Study on Methanation Performance of Biomass Gasification Syngas Based on a Ni/Al₂O₃ Monolithic Catalyst

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1. INTRODUCTION

Syngas methanation technology is the core of biomass to produce natural gas. Its main process is to convert H₂ and CO in biomass gasification of syngas into CH₄ by using a catalyst, which plays a dominant role in this process. At present, the catalysts used for methanation still have a series of problems such as high reaction temperature, low weight hourly space velocity (WHSV), and difficult replacement.¹ If a low-temperature catalyst can be used in the methanation reaction, it can not only reduce operational costs of the system but also improve the safety of the reaction. Therefore, the preparation of a low-temperature methanation catalyst is the key to the study of syngas methanation. Usually, porous materials are loaded with metals as methanation catalysts, which are mainly composed of active components and carriers. As for the active component, metallic nickel has high methanation activity, good methane selectivity, and low cost, so it is an ideal choice for the active component of the methanation catalyst.²⁻⁸

In recent years, most researchers have mainly studied the methanation performance of nickel-based catalysts under different single carriers such as Al₂O₃, CeO₂, SiO₂, ZnO, and TiO₂. The results showed that Al₂O₃ exhibited a larger specific surface area, which made the active component more dispersed, and the methanation performance of catalyst was better.⁹⁻¹² Cordierite has high mechanical strength, low pressure drop, good thermal stability, and low thermal expansion coefficient, so it has become one of the best choices for molding catalysts in recent years.¹³⁻¹⁵ Gryzbiak et al.¹⁶ studied the catalytic effect of the Co–Ni/cordierite monolithic catalyst on the decomposition reaction of N₂O using the structural advantage of cordierite; the results showed that the conversion rate of N₂O can reach 96% at 400–450 °C. Sollier et al.¹⁷ researched the oxidation coupling reaction of methane by loading Sr/La₂O₃ on cordierite, comparing the catalytic effect of the Sr/La₂O₃ monolithic catalyst with that of the Sr/La₂O₃ powder catalyst. The results showed that the contact area between the feed gas and catalyst increased because of the honeycomb structure of the monolithic catalyst, and the reaction rate improved. At the same time, Mg and Si contained in cordierite can effectively improve the catalytic performance of the catalyst, so that the monolithic catalyst has a better catalytic effect. By loading Pd on cordierite coated with graphene, Zhu et al.¹⁸ found that the monolithic catalyst had a good effect on the catalytic reaction of the hydrogenation of...
2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The cordierite needs to be preprocessed before the methanation experiment; cordierite was placed in 20% dilute nitric acid solution, soaked for 12 h at room temperature, then washed with deionized water until it became neutral, dried in oven, and stored for later use.

2.1.1. Catalyst Prepared by the Dipping Method. The pretreated cordierite is placed in a mixed solution of nickel nitrate and aluminum nitrate with a molar ratio of nickel and aluminum of 10:3, soaked for 12 h, dried at 105 °C for 12 h, and roasted at 500 °C in a muffle furnace for 4 h. The above operation is repeated twice to obtain the Ni/Al2O3 monolithic honeycomb catalyst, DIP-Ni/Al2O3 catalyst in short.

2.1.2. Catalyst Prepared by the Sol–Gel Method.
(1) Ni/Al2O3 powder is prepared using ref 21.
(2) preparation of the aluminum gel, a certain volume of deionized water was heated to 85 °C, a certain mass of pseudoboehmite powder was added, magnetically stirred into a suspension, continued to heat for 1 h, then 1 mol/L of dilute nitric acid was added, continued to stir 1.5–2 h until it became translucent, and it was aged 24 h at room temperature.
(3) load the nickel-based active component, the above Ni/Al2O3 powder was added to an appropriate amount of aluminum gel, stirred well, immersed the pretreated cordierite in the sol (the sol covers the entire cordierite matrix), and taken out after a certain period of time. The residual sol in the cordierite channel was blown off, let stand for 30 min after baking in an oven, and roasted for 4 h at 500 °C. The above operation was repeated twice to obtain the Ni/Al2O3 monolithic honeycomb catalyst, SG-Ni/Al2O3 catalyst in short.

