indicating that the interaction force of the adsorption molecule with the catalyst is higher than the interaction between the molecule and the used adsorbent, resulting in the enhancement of adsorption with the process. Additionally, in the range of \(P/P_0 = 0.4–1.0\), there is an obvious H3-type hysteresis loop for all four catalysts.

As shown in Figure 3a, the adsorption isotherms of Ni-Al2O3, Ca-Ni-Al2O3, and Co-Ni-Al2O3 samples show the same trend, while the isotherm of Ce-Ni-Al2O3 is relatively gentle. The hysteresis loop area of Ca-Ni-Al2O3 is larger, followed by Ni-Al2O3 and Ca-Ni-Al2O3, and the area of Ce-Ni-Al2O3 is very small. The pore size distribution of each catalyst is different, demonstrating that the promoter has a great impact on the pore size. The higher the value of \(dV/d \lg D\), the larger the number of holes present in the corresponding pore size range. Ce-Ni-Al2O3 has a smaller amount of holes than others, which might be related to the agglomeration of each species in the catalyst, forming an alloy (oxides) or nickel—aluminum spinel.

2.1.3.2. Pore Structure Parameters. The average pore size of the Ni-Al2O3 catalyst is around 16.54 nm (Table 3), belonging to mesoporous pores. However, the size of different promoted catalysts, especially Ca- and Co-promoted ones, is more than 50 nm, attributing to large pores. Furthermore, the pore size of each catalyst is quite different, resulting from different types of promoters. In addition, the area and pore volume of each promoted catalyst vary significantly, demonstrating that the incorporation of each promoter reduces the value of both pore structure parameters, which might be due to the metal oxide clusters blocking the pores.

Table 3. Specific Surface Area, Pore Volume, and Average Pore Diameter of the Catalysts

| catalyst          | \(A_{\text{BET}}\) (m2·g−1) | \(V\) (cm3·g−1) | \(d\) (nm) |
|-------------------|-------------------------------|-----------------|-----------|
| Ni-Al2O3          | 101.70                        | 0.320           | 16.54     |
| Ca-Ni-Al2O3       | 41.71                         | 0.270           | 213.71    |
| Co-Ni-Al2O3       | 65.70                         | 0.290           | 161.60    |
| Ce-Ni-Al2O3       | 27.38                         | 0.054           | 69.67     |
the contents of Ni and Ce in Ce-Ni-Al₂O₃ are 18.7 and 2.93, quite different from their theoretical loading, and both of them are decreased, which might be attributed to NiAl₂O₄ spinel in the sample, wrapping Ni and Ce elements. Additionally, the content of Co element in Co-Ni-Al₂O₃ is 21.86, far more than 4 (the theoretical value), which could be ascribed to the mobilization of Co species to the surface of the catalyst at high calcination and reduction temperatures.

Figure 4 shows the EDX-mapping photos of the prepared catalysts. It is not difficult to note that the dispersion effect of Ni and Ca elements on the Ca-Ni-Al₂O₃ catalyst is better and more uniform. The distribution of Co on Co-Ni-Al₂O₃ is more obvious, while the distribution of Ni is relatively poor, which may have resulted from the fact that the introduction of Co might partially cover the active component Ni, resulting in the decrease of the number of active centers, which is consistent with the high loading of Co element in EDX characterization (Table 4).

2.1.5. NH₃-Temperature-Programmed Desorption (NH₃-TPD) Profiles of the Catalysts. To test the surface acidity of the prepared catalysts, NH₃-TPD profiles were recorded as shown in Figure 5. From the interaction between the acid
center and NH₃ molecule on the surface of the catalyst, the acidity property of each sample is approximately determined by the NH₃ desorption temperature. Generally, the acid center with desorption temperature lower than 300 °C is ascribed to a weak acid, and the temperature of a strong acid center is higher than 600 °C, while the acid center with temperature between 300 and 600 °C is attributed to a medium—strong acid. For Ce-Ni-Al₂O₃ three NH₃ desorption peaks are detected around 220, 550, and 720 °C, while only one peak, higher than 600 °C, can be observed for both Ca-Ni-Al₂O₃ and Co-Ni-Al₂O₃ samples, indicating that weak, medium—strong, and strong centers can be observed on Ce-Ni-Al₂O₃ and that only strong centers can be found on Ca-Ni-Al₂O₃ and Co-Ni-Al₂O₃. There is no NH₃ desorption peak on the Ni-Al₂O₃ catalyst, indicating that the surface of the catalyst without a promoter does not show any acid property, indicating that the addition of the promoter could change the surface acid property of the material. The NH₃ desorption peak area of Ca-Ni-Al₂O₃ is larger than those of others, revealing that there are more strong acid centers on the catalyst, while the number of acid centers on Co-Ni-Al₂O₃ is relatively less, but their acid strength is very high from the peak temperature around 820 °C. Studies have reported that Al₂O₃ has both acid and alkali centers, and transition-metal oxides, vacant metal ions that are not covered by oxygen, can form coordination bonds with basic materials, exhibiting acid centers, and alkali centers also exist in the system. Compared with Ni-Al₂O₃, the incorporation of promoters increased the acidity of the catalysts, indicating that those metal oxides may change the electron distribution on the surface of the support.

