

Electronic Supplementary Information

Gold catalyzes the Sonogashira coupling reaction without the requirement of palladium impurities

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1. Experimental Section

1.1. Preparation of CeO₂ nanoparticles. Nanoparticulated ceria was prepared adding at ambient temperature under continuous magnetic stirring an ammonia aqueous solution (1.12 L, 0.8 M) over 375 mL of a Ce(NO₃)₄ (0.8 M). The colloidal dispersion of CeO₂ nanoparticles was heated in a polyethylene terephthalate vessel at 100 °C during 24 h. The resulting yellow precipitate was filtered and dried under vacuum overnight. The cerium oxide synthesized has, owing to the small size of the nanoparticles, a surface area 180 of m²·g⁻¹

1.2. Preparation of Au/CeO₂. Au supported on nanoparticulated cerium oxide was prepared using a solution of 2175 mg of HAuCl₄·3H₂O in 40 ml of deionised water that was brought to pH 10 by addition of a solution of NaOH 0.2 M. Once the pH value was stable the solution was added to a slurry containing colloidal CeO₂ (10 g) in H₂O (50 ml). After adjusting the pH to 10 with NaOH 0.2M, the slurry was left under vigorous stirring for 18 hrs at room temperature. The Au/CeO₂ solid was then filtered and exhaustively washed with distilled water until no traces of chlorides were detected by the AgNO₃ test. This is an important treatment since traces of Cl⁻ remain strongly bonded to gold and are highly detrimental for the overall activity. The catalyst was dried at room temperature under vacuum. The total Au content of the final catalyst was 4.35 % as determined by chemical analysis. Under this procedure, gold nanoparticles of 1.5 nm average size supported on CeO₂ are obtained.

1.3. Preparation of Au/CeO₂ ultrapure. Au ultrapure supported on nanoparticulated cerium oxide was prepared using a solution of 25.87 mg of gold (III) chloride hydrate 99.999 % metal basis in 100 ml of milliQ water that was brought to pH 10 by addition of a solution of NaOH 0.2 M. Once the pH value was stable the solution was added to a

slurry containing colloidal CeO₂ (1 g) in H₂O. After adjusting the pH to 10 with NaOH 0.2 M, the slurry was left under vigorous stirring for 18 hrs at room temperature. The Au/CeO₂ solid was then filtered and exhaustively washed with distilled water until no traces of chlorides were detected by the AgNO₃ test. This is an important treatment since traces of Cl⁻ remain strongly bonded to gold and are highly detrimental for the overall activity. The catalyst was dried at room temperature under vacuum. The total Au content of the final catalyst was 1.40 wt % as determined by chemical analysis.

1.4. Reaction procedure. Catalytic experiments were performed in reinforced glass reactors. For each reaction, the reactant mixtures were dissolved in DMF (1ml) and placed into the reactor (2 mL capacity) together with the corresponding catalyst (Au/CeO₂). The appropriate amount of PdCl₂ dissolved in DMF was spiked into the mixture. These solutions of PdCl₂ in DMF were prepared by weighing a known amount of PdCl₂, dissolving in DMF and diluting the mother solution to the exact required concentration. Iodobenzene, phenylacetylene used in this study are commercially available from Sigma-Aldrich with purities higher than 95 %. Na₂CO₃ is commercially available from Sigma-Aldrich, with Pd impurities analyzed by ETAAS being lower than 0.05 ppm. The samples were used as received. n-Dodecane was used as internal standard to determine conversions and selectivity by GC. The reactors were sealed and deeply introduced into the silicone bath preheated at the required temperature. During the experiment, the reaction mixtures were magnetically stirred at 1000 rpm. The course of the reaction was determined by analyzed aliquots at different reaction times. At the final times the catalyst particles were removed from the solution by filtration and the products were analyzed by GC-MS (Hewlett-Packard, 35 m capillary column of cross-linked 5 % phenyl methylsilicone). Only experiments with mass balances ≥ 95 % were considered.

