

## Catalytic and noncatalytic CO oxidation on Au/TiO<sub>2</sub> catalysts

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Received 6 February 2003; revised 11 April 2003; accepted 11 April 2003

### Abstract

The CO oxidation reaction has been studied on Au/TiO<sub>2</sub> catalysts prepared by incipient wetness (IW) and deposition–precipitation (DP) methods, with a range of metal loadings from 0.1 to 5 wt% for the former. We have found that there are three types of CO<sub>2</sub> production from fresh catalysts which have been calcined to only 120 °C, namely noncatalytic (types I and II) and catalytic (type III). The DP catalysts are far more active for type III reaction, showing activity at room temperature, whereas the IW catalysts generally do not show steady-state conversion until > 120 °C. However, IW catalysts with low loadings produce type I CO<sub>2</sub> (that formed at room temperature), whereas higher loadings produce only type II (that formed when heating), with intermediate loadings showing both. We associate type I CO<sub>2</sub> production with monolayer Au catalysts, which have intimate contact with the TiO<sub>2</sub>, and are probably already in some oxidic form. Type II behavior we associate with three-dimensional oxidic Au, the surface of which is no longer in direct contact with the support. The poor performance of IW catalysts compared with DP catalysts is ascribed to the presence of chloride in the former, which induces a larger average particle size, and vulnerability to extensive sintering.

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*Keywords:* Gold; Titania; CO oxidation; Gold catalysts

### 1. Introduction

Gold is generally regarded as being the least useful of the noble metals for catalytic purposes. The low chemical activity of gold is due to the filled 5d shell and the relatively high value of its first ionization potential, with the result that gold films hardly chemisorb any gas. Due to its nobleness, it has always been regarded as unsuitable for heterogeneous catalysis, apart from a few isolated reports [1,2]. However the 80s and 90s saw a huge growth in interest in gold as a catalyst. Probably the biggest surprise has been the ability for suitably prepared gold, supported on transition metal oxides, to catalyze the oxidation of CO to CO<sub>2</sub> at temperatures as low as –70 °C [3]. It was demonstrated that gold is better than conventional Pd and Pt catalysts and that the way gold acts catalytically is substantially different from other metals from the Pt group. It is now known that gold may catalyze

a wide variety of reactions under comparatively mild conditions. Nowadays gold catalysis has been receiving increasing attention from many research groups around the world and the subject has been recently reviewed by Thompson and Bond [4,5]. This relatively new field of gold catalysis has very promising applications but among them, CO oxidation is the reaction that has received most attention in the literature. Possible applications for CO oxidation include car exhaust systems for pollution control, fuel cells (CO purification in H<sub>2</sub> + O<sub>2</sub> streams [4,6]), gas sensing, chemical processing (CO oxidation in reforming gas [7]), and air purification systems (long-term space travel).

However, any practical application of a catalyst will require a reliable method of manufacture, long-term stability, good response to operating conditions, and more information on the kinetics and mechanism of the reaction. The explanation of the causes and mechanism of this outstanding low temperature activity for CO oxidation on gold catalysts is expected to be important, not only because of the practical applications of this reaction, but also because it will surely provide insight into the more general field of heterogeneous catalysis.

The major conclusions of the research on CO oxidation on gold catalysts so far are that

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- macroscopic gold is only weakly active for CO oxidation;
- Au in nanodispersed form, with strong metal-support interaction, leads to highly active catalysts; and
- the nature of the support is important.

Since the studies made so far pointed out that the reactivity of gold is highly structure sensitive, the preparation techniques play a major role in the synthesis of highly active gold catalysts. Successful methods are impregnation [8–11] (pretreatment reduction + calcination), deposition precipitation [12], coprecipitation [13,14], and the Iwasawa method [15]. With various degrees of success there are also colloidal methods [4,12], grafting and vapor deposition [12].

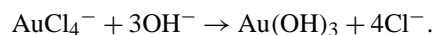
A mechanism for the reaction has been proposed by Bond and Thompson [5] and they suggest that both  $\text{Au}^0$ ,  $\text{Au}^{x+}$  and the oxide support all have a role to play in the catalysis of CO oxidation. They indicate that the interaction between gold and support is particularly important, since it dictates the nature of the interface at which the reaction takes place.

In our contribution to this field we want to point out a new feature of this reaction, namely the formation of oxidic states on the surface of these Au/TiO<sub>2</sub> catalysts which result in stoichiometric, noncatalytic reaction with CO to produce CO<sub>2</sub>. On the one hand this can be a problem for the measurement of catalytic activity for some systems, on the other hand these processes may give us new clues about the state of the catalyst surface after various types of preparation procedures.

## 2. Experimental

Most of the catalysts used in this work were prepared by the incipient wetness impregnation method (IW). An aqueous solution of chloroauric acid (HAuCl<sub>4</sub>) was added to TiO<sub>2</sub> P25 (50 m<sup>2</sup>/g, Degussa, pretreated at 500 °C in air for 2 h) until incipient wetness was achieved. The catalysts were then dried at 120 °C in air for 2 h.

