Supplementary Information

Unique Catalysis of Gold Nanoparticles in the Chemoselective Hydrogenolysis with H_2: 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. $HAuCl_4 \cdot xH_2O$ was obtained from N. E. Chemcat. Co., Ltd. MgO (GR for analysis) was purchased from Merck Chemical Industries Co., Ltd. Al_2O_3 (JRC-ALO-3), SiO_2 (JRC-SIO-6) and TiO_2 (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. ^{1}H and ^{13}C-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 k^3-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 H_2 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 (^{1}H and ^{13}C-NMR) of the products were in agreement with those of authentic samples (commercially available).

5) Hydrogenolysis of 1 with 2-propanol

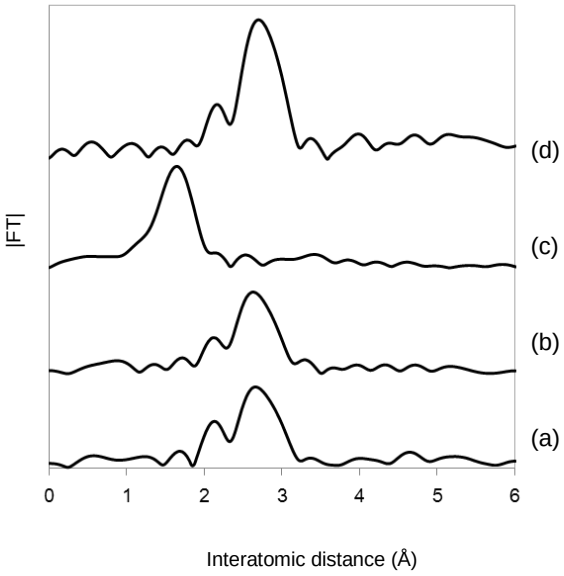
Au/HT (0.10 g) was placed in a reaction vessel, followed by the addition of toluene (5 mL), 2-propanol (0.6 mL) and **1** (0.2 mmol). The reaction mixture was vigorously stirred at 80 °C under Ar for 3 h. After the reaction, the Au/HT was removed by

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_2O

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



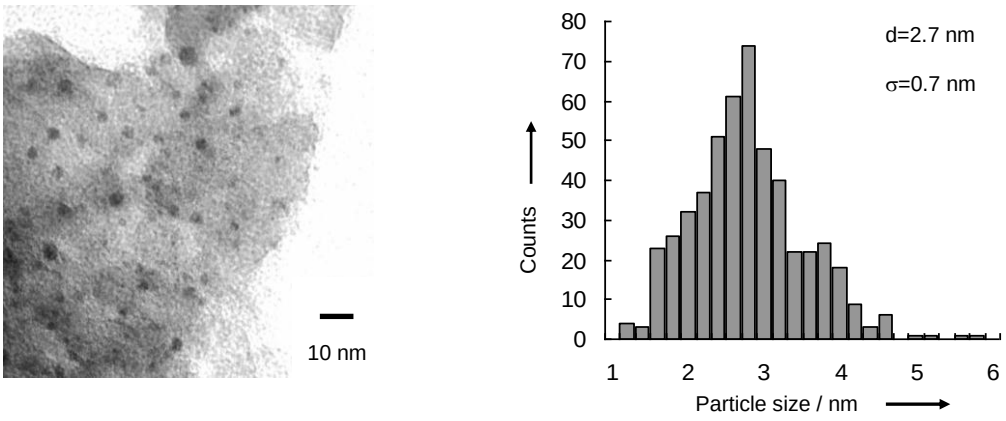
Curve fitting analysis of Au L-edge EXAFS

	Coord. no. (CN)	Interatomic dis. (Å)	$\Delta\sigma$/ Å ^{2}
Au/HT (fresh)	8.6	2.82	0.028
Au/HT (after two times reuse)	8.9	2.83	0.020
Au foil	12	-	-

Figure 1S. Fourier transformed k^3-weighted Au L-edge EXAFS for (a) Au/HT, (b) Au/HT after being reused twice, (c) Au_2O_3 and (d) Au foil.

