Effect of the Nickel Source on the Structure, Performance, and Carbon Deposition of the Ni/Al_2O_3 Catalyst for CO_2−CH_4 Reforming

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ABSTRACT: Ni/Al_2O_3 catalysts were prepared with Ni(NO_3)_2·6H_2O, NiSO_4·6H_2O, NiCl_2·6H_2O, and NiC_2H_4O_2·4H_2O as nickel sources by the solution combustion method. The catalysts were characterized by X-ray diffraction, H_2 temperature-programmed hydrogenation, TG-DTG, TPH, and transmission electron microscopy methods, and the effect of the nickel source on performance of the Ni/Al_2O_3 catalyst was investigated via the CO_2−CH_4 reforming experiment. Results showed that Ni dispersion, Ni size, and the metal−support interaction between active component Ni and the support were influenced significantly by anion in nickel sources, resulting in that the performance of each catalyst was different. Highly dispersed Ni species, small Ni crystallite size, and strong metal−support interaction were presented in the Ni/Al_2O_3 catalysts with Ni(NO_3)_2·6H_2O and NiSO_4·6H_2O as nickel sources. Evaluation results showed that the catalyst prepared with Ni(NO_3)_2·6H_2O exhibited higher activity and stability, with CH_4 and CO_2 conversions of 31.21 and 48.97%. Carbon deposition analysis demonstrated that the catalyst prepared with NiSO_4·6H_2O contained more graphite carbon.

1. INTRODUCTION

In recent years, because of the excessive exploitation and utilization of fossil energy, the content of greenhouse gases such as CO_2 and CH_4 in the atmosphere increased obviously, which has a great impact on the living environment of human beings. It is important to utilize the reaction of CH_4 reforming reaction, and syngas, a chemical raw material, can be produced. The reaction is considered to be an effective way for the conversion and utilization of CO_2 and CH_4. However, the reaction is an endothermic process and reaction conditions are harsh; thus, the preparation of a catalyst with high stability and activity is the key to effective utilization of this technology. A large number of studies have shown that noble metal catalysts (Ir, Pd, Pt, Rh, Ru, etc.) exhibited high activity and stability in the reforming reaction. In view of the high cost of these catalysts, it is difficult to use them on a large scale. Furthermore, it is found that the activity of nickel-based catalysts is comparable to that of precious metal catalysts, but it is easy to be deactivated because of metal sintering and carbon deposition. Due to its low cost and promising applications, the modification of nickel-based catalysts has received widespread attention.

The modification of the Ni/Al_2O_3 catalyst for CO_2−CH_4 reforming mainly focused on additives and supports, while the effect of sources on the structure and performance of catalysts was scarcely discussed. Studies showed that the source affected the structural characteristics of the prepared catalyst to a certain extent, thereby affecting the activity and stability of the catalyst. Ren et al. prepared Ni/γ-Al_2O_3 catalysts with nickel nitrate and nickel acetate as Ni sources by the impregnation method for catalytic hydrogenation of α-pinene. Results showed that the catalyst prepared with nickel acetate exhibited higher catalytic activity. Liu et al. used nickel nitrate, nickel acetate, and nickel citrate as nickel sources, respectively, to prepare Ni-based catalysts by the impregnation method, and the prepared catalysts were applied to hydrogenation of phthalic anhydride. It was found that the catalyst prepared with nickel acetate showed large Ni crystallite size and low activity, while the catalysts prepared with nickel nitrate and nickel citrate presented higher activity and selectivity. Zhong et al. prepared bimetallic catalysts Ni−Fe/γ-Al_2O_3 for CO methanation reaction with nickel nitrate, nickel acetate, and nickel chloride as nickel sources. Results showed that the catalyst prepared with nickel nitrate proposed a larger specific surface area and better NiO dispersion.
obtained Ni-modified HZSN-5 catalysts with nickel nitrate, nickel chloride, nickel sulfate, and nickel acetate by the impregnation method. Performance of the catalysts for toluene and methanol to synthesize p-xylene was investigated. Results showed that the catalyst with nickel nitrate as the precursor presented small Ni particle size, high dispersion, high activity, and well stability. Zhang et al. synthesized Ni/SBA-15 catalysts by the impregnation method using different nickel salts as nickel sources for dry reforming reaction. X-ray diffraction (XRD) demonstrated that the Ni/SBA-15 catalyst prepared with nickel acetate presented low Ni crystallinity and well dispersibility, showing high stability and selectivity in dry reforming of methane. Therefore, a proper nickel source was conducive to improve the performance of the catalyst.