The rest of the catalysts were prepared by a deposition–precipitation (DP) method, for which TiO<sub>2</sub> (Degussa P25) was suspended in a continuously stirred solution of HAuCl<sub>4</sub>. The pH was then increased by adding dropwise 49 ml of a solution of 0.1 M Na<sub>2</sub>CO<sub>3</sub>; this represents an excess of sodium carbonate over chloroauric acid (4.9 and 0.76 mmol, respectively). This increased the pH to 8 and after this the solution was allowed to age for 2 h in order to deposit Au(OH)<sub>3</sub> on to the surface of the catalyst [16]. The role of the carbonate is to extract protons from solution by forming bicarbonate, leaving an excess population of hydroxyl, which then hydrolyzes the gold salt, probably in the following manner:



The mixture was then vacuum filtered and dried at 120 °C in air for 2 h. All of the catalysts were ground, pelleted, and sieved to give a particle size range of 600 μm < d < 850 μm before use in the reactor.

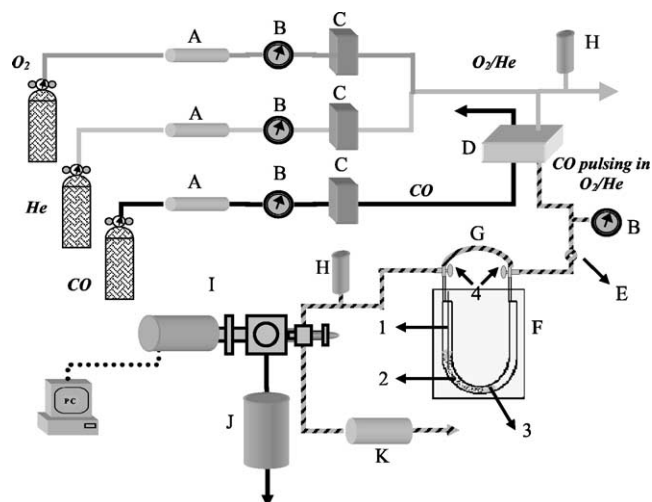


Fig. 1. The pulsed flow reactor (P.F.R.): A, molecular sieves; B, gauges; C, mass flow controllers; D, pulsing valve; E, PTFE septum; F, oven containing u-tube with sample; G, bypass; H, needle valve; I, quadrupole mass spectrometer; J, turbo pump; K, rotary pump; 1, thermocouple; 2, sample; 3, quartz-wool plug; 4, switching valves.

The performance of the catalysts was analyzed in a pulse flow reactor (P.F.R.) described in a previous publication [17]. The P.F.R. (Fig. 1), consists of a tubular microreactor (6.4 mm o.d., 10 cm long) containing the catalyst which is housed in a fan circulation oven where the temperature may be controlled. In a typical experiment one reactant gas flowed through the catalyst bed and one of the reactants was pulsed at regular intervals into the stream. Meanwhile the sample temperature was controlled isothermally, or a linear heating ramp can be applied. The products of the reaction were continuously analyzed by a quadrupole mass spectrometer and the data recorded for further analytical treatment. In this manner, a single run on the reactor provided enough data for the calculation of conversions/selectivities vs temperature.

The catalytic bed consisted of 1 g of catalyst held in place by quartz wool plugs. The flow rate was 21 ml/min of either 10% vol O<sub>2</sub>/He or He only. Pure CO was regularly pulsed into the stream, the frequency and duration of pulsing being computer controlled. Whenever yields of CO<sub>2</sub> are shown on the graphs, they were calculated according to the formula yield

$$\text{CO}_2(\%) = (A_{\text{CO}_2}/A_{\text{CO}_2,100\%}) * 100,$$

where  $A_{\text{CO}_2}$  = peak area of CO<sub>2</sub>, and  $A_{\text{CO}_2,100\%}$  = peak area of CO<sub>2</sub> corresponding to 100% conversion of CO.

Mass spectrometers are not as stable in sensitivity as other kinds of equipment such as gas chromatography so care was taken in the calibration of peak areas. In each graph shown here calibrations were applied that took into account daily changes in the sensitivity of the mass spectrometer.

The XPS data were collected using two different instruments. Some of the work, which was carried out at Reading, used a VSW 100 mm concentric hemispherical analyzer, op-

erating at a constant pass energy, and employing a VSW twin anode X-ray gun, providing nonmonochromated Mg( $K_{\alpha}$ ) radiation. The second instrument, based at AEA Technology, was a VG ESCALAB MkII, equipped with a  $150^{\circ}$  spherical sector analyzer and fitted with a triple-channel detector. Data were collected at a constant pass energy using a nonmonochromated Al( $K_{\alpha}$ ) X-ray source.

All of the XPS data were referenced to the adventitious C 1s signal, taken as 284.8 eV, since the catalyst samples experienced charging. Besides this both XPS machines were calibrated using Au foil, taking Au  $4f_{7/2}$  as 84.0 eV. Where the C 1s signal was found to be broadened the  $Ti^{4+} 2p_{3/2}$  peak of the underlying  $TiO_2$  was also used to assist in correcting for charging effects. The fitting procedure employed for deconvoluting the individual oxidation states contained within the Au 4f peak envelope was based on two doublets constructed from a combined Gaussian–Lorentzian line shape. The full-width at half-maximum (FWHM) values were fixed for both the Au  $4f_{7/2}$  and  $4f_{5/2}$  lines at the values obtained from Au metal foil in the same instrument. The doublet splitting was fixed at 3.67 eV for the Au 4f peaks [18], in addition to the area ratio being fixed at 3:4, between the  $f_{5/2}$  and  $f_{7/2}$ , respectively. The fit procedure was allowed to adjust the doublets until a best fit for position and area were obtained. Fitting, integration, and XPS data presentation was prepared using a commercial software package (CASAXPS, CASA Software Limited).

