Supplementary Material

N-doped graphitized carbon supported Co@Ru core-shell bimetallic catalyst for hydrogen storage of N-ethylcarbazole

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1. Characterization

Fig. S1 was the XRD pattern of Co@Ru/NGC, monometallic Ru and Co catalysts. As shown in Fig. S1, for the Ru/NGC samples (Fig. S1B), the diffraction peaks at 2θ=38.3°, 42.0°, 44.0°, 69.1°, 78.1° and 85.0° correspond to (100), (002), (101) (110), (103), (112) crystal planes of bulk hexagonal Ru, the characteristic peaks at around 35.0° and 54.5° was assigned to the (101) and (211) planes of RuO₂ (JCPDS no.06-0663). For Co/NGC samples (Fig. S1C), the diffraction peaks at 2θ=44.6° and 78.7° correspond to the (111) and (220) crystal planes of face-centered cubic Co (JCPDS No.05-0727), respectively. While the diffraction peaks at 31.2°, 36.8°, 55.7°, 59.2° and 65.2°, which belong to a characteristic feature of Co₃O₄ phase. According to the XRD patterns of monometallic Ru and Co catalysts, the diffraction peaks of Co@Ru/NGC (Fig. S1A) at 44.2° and 79.2° can be expressed as Co@Ru bimetallic phase.
Fig. S1. XRD patterns of various catalysts: (A) Co@Ru/NGC, (B) Ru/NGC, (C) Co/NGC.

Table S1 Physical properties of synthesis catalyst

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$g$^{-1}$)</th>
<th>$V_T$ (cm$^3$g$^{-1}$)</th>
<th>$S_{micro}$ (m$^2$g$^{-1}$)</th>
<th>$V_{micro}$ (cm$^3$g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC-550-2</td>
<td>1172</td>
<td>0.68</td>
<td>850</td>
<td>0.35</td>
</tr>
<tr>
<td>Co@Ru/NGC-450-2</td>
<td>1051</td>
<td>0.74</td>
<td>775</td>
<td>0.32</td>
</tr>
<tr>
<td>Co@Ru/NGC-550-2</td>
<td>1007</td>
<td>0.77</td>
<td>758</td>
<td>0.30</td>
</tr>
<tr>
<td>Co@Ru/NGC-650-2</td>
<td>972</td>
<td>0.82</td>
<td>717</td>
<td>0.26</td>
</tr>
<tr>
<td>Co-Ru/BC-NaBH$_4$</td>
<td>1077</td>
<td>0.56</td>
<td>827</td>
<td>0.31</td>
</tr>
</tbody>
</table>

In order to determine the relevant information of metal reduction in the carbothermic reduction process, we performed TG analysis on the sample in a nitrogen atmosphere. As shown in Fig. S2(a), where Co$_1$Ru$_4$/BC is a sample without carbothermal reduction. Increased peak water loss due to capillarity in the material, the weight loss before 130°C is mainly water vapor in the material. Fig. S2(b) is the DTG curve of the sample, which can be seen from the DTG curve of Co$_1$Ru$_4$/BC. When the reduction temperature reaches 450°C, the weight loss rate of the sample gradually increases, indicating that the metal is beginning to be reduced. As the temperature rises to 550°C, the weight loss rate of the sample is the highest, revealing that the metal is
largely reduced at this temperature. At the same time, combined with the investigation of the catalyst preparation conditions in Fig. 8, when the reduction temperature is 450 and 500°C, the activity of the catalyst is poor, so 550°C is chosen as the best reduction temperature in this article.

![Fig. S2. TG (a) and DTG (b) curves of the sample.](image)

<table>
<thead>
<tr>
<th>Quality/g</th>
<th>Volume/ml</th>
<th>Dilution</th>
<th>Element</th>
<th>Display</th>
<th>Unit</th>
<th>Final result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0427</td>
<td>25</td>
<td>1</td>
<td>Co</td>
<td>14.479</td>
<td>mg/L</td>
<td>8477.0 mg/kg</td>
</tr>
<tr>
<td>0.0427</td>
<td>25</td>
<td>50</td>
<td>Ru</td>
<td>1.1306</td>
<td>mg/L</td>
<td>33096.6 mg/kg</td>
</tr>
</tbody>
</table>

Calculation formula: Display × Volume × Dilution/Quality.

mg/kg unit conversion wt% formula: Content/10000 was wt%.

