

Unique gold chemoselectivity for the aerobic oxidation of alcohols.

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Supplementary Information

Catalysts Preparation

Synthesis of nanoparticulated ceria. A colloidal dispersion of CeO₂ nanoparticles was prepared by thermolysis of an acidified Ce(NO₃)₄ solution followed by re-dispersion. The dispersion was purified and concentrated using an ultra-filtration cell equipped with a 3KD membrane. The purification was monitored by the residual acidity of the dispersion, determined by an acid titration of the supernatant after ultra-centrifugation at 50000 rpm for 6h. The resulting cerium oxide has, owing the small size of the nanoparticles, a very high surface area (180m²·g⁻¹) as determined by isothermal nitrogen adsorption.

Synthesis of hydroxyapatite. Hydroxyapatite was prepared using a method described in the literature.^[1] A solution of (NH₄)₂HPO₄ (40.0 mmol) in deionized water (150 mL) was set at pH 11 with aqueous NH₃ solution. This solution was added dropwise over 30 min to a solution of Ca(NO₃)₂·4H₂O (66.7 mmol) in deionized water (120 mL) adjusted to pH 11 with aqueous NH₃ solution. Vigorous stirring at room temperature was maintained during the addition process. The resulting milky solution was heated at 90° C for 10 min. The precipitate was filtered, washed with deionized water, and dried at 110° C giving a solid with the stoichiometry of Ca₁₀(PO₄)₆(OH)₂ and a Ca/P ratio of 1.67.

Preparation of Au/CeO₂ catalyst. Au was deposited on the nanoparticulated ceria by the following procedure: A solution of HAuCl₄.3H₂O (296 mg) in 60mL of deionised water was brought to pH 10 by addition of a solution of NaOH 0.2M. Once the pH value was stable the solution was added to a gel containing of colloidal CeO₂ (4.01 g) in H₂O (50 mL). After adjusting the pH of the slurry at a value of 10 by addition of a 0.2 M solution of NaOH 0.2M, the slurry was continuously stirred vigorously for 18 hrs at room temperature. The Au/CeO₂ solid was then filtered and exhaustively washed with several litres of distilled water typically used to wash 4.0 g of Au/CeO₂ catalyst until no traces of chlorides were detected by the AgNO₃ test. The catalyst was dried at vacuum at room temperature for 1h. Then 3.5 g of the supported catalyst were added over 30 g of 1-phenylethanol at 160° C and the mixture were allowed for reduction during 20 minutes. The catalyst was filtered, washed, with acetone and water, and dried under vacuum at room temperature. The total Au content of the final catalyst Au/CeO₂ was 0.44 wt % as determined by chemical analysis. For the preparation of 1.87 wt % Au/CeO₂ the method used was the same above changing only the amount of HAuCl₄.3H₂O aqueous solution (20 mL instead of 60 mL for 2g of CeO₂) and the time that the slurry is left under stirring (3h instead of 18 h). This catalyst Au/CeO₂ is commercially available from ITQ (web page: www.upv.es/itq).

Preparation of Pd/hydroxyapatite. Hydroxyapatite (2.0 g) was stirred at room temperature for 3h in 150 mL of acetone solution of PdCl₂(PhCN)₂ (2.5×10^{-4} M). The obtained mixture was filtered, washed with acetone, and dried under vacuum at room temperature. Then 1.8 g of the supported catalyst was added over 15 g of 1-phenylethanol at 160° C and the suspension was allowed for reduction during 20 minutes. The Pd/(OH)apatite catalyst was filtered, washed, with acetone and water, and dried under vacuum at room temperature. The total Pd content of the final catalyst as

determined by chemical analysis was 0.18 %. For the preparation of 1.22 wt % Pd/Hydroxyapatite the same method was used with the only change of the volume and concentration of $\text{PdCl}_2(\text{PhCN})_2$ acetone solution (400 mL; 2.5×10^{-4} M for 2.0 g of hydroxyapatite).

Preparation of Au-Pd/CeO₂. Au-Pd/CeO₂ was prepared by deposition of 12 mg of $\text{PdCl}_2(\text{PhCN})_2$ over 2 g 0.44 wt %-Au/CeO₂ catalyst by the procedure described above for the preparation of Pd/(OH)apatite. The total Au content of the final catalyst Au-Pd/CeO₂ was 0.44 wt % of gold and 0.12 wt % of palladium as determined by chemical analysis.

Preparation of Au-Pd/TiO₂. 2.5 % Au- 2.5 % Pd/TiO₂ catalyst was prepared using a method described in the literature.^[2] Basically it consists in a incipient-wetness impregnation of TiO₂ (2 g) with 4 mL of an aqueous solution of 50 mg of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and 30 mg of PdCl_2 . The catalyst was then dried at 80° C during 17 h and calcined in air at 400°C during 6h.

Catalysts characterization.

For analysis of the crystal structure and indexation, the samples were examined by bright- and dark-field electron microscopy in a Jeol 2200 HRTEM operated at an accelerating voltage of 200 kV. Dark field consists on observing the image produced by diffracted electrons corresponding to a determined lattice spacing leaving the rest of the solid dark.

