ChemComm

Evidence for a surface gold hydride on a nanostructured gold catalyst†

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Inelastic neutron scattering shows formation of a surface Au–H species, of key importance for the study of catalytic mechanisms. Previous assignment of this feature in the infrared as a purely Ce^{3+} transition is shown to be erroneous on reducing the catalyst using hydrogen and deuterium.

Although gold was largely ignored as a catalytic metal before the mid 1980s, after highly active, practical catalysts were demonstrated for acetylene hydrochlorination[1] and CO oxidation,[2] the field rapidly expanded.[3,4] Key factors that have been identified in the production of highly active catalysts are the small diameter of gold particles[5] and their interaction with the support.[6,7] Often gold is supported on reducible metal oxides, such as TiO_2, Fe_2O_3, Co_3O_4 and CeO_2 with proposed mechanisms involving reaction between adsorbates on the gold and support oxygen at the metal boundary.[6,7] As size and support effects are important for catalytic activity, commonly used characterisation techniques may fail to provide useful information if they are unable to distinguish between changes to the metal and support. An example of such ambiguity is in the reduction of supported gold catalysts. Infrared (IR) spectroscopy and inelastic neutron scattering (INS) have shown that gold can activate hydrogen to form hydroxyl groups on ceria.[8] Hydroxyl group formation is generally seen on metal oxides where Au nanoparticles are present, but not on the bare support, indicating hydrogen spillover from gold is occurring. In addition, a weak band was observed in the infrared at 2126 cm^{-1}, which the authors assigned to an Au–H stretching vibration. The INS measurement did not cover this spectroscopic region. Similar bands have been observed by IR on gold supported on ceria[9] and

mixed CeO_2/ZrO_2,[9,10] by other groups and widely assigned to an electronic transition of the Ce^{3+} atoms in the reduced support.[11] This work aims to clarify the origin of this feature using inelastic neutron scattering and infrared spectroscopy with reduction by H_2 and D_2.

A 1% Au/CeO_2 catalyst by weight was prepared using a colloidal method from tetrakis-(hydroxymethyl)-phosphonium chloride (THPC) and $HAuCl_4$ (see ESI† for full experimental details) and dried after filtration. It was further calcined at 673 K before measurement. This was done in static air for 12 hours *ex situ* for INS measurement, and in 35 sccm flowing 10% O_2/He *in situ* for IR measurements to provide a similarly oxidised surface in both cases. Diffuse reflectance infrared spectra of the catalyst after 30 min reduction at 423 K with H_2, and D_2 are shown in Fig. 1. Fig. 1a displays the disputed band at 2125 cm^{-1}. Under H_2 reduction a weak, relatively broad band appears, which has been variously assigned in the literature to Au–H,[8] and the $^2f_{5/2} \rightarrow \,^2f_{7/2}$ electronic transition of Ce^{3+} formed by reduction of the CeO_2 support.[12] If the genesis of this feature is the production of Ce^{3+}, the final extent of reduction should be identical when using D_2 and produce an identical peak. After D_2 reduction with a fresh sample the band appears considerably weaker. Integration of the peak area between 2220 and 2050 cm^{-1} with a linear baseline showed the 2125 peak formed with D_2 to be 56% of that with H_2. Changing the integration range by $\pm 10 \text{ cm}^{-1}$ gave $56 \pm 4\%$. The apparent slope in the baseline is due to the tail of the broad absorbance of hydrogen-bonded deuteroxyl species and is well compensated for in the quantification described. Fig. 1b shows the changes in absorbance in the carbonate region. The various carboxylate, carbonate, and bicarbonate species that may be present as surface species produce ambiguous spectra and a full assignment is not attempted here. Significant differences are however apparent between the samples reduced with H_2 and D_2. The feature around 1609 cm^{-1} corresponds to an OH bend of hydroxyl groups on the ceria surface. This displays a strong loss peak under D_2 reduction, due to exchange to form OD. The corresponding OD bend is apparent as a shoulder at 1186 cm^{-1} ($1609/1.383 = 1163$). There is a significant negative peak at 1409 cm^{-1} on hydrogen reduction,