Gaussian fitting results from NH₃-TPD profiles of the catalysts are shown in Table 5. The temperature range before 400 °C belongs to weak acid sites, which can correspond with Lewis acids and has a little influence on improving the catalytic efficiency. It can be observed in Ce-Ni-Al₂O₃ that there are many weak acid sites after adding the promoter Ce. Strong acid sites can be related to Bronsted acid sites, which appeared at 650–900 °C. It is speculated that strong acid sites showed strong decomposition effects for C–C, C–H, and C–O. A higher amount of strong acid sites on Ca-Ni-Al₂O₃ and Co-Ni-Al₂O₃ may lead to better catalytic performance. Additionally, medium acid sites were present on Ca-Ni-Al₂O₃ and Co-Ni-Al₂O₃ in the temperature range of 400–650 °C.

### Table 5. Gaussian Fitting Results from NH₃-TPD Profiles of the Catalysts

| catalyst           | weak acid (200–400 °C) | medium acid (200–400 °C) | strong acid (200–400 °C) |
|--------------------|------------------------|--------------------------|-------------------------|
| Ca-Ni-Al₂O₃        | 556.75                 | 5493.61                  |                         |
| Co-Ni-Al₂O₃        |                        | 228.76                   |                         |
| Ce-Ni-Al₂O₃        | 1218.61                | 1349.19                  | 927.76                  |

Figure 6 shows the conversions of CH₄ and CO₂ for promoted catalysts are higher than those of Ni-Al₂O₃. Among them, the CH₄ conversion of Ce-Ni-Al₂O₃ is better with an average value of 68.56, and the values of Ca-Ni-Al₂O₃, Co-Ni-Al₂O₃, and Ni-Al₂O₃ are 53.99, 51.30, and 31.29, respectively. Naeem et al. reported that catalysts with a basic support could enhance the adsorption of acidic gas, such as CO₂. High performance of the modified catalyst might result from the enrichment of surface electrons and the presence of alkaline oxides in the Ni-based catalyst, which is beneficial for the adsorption of acid gas CO₂ and increasing the conversion of CO₂. In addition, the conversions of CH₄ and CO₂ fluctuate in a certain range, which might be due to the simultaneous occurrence of carbon deposition and removal in CO₂–CH₄ reforming, and the reforming reaction might be in the process of dynamic equilibrium.

Figure 7 shows H₂ and CO selectivity of each catalyst. The trend of H₂ and CO selectivity of all of the catalysts is in line with the conversion trend of feed gases. The H₂ and CO selectivity values of Co-Ni-Al₂O₃ are higher with 31.36 and 34.83, respectively, which are relatively poor for Ca-Ni-Al₂O₃ with values of only 28.93 and 29.64, respectively. And the values are 26.37 and 31.16 for Ni-Al₂O₃ and 17.53 and 20.81 for Ce-Ni-Al₂O₃.

Figure 8 shows H₂/CO ratios for the different catalysts. For Ni-Al₂O₃, Co-Ni-Al₂O₃, and Ce-Ni-Al₂O₃, the ratios of H₂/CO are less than unity, which may be due to the existence of the reverse water gas shift reaction (CO₂ + H₂ = CO + H₂O, RWGS) in the reforming process, resulting in the decreasing of H₂ generated by methane cracking and the increasing of CO. Compared to the unpromoted sample, the ratios of promoted ones basically showed an increasing trend, which may be due to the fact that the promoted catalysts inhibit the RWGS process. Additionally, the ratio of H₂/CO for Ca-Ni-Al₂O₃ is higher than unity, the reason of which needs to be further studied from the aspects of the microstructure of the used catalyst and the mechanism of the reforming reaction.

