Influence of Preparation Conditions on the Performance of Ni-Based Catalysts for Glycerol Steam Reforming

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ABSTRACT: The effect of preparation conditions on the performance of Ni-based catalysts was investigated for glycerol steam reforming. La0.7Ce0.3NiO3 mixed oxides were synthesized using different solution concentrations and calcination temperatures by a co-precipitation method. Brunauer—Emmett—Teller, inductively coupled plasma, X-ray diffraction, temperature-programmed reduction, field emission scanning electron microscopy, CO2-temperature-programmed desorption, thermal gravity analysis, and Raman spectroscopy were performed to characterize the catalysts. With an La2NiO4 phase at lowest solution concentration, a catalyst precursor included an LaNiO3 phase instead of La2NiO4 at other solution concentrations. At a low calcination temperature of 700 °C, it was found that the smaller particle size of CeO2 incorporated more lanthanum and higher surface basicity, and the La2O3CO3 phase could effectively inhibit and eliminate coking leading to the better performance of catalysts.

1. INTRODUCTION

With energy crisis and environmental issues, it is urgent to develop renewable energy resources. Currently, the use of biomass to obtain liquid fuels has received much interest, such as biodiesel with properties similar to diesel. Biodiesel as carbon neutral fuel is biodegradable and nontoxic and is derived from the transesterification of vegetable oils or animal fats by reacting with alcohol to produce approximately 10% (w/w) of crude glycerol. The profitability of biodiesel depends heavily on the economics of the byproducts. Nowadays, glycerol is used mostly in the pharmaceutical, personal care, food, and cleaning industries. Glycerol is employed as a source of renewable hydrogen, which provides a promising solution for the dilemma of surplus glycerol.

Various routes for the preparation hydrogen by glycerol, namely steam reforming,1 autothermal reforming,2–4 partial oxidation,5 aqueous-phase reforming,6,7 and supercritical water reforming,8 have been extensively investigated. Glycerol steam reforming (GSR) is a catalytic process and technology similar to those of methanol or ethanol steam reforming and provides higher hydrogen yield at atmospheric pressure,9 so, GSR is widely utilized. GSR can be represented by eqs 1 and 2

\[ C_3H_8O_3 \rightarrow 3CO + 4H_2 \quad (1) \]

\[ CO + H_2O \leftrightarrow CO_2 + H_2 \quad (2) \]

Different methods of process intensification and catalytic materials have been extensively studied for steam reforming. For example, Dou et al. studied several methods of process intensification, such as the sorption-enhanced steam reforming,10 chemical-looping steam reforming11,12 and the sorption-enhanced chemical-looping steam reforming.13

In GSR, the most investigated materials are Ni-, Pt-, Co-, and Ru-based catalysts,14–17 and less researched materials are Rh-, Ir-, and Pd-based catalysts.18–21 As a matter of fact, Ni-based catalysts are less costly and well-known to promote the rupture of C–C, O–H, and C–H bonds.22 However, the main challenges for Ni-based catalysts are sinter, carbon deposition, and rich hydrogen gas with a low CO concentration. Accordingly, three strategies were presented to address these challenges containing methodologies for the preparation of highly dispersed nickel catalysts with a strong metal—support interaction, promotion in the mobility of the surface oxygen, and then the removal of surface carbon deposition and process intensification via in situ absorption of CO2.23

Furthermore, perovskite-type mixed oxides, represented by the general formula ABO3, as catalyst precursors have received increasing attention due to their special crystal structures.24–29 In ABO3 structures, the A-site is a large rare earth cation and the B-site is a small cation of a d-transition metal, which may be partially substituted by A and B cations of similar oxidation state and ionic radius.23 These mixed oxides are able to produce highly dispersed metallic particles upon reduction,

Received: April 30, 2018
Accepted: June 29, 2018
Published: October 17, 2018
which inhibit the formation of carbon, and exhibit a high oxygen mobility (OM), which may be beneficial for the removal of carbon deposits.\(^{27}\) In addition, Kamonsuangkasem et al.\(^{24}\) reported that after reducing the catalysts, the CeAlO\(_3\) perovskite suppresses the interaction between Ni and Al\(_2\)O\(_3\), thereby increasing the number of active and Brønsted acid sites to improve the bifunctional metal–acid properties of Ni/CeO\(_2\)–Al\(_2\)O\(_3\) in the hydrogenolysis and dehydrogenation—dehydration of condensable intermediates that produce more \(\mathrm{H}_2\). However, Veiga et al.\(^{30}\) manifested that after reducing the catalysts, LaTiO\(_3\) perovskite has no effect on catalytic performance.

