Catalytic Steam Reforming of Biomass-Derived Acetic Acid over Two Supported Ni Catalysts for Hydrogen-Rich Syngas Production

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ABSTRACT: The catalytic steam reforming (CSR) of biomass-derived acetic acid over the commercial Ni-based catalyst (CNC) and the maize stalk ash-supported Ni catalyst (Ni/MSA) for hydrogen-rich syngas production was studied by means of a bench-scale fixed-bed unit combined with NDIR/TCD techniques. A maize stalk ash-supported Ni catalyst was developed for steam reforming of HOAc. The chemical composition and structural characteristics of CNC and Ni/MSA catalysts were compared. Evolution characteristics of H₂ and CO during CSR of HOAc were explored. Between 600 and 900 °C, the yields of H₂ and CO showed a similar trend over time, which first increased rapidly to the peak value, then began to decrease and finally tended to stabilize. The optimal reaction conditions were as follows: temperature = 800 °C, water to carbon molar ratio (WCMR) = 3, and weight hourly space velocity (WHSV) = 5 h⁻¹. Elevating the reforming temperature up to 900 °C gave rise to the continuously increased H₂ yield and enhanced catalyst ability for selective hydrogen production. The percentage of coke deposited on the catalyst decreased by 49.8% with the rise of temperature from 600 to 900 °C. The CO yield continued to decrease with increasing WCMR from 1 to 7. Ni/MSA gave similar CO yield to the CNC. The Ni/MSA exhibited better ability to selectively generate hydrogen than the CNC, resulting in significantly higher hydrogen yield.

INTRODUCTION

Hydrogen is one of the most promising clean energy sources and widely used in fuel cells, transportation, and power systems. As a basic chemical material, hydrogen has wide applications in chemical synthesis, food processing, petrochemical, and metallurgical industries. Currently, hydrogen is mainly derived from fossil fuels. Considering the importance of environmental issues and sustainable energy development, it is particularly important to explore clean and renewable hydrogen production methods.

The utilization of renewable biomass for hydrogen generation can reduce environmental pollution while reducing the reliance on fossil fuels. The methods of hydrogen production from biomass mainly include biological and thermochemical approaches. Among them, the catalytic steam reforming (CSR) of bio-oils produced by rapid pyrolysis of biomass is one of the most prospective routes to produce hydrogen from biomass on an industrial scale, which is mainly due to the advantages of this technology mentioned in several literature studies. In addition, the CSR of one part of the bio-oil can provide hydrogen to the hydrotreating process of the other part, thereby enabling the hydrogen source self-sufficiency in the catalytic hydrogenation conversion of the bio-oil and making the bio-oil refining technology more economical and practical. However, the bio-oil contains a wide variety of components, such as carboxylic acids, aldehydes, ketones, furans, phenols, and sugars, making the reforming process very complicated. Acetic acid (HOAc) is a typical carboxylic acid, whose content can be up to 20% in bio-oils. Moreover, HOAc can be produced in large quantities from biomass by fermentation. Therefore, HOAc has been recognized as the important and representative derivative of biomass to establish the correlations between the catalyst physicochemical characteristics and its reforming performance for hydrogen production.

Currently, although some progress has been made in the theoretical research and technology development of bio-oil CSR for hydrogen generation, there are still many deficiencies. The main constraint is catalyst deactivation due to carbon deposition, poisoning, and sintering. Therefore, to explore novel high-efficiency catalysts with high catalytic activity, high selectivity, high stability, and easy regeneration is the key to the development of bio-oil CSR technology, focusing on how to enhance the structure stability and catalytic activity of reforming catalysts and reduce the carbon deposition rate on the catalyst surface. The studies on reforming catalysts of bio-oils and their model compounds for hydrogen production have largely focused on noble metal catalysts (such as Pt, Rh, Pd,
Supported noble metal catalysts have high catalytic activity and good stability, but they are expensive and have limited reserves, which greatly limits their industrial application and is difficult to suffice the needs of large-scale production of industrial catalysts. Non-noble metal Ni-based catalysts are also fit for use as reforming catalysts for hydrogen production because of their low cost and good catalytic activity, but they still have problems such as weak stability, poor carbon deposition ability, and easy deactivation, which impose certain restrictions on their industrial applications. Therefore, there is an urgent need to develop a novel high-efficiency and inexpensive Ni-based catalyst which has excellent reactivity, high selectivity, long-term stability, and easy regeneration for inexpensive Ni-based catalyst which has excellent reactivity, high selectivity, long-term stability, and easy regeneration for bio-oil CSR to produce hydrogen.

