Effect of Ca Promoter on the Structure, Performance, and Carbon Deposition of Ni-Al₂O₃ Catalyst for CO₂-CH₄ Reforming

Huanhuan Wang, Wenlong Mo,* Xiaoqiang He, Xing Fan, Fengyun Ma, Shuai Liu, and Dihumar Tax

ABSTRACT: Ni-Al₂O₃ catalyst with different Ca abundance for CO₂-CH₄ reforming was prepared by the solution combustion method. By some mature characterization methods, such as XRD, H₂-TPR, EDX mapping, TEM, TPH and TG-DTG technologies, and the reforming experiment, the effect of Ca content on the structure, reforming performance, and carbon deposition of Ni-Al₂O₃ catalyst was investigated. Results showed that the grain size of active component Ni on the 4 wt % Ca-modified catalyst (Ni-Ca-4) was small (13.67 nm), presenting good dispersion, and that Ni and Ca elements were well distributed on the support, which was more conducive to the CO₂-CH₄ reforming. Evaluation results showed that activity of Ni-Ca-4 was higher than the others, with CH₄ and CO₂ conversions of 52.0 and 96.7%, respectively, and H₂/CO ratio close to unit. Carbon deposition performance, and carbon deposition of Ni-Al₂O₃ catalyst was investigated. Results showed that the grain size of active component Ni on the 4 wt % Ca-modified catalyst (Ni-Ca-4) was small (13.67 nm), presenting good dispersion, and that Ni and Ca elements were well distributed on the support, which was more conducive to the CO₂-CH₄ reforming. Evaluation results showed that activity of Ni-Ca-4 was higher than the others, with CH₄ and CO₂ conversions of 52.0 and 96.7%, respectively, and H₂/CO ratio close to unit. Carbon deposition proposed that the amount of carbon deposited on the surface of Ni-Ca-4 was lower (18%), and the type of carbon was attributed to amorphous carbon, indicating that 4 wt % Ca-promoted catalyst presented better anticarbon deposition performance.

