Hydrogen Production by Ethanol Reforming on Supported Ni–Cu Catalysts
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ABSTRACT: Supported bimetallic Ni–Cu catalysts with different Ni–Cu loadings on alumina (Al₂O₃), alumina–silica (Al₂O₃–SiO₂), alumina–magnesia (Al₂O₃–MgO), alumina–zinc oxide (Al₂O₃–ZnO), and alumina–lanthanum oxide (Al₂O₃–La₂O₃) were prepared and tested in ethanol steam reforming for the production of hydrogen (H₂). These catalysts were characterized by X-ray diffraction, H₂-temperature-programmed reduction, ammonia-temperature-programmed desorption, X-ray photoelectron spectroscopy, thermogravimetry, and differential scanning calorimetry. Cu addition improved the reducibility of NiO. Among the as-prepared catalysts, 30Ni5Cu/Al₂O₃–MgO and 30Ni5Cu/Al₂O₃–ZnO demonstrated much higher H₂ selectivity and excellent coke resistance compared to the other investigated catalysts. Over 30Ni5Cu/Al₂O₃–MgO and 30Ni5Cu/Al₂O₃–ZnO, the respective H₂ selectivity was 73.3 and 63.6% at 450 °C and increased to 94.0 and 95.2% at 600 °C. The strong interaction of Ni–Cu and Al₂O₃–ZnO (or Al₂O₃–MgO) led to the formation of smaller and highly dispersed CuO and NiO species on the carrier, which is conducive to improved catalytic performance. These Al₂O₃–MgO- and Al₂O₃–ZnO-supported bimetallic Ni–Cu materials can be promising catalysts for hydrogen production from ethanol steam reforming.

1. INTRODUCTION
The synthesis and use of hydrogen has received considerable attention due to carbon pollution from conventional fuels. Of special interest is ethanol obtained by fermentation of renewable substances, considering the reproducibility of biomass feedstocks, good processability of liquid ethanol, and high hydrogen conversion.⁴⁻⁶ Ethanol can be efficiently converted to the main product hydrogen (H₂) by the following reaction⁷⁻⁹

\[
\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 2\text{CO}_2, \Delta f_{298}^0 = +347.4 \text{ kJ/mol}
\]

The thermodynamic ethanol reforming reaction usually consists of several reactions, starting with a dehydrogenation or dehydration reaction. The dehydrogenation reaction produces acetaldehyde, which is transformed into carbon monoxide and methane by C–C bond cleavage. However, carbon deposition in the process of producing ethylene from ethanol is an urgent problem to be solved. Generated CH₄ can form H₂ and CO via steam reforming, and a water–gas shift (WGS) reaction can convert CO to carbon dioxide (CO₂).

In general, transition metals such as Ni, Co, Pt, Pd, and Rh are often used to catalyze the production of hydrogen from ethanol due to their good activity and selectivity.⁷⁻⁹ Ni is widely used as a catalyst thanks to its high activity in C–C bond cleavage, however, its use is limited by various disadvantages.¹⁰⁻¹² The reactivity of Cu is limited for hydrogen production from ethanol but good for dehydrogenation and the WGS reaction. In addition, mixing in Ni and Cu can reduce CO production and improve coking.
resistance for hydrogen production in ethanol using silica (SiO₂) as a carrier.

Among oxide carriers, alumina (Al₂O₃) carriers have excellent physical and chemical stabilities and are commonly used as catalysts for hydrogen production from ethanol. However, the deactivation of Al₂O₃ due to carbon deposition greatly reduces its catalytic activity. To address these shortcomings, the researchers developed alkaline additives that readily absorb water and improve the surface mobility of hydroxyl (OH) groups. Magnesium oxide (MgO) and solid solution magnesium oxide (MgAl₂O₄) have been developed and used to avoid coking on nickel-based carriers because they allow better dispersion of nickel powders. Zinc oxide (ZnO) has basic characteristics as well as redox properties that accelerate the dehydrogenation of ethanol to acetaldehyde, which is also promoted by lanthanum oxide (La₂O₃) and other lanthanide oxides. In addition, it was reported that SiO₂-stabilized Al₂O₃ used as the support for Pd catalysts can make the methane combustion more complete and employing SiO₂–Al₂O₃ as the support can slow down coking in the process of olefin hydrogenation. Although many metal catalysts have been studied for hydrogen production from ethanol, further intensive investigations are required to explore efficient catalysts with high coke resistance and selectivity in the production of H₂.

