Supporting Information:

Mild and efficient CO-mediated eliminative deoxygenation of epoxides catalyzed by supported gold nanoparticles

Ji Ni, Lin He, Yong-Mei Liu, Yong Cao,* He-Yong He, and Kang-Nian Fan

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China.

Experimental Details

I. Catalytic materials

Gold catalysts including 1.5 wt% Au/TiO_2 (type A, lot no. Au/TiO_2 no. 02-1) and 4.5 wt% Au/Fe_2O_3 (type C, lot no. Au/Fe_2O_3 no. 02-5) were supplied by the World Gold Council (WGC). 5 wt% Pd/C (stock # 38300), 5 wt% Ru/Al_2O_3 (stock # 11749) were provided by Alfa Aesar.

Preparation of Au/TiO_2-VS, Au/CeO_2 and Pt/TiO_2 catalysts: 1 wt% Au/TiO_2-VS, 1 wt% Au/CeO_2 and 1 wt% Pt/TiO_2 were prepared through previously reported methods (Ref. S1).

Preparation of Ag/TiO_2 and Ir/TiO_2 catalysts: 1 wt% Ag/TiO_2 and 1 wt% Ir/TiO_2 catalysts were prepared by incipient wetness technique. TiO_2 (1.0 g Degussa P25, specific surface area: 45 m^2/g nonporous, 70% anatase and 30% rutile, purity > 99.5%) was added to 10 mL of an aqueous solution containing appropriate amounts of $AgNO_3$ or H_2IrCl_6. After a perfect mixing of the corresponding slurries, samples were dried at 100 ^oC for 5 h and then reduced in a 5% H_2/Ar stream at 300 ^oC for 2 h.

Preparation of Au/TiO_2 catalysts with different gold particle size: Au/TiO_2 catalysts with varied average gold particle sizes at ca. 4.3 or 7.2 nm were prepared by calcination of Au/TiO_2-VS at elevated temperatures under a static air atmosphere at 500 ^oC for 2 h or at 500 ^oC for 6 h, respectively.

II. Catalytic activity measurements

General procedure for reductive deoxygenation of epoxides (or N-oxides and S-oxides) by CO/H_2O: A mixture of substrate, supported metal catalysts, and solvent (1 mL), water (0.05 mL) was put into a batch

autoclave reactor (25 mL). After sealing the reactor, CO was fed to the reactor through a gas inlet tube to the arranged pressure. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 25 °C. The conversion and product selectivity were periodically determined by GC-17A gas chromatograph and a flame ionization detector (FID) using *n*-decane as an internal standard.

Procedure for 20-mmol scale CO-mediated deoxygenation of styrene epoxide: A mixture of styrene epoxide (20 mmol), Au/TiO_2-VS (Au: 0.01 mol%), acetone (20 mL) and water (1 mL) was put into a batch reactor (100 mL). After sealing the reactor, CO (20 atm) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 60 °C for 24 h. The conversion and product selectivity were periodically determined by GC analysis.

Recovery and reuse of Au/TiO_2-VS: The reused catalyst was recovered by filtering the solid Au/TiO_2-VS from liquid phase after the reaction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried at 100 °C for 12 h.

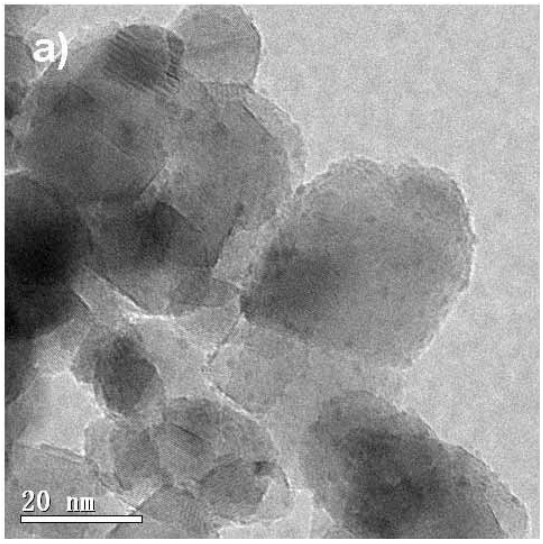
Procedure for deoxygenation of styrene epoxide by CO in anhydrous acetone in the absence of water: A mixture of styrene epoxide (1 mmol), Au/TiO_2-VS (Au: 0.5 mol%), and anhydrous acetone (1 mL) was put into a batch reactor (25 mL). After sealing the reactor, CO (2 atm) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 25 °C. Under these conditions, no conversion of styrene epoxide was observed up to 2 h of contact time.