TEM analysis

(a) Au/HT (fresh)



(b) Au/HT (after reuse experiment)

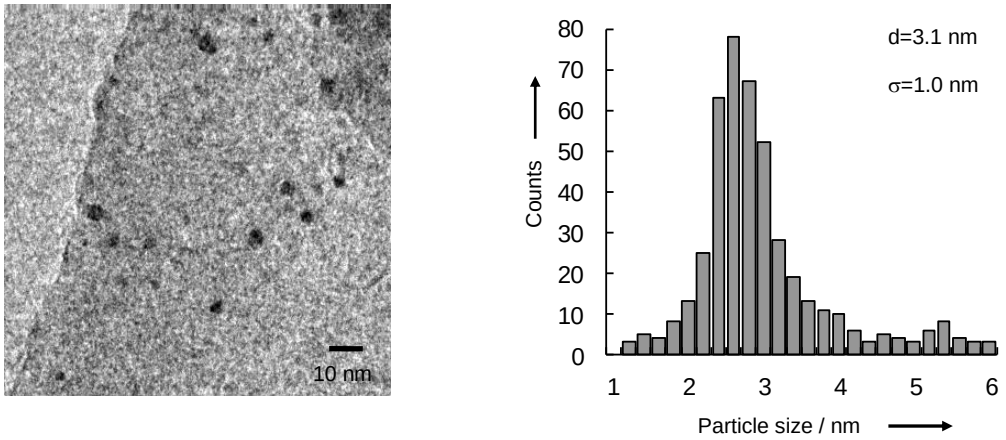
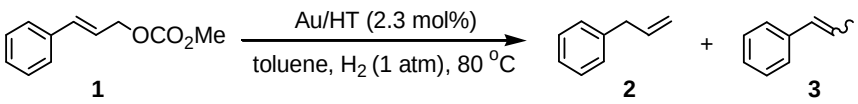


Figure 2S. Typical TEM images and size distribution diagrams (obtained by counting at least 500 particles) of (a) fresh Au/HT and (b) Au/HT after reuse.

Leaching Test



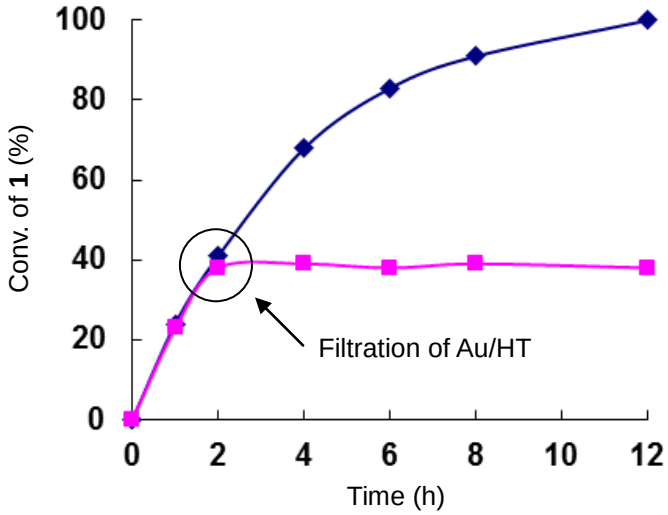


Figure 3S. Time profile for hydrogenolysis of **1** using Au/HT

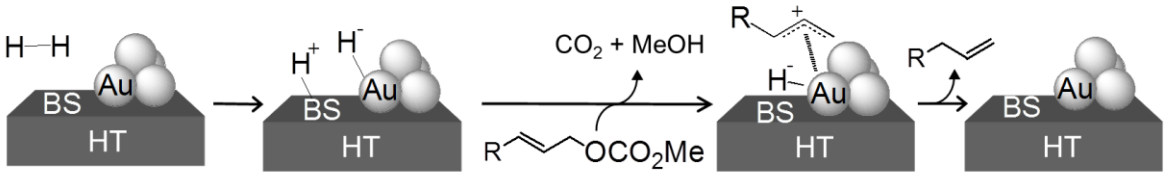


Figure 4S. Plausible reaction pathway