2.2. Evaluation of Catalyst Activity. The experimental system used for the evaluation of catalyst activity during the methanation reaction is shown in Figure 1a. It mainly consists of an intake system, reaction system, and detection system. Among them, the intake system is composed of feed gas, a mass flow meter, and its control device; the reaction system consists of a fixed-bed reactor and its temperature controller, and the detection system is mainly a gas chromatograph. The catalytic test is conducted in the fixed-bed reactor, which consists of a quartz tube and insulation system. The inner diameter of the quartz tube is 50 mm, the length of isothermal zone is 300 mm, and the catalyst bed is situated at the bottom of the constant temperature zone, with a thickness of 2 mm. More detailed dimensions of the fixed-bed reactor are shown in Figure 1b. In addition, the experiments of the methanation reaction are performed at room pressure, and the methanation performance of the catalyst is evaluated using CO conversion and CH4 selectivity.

The experimental procedure is as follows: First, the Ni/Al2O3 catalyst placed in the constant temperature zone of the quartz tube is purged with 50 mL/min of N2 and heated to 470 °C. Then, the catalyst is subjected to reduction treatment in a H2 atmosphere of 50 mL/min for 3 h when the temperature stabilizes. Next, the quartz tube is cooled to the reaction temperature, and the feed gas H2/CO/N2 with the molar ratio 3/1/1 is injected into it. In experiments, N2 is added as an

Figure 1. Schematic diagram of the experimental system (a) and the size of the fixed-bed reactor (b).
inert component for decreasing the gas-volume reduction rate and employed as internal standard gas. After the methanation reaction, the generated gas is collected using a gas bag, and the gas composition and content are analyzed by using gas chromatography.

The CO conversion (abbreviated as \( X_{\text{CO}} \)) and \( \text{CH}_4 \) selectivity (abbreviated as \( S_{\text{CH}_4} \)) can be calculated based on the formulas given below. In all formulas, \( A_{\text{x, in}} \) and \( A_{\text{x, out}} \) represent the flow rate of the \( \text{x} \) species, which flow into and out of the reactor, respectively.

\[
\text{CO conversion: } X_{\text{CO}}(\%) = \frac{A_{\text{CO, in}} - A_{\text{CO, out}}}{A_{\text{CO, in}}} \times 100
\]

\[
\text{CH}_4 \text{ selectivity: } S_{\text{CH}_4}(\%) = \frac{A_{\text{CH}_4, \text{ out}}}{A_{\text{CO, in}} - A_{\text{CO, out}}} \times 100
\]

3. RESULTS AND DISCUSSION

3.1. Effect of the Catalyst Preparation Method on the Catalyst Structure. 3.1.1. Microtopographic Analysis of Catalysts. The particle size of the catalysts was analyzed by a TF20 transmission electron microscope. The test steps are as follows: the catalyst is carefully ground and evenly dispersed in anhydrous ethanol and then treated in a microwave ultrasonic instrument for 20 min. The suspension is added dropwise on the copper network and observed after infrared drying.

In order to visually observe the distribution of the active component and the carrier of the catalyst, TEM characterization and particle size distribution analysis were performed on the DIP-Ni/Al₂O₃ and SG-Ni/Al₂O₃ catalysts after reduction. The results are shown in Figure 2. As can be seen from Figure 2a₁,b₁, the Ni grains are evenly distributed on the surface of the catalysts, and the Ni crystalline grain sizes range from 0 to 8 nm and from 0 to 12 nm, the average sizes are 4.10 and 5.21 nm, respectively, for the DIP-Ni/Al₂O₃ and SG-Ni/Al₂O₃ catalysts. The average crystalline grain size of Ni for the former is smaller than for the latter, which shows the DIP-Ni/Al₂O₃ catalyst has higher Ni dispersion, and the particle agglomeration occurs in the SG-Ni/Al₂O₃ catalyst. The existence of Ni grains is mainly determined by the interplanar spacing in the TEM diagram. It can be seen from Figure 2a₂,b₂ that there are obvious lattice fringes that exist on both catalysts with the interplanar spacing of 0.203 nm; it mainly corresponds to the Ni crystal surface (111).

