Advanced
Synthesis &
Catalysis

Supporting Information

Highly Chemo- and Regioselective Transfer Reduction of Aromatic Nitro Compounds Using Ammonium Formate Catalyzed by Supported Gold Nanoparticles

Xia-Bing Lou, Lin He, Yue Qian, Yong-Mei Liu, Yong Cao*, Kang-Nian Fan

Supporting Information

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry, Fudan University, Shanghai 200433, P. R. China, Fax: (+86-21) 65643774; e-mail: yongcao@fudan.edu.cn

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1. Catalytic Materials

Gold catalysts including 1.0 wt% Au/TiO_2, 1.0 wt% Au/ZnO and 0.9 wt% Au/Al_2O_3 were supplied by Mintek. 5 wt% Ru/Al_2O_3 was provided by Urchem. 5 wt% Pd/C was provided by Alfa Aesar.

Preparation of Au/CeO_2 catalyst: 1 wt% Au/CeO_2 catalyst was prepared by deposition-precipitation method. Firstly, 100 mL of a gold solution (0.2 g of $HAuCl_4 \cdot 4H_2O$ in 1 L of water) was heated to 80 ^{o}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 CeO_2 (Degussa, Adnano 90). Stirring was continued for 2 h, after which the suspension was cooled to room temperature. Solids were then filtrated and exhaustively washed with distilled water. The solid thus obtained was dried for 12 h at 50 ^{o}C under vacuum, and reduced in 5 % H_2/Ar at 300 ^{o}C for 2 h.

2. General procedures

General procedure for the reduction of aromatic nitro compounds: The mixture of nitro compound (1 mmol), metal catalysts (metal: 1 mol %), ethanol (10 mL), and anhydrous $HCOONH_4$ (5 mmol) was put into a flask (100 mL) fitted with a gas inlet tube for introducing N_2 by bubbling (10 mL/min). The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 25 °C. After completion of the reduction, the reaction mixture was filtered and the catalyst was washed thoroughly with ethanol. Then the filtrate was concentrated under vacuum and extracted by CH_2Cl_2 (3 × 3 mL). The combined CH_2Cl_2 fractions were concentrated under reduced pressure by using a rotator evaporator. The crude product was purified by column chromatography (silica 200-300; petroleum ether (60~90^{o}C)/ethyl acetate mixture) to afford the amine product. The product was identified by GC-MS and the spectra obtained were compared with the standard spectra. No variation in reduction rate was observed over a range of stirrer speeds (600-1500 rpm) indicating the absence of mass-transfer control. The conversion and product selectivity were periodically determined by GC analysis (Shimazu GC-17A equipped with a HP-FFAP column (30m × 0.25mm) and a flame ionization detector (FID)) using *n*-decane as an internal standard. All products were known and available.

General procedure for the formylation of aromatic nitro compounds: The mixture of nitro compound (1 mmol), Au/TiO_2 (Au: 1 mol %), 3 mL of anhydrous CH_3CN and anhydrous $HCOONH_4$ (7 mmol) was added to a flask (10 mL) equipped with a reflux condenser. The resulting mixture was allowed to reflux with vigorous stirring under a nitrogen atmosphere. After completion of the reaction, the mixture was filtered and the catalyst was washed thoroughly with CH_3CN. Then the filtrate was concentrated under vacuum. The residue was loaded on a silica gel (200-300) column and eluted with petroleum ether (60 ~ 90 °C) and ethyl acetate to afford the pure product. All the products were characterized by GC-MS and the spectra obtained were compared with the standard spectra.

Recovery and reuse of Au/TiO_2: Filtration of the catalyst and washings with ethanol were carried out in order to recover the catalyst. After drying under vacuum for 12 h, the catalyst was reused for the next reaction.

General procedure for the reduction of possible intermediates (phenyl hydroxylamine, nitrosobenzene, azobenzene and azoxybenzne): The mixture of a certain above intermediate (1 mmol), Au/TiO_2 (Au: 1 mol%), 10 mL of ethanol and anhydrous $HCOONH_4$ (5 mmol) was vigorously stirred in a flask under a nitrogen atmosphere at 25 °C for 3 h.

Intermolecular competitive reaction between nitrobenzene and other unsaturated substrates: A mixture of nitrobenzene (0.5 mmol), other unsaturated substrates (0.5 mmol), Au/TiO_2 (Au: 1 mol %), 10 mL of ethanol and anhydrous $HCOONH_4$ (5 mmol) was vigorously stirred at 1000 rpm under a nitrogen atmosphere at 25 °C for 3 h. The result showed that when the yield of aniline > 99%, all other unsaturated substrates exhibited no conversion at all.

3. Characterization of catalysts

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 Kα (*hv* = 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.

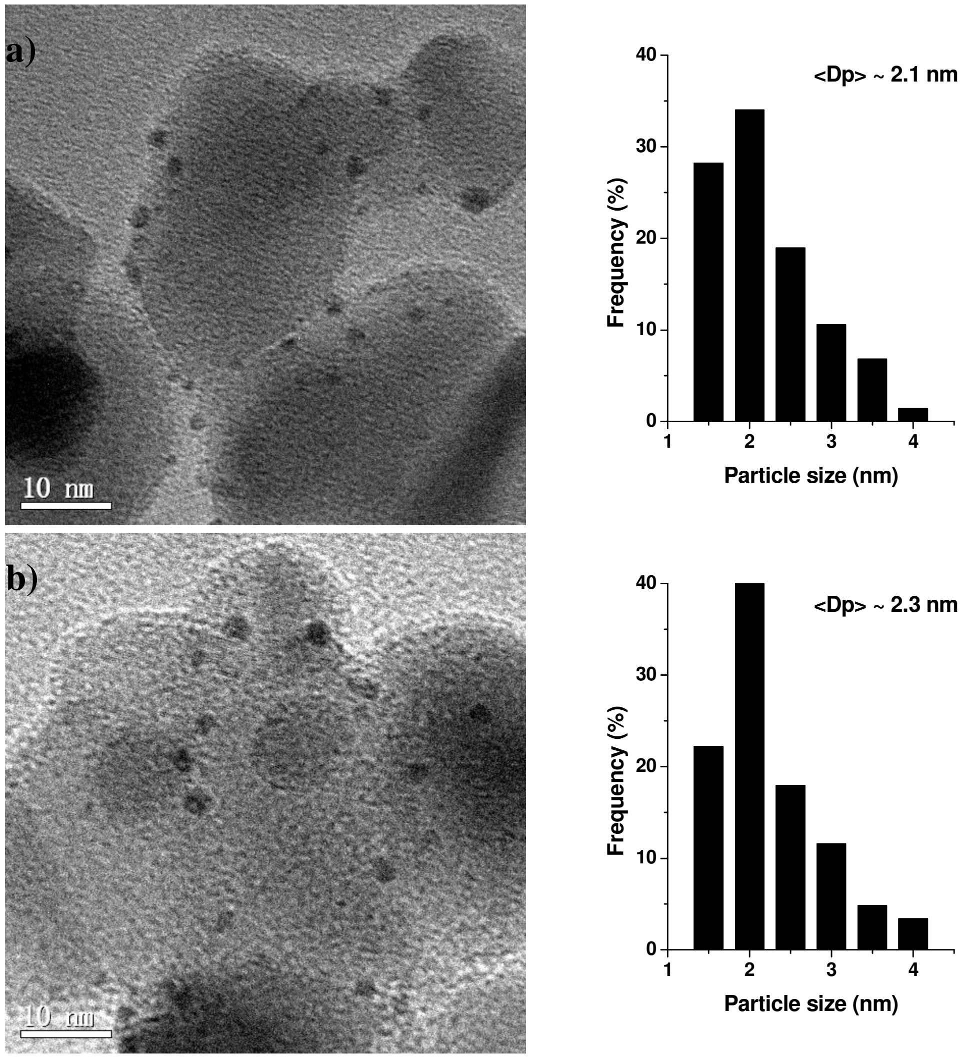
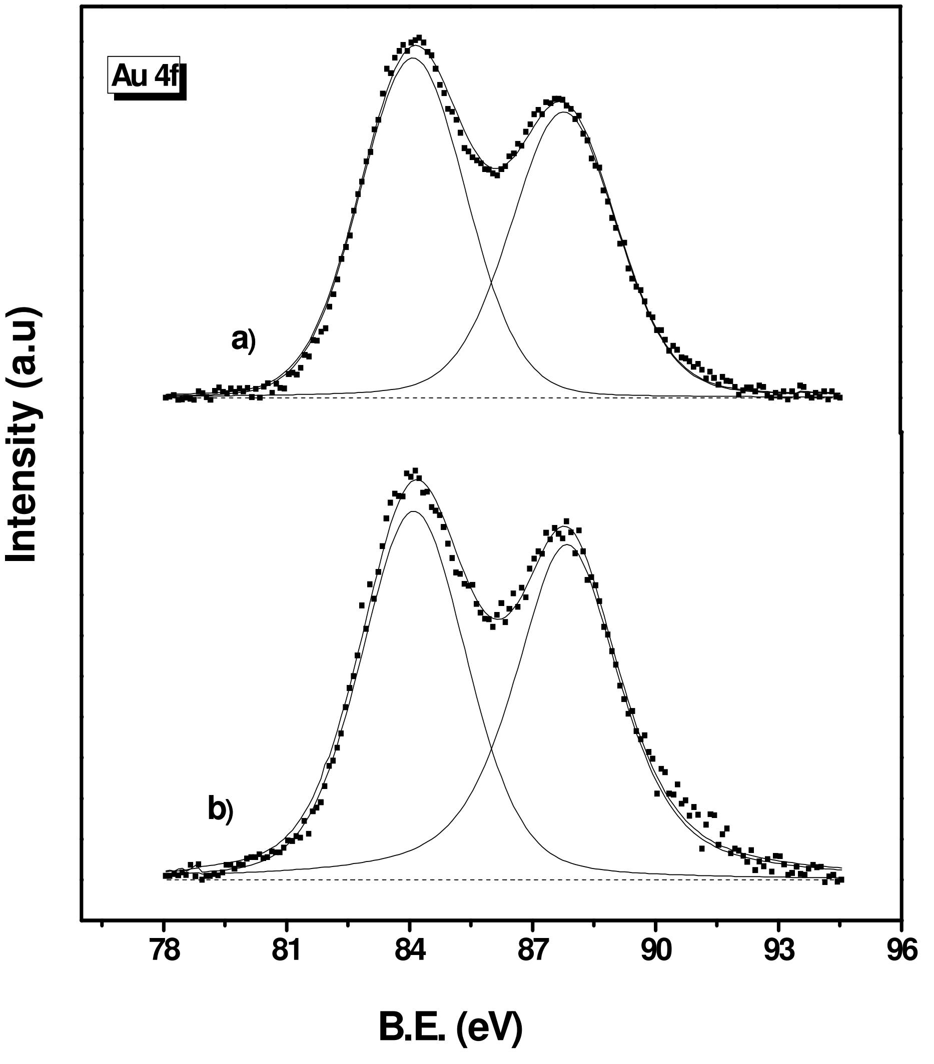


Figure S1. Representative TEM image and size distribution of a) fresh 1 wt % Au/TiO_2; b) 1 wt % Au/TiO_2 after three runs.


Au 4f
a)
b)
Intensity (a.u)
78
81
84
87
90
93
96
B.E. (eV)

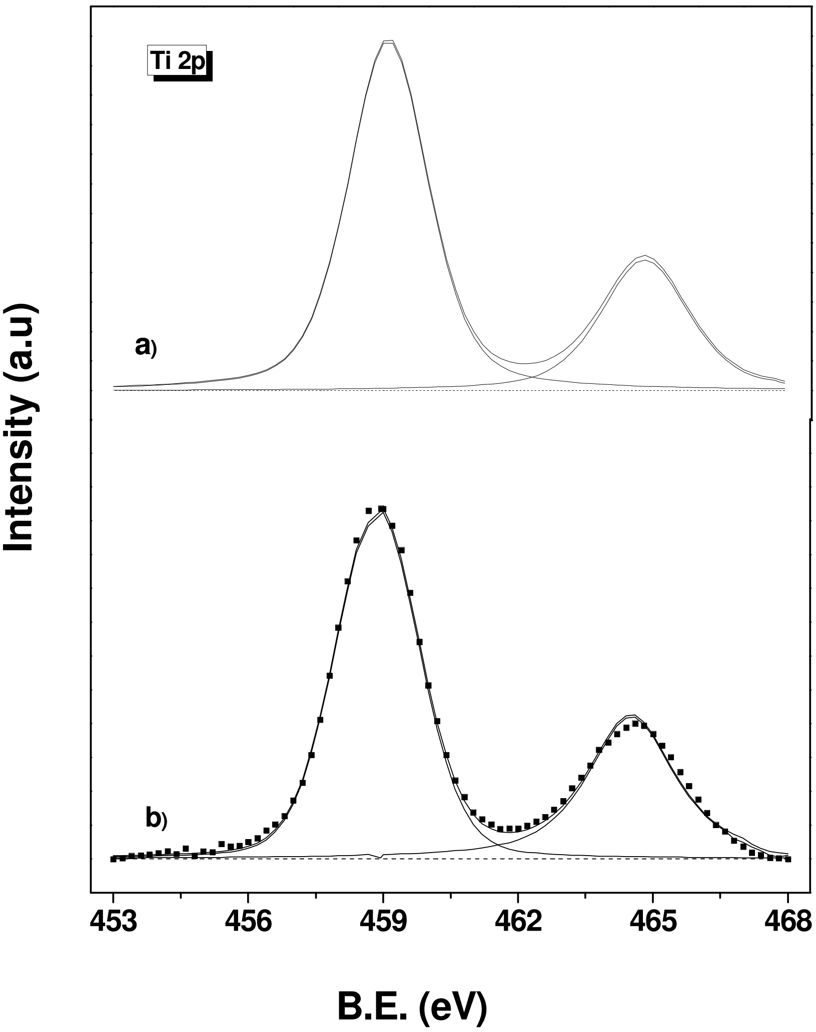


Figure S2. Au4f and Ti 2p XP spectra of Au/TiO_2 a) before reaction; and b) after three runs.

Table S1. XPS results of Au/TiO_2 catalysts.

Catalyst	BE of Au $4f_{7/2}$ (eV)	BE of Ti $2p_{3/2}$ (eV)	Au/Ti
Au/TiO_2 (before reaction)	83.7	459.0	0.042
Au/TiO_2 (after three runs)	83.8	458.9	0.041

4. Effect of reaction temperature

Table S2. Effect of reaction temperature on the reduction of nitrobenzene to aniline by $HCOONH_4$-Au/TiO_2.

Entry	T (°C)	Time (h)	Yield%	Average TOF (h^{-1})
1	0	30	98	3.3
2	25	3	> 99	33.3
3	50	1.6	> 99	62.5
4	75	0.5	> 99	200.0

Reaction conditions: substrate (1 mmol), Au/TiO_2 (Au: 1 mol%), ethanol (10 mL) and anhydrous NH_4COOH (5 mmol).

5. The reduction of possible intermediates

Table S3. The reduction of possible intermediates.

Entry	Substrate	Product	Yield%
1	Phenyl hydroxylamine	Aniline	60
2	Nitrosobenzene	Aniline	3
3	Azobenzene	Aniline	12
4	Azoxybenzene	Aniline	3

Reaction conditions: substrate (1 mmol), Au/TiO_2 (Au: 1 mol%), ethanol (10 mL) and anhydrous NH_4COOH (5 mmol), 25 °C.