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Electronic Supplementary Information for *Chemical Communications*

Dramatic effect of redox pre-treatments on the CO oxidation activity of Au/$Ce_{0.50}Tb_{0.12}Zr_{0.38}O_{2-x}$ catalysts prepared by deposition-precipitation with urea. A nano-analytical and nano-structural study

Eloy del Río*, Miguel López-Haro, José M. Cíes, Juan J. Delgado, José J. Calvino, Susana Trasobares, Ginesa Blanco, Miguel A. Cauqui, Serafín Bernal

Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica. Facultad de Ciencias. Universidad de Cádiz. Campus Río San Pedro. E-11510 Puerto Real (Cádiz). Spain. E-mails: serafin.bernal@uca.es, eloy.delrio@uca.es

*Corresponding author:
Eloy del Río, E-mail: eloy.delrio@uca.es

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1. *Catalyst Preparation*

The 1.5 wt% Au/$Ce_{0.50}Tb_{0.12}Zr_{0.38}O_{2-x}$ catalyst was prepared by deposition-precipitation with urea (DPU).[1,2] The mixed oxide support, $Ce_{0.50}Tb_{0.12}Zr_{0.38}O_{2-x}$, was kindly donated by Grace Davison. The gold precursor was 99.99% $H[AuCl_4]$ (Alfa Aesar). The preparation procedure may be summarized as follows: 10 g of the support was suspended in 0.31 L of a 2.5 x 10^{-3} mole L^{-1} aqueous solution of $H[AuCl_4]$ at room temperature. Then, urea was added until a concentration of 0.42 mole L^{-1} was reached. Immediately after, the suspension was heated at 353 K and was kept at this temperature under vigorous stirring for 20 h in complete absence of light. Along this time, the pH remained stabilized within the 8.0 and 8.5 range. The suspension was aged for 5 h at room temperature under stirring and filtered off. The resulting solid was washed several times with distilled water at room temperature until no evidence of chloride ions. Finally, it was dried overnight in an oven at 373 K, meshed at 125 μm, and stored in the dark under Ar until further use. This catalyst sample with a Brunauer/ Emmett/Teller (BET) surface area of 25 m^2 g^{-1} will be hereafter referred to *as prepared* Au/CTZ. AAS-ICP analysis confirmed that the initial gold present in solution was totally deposited on the oxide support.

2. *Experimental*

The BET surface area, pore size distribution, and pore volume of the investigated catalysts were determined by N_2 adsorption at 77 K. Experiments were performed on a

Micromeritics ASAP-2020 instrument.. The amount of sample was always 200 mg. Prior to adsorption, the catalysts were degassed under high vacuum for 2 h at 473 K.

Catalysts have also been characterised by means of High Resolution Transmission (HRTEM) and High-Angle Annular Dark Field–Scanning Transmission (HAADF-STEM) electron microscopies. HRTEM images were recorded on a JEOL2011 LaB_6 electron microscope with 0.23 nm spatial resolution at Scherzer Defocus conditions. This value is adequate to image the internal structure of nanosized gold particles. HAADF-STEM images were obtained on a JEOL2010F instrument by using an electron probe of 0.5 nm of diameter at a diffraction camera length of 10 cm. This STEM-HAADF imaging mode provides contrasts directly related to the average atomic number (Z) in the region under the electron beam. The difference in atomic number between Au ($Z = 79$) and the support cations ($Z_{Ce} = 58$, $Z_{Zr} = 40$, $Z_{Tb} = 65$) is large enough as to guarantee optimum imaging of gold nanoparticles with diameters even smaller than 1 nm. From the contrasts observed in both HAADF and HRTEM images, a simple discrimination of gold nanoparticles and support can be performed. In any case, the nature of the particles included in the size distribution was further confirmed by STEM-X-ray energy dispersive and Electron Energy Loss (EELS) spectroscopy. The JEOL 2010F, which has a structural resolution of 0.19 nm at 200kV, is equipped with a HAADF detector, an EELS spectrometer (GIF2000 Gatan Imaging Filter), and a X-EDS, Oxford INCA Energy 2000 system. Spectra corresponding to the individual particles were recorded using an Oxford INCA Energy TEM 200 system, which allows an energy resolution of 0.13 keV. To avoid any contact with solvents, samples for electron microscopy studies were prepared by depositing small amounts of the catalyst powder directly onto holey-carbon coated Cu grids. Excess was removed from the grids by gentle blowing with a nozzle. The carbon distribution on the nanoparticle was studied by combining HAADF images with Electron Energy Loss Spectroscopy (EELS) in STEM mode using a 0.5 nm probe size and a 10 cm camera length. The EELS spectra, covering the C-K (284eV) and Zr-M signal (330eV), were recorded with 0.5eV energy dispersion, were recorded using an acquisition time of 0.4 s and convergence and collection semiangles of 8 and 24 mrad, respectively. A power law model, using a window width of 20 eV was used to remove the background beneath Zr-M and C-K signals.