XRF measurements were carried out on a Phillips PW-1480 instrument and were calibrated from a plot of signal integral vs Au loading for the incipient wetness catalysts, which have a known loading of Au. Five standard samples of Au/ $TiO_2$  with known loadings of Au of 0, 0.5, 1, 2, and 5% by weight were used to obtain a calibration plot, and 0.5 g of each sample was mixed with 4.5 g of alumina to make it easier to press into XRF disks. The peak area of the Au XRF signal was fitted linearly by the standard equation  $y = mx$ , where  $y$  is the XRF integral,  $x$  is the Au loading, and  $m$  is the proportionality constant from which the DP loading can be determined. The DP catalyst loading was then determined from this calibration plot as 1.6 wt% loading of Au on titania.

### 3. Results and discussion

In Fig. 2, we show the results of a typical CO oxidation run, which was essentially the same sequence as used for all the experiments given here. It consisted of an initial isothermal period at near-ambient temperature, followed by a temperature ramp (heating rate  $10^{\circ}C/min$ ), and then by a high temperature isothermal period. In Fig. 2, CO was pulsed (0.5-ml pulses) into a continuous flow of 10%  $O_2$  in He. For the impregnated 1 wt% Au/ $TiO_2$  dried at  $120^{\circ}C$ ,  $CO_2$  production was already seen at room temperature. There were three stages of  $CO_2$  production. The first (type I), produced at ambient temperature, and the second (type II), at  $80^{\circ}C$ ,

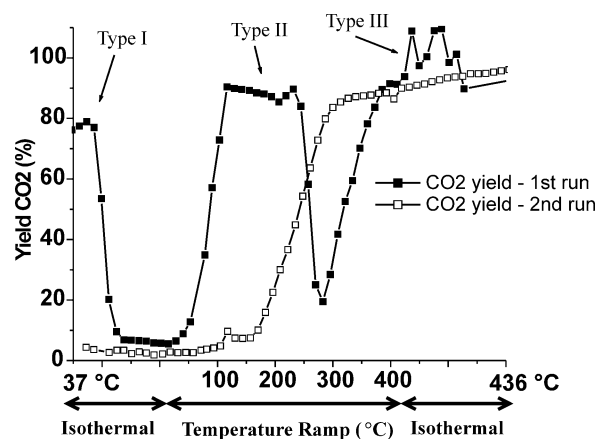


Fig. 2. Temperature-programmed pulsed reaction on 1 wt% Au/ $TiO_2$ , prepared by the impregnation method, dried at  $120^{\circ}C$ . The data points are integrals of the  $CO_2$  pulses produced during pulsing of CO into the continuous flow of 10%  $O_2$  in He. Consisting of a nearly isothermal period at  $37^{\circ}C$ ; a temperature ramp  $10^{\circ}C/min$ , and a nearly isothermal period at  $400$ – $436^{\circ}C$ .

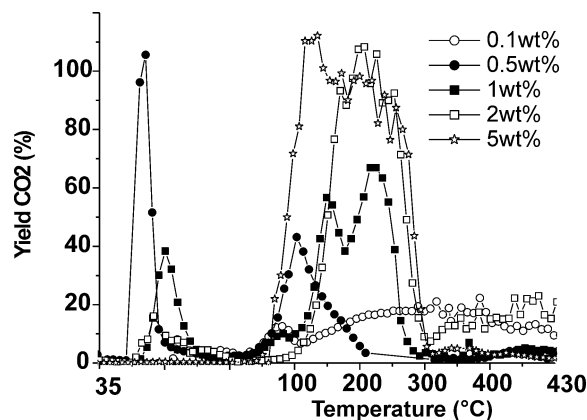


Fig. 3. Temperature-programmed pulsed reaction on Au/ $TiO_2$  prepared by the impregnation method, dried at  $120^{\circ}C$  and with different loadings. Pulsing CO in He stream. The yield of  $CO_2$  is given as percentage of the maximum (i.e., 100% CO conversion).

are irreversible processes; that is, they were not seen in a second run. In these two stages of  $CO_2$  production, CO conversion was around 100%, but oxygen was not consumed. Further, this  $CO_2$  production occurred even if there was no  $O_2$  present, which proves that the  $O_2$  available for CO oxidation came from the catalyst sample itself (Fig. 3). It should be noted that  $TiO_2$  alone has only low activity for CO oxidation (10% conversion at  $300^{\circ}C$ , 40% at  $400^{\circ}C$ ) and does not show the types I and II  $CO_2$  production. This suggests that CO is involved in the reduction of a gold precursor, using some form of reactive oxygen atoms bound to gold species (e.g.,  $AuO_x$  or  $Au(OH)_x$ ) yielding  $CO_2$ . This is discussed further below. The first two stages at different temperatures imply the existence of two forms of active, bound oxygen, one being more strongly held than the other. In effect this is a kind of temperature-programmed reduction experiment. It should be noted that, for the 1% catalyst, during the first

