Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Evidence for a Surface Gold Hydride on a Nanostructured Gold Catalyst

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Primary Catalyst synthesis

A 1% Au/CeO_2 catalyst by weight was prepared using a colloidal method. Aqueous solutions of 0.0675 M tetrakis-(hydroxymethyl)-phosphonium chloride (THPC) and 0.2 M NaOH were prepared, before being stirred together. After three minutes stirring, an aqueous solution of $HAuCl_4$ was added, with continued vigorous stirring. The formation of dark brown hydrosols of gold was observed. Solution quantities and concentrations were chosen to provide a final composition in the sol of [Au] = 1×10^{-3} M and a molar ratio of NaOH:THPC:metal of 5.91:1.33:1. After formation of the hydrosol, stirring was continued for 30 min. The desired amount of ceria support was then added (acidified to pH 2 by sulfuric acid) to obtain a 1 wt. % metal loading. The mixture was sonicated for 10 minutes before it was vigorously stirred for 12 hours, yielding a bright purple slurry. The slurry was filtered, the catalyst washed thoroughly with distilled water and dried at 393 K overnight under static air. The dried catalyst used for INS measurement was calcined *ex situ* at 673 K for 12 hours in static air . The dried catalyst used for IR measurements was calcined *in situ* in 35 sccm 10% O_2/He at 673 K for 1 hour.

Transmission Electron Microscopy

Samples of the catalyst calcined in static air were prepared for TEM by first dispersing the catalyst powder in high purity ethanol using sonication. 40 µL of the suspension was dropped on to a holey carbon film supported by a 300 mesh copper grid before the solvent was evaporated. The samples were then examined using a JEOL JEM 2100 EM model. Average gold particle size was given as 5.4 nm across 200 particles using ImageJ.[1] Representative images are shown in Figure S1.