1. INTRODUCTION

In the process of using fossil fuels, a large amount of CO₂ will be generated, resulting in increasingly serious global warming (e.g., greenhouse effect). Realizing efficient conversion and utilization of greenhouse gases CO₂ and CH₄ has become a widespread concerning problem. CO₂ reforming of CH₄ (CO₂ + CH₄ = 2CO + 2H₂, CRM) can produce a synthesis gas with the H₂/CO of about 1:1, which can be directly used to produce methanol and Fischer–Tropsch synthetic liquid fuels. CRM can not only effectively utilize CO₂ and CH₄ but also produce syngas (H₂ and CO). However, the reforming process has shown the characteristics of endotherm, reversibility, carbon deposition, and so on. On the other hand, high reaction temperature (more than 650 °C) would lead to sintering of the active component and deposition of carbon on the catalyst surface (CH₄ = C + 2H₂), resulting in catalyst deactivation. The key to the conversion of the two typical greenhouse gases into a valued product is to prepare a high-performance catalyst with high activity, good stability, and excellent anticokeing property. Precious metals (Ru, Pt, Ir, etc.) present good performance, especially high activity and anticarbon deposition ability, but it is difficult to realize industrialization because of their high cost. It has been reported that metals such as Ni and Co have catalytic properties comparable to those of precious metals, and their cost is relatively low, which have been widely used in the research of CRM reaction. However, at high temperature, the active component Ni grains of the nickel-based catalyst were prone to sintering, and the surface of the catalyst was prone to carbon deposition (CH₄ = C + 2H₂), leading to catalyst deactivation. It is known that promoters have great influence on the performance of catalyst. Literature showed that the catalyst with La content of 0.95 wt % presented small average Ni grain size of 7.71 nm and exhibited good catalytic performance at 800 °C with CH₄ and CO₂ conversions of 94.37 and 97.15%, respectively. Endurance test (150 h) demonstrated that the conversion of CH₄ on the La-Ni-1 catalyst was around 95%, higher than that of La-Ni-0 (without lanthanum addition). The carbon deposition rate of the catalyst was only 1.63 mg/(g cat h), showing both high activity and good stability, which were attributed to the “confinement effect” of La₂O₃ to Ni crystalline grain, inhibiting the sintering of active components, preventing the carbon deposition, and improving the catalytic reforming performance. Therefore, the small size of Ni grain can inhibit the formation of carbon deposition, prevent the sintering of active component, and improve the performance of catalyst, showing a good size effect. The effect of Cu and Zn on
Ni-Al₂O₃ catalyst for methane reforming to produce syngas was studied. It was found that the increase in Cu content would improve CO selectivity and reforming stability. Also, the addition of Zn promoter is beneficial to CH₄ conversion and H₂ yield. SEM results showed that the introduction of Cu made the distribution of Ni on Al₂O₃ more uniform. TGA results presented that the introduction of Cu and Zn made the catalyst activity more stable, and Cu was more positive on the stable effect of the catalyst than Zn. The catalytic effect of Rh as an additive on the Co-based catalyst for CRM reaction was reported, and it is found that reduction performance of Co oxides on CeO₂ can be greatly improved by adding 0.1% Rh.20 Ni-Ybₓ/SiC (x = 2%, 4%, 6%, 10%, x-mass fraction) catalyst was prepared by the impregnation method, and the influence of promoter Yb₂O₃ on the reaction performance of the catalyst for CH₄-CO₂ reforming was investigated.21 Results showed that the appropriate addition amount of Yb was 4%. At 800 °C, Ni-Yb₄/SiC and Ni-Yb₆/SiC presented excellent catalytic activity and stability, with high CH₄ and CO₂ conversions of 90%. It is explained that the introduction of promoter could effectively inhibit the sintering of Ni particles and reduce the amount of carbon deposition.

In this paper, Ni-Al₂O₃ catalyst with different Ca contents was prepared by the solution combustion method. By means of X-ray diffraction (XRD), H₂ temperature-programmed reduction (H₂-TPR), energy dispersive X-ray (EDX) mapping, transmission electron microscopy (TEM), thermogravimetric (TG-DTG) analysis, and other characterization methods, the influence of Ca additive on the catalyst structure, reaction performance, and carbon deposition of CO₂-CH₄ reforming was investigated. The effect of Ca promoter on the amount and type of carbon deposited on the catalyst was investigated, and carbon resistance by calcium has also been discussed. Furthermore, the effect of temperature on the conversion of carbon removal for the used catalysts was obtained, and thus, the main carbon removal temperature region of all samples was selected. Also, kinetic parameters of carbon removal reaction at 480–680 °C were calculated by the first-order kinetic model using the Coast–Redfern method, and the effect of Ca species on the activation energy of carbon removal was analyzed.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. 2.1.1. XRD Analysis. Figure 1 gives XRD patterns of the prepared catalysts. The diffraction peaks at 2θ = 37.1°, 45.2°, and 65.5° are ascribed to Al₂O₃ species, and all the catalysts show the same peak positions, indicating that Al₂O₃ as a support was not destroyed after being modified with different Ca contents. The peaks at 2θ = 43.2°, 62.7°, and 75.8° are attributed to crystalline NiO (JPCDS 73-1519), the Ni-Ca-0 catalyst presents the highest intensity, and its peak shape was relatively sharp. The NiO diffraction peak intensity of Ni-Ca-n (n = 1, 2, 4, 6) catalyst was decreased with the modification of calcium, indicating that Ca could promote the NiO dispersion on the support surface. In addition, the diffraction peaks of Ca species have not been identified for all the samples, implying that it might exist in amorphous form or enter into the lattice of Al₂O₃ rather than in the form of crystal.