At present, the studies on Ni-based catalysts have mainly focused on the influence and promotion mechanism of catalyst supports and promoters. The introduction of suitable supports and promoters can enhance the catalyst activity, structural stability, and carbon deposition resistance. Adding a certain amount of alkali metal and alkaline earth metal (such as K, Mg), rare earth metal (such as La, Ce) or transition metal (such as Fe, Co, Cu) promoters can increase the dispersion of active components, improve the structural and chemical properties of reforming catalysts, thereby enhancing their catalytic activity, stability, and anti-carbon deposition ability. Most studies on nickel-based catalyst carriers have focused on single metal oxide supports such as Al2O3, MgO, SiO2, ZrO2, and composite oxide supports, such as CeO2−Al2O3, La2O3−Al2O3, CeO2−ZrO2, MgO−La2O3−Al2O3, and so on.

Straw ash is a kind of solid waste generated after the burning of crop straws, which is produced in large quantities in biomass power plants and needs to be dealt with urgently. Otherwise, it will lead to a series of environmental and health problems. At present, the conventional treatment methods for straw ash include preparation of concrete building materials, adsorbents, fertilizers, and so forth, or improvement of soil by application to the field. It is emphasized that the high value utilization of straw ash as a catalyst or catalyst carrier needs to be further developed. As we all know, straw ash is mainly composed of various oxides with high thermal stability, such as SiO2, CaO, K2O, Al2O3, MgO, Na2O, Fe2O3, and so forth. They have good catalytic or cocatalytic effects, among which K, Na, Mg, and Fe are good promoters, while Al2O3 and SiO2 are good catalyst carriers. In particular, CaO has dual functions as both a catalyst and an absorbent, which can realize the in situ separation of CO2 in the reaction system. The above aspects confirm that straw ash has excellent catalytic performance and has been previously used for catalytic application in coalchar gasification. However, there are very few reports about its application in bio-oil CSR, and this aspect deserves further exploration.

The objective of this study is to develop an inexpensive and effective straw ash-supported Ni catalyst for hydrogen-rich syngas generation and explore its catalytic activities. In this study, the CSR of HOAc as a representative bio-oil derivative over commercial nickel-based catalyst and maize stalk ash-supported Ni catalysts for hydrogen production was studied by means of a bench-scale fixed-bed unit combined with the nondispersive infrared/thermal conductivity detection (NDIR/TCD) techniques. The effects of reforming temperature, water to carbon molar ratio (WCMR), and catalyst types on hydrogen production were explored. This study combines the catalytic utilization of straw ash with the clean generation of hydrogen from CSR of bio-oils.

### RESULTS AND DISCUSSION

#### Chemical Reactions Involved in the CSR of HOAc. The chemical reactions involved in the catalytic reforming of HOAc are very complex and can be described by R1–R20 shown in Table 1. Small molecular gases, such as H2, CO, CO2, CH4, and

