

A green and efficient oxidation of alcohols by supported gold catalysts using aqueous H₂O₂ under organic solvent-free conditions

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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), 4.5 wt % Au/Fe₂O₃ (type C, lot no. Au/Fe₂O₃ no. 02-5) and 0.8 wt % Au/C (type D, lot no. Au/C no. 38D) were supplied by the World Gold Council (WGC). 1 wt % Au/TiO₂ and 0.9 wt % Au/Al₂O₃ were supplied by Mintek. Unless otherwise specified, all catalysts were activated by calcination in air at 300 °C for 2 h before using.

Mintek Au/TiO₂ catalysts calcined at elevated temperatures: a series of 1 wt % Au/TiO₂ catalysts with mean gold particle size of ca. 2.7, 3.5, 4.3 and 7.2 nm was obtained by being respectively calcined in air at 300 °C, 400 °C and 500 °C for 2 h and 500 °C for 6 h.

Preparation of Au/CeO₂ catalysts: 1 wt % Au/CeO₂ catalysts were prepared by deposition-precipitation method. Firstly, 100 ml of a gold solution (0.2 g of HAuCl₄ • 4H₂O in 1 L of water) was heated to 80 °C under vigorous stirring. The pH of the solution was adjusted to 9.0 with 0.2 M NaOH, followed by addition of 1.0 g of CeO₂ (Degussa, Adnano 90, specific surface area: 90 m²/g). Stirring was continued for 2 h, after which the suspension was cooled to room temperature. Solids were then filtrated and exhaustively washed with 200 ml of distilled water. The solid thus obtained was dried for 12 h at 80 °C, and calcined in air at 300 °C for 3 h.

2. Oxidation of alcohols by supported gold catalysts using aqueous H₂O₂.

General procedure for the oxidation of alcohols: The alcohol (10 mmol), supported gold catalysts (Au: 0.1 mmol) and water (10 ml) was charged in a flask (50 ml) with a magnetic stirring bar and a reflux condenser. After the mixture was stirred at 90 °C for 10 min under N₂ atmosphere, an aqueous solution of H₂O₂ (5 %, 15 mmol for secondary alcohols and cinnamyl alcohol, 25 mmol for primary alcohols) was dropwise added over the course of 1 h, followed by heating at 90 °C for additional 5 min. The reactants and products were extracted with ethyl acetate, and analyzed on a Shimadzu GC-17A gas chromatograph equipped with an Agilent Technologies Inc. HP-FFAP column (30 m×0.25 mm) and a flame ionization detector (FID).

Recovery and reuse of Au/TiO₂: The catalyst was collected after filtration washed with water and heated at 120 °C for 12 h. Then the catalyst was used for next reaction.

Hectogram-scale oxidation of 1-hexanol: 1-hexanol (100g, 0.98 mol) and 1 wt % Au/TiO₂ (Au 10 mmol) were charged in a 2 L round-bottomed flask with a magnetic stirring bar and a reflux condenser. After the mixture was vigorously stirred at 90 °C for 10 min, an aqueous solution of H₂O₂ (5%, 3 mol) was added dropwise. The mixture was heated at 90 °C for 2.5 h, and then cooled to room temperature. The organic phase was separated and washed with saturated aqueous solution of Na₂S₂O₃ (50 ml). After distillation, hexanoic acid (105.6 g, 93%) was obtained as a colorless liquid.

3. Methods

TEM

Transmission electron microscopy (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.

XPS

XPS analysis was performed using a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The MgK 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.

4. TEM images of supported gold catalysts.

Fig. S1 TEM image and size distribution of Mintek 1 wt % Au/TiO₂ calcined at 300 °C for 2 h.

