Influence of Ceria Modified Support on Steam Reforming of Acetic Acid Using Ni-Ru/CeO₂-Al₂O₃ Catalysts

(BASE, Tokyo University of Agriculture and Technology)

Jianglong Pu, Katsuki Nishikado, Eika W. Qian

1. Introduction

Concerning the great demand for energy and depletion of fossil fuel reserves, as well as the environmental pollution problems caused by automobile exhausts and industrial production in recent years, finding a new and alternative energy is becoming very urgent. Hydrogen is regarded as a clean and highly efficient energy resource to generate electricity via a fuel cell ¹. Biomass can be easily transformed into bio-oil by fast pyrolysis, in which process biomass is heated to high temperature rapidly in the absence of oxygen. Then hydrogen can be produced by steam reforming of bio-oil with involvement of catalyst. However, the traditional catalysts can be easily deactivated because of the severe coke formation on the catalyst. Therefore, it is urgent to develop a novel catalyst with a high activity and good ability to inhibit the formation of coke.

Elemental analysis of the bio-oil demonstrated that acetic acid is one of the main components ². Thus a study of steam reforming of bio-oil using acetic acid as model oxygenates is meaningful. Previous researches indicated that, besides the active metals on the catalysts, supports also had a significant effect on the performance of catalysts. Some researchers focus on researches about CeO₂ catalyst to reduce the coke formation on the catalyst due to its perfect redox property and oxygen storage capacity (OSC). In this research, effect of Al₂O₃ supports modified by various amount of CeO₂ on the ability to remove coke of catalysts was investigated.

2. Experimental

2.1 Preparation of catalysts

To investigate the effect of CeO₂ doping amount on the catalyst activity and durability, catalysts with various amounts of CeO₂ impregnated on Al₂O₃ were prepared. Nickel-Ruthenium were used as the active metals.

2.2 Characterization of catalysts

The catalysts prepared were characterized by BET, XRD and H₂-TPR. To investigate the ability to inhibit coke formation for the catalysts, DTG of catalysts spent after activity test was conducted.

2.3 Activity test of catalysts

Catalytic activity test was conducted on a fixed bed flow reactor. Firstly, the catalysts were reduced with H₂ under 600 °C for 3 h. Then the steam reforming of acetic acid was started at 650, 700, 750 °C respectively under 1 MPa for 10 h.

3 Results and discussion

3.1 Properties of supports and catalysts with addition of CeO₂

The results of BET measurement for supports showed that the specific surface area slightly decreased with an increase of CeO₂ on support indicating the partial obstruction of the narrow pore on the Al₂O₃ support by CeO₂.

Results of XRD demonstrated that all the peaks were isolated metal oxide but had a lower intensity, implying that the crystal structures of these oxides did not suffer significant alterations or formed a new phase, but a mixture of these three phases.

H₂-TPR profiles showed that as the loading of CeO₂ on the support, the reduction peak of NiO at low temperature became sharper, indicating the addition of CeO₂ favored for the reduction of NiO.
3.2 Effects on the catalytic activity

Fig. 1 was the hydrogen yield for these three catalysts at different temperatures. Activity test of the catalysts indicated that catalysts with CeO₂ exhibited a higher activity and good stability as the time on the stream. As the temperatures increased, the hydrogen yield increased for all these three catalysts. The catalysts suffered from a severe coke accumulation at 650 °C leading to the hydrogen yield decreased along with the time on stream for 10h.

3.3 Effects on coke formation on the catalyst

Thermogravimetric analysis of the catalyst after activity test showed that the coke amount, and the species deposited on the catalysts were different as showed in Fig. 2. From Table 1 it can be seen that as the temperature increased, the total carbon on the catalysts after activity test decreased, indicating that high temperature is favorable for the alleviation of coke formation on the catalysts. At the same time, the addition of CeO₂ on the catalysts can also slow down the coke formation especially for filamentous carbon which was the main reason for catalyst deactivation.

4. Conclusions

The support had a vital effect on both activity and durability of the catalyst for steam reforming of the acetic acid. NiRu/CeAl catalyst had better stability than the NiRu/Al catalyst. NiRu/20CeAl catalyst had the highest hydrogen yield and the lowest coke formation. High temperature is favorable for the activity and stability of the catalysts by alleviating the coke formation on the catalysts. CeO₂ can inhibit the deposition of coke on the catalyst due to its oxygen storage capacity, which can improve the durability of the catalyst.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>T (°C)</th>
<th>Cₐ(%)</th>
<th>Cₕ(%)</th>
<th>Cₛ(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiRu/Al</td>
<td>700</td>
<td>12.25</td>
<td>12.13</td>
<td>24.38</td>
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<tr>
<td></td>
<td>750</td>
<td>6.82</td>
<td>4.49</td>
<td>11.31</td>
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<tr>
<td>NiRu/10CeAl</td>
<td>650</td>
<td>16.89</td>
<td>27.86</td>
<td>44.75</td>
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<tr>
<td>CeAl</td>
<td>700</td>
<td>8.98</td>
<td>1.68</td>
<td>10.65</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>4.18</td>
<td>1.02</td>
<td>5.20</td>
</tr>
<tr>
<td>NiRu/20CeAl</td>
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<td>17.37</td>
<td>14.79</td>
<td>32.16</td>
</tr>
<tr>
<td>CeAl</td>
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<td>0.72</td>
<td>4.05</td>
<td>4.77</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>2.70</td>
<td>0.00</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Note: a): Amorphous carbon, b): Filamentous carbon, c): Total carbon