2. Computational details. Calculations corresponding to the mechanism of oxidative addition to a Au^I complex were carried out with the Gaussian03 program package¹ using the density functional B3PW91 method^{2,3} and the standard 6-31G(d,p) basis set.^{4,5} The Au^I complex was simulated by means of a AuIP(CH₃)₃ molecular model, after having checked that its geometry and charge distribution is equivalent to that of a AuIPPh₃ model. The geometries of all species involved in the mechanism were fully optimized and the nature of every stationary point was characterized by means of frequency calculations and analysis of the vibrational modes. Atomic charges were calculated with Natural Bond Orbital methods.⁶

The mechanism on the neutral Au nanoparticle was investigated by means of periodic density functional theory, using the Perdew-Wang (PW91) exchange-correlation functional within the generalized gradient approach (GGA)^{7,8} as implemented in the VASP code.^{9,10} The neutral Au nanoparticle was simulated by means of a Au₃₈ cluster having a typical cuboctahedral shape and 1 nm diameter. It was placed in a 20 × 20 × 20 Å³ cubic box, large enough as to avoid interactions between periodically repeated nanoparticles or adsorbates, and during the geometry optimizations only the positions of the adsorbates were allowed to fully relax. Transition states were located using the DIMER algorithm^{11,12} and stationary points were characterized by pertinent frequency analysis calculations. The valence density was expanded in a plane wave basis set with a kinetic energy cutoff of 500 eV, and the effect of the core electrons in the valence density was taken into account by means of the projected augmented wave (PAW) formalism¹³. Integration in the reciprocal space was carried out at the Γ k-point of the Brillouin zone. Charge distributions were estimated using the theory of atoms in molecules (AIM) of Bader using the algorithm developed by Henkelman.^{14,15}

Table S1. Measured yield of the Sonogashira coupling between iodobenzene and phenylacetylene (in %) at different times (in min) for Au/CeO₂ catalysts having the same content of gold and increasing amounts of palladium and for a Au/CeO₂ catalyst prepared with ultra pure Au (99.999 %)

Au(mg)	Pd(ppm)	t (min)	Yield (%)
3.6	1.1	0	0
		20	1.9
		50	5.2
		85	8.9
		125	13.1
		180	20.4
		360	22.3
3.1	3.2	0	0
		25	2.2
		50	6.3
		85	13.5
		240	35.4
		360	45.2
3.3	5.8	0	0
		25	4.9
		50	7.5
		85	15.2
		360	38.4
3.6	8.2	0	0
		25	6.9
		80	13.0
		90	14.8
		240	38.0
		360	43.9
3.5	0.18	0	0
		50	6.8
		60	8.8
		90	11.6
		130	16.6
		300	16.7

Table S2. Optimized values of the most relevant distances (in Å) and calculated net atomic charges on selected atoms (in e) of the systems depicted in Figure 2.

	d(C-I)	d(C-Au)	d(I-Au)	q(I)	q(C ₆ H ₅)	q(Au)
I-Ph + [AuI(PPh ₃)]	2.149	-	-	0.145	-0.145	0.205
TS_Au ^I	2.449	2.277	2.908	-0.040	-0.105	0.488
[AuPhI ₂ (PPh ₃)]	3.377	2.078	2.746	-0.367	-0.203	0.627
(Au ₃₈ -I-Ph) _{adsorbed}	2.124	3.822	2.772	0.314	-0.054	-0.259
TS_Au ₃₈	2.475	2.208	2.781	0.044	0.001	-0.045
(Au ₃₈ -I-Ph) _{dissociated}	5.566	2.076	2.746	-0.153	-0.134	0.287

¹ Frisch, M. J.; et al. Gaussian 03, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

² Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

³ Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

⁴ Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.

⁵ Davis, L. P.; Guidry, R. M.; Williams, J. R.; Dewar, M. J. S.; Rzepa, H. S. *J. Comput. Chem.* **1981**, *2*, 433.

⁶ Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. NBO Version 3.1.

⁷ J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys Rev B* 48 (1993) 4978

⁸ J. P. Perdew, Y. Wang, *Phys. Rev. B* 45 (1992) 13244.

⁹ G. Kresse, J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.

¹⁰ G. Kresse, J. Hafner, *Phys. Rev. B*, 1993, **47**, 558.

¹¹ A. Heyden, A. T. Bell, F. J. Keil, *J. Chem. Phys.*, 2005, **123**, 224101.

¹² G. Henkelman, H. Jónsson, *J. Chem. Phys.*, 1999, **111**, 7010.

¹³ P. E. Blöchl, *Phys Rev B*, 50 (1994) 17953.

¹⁴ E. Sanville, S. D. Kenny, R. Smith, G. Henkelman, *J. Comp. Chem.*, 2007, **28**, 899.

¹⁵ G. Henkelman, A. Arnaldsson, H. Jónsson, *Comput. Mater. Sci.*, 2006, **36**, 254.