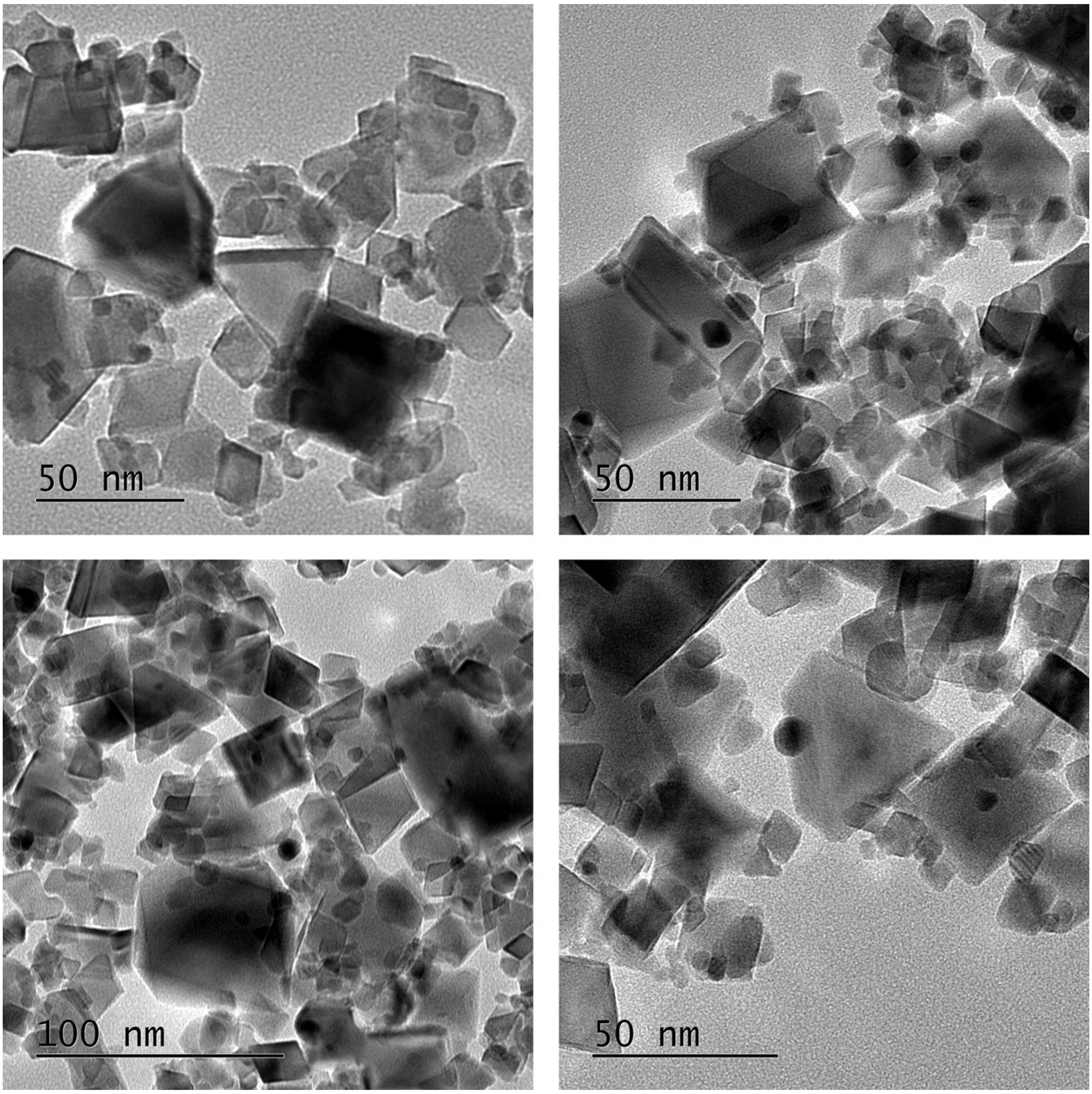

Figure S1: Electron micrographs of the calcined 1wt. % Au/CeO_2 catalyst

Infrared spectroscopy

Infrared spectra were obtained using a Harrick praying mantis high temperature reaction chamber diffuse reflectance accessory equipped with ZnSe windows. Data were recorded at 423 K under ambient pressure using an Agilent Cary 680 equipped with a liquid nitrogen-cooled MCT detector. H_2 10% O_2 in He and He were supplied by BOC. D_2 was supplied by CK gas. All were used without purification and controlled by mass flow controllers. Background spectra were recorded at 423K under 30 sccm He flow after pre-treatment at 673 K in 10% O_2/He. Spectra were recorded 30 min after 3 sccm of the H_2/D_2 reductant was co-added to the He stream.

Inelastic neutron scattering

Inelastic neutron scattering measurements used the MERLIN spectrometer at the ISIS neutron and muon facility.[2] 21.6 g of the catalyst was loaded into a stainless steel can and evacuated at room temperature for 2 days with a turbomolecular pump to remove any residual moisture. It was then pressurised with 4 bar H_2 at 423 K and data recorded at 15K. Hydrogen for the INS procedures was provided by CK gas.

Neutron diffraction

An attempt was made to directly measure the Au-D bond length using neutron diffraction on the GEM diffractometer[3] at the ISIS neutron source. The raw data were corrected and normalised in Gudrun. The produced D(r) were fitted in PDFGui and the reciprocal space data were fitted using the Rietveld method within TOPAS.

13.1 g of the 1% Au catalyst was loaded into a quartz cell and evacuated overnight. Deuterium was admitted to the cell until the pressure was stable at approximately 1 bar. When changes were not observed upon reduction of the 1% loaded catalyst, the procedure was repeated with 8.7 g of a 10% impregnated Au/CeO_2 catalyst obtained from Johnson Matthey. This was prepared following the method of Sakurai *et al.*[4] with two minor modifications. K_2CO_3 was substituted for Na_2CO_3 and calcination was at 500°C, rather than 350°C. Plots of this catalyst are shown in Figure S2. Only minor changes are apparent, with the lattice spacing increasing from 5.405 to 5.417 Å on D_2 reduction. Lattice expansion occurs on ceria reduction,[5] and this increase suggests that ceria reduction has occurred at ambient temperature. This is further evidence for the dissociation of hydrogen on Au to form AuH, as ceria reduction will not occur at such mild conditions with molecular hydrogen in the absence of gold. Gold must therefore be responsible for the deuterium activation.

