Oxidation by CO_2 of Au^0 species on La_2O_3-supported gold clusters

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The IR spectra that characterize La_2O_3-supported gold clusters show that the original Au^0 species can be oxidized by CO_2 during the catalytic CO oxidation reaction, indicating that CO_2 is the actual gold oxidizing agent.

Interest in catalysis by gold has grown enormously in recent times, motivated by discoveries of new catalytic properties.[1] Low-temperature CO oxidation has been used widely as a probe of catalytic sites,[2] but there is still no consensus regarding the oxidation states of the catalytically active gold species. Some authors have inferred that metallic gold is active,[3] and there is also evidence of the role of cationic gold.[4] Here we report the redox chemistry of supported gold clusters, showing that Au^0 species, although they are inert towards O_2 at room temperature (r.t.), are readily oxidized by CO_2.

La_2O_3-supported gold catalysts were prepared and characterized as described elsewhere.[5] Extended X-ray absorption fine structure (EXAFS) spectra indicated the existence of mononuclear gold species (a lack of detectable Au–Au contributions).[5] Upon treatment at temperatures exceeding *ca.* 473 K, Au–Au contributions appeared as gold was reduced and aggregated,[6] consistent with observations of gold on other supports.[7]

To investigate the redox properties of the gold species on Au/La_2O_3, we tested variously pre-treated samples with CO (2 kPa) at r.t. using a Bruker IFS-66 spectrometer at a spectral resolution of 2 cm^{-1}. The sample was initially activated by evacuation at 673 K. Subsequent CO adsorption resulted in the appearance of an Au^0–CO band[8–15] at 2095 cm^{-1} (Fig. 1a). This band always appeared when CO was adsorbed on a sample pre-evacuated at 673 K. Adsorption of CO at r.t. on lanthanum oxide activated at 673 K showed only one (very weak) band, characteristic of a La^{3+}–CO species, at 2167 cm^{-1}.

In preparation for the next experiment, the catalyst was evacuated at 673 K for 10 min, exposed to O_2 at r.t. and evacuated. Subsequent exposure to CO led to a spectrum essentially identical to that observed prior to contact of the sample with O_2 (Fig. 1b). These results show that O_2 did not oxidize the zerovalent gold at r.t.

Co-adsorption of CO and O_2 at r.t. onto the sample, again evacuated at 673 K, led to markedly different results. Initially, CO was adsorbed, and the spectrum of Fig. 1a was reproduced. Next, O_2 was added, and spectra were recorded as a function of time (Fig. 2A). The band at 2095 cm^{-1} was gradually converted into a new band at 2116 cm^{-1}, with a shoulder at 2136 cm^{-1}. Simultaneously, a band at 2355 cm^{-1}, assigned to adsorbed CO_2,[8] grew in. Initially, the reactions occurred at a very low rate, then followed by a higher rate (*i.e.*, there was an induction period, as evidenced in Fig. 2B).

Subsequently, the sample was evacuated at r.t. The spectrum of CO adsorbed on it (Fig. 1c) is similar to that of spectrum h of Fig. 2A.

The carbonyl bands in Fig. 1c and Fig. 2h are assigned to two kinds of $Au^{\delta+}$–CO species.[8–13] Blue shifts of the ν_{CO} bands in the presence of O_2 have previously been observed for CO on ZnO- and TiO_2-supported gold and assigned to $Au^{\delta+}$–CO species with various charge-compensating anions.[12,13] Recently, we suggested that the $Au^{\delta+}$ sites represented Au^+ ions located on the surface of the gold nanoparticles.[9–11,14] Because of electron transfer from subsurface gold to Au^+ ions, the properties of these surface cations are intermediate between those of Au^0 and isolated Au^+ sites bonded to the support. Thus, the frequency characteristic of CO

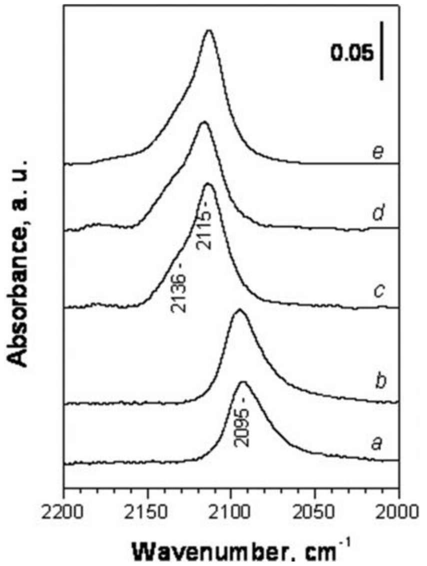

Fig. 1 IR spectra of CO (2 kPa) adsorbed at r.t. onto Au/La_2O_3 subjected to various treatments, carried out in sequence: (a) 1 h evacuation at 673 K; (b) introduction of O_2 (10 kPa, 20 min at r.t., evacuation at r.t.); (c) co-adsorption of CO and O_2 (2 and 0.1 kPa, respectively), 10 min at r.t., evacuation at r.t.; (d) introduction of CO_2 (2 kPa, 10 min at r.t., evacuation at r.t.); (e) introduction of O_2 (10 kPa, 10 min at 473 K, evacuation at r.t.). The sample was evacuated at 673 K for 10 min before each experiment (b–e).