To determine the effect of Cu and supports on the performance of bimetallic Ni–Cu catalysts in ethanol steam reforming, several metal-oxide-modified supports with varying Cu contents were investigated in this study. The composite supports Al₂O₃–SiO₂, Al₂O₃–MgO, Al₂O₃–ZnO, and Al₂O₃–La₂O₃ were prepared and used as bimetallic Ni–Cu catalyst supports. The catalysts were characterized by X-ray diffraction (XRD), H₂-temperature-programmed reduction (H₂-TPR), ammonia-temperature-programmed desorption (NH₃-TPD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The results showed that Al₂O₃–MgO- and Al₂O₃–ZnO-supported Ni–Cu catalysts possessed much better catalytic performance than the other investigated catalysts.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction Analysis. XRD patterns of the calcined 30Ni5Cu catalysts with different supports are shown in Figure 1. The major peaks at 2θ = 36, 46, and 67° are attributed to γ-Al₂O₃, and the peaks around 2θ = 18 and 60° are attributed to NiO species. The diffraction peaks of NiO and CuO are not observed in patterns (c) and (d), indicating that NiO and CuO might be well dispersed on the support. To further explore the relationship between the active species and the carrier structure, H₂-TPR experiments were conducted.

2.2. H₂-Temperature-Programmed Reduction. The H₂-TPR profiles of the catalysts are shown in Figure 2. Except for the 30Ni5Cu/Al₂O₃–La₂O₃ catalyst, the reduction curves of the catalysts generally contained two peaks. The low-temperature peak could be attributed to the reduction of dispersed small metal particle species (NiO or Ni–Cu mixed metal oxides), and the high-temperature peak probably resulted from the reduction of agglomerated coarse metal particle species. The two reduction peak intensities of the 30Ni5Cu/Al₂O₃–SiO₂ catalyst were similar, and it was assumed that the amounts of dispersed fine metal and agglomerated coarse metal particle species were roughly the same. For 30Ni5Cu/Al₂O₃–SiO₂, the intensity of the high-temperature reduction peak decreased, and the low-temperature reduction peak shifted to a higher temperature, which indicated that the introduction of SiO₂ can promote the dispersion of metal particles. For the 30Ni5Cu/Al₂O₃–MgO catalyst, the low-temperature reduction peak shifted to a lower temperature and was significantly stronger than the high-temperature reduction peak, which infers that most of the NiO species on the catalyst occurred in a well-dispersed form. For the 30Ni5Cu/Al₂O₃–ZnO catalyst, the low-temperature reduction peak shifted to a lower temperature and was significantly stronger than the high-temperature reduction peak, which infers that most of the NiO species on the catalyst occurred in a well-dispersed form. Moreover, for the 30Ni5Cu/Al₂O₃–La₂O₃ catalyst, the low-temperature reduction peak shifted to a lower temperature and was significantly stronger than the high-temperature reduction peak, which infers that most of the NiO species on the catalyst occurred in a well-dispersed form. However, the deactivation of Al₂O₃ due to carbon deposition greatly reduces its catalytic activity. To address these shortcomings, the researchers developed alkaline additives that readily absorb water and improve the surface mobility of hydroxyl (OH) groups. Magnesium oxide (MgO) and solid solution magnesium oxide (MgAl₂O₄) have been developed and used to avoid coking on nickel-based carriers because they allow better dispersion of nickel powders. Zinc oxide (ZnO) has basic characteristics as well as redox properties that accelerate the dehydrogenation of ethanol to acetaldehyde, which is also promoted by lanthanum oxide (La₂O₃) and other lanthanide oxides. In addition, it was reported that SiO₂-stabilized Al₂O₃ used as the support for Pd catalysts can make the methane combustion more complete and employing SiO₂–Al₂O₃ as the support can slow down coking in the process of olefin hydrogenation. Although many metal catalysts have been studied for hydrogen production from ethanol, further intensive investigations are required to explore efficient catalysts with high coke resistance and selectivity in the production of H₂.

