Supporting Information

In-situ Hydrogenation and Decarboxylation of Oleic Acid into Heptadecane over a Cu-Ni Alloy Catalyst using Methanol as Hydrogen Carrier

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Materials

Oleic acid (99%) was purchased from TCI, Japan. Stearic acid (99%), heptadecane (99%), octadecanol (99%), methyl stearate and Pt/C (5wt %) were purchased from Sigma-Aldrich, USA. Sodium carbonate anhydrous (analytic reagent grade), Sodium hydroxide (analytic reagent grade), Cu(NO$_3$)$_2$•3H$_2$O (analytic reagent grade), Anhydrous methanol (analytic reagent grade) and acetone (analytic reagent grade) were purchased from Sinopharm Chemical Reagent Co. Ltd, China; Ni(NO$_3$)$_2$•6H$_2$O (99.9%) was purchased from STREM Chemical. Al(NO$_3$)$_3$•9H$_2$O (99%) was purchased from Aladdin Industrial Corporation China. Gutter oil (>96%) was purchase from Xiamen Huayihong import and export Co. Ltd, China. Gutter oil hydrolysate was self-achieved by the hydrolysis reaction of gutter oil at 280 °C by near critical water continuous reaction unit, and residence time is 67 min. The main component of the hydrolysate products of gutter oil is palmitic acid, oleic acid and linoleic acid. Deionized water was prepared in house. All chemicals were used without further purification.

Catalyst synthesis

A series of Al$_2$O$_3$ supported Cu and Ni catalysts were prepared via a modified co-precipitation method. Briefly, the calculated amount of Cu(NO$_3$)$_2$•3H$_2$O, Ni(NO$_3$)$_2$•6H$_2$O, Al(NO$_3$)$_3$•9H$_2$O were dissolved together in 400 mL deionized water, forming a transparent solution, which was referred as solution A. Solution B was the mixture of NaOH and Na$_2$CO$_3$ with the concentration of 0.8 and 0.25 mol/L, respectively. Then solution A and B were simultaneously added drop-wise in a three-neck flask under vigorous stirring at 30 °C and a pH value of 9.5. After aging the precipitate for 7 h at 30 °C, the precipitate was separated by filtration and washed thoroughly with deionized water until the pH was around 7. The precipitate was further dried in a forced air oven at 110 °C for 12 h and then calcined at 600 °C for 4 h. Prior to reaction and testing, these catalysts were activated in a tube furnace with flowing hydrogen (a flow rate of 80 mL/min) at 650 °C for 1 h, and then cooled under N$_2$ flow. The total theoretical metal loading of the self-designed catalysts was 60 wt%.

Characterization techniques
Prior to its characterization, the catalyst was reduced using hydrogen in a tube furnace (flow rate of 80 mL/min) at 650 °C for 1 h.

XRD patterns were recorded on a PANalytical Empyrean 200895, using Ni filtered Cu Ka radiation ($\lambda=0.154$ nm) at 30 mA, 40 kV. The catalyst was reduced in a tube furnace with hydrogen (a flow rate of 80 mL/min) at 650 °C for 1 h before XRD analysis. The samples were scanned using a 20 range of 10-80°.

H$_2$-TPR studies of CuAl, Cu$_2$NiAl, CuNiAl, CuNi$_2$Al, NiAl were carried out by Micromeritics AutoChem II 2920 device. The reactor was heated to 750°C at the ramp of 10 °C/min with the hydrogen flow of 30.1 cm$^3$ STP/min. Effluent gas was dried by powder KOH and the consumption of hydrogen were recorded by thermal conductivity detector (TCD).

N$_2$ adsorption was performed at 77 K in a static volumetric apparatus (Micromeritics 3Flex, GA, USA). Samples were degassed at 250°C for 12 h before adsorption. Specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. Pore size and volume were calculated according to Barret-Joyner-Halenda (BJH) method. All calculations were based on the adsorption model.

The diffuse reflectance Fourier transform infrared spectra (DRIFT-IR) with CO probes were performed on a Nicolet-iS50 FT-IR. The reduced CuAl, Cu$_2$NiAl and CuNi$_2$Al were pretreated by Ar purging at 30°C for 30 min. The background spectrum for each sample was recorded at 30 °C. After collecting the background spectrum, the sample was then treated with pure CO at a gas flow rate of 20 mL/min at room temperature for 30 min and then purged with 50% CO balanced in Ar. The sample spectrum was recorded after purging the reaction cell with Ar for 10 min.

X-ray photoelectron spectra (XPS) were taken on a VG ESCALAB MARK II (ESCALAB), and the data was calibrated by C 1s (284.8 eV) and processed using Casa XPS software.