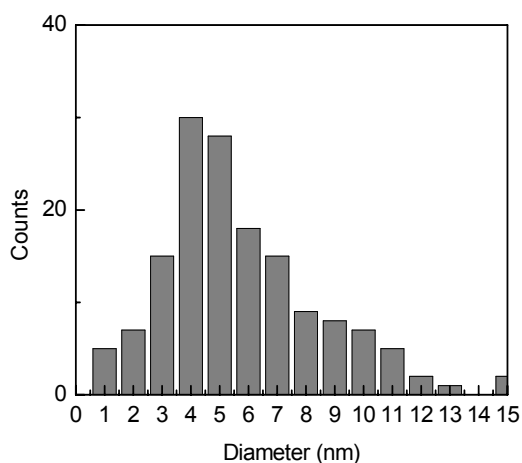


Fig S1. Au particle size distribution determined by statistical analysis of Au/CeO₂.

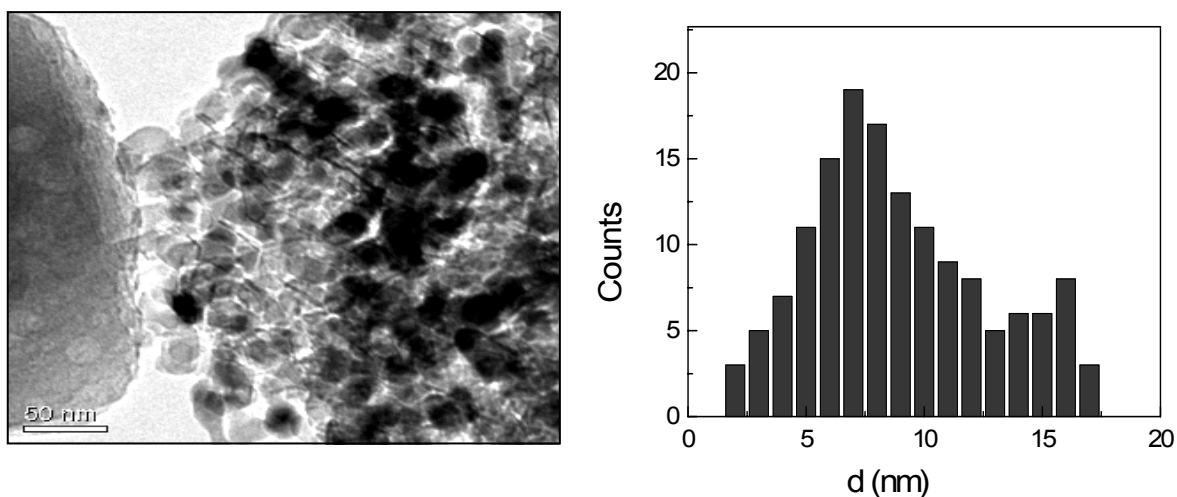


Figure S2. Left: High resolution TEM image of the Pd/(OH)apatite catalyst. Right: Pd particle size distribution determined by statistical analysis of Pd/OHapatite.

Chemical analysis of gold and palladium metals in the catalysts were carried out after dissolving the solids by attack with a 2:1 mixture of HNO₃/HF on a Varian-10 Plus Atomic Absorption Spectrometer or directly of the solid samples using on a Philips MiniPal 25 fm Analytic X-Ray apparatus and a calibration plot. Analysis of reaction products was carried out by GC on an HP-Agilent 5973 with a 6980N mass selective detector.

Alcohol oxidation. The corresponding alcohol (12.5 mmol) was added over 0.44%-Au/CeO₂ catalyst (0.056 g), molecular oxygen was bubbled continuously through the suspension (25 mL x m⁻¹). The resulting mixture was then heated at 393 K. After the reaction, acetone was added and the catalyst was separated by centrifugation. The

products in the solution were analysed by GC-MS and conversion and selectivity were determined by GC using undecane as external standard. Supported gold catalyst was washed with acetone and 1M aqueous solution of NaOH, and dried in vacuum before reuse.

Isomerization catalytic test. The isomerization reactions were carried out in a 25 mL scale pressurized batch reactor. The vessel was charged with 1-octen-3-ol (15mL). The autoclave was purged with nitrogen during 20 minutes leaving the vessel at $1.0 \cdot 10^5$ Pa pressure and then was charged with H₂ to the final $1.1 \cdot 10^5$ Pa pressure. The stirrer was set to 2000 r.p.m and the reaction mixture was raised to 393 K. After 30 minutes the reaction was cooled and the product distribution was analyzed by GC-MS and conversion and selectivity were determined by GC using undecane as internal standard.

Catalyst stability

To check the stability and reusability of the Au/CeO₂ catalyst, 0.22 g of 0.44%-Au/CeO₂ were used in the oxidation of 12.5 mmol of trans-carveol. After 24 h the catalyst was filtered, washed with acetone and 1M NaOH solution. The products in the solution were analysed by GC-MS and conversion (91%) and selectivity (99%) were determined by GC using undecane as internal standard. Less than 1% of the gold present in the catalyst was detected in the filtered reaction mixture by chemical analysis. The recovered catalyst (0.21 g) was used in another run, showing no loss of activity (89% conversion) and selectivity (99%).

- [1] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc* **2004**, *126*, 10657.
- [2] J. K. Edwards, B. E. Solsona, P. Landon, A. F. Carley, A. Herzing, C. J. Kiely, G. J. Hutchings, *J. Cat* **2005**, *236*, 69.