2.3. NH₃-Temperature-Programmed Desorption. NH₃-TPD curves of the catalysts in Figure 3 show that the
Figure 3. NH$_3$-TPD of the catalysts: (a) 30Ni5Cu/Al$_2$O$_3$, (b) 30Ni5Cu/Al$_2$O$_3$–SiO$_2$, (c) 30Ni5Cu/Al$_2$O$_3$–ZnO, (d) 30Ni5Cu/Al$_2$O$_3$–MgO, and (e) 30Ni5Cu/Al$_2$O$_3$–La$_2$O$_3$.

The chemical states of the elements Ni and Cu on the surfaces of various catalysts after reduction in H$_2$ at 650 °C were investigated by XPS, and the relevant information is shown in Table 2. The XPS spectra of all reduced catalysts contained the peak of Ni$^0$ (852.6 eV) and Ni$^{2+}$ in nickel aluminate entities (856.2 eV). According to literature, the Cu 2p$_{3/2}$ lines appear at 932.4, 932.6, and 934.6 eV and are typically assigned to Cu$^0$, Cu$^{+}$, and Cu$^{2+}$. In the reduced catalyst samples, Cu species are identified as Cu$^0$ or Cu$^{2+}$ species. On the surfaces of the Al$_2$O$_3$–ZnO and Al$_2$O$_3$–MgO carriers, the samples showed a relatively high Ni/Al ratio, while smaller Cu/Al ratios indicate the high dispersion of active species on these supports.

For the 30Ni5Cu/Al$_2$O$_3$, 30Ni5Cu/Al$_2$O$_3$–SiO$_2$, 30Ni5Cu/Al$_2$O$_3$–La$_2$O$_3$, and 30Ni5Cu/Al$_2$O$_3$, the higher Cu/Al atomic ratio indicates that Cu caused a large amount of aggregation on the carrier surface.

2.5. Catalytic Performance. 30Ni5Cu/Al$_2$O$_3$ ($x = 0, 5, 10, 15$) catalysts were assessed for the production of hydrogen from ethanol at 400–600 °C at a molar H$_2$O/ethanol ratio of 4.0 and a GHSV of 8.0 h$^{-1}$ Figure 4 compares the selectivities for products including H$_2$, CO, CH$_4$, and CO$_2$ over the catalysts 30Ni5Cu/Al$_2$O$_3$, the selectivities for H$_2$, CO, and CO$_2$ were 58.7, 33.4, 39.0, and 18.8% at 400 °C, respectively. The selectivity for H$_2$ and CO$_2$ increased while that for CH$_4$ decreased with temperature. CO selectivity exhibited a maximum of 9.4% at 450 °C, and the selectivities for H$_2$, CO, and CO$_2$ were 90.0, 24.1, 7.4, and 58.8%, respectively, at a temperature of 600 °C. The 30Ni5Cu/Al$_2$O$_3$ catalyst showed the highest selectivity for H$_2$ and CO$_2$ in the temperature range of 400–600 °C, i.e., the selectivity for H$_2$, CO, CH$_4$, and CO$_2$ of 61.2, 29.6, 42.7, and 26.3% at 400 °C changed to 92.0, 32.3, 7.2, and 59.9% at 600 °C. When the Cu content was increased to 10 or 15 wt %, the selectivity for H$_2$ and CO$_2$ decreased in comparison to 30Ni5Cu/Al$_2$O$_3$–SiO$_2$ at the investigated temperatures, implying that the rates of the ethanol steam reforming reaction (C$_2$H$_5$OH + 3H$_2$O $→$ 6H$_2$ + 2CO$_2$) and the WGS reaction (CO + H$_2$O $→$ CO$_2$ + H$_2$) decreased when the Cu concentration was high.

