Hydrogen production via steam reforming of bio-oil model compounds over supported nickel catalysts

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Abstract
The steam reforming of four bio-oil model compounds (acetic acid, ethanol, acetone and phenol) was investigated over Ni-based catalysts supported on Al\textsubscript{2}O\textsubscript{3} modified by Mg, Ce or Co in this paper. The activation process can improve the catalytic activity with the change of high-valence Ni (Ni\textsubscript{2}O\textsubscript{3}, NiO) to low-valence Ni (Ni, NiO). Among these catalysts after activation, the Ce-Ni/Co catalyst showed the best catalytic activity for the steam reforming of all the four model compounds. After long-term experiment at 700 °C and the S/C ratio of 9, the Ce-Ni/Co catalyst still maintained excellent stability for the steam reforming of the simulated bio-oil (mixed by the four compounds with the equal masses). With CaO calcinated from calcium acetate as CO\textsubscript{2} sorbent, the catalytic steam reforming experiment combined with continuous in situ CO\textsubscript{2} adsorption was performed. With the comparison of the case without the adding of CO\textsubscript{2} sorbent, the hydrogen concentration was dramatically improved from 74.8% to 92.3%, with the CO\textsubscript{2} concentration obviously decreased from 19.90% to 1.88%.

Key words
hydrogen production; bio-oil; model compounds; Ni catalyst; CO\textsubscript{2} capture

1. Introduction

Currently, hydrogen producing is mainly through steam reforming of fossil fuels containing nature gas, naphtha and coal. But due to the depletion of fossil fuels and the deterioration of the environment resulting from its utilization process, increasing attention is being paid to the development of clean and renewable energy [1]. Renewable biomass is recognized as an attractive alternative to fossil fuels, because of its rich reserves and neutral CO\textsubscript{2} emissions [2]. There are mainly two thermochemical processes to produce hydrogen from biomass, gasification and flash pyrolysis followed by steam reforming of the pyrolysis bio-oil. The latter was known as one of the more economically friendly methods for hydrogen production with the fairly mature pyrolysis technology and the easy transportability [3–9]. However, bio-oil is typically a complex mixture of low and high molecular weight oxygenated compounds, such as carbonxylic acids, alcohols, ketones, aldehydes and phenols [10–12]. So, it is difficult to directly perform the steam reforming of the entire bio-oil, and therefore, model compounds were often used to establish catalyst structure-activity correlations, such as ethanol, acetic acid, acetone, phenol, ethylene or the mixture of two or more compounds [1,10,13–18].

For the bio-oil, the steam reforming reaction is:

\[ C_nH_mO_k + (n - k)H_2O \rightarrow nCO + (n + m/2 - k)H_2 \] (1)

associated with the water gas shift (WGS) reaction:

\[ nCO + nH_2O \rightarrow nCO_2 + nH_2 \] (2)

Given the Equation (1) and Equation (2) happening successively, the overall reforming reaction can be represented as follows:

\[ C_nH_mO_k + (2n - k)H_2O \rightarrow nCO_2 + (2n + m/2 - k)H_2 \] (3)

From the above equations, there is almost equivalent carbon dioxide with hydrogen in the final products of steam reforming, thereby limiting the hydrogen purity, with the concentration lower than 70% in the most researches [1,19–21]. On the other hand, as the WGS reaction is limited by the equilibrium, it is expected that the removal of CO\textsubscript{2} from the gas phase in the steam reforming process will displace the equilibrium to higher H\textsubscript{2} production [22]. Hence, the steam reforming process of bio-oil with in situ CO\textsubscript{2} capture was put forward. In the related studies, most of CO\textsubscript{2} sorbents were
CaO-based substances [9,22–25]. And, the certain amounts of CO₂ sorbent, mixed with reforming catalysts, were often packed in a fixed bed reactor, and the results showed that the addition of CO₂ sorbents could obviously improve the hydrogen concentration before the adsorption capacity of CO₂ sorbents reached saturation [9,23,25]. However, the fixed amount of CO₂ sorbents limited the continuity of the SR process with high efficiency. Aimed to realize continuous CO₂ capture, for acetic acid, ethanol, acetone and phenol, respectively:

CH₃COOH + 2H₂O −→ 2CO₂ + 4H₂ (4)

CH₃COCH₃ + 5H₂O −→ 3CO₂ + 8H₂ (5)

CH₃OH + 11H₂O −→ 6CO₂ + 14H₂ (7)

In the SR process, some side reactions also took place, such as thermal decomposition reaction (Equation 8) and (carbon) disproportionation reaction (Equation 9):

\[ C_nH_mO_k \rightarrow C_xH_yO_z + \text{gas}(H_2, CO, CO_2, CH_4, \cdots) + \text{coke} \] (8)

\[ C + CO_2 \rightarrow 2CO \] (9)

In the catalyst test experiments, ethanol, acetic acid and acetone were mixed with deionized water into the aqueous solution with the mole ratio of steam to carbon (S/C) of 6. Because of the limited solubility of phenol in water at room temperature, the aqueous solution of phenol was made up with S/C ratio of 12. In the experiment of catalytic steam reforming with in situ CO₂ capture, the four compounds were mixed with the equal masses, and then the mixture, called simulated bio-oil, was mixed with deionized water at S/C ratio of 9 into the aqueous solution as the feed of this experiment.

2.2. Catalysts preparation

Eleven nickel-based catalysts (Ni, Ni/Mg, Mg-Ni, Mg-Ni/Mg, Mg-Ni/Ce, Mg-Ni/Co, Ce-Ni, Ni/Ce, Ce-Ni/Mg, Ce-Ni/Ce and Ce-Ni/Co) supported on the Al₂O₃ balls with 3–5 mm in diameter were prepared with the incipient wetness method. Mg, Ce and Co were as the auxiliary agent elements. The precursors used for Ni, Mg, Ce and Co metals were Ni(NO₃)₂·6H₂O, Mg(NO₃)₂·6H₂O, Ce(NO₃)₃·6H₂O, and Co(NO₃)₃·6H₂O, respectively. For Ni, Ni/Mg and Ni/Ce, they were prepared with just one-time impregnation. For other catalysts, they were impregnated for two times. Mg or Ce metal was firstly impregnated to improve thermostability of the Al₂O₃ carrier, and the mixed Ni and Mg or Ce or Co metals were then impregnated. In each impregnating process, the carrier particles were impregnated in the aqueous solutions of the precursors for 12 h and then were dried over night at 120 °C, and afterwards were calcined at 950 °C for 3 h. The nominal metal composition of the final catalysts was 10 wt% for Ni, 5 wt% for Mg and Ce in the first impregnation, and 5 wt% for Mg, Ce and Co in the second impregnation. Before the catalytic performance tests, these catalysts were activated at 600 °C in the atmosphere of H₂ (10% in N₂) for 6 h.

2.3. Apparatus

Figure 1(a) shows a schematic illustration of the experiment apparatus of catalytic test. The experiments were conducted in a fixed-bed reactor made of stainless steel (06Cr25Ni20). The catalysts were placed in the middle of the reactor.
steel tube, with the packing height of 15 cm. The aqueous solutions of the compounds were pumped into the reactor drop by drop through the peristaltic pump. The product gas from the reactor was in sequence cooled, dried and finally detected by gas meter and gas analyzer. Prior to the catalytic reaction, the catalysts were reduced in a H\textsubscript{2} flow from the hydrogen generator.

Figure 1(b) shows the schematic illustration of the experiment apparatus of catalytic steam reforming with in situ CO\textsubscript{2} capture. The preferred catalyst was packed in the middle of reactor tube with the same packing height with the catalyst test experiment. The CO\textsubscript{2} sorbent, calcium oxide powder, obtained by the calcination of calcium acetate at 900 °C for 3 h, was introduced into reactor from the screw feeder with nitrogen as carrier gas. The gaseous products from reactor were purified by filtering the solid powder. Then the subsequent equipments were the same with the experiment apparatus of catalytic test.

The crystalline phases of the catalyst samples were tested with the X-ray diffractometer (Shimadzu, XRD-7000) using Cu K\textsubscript{α} radiation operated at 30 kV and 40 mA, and diffraction data was recorded continuous scanning with a step of 2.0 °/s.

