

Direct one-pot reductive imination of nitroarenes using aldehydes and carbon monoxide by supported gold nanoparticles at room temperature

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Electronic Supplementary Information

Experimental Details

I. Catalytic materials

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).

Preparation of Au/TiO₂-VS catalysts: 0.5 wt % Au/TiO₂ catalysts were prepared by a routine deposition-precipitation method. An appropriate amount of aqueous solutions of chloroauric acid (1 g HAuCl₄•4H₂O in 100 mL deionized water) was added to 100 mL deionized water. The pH was adjusted to 8 by dropwise addition of NaOH (0.2 M), and then 1.0 g of TiO₂ (P25, Evonik) was dispersed in the solution. The mixture was aged for 1 h at 70 °C, after which the suspension was cooled to room temperature. Solid were then filtrated and exhaustively washed with distilled water until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h, and then calcined in static air at 300 °C for 4 h. The as-prepared Au/TiO₂ with very small Au nanoparticles (*ca.* 1.9 nm, see TEM data in Fig. S1) was denoted as Au/TiO₂-VS.

Preparation of Au/SiO₂ catalyst: 1.0 wt% Au/SiO₂ catalysts were prepared by following the modified DP procedure.^[S1] 1.0 g of SiO₂ (Evonic, Aerosil 380, specific surface area: 380 m² g⁻¹) was introduced into the appropriate amount of HAuCl₄ solution in order to prepare catalysts with 1.0 wt% gold content. After stirring at 75 °C for 1 h the solution was cooled down to room temperature (RT) and 0.2 M NH₄OH was added to the solution under stirring. After 6 h stirring at RT the catalyst was washed five times with deionized water and separated by centrifugation. The samples were dried under vacuum at RT for 12 h and reduced in flowing 5 vol% H₂/Ar at 350 °C for 2 h.

Preparation of Au/CeO₂ catalysts: 1 wt % Au/CeO₂ catalysts were prepared by a routine deposition precipitation method.^[S2] An appropriate amount of aqueous solutions of chloroauric acid (HAuCl₄) was

heated to 80 °C under vigorous stirring. The pH was adjusted to 10 by dropwise addition of NaOH (0.2 M), and then 1.0 g of CeO₂ (Evonic, Adnano 90, specific surface area: 90 m²/g) was dispersed in the solution. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to RT. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were filtrated and dried under vacuum at RT for 12 h, and reduced in 5 % H₂/Ar at 300 °C.

II. Catalytic activity measurements

General procedure for synthesis of imines: Equimolar amounts of nitro compound and aldehyde (1 mmol), anisole (10 μL) as internal reference in 2 mL solvent in the presence of appropriate amount of gold catalyst (1 mol % Au) and water were put into a batch autoclave reactor (25 mL). After sealing the reactor, it was purged with CO to completely remove air from the reactor. The reaction mixture was thermostatted at 25 °C in a water bath under continuous stirring (1000 rpm with a magnetic stir bar) under CO atmosphere ($P_{CO} = 5$ atm). The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID). For isolation, the combined organic layer was dried over anhydrous Na₂SO₄, concentrated, and purified by silica gel column chromatography.

Procedure for imination of nitrobenzene using benzaldehyde and 1 atm of CO: Equimolar amounts of nitrobenzene and benzaldehyde (1 mmol), anisole (10 μL) as internal reference in 2 mL triethylamine in the presence of appropriate amount of Au/TiO₂-VS catalyst (1 mol % Au) and water was put into a flask (25 mL) fitted with a gas inlet tube for introducing CO by bubbling (10 mL/min). The reaction mixture was stirred (1000 rpm with a magnetic stir bar) at 25 °C. The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID).

Procedure for imination of nitrobenzene using benzaldehyde and 5 atm H₂: Equimolar amounts of nitrobenzene and benzaldehyde (1 mmol), anisole (10 μL) as internal reference in 2 mL triethylamine in the presence of appropriate amount of Au/TiO₂-VS catalyst (1 mol % Au) and water were put into a batch autoclave reactor (25 mL). After sealing the reactor, it was purged with H₂ to completely remove air from the reactor. The reaction mixture was thermostatted at 25 °C in a water bath under continuous stirring (1000 rpm with a magnetic stir bar) under H₂ atmosphere ($P_{H_2} = 5$ atm). The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with

a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID).

Procedure for sole reduction of benzaldehyde with CO/H₂O: Benzaldehyde (1 mmol), anisole (10 μL) as internal reference in 2 mL triethylamine in the presence of appropriate amount of Au/TiO₂-VS catalyst (1 mol % Au) and water were put into a batch autoclave reactor (25 mL). After sealing the reactor, it was purged with CO to completely remove air from the reactor. The reaction mixture was thermostatted at 25 °C in a water bath under continuous stirring (1000 rpm with a magnetic stir bar) under CO atmosphere ($P_{CO} = 5$ atm). The conversion and product selectivity were determined by GC-17A gas chromatograph equipped with a HP-FFAP column (30 m × 0.25 mm) and a flame ionization detector (FID). It was verified by GC analysis that the sole reduction of benzaldehyde did not proceed under such mild reaction conditions.

One-Pot two-step aza Diels-Adler reaction: Equimolar amounts of nitrobenzene, benzaldehyde and water (1 mmol) in 2 mL triethylamine in the presence of appropriate amount of Au/TiO₂-VS catalyst (1 mol % Au) were put into a batch autoclave reactor (25 mL). After sealing the reactor, it was purged with CO to completely remove air from the reactor. The reaction mixture was thermostatted at 25 °C in a water bath under continuous stirring under CO atmosphere ($P_{CO} = 5$ atm). After 1 hour reaction, the reactor was depressurized, Danishefsky's diene (1 mmol) was added into the system and the mixture was stirred for 6 h at 25 °C. Then the catalyst was separated by centrifugation, and the organic layer was dried over anhydrous Na₂SO₄, concentrated, and purified by silica gel column chromatography to give 1,2-diphenyl-2,3-dihydropyridin-4-one (85% yield).

Recovery and reuse of Au/TiO₂-VS: The reused catalyst was recovered by filtering the solid Au/TiO₂-VS from liquid phase after the reaction. The recovered catalyst was washed with ethanol for three times and then with deionized water for several times. The catalyst was then dried under vacuum at room temperature overnight before the next recycle run.

III. Characterization

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. The measurement result shows that the real gold content, 0.48 wt % was essentially the same as the nominal loading for TiO₂ supported gold catalyst.

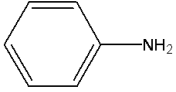
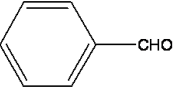
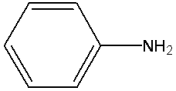
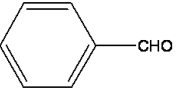
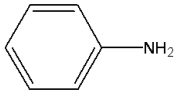
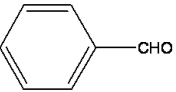
Transmission electron microscopy (TEM): TEM images for supported gold catalysts were taken with a JEOL 2011 electron microscope operating at 200 kV. Before being transferred into the TEM

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 150 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.

^1H NMR spectroscopy: ^1H NMR spectra were recorded in CDCl_3 on a DMX 500 at 25 °C and chemical shifts were expressed in ppm with TMS as an internal standard ($\delta = 0$ ppm).

Table S1 Synthesis of N-benzylidenebenzenamine by direct condensation between aniline and benzaldehyde over various catalysts.^a

Entry	Aniline	Benzaldehyde	Catalyst	Conversion ^b [%]	S [%] ^b
					Imine
1			/	32	100
2			TiO ₂	89	100
3			Au/TiO ₂ -VS	95	100

^a Reaction conditions: 1 mmol aniline, 1 mmol benzaldehyde, 2 mL triethylamine, 1 mmol H₂O, 5 atm CO, 25 °C, 1 h. ^b GC conversion and selectivity obtained by using anisole as internal reference.

Table S2 Yields of N-benzylidenebenzenamine versus the pKa values of various solvents.^[S3]

Entry	Ethanol	Acetonitrile	DMF	Toluene	Tetrahydrofuran	Triethylamine
pKa	16	25	2.1	40	1.3	11
Yield of imine (%)	65	23	17	62	85	95

Table S3 Synthesis of N-benzylidenebenzenamine from nitrobenzene and benzaldehyde over various catalysts.^a

Entry	Catalyst	d_{Au}^b (nm)	Conversion [%] ^c	S [%] ^c		
				Imine	Aniline	Nitrone
1	Au/Fe ₂ O ₃	3.5	11	66	34	0
2	Au/CeO ₂	2.6	32	79	21	0
3	Au/SiO ₂	1.9	n.r.	-	-	-
4	Au/C	12.2	n.r.	-	-	-

^a Reaction conditions: 1 mmol nitrobenzene, 1 mmol benzaldehyde, 2 mL triethylamine, 1 mmol H₂O, 5 atm CO, 25 °C, 1 h. ^b Average gold particle size estimated by statistical analysis from TEM results. ^c GC conversion and selectivity obtained by using anisole as internal reference, n.r. = no reaction.

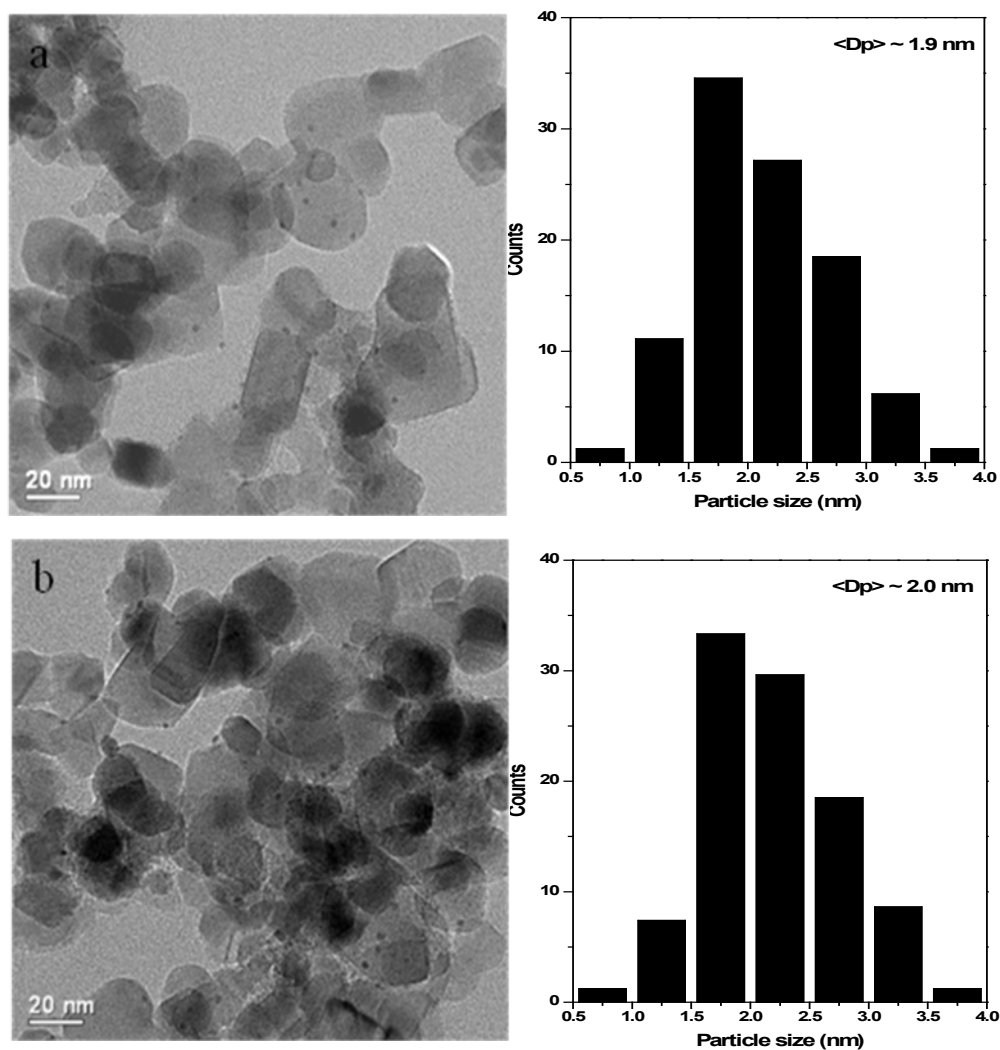


Fig. S1 TEM image and gold particle size distribution of 0.5 wt% Au/TiO₂-VS: (a) fresh catalyst, (b) after five runs. The TEM results clearly demonstrate that the gold particles are finely dispersed on the surface of TiO₂ before and after five runs. The average gold particle sizes of the fresh and used catalysts are estimated to be *ca.* 1.9 and 2.0 nm, respectively. Thus the catalyst is stable and reusable under our reaction conditions.

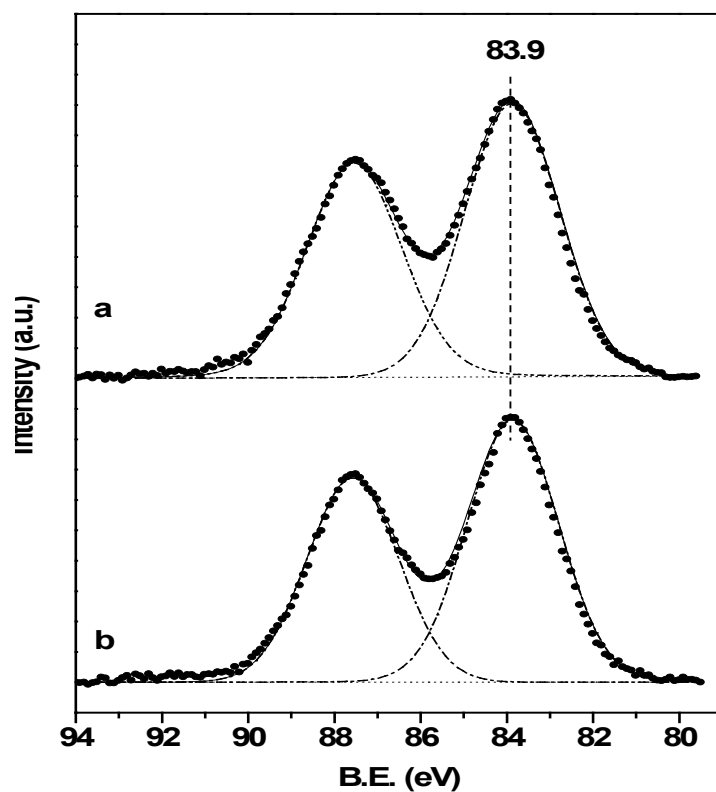
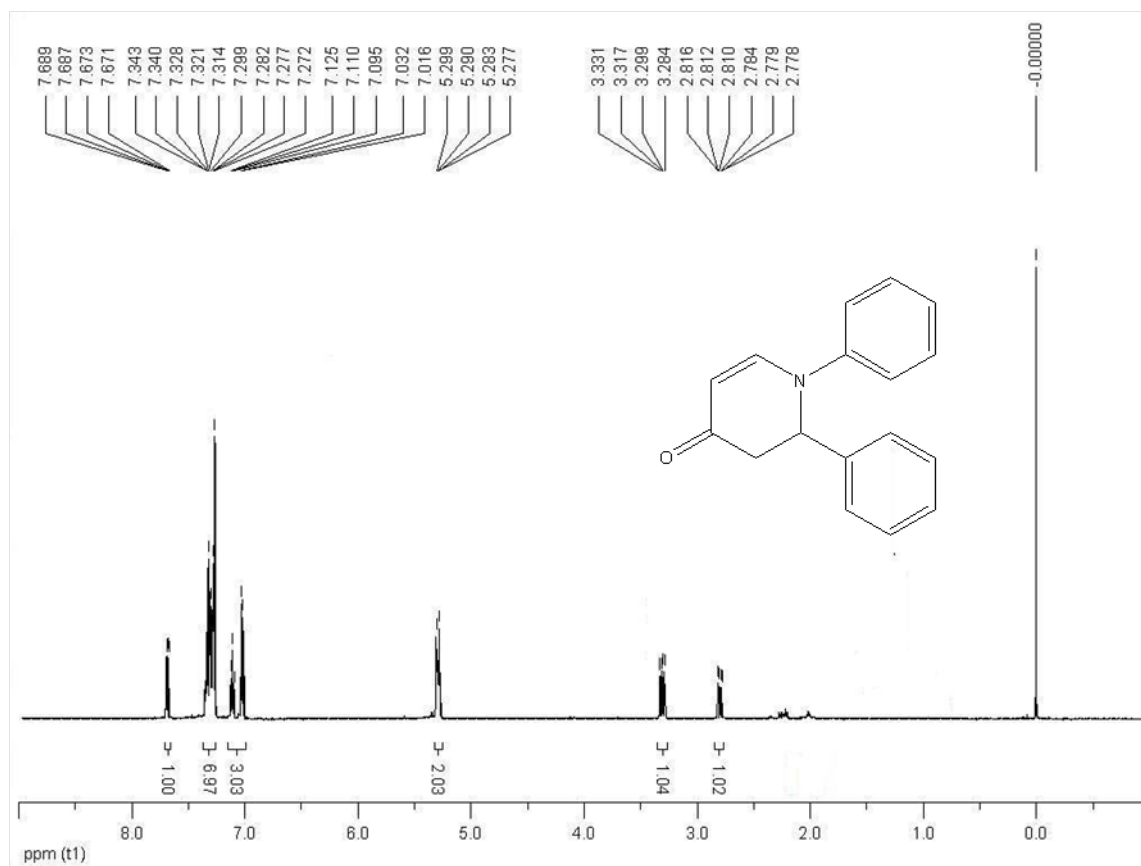


Fig. S2 Au 4f XPS spectra of 0.5 wt % Au/TiO₂-VS: (a) fresh catalyst, (b) after five runs. The binding energy of Au 4f_{7/2} for the fresh and used catalysts is *ca.* 83.9 eV which is the characteristic of Au⁰ (84.0 eV). Deconvolution of the Au spectra indicates that only metallic gold species is present in the both samples. Combined with the TEM results, it again confirms the stability and reusability of the catalyst.

¹H NMR spectroscopy of 1,2-diphenyl-2,3-dihydropyridin-4-one

¹H NMR (500 MHz, CDCl₃, ppm): δ 2.80 (dd, 1H, J₁ = 16 Hz, J₂ = 3 Hz), 3.30 (dd, 1H, J₁ = 16 Hz, J₂ = 7 Hz), 5.30-5.27 (m, 2H), 7.13-7.01 (m, 3H), 7.34-7.27 (m, 7H), 7.68 (dd, 1H, J₁ = 8 Hz, J₂ = 1 Hz).



References:

- [S1] F. Somodi, I. Borbáth, M. Hegedús, A. Tompos, I. E. Sajó, Á. Szegedi, S. Rojas, J. L. G. Fierrob and J. L. Margitfalvi, *Appl. Catal. A*, 2008, **347**, 216.
- [S2] M. Haruta, *Catal. Today*, 1997, **36**, 153.
- [S3] M. B. Smith and J. March, *Advanced Organic Chemistry: Reactions, Mechanisms and Structure*, John Wiley & Sons, Inc., Hoboken, New Jersey, 2007, 359.