The metal contents of catalysts were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES) on Agilent 730 device. Prior to the analysis, catalysts were dissolved in a mixture of HCl and HNO$_3$. ICP-OES results of different catalysts was shown in table 4.
Scanning-transmission electron microscopy (STEM) images, HADDF-STEM and energy dispersive X-ray spectroscopy (EDS) of reduced Cu-Ni alloy catalysts was obtained in Field Emission Transmission Electron Microscope (JEM-2100F) with 200 kV operating voltage. Before characterization, Cu-Ni alloy and Ni-based catalysts was embedded by phenol formaldehyde resin which was prepared by Department of Chemistry, Zhejiang University, and sliced up owing to its strong magnetism.

Temperature programmed desorption (TPD) of CO, propane (C$_3$H$_8$), ethylene (C$_2$H$_4$) and acetic acid was measured by FineSorb-3010 equipped with a thermal conductivity detector (TCD), Zhejiang FINETEC INSTRUMENTS co., LTD. For CO, propane (C$_3$H$_8$) and ethylene (C$_2$H$_4$), before characterization, the catalysts were preheated to 120°C and the temperature decreased to 60°C under argon atmosphere with the argon flow of 20 sccm for 262 min. And then gas was adsorbed on the catalysts for 40 min with 5% C$_3$H$_8$/ C$_2$H$_4$ and 95% N$_2$, and swept the gas for 20 min. The reactor was heated to 750°C at the ramp of 10°C/min with the argon flow of 20 sccm. For acetic acid desorption, before characterization, the 50 mg of catalysts were soaked by 10μL acetic acid and preheated to 80°C with the argon flow of 20 sccm for 60 min. And then, the reactor was heated to 650°C at the ramp of 20°C/min with the argon flow of 20 sccm.

Differential scanning calorimetry-Thermogravimetric (DSC-TGA) results were collected by a SDT Q600 with V20.9 Build 20 software. Fresh and used CuNi$_2$Al were heated to 120 ºC at the ramp of 10 ºC /min, and then the temperature increased to 750 ºC at the ramp of 10 ºC /min after lasting for 30 min at 120 ºC at an air velocity of 100 mL/min.
Catalyst stability

The stability of CuNi$_2$Al has been examined on the in-situ hydrogenation and decarboxylation of oleic acid. CuNi$_2$Al exhibited a certain degree of deactivation after recycle, and the heptadecane yield decreased from 92.6 to 63.4% over the used catalyst in Figure S9. In Figure S10, XRD results indicate that the diffraction peaks of Al$_2$O$_3$ at 37.5 and 66.6° (JCPDS #29-0063) disappear after use and main diffraction peaks at 14.5°, 28.2°, 38.3°, 49.0° are discovered, which belongs to boehmite AlOOH (JCPDS #21-1307). DSC-TGA of fresh and used CuNi$_2$Al was used to prove the existence of AlOOH and the amount of carbon deposit. In Figure S11, weight of used CuNi$_2$Al decreased at around 500 °C, and the endothermic peak are found at the same time. Kuang et.al (J. Mater. Chem., 2003, 13, 660) have reported the alumina is formed upon dehydration of the AlOOH by calcination at 520 °C. In addition, about 4.5% carbon deposition was found according to the weight loss from 200 °C to 280 °C, and exothermic peak can be clearly seen at the same time. Figure S12 shows the TEM image of used CuNi$_2$Al, and the results indicate that CuNi$_2$ alloy is surrounded by a large number of substance, which should be ascribed to AlOOH. CO-TPD results show the adsorption amount of CO on used CuNi$_2$Al decreased remarkably relative to fresh catalyst in Figure S13, confirming a part of CuNi$_2$ alloy active site has been covered after recycle. Therefore, hydration of support Al$_2$O$_3$ and 4.5% carbon deposition is probably the main causation for the deactivation of CuNi$_2$Al.
Figure S1. Left: the dark filed TEM image of CuAl and its corresponding X-ray map of Cu, O and Al;
Right: Line scanning of single particle and support of CuAl
Figure S2. The dark filed TEM image of NiAl; Line scanning and its corresponding single particle of NiAl. The intensity of O is higher than Al, it may be caused by the oxidation of Ni during the preparation process of TEM test, since nickel is easy to be oxidized in air atmosphere.
Figure S3. HRTEM image of CuAl, Cu$_2$NiAl, CuNi$_2$Al and NiAl in sequence and its inter-planar spacing are calculated by Gantan Digital Micrography.
Figure S4. Left: the TEM image of CuNi$_2$Al, and Right: the CuNi$_2$ alloy particle size distribution calculation by the area of left picture.
Figure S5. Chromatograms for gutter oil hydrolysate (a) and products after reaction (b). Reaction condition: T=330 °C, reactant loading=50 mg, CuNi$_2$Al=15 mg, methanol loading=10 mg, water =0.5 mL, reaction time: 1h.
(a) FID signal (a.u.)

Reaction time = 60 min

C_{10} C_{11} C_{12} C_{13} C_{14} C_{15} C_{16}

Stearic acid

octadecanol

(b) FID Signal (a.u.)