For LaNiO\(_3\), the effect of partial substitution of La with a great range of metal cations (Ce, Ca, Sr, Sm, Nd, etc.) was widely investigated.\(^{22,51,32}\) But less investigations about the effect of preparation conditions on the performance of perovskite-type mixed oxides are found. In this work, solution concentrations and calcination temperatures were studied over a series of La\(_{0.7}\)Ce\(_{0.3}\)NiO\(_3\) mixed oxides prepared by the co-precipitation method. Several characterization techniques and online analyses of gas phase products were used to determine the performance of catalysts in GSR.

2. RESULTS AND DISCUSSION

2.1. Characterization of Catalysts. The analysis results of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and Brunauer–Emmett–Teller (BET) are summarized in Table 1. A 6 wt % loading of Ni on L900-0.03-0.1 is much less than that on other catalysts in the range of 12–14 wt %, which exhibits that Ni loading decreases dramatically with solution concentration declining to a certain extent. It is found that calcination temperature influences the textural properties of catalysts. When catalysts are calcined at 700 °C, the solution concentration remarkably affects the textural properties. L700-3-1.9 shows the highest specific surface area, pore volume, and pore diameter.

The X-ray diffraction (XRD) patterns of calcined samples are shown in Figure 1. The CeO\(_2\) phase shifting to lower Bragg angles due to lanthana doping, and the perovskite phase were found in all samples without the detection of the NiO phase, which indicated that the used co-preparation method was efficient to produce the perovskite structure.\(^{22}\) The appearance of the perovskite structure was not affected by the investigated calcination temperature, which was consistent with the study result of Glisenti et al.\(^{26}\) The La\(_2\)NiO\(_4\) phase (2\(\theta\) = 32.5°) was presented only in L900-0.03-0.1, with the LaNiO\(_3\) phase (2\(\theta\) = 23.2, 32.8, 47.3, 58.6°) instead of the La\(_2\)NiO\(_4\) phase in other catalysts. For preparing catalysts with constant mole numbers of nitrate and precipitant, the formation of La\(_2\)NiO\(_4\) requires less nickel than that of LaNiO\(_3\). Thus, L900-0.03-0.1 had the lowest Ni content in agreement with the ICP result. At a low calcination temperature of 700 °C, it was obvious that the diffraction peaks of the CeO\(_2\) phase were more diffusive. Smaller particles of CeO\(_2\) possess significantly more Ce\(^{3+}\) sites, which contributes to the higher reducibility of the ceria.\(^{33}\) Tang et al.\(^{34}\) had reported that the Ce\(^{3+}\) content was higher, implying the higher oxygen vacancy density, which enhanced the oxygen storage capacity (OSC) and surface oxygen mobility (OM).

After reduction treatment (Figure 2A,B), all catalysts mainly decomposed to Ni (2\(\theta\) = 44.6, 51.8, 76.4°), La(OH)\(_3\), (2\(\theta\) = 15.6, 27.5, 39.5, 48.6°), and CeO\(_2\) with lanthana doping. As shown in Figure 2B, a shift of the diffraction peaks of CeO\(_2\) was larger at a calcination temperature of 700 °C, which manifested CeO\(_2\) by doping more lanthana. The introduction of other metal cations as dopants (such as La\(^{3+}\)) can also modify OSC and surface oxygen mobility OM of the oxide by lowering the barrier for oxygen migration and decreasing the activation energy for the reduction of the ceria species.\(^{25,35}\) Therefore, higher OSC and OM in L700-3-0.6 and L700-3-1.9 could only be inferred from the available data, which contributed to the gasification of the carbonaceous deposits. The mean Ni crystal sizes were 11, 11, 12, 13, and 13 nm corresponding to L900-0.03-0.1, L900-0.3-0.6, L900-3-1.9, L700-3-0.6, and L700-3-1.9, respectively, which revealed that Ni crystal sizes did not have clear correlation with calcination temperature and solution concentration. L900-0.03-0.1 had the weakest intensity of the diffraction peak of Ni due to the lowest Ni content as discussed above.