Figure 1b depicts the XRD profiles of the samples after reduction. The characteristic peaks of Al₂O₃ at 2θ = 37.1°, 45.4°, and 66.4° still exist, the peak position and intensity of which are basically the same as previous reduction, indicating that Al₂O₃ is stable in the reduction process at high temperature (T = 650 °C), and its crystal structure has not been significantly damaged. Meanwhile, the peaks of active component Ni that appear at 2θ = 44.3°, 52.2°, and 76.4° almost disappear, demonstrating that all the catalysts have been successfully reduced. Among them, the Ni peak intensity of Ni-Ca-0 is higher than the others, which was due to the agglomeration of Ni metal on the surface of the support without any promoter at high temperature. Promoted with calcium, the peak intensity of Ni on the support decreases obviously; this might be attributed to the fact that Ca can form a fortress around the active component Ni to prevent the aggregation of Ni grains at high temperature. As the content of Ca is ≤4 wt %, the peak intensity of Ni at 2θ = 52.2° decreases gradually, which may be attributed to the introduction of Ca, inhibiting the crystallization of the active component. As the content of Ca is >4 wt %, the diffraction peak of Ni becomes sharper, which might be ascribed to the agglomeration of Ni due to the excessive content of Ca, not conducive to the improvement of the dispersion of active component.22

In addition, according to Scherrer’s law (d = 0.89λ/βcosθ), the Ni grain size at 2θ = 52.2° is calculated, and the results are shown in Table 1. It can be seen from Table 1 that the grain size of the active component Ni on all the promoted catalysts is smaller than that of Ni-Ca-0, with the size of Ni-Ca-4 of 13.67 nm only, indicating that better Ni dispersion has been realized by the confinement effect by the used promoter. 2.1.2. H₂-TPR Analysis. Figure 2 shows the H₂-TPR profiles of the fresh catalysts. It can be seen from Figure 2 that there are three types of reduction peaks in the catalyst. Generally speaking, different types of reduction peaks represent the different degrees of interaction between the active component

Figure 1. XRD patterns of the catalysts: (a) after calcination and (b) after reduction.
and support. The reduction peak around 400 °C illustrates weak interaction between NiO (labeled as α-type) and Al2O3. Although the catalyst has good reducibility, it is easy to be inactivated by sintering under high temperature or long-time reaction process. The reduction peak observed at about 600 °C demonstrates strong interaction of NiO (β-type) with Al2O3 support, showing better stability. The peak around 800 °C is attributed to Ni species (γ-type) that have a more strong interaction with Al2O3, such as NiAl2O4 spinel, or attributed to NiO (or lattice NiO) entering the crystal phase of Al2O3 support. No characteristic diffraction peak of NiAl2O4 was observed in Figure 2. It is consistent with the result of the reported reference;23 that is, the introduction of Ca into the catalyst could inhibit the formation of spinel, indicating that the active component precursor in the promoted catalyst mainly existed in the form of β-type and lattice NiO. It could be reduced at the temperature higher than 600 °C.

According to Figure 2, the Ni-Ca-0 catalyst has a small hydrogen consumption peak at around 430 °C, belonging to α-type NiO. A relatively big peak appears at 600 °C, presenting strong interaction with the support. Also, an obvious γ-type reduction peak can be observed at about 800 °C. The reduction peak temperature of the modified catalyst is higher than the unmodified one, and with the increase in calcium addition, the temperature of γ-type peak increases first to the maximum value of 850 °C for Ni-Ca-2 and then decreases slightly. The difference of the reduction peak temperature for the promoted catalysts may be due to the variation of the interaction between the active component and support that resulted from different calcium content. It can also be seen from Figure 2 that the reduction peak area of Ni-Ca-4 is larger, indicating that there might be more active sites on the catalyst after reduction, which is beneficial to reduce the amount of carbon deposition.24