Based on the established optimal catalyst composition of 30Ni5Cu/Al$_2$O$_3$, the performance of different composite supports for hydrogen production from ethanol was compared. Figure 5 shows the selectivity of various metal catalysts for H$_2$ from 400 to 600 °C. The catalysts with the composite supports Al$_2$O$_3$–MgO and Al$_2$O$_3$–ZnO demonstrated higher H$_2$ selectivity than other composite supports. The difference in H$_2$ selectivity of these metal catalysts becomes insignificant after the temperature reaches 600 °C.

For the 30Ni5Cu/Al$_2$O$_3$–MgO and 30Ni5Cu/Al$_2$O$_3$–ZnO catalysts, the effect of reaction temperature was further studied. Figure 6 shows the experimental results for 30Ni5Cu/Al$_2$O$_3$–MgO. When the temperature was lower than 300 °C, acetaldehyde was produced in the system due to the low conversion rate of ethanol conversion. When the temperature was increased from 300 to 600 °C, ethanol was completely converted, and thus, no ethylene and acetaldehyde were found in the system. These results show that Al$_2$O$_3$ supports containing MgO do not possess sufficient acidic sites for ethanol dehydrogenation. The Al$_2$O$_3$–MgO-supported catalyst was catalyzed by the following mechanisms: (i) dehydrogenation reaction on Cu sites and (ii) C–C bond breaking of acetaldehyde, formed as an intermediate product by the
dehydrogenation reaction, and generation of CO and CH4 on the Ni site.27

As shown in Figure 6, H2 selectivity increases with temperature. The selectivity to H2 increased from 52.6% at 300 °C to 94.0% at 600 °C, indicating that the catalytic system has better selectivity to H2. As the temperature increased from 300 to 600 °C, the water conversions were 10.7% (300 °C), 40.1% (450 °C), and 55.0% (600 °C). At the same time, the selectivity of CO and CO2 also increases with the increase of temperature in the range of 300−600 °C. Meanwhile, the selectivity of the catalytic system to CH4 reaches a maximum value as the temperature increases and then decreases to 11.0%

**Table 2. Binding Energies of Ni 2p3/2 and Cu 2p3/2 and Atomic Ratios on the Catalyst Surfaces**

| samples               | Ni 2p3/2 (eV) | Ni species | ratio (mol %) | Cu 2p3/2 (eV) | Cu species | ratio (mol %) | Ni/Al<sup>a</sup> | Cu/Al<sup>b</sup> |
|-----------------------|---------------|------------|---------------|---------------|------------|---------------|-------------------|-------------------|
| 30Ni5Cu/Al2O3         | 852.6         | Ni<sup>0</sup> | 49.19         | 932.7         | Cu<sup>0</sup> | 100%          | 0.29              | 0.094             |
|                       | 855.7         | Ni<sup>2+</sup> | 50.81         |               |             |               |                   |                   |
| 30Ni5Cu/Al2O3−MgO     | 852.5         | Ni<sup>0</sup> | 55.6          | 932.6         | Cu<sup>0</sup> | 100%          | 0.61              | 0.067             |
|                       | 855.9         | Ni<sup>2+</sup> | 44.4          |               |             |               |                   |                   |
| 30Ni5Cu/Al2O3−ZnO     | 852.2         | Ni<sup>0</sup> | 60.6          | 932.6         | Cu<sup>0</sup> | 100%          | 0.67              | 0.049             |
|                       | 855.8         | Ni<sup>2+</sup> | 39.4          |               |             |               |                   |                   |
| 30Ni5Cu/Al2O3−La<sub>2</sub>O<sub>3</sub> | 852.3 | Ni<sup>0</sup> | 41.6          | 932.3         | Cu<sup>0</sup> | 100%          | 0.20              | 0.13              |
|                       | 855.7         | Ni<sup>2+</sup> | 58.4          |               |             |               |                   |                   |
| 30Ni5Cu/Al2O3−SiO<sub>2</sub> | 852.6 | Ni<sup>0</sup> | 67.6          | 932.5         | Cu<sup>0</sup> | 100%          | 0.34              | 0.12              |
|                       | 856.1         | Ni<sup>3+</sup> | 32.4          |               |             |               |                   |                   |