X-ray photoelectron spectra were acquired with a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al-Kα X-ray source (hν = 1,486.6 eV), a 2 x 1 mm spot size for the analysis; a pass energy of 20 eV was used to collect the spectra. The *quasi-in-situ* pre-treatment was carried out in a catalytic cell chamber attached to the XPS spectrometer, to avoid any contact with air. X-ray satellites and Shirley backgrounds were subtracted. The peak areas were normalized with the corresponding cross-sections to obtain the relative surface compositions. The binding energy scale was calibrated using the internal reference Zr $3d_{5/2}$

(182,64 eV)[3] inherent of the oxide support. The peaks were fitted using Gaussian-Lorentzian curves.

The catalytic assays were performed under the following conditions: amount of catalyst: 25 mg diluted with 100 mg of crushed quartz; total flow rate of a reaction mixture consisting of 1% CO, 0.6% O2, and He to balance was 100 mL min^{-1}; temperature range: 233 K – 413 K; and heating rate: 10 K.min^{-1}. The temperature was controlled by immersion of the reactor in a cooling/heating bath Lauda, model Proline RP-845, filled with poly-methylsiloxane. The gas composition at the reactor exit was continously monitored by a mass spectrometer Pfeiffer, model QME-200-D. Prior to running the activity assays, the catalyst samples were activated *in situ* under the oxidising and reducing conditions discussed in the main text of this communication.

Supplementary Figures

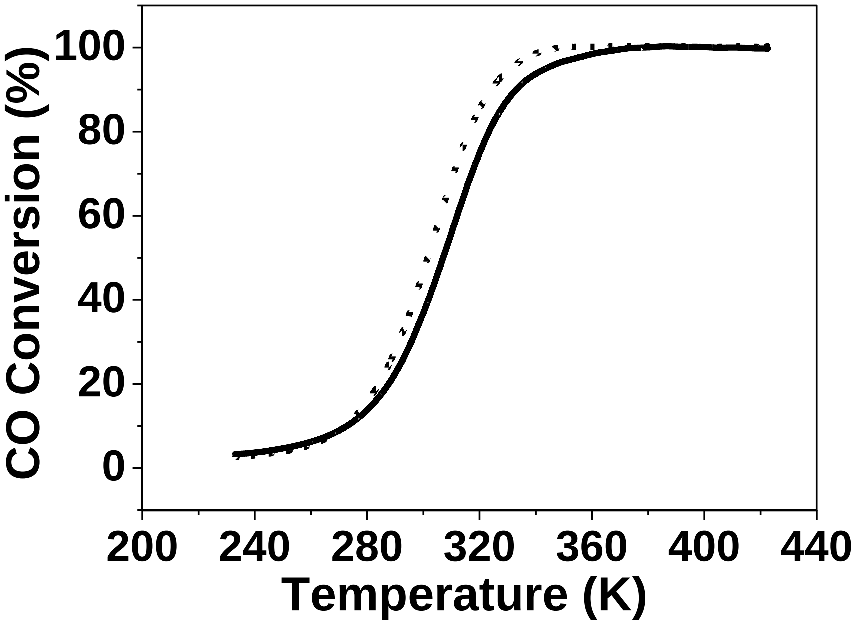

Figure S1. Influence of the activation pretreatment on the CO oxidation activity of a Au/CTZ sample prepared by deposition-precipitation with sodium carbonate (DPC). Light-off curves for the pre-reduced, RE473 (dashed line), and pre-oxidised, OE523 (solid line) catalysts. We conclude that the redox nature of the activation pre-treatments has a very minor effect on the catalytic behaviour of the Au/CTZ-DPC samples. This strongly contrasts with In contrast with the response of the Au/CTZ-DPU sample whose activity is dramatically modified by the oxidising or reducing nature of identical pretreatments.