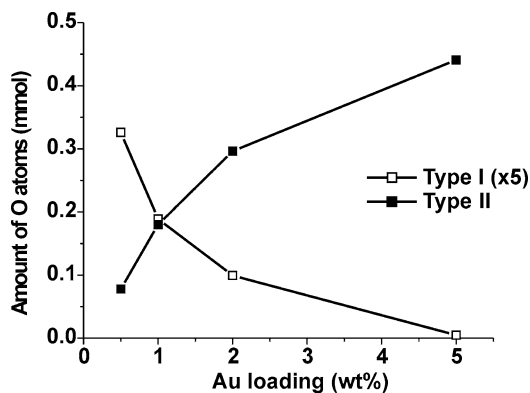


Fig. 4. Integrated pulsed yields of CO<sub>2</sub> from the data of Fig. 3 as a function of Au loading for the incipient wetness catalysts. Note that the data for the type I species have been exaggerated by a factor of 5 for clarity.

stage of CO oxidation, the catalyst color changed from yellow to green.

The final stage of the reaction (type III) occurred above about 300 °C when the true catalytic CO oxidation began, with both gas-phase CO and O<sub>2</sub> conversions evident. By 400 °C the CO conversion was complete and in this temperature range the CO oxidation continued at steady state. Fig. 2 shows that this catalytic stage still occurred (indeed, at about 80 °C lower in temperature) during a second heating ramp to 450 °C, but that the first two stages of CO<sub>2</sub> production were lost, presumably because the active surface oxygen which produced them is no longer present, and was not recovered through gas-phase oxygen. After high temperature calcination the catalysts tended to range in color from very pale blue to deep blue to mauve, depending on the exact loading, preparation method, and treatment conditions.

We believe these findings are important in relation to the current interest in low temperature CO oxidation, and care must be taken to identify whether the CO<sub>2</sub> production seen is truly catalytic in nature, or is a stoichiometric reaction with this special form of surface oxygen, which is still around after low temperature heating. It is the case that many catalyst studies are carried out after high temperature calcination and so then this problem is largely avoided. However a significant number of researchers avoid calcination.

In order to investigate the two types of irreversible CO<sub>2</sub> production, we varied the loading of Au and performed CO pulsing in a He stream only (Figs. 3 and 4). Here it was seen that the amount of types I and II CO<sub>2</sub> production varied strongly with loading. Type I increased with loading up to ~ 0.5 wt% Au and then diminished again, with little CO<sub>2</sub> of this type produced above 2%, whereas the type II CO<sub>2</sub> appeared to increase with metal loading in a near-linear fashion. Allied with this there was desorption of HCl from the catalysts and this is shown in Fig. 5. There appeared to be little desorption of HCl from the low loading catalysts, but significant amounts at higher loadings. It may be that, at low loadings, all the Au is intimately associated with the support and that the Cl from the preparation was easily lost resulting in Au oxidation (perhaps the Cl was removed to the support

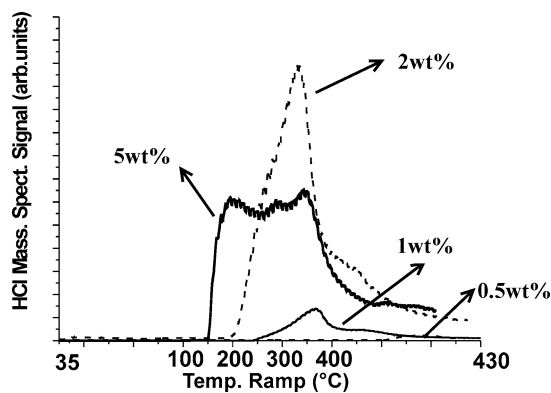


Fig. 5. Temperature-programmed desorption (TPD) of HCl, while pulsing CO into a He stream passing over Au/TiO<sub>2</sub> prepared by the impregnation method, dried at 120 °C, and with different gold loadings.

by Cl–O exchange). As the loading increased, it may be that three-dimensional Au particles form in which the top layers are no longer directly associated with the titania and so show different reaction characteristics with CO. These layers may well still be chlorided (as evidenced from the HCl TPD) and the CO<sub>2</sub> production may be associated with changes in these layers which include reaction with the support as provider of O. It is possible that types I and II are associated with surface and bulk oxygen, respectively; as the loading goes up, so does the bulk oxygen (type II), whereas the higher loadings do not show type I because of surface poisoning by the large amounts of Cl available and the lower surface:bulk ratio (i.e., higher Cl:surface ratio). The exact distribution of Cl between the support and the Au is uncertain. These ideas are schematically summarized in Fig. 9 later and discussed further below.