Figure 9 gives the time average results of catalyst performance. It can be seen that the comprehensive properties of the four catalysts are quite different. According to calculation, the H₂ yields (product of conversion and
selectivity) of Ni-Al₂O₃, Ca-Ni-Al₂O₃, Co-Ni-Al₂O₃, and Ce-Ni-Al₂O₃ are 8.25, 15.62, 16.09, and 5.01, respectively. The better performance of Ca-Ni-Al₂O₃ might be related to the uniform distribution of Ca and Ni elements on the surface of the support. And the higher performance of Co-Ni-Al₂O₃ may be due to the synergistic effect between Co and Ni species, resulting in the fact that the active component Ni is not easy to accumulate together in the reaction process. In addition, compared with Ni-Al₂O₃ all promoted samples present high CH₄ and CO₂ conversions, which is similar to Mehran's research;¹⁴ that is, the incorporation of the promoter could enhance the RWGS process, remarkably reducing the H₂ yield. And the RWGS also contributed to the higher CO₂ partial pressure in the reforming products.³⁸

2.3. Characterization of the Spent Catalysts (Carbon Deposition)

2.3.1. X-ray Diffraction (XRD). Figure 10 shows the XRD profiles of the catalysts after the reforming reaction. All four catalysts preserve good stability at a high reaction temperature (800 °C). The spent catalysts show a diffraction peak at 2θ = 25.7°, which is attributed to carbon deposition, with the intensity order of Ca-Ni-Al₂O₃, Co-Ni-Al₂O₃, and Ce-Ni-Al₂O₃. However, the absence of the carbon deposition peak in Ni-Al₂O₃ did not result from its high antoking performance, but the lower catalytic performance (Figure 6) might be responsible for its little carbon deposition.

The Ni crystal size of the spent catalyst is also calculated at 2θ = 51.6° and shown in Table 1. It can be seen that the Ni size of Ca-Ni-Al₂O₃ and Co-Ni-Al₂O₃ is smaller than that of Ni-Al₂O₃, indicating that promotion by Ca or Co species could effectively improve the “dispersion effect” of the Ni-based catalyst. After the reforming process, the Ni size increasing rates of Ni-Al₂O₃, Ca-Ni-Al₂O₃, and Co-Ni-Al₂O₃ are 41.51, 41.99, and 65.88, respectively. Obviously, the Ni metal in Co-Ni-Al₂O₃ is agglomerated seriously after the reforming process at a high temperature, presenting a poor sintering resistance. However, the size of the Ni crystal in Ce-Ni-Al₂O₃ is reduced from 34.63 to 32.28 nm with an increasing rate of ~7.29, which might have resulted from the formation of NiAl₂O₄ spinel observed in Figure 10.

2.3.2. Thermogravimetric-Differential Thermal Analysis (TG-DTG). Figure 11 shows the TG-DTG profiles of the used catalysts after the reforming process. TG profiles of Ni-Al₂O₃, Ce-Ni-Al₂O₃, and Co-Ni-Al₂O₃ are basically the same, with the weight loss of 1.3, 5.9, and 7.0, respectively, while the weight loss of Ca-Ni-Al₂O₃ is about 35. The TG profiles of all of the used catalysts first show a decreasing trend and then an increasing one before 500 °C, and after which the profiles decrease again. The first decline is due to the desorption of some small molecular gases (N₂, O₂, H₂O, ...
obviously, among which the peak of Ca-Ni-Al2O3 appears at loss rate peak temperature of each used catalyst is different. In our previous work,38 which presented a fibrous or rodlike morphology. In addition, the increase of the TG profile could be attributed to the increase of the catalyst mass caused by the oxidation of metals Ni and Co in the catalyst at high temperatures in air.

It can be seen from Figure 11b that the maximum weight loss rate peak temperature of each used catalyst is different obviously, among which the peak of Ca-Ni-Al2O3 appears at about 575 °C, demonstrating that the deposited carbon is probably in the form of filamentous one. However, the peak temperature of Co-Ni-Al2O3 and Ce-Ni-Al2O3 appears around 650 °C, indicating that the deposited carbon might have been converted into graphitic carbon. Graphitic carbon has been verified by Raman test from our previous literature15 and it can also be observed by XRD (Figure 12), which cannot be

Figure 11. TG-DTG profiles of the spent catalysts: (a) TG profiles and (b) DTG profiles.

Figure 12. Temperature-programmed hydrogenation (TPH) profiles of the catalysts after the reaction.

removed by CO2 (C + CO2=2CO) and needs a higher temperature to be oxidized with air. Additionally, the second weight loss rate peak of Ce-Ni-Al2O3 appears at about 800 °C, indicating that the graphitization degree of the carbon deposit on Ce-Ni-Al2O3 is higher, which might be the important reason for its poor catalytic performance (Figure 9).