| no. | reaction | reaction type |
|-----|----------|---------------|
| R1  | C2H4O2 + 2H2O → 2CO2 + 4H2 | complete steam reforming of HOAc |
| R2  | C2H4O2 + H2O → CO + CO2 + 3H2 | steam reforming of HOAc |
| R3  | 2C2H4O2 → C2H6O + CO2 + H2O | ketonization of HOAc |
| R4  | C2H4O2 → C2H2O + H2O | thermal decomposition |
| R5  | C2H4O2 → CH4 + CO2 | water gas shift reaction |
| R6  | C2H4O2 → CO2 + 2H2 + C | methane steam reforming |
| R7  | CO + H2O → CO + H2 | methane dry reforming |
| R8  | CH4 + 2H2O → CO + 4H2 | hydrogenation or methanation reactions |
| R9  | CH4 + H2O → CO + 3H2 | |
| R10 | CH4 + CO2 → 2CO + 2H2 | |
| R11 | CO + 3H2 → CH4 + H2O | |
| R12 | CO2 + 4H2 → CH4 + 2H2O | |
| R13 | 2CO + 2H2 → CO + CH4 | |
| R14 | C + 2H2 → CH4 | |
| R15 | CO + H2 → C + H2O | carbon monoxide reduction reaction |
| R16 | CO3 + 2H2 → C + 2H2O | carbon dioxide reduction reaction |
| R17 | CO2 + H2 → CO + H2O | reverse water gas shift reaction |
| R18 | CH4 → 2H2 + C | coke formation by CH4 decomposition |
| R19 | 2CO → CO2 + C | coke formation by Boudouard reaction |
| R20 | C + H2O → CO + H2 | coke gasification |
before, the main components of the MSA are SiO$_2$, CaO, K$_2$O, P$_2$O$_5$, Al$_2$O$_3$, and MgO, which make up more than 90% of MSA.$^{32}$ In addition, a small amount of Fe$_2$O$_3$ and Na$_2$O are also present in the MSA. SiO$_2$ and Al$_2$O$_3$ have been experimentally proven to be good catalyst supports. K, Na, Mg, and Fe can be used as additives of reforming catalysts and have been proven to have good catalytic or cocatalytic effects.$^{29}$ In particular, the content of CaO in the MSA is as high as 10%. CaO has dual functions as both a catalyst and an absorbent, which can realize the in situ separation of CO$_2$ in the reaction system and help to increase H$_2$ yield and purity.

The two catalysts, CNC and Ni/MSA, are similar in that they both contain a higher amount of NiO (11.80 and 26.00% for CNC and Ni/MSA, respectively), SiO$_2$ (25.50, 30.60%), and Al$_2$O$_3$ (17.70, 2.25%). They differ in that the CNC contains a higher amount of ZrO$_2$ (10.80%) and WO$_3$ (32.20%), while Ni/MSA contains a higher amount of K$_2$O (14.50%), CaO (9.95%), MgO (4.29%), and Fe$_2$O$_3$ (2.14%). The catalyst CNC is a rod-like catalyst with a specific surface area and a pore volume of 72.25 m$^2$/g and 0.156 cm$^3$/g, respectively, while the catalyst Ni/MSA is a powdery catalyst with a specific surface area of 2.46 m$^2$/g and a pore volume of 0.011 cm$^3$/g, which are significantly smaller than those of the CNC.

According to the physical adsorption isotherm classification method proposed by the International Union of Pure and Applied Chemistry (IUPAC), the adsorption isotherms for the fresh and reformed catalysts can be classified as IV type, indicating that they belong to mesoporous materials, which can also be confirmed from the data shown in Figure 1. From Figure 1a, in the lower relative pressure ($P/P_0$) region, the adsorption isotherm is convex upward, similar to the type II isotherm, and the adsorption mechanism is also basically the same. When $P/P_0$ reaches about 0.4, the adsorbate undergoes capillary condensation in the mesopores and the adsorption capacity suddenly rises. When the capillary condensation of all the mesopores is completed, the adsorption occurs only on the outer surface much smaller than the inner surface, and the increasing trend of adsorption capacity gradually slows down. The capillary condensation phenomenon makes the adsorption/desorption isotherms unable to coincide and gives rise to the occurrence of adsorption hysteresis and thus the formation of hysteresis loops shown in Figure 1a. Compared to the fresh CNC catalyst, CNC600 gives the higher amount of gas adsorbed. This is mainly due to the formation of some new pores and the opening of the part of closed pores caused by increasing temperature. However, when the temperature is further increased, the adsorbed quantity is always reduced.