3.1.2. Crystal Phase Analysis of Catalysts. The crystal component and micrograph of catalysts were analyzed by XRD, and the model is known as XRD-7000S. The excitation source was Cu Kα radiation with a scan rate of 5°/min and the diffraction angle 2θ values ranged from 5 to 90°. The crystallite size was calculated via the Scherrer equation.

Figure 3 shows XRD patterns of the cordierite and the SG-Ni/Al₂O₃ and DIP-Ni/Al₂O₃ catalysts after reduction. It can be seen that there are no characteristic peaks of NiO and Al₂O₃ for cordierite; the diffraction peaks at 2θ = 36.9, 43, and 66.7° are attributed to the alumina phase (PDF no. 50-1496); the corresponding particle sizes of Al₂O₃ are 26.3, 21.2, and 28.0 nm; they are present in both catalysts. Also, the diffraction peaks of the NiO phase appear at 2θ = 36.6, 62.9, and 75.4° (PDF no. 47-1049) for the DIP-Ni/Al₂O₃ catalyst. No NiO peak appears in the detection result of the SG-Ni/Al₂O₃ catalyst, but there is a very obvious reduction peak in the \( \text{H}_2\)-TPR results; these results indicate that incorporation of nickel oxide occurs in the SG-Ni/Al₂O₃ catalyst. It is closely related to the reasons that are as follows: (1) this might happen because the diffraction peaks of Al₂O₃ are close to NiO in the XRD spectrum; the diffraction peak of Al₂O₃ covers the diffraction peak of NiO, making NiO unable to distinguish. (2) The fine NiO particles are highly dispersed on the carrier Al₃O₉, which is below the detection limit of the instrument, resulting in no characteristic diffraction peak of NiO in the test results. (3) The microporous structure of the gel itself increases the possibility of active ingredient coverage, and the coverage of the active ingredient is generated in the XRD test results, which is consistent with the TEM results in Section 3.1.1: the NiO particle agglomeration occur in the SG-Ni/Al₂O₃ catalyst.

3.1.3. Active Site Analysis of Catalysts. \( \text{H}_2\)-TPD can be used for quantitative analysis of active sites on catalyst samples. The experiment of \( \text{H}_2\)-TPD was carried out on a PCA-1200 chemical adsorption instrument, and 100 mg of the catalyst was loaded into the reactor. First, the catalyst sample was blown by a \( \text{H}_2 \) flow rate of 50 mL/min for 1 h at room temperature. After that, the gas was changed into helium for removing the physical adsorption of \( \text{H}_2 \). Then, the sample was heated to 900 °C (heating rate of 20 °C/min) in helium with a flow rate of 50 mL/min.
Figure 4 shows the H2-TPD patterns of the reduced catalysts. The temperature of hydrogen desorption are different for the DIP-Ni/Al2O3 and SG-Ni/Al2O3 catalysts, as can be seen from the figure. It was reported that the hydrogen adsorption took place in the adsorption site of both the active component and carrier. The DIP-Ni/Al2O3 catalyst shows four desorption peaks at 150, 250, 330, and 480 °C, and the amount of hydrogen chemisorbed is very considerable. Research shows that the H2 desorption in the low-temperature region is from the hydrogen adsorption on highly dispersed Ni nanoparticles, whose surface often has high-density surface defects. These defect sites can be used as the capture centers of hydrogen to reduce the activation energy of hydrogen dissociation and make the methanation reaction easier. For the SG-Ni/Al2O3 catalyst, the adsorption capacities of hydrogen are obviously low, and this indicates poor dispersion of Ni. Although many nickel species are reduced at low temperature in the results of H2-TPR, the aggregation of nickel into large particles after reduction occurs, which will have a bad effect during the methanation reaction. For the DIP-Ni/Al2O3 catalyst, the desorption peaks are more obvious in the low temperature region; this indicates that the active metal Ni is highly dispersed, thereby improving the catalytic performance of CO methanation. The results are in agreement with the conclusion given by H2-TPR.

3.1.4. Reduction Characteristic Analysis of Catalysts. The reduction characteristic of the catalysts was tested and analyzed on a Micromeritics AutoChem II 2920 adsorption apparatus by the temperature-programmed reduction (TPR) technique. The powder form of the catalyst sample (120 mg) was heated from room temperature to 900 °C (heating rate of 10 °C/min) under 10% H2/90% He with a flow rate of 30 mL/min. The H2 concentration was estimated by TCD.

