

Supporting Information

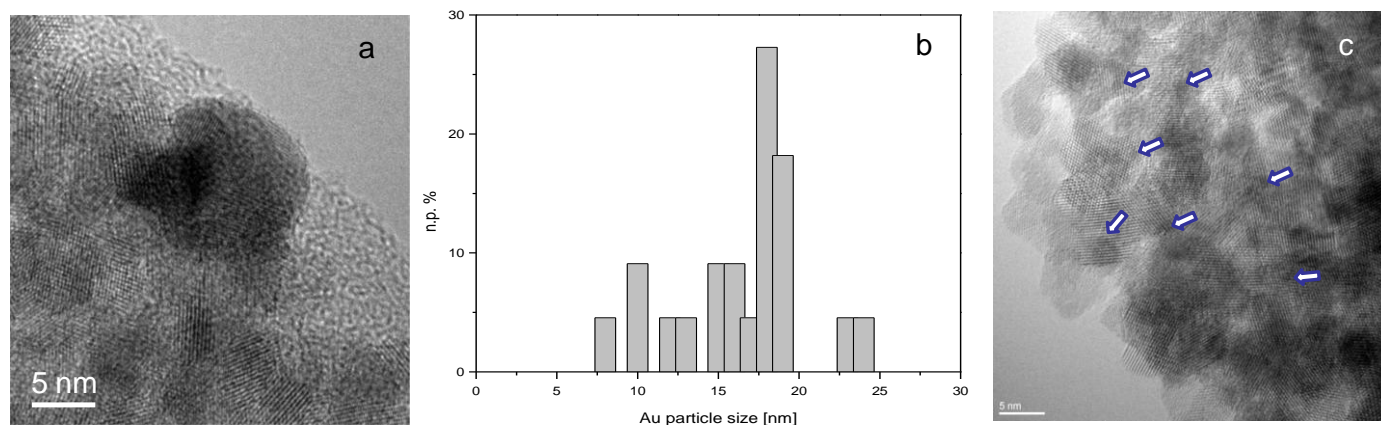


Figure S1. HRTEM images collected on AuCeUGC showing a bimodal gold particles size population: a typical big Au particle (section a), the related big particles size distribution (section b) and highly dispersed Au particles with size around 1 nm (section c). Instrumental magnification: 500000X and 800000X, respectively.

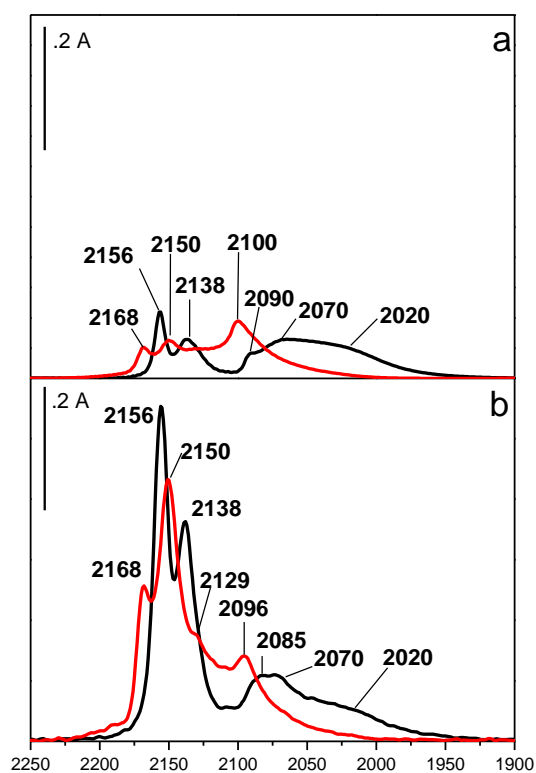


Figure S2: FTIR spectra of CO adsorbed at 120 K on AuCeCP (section a) and AuCeUGC (section b), before (black curves) and after (red curves) WGS reaction.

