The Au-Cu bimental catalyst by renewable $\gamma$-Al$_2$O$_3$ as supports for acetylene hydrochlorination

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Characterization

XRD data was collected using a Bruker D8 advanced X-ray diffract meter with Cu-K$\alpha$ irradiation at 40 kV and 40 mA in the scanning range of 10$^\circ$ and 80$^\circ$. H$_2$-TPR was performed using a Micromeritic ASAP 2920 instrument, using 10% H$_2$ in argon (flow 50 ml/min) as a reductive gas and a temperature ramp of 50 to 600 $^\circ$C (ramp rate, 10 $^\circ$C/min) with the TCD detector recording the signal. Metal content analysis using Varian's 710ES inductively coupled plasma atomic emission spectrometry (ICP-AES) measurement instrument. Plasma gas flow rate of 15 ml/min, atomizing air pressure 200 kPa.
Result and discussion

The actual loading amount of active component

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu, wt%</th>
<th>loss ratio, %</th>
<th>Au, wt%</th>
<th>loss ratio, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh sample</td>
<td>1.37</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Deactivated sample</td>
<td>1.25</td>
<td>8.76</td>
<td>0.09</td>
<td>10.00</td>
</tr>
</tbody>
</table>

Structure and textural properties

The profiles were similar and showed broad peaks belonging to the faces (3 1 1), (4 0 0) and (4 4 0) of the γ-Al₂O₃ phase (JCPDS card No. 43-1308), which indicated that all the supports have similar crystal structure.

![Fig. S1 XRD patterns of sample A, B, C and D.](image)

The nitrogen adsorption desorption isotherms of four γ-Al₂O₃ are illustrated in Fig. S2a. In all cases, the isotherms were ascribed to the type IV according to the IUPAC classification, which were produced by the mesoporous materials. A typical feature could be observed that a hysteresis loop and a platform in a region of higher p/p₀
values, sometimes ended with isotherm eventually turned up. The isotherms of sample A and D exhibited an hysteresis loop intermediate between H2 and H4 (IUPAC classification) due to open tubular pores with circular or polygonal sections and a pore size distribution with a maximum frequencies of pore diameters between 6 and 20 nm (Fig.S2b). The isotherm of sample B and C, which had a similar hysteresis loop, could be classified as type H2. The pores showed a smaller pore size distribution than sample A and D.

Fig. S2 Porosity profiles (a) Nitrogen adsorption–desorption isotherms; (b) pore size
distribution.

Possible mechanism for the influence of the base site to the activity

H$_2$-TPR analysis provided some evidence that the base site of the Al$_2$O$_3$ support played an important role in the dispersion of the Au$^{3+}$. Nkosi$^{1, 2}$ had confirmed that Au$^{3+}$ is the main activity site in the acetylene hydrochlorination. H$_2$-TPR profiles for fresh catalysts are shown in Fig. 5. The reductive peak at approximately 228 °C was attributed to the reduction of Au$^{3+}$ to Au$^0$. Compared with ACAID, the others had different degree of forward migration of peak which was due to the relative poorer dispersion of the active ingredient Au$^{3+}$, and it was consistent with their catalyst activity. The second reductive peak at approximately 330 °C was attributed to the reduction of Cu$^{2+}$ to Cu$^0$. It was obvious that they also have migration phenomenon, just as the Au$^{3+}$.

![Diagram](image)

Fig. S3 H$_2$-TPR profiles of AuCl$_3$-CuCl$_2$ supported on γ-Al$_2$O$_3$

TEM

The TEM images of fresh catalysts were shown in Fig. 6. No significant highly
metal dispersion was observed in ACAIA and ACAIB, which attributed to areunion phenomenon for the activity metal. To the fresh ACAIC, ACAID, small black dots appeared on the substrate, they were dispersed Au particles. It indicated more obvious aggregation of Au particles associated with surface groups, which showed a positive relationship between the metal dispersion and the catalysis activity, which was consistent with the TPR results.
Fig. S4  TEM images of fresh catalyst (a) ACAIA;(b)ACAlB;(c)ACAlC;(d)ACAlD.

**Schematic plot**

The possible mechanism sketch for the enhanced stability and catalytic efficiency was shown in Fig. S5

![Schematic plot](image)

**The support modification initially by potassium hydroxide**

The CO$_2$-TPD profile of MB was shown in Fig. S6, it can be seen that an obvious strong base site appeared.

![CO$_2$-TPD profile of MB](image)

**Reference**

386.