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† Electronic supplementary information (ESI) available: Primary catalyst preparation, experimental methods and neutron diffraction of second Au/CeO_2 catalyst. See DOI: 10.1039/c5cc06118k
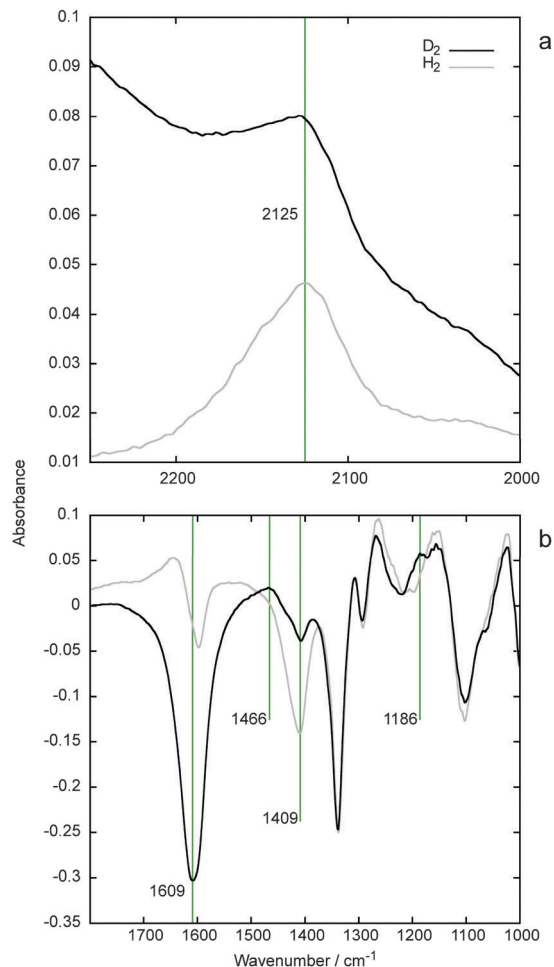
Fig. 1 Difference infrared spectra obtained on reduction of Au/CeO$_2$ with H$_2$ and D$_2$.

Fig. 2 INS spectrum of Au/CeO$_2$ catalyst with adsorbed H$_2$.

which appears with reduced intensity under D$_2$. A weak positive feature can be seen at 1466 cm^{-1} which may be assigned to the Au–D stretch that corresponds to the 2125 cm^{-1} peak under hydrogen (2125/1.411 = 1506). Convolution of these features makes precise wavenumber assignment difficult, but the difference in intensity around 1409 cm^{-1} is clearly visible and may be assigned to Au–D.

Inelastic neutron scattering (INS) data were recorded on the MERLIN spectrometer[13] at the ISIS neutron source. This instrument has exceptional sensitivity due to the 3.1 steradian detector coverage. As neutrons scatter from the nuclei of atoms, electronic transitions should not be visible with this technique, and any peak should be assigned to a vibration involving hydrogen. However, neutrons scatter only weakly, so the instrument sensitivity is key in detection of minority species. The data obtained using neutron incident energy of 600 meV (4840 cm^{-1}) is shown in Fig. 2. It should be noted that error bars are included in this plot, which shows the feature to be above the noise level. We consider this feature, despite its low intensity, to be evidence for the existence of an AuH species with a stretching vibration frequency of approximately 2130 cm^{-1} upon nanoparticulate gold catalysts.
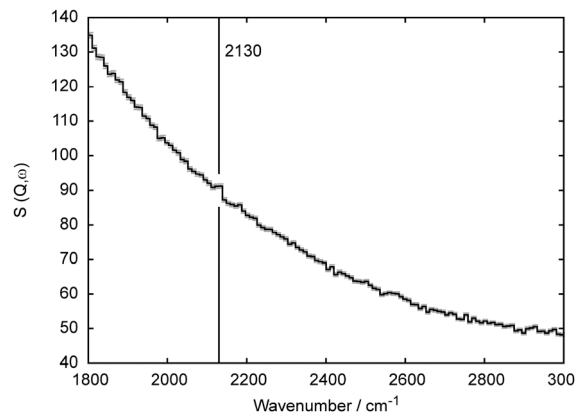
The current dominant interpretation for a band at *ca.* 2130 cm^{-1} on ceria supported Au catalysts is the $^2f_{5/2} \rightarrow \, ^2f_{7/2}$ electronic transition of Ce^{3+} after Binet *et al.*, who observed a band at 2127 cm^{-1} in the absence of gold when reduced at high temperature.[14] Although this is a forbidden transition, it is suggested that a weak crystal field effect makes this allowed. As the band appears as a single absorbance, the magnitude of the crystal field splitting must be low, or the splitting of the energy levels would be resolved in the spectrum. Consequently the transition was assigned to subsurface Ce^{3+} in an approximately spherical crystal field. The authors report that the peak becomes visible on reduction at 623–673 K as this is the temperature range where oxygen migration is occurring and the Ce^{3+} is accommodated into the bulk.

