A Collaborative Effect between Gold and Support Induces Selective Oxidation of Alcohols

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MATERIALS

Preparation of Au–CeO₂ catalyst.

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 to the small size of the nanoparticles, a very high surface area (180m²×g⁻¹).

Synthesis of regular-size ceria.

A solution of 25.2 g of Ce(NO₃)₃ in 200mL of deionised water was heated at 70° C, then pH was adjusted to 9 with an ammonia solution (25 % wt) and the mixture was allowed to
react for 1 h. After this time the solution was filtered and dried at 100º C overnight. The resulting solid is calcined at 550º C for 6h. Surface area (70 m²/ g).

**Formation of AuCeO₂.**

Au was deposited on the nanoparticulated or regular particle size cerium oxide by the following procedure: A solution of HAuCl₄·3H₂O (200mg) made in 40mL 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 slurry containing of colloidal CeO₂ (2.01 g or 10.02g) in H₂O (50 ml). After adjusting the pH of the slurry at a value of 10 by addition of a solution of NaOH 0.2M, the slurry was left under vigorous stirring for 18 hrs at room temperature. The AuCeO₂ solid was then filtrated 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 Au⁺ and are highly detrimental for the overall activity. The catalyst was dried at vacuum at room temperature. The total Au content of the final catalyst was 2.4% or 0.38% as determined by chemical analysis.

**Preparation of Au/C catalyst.**

A colloidal solution of gold nanoparticles stabilized by polyvinyl alcohol were deposited on activated carbon (KB-B,-100, provided by Aldrich), following the procedure...
METHODS

TEM

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

Typical procedure for the aerobic oxidations of alcohols:

All alcohols provided by Aldrich were used without further purification.

a) Solvent-less oxidation. The corresponding alcohol (4.85 mmol) was added over AuCeO₂ catalyst (0.2 g; 2.4 % Au), molecular oxygen was bubbled continuously through the suspension (25 mL·min⁻¹). The resulting mixture was then heated at 80°C for 2.5 h. 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 nonane or nitrobenzene as external standards.
In order to compare the performance of Au⊂CeO$_2$ and Pd/hydroxyapatite catalyst, 1-phenylethanol (30g, 250 mmol) and Au⊂CeO$_2$ (0.06g, Au 1 µmol) were placed in a reaction vessel with a reflux condenser. The resulting mixture was stirred at 160 ºC in the presence of O$_2$ under Dean-Stark conditions. After 24h, Au⊂CeO$_2$ was separated by filtration, and the liquid was analysed as described below.

b) Oxidation in aqueous media: A suspension of Au⊂CeO$_2$ (0.109 g, 0.66 mol% Au) in 25 mL of an aqueous solution of sodium carbonate (0.55 M) was stirred under O$_2$ flow (25 mL×m$^{-3}$) for 5 minutes. Then, the corresponding alcohol (2mmol) was added and the mixture heated at 50º C for 2h. After this time, the reaction mixture and the catalyst were separated by centrifugation. The products in the solution were analysed by HPLC-MS and conversion and selectivity were determined by HPLC. The separated Au⊂CeO$_2$ catalyst was washed with 1M aqueous solution of NaOH, and dried in vacuum before reuse.

**XPS Spectroscopy**

X-ray photoelectron spectra (XPS) were obtained in a VG Escalab 210 spectrometer using MgKα (hν =1253,6 eV) X-ray radiation at an energy of 200W. Photoreduction of Au$^{3+}$ to Au$^0$ due to the X-ray beam was observed, while the amount of Au$^+$ remains constant. Spectra were collected at room
temperature and at a pressure in the analyzer chamber of 2 \(10^{-9}\) mbar. Kinetic energies of the photoelectron were measured with an hemispherical energy analyzer working at constant pass energy of 50eV. The binding energy scale was calibrated by setting the C1s transition at 284.5eV.

FT-IR EXPERIMENTS

Fourier transform infrared (FTIR) experiments were performed with a quartz infrared cell fitted with KRS-5 windows and connected to a conventional vacuum system. Calibrated volume (1.55 cm\(^3\)), were used for addition of the probe molecule. The spectra were recorded on a PC controlled Bio-Rad FTS-40AFTIR spectrophotometer. Prior to the IR experiments the sample wafer were evacuated at \(10^{-4}\) mbar and 80°C, similar to the sample activation prior to the catalytic test. Isopropanol (Aldrich, +99%), previously purified by a frozen pump method, were adsorbed onto the sample at 11 mbar. No change of the intensity of the IR bands associated to isopropanol adsorption (hydride and alkoxide bands) were observed from the first minutes of spectra collection to two hours latter. After degassing in order to remove physisorbed isopropanol species, molecular oxygen (Linde, 99.99%) was adsorbed at 65 mbar. Spectra were collected from the first minutes of oxygen admission to one hour later. Again no change in the intensity of the bands since the first time was observed.
CO adsorption experiment were carried out at room temperature on previous evacuated sample at $10^{-4}$ mbar and 80° C. IR spectra was collected immediately after adsorption of 10 mbar of CO.
**Fig S1.** FTIR spectra of the CeO₂ catalyst in the 2700-1900 cm⁻¹ region of a) activated sample; b) After absorption of isopropanol; c) evacuation and consequently insertion of oxygen.
Fig S2. FTIR spectra of the CeO$_2$ catalyst in the 1900-1000 cm$^{-1}$ region of a) activated sample; b) After absorption of isopropanol; c) evacuation and consequently insertion of oxygen and d) final evacuation.
Figure S3. XPS spectra of Au 4f core level line of the Au⊂CeO$_2$ catalyst.
Figure S4. FTIR spectra of CO adsorbed on the Au⊂CeO₂ at 25° C.
Figure S5. High resolution TEM image of the 2.4% AuCeO$_2$ catalyst. Left: the white lines correspond to the (202) Ce$_6$O$_{11}$ (3.3 Å) and the (200) CeO$_2$ (2.7 Å) lattice spacing. Right: a hexagonal faceted (111) Au crystal is indicated. The inset show the Au particle size distribution.
Fig S6. FTIR spectra of the Au⊂CeO₂ catalyst in the 2700–1900 cm⁻¹ region of a) activated sample; b) After absorption of isopropanol; c) evacuation and consequently insertion of oxygen and d) final evacuation.
**Fig S7.** FTIR spectra of the AuCeO$_2$ catalyst in the 1900–1000 cm$^{-1}$ region of a) activated sample; b) After absorption of isopropanol; c) evacuation and consequently insertion of oxygen and d) final evacuation.