

A novel gold-catalyzed chemoselective reduction of α,β -unsaturated aldehydes using CO and H₂O as the hydrogen source

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Electronic Supplementary Information

1. Catalytic materials.

Gold catalysts including 1.5 wt% Au/TiO₂ (type A, lot no. Au/TiO₂ no. 02-1) and 4.5 wt% Au/Fe₂O₃ (type C, lot no. Au/Fe₂O₃ no. 02-5) were supplied by the World Gold Council (WGC). 5 wt% Pd/C (stock # 38300), 5 wt% Ru/Al₂O₃ (stock # 11749) were provided by Alfa Aesar.

Preparation of Au/CeO₂ catalysts: 2.1 wt% Au/CeO₂ catalysts were prepared by a routine deposition precipitation (DP) method. An appropriate amount of aqueous solutions of chloroauric acid (HAuCl₄) was heated to 80 °C under vigorous stirring. The pH was adjusted to 9 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO₂ (Degussa, Adnano 50, specific surface area: 50 m²/g) was dispersed in the solution. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and reduced in 5% H₂/Ar at 300 °C for 2h.

Preparation of Pt/CeO₂ catalysts: 1 wt% Pt/CeO₂ catalysts have been prepared by wet impregnation of the CeO₂ support with an aqueous solution of H₂PtCl₆, dried at 80 °C, and calcined in air at 300 °C for 4 h.

2. Catalytic activity measurements

General procedure for reduction of α,β -unsaturated aldehydes under 5 atm of CO: A mixture of α,β -unsaturated aldehydes (1 mmol), metal catalysts (2.8 mol% metal), and H₂O (20 mL) or H₂O /EtOH (10 mL /10 mL) was put into a stirred autoclave reactor (100 mL). The reactor was sealed, CO (5 atm) was introduced to the system. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 96 °C. No variation in reduction rate was observed over a range of stirrer speeds (400-1000 rpm) indicating the lack of external diffusion limitations. The conversion and product selectivity were determined by Shimadzu GC-17A gas chromatograph equipped with a HP-FFAP column (30 m \times 0.25 mm) and a flame ionization detector (FID). (When H₂O as sole solvent, the product mixtures were extracted with Et₂O for 3 times and analyzed.) The identification of the products was performed in a GC-MS spectrometer. For isolation, the combined organic layer was dried over anhydrous Na₂SO₄, concentrated, and purified by silica gel column chromatography to give the product.

Procedure for reduction of crotonaldehyde under 1 atm of CO: A mixture of crotonaldehyde (1 mmol), Au/CeO₂ catalysts (2.8 mol% Au), and H₂O (20 mL) was put into a flask (100 mL) fitted with a reflux condenser and a gas inlet tube for introducing CO by bubbling (10 mL/min). The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 96 °C. The product mixtures were extracted with Et₂O for 3 times and analyzed on a Shimadzu GC-17A gas chromatograph equipped with a HP-FFAP column (30 m \times 0.25 mm) and a flame ionization detector (FID).

Recovery and reuse of Au/CeO₂: The reused catalyst was recovered by separation of solid Au/CeO₂ catalysts from liquid after filtering. Washing the recovered catalyst with acetone for three times and then wash with distilled water for several times. The catalyst was then dried at 100 °C for 12 h. Then the catalyst was used for next reaction.

Procedure for reduction of crotonaldehyde under 5 atm of H₂: A mixture of crotonaldehyde (1 mmol), Au/CeO₂ catalysts (2.8 mol% Au), and H₂O (20 mL) was put into a stirred autoclave reactor (100 mL). The reactor was sealed, H₂ (5 atm) was introduced to the system. Then the reaction

mixture was stirred (800 rpm with a magnetic stir bar) at 96 °C. The product mixtures were extracted with Et₂O for 3 times and analyzed.

3. Characterization methods

Elemental analysis: The Au loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer.

Transmission electron microscopy (TEM): TEM images for supported gold catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal nanoclusters was determined by measuring about 200 random particles on the images.

X-ray photoelectron spectroscopy (XPS) : XPS analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The Mg K α ($h\nu = 1253.6$ eV) was operated at 15 kV and 20 mA. The energy scale was internally calibrated by setting the C1s peak at 284.6 eV.