Pore size distribution (PSD) and specific surface area distribution (SSAD) diagrams for the fresh and used CNC catalysts under steam reforming of different feedstocks are displayed in Figure 1b,c, respectively. As observed, compared to the fresh catalyst, the steam reforming reaction results in

| catalyst  | Na$_2$O | MgO  | Al$_2$O$_3$ | SiO$_2$ | P$_2$O$_5$ | K$_2$O | CaO  | Fe$_2$O$_3$ | NiO  | ZrO$_2$ | WO$_3$ |
|-----------|---------|------|-------------|---------|-----------|-------|------|-------------|------|--------|-------|
| CNC       | 0.13    | 0.07 | 17.70       | 25.50   | 0.08      | 0.34  | 0.04 | 0.10        | 11.80| 10.80   | 32.20 |
| Ni/MSA    | 0.77    | 4.29 | 2.25        | 30.60   | 3.96      | 14.50 | 9.95 | 2.14        | 26.00| 0.02    |       |

Figure 1. (a) Isothermal curves, (b) PSD diagram, (c) SSAD diagram, and (d) porosity characteristics for the fresh and reformed CNC catalyst.
considerable variation in the PSD and SSAD of reformed catalysts, thus leading to the visible changes in catalyst specific surface area values (see Figure 1d). The specific surface area of the fresh catalyst is 72.25 m²/g, while that of the reformed catalysts are 83.57, 69.24, 53.43, and 36.92 m²/g for CNC600, CNC700, CNC800, and CNC900, respectively. The specific surface area and pore volume of the reformed catalysts are decreased by 55.8 and 16.8% with increase in temperature from 600 to 900 °C. Correspondingly, the average pore diameter of the reformed catalysts is increased with temperature.

XRD Analysis. The X-ray diffraction (XRD) spectra of the fresh CNC, Ni/MSA, and used CNC, Ni/MSA catalysts under steam reforming at temperature = 800 °C, WCMR = 3, and weight hourly space velocity (WHSV) = 5 h⁻¹ are shown in Figure 2. As the fresh and used catalysts contain very complex substances, the XRD patterns shown are the superposition of the diffraction peaks of various internal phases. The absorption or reflection of X-ray is different for each component in a catalyst, which is related not only to the content and crystallinity of the substance but also to the existence of other substances in the catalyst. In addition, there may be diffraction peaks at the same angle for different substances, but the peak intensities are different. The occurrence of XRD peak overlap makes it difficult to accurately analyze the catalyst crystal structure. Therefore, the detected substances cannot cover all the substances in the catalysts. The three peaks in the XRD spectrum of the fresh Ni/MSA are clearly visible at 2θ = 37.1°, 43.3, and 62.9°, as shown in Figure 2. As mentioned by Li et al., the three peaks at 2θ = 37.1°, 43.3, and 62.9° are assigned to the NiO(111), NiO(200), and NiO(220) bands, respectively. For the fresh CNC catalyst, the band assigned to NiO(111) can be observed, while the other two bands are not obvious. Furthermore, CNC has the characteristic diffraction bands of NiWO 4 with 2θ of 24.9°, 30.9°, and 36.6°. Moreover, there are diffraction peaks of Al₂O₃ observed at 2θ = 31.1°, 32.8°, and 37.0°. The weak peak corresponding to Ni(111) at 2θ = 44.7° can be observed, which means that the content of active constituent metal Ni is relatively low, suggesting the weak catalytic activity of the CNC at 600 and 700 °C. This is consistent with the experimental results shown in Figure 4. When the reforming temperature is increased above 800 °C, the intensity of the Ni(111) peak is significantly increased. At the same time, a new diffraction peak appears at 2θ = 51.8°, corresponding to the Ni(200) peak. These results indicate a continuous increase in the reduction degree of NiO in the catalyst with elevating temperature. Raising temperature favors the reduction of more NiO in the catalyst to Ni, which is attributed to the reaction of NiO + H₂ → Ni + H₂O. Therefore, increasing the reforming temperature is beneficial for increasing the catalyst activity. However, the temperature should not be too high because too high temperature will lead to the aggregation and sintering of catalyst particles, resulting in its deactivation.