Figure 1. The schematic illustrations of experiment apparatus (a) for catalytic test and (b) for catalytic steam reforming combined with in situ CO\textsubscript{2} capture

2.4. Data analysis

The activities of the catalysts for the reforming reaction of bio-oil model compounds were compared in term of the yields and contents of H\textsubscript{2}, CO, CO\textsubscript{2} and CH\textsubscript{4}. The hydrogen yield (Equation 10) was defined as the mole ratio of H\textsubscript{2} in the actual gaseous products to the theoretical amount of hydrogen that can be obtained when complete reforming to CO\textsubscript{2} and H\textsubscript{2} occurs (Equations 3–7):

\[
\text{H}_2 \text{ yield (\%)} = \frac{\text{Moles of H}_2\text{ obtained in actual gaseous products}}{(2n + m/2 - k)/n \times \text{moles of carbon in the feed}} \times 100\% \tag{10}
\]

For the three carbonous gaseous products, each yield was defined as the number of moles of itself in effluent gas per mole carbon feed:

\[
\text{CO, CO}_2 \text{ or CH}_4 \text{ yield (\%)} = \frac{\text{Moles of CO, CO}_2 \text{ or CH}_4 \text{ in the gas obtained}}{\text{Moles of carbon in the feed}} \times 100\% \tag{11}
\]

The total yield of the three carbonous gases, was also called carbon selectivity. The higher carbon selectivity means the fewer carbon deposits or other hydrocarbons (C\textsubscript{n}H\textsubscript{m}) produced. However, because of CO\textsubscript{2} adsorption, the total yield of the carbonous gases can no longer represent the carbon selectivity in the experiment of catalytic steam reforming with in situ CO\textsubscript{2} capture. Therefore, besides the actual hydrogen yield (Equation 10), the other two kinds hydrogen yields (H\textsubscript{2}(+CO) and H\textsubscript{2}(+CO+CH\textsubscript{4})) were also studied. The H\textsubscript{2}(+CO) yield (Equation 12) was defined as the sum of the actual hydrogen yield and the potential hydrogen yield from the complete reaction of carbon monoxide in the gaseous products through the WGS reaction; the H\textsubscript{2}(+CO+CH\textsubscript{4}) yield (Equation 13) was defined as the sum of the H\textsubscript{2}(+CO) yield and the potential hydrogen yield from the complete reaction of methane in the gaseous products through the methane steam reforming reaction (MSR, Equation 14).

\[
\text{H}_2(+/CO) \text{ yield (\%)} = \frac{\text{Moles of (H}_2\text{ + CO) in gaseous products}}{(2n + m/2 - k)/n \times \text{moles of carbon in the feed}} \times 100\% \tag{12}
\]
\[
\text{H}_2(+/CO+CH}_4\text{) yield (\%)} = \frac{\text{Moles of (H}_2\text{ + CO + 4CH}_4\text{) in gaseous products}}{(2n + m/2 - k)/n \times \text{moles of carbon in the feed}} \times 100\% \tag{13}
\]
Because the exothermic WGS reaction readily took place, the H$_2$(+CO) yield was studied, generally called potential hydrogen yield. The SR reaction of methane will be promoted under the suitable conditions (such as efficiency catalyst, sufficient steam), although the reaction is endothermic. Moreover, the H$_2$(+CO+CH$_4$) yield to some extent can reflect the degree of carbon selectivity.

The liquid hourly space velocity was defined by the formula in Equation (15):

$$\text{LHSV} = \frac{\text{Volumetric flow rate of aqueous solution of model compound}}{\text{Volume of catalyst}}$$ (15)

In this paper, all volumes were calculated at 1 atm and room temperature, and the catalytic reforming reaction was performed at the LHSV of 850 h$^{-1}$ and 700 $^\circ$C.

