

Au/Ag-Mo Nano-Rods Catalyzed Coupling Reaction of Nitrobenzenes and Alcohols Using Glycerol as Hydrogen Source

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1. Experimental

All solvents and chemicals were obtained commercially and were used as received.

NMR spectra were measured using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (¹H) and 100 MHz (¹³C). All spectra were recorded in CDCl₃ and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks. Mass spectra were in general recorded on an HP 6890/5973 GC-MS and Agilent 1100-MSD-Trap-VL. High-resolution TEM analysis was carried out on a JEM 2010 operating at 200 KeV. The catalyst samples after pretreatment were dispersed in methanol, and the solution was mixed ultrasonically at room temperature. A part of solution was dropped on the grid for the measurement of TEM images. Scanning electron microscopy (SEM) was performed with a Hitachi S4800 with a cold FEG (Field Emission Gun). The setup was equipped with an Energy Dispersive X-ray system EDAX Genesis 4.52. Samples were mounted on Al-holder with conducting carbon tape. XRD measurements are conducted by a STADI P automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting Cu Kα1 radiation and a 6° position sensitive detector (PSD). The XRD patterns are scanned in the 2θ range of 10-50°. For the data interpretation the software WinXpow (STOE) and the database of Powder Diffraction File (PDF) of the International Centre of Diffraction Data (ICDD) were used. The XPS measurements were performed with a VG ESCALAB 210 instrument provided with a dual Mg/Mg anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar⁺ ion-gun. All spectra were recorded using non-monochromatic Mg Ka (1253.6 eV) radiation. Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Ag and Mo contents

of the catalysts were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device.

2. Preparation of Ag-Mo nano-rods

Firstly, 30 mL of 0.25 M AgNO_3 was added drop wise into 30 mL of 0.0175 M $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ solution under magnetic stirring in 10 min. Then the acidity of the solution was tuned finely with the addition 11 mL nitric acid (2 M) to form a green-yellow solution. Then, the resulting precursor solution was transferred into a 150 mL Teflon-lined stainless autoclave. After being hydrothermal treated at 140 °C for 12 h, the reaction mixture was cooled to room temperature, filtrated and washed with 50 mL distilled water for three times. The straw yellow solid sample was further dried at 100 °C in air for 4 h to obtain the final Ag-Mo nano-rods (Ag-Mo-NR).

3. Preparation of Au NPS

For a typical synthesis the Au NPs, 10 mg of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ were dissolved in 2mL of BMImBF₄, which reacted under 1 MPa CO pressure and 180 °C for 1 h. After cooling to room temperature by nature, 0.2 mL of water was employed to the system with drastic shaking at room temperature, and in a minute, 5mL of benzene that dissolved 26 mg (0.12 mmol) of n-tetradecylamine was introduced to transferring AuNPs from BMImBF₄.

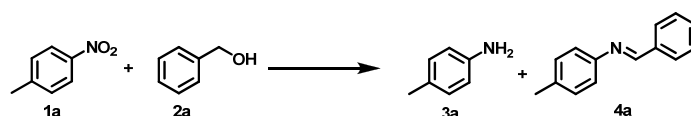
4. Preparation of Au/Ag-Mo-NR

The pre-synthesized Au seeds in toluene solution were placed at room temperature. Under a N₂ blanket, 1.5g pre-synthesized Ag-Mo-NR was added to the Au seeds containing solution under magnetic stirring for 1 h. The catalysts were separated and washed with ethanol and deionized water three times respectively. The final product was separated by centrifugation.

5. Representative procedure for the coupling reaction of nitrobenzenes with alcohols to synthesize of imines: To an oven-dried, argon purged reaction tube containing Au/Ag-Mo-NR (40 mg), K₂CO₃ (13.9 mg, 0.1 mmol), 1.0g glycerol and 2mL toluene was added the representative nitrobenzene (1 mmol) and representative alcohol (1 mmol). Then, the tube was sealed and the reaction mixture was stirred under refluxing for 12 h. Then it was cooled to room temperature, 40 mg biphenyl was added as internal standard. ~20 mL ethanol was added to dissolve the reaction mixture and the conversion and product selectivity were periodically determined by GC analysis (Agilent GC-7890A with a column (30 m×0.25 mm×0.32 μm) and a flame ionization detector (FID)).