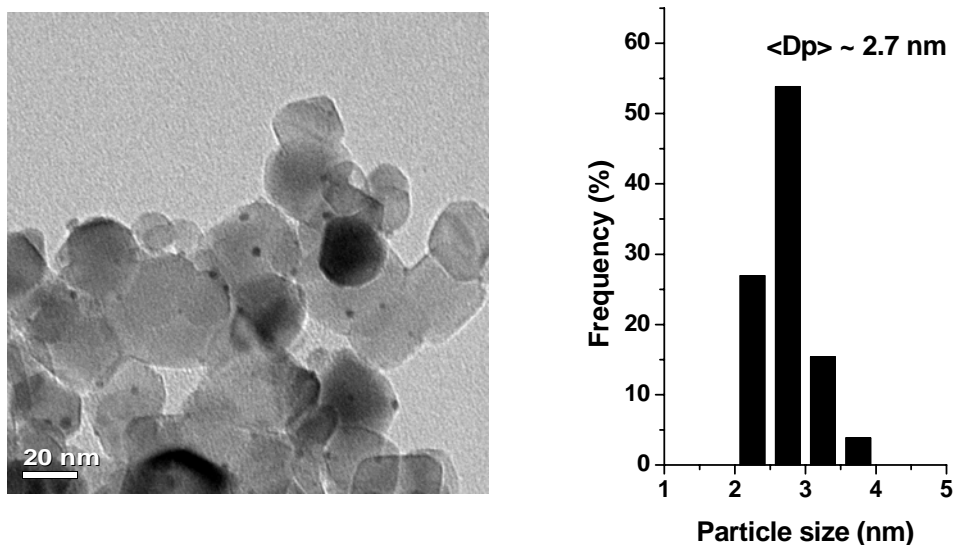


Fig. S2 TEM image and size distribution of Mintek 1 wt % Au/TiO₂ calcined at 400 °C for 2 h.

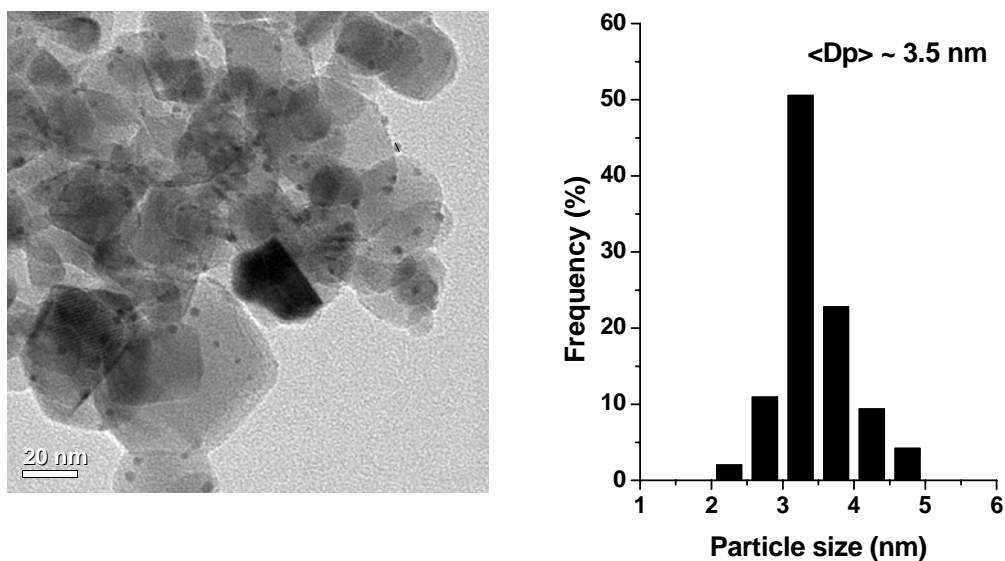


Fig. S3 TEM image and size distribution of Mintek 1 wt % Au/TiO₂ calcined at 500 °C for 2 h.