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

| catalyst | Ni-cluster (d/nm) | after reduction | after reaction | increasing rate (%) |
|----------|------------------|----------------|---------------|---------------------|
| Ni-Ca-0  | 26.53            | 45.36          | 41.51         |
| Ni-Ca-1  | 16.54            | 30.82          | 46.33         |
| Ni-Ca-2  | 13.76            | 23.16          | 40.57         |
| Ni-Ca-4  | 13.67            | 25.17          | 45.68         |
| Ni-Ca-6  | 16.77            | 24.51          | 31.59         |

2.1.3. EDX-Mapping Analysis. To analyze the distribution of each element on the surface of catalyst, EDX mapping test was carried out, as shown in Figure 3. It can be seen from Figure 3 that all elements (Al, Ca, Ni, and O) were uniformly dispersed within the entire surface of the promoted catalysts, indicating that the solution combustion method is suitable for the preparation of catalyst system with high dispersion. It can also be seen from Figure 3 that with the increase in calcium content, the number of Ca element particle on the surface of catalyst shows an obvious increasing trend, and the homogeneity of the distribution of Ni element has not changed obviously, which shows that the addition of promoter has little effect on the dispersion of active metal. In addition, the distributions of Ni and Ca elements are more uniform as the high content of Ca of 4 wt %, which might be more conducive to CO2-CH4 reforming.

2.2. Catalytic Performance Test. Figure 4 shows the results of CH4 and CO2 conversions of the prepared catalysts in 5 h. CH4 conversion of each promoted catalyst is between 45 and 60%, higher than that of Ni-Ca-0, while CO2 conversion of the modified catalyst ranges from 80 to 95%, well higher than that of CH4 conversion, which may be due to the reverse water gas shift conversion reaction (CO2 + H2 = CO + H2O, RWGS). Specifically, with the increase in Ca content, CH4 conversion increased first and then decreased. Among them, the CH4 conversion of Ni-Ca-2 is up to 60%, while the activity of Ni-Ca-6 sample (CH4 and CO2 conversions) is lower, which might be caused by the loss of dispersion effect due to the aggregation of Ca species or by the covering of active component sites on the catalyst (the dispersion of Ni in Ni-Ca-6 in the EDX mapping diagram is poor). CO2 conversions of Ni-Ca-1, Ni-Ca-4, and Ni-Ca-2 are relatively high in the range of 92.5 to 97.5%, indicating that the activity of the Ni-based catalyst can be improved with the addition of calcium less than 4 wt %. As the amount of Ca added is more than 6 wt %, the conversions of CH4 and CO2 are obviously reduced.

Figure 5 shows the H2 and CO selectivity of the catalyst. H2 selectivity of Ni-Ca-1 is more than 32.5%, while the selectivity of Ni-Ca-4 and Ni-Ca-6 is between 28 and 35%, and Ni-Ca-2 and Ni-Ca-0 show lower H2 selectivity. It is noted that the variation rule of the selectivity for each catalyst with the addition of Ca is not consistent with the rule of activity, which may be caused by the different diffusion performances of the product molecules in the catalyst. In contrast, CO selectivity of the catalyst is higher than that of H2. Combined with high CO2 conversion, it is speculated that the difference might be related to the formation of water (H2 + CO2 = CO + H2O) in the by-product; that is, the reverse reaction of water and gas exists in the reforming reaction.

According to Figures 4 and 5, time average evaluation results of the promoted catalysts are calculated, as shown in Figure 6. H2/CO values of Ni-Ca-1 and Ni-Ca-4 are close to unit, while the values of Ni-Ca-0, Ni-Ca-2 and Ni-Ca-6 are less than unit with CO selectivity higher than H2 and the water gas shift reaction (CO2 + H2 = CO + H2O) may be responsible for the lower H2/CO value, reducing the H2 amount in the product and increasing the CO content. Figure 6b shows that the conversions of CH4 and CO2 of Ni-Ca-4 catalyst are 52.0 and 96.7%, respectively, and that the H2/CO value of synthesis gas is closer to 1, so the comprehensive performance of Ni-Ca-4 catalyst is better than the others.25,26 Combined with the catalyst characterization, excellent performance of Ni-Ca-4...
Figure 3. EDX mapping photos of the catalysts after reduction.