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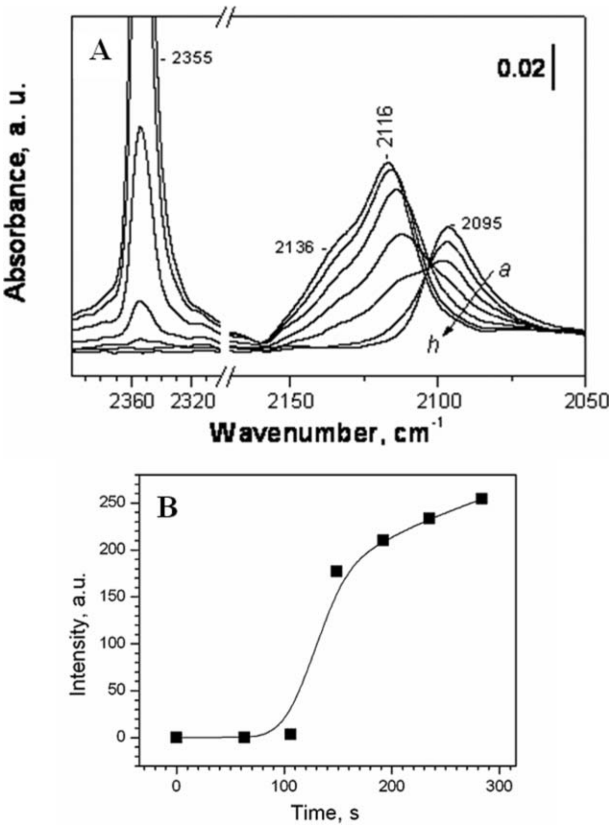

Fig. 2 (A) IR spectra of CO (2 kPa) adsorbed at r.t. onto Au/La_2O_3 (evacuated at 673 K) (a) before the introduction of O_2; (b) 60 s after the subsequent introduction of O_2 (0.1 kPa) at r.t.; (c–h) spectra recorded subsequently at 40 s intervals. (B) Change of the integral intensity of the CO_2 band with time during CO oxidation.

adsorbed onto $Au^{\delta+}$ sites is expected to depend on the charge-compensating anion (*e.g.*, O^{2-}, O_2^{-}, O^{-}, O_2^{2-}, *etc.*) and on the density of these anions associated with the gold clusters.[8]

The above results demonstrate that a CO + O_2 mixture is a more efficient oxidizing agent than O_2 alone for the zerovalent gold sites that act as CO adsorption centres. Thus, it is reasonable to suppose that the actual oxidizing agent was CO_2. To test this hypothesis, we treated the activated sample with CO_2 alone; next, following evacuation, CO was introduced into the cell. The resultant spectrum (Fig. 1d) matched that of CO adsorbed onto the (CO + O_2)-treated sample (Fig. 1c). These data show that CO_2 alone at r.t. oxidizes zerovalent gold sites (at least the CO adsorption sites). A comparable oxidation of gold by O_2 could be achieved only at much higher temperatures (*e.g.*, 473 K; Fig. 1e).

To check whether these conclusions extend beyond Au/La_2O_3, we investigated similarly prepared samples of Au/MgO and Au/NaY zeolite. Similar results were indeed observed with these samples, indicating that the observations could be general for supported gold catalysts.

The fact that CO_2 oxidizes reduced gold sites, combined with our IR observation of CO in the gas phase as the only observed product of this reaction, suggests that CO_2 reacted with the gold to give a CO molecule and leave an oxygen atom at the surface. Thus, we suggest that the charge-balancing anion is mononuclear oxygen, although we cannot rule out other possibilities.

Fig. 2A shows that the intensity of the $Au^{\delta+}$–CO bands at 2116 and 2136 cm^{-1} exceeds that of the initial Au^0–CO band at 2095 cm^{-1}. This result might be explained by the inference that the extinction coefficient of the band at 2116 cm^{-1} is greater than that of the band at 2095 cm^{-1}. However, the extinction coefficient of a Au^0–CO species is expected to be greater that of a $Au^{\delta+}$–CO species;[8] thus, the results suggest that, in addition to the Au^0 sites that act as CO adsorption sites, some additional metal sites (inert gold atoms) are oxidized, thus becoming reactive for CO adsorption.

The results point to the following reaction:

$$2\,Au^0 + CO_2 \rightarrow Au^{+}\text{–}O^{2-}\text{–}Au^{+} + CO \qquad (1)$$

which does not describe the catalytic decomposition of CO_2, because oxygen remains bound to the surface.

These oxidation reactions help to elucidate the interactions between CO_2 and gold clusters, which are distinct from the oxygen exchange reaction between CO_2 and support lattice oxygen. This is demonstrated by $C^{18}O^{16}O$ scrambling reactions.[16,17] Our results provide an explanation for the following scrambling reaction, proceeding on supported gold:[13,18]

$$C^{16}O + {}^{18}O_2 \rightarrow C^{18}O + {}^{16}O^{18}O \qquad (2)$$

which could occur by dissociation of $C^{16}O^{18}O$, formed during CO oxidation.

Activation of O_2 may be expected to occur on gold clusters,[13] on the support[19] or at the metal–support interface.[16] Our results demonstrate that for the catalysts investigated, O_2 is not activated on metallic gold. This result suggests that oxidized gold sites may play a role in the catalytic CO oxidation reaction. Indeed, as shown by the induction period in Fig. 2, both the CO oxidation reaction and the formation of oxidized gold sites are favoured by the presence of cationic gold. Therefore, we infer that the CO oxidation may be autocatalytic and that cationic gold sites somehow assist in the activation of O_2. At present, we cannot draw conclusions about whether adsorbed CO (*i.e.*, $Au^{\delta+}$–CO species) is needed for the reaction.

In summary, CO_2 oxidizes gold sites at room temperature that cannot be oxidized by O_2; activation of O_2 requires cationic gold. These results suggest that oxidized gold sites play a role in the catalytic CO oxidation reaction.

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