The reduction profiles of catalysts are shown in Figure 3. The peaks of other catalysts except L900-0.03-0.1 within 300–400 and 500–550 °C were defined for the LaNiO\(_3\) perovskite-type oxides,\(^{22,51}\) although there were more than three peaks attributing to the fluctuation of the temperature-programmed reduction (TPR) system and the reduction of CeO\(_2\).\(^{36}\) The reduction peak of L900-0.03-0.1 at highest temperature was ascribed to the existence of La\(_2\)NiO\(_4\),\(^{35}\) which indicated that L900-0.03-0.1 had the strongest metal–support interaction. Moreover, L900-0.03-0.1 had the lowest amount of hydrogen consumption in all samples because of the lowest Ni content (Table 1).

The CO\(_2\)-temperature-programmed desorption (TPD) profiles of reduced catalysts are shown in Figure 4. Two major peaks were observed at 67–152 °C originating from the
decomposition of a monodentate carbonate and at 267–647 °C probably arising from the decomposition of bidentate and/or bridged carbonates. It was concluded that calcination temperature and solution concentration could affect the surface basic properties of the catalysts. At a calcination temperature of 700 °C, a large amount of strong basic sites of catalysts could be inferred from their high specific surface area. The maximum amount of weak basic sites was obtained, at the highest solution concentration. As the solution concentration decreased, the strong basic sites of the catalysts increased. Charisiou et al. revealed that active sites for glycerol conversion are not necessarily based on Ni⁰, but it is the basicity of the catalysts (oxygen anion sites) which is the key parameter to form acetol and even break the C–C bonds to a certain extent. Vizcaino et al. provided that coke formation from ethylene decreased, thanks to the basic properties of Ca/SBA-15 and Mg/SBA-15 supports. Sahraei et al. concluded that the enhanced steam adsorption in the presence of basic materials could also help the oxidation of carbonaceous deposits.

2.2. Catalytic Performance. Catalytic performance was investigated at 575 °C for GSR with S/C = 5 after 2.5 h of feeding in all samples. The blank experiment in the absence of the catalysts was run under the same conditions to observe that the hydrogen product was negligible. In addition, C₂H₄ and C₂H₆ were not detected in all experiments. The yield of the gas product and Xₚ are given in Figure 5. The CH₄ yield was about temperature and solution concentration could affect the surface basic properties of the catalysts. At a calcination temperature of 700 °C, a large amount of strong basic sites of catalysts could be inferred from their high specific surface area. The maximum amount of weak basic sites was obtained, at the highest solution concentration. As the solution concentration decreased, the strong basic sites of the catalysts increased. Charisiou et al. revealed that active sites for glycerol conversion are not necessarily based on Ni⁰, but it is the basicity of the catalysts (oxygen anion sites) which is the key parameter to form acetol and even break the C–C bonds to a certain extent. Vizcaino et al. provided that coke formation from ethylene decreased, thanks to the basic properties of Ca/SBA-15 and Mg/SBA-15 supports. Sahraei et al. concluded that the enhanced steam adsorption in the presence of basic materials could also help the oxidation of carbonaceous deposits.

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2% for all samples, which indicated that hydrogenation reactions between CO/CO₂ and H₂ formed were inhibited.⁴⁰ The molar CO/CO₂ ratio was about 0.5 on L900-0.03-0.1, whereas the ratio was approximately 0.2 on other samples. This result illustrated that all catalysts facilitated the water-gas-shift reaction (WGSR). L900-0.03-0.1 had a relatively lower molar CO/CO₂ ratio which might due to different catalyst precursors. The H₂ yields were 57, 79, 82, 88, 95, and 100%, respectively. L700-3-1.9 with the highest Ni content and specific surface area had the highest initial H₂ yield and Xₐ. L900-0.03-0.1 with the minimum Ni content had the lowest initial H₂ yield and Xₐ. The result elucidated that the catalytic activity positively correlated with the primary Ni content and the specific surface area, but was unrelated to the particle size of Ni. Meanwhile, Goula et al.⁴¹ proved that despite much lower specific surface area of apatite-type lanthanum silicates (ATLSs) compared to the Al₂O₃ support and their eventually larger Ni crystallites, Ni-ATLS exhibit excellent low temperature conversion rates and selectivity towards H₂ production.