Figure 4. Conversions of (a) CH$_4$ and (b) CO$_2$ of the catalysts.
may be related to the following reasons. On the one hand, the distributions of Ni and Ca elements on the 4 wt % calcium-modified catalyst are more uniform, which is more conducive to the reforming reaction. On the other hand, the reduction peak area of Ni-Ca-4 is larger, resulting in more active sites for CO$_2$-CH$_4$ reforming.

Figure 7 discusses the effect of the auxiliaries on catalyst performance. Relevant reports showed that the active component Ni in the supported catalyst unmodified by the promoter would be subjected to serious sintering. In addition, the addition of promoter would increase the reaction activity and improve the specific surface area of the catalyst, preventing carbon deposition on the surface of the modified catalyst, showing higher performance.\textsuperscript{27–30} As shown in Figure 7, Ni/Al$_2$O$_3$ catalyst modified by CaO shows preferable dispersion by the confinement effect and exhibits better catalytic performance during the high-temperature reaction process. The reason might be derived from that the presence of CaO would reduce the particle size of the metal Ni, improve the antisintering property of the active metal, and ensure the catalyst stability. Additionally, the addition of CaO would provide more active sites by the confinement effect and enhance CO$_2$ adsorption.\textsuperscript{16,51}

In conclusion, the difference of the performance of each modified catalyst is not significant. To further compare the potential stability of the catalyst, the surface carbon deposition of each sample after the reaction was characterized and analyzed.

2.3. Analyses of the Spent Catalysts. 2.3.1. XRD Analysis. Figure 8 shows the XRD profiles of the spent catalysts. Compared to Figure 1b, the spent catalysts present the similar Al$_2$O$_3$ XRD peaks at 20 = 37.1°, 45.1°, and 65.6°, indicating good stability of the Al$_2$O$_3$ support during the CO$_2$-CH$_4$ reforming process. The diffraction peaks of nickel for the
spent catalysts appear at 2θ = 44.3°, 52.2°, and 76.4°, the same as the fresh ones, while the peak intensity of Ni is significantly increased, indicating that dispersion of the active component Ni is weakened after the reforming reaction. This might be attributed to the agglomeration of Ni particles on the surface of the support as the catalyst served at high temperature (800 °C) for a long time. Among them, the Ni peak of Ni-Ca-0 was also sharp, presenting that the crystallinity of the Ni metal is higher. Also, the peak intensity of Ni crystal of the promoted catalyst is also relatively weak, demonstrating that the introduction of Ca is beneficial to inhibiting the sintering of Ni. According to Scherrer’s law, the Ni grain size of the used catalyst at 2θ = 52.2° was calculated, as shown in Table 1. It can be seen that the Ni grain size on each catalyst increases in varying degree after the reforming reaction, which is due to the sintering of Ni. Also, the Ni size on all the promoted catalysts is also smaller than that of Ni-Ca-0, which shows that the introduction of Ca is beneficial for inhibiting the sintering of active component. In addition, the Ni size increasing rate can be used to specify the sintering degree of metal supported on the support. Among them, Ni-Ca-0 presents larger Ni grain size of 45.36 nm, with the increasing rate of 41.51%, while the increasing rate of Ni on Ni-Ca-6 is lower (31.59%), indicating good stability.

It can also be seen from Figure 8 that the spent promoted catalysts show an obvious characteristic peak at 2θ = 25.4°, which is ascribed to carbon deposition, and the peak type varies with the amount of calcium loading. Among them, the peak intensity of Ni-Ca-2 and Ni-Ca-6 is smaller, indicating better anticoking performance. While the amount of carbon deposited on Ni-Ca-4 is more serious, which might be related to the low CO selectivity of the catalyst, and the formation of carbon deposition may probably be resulted from the disproportional reaction (2CO = C + CO₂).