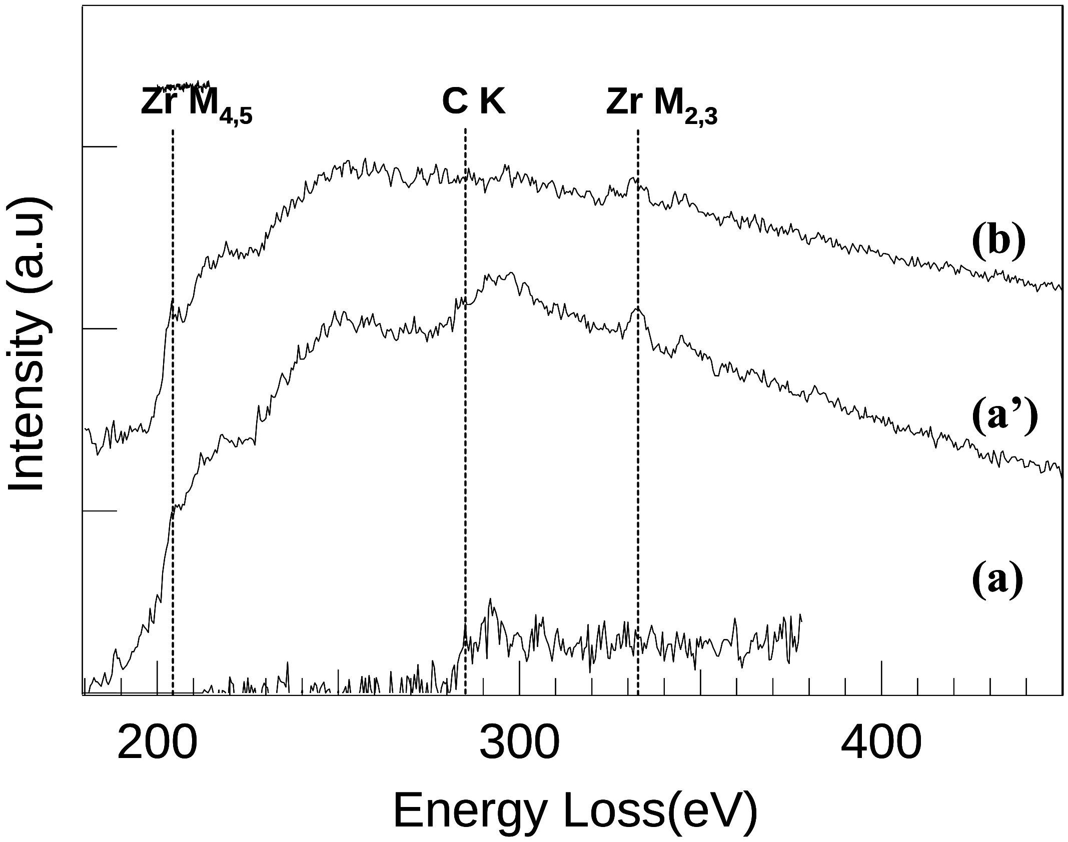

Figure S2. EEL-spectra acquired on Au/CTZ-RE473 and -OE523 catalysts. Two areas were studied on RE473, Au nanoparticle surface (a) and CTZ support (a'), whereas a wider area including both metal and support was analysed on the OE523 catalyst (b). Note how after RE473 treatment the C-K edge appears in both a and a' spectra indicating that the catalyst is covered by a very thin layer of carbon. In contrast, no C-K edge is observed on the Au/CTZ-OE523 sample. These results are in good agreement with the corresponding HREM images reported in this work.

References

[1] R. Zanella, S. Giorgio, C. R. Henry, and C. Louis, *Journal of Physical Chemistry B*, 2002, **106**, 7634.
[2] R. Zanella, L. Delannoy, and C. Louis, *Applied Catalysis A: General*, 2005, **291**, 62.
[3] J. M. Cíes, E. del Río, M. López-Haro, J. J. Delgado, G. Blanco, S. Collins, J. J. Calvino, and S. Bernal, *Angewandte Chemie International Edition*, 2010, **49**, 9744.