Stability tests of catalysts with similar Ni content were performed for 21.5 h. The yield of the gas product and Xₐ are displayed in Figure 6. There is always a gap between the data obtained after 10.5 and 20 h in Figure 7, because the data were not collected at night. The average CH₄ yield was near 2%, and the average molar CO/CO₂ ratio was about 0.3 in all catalysts. Hence, the prepared catalysts could hinder methanation reaction and promote WGSR. The H₂ yield declined smoothly from 80 to 66%, and Xₐ decreased from 92 to 70% for L900-0.3-0.6 during stability experiment. There was a rapid decline in H₂ yield from 82 to 44%, and Xₐ had the same change trend for L900-3-1.9. After the H₂ yield reduced from 82 to 70% within the initial 4.5 h, the H₂ yield was basically stable at around 70% for L700-0.3-0.6. Meanwhile, the same change trend was observed in Xₐ. There was a rapid decrease in H₂ yield from 91 to 60% and in Xₐ from 100 to 61% during 21.5 h for L700-3-1.9. Furthermore, the reductions of H₂ yield and Xₐ were extremely slow after 9.5 h.

The reaction temperature from 400 to 700 °C was studied after 3 h of feeding over L700-0.3-0.6 with the best performance. The experimental result is illustrated in Figure 7. Xₐ increased with the increasing temperature below 575 °C and it underwent a drop from 575 to 700 °C. H₂ yield raised with the increasing temperature below 500 °C, and it underwent a drop from 500 to 700 °C; H₂ yields at 500 and 575 °C were rather close. Possible explanations for the above results were the C–C bond cleavage favored at higher temperatures, the thermodynamic equilibrium and carbon deposits.²³,³²,⁴²,⁴³ CH₄ yield was very low over the whole temperature range, which clarified that the prepared catalysts had a sufficient capacity for reforming CH₄ into hydrogen and carbon oxide.³⁸,⁴⁴,⁴⁵ It was worth noting that H₂ yield could reach around 60% at 450 °C.

2.3. Characterization of the Used Catalysts. The XRD patterns (Figure 8) show main phases of all used catalysts including Ni, La₂O₃CO₃ (2θ = 11.1, 22.2, 25.8, 30.3, 44.4°), and CeO₂ with lanthana doping. It was only inferred from the available data that the appearance of the La₂O₃CO₃ phase rather than the La(OH)₃ phase was assigned to the existence of CO₂ under reaction conditions.³¹,⁴⁶,⁴⁷ Verykios et al.⁴⁸ discovered that the catalytic activity occurs at the Ni–
La$_2$O$_2$CO$_3$ interface, whereas the oxycarbonate species participate directly by reacting with deposited carbon, thus restoring the activity of the Ni sites at the interface. Simultaneously, de Lima et al. reported that La$_2$O$_2$CO$_3$ strongly interacts with Ni particles, inhibiting sintering during the reaction. The lines of Ni phase overlap with those of the La$_2$O$_2$CO$_3$ phase, thus, it is difficult to estimate the particle size of Ni on used samples.

Raman spectroscopy of the used catalysts (Figure 9) is performed to characterize the structure of the deposited coke after stability tests. All samples had two characteristic peaks located at around 1338 cm$^{-1}$ (D band) and 1587 cm$^{-1}$ (G band), usually assigned to phonons of E$_{2g}$ and A$_{1g}$ symmetry, respectively. It was obvious that the D band area was greater than the G band area, which indicated a predominance of a low degree of crystalline carbon species in all samples.