2.3.2. TEM Analysis. Figure 9 gives the TEM image of the catalyst after reaction. It could be seen that there is obvious carbon deposition on the catalyst surface. It is reported that there are four types of carbon deposited on the surface of Ni-based catalyst in the CO₂-CH₄ reforming process, including amorphous carbon, filamentous carbon, coated carbon, and graphite carbon. Among them, the activity of amorphous carbon is higher, which is conducive to the process of carbon elimination (CO₂ + C = CO). The filamentous carbon will not lead to catalyst deactivation and thus not affect the activation of CH₄ but with the increase in carbon deposition, it will transform to coated carbon and graphite carbon, covering the effective surface area of the catalyst, reducing active sites, and inhibiting the process of reforming. It can be seen from Figure 9 that all the prepared catalysts present carbon nanotubes, belonging to filamentous carbon. Although this type of carbon will not lead to catalyst deactivation, its aggregation on the pores of catalyst would increase the pressure drop in the fixed-bed.

2.3.3. TG-DTG Analysis. 2.3.3.1. TG-DTG Profiles. TG-DTG analysis of the spent catalyst is given in Figure 10. All the catalysts showed slight weight loss before 105 °C, which was due to the removal of water absorbed by the catalyst. The weight loss in the range of 105–250 °C could be ascribed to the relatively active amorphous carbon, which can be removed with oxygen to generate CO₂. Metal Ni might react with oxygen at high temperature (more than 250 °C) to generate NiO, making the weight of the catalyst increase. Also, the weight loss around 700 °C was attributed to the filament carbon deposited on the catalyst reacting with oxygen to produce CO₂, resulting in mass decline. The Ni-Ca-1 catalyst shows almost no carbon deposition, while the four promoted catalysts present the same obvious weight loss curve. Weight losses of Ni-Ca-1 and Ni-Ca-2 are more than 50 and 30%, respectively, while the loss of Ni-Ca-4 and Ni-Ca-6 is around 18%, indicating that the addition of calcium could obviously promote the formation of carbon, which is derived from the high activity of the modified catalyst, improving the conversions of CH₄ and CO₂, which promote carbon deposition at the same time. In addition, the catalyst promoted with 4 wt % calcium shows a higher carbon resistance performance.

2.3.3.2. Carbon Removal Kinetics. According to ref 36, the effect of temperature on carbon removal conversion of the catalysts is shown in Figure 11a. The kinetic parameters of carbon removal reaction at 480–680 °C were calculated by the first-order kinetic model using the Coast–Redfern method, as given in Figure 11b and Table 2. It could be seen from Figure 11a that the carbon removal process could be divided into three stages: 50–480 °C, 480–680 °C, and 680–980 °C. In the low-temperature region (50–480 °C), the conversion does not change obviously with the increase in reaction temperature. In the second stage (480–680 °C), the temperature has a significant effect on the carbon removal conversion, as shown in the figure that the conversion curve changes steeply, indicating that the carbon removal reaction of the used catalyst is easy to proceed at 480–680 °C. At 680–980 °C, the influence of temperature on the carbon removal conversion gradually decreases, with the profile going flat.

To analyze kinetic parameters of the carbon removal process, kinetic fitting profiles have been carried out as the reaction order n = 1 at 480–680 °C, which are shown in Figure 11b, and the kinetic parameters were calculated accordingly, as shown in Table 2. From the points of 2RT/E value → 0 and correlation coefficient R² → 1, the Coast–Redfern model is suitable for the carbon removal process. The activation energy of carbon removal decreases with the increase in Ca addition, indicating that the addition of Ca promoter is beneficial for the removal of carbon deposited on the Ni-based catalyst. Also, there is a similar trend for the pre-exponential factor, demonstrating that there is a compensation effect between the activation energy and pre-exponential factor.
2.3.4. TPH Analysis.