6. Representative procedure for the coupling reaction of nitrobenzenes with alcohols to synthesize of substituted amines: To an oven-dried, argon purged reaction tube containing Au/Ag-Mo-NR (40 mg), K₂CO₃ (13.9 mg, 0.1 mmol), 1.0g glycerol and 2 mL xylene was added the representative nitrobenzene (1 mmol) and representative alcohol (1 mmol). Then, the tube was sealed and the reaction mixture was stirred under refluxing for 24 h. Then it was cooled to room temperature, 40 mg biphenyl was added as internal standard. ~20 mL ethanol was added to dissolve the reaction mixture and the conversion and product selectivity were periodically determined by GC analysis (Agilent GC-7890A with a column (30 m×0.25 mm×0.32 μm) and a flame ionization detector (FID)).

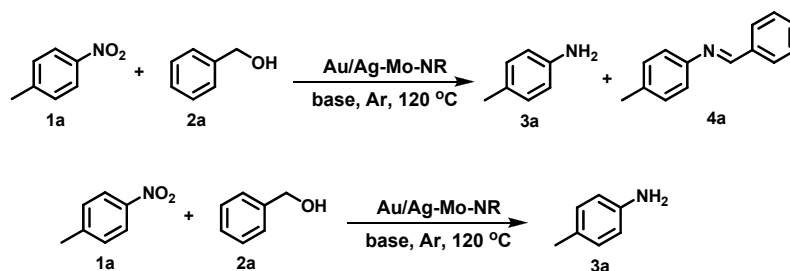
Table S1. Optimization of the condition of the coupling reaction of benzyl alcohol and p-methyl-nitrobenzene



Entry	Catalyst	Base	Solvent	Con (%)	Sel(%) ^b	
					3a	4a
1	---	K ₂ CO ₃	Toluene	5	0	>99
2	Au/Ag-Mo-NR	---	Toluene	5	20	80
3	Au/Ag-Mo-NR	K ₂ CO ₃	Toluene	55	4	96
4	Au/Ag-Mo-NR	Na ₂ CO ₃	Toluene	30	8	92
5	Au/Ag-Mo-NR	KOH	Toluene	3	0	>99
6	Au/Ag-Mo-NR	NaOH	Toluene	3	0	>99
7	Au/Ag-Mo-NR	K ₂ CO ₃	THF	21	0	>99
8	Au/Ag-Mo-NR	K ₂ CO ₃	DMF	39	10	90
9	Au/Ag-Mo-NR	K ₂ CO ₃	1,4-dioxane	25	14	86
10	Au/Ag-Mo-NR	K ₂ CO ₃	TFMB	40	13	87
11 ^c	Au/Ag-Mo-NR	K ₂ CO ₃	Toluene	100	0	98 ^d
12 ^c	AgO	K ₂ CO ₃	Toluene	20	100	0
13 ^c	MoO ₃	K ₂ CO ₃	Toluene	42	4	96
14 ^c	Ag ₂ MoO ₄	K ₂ CO ₃	Toluene	50	6	94
15 ^c	Ag-Mo-NR	K ₂ CO ₃	Toluene	73	27	73
16 ^c	Au/TiO ₂	K ₂ CO ₃	Toluene	6	0	>99
17 ^c	Au/Fe ₂ O ₃	K ₂ CO ₃	Toluene	26	0	>99

Reaction conditions: a) 1mmol benzyl alcohol, 1mmol nitrobenzene, 40 mg catalyst, 10 mol% base, 1.0 g glycerol, 0.5 mL solvent 12 h; b) the products were confirmed by GC-MS, The yields was determined by GC, using naphthalene as internal standard. c) The reaction was prolonged to 24 h, d) N-benzyl-4-methylaniline (5a) formed

Table S2. Comparative tests of the reductive capacity of alcohol and glycerol.