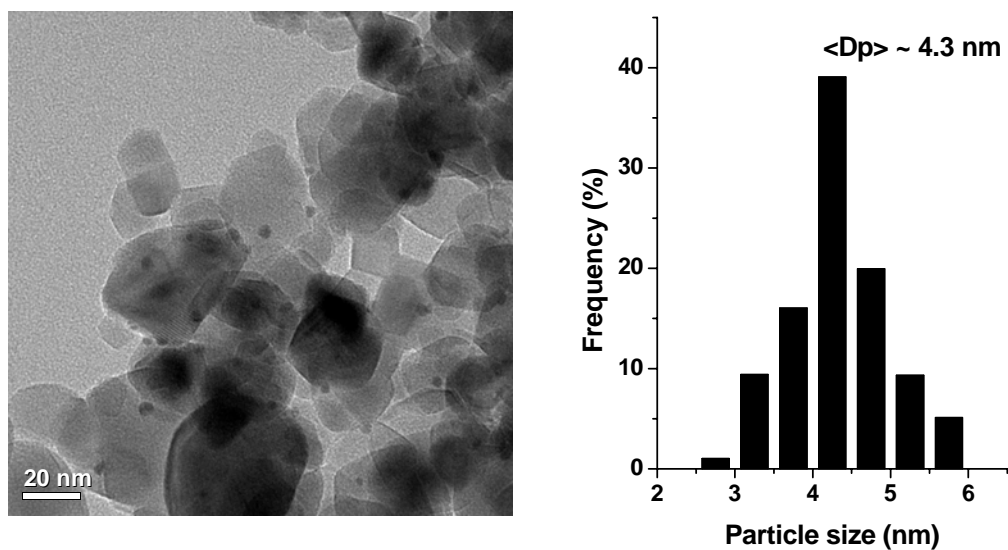


Fig. S4 TEM image and size distribution of Mintek 1 wt % Au/TiO₂ calcined at 500 °C for 6 h.

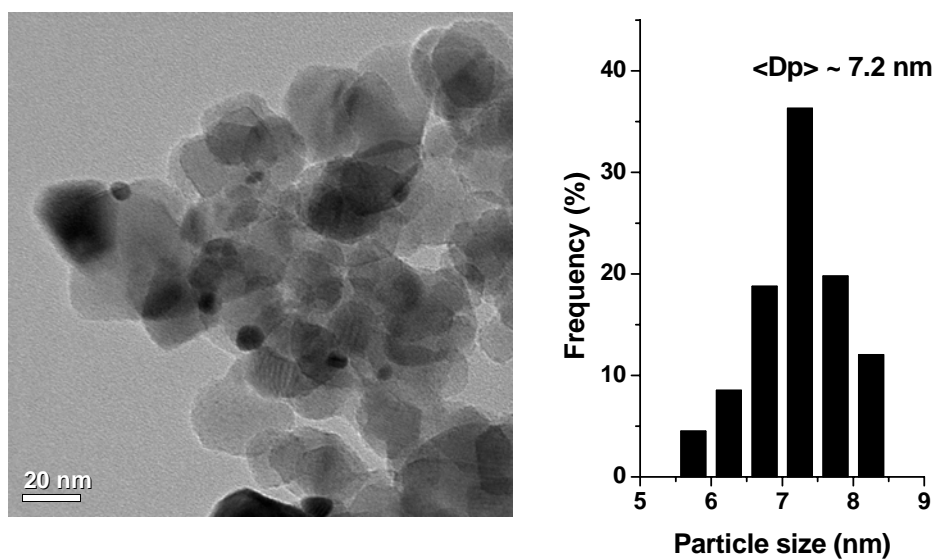


Fig S5 TEM image and size distribution of Mintek 1 wt % Au/TiO₂ after five runs.

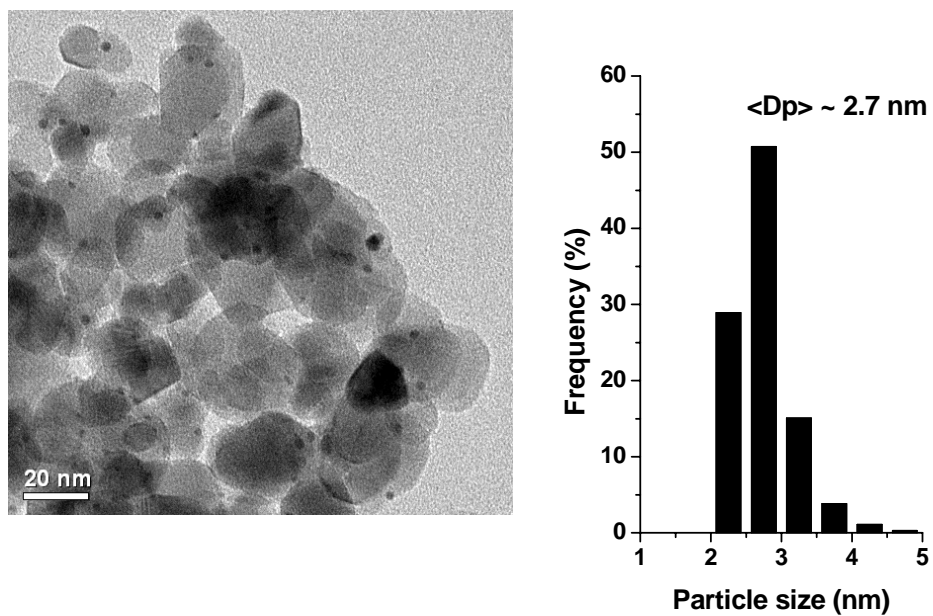


Fig S6 TEM image and size distribution of 1.5 wt % TiO₂ (WGC).