Figure 5 gives the reduction characteristic curves of the SG-Ni/Al2O3 and DIP-Ni/Al2O3 catalysts. It can be seen that the different preparation methods have a significant effect on the phase formation of the sample. According to reports in the literatures, the peak of TPR below 450 °C is due to reduction of free NiO (denoted as α peak); the peak at or above 750 °C is due to reduction of spinel NiAl2O4 (γ peak). The broad peak in temperature ranging from 450 to 750 °C (β peak) can be assigned to reduction of nonstoichiometric nickel aluminate, which are largely classified into Ni2+-rich nickel aluminate (β1 peak) and Al3+-rich nickel aluminate (β2 peak); the former has a relatively higher reducibility than the latter.

In addition, the SG-Ni/Al2O3 catalyst has a strong reduction peak at 348 °C and a weak shoulder peak at 430 °C, both of them correspond to the α-NiO species. The free α-NiO interacts weakly with the carrier Al2O3, which makes NiO easy to be reduced. In addition, the migration and aggregation may occur during the reduction and methanation reactions because the α-NiO species have a large particle size, and this leads to a decrease in the effective specific surface area and catalyst activity. However, the DIP-Ni/Al2O3 catalyst has four reduction peaks, and the overall reduction temperature is higher than that of the SG-Ni/Al2O3 catalyst. Reduction peaks correspond to the Ni2+-rich nickel aluminate, Al3+-rich nickel aluminate, and stable NiAl2O4 phase; these three species have a stronger degree of interaction with the carrier, indicating the formation of hard reduced species in the DIP-Ni/Al2O3 catalyst. It is known that the strong interaction plays a key role in suppressing the metallic sintering and carbon formation. This makes the DIP-Ni/Al2O3 catalyst have good heat resistance and stability in the methanation reaction. This can be confirmed in the catalyst activity test.

3.1.5. TG Analysis of Catalysts. The TG analysis of the catalysts after the methanation reaction was carried out in the TGA/DTA system of model QMA200M. The reaction atmosphere was O2, the flow rate was 10 mL/min, and the analysis temperature was from room temperature to 900 °C. Carbon deposition on the surface of the catalyst during methanation reaction mainly comes from the CO disproportionation reaction and CH4 cracking process. Figure 6 gives the TG curves of the catalysts after methanation. The result shows that the SG-Ni/Al2O3 catalysts exhibit different degrees of weight loss. The TG curve of the SG-Ni/Al2O3 catalyst is divided into stage I and stage II according to the research of Li et al. A lot of gases and organic matter escape during the drying process in the first stage, and then the carbon attached to the surface of
the catalyst is released by oxidation in the second stage. This shows that the amounts of carbon deposits of the SG-Ni/Al₂O₃ and DIP-Ni/Al₂O₃ catalysts after the methanation reaction are 1.3 and 1.2 wt %, respectively. The weight loss of the SG-Ni/Al₂O₃ catalyst comes mainly from the adsorbed water and structured water. It is closely related to the microporous structure of the gel itself. Massive micropores in the gel provide a large contact area during the methanation reaction process, but it also absorbs more adsorbed water and structured water at the same time. Hence, a slight carbon deposit is produced in the SG-Ni/Al₂O₃ catalyst.