<sup>a</sup>Nominal value: 0.59.  <sup>b</sup>Nominal value: 0.09.

**Figure 4.** Effect of copper content on the 30Ni5Cu/Al2O3 catalyst performance for hydrogen production from ethanol reforming: (A) H2 selectivity, (B) CO selectivity, (C) CH4 selectivity, and (D) CO2 selectivity.
as the temperature increases to 600 °C. It is shown that the reforming and reverse shift reactions of CH₄ are accelerated at the same time at elevated temperatures.
converted, while acetaldehyde is only present at temperatures below 350 °C. At the same time, no ethylene was found in the whole testing process, indicating that 30Ni5Cu/Al2O3−ZnO greatly reduced the possibility of ethanol dehydration to ethylene due to its weak acidity.28 As shown in Figure 7, H2 selectivity increased with temperature. When the temperature was increased to 450 °C, the conversion of water was 32.5%, and the selectivities for H2, CO2, and CH4 were 63.6, 37.5, and 39.1%, respectively. The results also indicate that the WGS reaction occurs and causes a decrease in CO selectivity. When the temperature increased to 600 °C, H2 selectivity was 95.2%, while CH4 selectivity was below 7.2%, and CO2 selectivity increased to 63.3%; meanwhile, the selectivity to CO increased to 33.3%. These results suggest that CH4 reforming and the reverse shift reaction were accelerated, while the WGS reaction gradually decreased.29

2.6. Thermogravimetric Analysis and Differential Scanning Calorimetry. In the process of ethanol reforming, ethanol dehydration probably occurred and produced ethylene, which was easily decomposed on the catalyst surface to form coke (C2H4 → 2C + 2H2).30,31 To investigate the anticoking performance of the catalysts, TG and DSC experiments were conducted. Before the test, the 30Ni5Cu/Al2O3, 30Ni5Cu/Al2O3−MgO, and 30Ni5Cu/Al2O3−ZnO catalysts were catalyzed in the range of 250−600 °C at a temperature interval of every 50 °C for 2 h in the production of hydrogen from ethanol. Figure 8 shows the TG curves of the reacted catalyst to evaluate the moderate coking effect during the reaction. According to previous studies,32,33 three forms of carbon are typically deposited on the catalyst during ethanol reforming, which are monoatomic carbon, filamentous coke, and graphitized carbon. But monoatomic carbon and filamentary coke can be easily removed by oxidation due to their high reactivity. However, as with increasing deposition of these two forms of carbon in catalytic systems, the possibility of graphitization of carbon is greatly increased. On the other hand, the formed graphitized carbon requires a higher temperature than the other two carbon species to react with O2.24 Therefore, we can know from the TGA curve that the peak below 550 °C is the oxidation of monoatomic carbon or filamentous coke in the catalytic system, while the higher temperature peaks are attributed to the oxidation of graphitized coke in the catalytic system. Such graphitic carbon would greatly reduce the catalytic activity of this supported catalyst.34 As calculated from the TG data, about 53% of the deposited coke present in 30Ni5Cu/Al2O3 is graphitic coke and a portion is other carbon coke. The monoatomic carbon and filamentary coke of 30Ni5Cu/Al2O3−MgO and 30Ni5Cu/Al2O3−ZnO account for most of them, so the proportion of graphite coke was below 10%. The supports of Al2O3−MgO and Al2O3−ZnO greatly decreased the formation of coke in the catalytic system, which was probably that the active metals are well dispersed on the support, so the catalyst has stronger adsorption performance.35,36