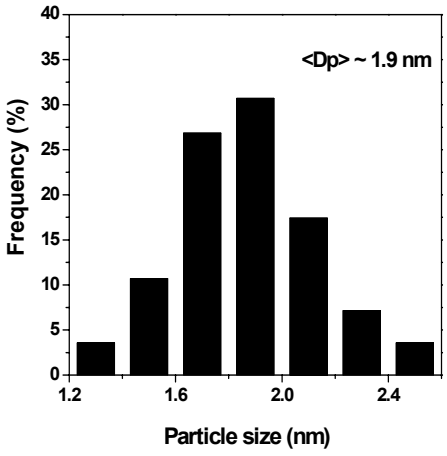
Procedure for deoxygenation of styrene epoxide with 2 atm H_2 using gold catalyst: A mixture of styrene epoxide (1 mmol), Au/TiO_2-VS (Au: 0.5 mol%), acetone (1 mL), and water (0.05 mL) was put into a batch reactor (25 mL). After sealing the reactor, H_2 (2 atm) was fed to the reactor via a gas inlet tube. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 25 °C. The conversion and product selectivity were periodically determined by GC analysis.

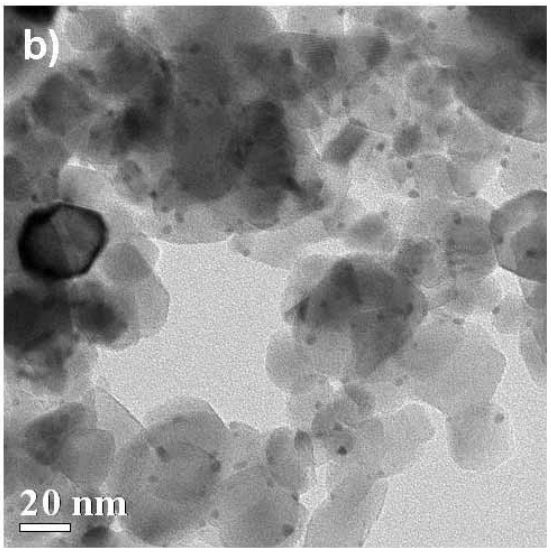
Procedure for CO oxidation by Au/TiO_2: A mixture of catalyst, acetone (1 mL), and water (0.05 mL) was put into a batch reactor (25 mL). After sealing the reactor, the reactor was filled with CO and O_2 to give a CO to O_2 ratio of 1:9 at a total pressure of 20 atm. The reaction mixture was stirred (800 rpm with a magnetic stir bar) at 25 °C. The initial rate of CO conversion was calculated by gas analysis after reaction.

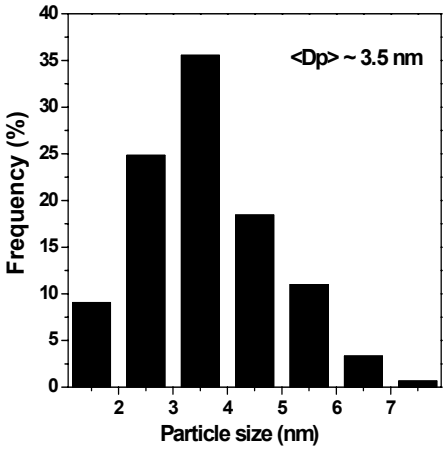
III. Characterization

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.