3. Results and discussion

3.1. Selection of catalysts

3.1.1. Effect of activation

Figure 2 shows the effect of non-activated Ni, activated Ni and pure Al$_2$O$_3$ balls (as blank sample) on the yields of gaseous products for four model compounds. From Figure 2, the hydrogen yields of the Al$_2$O$_3$ balls for all the compounds were the lowest, and after the adding of Ni, the hydrogen yields were improved, other than that of non-activated Ni for acetic acid. For acetic acid, the hydrogen yield over the non-activated Ni was almost the same low in the yield with Al$_2$O$_3$, indicating that the non-activated Ni catalyst had a very weak catalytic effect on the steam reforming of acetic acid. For the two samples, the main products of acetic acid were CH$_4$, CO$_2$ and small amount of H$_2$ with scarcely any CO, which were attributed to the following thermal decomposition reaction (Equation 16).

$$\text{CH}_3\text{COOH} \rightarrow \text{CO}_2 + \text{CH}_4$$ (16)

But with the comparison of the former two catalysts, the hydrogen yield of acetic acid over the activated Ni catalyst as obviously increased, with the improved CO$_2$ and CO yields and the decreased CH$_4$ yield, indicating that the steam reforming of acetic acid was dominant, or the activated Ni was favorable for the processing of the methane steam reforming (Equation 17):

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}$$ (17)

For the other three compounds, the similar rule was also gotten that their hydrogen yields over the activated Ni catalyst were higher than those over the non-activated Ni catalyst,
with the CO\textsubscript{2} and CO yields increased and the CH\textsubscript{4} yields decreased, although the hydrogen yield of ethanol was just slightly increased.

Figure 3 shows the X-ray diffraction patterns of non-activated and activated Ni catalysts. For the activated Ni catalyst, Ni element mainly in the form of lower valence (Ni, NiO) was loaded on the Al\textsubscript{2}O\textsubscript{3}. On the contrary, Ni element of the non-activated Ni catalyst, mainly in the form of higher valence (Ni\textsubscript{2}O\textsubscript{3}, NiO), was loaded on the Al\textsubscript{2}O\textsubscript{3}.

According to the above results, the conclusion was drawn that low-valence Ni-based catalyst was favorable for the steam reforming processing of bio-oil model compounds. Therefore, before the catalytic performance tests of the other 10 Ni-based catalysts (Ni/Mg, Mg-Ni, Mg-Ni/Mg, Mg-Ni/Ce, Mg-Ni/Co, Ce-Ni, Ni/Ce, Ce-Ni/Mg, Ce-Ni/Ce and Ce-Ni/Co), all of them were activated.

3.1.2. Steam reforming of acetic acid

Figure 4 shows the effects of various catalysts on the yields and concentrations of gaseous products for acetic acid steam reforming. The hydrogen yields and concentrations of the magnesium-containing catalysts (Figure 4a and 4c) were lower than those of the cerium-containing catalysts (Figure 4b and 4d), and the hydrogen yields of Mg-Ni and Ni/Mg were even lower than pure Ni catalyst without any auxiliary agent element (see Figure 2a). It was because that MgNiO\textsubscript{2} spinels were formed in these catalysts (see Figure 5), which could decrease the number of active sites of these Ni-base catalyst. For Mg-Ni and Ni/Mg catalysts, the carbon selectivities and CH\textsubscript{4} yields were obviously higher than those of the other catalysts, mainly due to the thermal decomposition reaction of acetic acid.
acid (Equation 16). For the catalysts with two-time impregnation, the catalysts of first impregnation of cerium have higher hydrogen yields and carbon selectivity than those of first impregnation of magnesium, illustrating that Ce was more favorable than Mg to improve the carrier stability and the dispersion of active components on or in the carrier particles. Among all the catalysts, the Ce-Ni/Ce and Ce-Ni/Co having very similar yields and concentrations of gaseous products coincidentally, were the most active and selective for H₂ and CO₂, with about 73% hydrogen yield, about 76% carbon selectivity. And both of them had the highest hydrogen concentrations, around 69%.