It is known that catalysts prepared by the incipient wetness route are generally less active than those prepared by deposition precipitation [12]; the latter tend to be the best catalysts for low-temperature CO oxidation. Thus we prepared catalysts by the DP method to compare with the results shown above for the impregnation method. In contrast with the catalysts prepared by the IW method, the samples prepared by the DP method showed activity for catalytic CO oxidation even at room temperature (Fig. 6), as described previously by Haruta and others [3,14]. Here the conversion of CO appeared to be very high and continuous at room temperature in an oxygen flow, making it difficult to distinguish whether any noncatalytic CO<sub>2</sub> is produced. However, it is, as was clearly demonstrated by an experiment carried out in the absence of oxygen, which showed significant CO<sub>2</sub> production of both types I and II (Fig. 6b). Nevertheless it may be that the active types of oxygen can be readsorbed for the DP catalysts and hence why these catalysts are active at ambient temperature. Active oxygen cannot apparently be readsorbed on IW catalysts in a significant amount, probably due to loss of surface area and poisoning by Cl, as discussed further below. It must be remembered that the DP catalysts produced no HCl in initial desorption experiments.

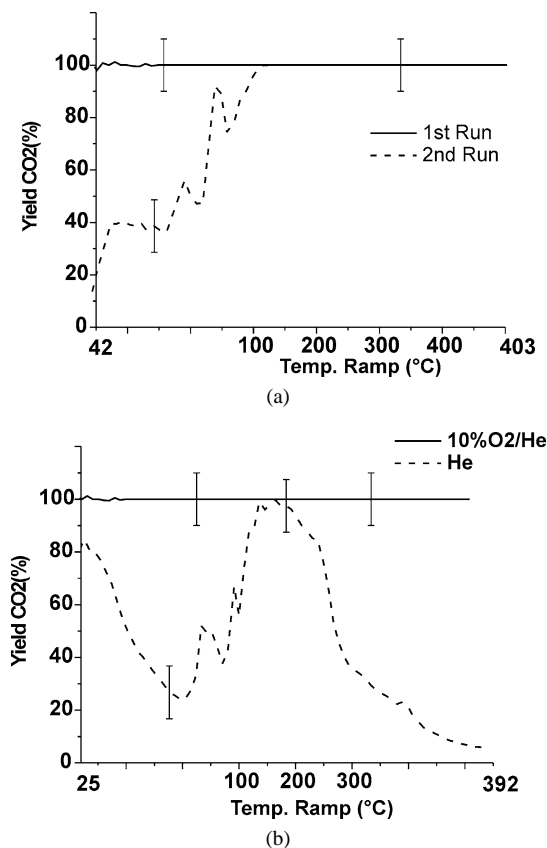


Fig. 6. (a) Temperature-programmed pulsed reactions of CO in 10% O<sub>2</sub>/He passing over 1.6% Au/TiO<sub>2</sub>, dried at 120 °C in air, prepared by the DP method. (b) A comparison of the temperature-programmed pulsed reaction of CO in He and 10% O<sub>2</sub>/He over the same catalyst.

Whether the Au is in the form of (i) Au(OH)<sub>3</sub>, (ii) Au<sub>2</sub>O<sub>3</sub>, (iii) mixed oxyhydroxide/chloride, or (iv) Au metal is not clear at this point, though the appearance of non-catalytic CO<sub>2</sub> production implies at least some oxidation/hydroxylation of Au during the preparation stage. We attempted some XPS measurements of the IW catalysts, but there was significant static and differential charging of these samples which made clear identification of oxidation states difficult. However, experiments with two different machines, as described above, gave essentially the same results when treated in the same way. These are shown in Fig. 7a and it can be seen that at lower temperatures the Au exists as a combination of components. The majority of the Au 4f envelope is situated above 86 eV for the 4f<sub>7/2</sub> peak, with a small component seen at approximately 84 eV. Fig. 7b shows XPS data taken from the precursor compound used as a kind of calibration material, since the Au should be completely Au<sup>3+</sup>, but two oxidation states are observed. Au<sup>3+</sup> is likely to be the source of the peak at 87.5 and 91 eV [20,21]. The other peaks at 85.5 and 89 eV are likely to be due to a Au<sup>1+</sup> state [20]. The Au<sup>1+</sup> signal may have come from a reaction between the chloroauric acid and the Si wafer on which it was held, or more likely, it was due to a genuine loss of Cl

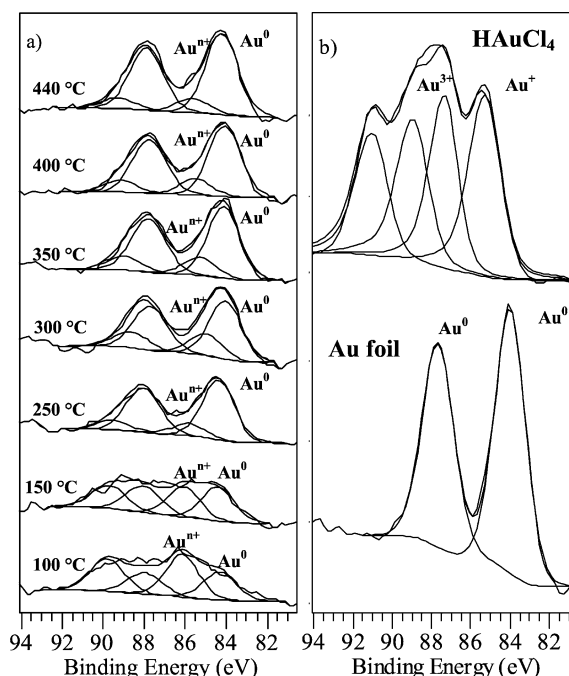
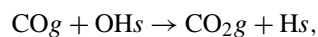