3. CONCLUSIONS

Catalysts loaded with two metals (Ni and Cu) on Al2O3 and Al2O3−M2O (M = Si, La, Mg, or Zn) supports were prepared and their catalytic performances in the production of hydrogen from ethanol were investigated. The experimental results show that among these bimetallic supported catalysts, Cu, the one loaded with 5 wt % has the best catalytic performance. We prepared Ni−Cu-based bimetallic catalyst supported on Al2O3−M2O (M = Si, La, Mg, or Zn) based on a Cu content of 5 wt % and investigated the catalytic activity of the composite support on reforming of ethanol to hydrogen. Among them, Al2O3−MgO-and Al2O3−ZnO-supported catalysts demonstrated better catalytic activity than those supported on other research supports because of their better selectivity for H2. For 30Ni5Cu/Al2O3−MgO and 30Ni5Cu/Al2O3−ZnO, H2 selectivities were 73.3% and 63.6% at 450 °C and increased to 94.0 and 95.2%, respectively, when the temperature was increased to 600 °C. Furthermore, the two catalysts exhibited much lower coking amounts and could probably be used as promising catalysts for hydrogen production by ethanol steam reforming.

4. EXPERIMENTAL SECTION

4.1. Catalyst Preparation. Al2O3−M2O carriers (M = La, Mg, or Zn) were prepared by a precipitation−impregnation method using a commercial γ-Al2O3 (Dow Chemicals, S BET = 180 m2/g) powder, and the molar ratio of M/Al in mixed oxide was fixed at 0.25. A 0.1 M aqueous urea solution was dropped into a 0.1 M aqueous solution of lanthanum(III) nitrate, magnesium(II) nitrate, or zinc(II) nitrate and mixed well at 100 °C with constant stirring. Then, γ-Al2O3 powder was added to the above solution, and stirring was continued at 100 °C for 6 h. The mixture was filtered and the resulting solid was dried at 120 °C and then calcined in air at 650 °C for 6 h. The mixed solid was ground and sieved to obtain the catalyst carriers with a size of 0.2−3 mm. They were labeled Al2O3−M2O, where M refers to the metal element (Mg, Zn, and La) of the second oxide. In a typical experiment, Al2O3−SiO2 supports were prepared by the sol−gel method. First, Al(NO3)3·9H2O was dissolved in distilled water, and the pH of the solution was adjusted to 3.0−3.5 with dilute nitric acid, and a stoichiometric amount of tetraethoxysilane (TEOS) (SiO2/Al2O3 molar ratio of 0.25) was added to 0.347 g/mL Al(NO3)3. After mixing for 5 h, the pH of the solution was adjusted to 3.0 to obtain a floc, which was finally adjusted with dilute nitric acid.

Ni and Ni−Cu catalysts were synthesized by a precipitation−impregnation method using the prepared Al2O3−SiO2,
**Al₂O₃−MgO, Al₂O₃−ZnO, and Al₂O₃−La₂O₃ supports as well as the commercial γ-Al₂O₃ support. The nominal Ni loadings on the supports were fixed at 30 wt %. Stoichiometric amounts of an aqueous nickel(II) nitrate solution (0.1 M) and an aqueous copper(II) nitrate solution (0.1 M) were added to the supports, and then, aqueous urea solution (0.1 M) was added at 100 °C. The suspension was filtered, and the obtained solid was dried at 120 °C and calcined in air at 650 °C for 6 h. This supported metal catalyst was designated 30NiₓCuₓ/Al₂O₃−MₐO₂ (x = 0, 5, 10, 15, M = Mg, Zn, La, and Si), where the catalyst 30Ni₅Cu/Al₂O₃−MgO is represented as an Al₂O₃−MgO carrier containing 30 wt % Ni and 5 wt % Cu.