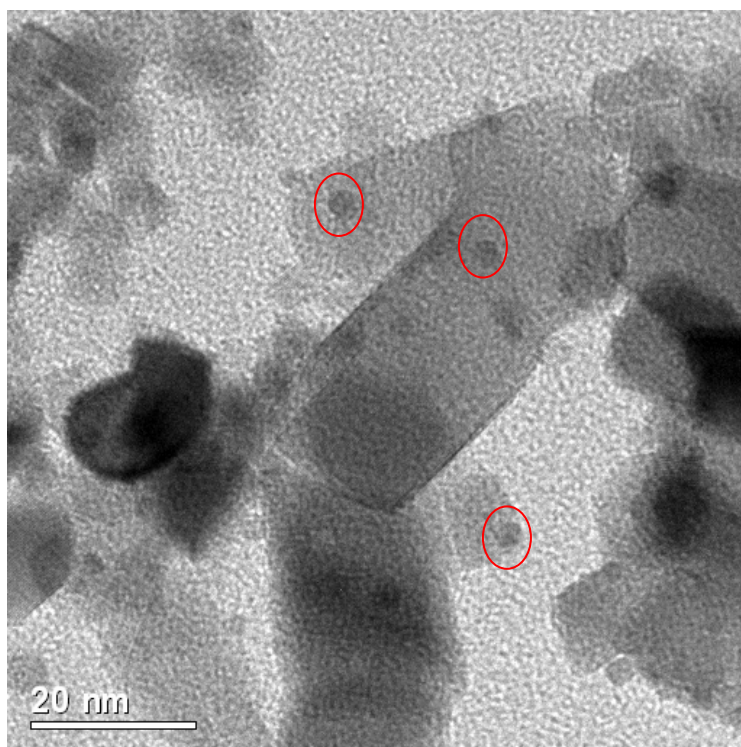


Fig. S1 Representative TEM image of 2.1 wt% Au/CeO₂

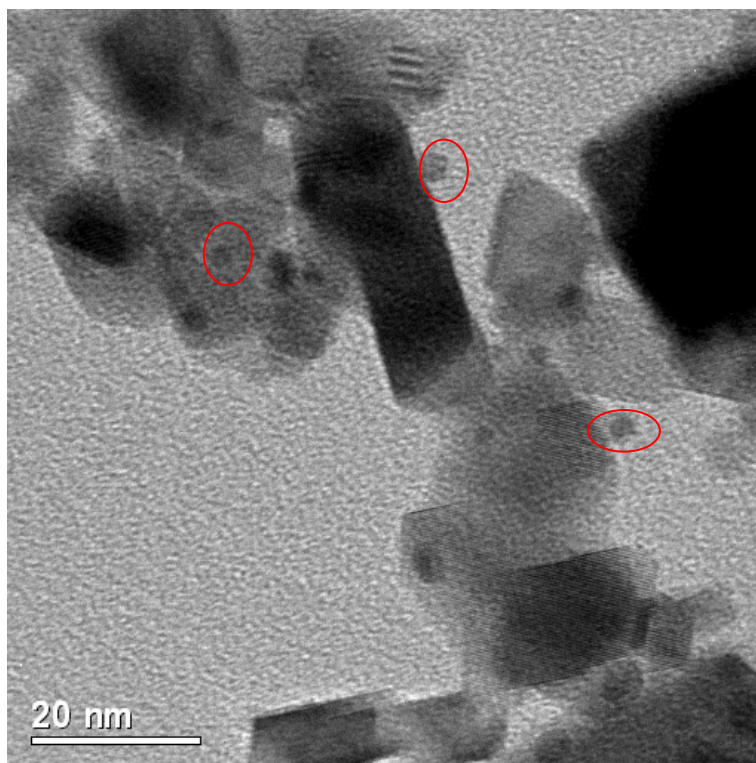


Fig. S2 Representative TEM image of 2.1 wt% Au/CeO₂ after three runs

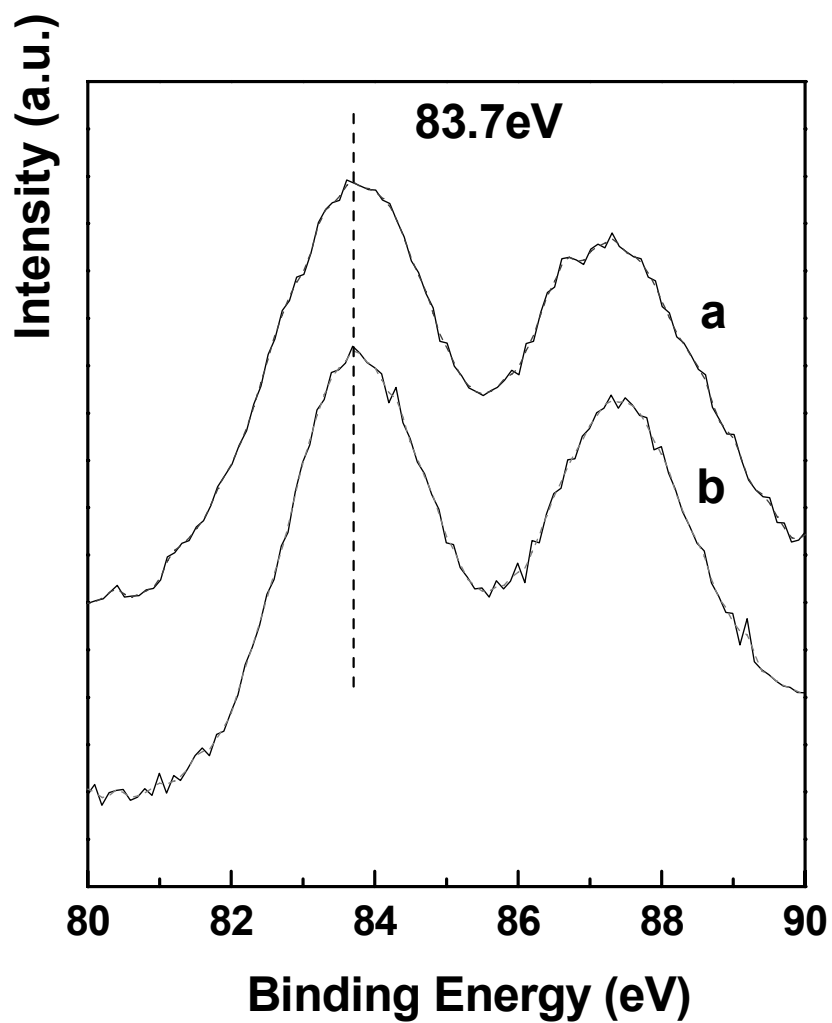