3.1.3. Steam reforming of ethanol

Similarly to the case of acetic acid, for ethanol steam reforming with the various catalysts, the hydrogen yields and concentrations of the cerium-containing catalysts (Figure 6a and 6c) were higher than those of the magnesium-containing catalysts (Figure 6b and 6d), especially in the case of the catalysts with two-time impregnation. Noteworthily, the hydrogen yield and concentration, and carbon selectivity of the Mg-Ni/Co catalyst were all the lowest among all the six catalysts with two-time impregnation, but with the highest methane yield, and such a case also was found for acetic acid (see Figure 4). It was speculated that besides MgNiO₂ spinels, another kind of spinel containing (Co, Mg) or (Ni, Mg) may existed on or in the catalyst, thereby resulting in the undesirable catalytic activity. For Mg-Ni, Ni/Mg and Mg-Ni/Co catalysts with higher methane yields, the main reactions of ethanol should be the thermal decomposition reaction (Equation 18) and the WGS reaction (Equation 2), which are more liable to happen than the methane steam reforming (Equation 17 or Equation 12).
$$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2 \quad (18)$$

Among all the catalysts, the Ce-Ni/Co shows the best catalytic performance for ethanol steam reforming, with the hydrogen yield up to 90%, the carbon selectivity up to 95%, and the hydrogen concentration up to 76.6%.

### 3.1.4. Steam reforming of acetone

Figure 7 shows the effects of various catalysts on the yields and concentrations of gaseous products for acetone steam reforming. As in the case of acetic acid and ethanol, for acetone steam reforming, the catalysts showing the best catalytic performances were still Ce-Ni/Co and Ce-Ni/Ce, with the similar yields and distribution (their hydrogen yields up to 72%). The Mg-Ni, Ni/Mg and Mg-Ni/Co catalysts still showed the worst performances, with the hydrogen yields less than 40% and the methane yields over 29%, attributed to the decomposition of acetone to ketene (Equation 19), the hydration of ketene to acetic acid (Equation 20) and the decomposition of acetic acid (Equation 16) [15].

$$\text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_2\text{CO} + \text{CH}_4 \quad (19)$$
$$\text{CH}_2\text{CO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} \quad (20)$$

![Figure 7](image-url)

**Figure 7.** Yields and concentrations of gaseous products of acetone steam reforming over various catalysts: (a) and (c) for the catalysts with first impregnation of Mg and Ni/Mg, (b) and (d) for the catalysts with first impregnation of Ce and Ce/Ni

### 3.1.5. Steam reforming of phenol

The effects of various catalysts on the yields and concentrations of gaseous products for phenol steam reforming are shown in Figure 8. Because of the limited solubility of phenol in water, the catalytic performance experiments of phenol steam reforming were conducted at S/C ratio of 12, causing the higher yields over almost all the catalysts, compared with the other three compounds. Since there was in phenol no CH$_3$ group which is liable to form CH$_4$ by combining with H, the amount of methane produced in phenol reaction over all the catalysts in this paper was less. CO was formed most likely from the direct decomposition of phenol containing a C–O bond, or as a result of the steam reforming of CH or C from the decomposition of benzene ring in phenol [1]. As the cases of the other three compounds, the Ce-Ni/Ce catalyst showed the best catalytic performance for phenol steam reforming, with the hydrogen yield up to 87.5% and the hydrogen concentration up to 74.5%.
3.1.6. Assessment of catalytic activity

According to the above, the hydrogen concentrations for the four compounds over all the catalysts in the present study were without any significant change, so in the present study the hydrogen yields over all the catalysts for the steam reforming of the four compounds is symbolically summarized in the Table 1. Among these catalysts, the Ce-Ni/Co catalyst showed the most versatile performance for the steam reforming of model compounds to produce hydrogen.

### Table 1. Activity of various catalysts for steam reforming of model compounds in terms of hydrogen yield

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Acetic acid</th>
<th>Ethanol</th>
<th>Acetone</th>
<th>Phenol</th>
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<tr>
<td>Ni</td>
<td>D</td>
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<td>B</td>
<td>A</td>
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<tr>
<td>Mg-Ni</td>
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<td>Ni/Mg</td>
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<td>Mg-Ni/Mg</td>
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<td>C</td>
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<tr>
<td>Mg-Ni/Ce</td>
<td>D</td>
<td>B</td>
<td>C</td>
<td>A</td>
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<td>Ce-Ni</td>
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<td>Ni/Ce</td>
<td>C</td>
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<td>B</td>
<td>A</td>
</tr>
<tr>
<td>Ce-Ni/Mg</td>
<td>B</td>
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<td>C</td>
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<tr>
<td>Ce-Ni/Ce</td>
<td>A</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>Ce-Ni/Co</td>
<td>A</td>
<td>S</td>
<td>A</td>
<td>S</td>
</tr>
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</table>

S is represented for the yield between 85%—100%, A for 70%—85%, B for 60%—70%, C for 50%—60% and D for 20%—50%.