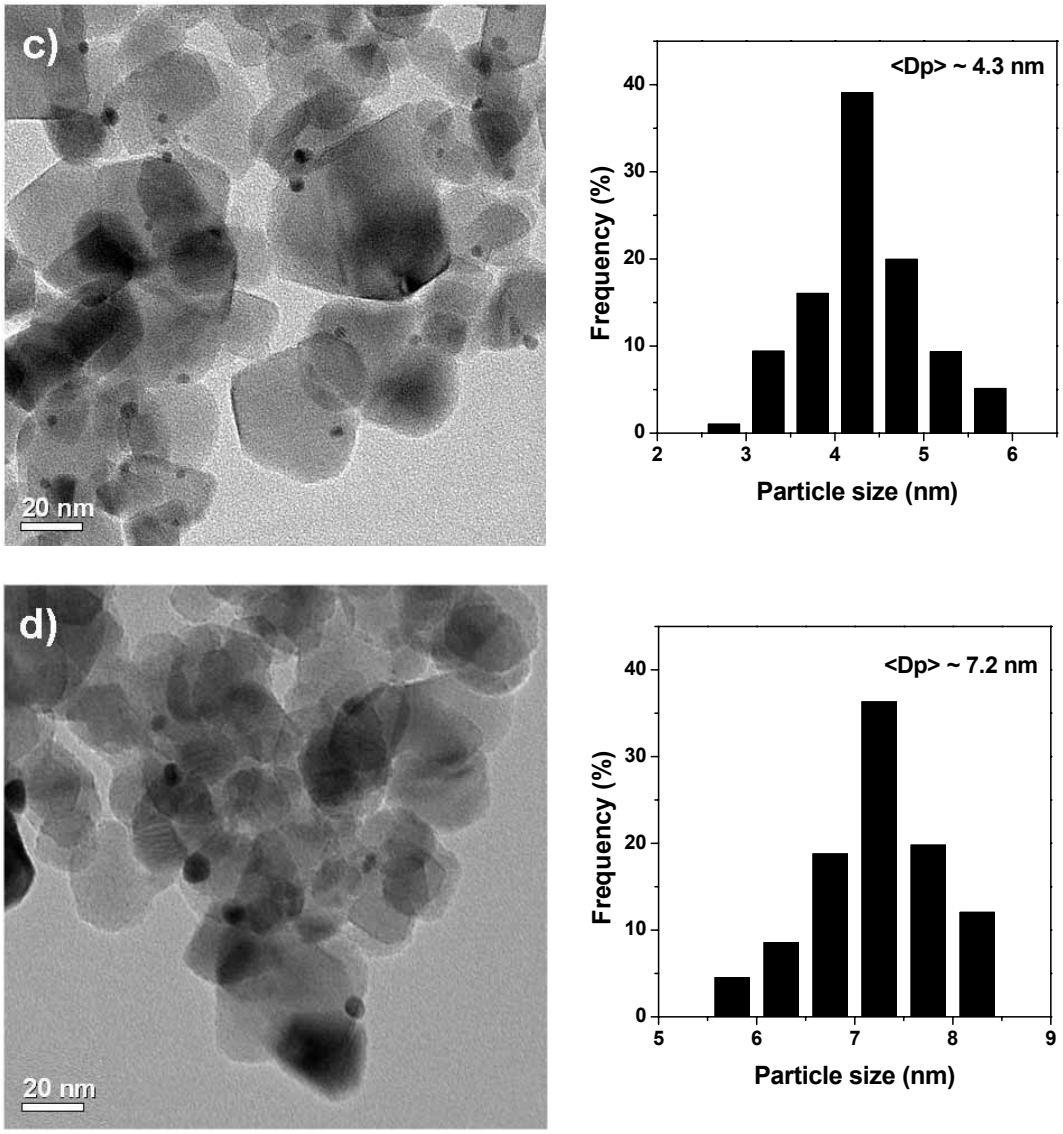


Fig. S1 TEM images and size distribution of Au/TiO_2 catalysts with average gold particle size of a) 1.9 nm (Au/TiO_2-VS); b) 3.5 nm (Au/TiO_2-WGC); c) 4.3 nm and d) 7.2 nm.

Table S1: The influence of solvent on the deoxygenation of styrene epoxide by CO/H_2O using Au/TiO_2-VS.

Entry	Solvent	Conv. (%)	Sel. (%)
1	Acetone	99	>99
2	THF	77	>99
3	Ethyl acetate	31.5	>99
4	Toluene	3.2	>99

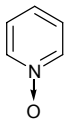
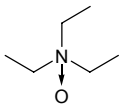
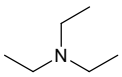
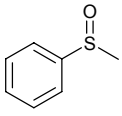
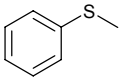
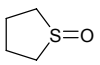
Reaction conditions: 1 mmol styrene epoxide, Au/TiO_2-VS (Au: 0.5 mol%), solvent (1 mL), H_2O (0.05 mL), 1.2 h, CO (2 atm), 25 °C.

Table S2: Deoxygenation of styrene epoxide and other unsaturated substrate by CO/H_2O using Au/TiO_2-VS.