2.3.3. Temperature-Programmed Hydrogenation (TPH). Figure 12 shows the TPH profiles of the spent catalysts. There are two hydrogenation peaks for Ce-Ni-Al2O3 at 390 °C and 800 °C, and only one peak for Ni-Al2O3 and Co-Ni-Al2O3 around 340 °C. Literature studies39,40 showed that the hydrogenation peak between 200 and 300 °C is ascribed to amorphous carbon (α type), the peak ranging from 300 to 500 °C is attributed to filamentous carbon (β type), and the peak above 600 °C belongs to inert graphitic carbon (γ type). It can be seen from the TPH profiles that the β-type carbon exists in all of the catalysts and that the α-type carbon is absent. A hydrogenated peak around 800 °C can be observed on Ce-Ni-Al2O3, which might be due to the electronic effect of the strong redox performance of Ce species that enabled implantation of the deposited carbon species into the support with strong interaction with the catalyst. Therefore, γ-type carbon is difficult to remove at high temperatures through hydrogenation. In addition, there is almost no hydrogenation peak for Ca-Ni-Al2O3, but there is a large amount of carbon deposited on the catalyst according to the TG-DTG profile. This might have resulted from the fact that the carbon deposit on the catalyst is mainly composed of filamentous carbon, which went deep into the complex pore structure of the catalyst in the reforming process and could not react with H2 in the hydrogenation test.41

3. CONCLUSIONS
Catalysts promoted by different additives prepared by the solution combustion method present great difference in crystal structure, surface acidity, specific surface area, pore structure parameters, and so on, which affect the performance of the CO2−CH4 reforming reaction. Ca-Ni-Al2O3 showed a small Ni crystal size, strong interaction between the metal and the support, and large specific surface area. The good distribution of Ca and Ni on the surface of the catalyst makes the CO2−CH4 reforming performance better. Additionally, carbon deposition on the Co-Ni-Al2O3 surface is dominated by type β, and the poor catalytic performance of the Ce-Ni-Al2O3 catalyst is due to the existence of NiAl2O4.

4. EXPERIMENTAL SECTION
4.1. Catalyst Preparation. Ni-Al2O3 catalysts with different promoters were prepared by the combustion method.18 With Ni, Al, and Ca (Ce or Co) elements in stoichiometric ratios of 20, 76, and 4 wt %, respectively, the reaction mixture was stirred for 2 h and aged for 3 h. The prepared catalysts were labeled Ca-Ni-Al2O3, Ce-Ni-Al2O3, and Co-Ni-Al2O3.

4.2. Catalyst Characterization. The crystal structure of the catalyst was analyzed by the XRD method with a Rigaku D/max2500 X-ray diffractometer from Japan. An Autosorb-2 physical adsorption instrument (Quantachrome Instruments) is used for N2 adsorption–desorption
characterization and N2 is used as the adsorbate, and the isothermal adsorption–desorption determination was performed at −196 °C. The specific surface area of the catalyst can be obtained by the Brunauer–Emmett–Teller (BET) formula, and the pore volume and pore size distribution can be obtained by the Barrett–Joyner–Halenda (BJH) formula.

The actual content of the active component Ni was determined using an EDX3600B element analyzer from Jiangsu Tianrui Co., Ltd., China. The tube voltage and current were 45 kV and 300 mA, respectively.

H2-TPR characterization of the catalyst was performed on a Chem-BET pulse TPR/TPD from Quantachrome Instruments company.

NH3-TPD was used to characterize the surface acidity of the catalyst with a Tianjin Xianquan TP-5080 adsorption instrument from China as the experimental device, which was carried out with a sample mass of 100 mg and He as the carrier gas.

TG-DTG profiles of the used catalysts were recorded with an SDTQ600 instrument of TA company (USA) in an air atmosphere, with the flow speed of 100 mL·min−1.

The amount and type of carbon deposited on the used catalyst were also tested by the TPH method. The test was carried out also on a Chem-BET pulsar TPR/TPD instrument from Quantachrome Instruments company. The sample (50 mg) was pretreated at 673 K in He flow for 1 h, and then the atmosphere was switched to a 5% H2 + 95% Ar mixture. The TPH experiment was performed in a 100 mL·min−1 mixture gas flow, and the temperature was increased to 1273 K at a heating rate of 10 °C·min−1 from ambient temperature.

4.3. Catalyst Evaluation. The reactor is a fixed-bed quartz tube (6 mm, inside diameter (i.d.); Figure 13) with a catalyst particle size of 40–60 mesh and loading amount of 1.00 g. Before the reaction, the catalyst was reduced in H2 (30 mL·min−1) for 3 h at t = 650 °C. Then, the feed gas was introduced to the reaction tube under the conditions of t = 800 °C, atmospheric pressure, CH4 flow rate of 60 mL·min−1, CO2/CH4 = 1 (volume ratio), GHSV = 14 400 h−1 and reaction time of 5 h. Product gases were detected online by a gas chromatograph.

Figure 13. Catalyst evaluation device.

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Notes
The authors declare no competing financial interest.
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