Fig. S3 XPS spectra of 2.1 wt% Au/CeO₂: a) before reaction; b) after three runs.

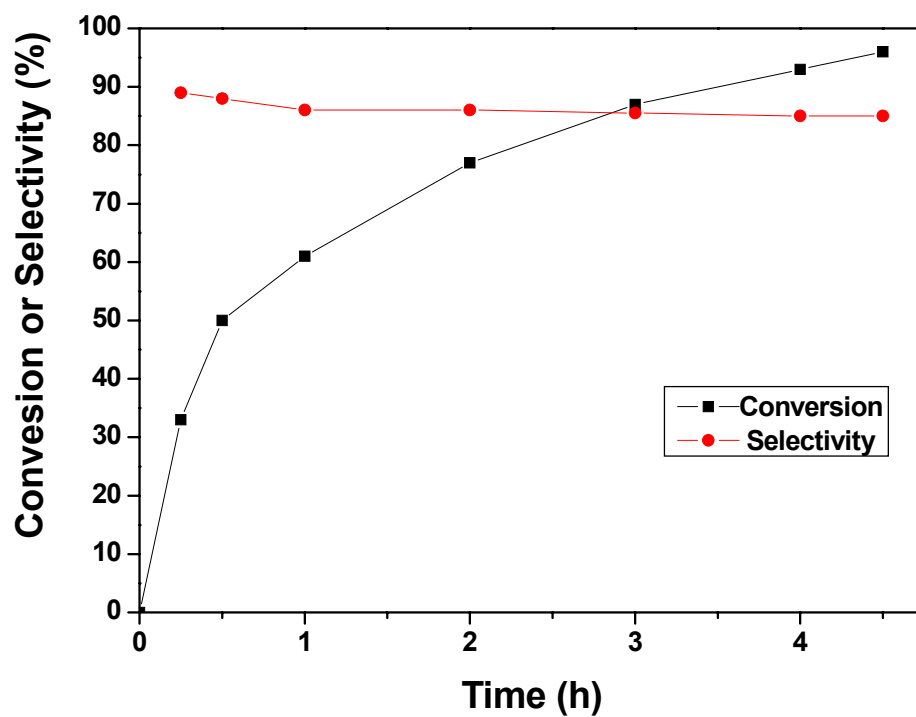


Fig. S4 Reduction of crotonaldehyde to crotyl alcohol. Reaction conditions: 1 mmol crotonaldehyde, Au/CeO₂ (2.8 mol% Au), 20 mL H₂O, 96 °C, 5 atm CO.