Supplementary Information

Unique Catalysis of Gold Nanoparticles in the Chemoselective Hydrogenolysis with H₂: Cooperative Effect between Small Gold Nanoparticles and a Basic Support

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Experimental

1) General

All organic reagents were purified before use. Allylic carbonates were prepared by the reaction of the corresponding allylic alcohol with methyl chloroformate in the presence of pyridine. HAuCl₄·xH₂O was obtained from N. E. Chemcat Co., Ltd. MgO (GR for analysis) was purchased from Merck Chemical Industries Co., Ltd. Al₂O₃ (JRC-ALO-3), SiO₂ (JRC-SIO-6) and TiO₂ (JRC-TIO-4) were supplied by the Catalysis Society of Japan. GC-FID and GC-MS were performed on a Shimadzu GC-2014 instrument equipped with a KOCL-3000T column (3 m) and a Shimadzu GC-17A instrument equipped with a ULBON HR-1 capillary column (30 m × 0.25 mm × 0.25 μm), respectively. Inductively coupled plasma measurements were performed using a SII Nano Technology SPS7800 instrument. ¹H and ¹³C-NMR spectra were recorded on a JEOL JNM-ESC400 spectrometer and a JNM-GSX270 spectrometer, respectively. Transmission electron microscopy (TEM) micrographs were obtained with a Hitachi HF-2000 microscope. Au L-edge X-ray absorption spectra were collected in the quick mode and recorded at room temperature in transmission mode at the facilities installed on the BL-01B1 line attached with a Si (311) monochromator at the SPring-8, Japan Atomic Energy Research Institute (JASRI), Harima, Japan. Data analysis was performed using the REX 2000 program, ver. 2.5.7 (Rigaku). Fourier transformation (FT) of the k²-weighted extended X-ray absorption fine structure (EXAFS) data was performed to obtain the radial structural function.
2) General reaction procedures

A typical procedure for the hydrogenolysis of 1 using the Au/HT catalyst was as follows. Au/HT (0.10 g, 0.0045 mmol Au) was placed in a reaction vessel, followed by the addition of toluene (5 mL) and 1 (0.2 mmol). The reaction mixture was vigorously stirred at 80 °C under an H₂ balloon for 12 h. After the reaction, the Au/HT was removed by filtration, and naphthalene (0.2 mmol) was added as an internal standard. The obtained mixture was analyzed by GC and GC-MS.

3) Reuse experiments for the hydrogenolysis of 1

After the hydrogenolysis of 1 under the above typical reaction conditions, Au/HT was separated by filtration and washed with toluene (3 x 10 mL). Next, additional portions of 1 (0.2 mmol) and toluene (5 mL) were added, followed by stirring under the identical conditions. The yields of 2 in the two reuse experiments were 90% and 88%, respectively.

4) Product identification

The products were identified by GC, GC-MS and NMR analyses. Retention times (GC or GC-MS) and chemical shifts (¹H and ¹³C-NMR) of the products were in agreement with those of authentic samples (commercially available).

5) Hydrogenolysis of 1 with 2-propanol

Au/HT (0.10 g) was placed in a reaction vessel, followed by the addition of toluene (5 mL), 2-propanol (0.6 mL) and 1 (0.2 mmol). The reaction mixture was vigorously stirred at 80 °C under Ar for 3 h. After the reaction, the Au/HT was removed by
centrifugation, and naphthalene (0.2 mmol) was added as an internal standard. The yields of 2 and 3 were 89% and 10%, respectively.

6) Hydrogenolysis of 1 with CO/H\textsubscript{2}O

Au/HT (0.10 g), THF (5 mL), water (0.1 mL) and 1 (0.2 mmol) were placed in an autoclave tube, and the mixture was vigorously stirred at 100 °C for 3 h under a 5 atm CO atmosphere. After the reaction, the Au/HT was removed by centrifugation, and naphthalene (0.2 mmol) was added as an internal standard. The yields of 2 and 3 were 88 % and 10%, respectively.
EXAFS analysis

Figure 1S. Fourier transformed \( k^3 \)-weighted Au L-edge EXAFS for (a) Au/HT, (b) Au/HT after being reused twice, (c) \( \text{Au}_2\text{O}_3 \) and (d) Au foil.

<table>
<thead>
<tr>
<th></th>
<th>Coord. no. (CN)</th>
<th>Interatomic dis. (Å)</th>
<th>( \Delta\sigma/\text{Å}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/HT (fresh)</td>
<td>8.6</td>
<td>2.82</td>
<td>0.028</td>
</tr>
<tr>
<td>Au/HT (after two times reuse)</td>
<td>8.9</td>
<td>2.83</td>
<td>0.020</td>
</tr>
<tr>
<td>Au foil</td>
<td>12</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

Curve fitting analysis of Au L-edge EXAFS

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TEM analysis

(a) Au/HT (fresh)

(b) Au/HT (after reuse experiment)

Figure 2S. Typical TEM images and size distribution diagrams (obtained by counting at least 500 particles) of (a) fresh Au/HT and (b) Au/HT after reuse.
Leaching Test

**Equation:**

\[
\text{PhCH}_2\text{CO}_2\text{Me} \xrightarrow{\text{Au/HT (2.3 mol%)}} \text{PhCH}_2\text{CH}_2 + \text{PhCH}_3
\]

toluene, H\textsubscript{2} (1 atm), 80 °C

**Figure 3S.** Time profile for hydrogenolysis of 1 using Au/HT
Figure 4S. Plausible reaction pathway