3.2. Effect of Temperature on Methanation Performance of Catalysts. The catalysts prepared by the dipping and the sol–gel methods were used to carry out the methanation reaction of syngas H₂/CO/N₂ with a molar ratio of 3/1/1 and a WHSV of 10,000 mL g⁻¹ h⁻¹; the reaction temperature ranged from 250 to 550 °C. Figure 7 shows the effect of different reaction temperatures on the methanation performance of the catalyst. It can be seen that in the range of experimental temperature, the CO conversion rate and CH₄ selectivity of the catalysts prepared by the two methods have basically the same trends, that is, both of them increase with increasing temperature between 250 and 400 °C and then decrease at 400–550 °C. The methanation performance of the SG-Ni/Al₂O₃ catalyst is the best at 400 °C, and the CO conversion and CH₄ selectivity are 81.8 and 80.7%, respectively, which refer to the maximum values during the process of methanation reaction. While the CH₄ selectivity of the DIP-Ni/Al₂O₃ catalyst is slightly higher at 350 °C than at 400 °C, the CO conversion is obviously higher at 400 °C. Overall, the DIP-Ni/Al₂O₃ catalyst has the best methanation performance at 400 °C; the CO conversion and CH₄ selectivity are 98.6 and 90.9%, respectively, under the optimum condition. Xiong et al.35 studied the methanation performance of different Ni-based catalysts for pyrolysis gas of biomass; the results showed that the Ni/Al₂O₃ powder catalyst has the best methanation activity at 400 °C, and the CO conversion was about 85% when the volume composition of biomass pyrolysis gas was 9.98% CH₄, 1.85% C₂H₆, 27.51% CO₂, 5.18% N₂, 40.17% CO, and 15.31% H₂ with a space velocity of 6000 h⁻¹. By contrast, the Ni/Al₂O₃ monolithic catalyst prepared with cordierite honeycomb ceramics as the substrate can effectively improve the catalytic performance of the catalyst. However, the methanation performance of the catalyst declines gradually between 400 and 550 °C. This is mainly related to the CO stability; the number of active molecules in the methanation reaction will increase with the increase of temperature to promote the reaction. However, the methanation reaction is a strongly exothermic reaction, and the high temperature is not conducive to CO conversion into methane because of the limitation of thermodynamics and the occurrence of carbon deposition reaction; hence, the methanation performance decreases.36

The stability of the SG-Ni/Al₂O₃ and DIP-Ni/Al₂O₃ catalysts was tested at 400 °C and a WHSV of 10,000 mL g⁻¹ h⁻¹, as shown in Figure 8. The DIP-Ni/Al₂O₃ catalyst has good stability after 25 min of the methanation reaction, and the CO conversion rate is stable around 94%. While the stability of the SG-Ni/Al₂O₃ catalyst gradually decreases after 25 min, and the CO conversion is only 66% when the reaction proceeds to 320 min. In summary, the Ni/Al₂O₃ catalyst prepared by the dipping method has higher methanation performance and good stability at 400 °C.

3.3. Effect of WHSV on Methanation Performance of Catalysts. The effect of WHSV on methanation performance of the catalyst was investigated at 400 °C. The results are shown in Figure 9; it can be seen that the CO conversion and CH₄ selectivity of the DIP-Ni/Al₂O₃ catalyst are basically maintained at around 90% with the increasing WHSV, indicating that the catalytic activity and selectivity of the catalyst prepared by the dipping method is relatively stable. However, the CO conversion and CH₄ selectivity for the SG-Ni/Al₂O₃ catalyst show a decreasing trend; the CO conversion decreases from 81.9 to 62.7% and CH₄ selectivity decreases from 73.4 to 56.2% when the WHSV increases from 6000 to 14,000 mL g⁻¹ h⁻¹. We know that the WHSV of the reaction gas can affect the external diffusion and thus the residence time of the reaction gas on the catalyst surface to further affect the methanation effect. The results of this study indicate that the effect of external diffusion on the catalyst gradually weakens with the gradual increase of WHSV, resulting in short residence time of feed gas on the catalyst surface and incomplete methanation reaction. In other words, part of the feed gas is taken away by the airflow before it diffuses to the inner surface of the catalyst for sufficient reaction, leading to a
decrease in catalyst activity. In conclusion, the overall catalytic performance of the DIP-Ni/Al₂O₃ catalyst prepared by the dipping method is significantly better than that of the SG-Ni/Al₂O₃ catalyst prepared by the sol–gel method. Combining with characterization analysis of the catalyst, the DIP-Ni/Al₂O₃ catalyst has a stronger interaction between the carrier and active component. It can effectively suppress the catalytic sintering and make the catalyst with good stability. Therefore, the DIP-Ni/Al₂O₃ catalyst shows better methanation performance.