In this work, Ni/Al2O3 catalysts with different nickel sources were prepared for CO2−CH4 reforming. To investigate the effect of the nickel source on the performance of the Ni/Al2O3 catalyst, the state of NiO species on support, the interaction between metal and support, and carbon deposition on the catalyst were characterized by XRD, H2 temperature-programmed hydrogenation (H2-TPR), TG-DTG, TPH, and transmission electron microscopy (TEM) technologies. This work is conducive to the selection of a suitable nickel source to prepare effective Ni-based catalysts for dry reforming of methane.

2. RESULTS AND DISCUSSION

2.1. Catalyst Characterization. 2.1.1. XRD Analysis. The XRD spectra of calcined and reduced samples are given in Figure 1. As shown in Figure 1a, the characteristic diffraction peaks of NiO appear at 37.3, 43.4, 62.3, and 75.5°, and the intensity of the peaks of each catalyst is different. Among them, the peaks of AlNO−NiCl are higher and sharper, indicating that NiO in the catalyst has a more complete crystal form, large grain size, and poor dispersion. The peaks of AlNO−NiSO are lower and dispersed, demonstrating that it proposes both small grain size and well dispersion. However, the characteristic diffraction peaks of Al2O3 are not observed in Figure 1a, presenting that the carrier Al2O3 is in an amorphous state, which might be related to the low calcination temperature (600 °C). In Figure 1b, the diffraction peaks of Al2O3 at 37.5, 45.5, and 66.3° can be clearly observed, which might be resulted from that the amorphous Al2O3 underwent a crystalline phase transformation, resulting in the formation of γ-Al2O3 form at the higher reduction temperature (650 °C). Meanwhile, it was also found that the characteristic diffraction peaks of active component Ni appeared at 44.3, 51.8, and 76.4° for all the reduced catalysts, which indicated that NiO was well reduced. The characteristic diffraction peaks of AlNO−NiCl, AlNO−NiCH, and AlNO−NiNO is more obvious, and the half peak width is smaller than that of AlNO−NiSO, demonstrating that the active metal Ni on the former of catalysts is more complete and that metal Ni dispersion on the surface of AlNO−NiSO is better. Crystallite size of the active component Ni at 51.8° is calculated according to Scherrer’s equation, and the results are shown in Table 1. The crystallite size of active component Ni on the surface of AlNO−NiCl is larger, and the size of other samples is not much different, showing that the nickel source can affect the dispersion and crystallite size of active component Ni on the carrier.

2.1.2. H2-TPR Analysis. Figure 2 shows the H2-TPR profiles of calcined samples. It can be seen from Figure 2 that the NiO reduction peaks of calcined samples are clearly observed in the range of 400−880 °C. According to the strength of interaction size of active component Ni on the surface of AlNO−NiCl is larger, and the size of other samples is not much different, showing that the nickel source can affect the dispersion and crystallite size of active component Ni on the carrier.
between NiO and the carrier, NiO species can be divided as $\alpha$-NiO, $\beta$-NiO, and $\gamma$-NiO. The reduction peak in the range of 400–450 °C is attributed to the reduction of $\alpha$-NiO (free NiO) species, which is easy to be reduced due to its weak interaction with the carrier. The reduction peak of $\beta$-NiO is caused by NiO reduction of the cubic crystal phase on the carrier surface, which appears at 450–700 °C. The reduction peak of $\gamma$-NiO species between 700 and 900 °C is considered to be caused by the reduction of NiAl$_2$O$_4$ spinel. However, NiO is only detected in Figure 1a, and the NiAl$_2$O$_4$ spinel is not detected. Therefore, it is speculated that the strong interaction may be caused by the reduction of NiO entering the inner pores of the carrier Al$_2$O$_3$. Figure 1a shows that the intensity of the NiO characteristic diffraction peak on the surface of AlNO−NiNO and AlNO−NiSO is relatively low, indicating that the NiO grain size is smaller than other samples. The smaller the grain size of NiO is, the easier NiO can enter into the inner channels of the support, resulting in that this part of NiO is difficult to be reduced and reduction of which should be at higher temperature. In addition, it is found that the reduction peak temperature of AlNO−NiNO is higher, and its reduction peak area is larger, indicating that NiO on the catalyst has a strong interaction with the carrier, and more stable Ni species could be obtained after reduction, which could improve the stability of the catalyst by inhibiting the migration and agglomeration of active component Ni.