Fig. 7. (a) XPS for a 5 wt% Au/TiO<sub>2</sub> IW catalyst showing the Au 4f region, taken at a range of temperatures using nonmonochromated Mg(K<sub>α</sub>) radiation. A Shirley background and component peaks have been fitted for deconvolution of the different Au oxidation states. (b) XPS data for H[AuCl<sub>4</sub>] and Au foil taken at room temperature using Al(K<sub>α</sub>) radiation.

during the preparation and drying procedure. Returning to the catalyst XPS, the main component of the Au 4f envelope above 250 °C in Fig. 7a is Au<sup>0</sup>, with a considerable reduction in the higher binding energy peaks from the precursor compound. However, even after heating to 440 °C, around 20% of the 4f peak was still present at high binding energy. This higher binding energy contribution is shifted from the Au<sup>0</sup> peak by ~ 2 eV, which is within the range of values expected for Au<sup>3+</sup> in association with some form of oxygen [19–21], though it may also be due to Au<sup>+</sup> associated with chloride. It is most unlikely to be due to Au(III) chloride, which should be shifted to much higher binding energies. However, some charge transfer could also occur at the Au/TiO<sub>2</sub> interface which could affect the binding energy shifts. We also carried out similar XPS measurements on the DP catalysts and it is significant that, even though the catalyst was only pretreated to 120 °C, the Au appeared to be completely Au<sup>0</sup> and remained so after heating to 450 °C. Further, the XPS showed a much higher Au/Ti ratio than the IW catalysts, indicating much better dispersion. The presence of Au<sup>0</sup> is surprising in view of the large amounts of types I and II CO<sub>2</sub> produced by these catalysts in the absence of gas-phase oxygen. This may imply that the very small Au particles in the DP catalyst (see below) are easily reduced in the X-ray beam; while the larger Au particles in the IW catalysts are not. In respect of the latter it should be noted that there is a significant level of Cl detected for the IW catalysts, even after calcination, which is not the case for the DP sample. For the DP catalysts, then, it is still not clear at what point they are converted to Au<sup>0</sup>.

Nevertheless our overall interpretation of the data for the IW catalysts is that during the temperature range of the type II CO<sub>2</sub> production the gold oxidation state shifts largely from Au<sup>*n*+</sup> to close to Au<sup>0</sup>. It is likely that the value of *n* is 3, since the low-temperature Au peak is shifted by ~ 2.0 eV from Au foil and this appears to be a larger shift than for Au<sup>+</sup> species (~ 1.0 eV) [20]. However the shift is in the range which might be expected also for Au(I) chloride. Although the nature of the active Au on the surface is not clear, we have experimented with Au<sub>2</sub>O<sub>3</sub> and Au(OH)<sub>3</sub> and find that both produce CO oxidation of types I and II when exposed to CO in the pulsed flow reactor [22]. Thus the species present at room temperature must be in (at least) a partially oxidized form.

A remaining question is, what is the nature of the reaction involved in the irreversible CO<sub>2</sub> production? If it is a hydroxyl group which reacts, it occurs in the following manner:



where *g* and *s* refer to gas phase and surface species, respectively. The fate of the H<sub>s</sub> released by this reaction is unclear. There was no evidence of H<sub>2</sub> production from the surface during stage I. A good possibility is that this H was lost to other parts of the catalyst (i.e., TiO<sub>2</sub> remote from the Au particles), either by direct diffusion of H<sub>s</sub>, or, more likely, by H + HO recombination, which produced water, which, in turn could have readsorbed on other parts of the catalyst. Indeed, some water is produced on further heating, but most of this is likely to be from the preparation stage; that is, drying alone is insufficient to remove all water from the catalyst. If it were simply atomic oxygen at the surface of the Au which reacted, then it is not clear why it could not easily be reformed by dosing oxygen. When we used Au<sub>2</sub>O<sub>3</sub> as the reactant with CO, it produced large amounts of types I and II CO<sub>2</sub>, essentially the whole of the catalyst was reduced to Au<sup>0</sup>. Thus it seems likely that the reactant is this kind of oxygen, though hydroxylation of oxide catalysts is likely to occur under ambient conditions to some degree.

A major difference between the IW and DP catalysts is that, by the very nature of the preparation method, the Cl associated with the Au precursor was still present in the former, but largely absent from the latter. The presence of easily removable chlorine is shown in Fig. 5 for the higher loading IW catalysts. Note that for the DP catalysts no such HCl was produced (since chloride was lost into the solution in the high-pH preparation stage). However, a large desorption of H<sub>2</sub> was observed during CO pulsing in a similar temperature window to HCl production. This is likely to have arisen from surface hydroxide reaction with CO. The reason these DP catalysts are much more active for CO oxidation is probably (at least) twofold, namely (i) most chloride is removed from these types of catalysts during preparation, and (ii) they are in appropriately dispersed form. In respect of the latter it is interesting to examine high-resolution TEM