4.2. Catalyst Characterization. The crystals of the materials were analyzed by X-ray diffraction (XD-3 diffractometer, Beijing Purkinje General Instrument Co., Ltd., China). The instrument used Cu Kα radiation (λ = 0.15418 nm) and was operated at 40 kV and 40 mA. XRD patterns were collected at 20 angles from 5 to 85°. X-ray photoelectron spectroscopy (XPS) was conducted with a Kratos Axis Ultra DLD spectrometer with a Mg Kα X-ray source. The reduction temperature of different supported metal catalysts was investigated using H₂-TPR and NH₃-TPD Micromeritics AutoChem 2920 V3.05 instruments. Specifically, H₂-TPR was used at a heating rate of 10 °C/min from room temperature to 900 °C. The NH₃-TPD experiments were carried out by heating samples to 650 °C at a heating rate of 10 °C/min at a He flow rate of 50 mL/min while using a thermal conductivity detector (TCD) to determine the NH₃ concentration in the system.

4.3. Activity Tests. The experiments for the production of hydrogen from ethanol reforming were conducted in a stainless steel tubular reactor (inner diameter = 12 mm, length = 360 mm) operating at atmospheric pressure. The catalyst (150 mg) was diluted in a volume ratio of 3:1 using SiC (0.2–0.3 mm) per experiment to avoid unfavorable thermal reactions. After placement of the diluted supported catalyst, the reactor was purged with N₂ at 200 °C and then reduced with H₂ (30 mL (STP)/min) at 650 °C for 40 min at a heating rate of 10 °C/min. After the pretreatment gas was removed by flushing the reactor with N₂, a mixture of water and ethanol at a molar ratio of 4.0 was fed into the evaporator at a rate of 1.2 mL/h by a syringe pump, and then, a mass flow controller was used with the N₂ mix supplied at a flow rate of 80 mL/min. After gasification at 150 °C, the reaction products were analyzed by online GC-TCD (chromatograph model 3420, Agilent) using a Porapak Q packed column (id = 2 mm, length = 5.0 m, CO₂, ethane, ethylene, water, acetaldehyde, ethanol, acetone, acetic acid, diethyl ether, ethyl acetate, and crotonaldehyde) and a TDX-01 packed column (id = 2 mm, length = 3.0 m, H₂, N₂, CO, CH₄, CO₂, and ethylene) in series with He as the carrier gas. Ethanol conversion denoted as X ethanol, H₂ selectivity denoted as S H₂, and the selectivity to carbon products denoted as S carbon−containing product are evaluated according to the following equations:

\[
X_{\text{ethanol}} = \frac{F_{\text{ethanol-in}} - F_{\text{ethanol-out}}}{F_{\text{ethanol-in}}} \quad (1)
\]

\[
S_{\text{H}_2} = \frac{F_{\text{gas}} \cdot V_{\text{H}_2}}{6(F_{\text{ethanol-in}} - F_{\text{ethanol-out}})} \quad (2)
\]

where \( F_{\text{ethanol}} \) is the molar flow rate of ethanol, \( F_{\text{gas}} \) is the total gas flow rate, \( V_{\text{H}_2} \) is the volume content of \( \text{H}_2 \) in the gas products, and \( n \) denotes the ratio of the calculated number of carbon atoms in ethanol to the number of carbon atoms in the product.

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

This work was supported by the NFCS (21376280) and Guangdong Provincial Science and Technology Plan (2016A010105022 and 2017A010103024).

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