2.2. Performance Evaluation of the Catalyst. Figure 3 shows the change of CH$_4$ and CO$_2$ conversions with time within 5 h. As shown in Figure 3a, the conversion of CH$_4$ of AlNO−NiNO is higher, which is about 31%; AlNO−NiCH is followed, with the CH$_4$ conversion of 28%, while the conversion of other two catalysts is much lower. CH$_4$ conversion of AlNO−NiSO increased at the beginning of the reaction and did not change significantly in the later stage of the reaction. However, the CH$_4$ conversion of AlNO−NiSO increased slightly after 3 h of reaction. It can be seen from Figure 3b that the CO$_2$ conversion of AlNO−NiNO is higher, about 49%, followed by AlNO−NiSO. In addition, it is found that the CO$_2$ conversion of each sample is obviously higher than that of CH$_4$, which resulted from that there are side reactions, carbon elimination ($\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$), and the reverse water–gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$), in the CH$_4$−CO$_2$ reforming reaction. The average conversion ratio of CO$_2$/CH$_4$ in the reforming reaction for AlNO−NiNO, AlNO−NiCH, AlNO−NiCl, and AlNO−NiSO is 1.58, 1.61, 2.25, and 2.35, respectively. The smaller the average conversion ratio, the weaker side reactions occurred in the reforming reaction, indicating that AlNO−NiNO may show better selectivity.

H$_2$ and CO selectivity of the samples are illustrated in Figure 4. AlNO−NiNO and AlNO−NiSO exhibit higher H$_2$ and CO selectivity in the reforming experiment, showing higher catalytic activity. Additionally, the H$_2$ and CO selectivity of AlNO−NiNO increased slightly after 1 h of reaction, while the other samples had no obvious change. Besides, it is found that the selectivity of CO is about five points higher than that of H$_2$, which could be linked to the reverse water–gas shift reaction ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$).

It can be seen from Figure 5 that the H$_2$/CO ratio of each sample is less than 1, which is also attributed to the reverse water–gas shift reaction. The H$_2$/CO ratio of AlNO−NiNO is about 0.84 and increases slightly with the increase of reaction.
Figure 5. Ratio of H$_2$ to CO of samples.

time. However, the H$_2$/CO ratio of AlNO$_3$NiSO decreased with the increase of time, and the ratio of others did not fluctuate significantly. Generally, the H$_2$/CO is close to 1; it means that there are fewer side reactions in the reforming reaction, which is more conducive to the reforming reaction. In addition, the H$_2$/CO ratio of AlNO$_3$NiNO is obviously higher than that of other catalysts, indicating that AlNO$_3$NiNO can inhibit the occurrence of the reverse water–gas shift reaction. Figure 6 presents the activity and selectivity of the catalysts. The order of activity (conversion of CO$_2$) of the catalysts is as follows: AlNO$_3$NiNO > AlNO$_3$NiSO > AlNO$_3$NiCl > AlNO$_3$NiCH. The reason for this difference could be related to the dispersion of the active component Ni and the interaction with the support. The structure difference between different nickel source catalysts might be caused by the pH of different nickel salt solutions; some researchers believed that the difference might be related to the anion radius in the nickel salt, and studies on the electronegativity of anions in nickel salts have also been reported, which showed that the anions in the nickel salt play an important role in the formation of the catalyst structure.

2.3. Characterization of Catalyst after Reaction. 2.3.1. XRD Analysis. Figure 7 shows the XRD spectra of the spent catalysts. The characteristic diffraction peaks of active metal Ni appear at 44.3, 51.8, and 76.4°, as same as the fresh ones, and the intensity of which increased slightly. In addition, crystallite size of Ni was also calculated according to Scherrer’s equation, as shown in Table 1. Results showed that the crystallite size of active component Ni increases after the reaction, which might be related to the sintering of the Ni cluster at high temperatures. Among which, the crystallite size of AlNO$_3$NiNO and AlNO$_3$NiSO increased obviously by 21.98 and 31.11%, respectively, while the size of AlNO$_3$NiCl only increased by 2.24%, indicating that the latter catalyst shows well anti-sintering ability.

2.3.2. TG-DTG. Figure 8 shows the TG-DTG curves of the spent catalysts after 5 h on stream at 800 °C. It can be observed that the weight loss for each sample is different. The mass of all samples decreased before 250 °C, which is mainly associated with the removal of amorphous carbon or filamentous carbon deposited on the catalyst surface. According to the mass loss, the content of amorphous carbon or filamentous carbon on the surface of AlNO$_3$NiNO is lower and that of AlNO$_3$NiCl is higher. The mass of each sample increases between 300 and 700 °C, which is the oxidation process of active metal nickel on the catalyst surface. The increase of AlNO$_3$NiNO and AlNO$_3$NiSO is more obvious at this stage, indicating that the oxidation of active metal Ni on the support is more serious, which might be linked to the small grain size and high dispersion of the active component. The mass of AlNO$_3$NiCl nearly did not change between 300 and 450 °C, and increased significantly after 500 °C, which may be explained by the larger size of Ni particles (25.04 nm) on the surface of the sample. The mass of each sample decreases after 700 °C, which might be caused by the removal of graphite carbon on the catalyst. Among them, mass of AlNO$_3$NiSO was reduced by four points in this process, while the AlNO$_3$NiCl was about 2%, and AlNO$_3$NiCl was slightly higher than that of AlNO$_3$NiNO. Therefore, the nickel source can affect the carbon deposition on the catalyst.

2.3.3. TPH Analysis. Figure 9 shows TPH profiles of the spent catalysts. It can be noted that two hydrogenation peaks of the spent catalysts are located at the low-temperature region (around 300 °C) and high-temperature region (800 °C), respectively. The first hydrogenation peak is due to the hydrogenation of amorphous carbon or filamentous carbon. The subsequent hydrogenation peak is ascribed to the hydrogenation of graphite carbon. The area of the hydrogenation peak at about 300 °C is larger than the peak at 800 °C, demonstrating that the carbon deposition on the catalyst
surface is mainly amorphous carbon or filamentous carbon. Hydrogenation peaks of AlNO−NiNO and AlNO−NiSO ranged from 200 °C, while the other samples was from 250 °C, suggesting that the amount of amorphous carbon deposited on the surface of AlNO−NiNO and AlNO−NiSO is more than that of the others, which might be resulted from that the activity of amorphous carbon is higher than that of filamentous carbon. In addition, it is found that the hydrogenation peak area of AlNO−NiSO at 800 °C was larger than that of other catalysts, and the former peak temperature of the catalyst was higher than 400 °C, indicating that the content of graphite carbon on the catalyst was higher than that of other catalysts.

2.3.4. TEM. Figure 10 presents the TEM images of spent catalysts. It can be observed that carbon deposition occurs on the surface of each spent catalyst. However, the amount of carbon deposition on the catalyst surface is relatively small, which should be related to the shorter reaction time. Filamentous carbon can be observed in Figure 10a,d, while the filamentous carbon are entangled and stacked together in Figure 10b. Clear graphite carbon is observed in Figure 10c, and the active metal Ni is covered by the gray shell of graphite carbon. Amorphous carbon and filamentous carbon can generally be removed by carbon elimination reaction, which will not lead to catalyst deactivation, but a large amount of accumulation of which can affect the progress of the reaction. In view of that graphite carbon can closely and tightly coat the active metal, it is the main reason for catalyst deactivation.

3. CONCLUSIONS

Ni/Al2O3 catalysts with different nickel sources were prepared for the CO2−CH4 reforming reaction. Results showed that the structure of the catalysts is greatly affected by the anions of nickel salts, especially the Ni crystallite size, Ni dispersion and metal−support interaction, which are the main reasons for the great differences in the performance of each catalyst. Highly dispersed Ni species, small Ni crystallite size, and strong metal−support interaction were presented in the Ni/Al2O3 catalysts with Ni(NO3)2·6H2O and NiSO4·6H2O as nickel sources. The catalyst prepared with Ni(NO3)2·6H2O exhibited higher activity and stability in the CO2−CH4 reforming reaction, with CH4 and CO2 conversions of 31.21 and 48.97%, respectively. The catalyst prepared with NiSO4·6H2O produced more graphite carbon in the CO2−CH4 reforming reaction and presented poor stability. Therefore, Ni(NO3)2·6H2O is a promising raw material for the preparation of a Ni-based catalyst for CO2−CH4 reforming.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. The used catalysts for CO2−CH4 reforming were prepared by the solution combustion method. 25 mL of distilled water and ethylene glycol (analytical agents, Tianjin Yongcheng Fine Chemical Co. Ltd., China) were mixed in equal volume to prepare glycol aqueous solution. A certain amount of Ni(NO3)2·6H2O (analytical agents, Shanghai Shangpu Chemical Co. Ltd., China) and Al(NO3)3·9H2O (analytical agents, Tianjin Zhiyuan Chemical Reagent Co. Ltd., China) were dissolved
in the solution. After stirring for 3 h at room temperature, the mixed solution was put into crucible and aged for 3 h. The sample was heated from room temperature to 600 °C in a muffle furnace, maintained at the temperature for 2 h, followed by cooling down to room temperature. The catalyst with 20 wt % Ni was obtained and labeled as NiNO−AlNO. With the same procedure, NiSO−AlNO, NiCl−AlNO, and NiCH−AlNO catalysts with the same Ni content were prepared with NiSO4·6H2O, NiCl2·6H2O, and NiC4H6O4·4H2O (analytical agents, Tianjin Zhiyuan Chemical Reagent Co. Ltd., China) as the nickel source, respectively.