images of DP catalysts (Fig. 8). These show that after calcination to 120 °C we have a dispersion of small particles, with an average (over 21 particles) of 7 nm diameter, but with no clear internal structure. After heating to 400 °C the particles appear to be somewhat smaller (average size 4 nm, 77 particles), with clear fcc internal structure and, occasionally, with well-defined hexagonal shape, as shown in the insert of Fig. 8, though the electron beam may have assisted in faceting of such particles. Note that this size is in the range reported by Haruta [3] and Goodman et al. [23] to be appropriate for maximized activity. The TEM of the IW catalysts showed an array of small particles of around 9 nm diameter on average for the sample before use, but only a few, very large agglomerates (~ 100 nm in diameter, though apparently composed of 10- to 20-nm-diameter fused particles) after calcination to 400 °C. Thus the reason for the low activity of IW catalysts is a combination of high chloride level and low dispersion, and the former probably aids sintering also. However, as shown in Fig. 2 the IW material calcined in situ to 440 °C was apparently a little more active than on the first run. This may be due to loss of poisoning Cl from the Au during the calcination procedure (Fig. 5).

Fig. 9 is a schematic figure summarizing our conclusions regarding the nature of the various catalysts employed in this work. It has some similarities with the proposals of Bond and Thompson [5] especially since it implies that IW catalysts consist of particles of Au interfaced to the support through Au<sup>3+</sup> species. However, the much more active DP catalyst shows little signs of such oxidized gold species. For the IW catalysts the oxidized Au may be associated with Cl remaining in the catalyst, and the particle size after heating is very large, whereas the particle size for the DP catalysts appears to remain small.

It should be noted that our conclusion that low-loading IW catalysts are monolayer, two-dimensional Au catalysts, whereas higher loadings result in three-dimensional catalyst particles, agrees with the proposal of Goodman et al. [23] who worked on model catalysts of Au on single crystal rutile TiO<sub>2</sub>(110). They prepared their nanoparticle by metal vapor deposition (MVD) onto single-crystal TiO<sub>2</sub>(110). They carried out STM/STS measurements of the properties of small Au nanoparticles (~ 1–5 nm diameter). They propose that single-layer catalysts have significantly different activity than three-dimensional ones, due to a quantum size effect and hence significantly different electronic structure and band gap (and therefore reactivity). In fact for CO oxidation the single-layer catalysts are judged to be ineffective. For our catalysts, after heating, the IW materials form large particles which results in much lower activity, and this is presumably due to the presence of Cl in the catalysts.

We recognize that some of the conclusions here regarding single-layer and three-dimensional, particulate Au catalysts are somewhat tentative. We will shortly embark on more studies to try to gain more insight into the structure and composition of these materials, and look forward to the appearance of other work to clarify or deny such proposals.