Effect of Reforming Temperature on Steam Reforming of HOAc. Temperature is a very crucial parameter affecting the CSR of the bio-oil. The influence of reforming temperature on the evolution characteristics of H₂ and CO from the CSR of HOAc at WCMR = 3 and WHSV = 5 h⁻¹ is shown in Figure 4. At the beginning of the reforming process, the reforming reaction is very intense, and the H₂ yield increases sharply with reaction time to the peak values of 14.9, 22.5, 24.7, and 27.1%, corresponding to 600, 700, 800, and 900 °C. After that, the yield of H₂ exhibits a downward trend, indicating that the catalyst ability for selective H₂ production gradually decreases. Because as the reaction proceeds, the intermediates are generated in large amounts during the CSR.

![Figure 2](image-url)  
**Figure 2.** XRD spectra of the fresh CNC, Ni/MSA, and reformed CNC, Ni/MSA catalysts at temperature = 800 °C, WCMR = 3, and WHSV = 5 h⁻¹.

![Figure 3](image-url)  
**Figure 3.** XRD patterns of fresh and reformed CNC catalysts at different temperatures.
of HOAc and cover the catalyst surface, which hinder the effective contact of the reactants (e.g., HOAc, H2O, CO, and so forth.) with the catalyst. In addition, different reactions are competitive at the catalyst active sites. The above factors inhibit the reactions [HOAc steam reforming (R1 and R2), thermal decomposition (R6), water gas shift reaction (R7), methane steam/dry reforming (R8−R10), and coke gasification (R20)] associated with hydrogen generation, resulting in the decrease of hydrogen yield and the lessened ability of the catalysts to selectively generate hydrogen. When the reaction time exceeds 10 min, the decreasing trend of H2 yield gradually slows down in response to the increase of reaction time. In the range of 600−900 °C studied, the yields of both H2 and CO show a similar trend, which rapidly increase to the highest values, then decrease continuously, and finally stabilizes.

Raising the reforming temperature up to 900 °C gives rise to the continuous increment of H2 yield and the enhanced ability of the catalysts for selective hydrogen production. Such observations were also mentioned by Salehi et al.34 when conducting the CSR of bio-oil over Ni/Al2O3 catalysts in the range of 750−950 °C. Therefore, the suitable reforming temperature should be above 800 °C. Considering that the yield of CO is the highest at 800 °C, and CO can be converted to H2 by water gas shift reaction under suitable conditions, 800 °C is the optimal temperature from the perspective of potential H2 yield and energy saving.

Coke deposition on the catalyst is one of the major obstacles of bio-oil CSR technology, which not only leads to the reduction of H2 yield but also to catalyst poisoning, deactivation, and even reactor blockage. Therefore, it is very important to avoid or inhibit coke formation. The amount of coke formed on the reforming catalyst was analyzed by DTG. Figure 5 shows the effect of reforming temperature on the percentage of catalyst coke deposits at the operational conditions of WCMR = 3 and WHSV = 5 h−1. When HOAc and steam are completely catalytically reformed to H2 and CO2 under ideal circumstances, the corresponding WCMR is 1. H2 yields at WCMR = 3 and 7 are close to that at WCMR = 1. This research finding is different from those reported in other studies.37,38 Wang et al.37 performed the CSR of HOAc over Ni/La2O3−Al2O3 catalysts and found that raising the WCMR from 1 to 5 gave rise to a continuous increase in H2 yield. Wang et al.38 examined the effect of WCMR on the CSR of HOAc over coal ash-supported Ni catalyst and pointed out that the H2 yield constantly increased from 44.2% to approximately 60% with raising the WCMR from 1 to 7.5. Considering the fact that HOAc is difficult to fully and effectively contact with steam and to be completely converted to H2 and CO2 in actual situations, the WCMR of 3 is an optimum choice to ensure good hydrogen production effect.