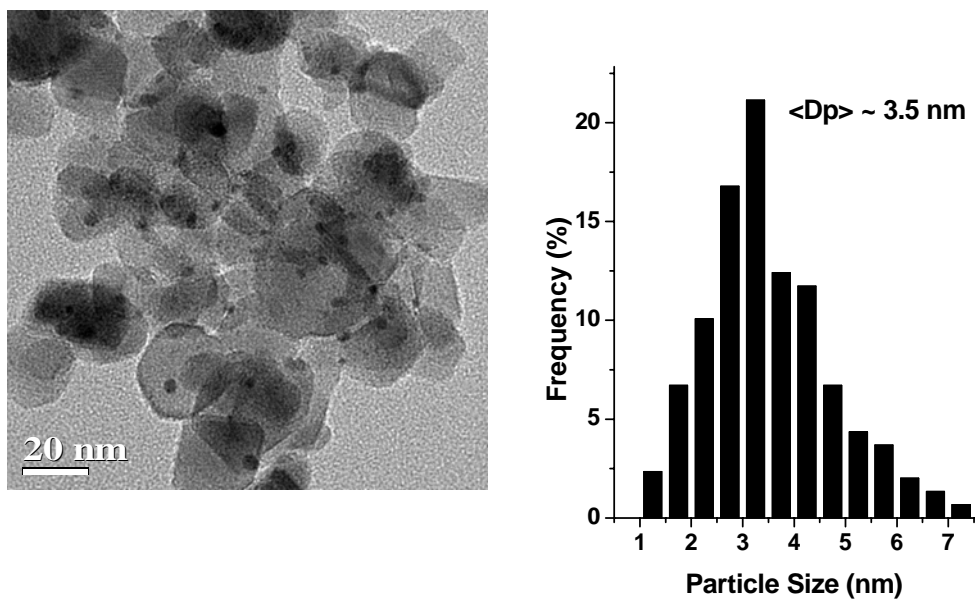


Fig. S7 XPS spectra of Mintek 1 wt % Au/TiO₂: a) before reaction; b) after five runs.

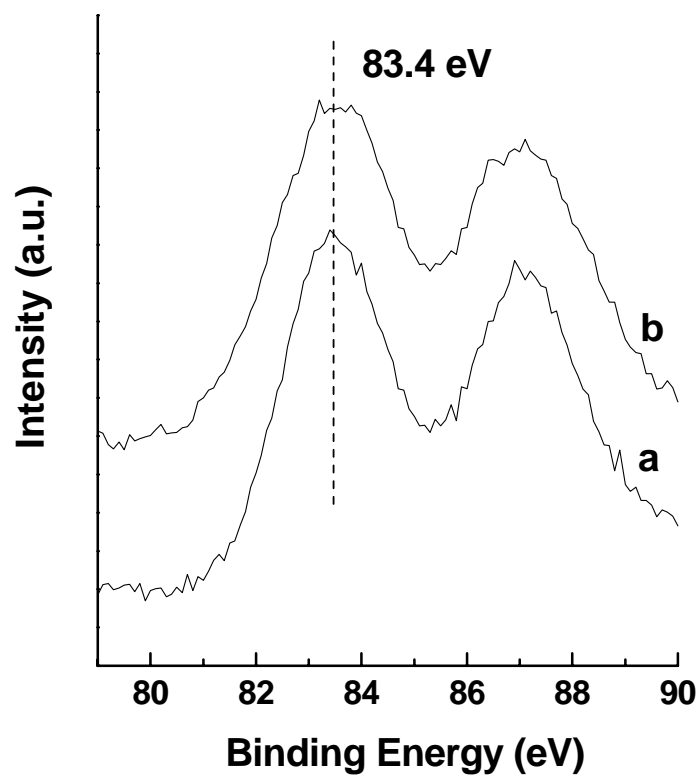


Fig. S8 Proposed mechanism of the alcohol oxidation by supported gold catalysts using aqueous H₂O₂:

