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Supporting Information

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Efficient and Clean Gold-Catalyzed One-Pot Selective N-Alkylation of Amines with Alcohols

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Supporting Information for

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Experimental Details

1. Catalytic materials

Au/TiO₂-WGC (1.5 wt% Au, type A, lot no. Au/TiO₂ no. 02-1) was supplied by the World Gold Council (WGC). 0.9 wt% Au/Al₂O₃ and 1 wt% Au/ZnO were provided by Mintek.

Preparation of Au/TiO₂-VS catalysts: A slightly modified deposition-precipitation (DP) procedure has been employed to prepare the 0.5 wt% Au/TiO₂-VS sample. TiO₂ (1.0 g, Degussa P25, specific surface area: 45 m²/g nonporous, 70% anatase and 30% rutile, purity > 99.5%) was added to 100 mL of an appropriate amounts of aqueous solution of chloroauric acid (HAuCl₄) at a fixed pH = 8 adjusting with 0.2 M NaOH. The mixture was aged for 2 h at 80 °C under vigorous stirring, after which the suspension was cooled to room temperature. Extensive washing with 0.2 M NH₄NO₃ and then deionized water was followed to remove Na⁺ and Cl⁻. The samples were dried under vacuum at room temperature for 12 h before calcination at 300 °C for 4 h in static air. All of the preparations were performed in the absence of light. The Au/TiO₂ catalyst as-prepared with very small Au nanoparticles (*ca.* 1.8 nm, see TEM data in Fig. S1) was denoted as Au/TiO₂-VS. Elemental analysis results revealed that the real gold loading was 0.49 wt% in Au/TiO₂-VS.

Preparation of Au/MgO catalysts: The 0.5 wt% Au/MgO sample was prepared by the modified DP procedure as described above. MgO (1.0 g, Merck Chemical Industries Co. Ltd.) was added to 100 mL of an appropriate amounts of aqueous solution of chloroauric acid (HAuCl₄) at a fixed pH = 9.6 adjusting with 0.2 M NaOH. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with 0.2 M NH₄NO₃ and then deionized water was followed to remove Na⁺ and Cl⁻. The samples were dried under vacuum at room temperature for 12 h before reduced in 5% H₂/Ar at 300 °C for 2 h. Elemental analysis results revealed that the real gold loading was 0.48 wt% in Au/MgO.

Preparation of Au/CeO₂ catalysts: The 0.5 wt% Au/CeO₂ sample was prepared by the modified DP procedure as described above. CeO₂ (1.0 g, Degussa, Adnano 90, specific surface area: 90 m²/g) was added to 100 mL of an appropriate amounts of aqueous solution of chloroauric acid (HAuCl₄) at a fixed pH = 9 adjusting with 0.2 M NaOH. The mixture was aged for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with 0.2 M NH₄NO₃ and then deionized water was followed to remove Na⁺ and Cl⁻. The samples were dried under vacuum at room temperature for 12 h before reduced in 5% H₂/Ar at 300 °C for 2 h. Elemental analysis results revealed that the real gold loading was 0.5 wt% in Au/CeO₂.

Preparation of hydroxyapatite and Au/HAP catalysts: Hydroxyapatite (HAP) was prepared through a liquid-precipitation method.^[S1] A solution of calcium nitrate tetrahydrate (6.3 g) in 60 mL mixed solvent (ethanol/water = 1/1 in volume) and a solution of diammonium hydrogenphosphate (2.112 g) in 60 mL water were prepared. Both of the two solutions were brought to pH = 10.5 by using aqueous ammonia before mixing. Then the phosphate solution was added dropwise into the calcium salt solution (drop rate < 5 mL/min) at 80 °C to produce a milky white precipitate and during the process the pH of the solution was also maintained at 10.5. After filtration, the precipitate was washed with distilled water for several times and dried overnight and finally calcined at 500 °C for 3 h. Homogeneous deposition-precipitation (HDP) method using urea as the precipitation agent has been employed to prepare the 0.5 wt% Au/HAP sample. Typically, 1 g of HAP was added to an aqueous solution with an appropriate amounts of aqueous solution of HAuCl₄ and urea (urea/Au = 100, molar ratio). The suspension was heated to 90 °C and stirred for 4 h, followed by filtering and washing for several times with distilled water. The resulting solid product was dried overnight and finally the purple catalyst was obtained by calcination at 300 °C for 4 h.

Preparation of Pd/TiO₂ and Ru/TiO₂ catalysts: 0.5 wt% Pd/TiO₂ and 0.5 wt% Ru/TiO₂ catalysts were prepared by incipient wetness impregnation of the support (Degussa P25, specific surface area: 45 m²/g nonporous, 70% anatase and 30% rutile, purity > 99.5%), with aqueous solution of Pd (NO₃)₂·6H₂O or RuCl₃ (Aldrich) of appropriate

concentrations (typically 1.0 mL/g support). After a perfect mixing of the corresponding slurries, samples were dried at 100 °C for 5 h and then reduced under 5% H₂/Ar (flow rate 30 mL/min) at 450 °C for 3 h.

2. Catalytic activity measurements

General procedure for the direct N-alkylation of alcohols and amines: A mixture of amine (1.5 mmol), alcohol (1.5 mmol), metal catalysts (0.5 mol% metal), toluene (1 mL), and *n*-dodecane (10 µL) as internal standard were placed into a Teflon-lined autoclave (4 mL capacity). The resulting mixture was vigorously stirred at 120 °C under N₂ atmospheres (5 atm) for given reaction time. The product was identified by GC–MS and the spectra obtained were compared with the standard spectra. 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.

Recovery and reuse of Au/TiO₂-VS: The reused catalyst was recovered by filtering the solid Au/TiO₂-VS from liquid phase after reduction. The recovered catalyst was washed with acetone for three times and then with distilled water for several times. The catalyst was then dried under vacuum at room temperature for 12 h.

Direct N-alkylation of pyrrolidine with benzyl alcohol by using Au/TiO₂-VS: A mixture of pyrrolidine (1.5 mmol), benzyl alcohol (1.5 mmol), Au/TiO₂-VS (1 mol% Au), toluene (1 mL) and *n*-dodecane (10 µL) as internal standard were placed into a Teflon-lined autoclave (4 mL capacity). The resulting mixture was vigorously stirred at 140 °C under N₂ atmospheres (5 atm) for given reaction time. The product was identified by GC-MS.

100 mmol scale N-alkylation of aniline with benzyl alcohol under solvent-free conditions: A mixture of aniline (100 mmol), benzyl alcohol (100 mmol), and Au/TiO₂-VS (0.0083 mol% Au) were placed into an autoclave (50 mL capacity). The resulting mixture was vigorously stirred at 180 °C under N₂ atmospheres (5 atm) for given reaction time. For isolation, the combined organic layer was dried over anhydrous Na₂SO₄, concentrated, and purified by silica gel column chromatography. 17.6 g of the corresponding benzylphenylamine was isolated.

The reaction of aniline with benzyl alcohol in the presence of Cs₂CO₃ by using Au/TiO₂-VS: A mixture of aniline (1.5 mmol), benzyl alcohol (1.5 mmol), Cs₂CO₃ (1.5 mmol), toluene (1 mL), and Au/TiO₂-VS (0.5 mol% Au) were placed into a Teflon-lined autoclave (4 mL capacity). The resulting mixture was vigorously stirred at 120 °C under N₂ (5 atm) for 14 h.

The crossover reaction of aniline with benzyl alcohol and benzaldehyde: A mixture of aniline (1.5 mmol), benzyl alcohol (0.75 mmol), benzaldehyde (0.75 mmol), toluene (1 mL), and Au/TiO₂-VS (0.5 mol% Au) were placed into an autoclave (a Teflon vessel, 4 mL). The resulting mixture was vigorously stirred at 120 °C under N₂ atmospheres (5 atm) for given reaction time. The aldehyde was immediately converted into the imine, while the alcohol reacted slowly to form the corresponding amine with about only 5% yield after 14 h.

The reaction of aniline with benzaldehyde in the presence of 2-propanol by using Au/TiO₂-VS: A mixture of aniline (1.5 mmol), benzaldehyde (1.5 mmol), 2-propanol (3.0 mmol), toluene (1 mL), and Au/TiO₂-VS (0.5 mol% Au) were placed into a Teflon-lined autoclave (4 mL capacity). The resulting mixture was vigorously stirred at 120 °C under N₂ atmospheres (5 atm) for 14 h and gave benzylideneaniline in 96% yield.

The transfer hydrogen (TH) reaction of benzylideneaniline with benzyl alcohol: A mixture of benzylideneaniline (1.5 mmol), benzyl alcohol (1.5 mmol), toluene (1 mL), and Au/TiO₂-VS (0.5 mol% Au) were placed into a Teflon-lined autoclave (4 mL capacity). The resulting mixture was vigorously stirred at 120 °C under N₂ atmospheres (5 atm) for 14 h and gave N-benzylaniline in < 3% yield.

3. 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.

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): The XPS measurements were performed with a Perkin Elmer PHI 5000C spectrophotometer with Mg K α radiation (1253.6 eV). The samples were pressed into a pellet and transferred to a test chamber. The spectra were collected with an analyzer pass energy of 23.5 eV and an electron takeoff angle of 45°. The vacuum in the test chamber was maintained below 1×10^{-9} Torr. The binding energies scale was calibrated taking, as a reference, the adventitious C 1s peak at 284.6 eV.

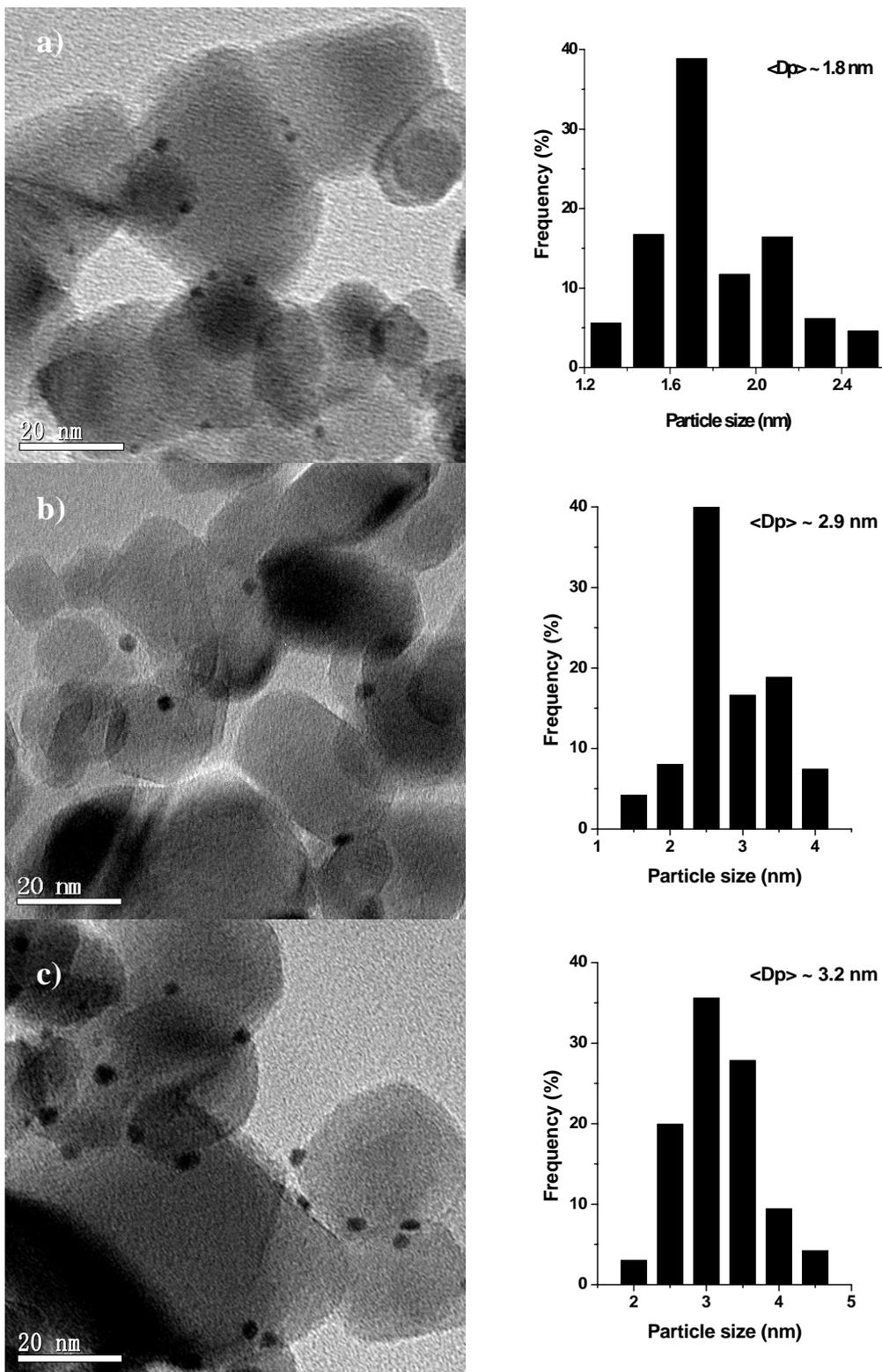


Figure S1. Representative TEM image and size distribution of a) 0.5 wt % Au/TiO₂-VS; b) 0.5 wt % Au/TiO₂-VS after three runs; c) 1.5 wt % Au/TiO₂-WGC.

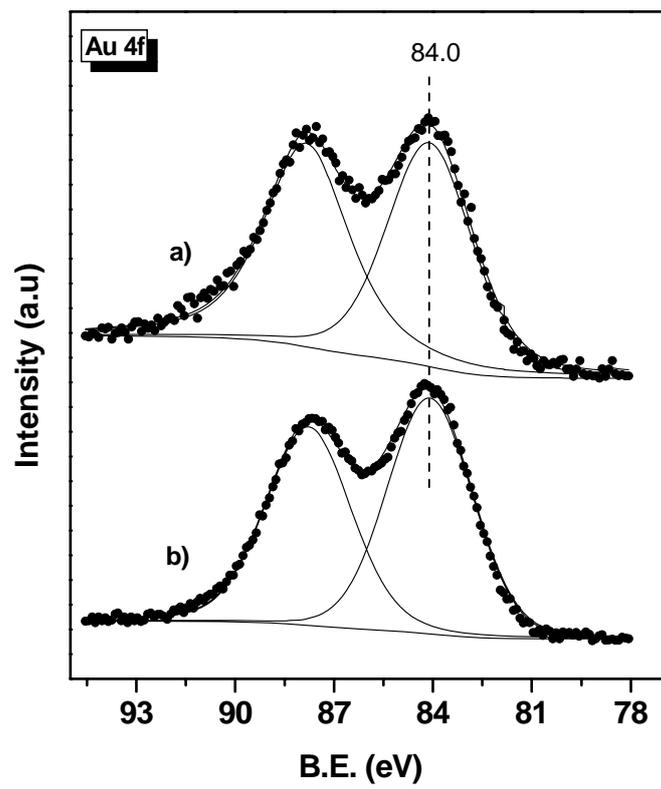


Figure S2. XP spectra of Au/TiO₂ -VS a) before reaction; b) after three runs.

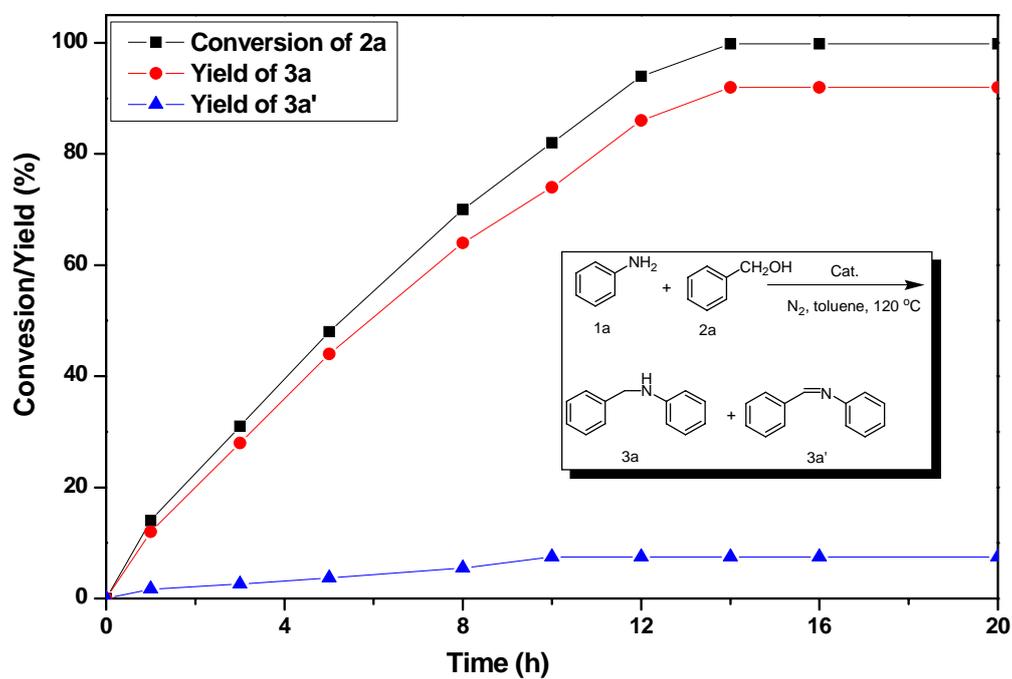


Figure S3. Direct N-alkylation of aniline with benzyl alcohol. Reaction conditions: aniline (1.5 mmol), benzyl alcohol (1.5 mmol), Au/TiO₂-VS (Au: 0.5 mol%), toluene (1 mL), 120 °C, 5 atm N₂.

Results of mechanistic studies

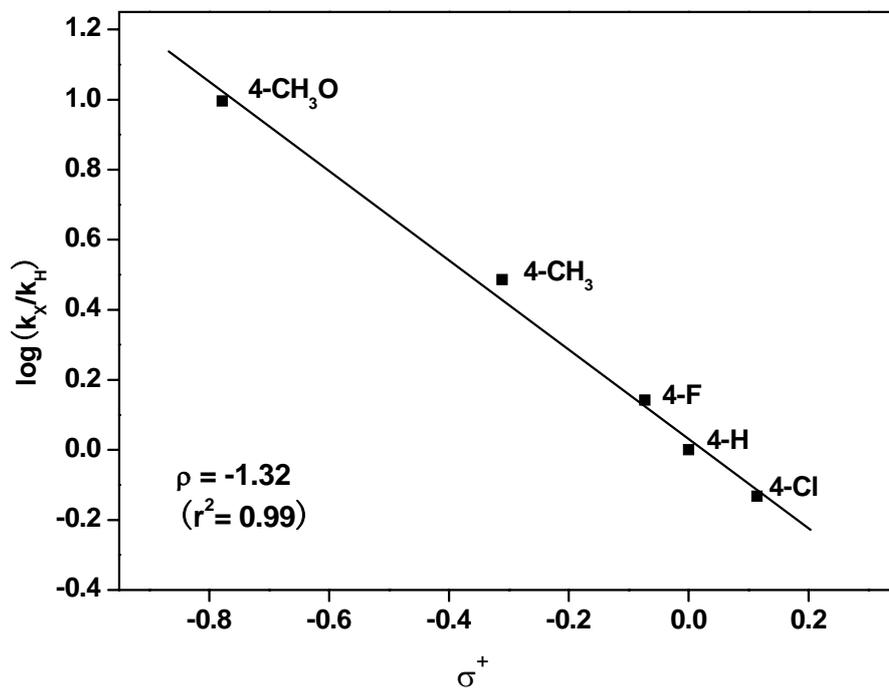


Figure S4. Brown-Okamoto plot for the competitive reaction of N-alkylation aniline with benzyl alcohol and 4-substituted benzyl alcohols. Slope (the Hammett ρ value) = -1.32 , $r^2 = 0.99$. Reaction conditions: aniline (1.5 mmol), benzyl alcohol (0.75 mmol), 4-substituted benzyl alcohol (0.75 mmol), Au/TiO₂-VS (Au: 0.5 mol%), toluene (1 mL), 140 °C, 5 atm N₂.

References

[S1] H. Sun, F. Z. Su, J. Ni, Y. Cao, H. Y. He, K. N. Fan, *Angew. Chem. Int. Ed.* **2009**, *48*, 4390.