3.4. Effect of Ni Content on Methanation Performance of the Catalyst. 3.4.1. Characterization of the Catalyst Structure. 3.4.1.1. Analysis of Specific Surface Area and Pore Structure. N₂ physical adsorption was used to characterize the specific surface area and pore structure characteristics of the reduced catalyst, which contained different Ni contents. The results are shown in Table 1 and Figure 10. The Ni/Al₂O₃ catalyst with 15% Ni content has the highest specific surface area, total pore volume, and average pore diameter up to 7.139 m²/g, 0.017 cm³/g, and 9.764 nm, respectively. However, the specific surface area of the Ni/Al₂O₃ catalyst with 10% Ni content is minimal, only 4.795 m²/g, and the total pore volume and average pore diameter are 0.016 cm³/g and 9.297 nm. It helps the gas molecules to break away from the catalyst. The specific surface area of the Ni/Al₂O₃ catalyst with 20% Ni content is between 15% Ni and 10% Ni.

3.4.1.2. Analysis of Microtopography. TEM characterization and particle size distribution analysis were carried out for the three catalysts with different Ni contents after reduction, and the results are shown in Figure 11. The Ni grains are not evenly distributed on the surface of the Ni/Al₂O₃ catalyst with 10% Ni content; the metal Ni particle size distribution ranges from 1 to 20 nm, and average particle diameter is 2.59 nm. For 15% Ni/Al₂O₃ and 20% Ni/Al₂O₃ (as shown in Figure 11b,c), the Ni particle size ranges from 0 to 8 nm and from 0 to 35 nm, respectively, and the average particle sizes are 4.10 and 11.33 nm, respectively. While, the Ni grains are uniformly distributed on the surface of the 15% Ni/Al₂O₃ catalyst. In summary, although the particle size of the active component of the 10% Ni/Al₂O₃ catalyst is small, the particle size distribution is not uniform, while the particle size of the 15% Ni/Al₂O₃ catalyst is smaller than that of the 20% Ni/Al₂O₃ catalyst, indicating that the 15% Ni/Al₂O₃ catalyst has a higher dispersion of Ni.

3.4.1.3. Analysis of the Crystal Phase. The XRD patterns of the catalysts with different Ni contents after reduction are shown in Figure 12. The diffraction peaks of Al₂O₃ are only detected at 18 and 37° diffraction angles for the 10% Ni/Al₂O₃ catalyst, and those of NiO are only detected at 37 and 43° for the 20% Ni/Al₂O₃ catalyst. There might be the diffraction peak of Al₂O₃ that coincides with that of NiO particles, and the diffraction peaks of NiO and Al₂O₃ are, respectively, covered.

Table 1. Physical Properties of the Reduced Catalyst

| Ni content (mole fraction) (%) | Specific surface area (m²/g) | Total pore volume (cm³/g) | Average pore diameter (nm) |
|-------------------------------|-------------------------------|---------------------------|---------------------------|
| 10                            | 4.795                         | 0.016                     | 9.297                     |
| 15                            | 7.139                         | 0.017                     | 9.764                     |
| 20                            | 6.262                         | 0.017                     | 9.078                     |

Figure 10 gives the N₂ adsorption/desorption isotherms and pore size distribution of Barret–Joyner–Halenda adsorption for reduced catalysts. It can be seen that the adsorption and desorption isotherms of the Ni/Al₂O₃ catalysts with different Ni contents exhibit hysteretic loops. They belong to the typical type IV isotherms and H3 hysteresis loops. Most of the pore widths focus on 2–20 nm; this shows that the catalysts are all composed of slit-like pores formed by polymer flake particles, and internal pores of catalysts have a mesoporous characteristic.

Figure 10. Isotherms and pore size distribution results for reduced catalysts. (a) Adsorption/desorption isotherms. (b) Pore size distribution.
by the diffraction peaks of Al₂O₃ and NiO. For the 15% Ni/Al₂O₃ catalyst, the NiO diffraction peaks are detected at 37, 43, and 62.5°. Combined with TEM results, one possible reason is the smaller particle size of the NiO particle and Al₂O₃ carrier, which are highly dispersed on the surface of the catalyst, and the levels are below the limit of detection for XRD. In addition, it may also be because of the NiO diffraction peak over that of Al₂O₃ so that Al₂O₃ is not detected.