Additionally, the deposited carbon was determined by thermal gravity analysis (TGA). The derivative thermograms are shown in Figure 10. To exclude the influence of La$_2$O$_2$CO$_3$, all samples were pretreated at 800 °C for 30 min, the mass losses were 3.2, 3.5, 4.3, and 4.0% corresponding to L900-0.3-0.6, L900-3-1.9, L700-0.3-0.6, and L700-3-1.9, respectively. In Figure 10, the slight mass gain of L900-3-1.9 was observed, whereas other catalysts had an obvious increase in the mass, reaching the maximum mass at 403 °C for all catalysts. The result could be due to the oxidations of metal nickel and Ce$^{3+}$. Different carbon types were obtained for each catalyst, because of amorphous carbon oxidizing below 550 °C and the oxidation of graphitic/filamentous carbon required higher temperature. It was reported that the catalyst/support system governed the type of the carbon deposited as coke at the end of the reaction. The mass of carbon deposition was represented by the difference between the maximum mass due to oxidation and the minimum mass. Therefore, L700-0.3-0.6 had the lowest coking amount contributed to high basic site density, highest La$_2$O$_2$CO$_3$ mass, CeO$_2$ with more lanthana doping, and smaller particle size of CeO$_2$. L900-0.3-0.6 had the...
highest coking amount ascribed to the lowest basic site density and La2O3·CO3 mass. While there was still high H2 yield (66%) for L900-0.3-0.6 after 21.5 h of reaction. This result could be due to most carbonaceous species covering the surface of supports rather than Ni active centers. Coking was mainly influenced by surface basicity of the catalysts and the mass of La2O3·CO3 in this work, but coking was significantly associated with the particle size of Ni in other literature studies.\(^{57}\)

The co-precipitation method with a fixed molar ratio was effective for the appearance of La2O3·CO3 in catalysts, because there was a reaction between La(OH)\(_3\) in reduced and fresh catalysts and CO\(_2\) in the reaction system. The synthesis method affected the textural, structural, and surface properties of the catalysts.\(^{57}\) In this work preparation conditions also influenced the physicochemical properties of catalysts. It was corroborated that catalytic deactivation was determined by growth situation and amount of coke. Amadeo et al.\(^{58}\) demonstrated that filaments are not generated by the direct involvement of the surface metal but rather they grow with the mechanisms involving a surface containing both acid and base functionality.

3. CONCLUSIONS

In this work, the solution concentration and calcination temperature could influence physicochemical, structural, and textural properties of the synthesized catalysts. L900-0.03-0.1 with the lowest Ni content had the lowest initial activity, so, the decline in solution concentration to a certain extent was adverse to nickel deposition. L700-3-1.9 had excellent initial activity contributed to the highest Ni content and specific surface area. L700-0.3-0.6 exhibited optimal catalytic performance, because of the lowest coking content due to the highest La2O3·CO3 mass, high density of basic sites, and small particle size of CeO\(_2\) doping more lanthana. The correlation of the physicochemical properties of catalysts with catalytic performance revealed that the co-precipitation method with a fixed molar ratio in proper solution concentration and low calcination temperature induced great catalytic performance for glycerol steam reforming. The growth situation of carbon deposition should be further studied for future work.

4. EXPERIMENTAL SECTION

4.1. Preparation Method. When La\(_{0.7}\)Ce\(_{0.3}\)NiO\(_3\) mixed oxides were prepared by the co-precipitation method, the molar ratio of 0.7:0.3:1.5 for La\(_3\), Ce\(_{1.5}\), Ni\(_2\), and HCO\(_3\)\(_2\) was kept constant. Only solution concentration and calcination temperature were varied in the co-precipitation procedure. The specific synthesis procedures were as follows. La(NO\(_3\))\(_3\)+6H\(_2\)O (99.0%, Kelon), Ce(NO\(_3\))\(_3\)+6H\(_2\)O (99.0%, Kelon), and Ni(NO\(_3\))\(_2\)+6H\(_2\)O (99.0%, Kelon) were dissolved in distilled water together to receive three different total concentrations with 0.03, 0.3, and 3 mol/L. Meanwhile, ammonium hydrogen carbonate was dissolved in distilled water to obtain three different concentrations with 0.1, 0.6, and 1.9 mol/L. Then, the three resulting precipitates obtained by adding the corresponding precipitant to nitrate solution were filtered, washed with distilled water, and dried at 80 °C for 2 h and at 110 °C for 6 h. After this, the materials were carefully ground in a mortar, and then calcined for 6 h at a certain temperature, labeled as LT-x-y (T is the calcination temperature, T = 900 or 700 °C, x is the concentration of nitrate solution, x = 0.03, 0.3, and 3 mol/L, y is the precipitant concentration, y = 0.1, 0.6 and 1.9 mol/L). Finally, L900-0.03-0.1, L900-0.3-0.6, L900-3-1.9, L700-0.3-0.6, and L700-3-1.9 were synthesized.