The behavior of AuCeUGC catalyst after the WGS reaction (Figure S2, red curve) is almost the same shown by AuCeCP. According to our previous findings on this latter catalyst¹, we can deduce that a re-oxidation of the support sites occurred during the reaction. In particular, the disappearance of the 2156 cm⁻¹ band together with the growth of a new band at 2150 cm⁻¹, due to the low temperature CO-OH interaction, can be related to the simultaneous appearance of a huge absorption in the 1900-800 cm⁻¹ range (not shown), due to the formation of carbonate/bicarbonate species during the WGS reaction. In addition, the band at 2138 cm⁻¹, associated to the Ce³⁺-CO interaction, disappears and a peak at 2168 cm⁻¹ increases contemporaneously. This frequency is congruent with the interaction between CO molecules and uncoordinated Ce⁴⁺ sites, supporting the support sites re-oxidation during the reaction. This hypothesis is also confirmed looking at the carbonylic bands due to Au species on both samples (Figure S2, red lines). In particular, an increase of the 2100/2096 cm⁻¹ band, associated to CO adsorbed on Au nanoparticles, occurs and at the same time an erosion of the component at low frequency is evident after WGS reaction. The erosion of the 2060-2040 cm⁻¹ component is an indication that the Au clusters are no longer negatively charged. In fact, no charge transfer from the reduced support to the clusters can occur since ceria is re-oxidised. The simultaneous increase of the band at 2100/2096 cm⁻¹ confirms the presence of rounded gold nanoparticles that had flattened shape before the reaction, due to the strong interaction with reduced ceria.

1. F. Vindigni, M. Manzoli, T. Tabakova, V. Idakiev, F. Boccuzzi and A. Chiorino, *Applied Catalysis B-Environmental*, 2012, **125**, 507-515.

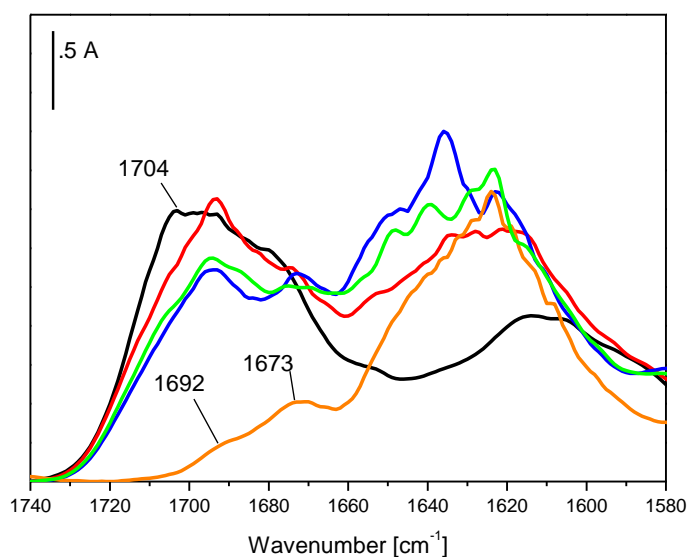


Figure S3. FTIR spectra of acetone (10 mbar) adsorbed at r.t. on CeO₂ (UGC), collected at increasing contact time: 5' (black curve), 10' (red curve), 20' (green curve), 30' (blue curve) and after 30' of outgassing (orange curve).

A band at 1704 cm⁻¹ due to acetone absorption in a “liquid like” phase (see ref. 43) is observed in the FTIR spectrum collected on AuCeUGC after 5 min in contact with acetone (black curve). This band does not increase with contact time, on the contrary it disappears after 10 min of interaction (red curve) when condensed species are formed. At the same time, the intensity of the components at 1692 and 1673 cm⁻¹ assigned to chemisorbed acetone remain constant if comparing the two spectra (black curve and red curve). These features indicate that the inlet of 10 mbar acetone is enough to survey all support sites exposed at the surface of ceria, in fact we are working in the presence of an excess of probe amount, since we observe the liquid like phase. Finally, the gradual decrease of the bands in the C=O stretching region of acetone (i.e. 1720-1650 cm⁻¹) with the simultaneous increase of the bands related to the condensed species (i.e. 1650-1550 cm⁻¹) at increasing contact times (green and blue curves), is an indication that the condensation reaction occurs.