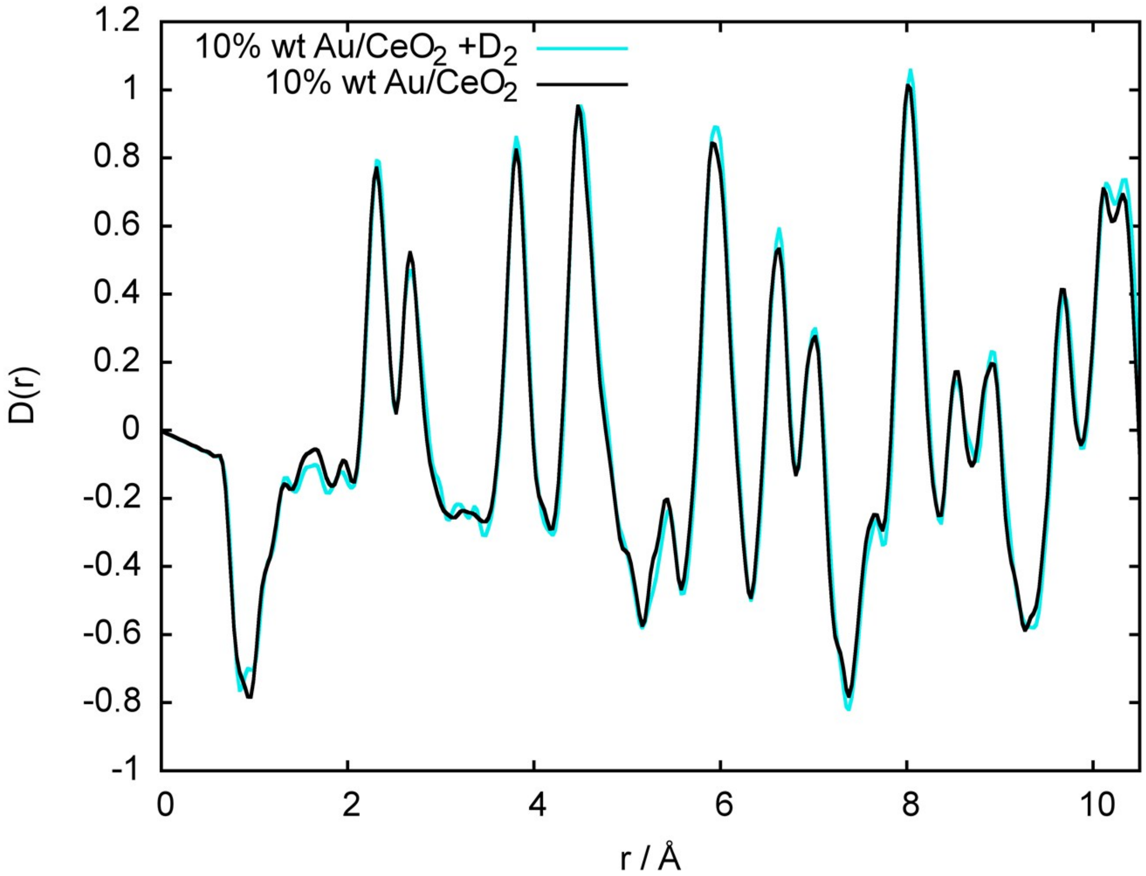

Figure S2: The radial pair distribution function of 10% Au/CeO_2 catalyst with and without

References

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