Entry	Substrate	Conv. (%)	Yield (%)
1	Stryene epoxide	99	>99
2	styrene	no reaction	-
3	acetophenone	no reaction	-
4	benzaldehyde	no reaction	-

Reaction conditions: 1 mmol substurate, Au/TiO_2-VS (Au: 0.5 mol%), acetone (1 mL), H_2O (0.05 mL), 1.2 h, CO (2 atm), 25 °C.

Table S3: Deoxygenation of N-oxides and sulfoxides by CO/H_2O using Au/TiO_2-VS

Entry	Substrate	Product	Time (h)	Conv. (%)	Yield (%)
1			10	84	>99
2			10	86	>99
3			5	99	>99
4			5	92	>99

Reaction conditions: 0.3 mmol substrate, Au/TiO_2-VS (Au: 3 mol%), acetone (1 mL), H_2O (0.05 mL), CO (10 atm), 60 °C.

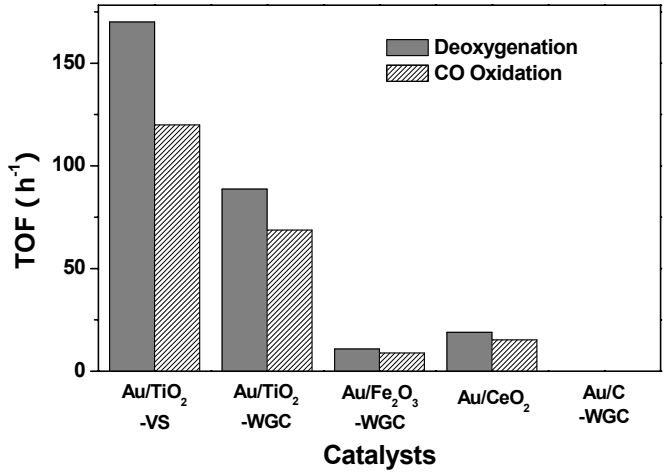


Fig. S2 Support effect of Au catalysts for deoxygenation of styrene epoxide and CO oxidation. Deoxygenation of styrene epoxide: 1 mmol substrate, Au 0.5 mol%, acetone (1 mL), H_2O (0.05 mL), CO (2 atm), 25 °C; CO oxidation: Au 5×10^{-3} mmol, acetone (1 mL), H_2O (0.05 mL), CO (2 atm), O_2 (18 atm), 25 °C. All TOF calculations were based on initial activities below 15 % conversion of the substrates or CO.

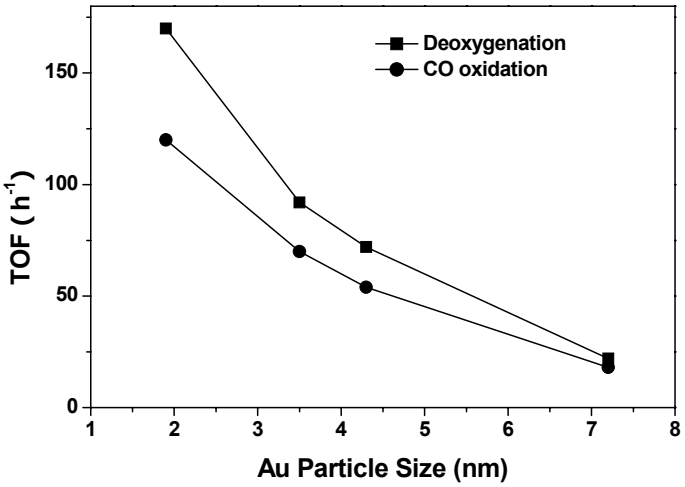


Fig. S3 Particle size effect of Au catalysts for deoxygenation of styrene epoxide and CO oxidation. Deoxygenation of styrene epoxide: 1 mmol substrate, Au 0.5 mol%, acetone (1 mL), H_2O (0.05 mL), CO (2 atm), 25 °C; CO oxidation: Au 5×10^{-3} mmol, acetone (1 mL), H_2O (0.05 mL), CO (2 atm), O_2 (18 atm), 25 °C. All TOF calculations were based on initial activities below 15 % conversion of the substrates or CO.

Reference

[S1] L. He, L. C. Wang, H. Sun, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem. Int. Ed.,* 2009, **48**, 9538.