3.4.1.4. Analysis of Reduction Characteristics. The TPR test for reduction characteristics of the three catalysts was carried out, and the results are shown in Figure 13. It is revealed that β₁-type and β₂-type NiO are the dominant species in the 10% Ni/Al₂O₃ catalyst. The above two species show a trend of transformation to α-NiO and γ-NiO in the 15% Ni/Al₂O₃ catalyst with the increase of Ni loading. For the 20% Ni/Al₂O₃ catalyst, the three reduction peaks indicate the existence of three NiO species, and the interaction between NiO and the carrier decreases correspondingly with the disappearance of γ-NiO in the 20% Ni/Al₂O₃ catalyst, and the reduction of NiO (NiO → Ni) occurs in the reduction reaction. Meanwhile, the results also show that the Ni loading has a great influence on the reduction characteristics of the catalysts. It affects the interaction between the active ingredients and carrier by changing the NiO species on the catalyst surface, thereby affecting the methanation reaction activity.

In addition, with the increase of Ni loading, the hydrogen-consuming peak gradually increased in the lower temperature region. When the Ni loading ranges from 10% Ni to 15% Ni, the reduction temperature moves toward the high-temperature region, which leads to the enhanced interaction between the species and carrier. This kind of strong interaction restrains sintering well in overreaction. However, with the further increase of Ni loading, the hydrogen-consumption peaks decrease gradually and transfer to the low-temperature section, which results in the weaker interaction between nickel oxide and the carrier. The carrier surface may be stacked with active components, which limits the “reaction site” of methanation, and this leads to easier sintering of active components.

3.4.2. Methanation Performance of Catalysts. The effect of Ni content on the methanation performance of the catalyst was investigated under the condition that the molar ratio of H₂/CO/N₂ was 3/1/1, and the WHSV was 10,000 mL g⁻¹ h⁻¹ at 250−550 °C. The Ni-based catalysts were prepared by using the dipping method, and the mole fractions of Ni are, respectively, 10, 15, and 20%. The results are shown in Figure 14; it can be seen that whole variant trends of the CH₄ selectivity and CO conversion are similar; all of them show the change in the trend of “volcanic type” for catalysts with different Ni contents. The results of the CH₄ selectivity and CO conversion at 250 °C show that the feed gas of H₂/CO is converted to hydrocarbons other than methane under the action of a catalyst, and it is certainly possible that the concentration of methane is below detection limit of the gas chromatograph. The CH₄ selectivity and the CO conversion first increase and then decrease with increasing temperature in this study. Overall, the order of methanation performance from high to low is 15% Ni, 20% Ni, and 10% Ni, and the Ni/Al₂O₃ catalyst with 15% Ni content has the highest CO conversion and CH₄ selectivity, 96.8 and 96%, respectively, at 400 °C; this result is consistent with the conclusions of characterization of the catalyst structure.

4. CONCLUSIONS

(1) The overall methanation performance of the Ni/Al₂O₃ catalyst prepared by the dipping method is significantly better than that of the Ni/Al₂O₃ catalyst prepared by the sol−gel method. The DIP-Ni/Al₂O₃ catalyst shows good resistance to
carbon deposition and antisintering performance, showing good temperature resistance and stability.

(2) When the H₂/CO molar ratio is 3/1 and the temperature is 400 °C, the CO conversion rate and CH₄ selectivity of the Ni/Al₂O₃ catalyst prepared by the dipping method are basically stable at around 90% within the experimental WHSV range, which has better methanation performance stability.

(3) Under the reaction conditions of H₂/CO molar ratio of 3/1 and WHSV of 10,000 mL g⁻¹ h⁻¹, the Ni/Al₂O₃ monolithic catalyst exhibits the best methanation performance at 400 °C. Under these conditions, the CO conversion and CH₄ selectivity of the DIP-Ni/Al₂O₃ catalyst were 98.6 and 90.9%, respectively.

(4) The loading of nickel also has a great influence on the methanation effect. The catalyst with a loading of 20% has higher CO conversion and CH₄ selectivity, and the best effect is observed at 400 °C, with a CO conversion of 96% and a CH₄ selectivity of 97%.

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Notes

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