Entry	Alcohol	Time (h)	Con (%)	Sel(%) ^b	
				3a	4a
1	Benzyl alcohol ^a	2	6	96	4
2	Benzyl alcohol ^a	12	15	25	75
3	Benzyl alcohol ^a	24	23	6	94
4	Glycerol ^b	2	5	100	0
5	Glycerol ^b	12	15	100	0
6	Glycerol ^b	24	17	100	0

Reaction conditions: Reaction conditions: a) 1 mmol benzyl alcohol, 1 mmol nitrobenzene, 40 mg catalyst, 10 mol% base, 0.5 mL toluene; b) 1 mmol nitrobenzene, 40 mg catalyst, 10 mol% base, 1.0 g glycerol, 0.5 mL solvent; c) the products were confirmed by GC-MS, The yields was determined by GC-FID using naphthalene as an internal standard.

Figure S1. XRD diffraction patterns of Au/Ag-Mo-NR

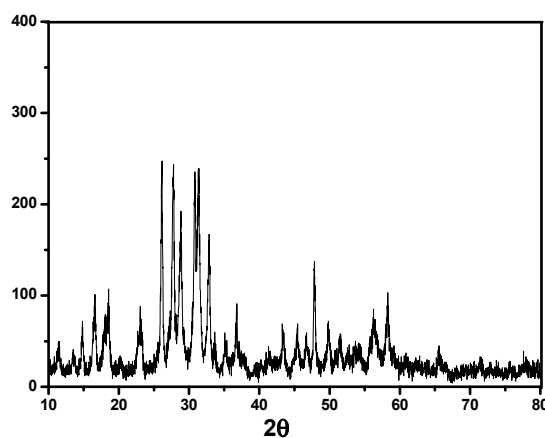


Figure S2. STEM and EDX pictures of Au/Ag-Mo-NR

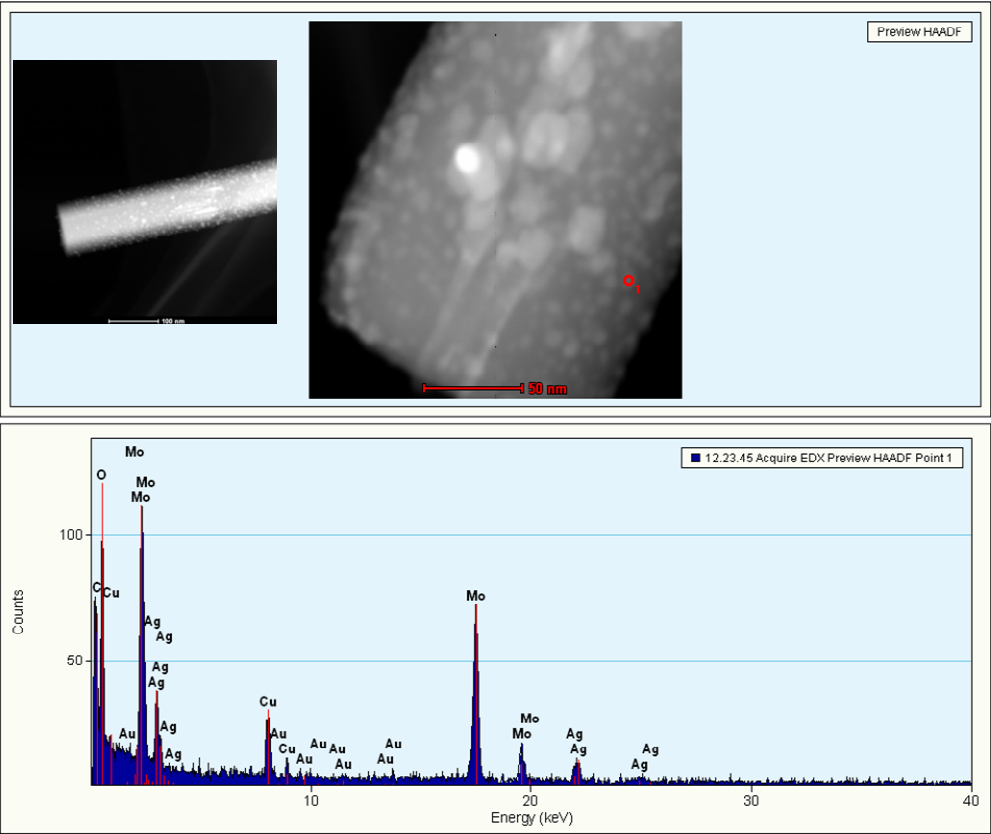


Figure S3. LC-MS analysis spectra of the reaction system

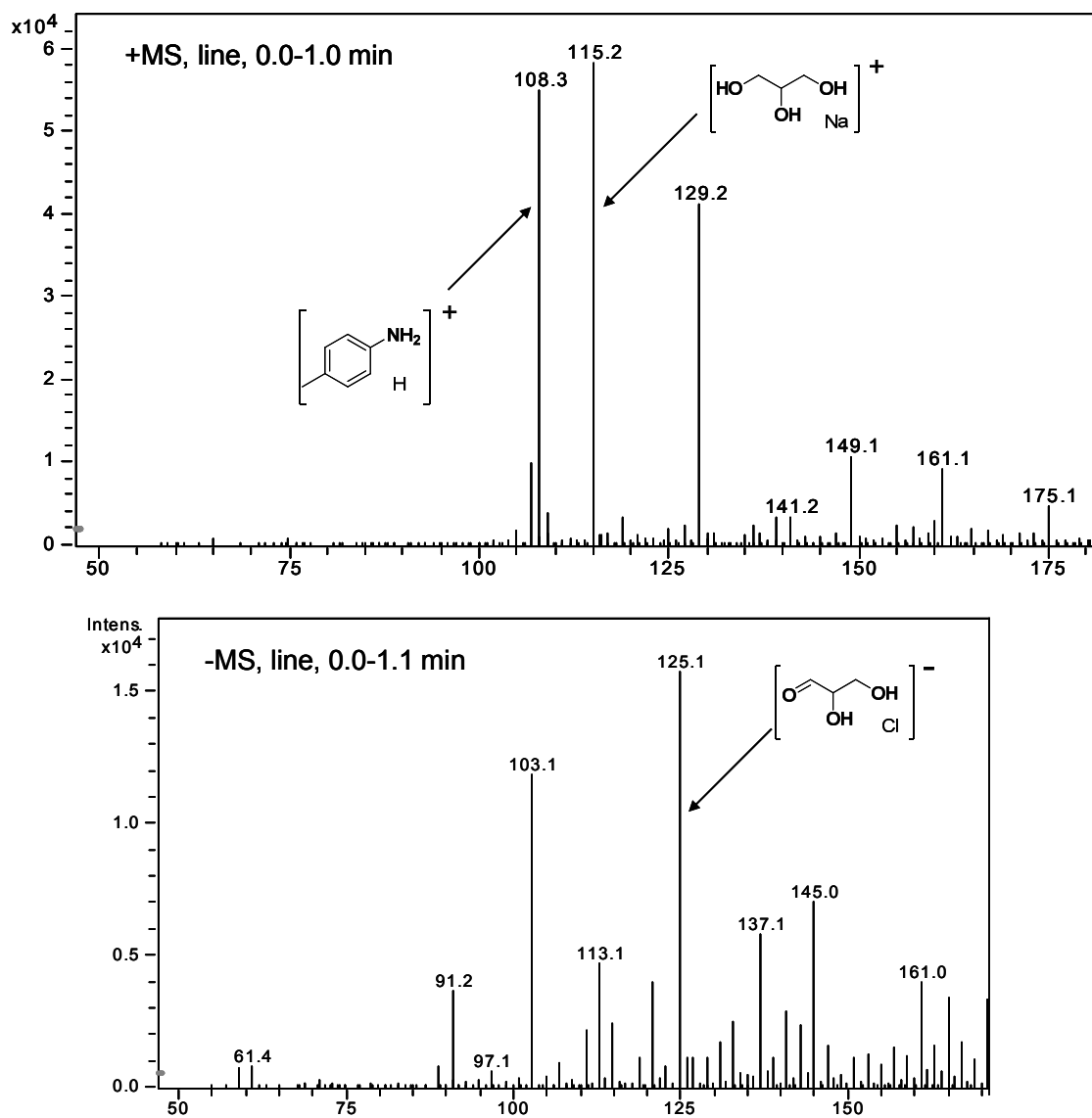


Figure S4. The ^1H NMR analysis spectrum of reaction system