3.2. Stability of Ce-Ni/Co catalyst

Long-term activity test was performed for the Ce-Ni/Co catalyst in order to study its stability under steam reforming conditions. In the present study, the simulated bio-oil was as the feed with the S/C ratio of 9. Figure 9 shows the three hydrogen yields and the concentrations of gaseous products as function of reaction time. Since with the peristaltic pump the delivery of the aqueous solution of the simulated bio-oil was not strictly continuous (i.e. the droplets were fed to the reactor every 3—5 s), the hydrogen yields showed some fluctuations with time. But the overall trends of the three types of hydrogen yields over the Ce-Ni/Co catalyst were stable for the whole reaction time range of 8 h (see Figure 9a). The average values of the actual H₂ yield, H₂(+CO) yield and H₂(+CO+CH₄) yield were obtained up to 83.8%, 88.7% and 92.5%, respectively. The distribution of the gaseous products also shows the excellent stability for the whole reaction time range, with the average values of H₂, CO, CO₂ and CH₄ being 74.8%, 4.4%, 19.9% and 0.9%, respectively.
3.3. Steam reforming over Ce-Ni/Co catalyst combined with continuous in situ CO₂ capture

With the Ce-Ni/Co catalyst, the steam reforming of the simulated bio-oil with in situ CO₂ capture was conducted at 700 °C, the S/C ratio of 9. The CO₂ sorbent, CaO calcined from calcium acetate, as well as the aqueous solution of the simulated bio-oil, was continuously fed into the reactor with the CaO/C ratio (i.e. the ratio of CaO moles and the carbon moles in the simulated bio-oil per unit feeding time) of 3, and the case of the stable stage was used to analyze. Figure 10 shows the hydrogen yields and the distribution of gaseous products with and without the adding of CO₂ sorbent. After adding CO₂ sorbent, the three hydrogen yields were not with big change, with the increase of the actual H₂ yield to 84.2%, the increase of H₂+(CO+CH₄) yield to 96.7%, and the decrease of the H₂+(CO) yield to 87.4%. However, the CO₂ concentration was obviously decreased from 19.9% to just 1.88%, and H₂ concentration was dramatically increased from 74.8% to 92.3%, due to simultaneous CO₂ capture.

4. Conclusions

Aimed at meeting the steam reforming process combined with continuous in situ CO₂ capture, various Ni-based catalysts supported Al₂O₃ particles with 3−5 mm in diameter were prepared with the incipient wetness method and then selected. Over these catalysts, the steam reforming of acetic acid, ethanol, acetone and phenol as bio-oil model compounds was investigated. With the comparison of the non-activated Ni catalyst, the activated Ni catalyst mainly containing the low-valence Ni (Ni, NiO) showed the better catalytic performance. After activation, the hydrogen yields and concentrations of the cerium-containing catalysts were overall higher than those of the magnesium-containing catalysts, especially in the case of the catalysts with two-time impregnation, attributed to the higher metal dispersity. Among all the catalysts, the Ce-Ni/Co catalyst showed the most versatile performance for the steam reforming of all the four model compounds. The simulated bio-oil, mixed by the four compounds with the equal masses, was used for the long-term experiment of the Ce-Ni/Co catalyst at 700 °C and the S/C ratio of 9, showing the excellent stability. Finally, the Ce-Ni/Co catalyst was applied into the steam reforming process combined with continuous in situ CO₂ capture with the simulated bio-oil as feedstock and CaO as sorbent at 700 °C, the S/C ratio of 9 and the CaO/C ratio of 3. Although the hydrogen yield was with just slight increase, the hydrogen purity was dramatically improved, up to 92.3%, with the CO₂ concentration obviously decreased to 1.88%.

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