Electronic Supplementary Information (ESI).

Materials

The silica (70 m² g⁻¹), titania (50 m² g⁻¹), ceria (20 m² g⁻¹), ceria-zirconia (85 m² g⁻¹) and lanthana (30 m² g⁻¹) were supplied by, Davison, X, Aldrich, Johnson Matthey and Aldrich respectively. The 0.2 wt.% Au supported catalysts were prepared by deposition-precipitation method. A solution of HAuCl₄ (Johnson-Matthey, UK) was added to an aqueous suspension of the support. The pH of the suspension was adjusted to a pH value between 8-9 with dil.Na₂CO₃ (Fluka) solution. The resultant suspension was kept under stirring for 12 h and was then filtered, washed with water for four times and dried at 70 °C in an oven for 12 h before further use.

Sulfation of Au supported catalysts was performed by incipient wetness impregnation method. The catalyst was added to a solution of $1M H_2SO_4$ (Fisher Scientific, 98%) such that the mass of sulphate would generate 1wt% of surface sulfate groups and stirred for 4 h at room temperature. The resultant slurry was then dried at 70 °C in air for 12 h.

Calcination treatments were performed under static air in carbolite CWF 1300 oven. Typically, the sample temperature was raised between room temperature and 550 °C at ramp rate of 15 °C min⁻¹ and subsequently maintained at 550 °C for 30 minutes before being brought back to room temperature.

X-ray Absorption Spectroscopy (XAS) and X-ray Photoelectron Spectroscopy (XPS) and Ion Scattering Spectroscopy (ISS)

In-situ XAS data were collected at the Synchrotron Radiation Source in Daresbury, U.K., using station 9.3 in fluorescence with a 9 channel solid state detector. The spectra were recorded at the gold L_{III} edge using a double crystal Si(111) monochromator set at 50% harmonic rejection. The incident X-ray intensity was measured using an ionization chambers filled with argon. A minimum of five scans per sample were required to obtain sufficiently good signal to noise. Each scan was examined separately to check whether any change in the Au speciation with the X-ray exposure. Scans were collected and

averaged using EXCALIB which was also used to convert raw data into energy vs. absorption data. EXBROOK was used to remove the background. The analysis of the EXAFS was performed using EXCURV98 on the k^3 weighted raw data using the curved wave theory. Phase shifts were derived from ab initio calculations using Hedin-Lundqvist exchange potentials and von Barth ground states. During the fitting procedure the absorber-scatterer distances, the Fermi energy correction and either the Debye-Waller factors or the coordination numbers were refined using a least squares refinement XPS was performed in a Kratos AXIS Ultra DLD equipped with a procedure. hemispherical electron analyzer and charge neutralizer. The working pressure was $< 10^{-8}$ mbar and the Au 4f region was measured with a sweep rate of 0.1 eV/s for at least 100 sweeps, with a pass energy of 40 eV. Monochromated Al K_{α} radiation was used as source. Charging was corrected with respect to C 1s (284.6 eV). The peaks were fitted using constraints for area ratio, doublet separation and half width². Background subtraction was performed using a Shirley background³ and CasaXPS. Ion Scattering Spectroscopy (ISS) data were obtained with a Kratos AXIS Ultra DLD. 1 KeV He⁺ ions were used to perform the ISS with the chamber pressure of $\sim 2.5 \times 10^{-7}$ mbar.

Results

Table S1

Structural parameters from the fitted EXAFS spectra shown for the fresh and calcined Au/sulfated La₂O₃(CD) catalysts shown in Figure S1. The data were fitted between $k = 3 - 10 \text{ Å}^{-1}$.

Catalyst	Atom	Shell	Co-ordination	Debye-Waller	Fit Factor / %
		Distance / Å	Number	Factor / $Å^2$	
Fresh	0	1.97	3.8	0.006	
	S	2.95	0.9	0.076	35.5
	La	3.28	3.3	0.032	
Calcined	0	2.00	3.4	0.008	
	S	2.89	0.7	0.004	39.5
	La	3.31	4.0	0.030	

Figure S1 Comparison of the experimental (solid line) and fitted (dashed line) (a) Au L_{III} EXAFS and (b) *pseudo*-radial distribution functions for the fresh and calcined Au/sulfated La₂O₃(CD) catalysts.



References

- (1) N. Binstead, EXCURV98: CCLRC Daresbury Laboratory computer program, 1998.
- (2) http://srdata.nist.gov/xps/selEnergyType.aspx
- (3) D.A. Shirley, *Phys. Rev. B*, 1972, **5**, 4709.