4.2. Catalyst Characterization. XRD and H2-TPR analyses were characterized for the fresh catalyst structure and nature, while TG-DTG, TPH, and TEM analyses were performed for the spent catalysts to quantify the amount of carbon deposition and the type/nature of carbon.

4.2.1. XRD. Crystal structure of each catalyst was determined using XRD (Ultima IV, Rigaku, Japan) with a Ni-filtered Cu Kα radiation source (λ = 0.15046 nm) with operation conditions of 40 kV and 40 mA. The diffraction pattern was recorded in the scan range of 10−80° with a scan step of 0.01°. The average crystalline size of Ni was calculated by Scherrer’s equation.

4.2.2. H2-TPR. H2 temperature-programmed reduction profiles of the samples were measured by chemical adsorption instrument (TP-5080, Xianquan Industry and Trade Development Co., LTD., Tianjin, China). Each sample was heated in a quartz reaction tube from room temperature to 100 °C and kept for 1 h in N2 flow (30 mL/min) and cooled down to room temperature. Then, the temperature was raised from room temperature to 800 °C under a mixed gas flow (10% H2 and 90% Ar) with 40 mL/min at a heating rate of 7 °C/min. And the hydrogen consumption signal was recorded by a GC-7890 gas chromatograph (TCD detector, Shanghai Tianmei Instrument Factory, China).

4.2.3. TPH. H2-TPH curves of the samples were also obtained by the chemical adsorption instrument (TP-5080, Xianquan Industry and Trade Development Co., LTD., Tianjin, China). The samples were heated from room temperature to 400 °C in a He flow, maintained for 1 h. The samples were cooled down to room temperature, and the carrier gas was replaced by mixed gas flow (5% H2 and 95% Ar) at a flow rate of 100 mL/min. Then, the samples were heated from room temperature to 1000 °C at a heating rate of 10 °C/min. The hydrogen consumption signal was recorded by a GC-7890 gas chromatograph (TCD detector, Shanghai Tianmei Instrument Factory, China).

4.2.4. TG-DTG. Thermogravimetric analysis (TG-DTG) of the samples were conducted on a SDTQ600 (TA Instruments, U.S.) thermogravimetric analyzer in a temperature range of room temperature to 1000 °C at a heating rate of 10 °C/min in air flow.

4.2.5. TEM. TEM image was performed on a Hitachi H-600 with an accelerated voltage of 100 kV. The sample for TEM observation was dispersed in ethanol solution, and the dispersed solution was dripped onto the 200 mesh Cu grid for drying.

4.3. Catalytic Performance Test. The schematic diagram of the catalyst evaluation device is shown in Figure 11. The reactor is an atmospheric fixed bed quartz tube with a length of 400 mm and an inner diameter of 6 mm. First, the catalyst was reduced at 650 °C, with H2 flow of 30 mL/min for 3 h. Then, the furnace was heated to 800 °C, and a mixture gas (50% CO2 and 50% CH4) with a flow rate of 60 mL/min was introduced to replace H2, and as reaction feed, the reaction was maintained for 5 h under GHSV = 14400 h−1. The tail gas produced after the reaction is detected by a gas chromatograph (Beijing Purui GC6890, ParapakQ column, TCD detector). It should be pointed out that each tail gas is tested three times, and the average value is taken as the experimental result. The calculation formulas for conversion and selectivity are as follows:

| Substance | Conversion | Selectivity |
|-----------|------------|-------------|
| CH4 | XCH4 = \( \frac{n_{CH4,\text{in}} - n_{CH4,\text{out}}}{n_{CH4,\text{in}}} \) × 100% | S = \( \frac{n_{CH4,\text{out}}}{2n_{CH4,\text{in}} - 2n_{CH4,\text{out}}} \) × 100% |
| CO | XCO = \( \frac{n_{CO,\text{in}} - n_{CO,\text{out}}}{n_{CO,\text{in}}} \) × 100% | S = \( \frac{m_{CO,\text{product}}}{m_{CH4,\text{feed}} - m_{CH4,\text{product}} + m_{CO,\text{feed}} - m_{CO,\text{product}}} \) × 100% |
| H2 | S(H2)/S(CO) = \( \frac{S(H2)}{S(CO)} \) |

**Figure 11. Schematic diagram of the catalyst evaluation device.**

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Notes
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