For gold supported on ceria, there are reports of ceria reduction at lower temperature. The generation of hydroxyl groups below 373 K is apparent, and the 2130 cm^{-1} band has been proposed as evidence that Ce^{3+} has formed.[15] If the band at 2130 cm^{-1} is dependent on Ce^{3+} diffusion into the bulk, then it would seem unlikely to occur at such low temperatures. Any Ce^{3+} formed at the surface would remain there in a highly asymmetric crystal field, leading to multiple bands. Under similar conditions it has recently been shown that Ce^{3+} segregates at the surface of a reduced Pt/CeO$_2$ catalyst by XPS depth profiling,[16] and there is strong evidence from calculations that Ce^{3+} is thermodynamically more stable at the surface.[17] If the reported band can not be assigned to the electronic transition for these reasons, an alternative explanation is needed.‡

A possible interpretation for the 2130 cm^{-1} band on bare ceria is the conversion of surface carbonates on the ceria to form an occluded carbonyl group on reduction,[18] although this interpretation has been disputed.[19] If this is the nature of the absorbance, a lower formation temperature with hydrogen atoms activated by supported gold than with molecular hydrogen would be reasonable. However, the unique sensitivity of the inelastic neutron scattering technique to hydrogenous modes strongly suggests the peak observed is due to displacement of a hydrogen atom.

Spectra in the literature do not contradict the theory that the peak at 2130 cm^{-1} that forms upon low temperature reduction on Au/CeO$_2$ catalysts is due to an Au–H stretching vibration. Its

presence in samples reduced at higher temperatures may be explained as an electronic transition, or an occluded carbonyl. The most credible explanation for the lowering of ceria reduction temperature, as shown by the production of hydroxyl bands is the activation of hydrogen on the gold surface through dissociative adsorption and spillover.[20] It would then logically follow that an AuH vibrational fingerprint should be present in the spectra of these materials. The observation of such a species has been claimed, by Garcia et al.[8] and Boccuzzi et al.[21] Both cite Wang and Andrews,[22] who used laser ablation to generate gold hydride species, but choose different frequencies as evidence for an AuH species, with 2126 and 1620 cm^{-1} respectively. Attempts to confirm these assignments through reduction with deuterium have been limited. The strong absorbance from carbonate type species in the support have hampered previous measurement.[8] Although the 2130 cm^{-1} band has only been reported on gold catalysts with ceria support, the interaction between metal and support is key to catalyst activity. This peak may provide an insight into the subtle differences between Au catalysts. Further evidence of AuH with other supports may already have been recorded by experimentalists who have overlooked a basic reduction test. For example, a peak is apparent at an estimated 2130 cm^{-1} on Au/TiO$_2$, but not discussed, in Fig. 3 of a paper by Panayotov and Yates.[20] Support for an Au–H species also appears in literature regarding the selective oxidation of alcohols.[23] Electron paramagnetic resonance using spin traps[24] and kinetic isotope effect by deuteration[25] suggest that oxidation of AuH is the rate determining step of the reaction.

A large portion of the relevant literature deals with adsorbed CO, either in isolation, or as part of the investigation into the (reverse) water gas shift reaction [(R)WGS]. The assignment of infrared absorbance peaks to CO on gold has occurred across a broad spectral range. This is proposed as evidence of adsorption on such species as Au$^{\delta+}$, Au$^{\varepsilon+}$, Au$^{\delta-}$, Au^{3+}, Au^0 and Au edge/defect sites in addition to adsorption on the support.[10,21,26–29] Most of these accounts neglect the possibility of a Ce^{3+} or AuH species in peak assignment. The region is congested with bands, leading to convoluted peak envelopes, and weak bands could easily be overlooked. A noteworthy exception is a report by Piccolo et al.[29] that demonstrated the presence of a broad weak band that did not shift with isotopic substitution using ^{12}CO and ^{13}CO. This band was assigned to the Ce^{3+} electronic transition, but would also be compatible with an AuH stretch.

The evidence presented suggests the existence of an Au–H band at 2125 cm^{-1} that forms under reduction with hydrogen at low temperature due to gold activating the H–H bond. More curious is the fact that this also appears under D$_2$ reduction. The band shape under both reduction regimes appears similar, although superimposed on the OD bend in the case of D$_2$. This appears to represent a single species in both cases, rather than presenting as a convoluted band envelope of many components. Hydrogen is present as OH on the ceria surface, and whilst stable in inert gas, may become mobile under D$_2$, resulting in reverse spillover onto the gold, or forming HD gas that chemisorbs. The alternative is that another of the previously discussed species is present at precisely the coincident energy, such as the band

previously assigned to the Ce^{3+} transition or occluded CO that occurs during high-temperature reduction. The isotopic shift in the IR and the peak in the INS demonstrate that AuH is at least a component of this band, and so gold hydride species must be considered as a possible intermediate in this area of catalysis, particularly in reference to research relating to the water gas shift.

Notes and references

‡ Evidence for the reduction of ceria was obtained using a different Au/CeO$_2$ catalyst using neutron diffraction. See ESI† for further details.

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