2. Results and Discussion

Hydrogen storage mechanism of NEC

The hydrogenation of NEC is stepwise through multiple partially hydrogenated intermediates (as shown in Fig. S3). NEC has a large planar polycyclic structure and is favorable for adsorption on the flat surface of Ru surface. At the beginning of the
reaction, NEC reacts with hydrogen rapidly to generate 4H-NEC and 6H-NEC. Compared with 6H-NEC, the content of 4H-NEC is very small and the consumption rate of 6H-NEC is slower than that of 4H-NEC, which is due to its strong adsorption on the Ru surface, making the catalyst surface more difficult to desorb compared to 4H-NEC. This behavior is attributed to the unstable structure of 6H-NEC, which destroys the original resonance system. As the hydrogenation proceeds to the 8H-NEC intermediate, the planar geometry is largely lost and adsorption on the catalyst surface is no longer favorable. The 8H-NEC intermediate is likely to be desorbed from the catalyst surface, resulting in poor selectivity. Therefore, the main products of NEC hydrogenation are 12H-NEC and 8H-NEC.

**Fig. S3.** NEC hydrogen storage reaction pathway.

**NEC hydrogen storage capacity calculation**

\[
\text{NEC hydrogen storage capacity} = \left(\frac{2}{M_{2\text{H}-\text{NEC}}} \times Y_{2\text{H}-\text{NEC}}\right) + \left(\frac{4}{M_{4\text{H}-\text{NEC}}} \times Y_{4\text{H}-\text{NEC}}\right) + \left(\frac{6}{M_{6\text{H}-\text{NEC}}} \times Y_{6\text{H}-\text{NEC}}\right) + \left(\frac{8}{M_{8\text{H}-\text{NEC}}} \times Y_{8\text{H}-\text{NEC}}\right) + \left(\frac{10}{M_{10\text{H}-\text{NEC}}} \times Y_{10\text{H}-\text{NEC}}\right) + \left(\frac{12}{M_{12\text{H}-\text{NEC}}} \times Y_{12\text{H}-\text{NEC}}\right)
\]
Among them \( M_{2H-NEC}, M_{4H-NEC}, M_{6H-NEC}, M_{8H-NEC}, M_{10H-NEC}, \) and \( M_{12H-NEC} \) represent the relative molecular mass of 2H-NEC, 4H-NEC, 6H-NEC, 8H-NEC, 10H-NEC and 12H-NEC; \( Y_{2H-NEC}, Y_{4H-NEC}, Y_{6H-NEC}, Y_{8H-NEC}, Y_{10H-NEC}, \) and \( Y_{12H-NEC} \) represent the corresponding yields of each hydrogenation product, respectively, data obtained by gas chromatography.

**NEC theoretical hydrogen storage capacity calculation**

\[
= \frac{M_{12H-NEC} - M_{NEC}}{M_{12H-NEC}} \times 100\% = 5.80 \text{ wt\%}
\]

**NEC hydrogen storage rate calculation**

\[
= \frac{\text{NEC actual hydrogen storage}}{\text{NEC theoretical hydrogen storage}} \times 100\%.
\]

As described in the article, the Co@Ru/NGC catalyst catalyzed NEC hydrogenation with 99.1% 12H-NEC and 0.9% 8H-NEC yields. Combining the above two equations, we can see that:

\[
= \left( \frac{8}{203} \times 0.9 + \frac{12}{207} \times 99.1 \right) \times \frac{5.80}{100} = 99.7\%
\]

In order to considering that low pressure is more in line with the safety considerations in actual industrial production and high temperature is more conducive to the hydrogenation reaction, the obtained reaction conditions are heated and depressurized treatment. The result is shown in Fig. S4, as the reaction temperature increases, the initial hydrogenation rate of the hydrogenation reaction enhances. When the temperature increased to 150°C and the pressure decreased to 5 MPa, the yield of 12H-NEC was 9.52%, and the hydrogen storage percentage of NEC was 99.2%. As the pressure continues to decrease to 4 MPa, the NEC hydrogenation reaction rate is
significantly reduced. This is due to the decrease of H concentration in the liquid at low pressure, which hinders the forward progress of the reaction.

**Fig. S4.** Investigation on the hydrogenation conditions of Co@Ru/NGC-550-2 in NEC.