4.2. Characterization Method. Nitrogen physisorption measurements were conducted using a surface area analyzer (Belsorp-max). Catalysts were degassed at 350 °C for 4 h before N\(_2\) adsorption–desorption measurements. The textural properties of the catalysts were obtained by the BET and BJH methods.

After microwave digestion of reduced samples in aqua regia, the nickel content was determined by ICP-AES (Agilent 7700x).

XRD data were collected using an X’Pert3 Powder Diffractometer operated at 40 kV and 40 mA with Cu K\(_\alpha\) radiation (\(\lambda = 0.154\) nm). The Scherrer equation was used to calculate the mean Ni crystal size based on the diffraction peak of the Ni(111) facet.

The reducibility of the catalyst precursor was evaluated by TPR using a 6 vol % H\(_2\)/Ar flow. 30 mg of sample in a U-shaped quartz tube was heated from 50 to 900 °C at a heating rate of 10 °C/min.

Surface basicity of the reduced catalyst was measured by the CO\(_2\)-temperature-programmed desorption (CO\(_2\)-TPD). 50 mg of the catalyst was reduced at 650 °C for 30 min, followed by flushing with 50 mL/min Ar for 30 min at 650 °C and then cooling down. A 10 vol % CO\(_2\)/Ar flow (50 mL/min) was adsorbed at 50 °C for 1 h, and then the sample was purged by 50 mL/min Ar for 30 min. Finally, the TPD of CO\(_2\) was performed from 50 to 700 °C at a heating rate of 10 °C/min in an Ar flow (50 mL/min).

TGA (STAR® System METTLERTOLEDO Corp.) was used to investigate the carbon deposition of the used catalyst. The catalyst was pretreated at 800 °C for 30 min and then cooled to room temperature in 50 mL/min N\(_2\). Next, the catalyst was heated from room temperature to 900 °C at a heating rate of 10 °C/min in 50 mL/min air.

Raman spectroscopy was performed to characterize the carbon deposition of 10 mg of the used catalyst. Raman spectra were obtained using an inVia Raman Microscope (inVia Reflex) with a He–Ne green laser (532.14 nm) at ambient conditions in the range of 1000–2000 cm\(^{-1}\).

4.3. Catalysis Measurement. The catalytic tests were investigated in a quartz fixed-bed reactor (inner diameter 8 mm) loaded with 100 mg of powder catalyst. Prior to starting a test, catalyst was reduced in situ at 650 °C under a 5 vol % H\(_2\)/N\(_2\) flow (30 mL/min) for 40 min. The feed liquid with a steam to carbon molar ratio equaling 5 (S/C = 5), was fed at 0.012 mL/min through a peristaltic pump at a space time of 49.7 g mol/h. Besides, N\(_2\) carrier gas was kept at 30 mL/min by a mass flow controller. The products passed through a cold trap for liquid product capture and then a bed of silica gel (16 cm). The gas products were analyzed online by gas chromatography (Pgeneral GC 1100) equipped with a thermal conductivity detector and a TDX-01 column (80–100 mesh) with N\(_2\) carrier gas. The catalytic performance was evaluated by hydrogen yield (\(Y_{\text{H}_2}\)), glycerol conversion to gaseous products (\(X_g\)), and yield of C-containing gas product (\(Y_Y\)).

\[
Y_{\text{H}_2} (\%) = \frac{F_{\text{H}_2,\text{out}}}{7F_{\text{glycerol, in}}} \times 100
\]

\[
X_g (\%) = \frac{F_{\text{out}}}{3F_{\text{glycerol, in}}} \times 100
\]
where, \(i\) is the CO, CO\(_2\), or CH\(_4\).

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This work is supported by the National Natural Science Foundation of China under grant number 21473180.

**ACKNOWLEDGMENTS**

The authors declare no competing financial interest.

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