At a constant feeding rate of HOAc, increasing the WCMR means that the water feeding rate is increased, which, on the one hand, ensures the effective contact of HOAc with steam and maximizes the carbon conversion; on the other hand, it promotes the water gas shift reaction equilibrium toward the positive direction of hydrogen generation and the catalytic gasification of coke deposits on the catalyst. The aspects described above are beneficial to increase the H2 yield. However, the WCMR should not be too large. This, on the one hand, causes too much water vapor to be wasted because
of not participating in the reforming reaction and has a detrimental effect on the purification of the downstream gas; on the other hand, the residence time of the reactants on the catalyst bed is reduced so that some of the reactants are too late to be converted and carried away by excess water vapor, causing carbon conversion to decrease with increase in the WCMR, as evidenced by the experimental data shown in Figure 6.

At a WCMR of 1, the yield of CO is highest for a given time, and as the WCMR increases, the CO yield decreases. This observation is consistent with our previous study when testing Ni–Ce/Al₂O₃ catalysts for bio-oil CSR in the WCMR range of 1–9. The main gas products produced by catalytic reforming of HOAc at WCMR = 1 are H₂ and CO. The increase in WCMR causes the water gas shift and methanation reaction equilibrium toward the positive direction, resulting in the continuous consumption of CO and H₂ and the generation of more CO₂ and CH₄. This may explain why there is no significant increase in H₂ yield with increase in the WCMR. With further increase of the WCMR, the water vapor has an increased feeding rate without changing that of HOAc and can carry some of the reactants away so that the residence time of the reactants in the catalyst bed is reduced, causing the decrease of carbon conversion and main gas yields with the increase of the WCMR.

Effect of Catalysts on Steam Reforming of HOAc. In the three cases of no catalyst, CNC, and Ni/MSA, the evolution characteristics of H₂ and CO with time at temperature = 800 °C, WCMR = 3, and WHSV = 5 h⁻¹ are exhibited in Figure 7. From the perspective of H₂ yield and carbon conversion, the catalytic reforming of HOAc over CNC and Ni/MSA is much better than that in the absence of the catalyst. In the presence of the CNC and Ni/MSA catalysts, the H₂ yield increases rapidly to a maximum with reaction time, then slowly decreases, and finally gradually stabilizes. Ni/MSA gives significantly higher H₂ yields than the CNC. However, almost the same carbon conversions are obtained over the two catalysts. The above information proves that Ni/MSA has the better ability to selectively generate hydrogen than CNC, resulting in significantly higher H₂ yield. The yield of CO has a similar trend to that of H₂, which increases rapidly to a maximum at the initial stage of the reforming process, then decreases with the progress of reforming reaction, and finally stabilizes. The CO yield is much greater in the presence of the CNC and Ni/MSA than that without the catalyst. To explore the stability of Ni/MSA, the CSR of HOAc was carried out for 7 h at 800 °C with a WCMR of 3 and WHSV of 5 h⁻¹. Figure 8 shows H₂, CO yields, and carbon conversion as a function of time on stream. The Ni/MSA catalysts are relatively stable for the CSR of HOAc within 7 h, corresponding to the slight decrease of H₂ and CO yields, which can be confirmed by the carbon conversion data exhibited in Figure 8. The above information confirms that Ni/MSA has good resistance to carbon deposition. In addition, Ni/MSA has the better ability.
to selectively generate hydrogen than the CNC. Therefore, Ni/MSA shows great potential because of its low cost and environmental benefit by utilizing the maize stalk ash as its support.

## CONCLUSIONS

A maize stalk ash-supported Ni catalyst was developed for steam reforming of HOAc. The chemical composition and structural characteristics of the CNC and Ni/MSA catalysts were compared. Evolution characteristics of H₂ and CO during CSR of HOAc were explored. Between 600 and 900 °C, the yields of H₂ and CO showed a similar trend over time, which first increased rapidly to the peak value, then began to decrease, and finally tended to stabilize. The optimal reaction conditions were temperature = 800 °C, WCMR = 3, and WHSV = 5 h⁻¹. Elevating the reforming temperature up to 900 °C gave rise to the continuously increased H₂ yield and the enhanced catalyst ability for selective hydrogen production. The percentage of coke deposited on the catalyst decreased by 49.8% with the rise of temperature from 600 to 900 °C. The CO yield continued to decrease with increasing the WCMR from 1 to 7. Ni/MSA gave a similar CO yield to the CNC. Ni/MSA exhibited better ability to selectively generate hydrogen than the CNC, resulting in significantly higher hydrogen yield.