Methyl stearate
Methyl oleate
Oleic acid
Stearic acid

Pt/C
Pt/C-methanol
CuNi:Al
CuNi:Al-methanol

(c) FID Signal (a.u.)

Methyl stearate
Methyl oleate
Stearic acid
Oleic acid

NiAl
CuNi:Al
CuAl
Figure S6. (a) GC-FID chromatograms for in-situ hydrogenation and decarboxylation of oleic acid over CuAl and NiAl at 330 °C for 1 h. (b) GC-FID chromatograms for the conversion of oleic acid over Pt/C and CuNi$_2$Al with and without methanol at 250 °C for 0.5 h; (c) GC-FID chromatograms for the conversion of oleic acid over CuAl, CuNi$_2$Al and NiAl at 250 °C for 0.5 h.
Figure S7. The ball and stick model of stearic acid and octadecanol, C linked to O was marked as C$_1$, and next one was marked as C$_2$, and so forth.
Figure S8. GC/FID chromatograms for the conversion of oleic acid and heptadecane over NiAl.
Reaction condition: T=330 °C, reactant loading=50 mg, 15 mg NiAl, methanol loading=10 mg, water
=0.5 mL, reaction time=1 h.
Figure S9. Mole yield of different products for the conversion of oleic acid over fresh and used CuNi$_2$Al.

Reaction condition: T=330 °C, reactant loading=50 mg, catalyst loading=15 mg, methanol loading=10 mg, water =0.5 mL, reaction time=1h.
Figure S10. XRD patterns of fresh and used CuNi$_2$Al.
Figure S11. DSC-TGA results of fresh and used CuNi$_2$Al
Figure S12. The different magnification of TEM image of used CuNi₂Al catalyst
Figure S13. Temperature-programmed desorption (TPD) of CO over the fresh and used CuNi$_2$Al catalyst.
Table S1. ICP-OES results of the catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu % (actual)</th>
<th>Ni% (actual)</th>
<th>Cu and Ni (%) (actual)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAl</td>
<td>57.1 (60)</td>
<td>0a (0)</td>
<td>57.1 (60)</td>
</tr>
<tr>
<td>Cu₂NiAl</td>
<td>37.7 (40)</td>
<td>14.2 (20)</td>
<td>51.9 (60)</td>
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<tr>
<td>CuNiAl</td>
<td>27.3 (30)</td>
<td>22.0 (30)</td>
<td>47.3 (60)</td>
</tr>
<tr>
<td>CuNi₂Al</td>
<td>18.6 (20)</td>
<td>32.1 (40)</td>
<td>50.7 (60)</td>
</tr>
<tr>
<td>NiAl</td>
<td>0a</td>
<td>51.3 (60)</td>
<td>51.3 (60)</td>
</tr>
</tbody>
</table>

a metal loading ration<0.1%

The results of ICP-OES were shown in Table S1. The errors between measurement value and actual value can be explained by the different precipitate rate between and experimental error.
Table S2. ICP-OES results of solutions after reactions

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu&lt;sup&gt;a&lt;/sup&gt; (ppm)</th>
<th>Cu&lt;sup&gt;b&lt;/sup&gt; (ppm)</th>
<th>Ni&lt;sup&gt;a&lt;/sup&gt; (ppm)</th>
<th>Ni&lt;sup&gt;b&lt;/sup&gt; (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuNi&lt;sub&gt;2&lt;/sub&gt;Al</td>
<td>-0.0834</td>
<td>279.0</td>
<td>0.0919</td>
<td>481.5</td>
</tr>
</tbody>
</table>

Cu<sup>a</sup>, Ni<sup>a</sup>: Actual leaching amount of Cu or Ni after reaction with dilution to 10 mL.
Cu<sup>b</sup>, Ni<sup>b</sup>: Total leaching amount of Cu or Ni calculated by actual Cu and Ni loading amount.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area(^a) (m(^2)/g)</th>
<th>Pore Volume(^b) (cm(^3)/g)</th>
<th>Pore size(^c) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAl</td>
<td>61.4</td>
<td>0.414</td>
<td>29</td>
</tr>
<tr>
<td>Cu(_2)NiAl</td>
<td>55.4</td>
<td>0.345</td>
<td>28.7</td>
</tr>
<tr>
<td>CuNiAl</td>
<td>78.9</td>
<td>0.415</td>
<td>22.5</td>
</tr>
<tr>
<td>CuNi(_2)Al</td>
<td>82.8</td>
<td>0.576</td>
<td>29.7</td>
</tr>
<tr>
<td>NiAl</td>
<td>125.1</td>
<td>0.616</td>
<td>19.5</td>
</tr>
</tbody>
</table>

\(^a\) BET Surface Area

\(^b\) BJH Adsorption cumulative volume of pores between 1.7000 nm and 300.000 nm diameter

\(^c\) BJH Adsorption average pore diameter (4V/A)