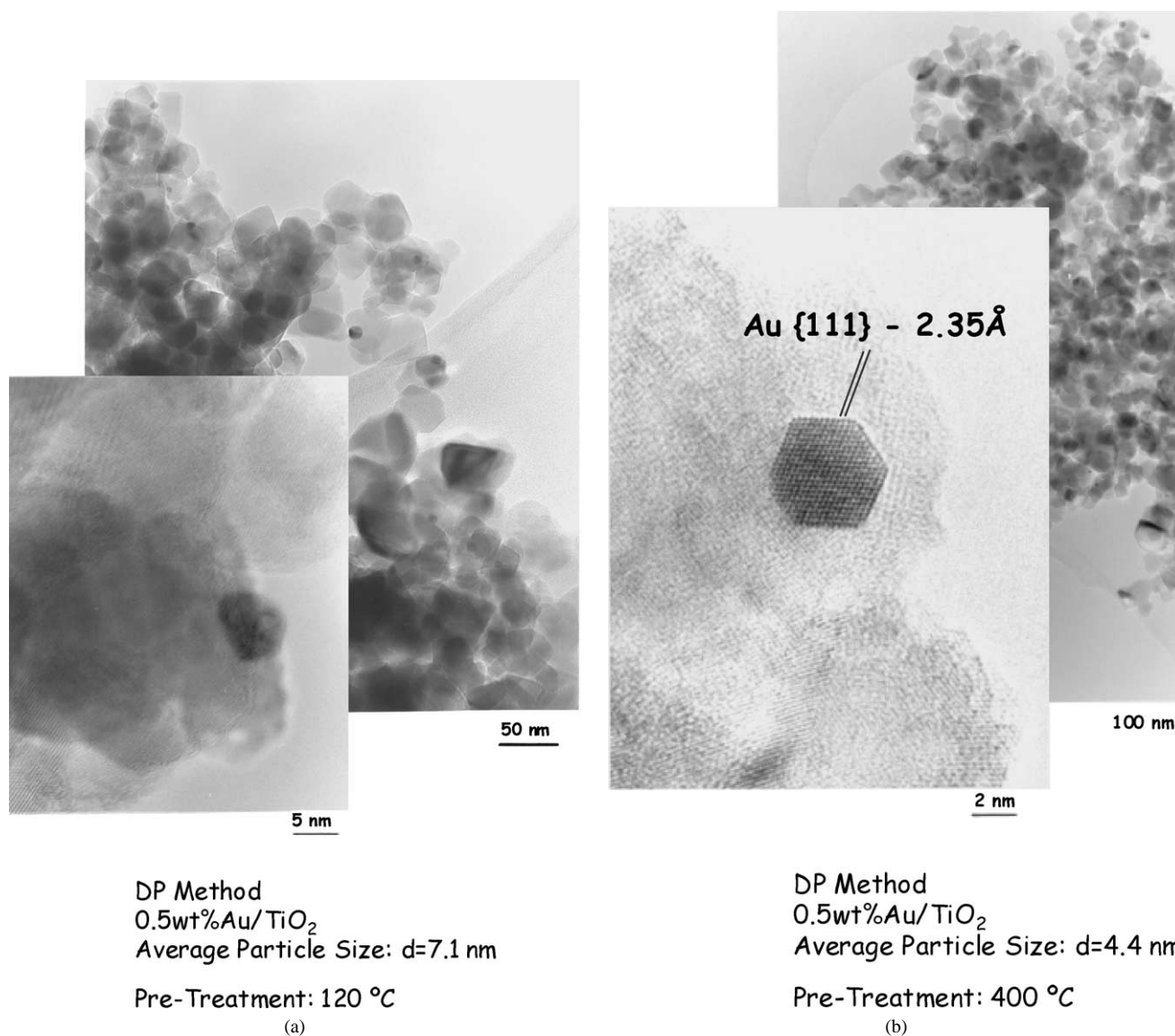


Fig. 8. High-resolution TEM images of the DP Au/TiO<sub>2</sub> catalyst before and after calcination.

#### 4. Conclusions

CO can be oxidized on both incipient wetness and deposition–precipitation catalysts in both reversible (steady-state) and irreversible (non-steady-state) ways. It is possible to prepare catalysts by both methods which are active at ambient temperature for the latter reaction. However the DP catalysts are much more active for the steady-state catalysis. These results have shown also that CO can be oxidized on Au/TiO<sub>2</sub> by at least two ways:

(a) *Through reaction of surface active oxygen species activated by gold during the preparation of the catalysts (types I and II).* These steps are irreversible and not catalytic. In the case of the dried impregnation method, the surface oxygen is available in two types: one which reacts readily at room temperature (type I) and another which requires a higher activation energy (type II). We associate these two

types with one-layer, two-dimensional Au particles at low loading (type I) and three-dimensional Au particles at higher loading (type II). In turn we consider it likely that type I state is associated with surface oxygen, whereas the type II state is associated with the conversion of bulk oxygen in the Au nanoparticles.

(b) *Through catalytic reaction mediated by gold (type III).* The dispersion of gold is the key factor for obtaining low-temperature CO oxidation, possibly by obtaining gold nanoparticles which provide enough interfacial sites for oxygen activation. A high gold dispersion can be obtained by a suitable choice of the experimental variables. We propose that this preparation method results in catalysts that are more free of chloride and are predominantly in the correct Au form, requiring good interfacial adhesion and the appropriate, very small particle size.

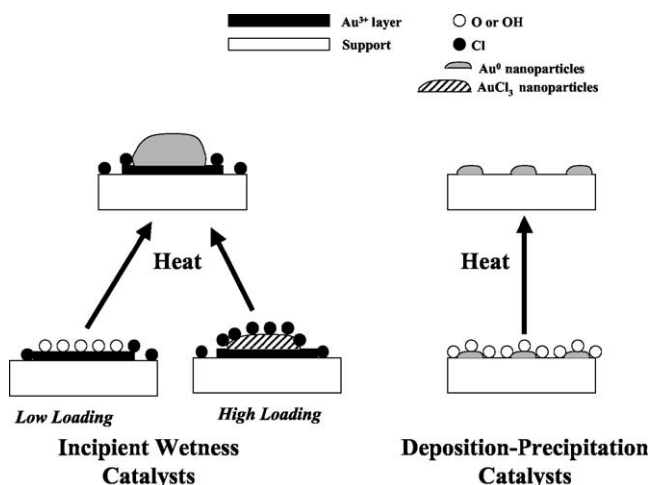


Fig. 9. Schematic diagram showing the effect of preparation and heating on the Au catalysts. For the incipient wetness catalysts calcination produces large  $\text{Au}^0$  nanoparticles, but much smaller ones are produced by deposition precipitation. There appears to be an interface layer of  $\text{Au}^{3+}$  for the IW catalysts, even after calcination. Low loadings of Au by IW produce a thin layer of oxidized Au, which sinters during calcination, while higher loadings produce initially chlorided catalysts. Some of the Cl is lost during heating. There are very low levels of Cl on the DP catalysts.

Since attention in the literature has mainly been devoted to the CO oxidation in the sense of the catalytic reaction (type III), we believe these preliminary results are significant because they show the importance of eliminating non-catalytic CO oxidation from rate measurements on such systems. Although high-temperature calcination eliminates these states, this can also result in catalytic deactivation if carried out in too extreme a manner.

### Acknowledgments

We thank the Portuguese government for funding J. Soares under Grant SFRH/BD/831/2000 and the University of

Reading for the provision of reactor facilities and analysis equipment. We also thank Franz Street of the Postgraduate Research Institute of Sedimentology, University of Reading, for the XRF measurements.

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