## EXPERIMENTAL SECTION

**Experimental Apparatus and Procedure.** The reforming experiments were performed in a bench-scale fixed-bed unit combined with the NDIR/TCD techniques. The schematic diagram of the reforming system and the related details could be found in our previously published paper. In each run, the catalysts were first reduced in situ under a N₂/H₂ atmosphere. Afterward, the reactor was purged with N₂ and heated to the target temperature between 600 and 900 °C. The bio-oil and steam were then introduced to the reaction system through two peristaltic pumps. The produced gas passed through a condensing system to mostly separate excess water and some unconverted reactants. A cotton filter was employed to capture residual condensable vapors to minimize interference with the rear gas analyzers. The cleaned gas was dried through a silica gel filter and then fed to a Gasboard-3100 analyzer based on the NDIR/TCD method, a detailed explanation of which can also be found in our previous paper. After each experiment, the catalyst bed was purged and cooled to room temperature in a stream of N₂. Subsequently, the catalyst bed, condenser, pipes, and filters were removed and weighed. Finally, the air was sent into the reforming reactor by combustion to clear away heavy tar from the tube wall. The condenser and all possible condensation lines were cleaned with acetone and the solvent was evaporated at 60 °C.

**Catalysts Preparation, Characterization, and Catalytic Performance Evaluation.** Maize stalk (MS) was collected from Zibo, central region of Shandong province (China). After harvesting maize plants, MS was air-dried, crushed, and then sieved to obtain particles below 80 mesh. The sieved particles were calcined at 815 °C for 30 min and then cooled to room temperature to obtain MS ash, which was chosen as the catalyst support. The MS ash-supported Ni catalysts were prepared by impregnation using the aqueous solution of nickel nitrate supported on MS ash. A known amount of Ni(NO₃)₂·6H₂O was dissolved in deionized water to obtain an aqueous solution of nickel nitrate. Then, a certain amount of prepared MS ash was slowly added to the above solution. The obtained slurry was continuously stirred at room temperature for 3 h, then dried at 110 °C for 48 h in a drying oven, and subsequently calcined at 600 °C for 4 h in a muffle furnace. Finally, the MS ash-supported Ni catalysts were obtained. The prepared MS ash, commercial nickel-based catalyst, and MS ash-supported Ni catalyst were denoted as MSA, CNC, and Ni/MSA, respectively. The reforming CNC catalysts were denoted as CNCT, where T represents the reforming temperature.

The catalyst chemical composition was measured by a ZSX-100e X-ray fluorescence spectrometer. The specific surface area and pore structure characteristics of the catalysts were measured using an ASAP 2020 analyzer. The XRD measurements were conducted by using a Bruker AXS D8 ADVANCE X-ray diffractometer. The amount of coke deposited on the catalyst surface was analyzed by a WCT-1C thermogravimetric analyzer. The temperature program was set to increase from room temperature to 800 °C and maintained at this temperature for 10 min. The weight loss of the catalyst was recorded online in real time. According to the weight loss curves, the percentage of coke deposited on catalyst could be obtained by calculation.

The performance evaluation of the catalysts was carried out according to the evolution characteristics of the main gas products and carbon conversion. The H₂ yield was defined as the ratio of the moles of H₂ produced to the theoretical maximum H₂ amount corresponding to complete reforming of HOAc to CO₂ and H₂. The yields of CO, CO₂, and CH₄ were defined as the ratio of the moles of corresponding gas produced to the moles of carbon in the feed. The carbon conversion could be obtained by dividing the moles of carbon in the gaseous products by the moles of feed carbon. The WCMR and WHSV were defined according to the methods provided in our previous paper.

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**Notes**

The authors declare no competing financial interest.
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