Results from temperature-programmed hydrogenation (TPH) of the spent catalysts are shown in Figure 12. Compared with the Ni-Ca-0 catalyst, the promoted catalysts have two obvious hydrogen consumption peaks. It has been reported that there are three types of carbon deposited on the catalyst. The first peak in the range of 200–350 °C belonged to the amorphous carbonaceous species related to α-type carbon with high activity. It is the active intermediate of carbon elimination reaction (CO₂ + C = 2CO), which is conducive to the promotion of catalytic reaction. The second peak at the range of 350–600 °C could be assigned to β-type carbon, which might enter into the catalyst lattice to form carbon nanotubes or filamentous carbon. Unfortunately, β-type carbon would be transformed into stable γ-type carbon within a long-time reaction at high temperature, and it is one of the main types of carbon deposition that will lead to catalyst deactivation. The last peak at the range of 600–900 °C was identified as γ-type carbon (e.g., graphitic carbon), which showed the lowest reactivity in three types of carbon species and was conducive to the deactivation of catalyst.

It can be seen from Figure 12 that the low-temperature hydrogen consumption peaks of Ni-Ca-0, Ni-Ca-1, and Ni-Ca-6 at about 300 °C are obvious, indicating that there was more amorphous carbon on the above catalysts. High-temperature hydrogen consumption peak areas of Ni-Ca-1 and Ni-Ca-2 catalysts at about 600 °C are larger than the others, indicating...
that the results of TPH characterization are in accordance with the inferences of TG-DTG analyses.

3. CONCLUSIONS

Optimization of Ni-Al2O3 catalyst with the addition of Ca by the solution combustion method was performed to improve the catalytic performance for the CO2-CH4 reforming reaction. Results showed that reduction peak area of Ni-Ca-4 was larger among all the catalysts, illustrating more active components on the used support. Distributions of Ni and Ca elements from EDX mapping were more uniform with the content of Ca of 4 wt %. Carbon deposition analysis showed that the surface of Ni-Ca-4 sample presented less filamentous carbon with TG weight loss of only 18%. The endurance time of catalyst evaluation test was only 5 h, which was too short to meet the standard of industrialization, and thus, the relevant research conclusions in our study were only attributed to the initial stage. Therefore, it is necessary to extend the reforming reaction time to provide more basic data for industrialization.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. Ni-Al2O3 catalyst modified by calcium was prepared by the solution combustion method. Twenty-five milliliters of distilled water and 25 mL of glycol were mixed evenly to get glycol aqueous solution. A certain amount of Ni(NO3)2·6H2O, Al(NO3)3·9H2O, and Ca(NO3)2·6H2O with a Ca element stoichiometric ratio of 1.0−6.0 wt % was added to the solution, and the mixture was stirred for 2 h, aged for 3 h at room temperature, and roasted for 3 h in a muffle furnace at 600 °C. The promoted catalyst is obtained after cooling the furnace to room temperature. According to the different loading amounts of promoter, the catalysts were named as Ni-Ca-1, Ni-Ca-2, Ni-Ca-4, and Ni-Ca-6 (with the same Ni loading). In addition, as a contrast, the Ni-Al2O3 catalyst was prepared under the same conditions and denoted as Ni-Ca-0.

4.2. Catalyst Characterization. XRD patterns of the catalysts were recorded on a Rigaku diffractometer (D/max2500, Japan) with Ni-filtered Cu Kα radiation (λ = 1.54056 nm) at 40 kV and 100 mA in the 2θ range of 10−80°, with a scan speed of 8°/min. H2 temperature-programmed reduction and hydrogenation (H2-TPR and TPH) curves were obtained using a chemical adsorption instrument (Chem-BET pulse TPR/TPD, Kantar LTD, U.S.). Prior to the test, all the samples were treated with He (100 mL/min) at 300 °C for 1 h, and the test was performed from room temperature to 1000 °C in H2/Ar mixture (H2/Ar = 0.05:0.95, 100 mL/min) with a ramping rate of 10 °C/min. The morphology of the catalyst was observed using a transmission electron microscope with an accelerating voltage of 200 kV, working distance of 15 mm, and collection time of 120 s. To quantitatively analyze the carbon amount deposited on the catalyst after reaction, TG-DTG analysis of the used catalyst was recorded on a SDTQ600 (TA Instruments, U.S.) instrument from room temperature to 1000 °C (10 °C/min, air atmosphere).

4.3. Catalyst Performance Test. The schematic diagram of catalyst evaluation device is shown in Figure 13. The performance test was carried out in a fixed-bed quartz tube reactor (i.d., 6 mm; l., 400 mm) at ambient pressure. One gram of catalyst (40−60 mesh) was loaded into the reactor. Prior to the reaction, the calcined catalyst was reduced for 3 h at T = 650 °C and P = 1 atm with a hydrogen flow rate of F = 30 mL/min. Then, the system was switched to the reaction gases for 5 h, and the volume ratio of the feed gas mixture CH4/CO2, reaction temperature, CH4 flow rate, gas hourly space velocity (GHSV), and pressure in the reactor were set as 1:1, 800 °C, 60 mL/min, 14,400 h−1, and 1 atm, respectively. The products were analyzed using an online chromatograph (GC-6890, Beijing Purui Analytical Instrument Co., Ltd., Beijing, China) equipped with a Porapak Q packed column and TCD detector. The conversions of CH4 and CO2, selectivities of H2 and CO, and ratio of H2 to CO are calculated as follows:

Conversion of methane:

\[ X_{\text{CH}_4} = \frac{n_{\text{CH}_4,\text{in}} - n_{\text{CH}_4,\text{out}}}{n_{\text{CH}_4,\text{in}}} \times 100\% \]

Conversion of carbon dioxide:

\[ X_{\text{CO}_2} = \frac{n_{\text{CO}_2,\text{in}} - n_{\text{CO}_2,\text{out}}}{n_{\text{CO}_2,\text{in}}} \times 100\% \]

Selectivity of H2:

\[ S(H_2) = \frac{n_{H_2,\text{out}}}{2n_{\text{CH}_4,\text{in}} - 2n_{\text{CO}_2,\text{in}}} \times 100\% \]

Selectivity of CO:

\[ S(CO) = \frac{[(\text{CO mass in product})/\text{(CH}_4 \text{ mass in feed − CH}_4 \text{ mass in product}) + \text{(CO масс in feed − CO}_2 \text{ mass in product})]}{100\%} \]

Ratio of H2 to CO:

\[ \frac{H_2}{CO} = \frac{S(H_2)}{S(CO)} \]
Corresponding Author

Huanhuan Wang — Key Laboratory of Coal Clean Conversion & Chemical Engineering Process (Xinjiang Uygur Autonomous Region), College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, China; Phone: 15022994903; Email: mowenlong@xju.edu.cn

Xiaojing He — Key Laboratory of Coal Clean Conversion & Chemical Engineering Process (Xinjiang Uygur Autonomous Region), College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, China; orcid.org/0000-0002-3758-3778

Xing Fan — Key Laboratory of Coal Clean Conversion & Chemical Engineering Process (Xinjiang Uygur Autonomous Region), College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, China; orcid.org/0000-0001-9714-2571

Fengyun Ma — Key Laboratory of Coal Clean Conversion & Chemical Engineering Process (Xinjiang Uygur Autonomous Region), College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, China

Shuai Liu — Xinjiang Tianyun Chemical Co. Ltd., Luntai, Xinjiang 841600, China

Dihumar Tax — Key Laboratory of Coal Clean Conversion & Chemical Engineering Process (Xinjiang Uygur Autonomous Region), College of Chemistry and Chemical Engineering, Xinjiang University, Urumqi, Xinjiang 830046, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02558

Notes

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