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Gold on titania catalysts for the oxidation of carbon monoxide: control of pH during preparation with various gold contents

François Moreau [*], Geoffrey C. Bond, Adrian O. Taylor

Institute for Materials Research, University of Salford, The Crescent Salford, Greater Manchester, M5 4WT, UK

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Abstract

Au/TiO_2 catalysts have been prepared by deposition-precipitation, with the initial pH of a $HAuCl_4$ solution raised to various values between 4 and 11 by the addition of NaOH at room temperature. The optimum pH for high activity proved to be 9; at this pH the main species in solution were anionic Au complexes, from which most of the chlorine had been removed by hydrolysis. At lower pH, the gold complexes contained more chlorine, Au particles were larger, and activities were lower. Whereas other workers have used catalysts with more than 2% gold, we have focused on lower loadings: catalysts containing only 0.05–1.9 wt% gold were prepared, and the pH was kept constant at 9 throughout the preparation. When their activities for CO oxidation were determined under conditions of kinetic control, all of them had about the same activation energy and the same high specific activity, suggesting that our method of preparation gave similar distributions of gold particle sizes at all loadings. Their activities were unchanged by calcination up to 573 K; however, a catalyst prepared at pH 6 lost activity progressively as the calcination temperature was raised. By withdrawing samples at critical points during the preparation, we have shown that the adsorbed precursor (the form of which determines the size of the gold particles) is in fairly rapid equilibrium with gold species in solution. This permits easy control of the gold particle size during the preparation and even allows the poor activity of a dried catalyst initially prepared at non-optimum pH to be substantially improved.

1. Introduction

The discovery by Haruta [1] and his associates that suitably prepared gold catalysts have activity for the oxidation of CO that is much higher than that shown by the noble metals of Groups 8–10 has stimulated extensive work in a number of laboratories [2–4]. The consensus is that high activity requires the metal particles to be very small, ideally 2–3 nm: for wet chemical methods of preparation this seems to be most readily achieved with oxides of certain transition metals. It is possible that the transition-metal oxide is also able in some way to assist in the reaction, but it should be noted that high activity has also been reported for silica-supported gold (prepared by chemical vapour deposition) [5]. Two preparative methods in particular have been shown to be effective for the synthesis of transition-metal oxide-supported gold catalysts for CO oxidation: (i) the so-called deposition-precipitation (DP) method used by Haruta's group and (ii) coprecipitation [6]; the former has been more widely used. Classical methods employing impregnation [7–9], reduction, and ceramic oxide supports have had very limited success in this reaction, at least in part because the procedures yield gold particles that are too big to be effective.

The DP method used to date entails, in essence, placing the support in contact with an aqueous solution of $HAuCl_4$, the pH of which has been raised by the addition of a base, so that upon heating an oxidic precursor is formed on the support. This seemingly simple procedure is capable of numerous variations, some of which have been described in the literature, but all too often the published accounts omit details that might be important or even critical, and the rationale behind the conditions selected is rarely explained. The

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[*] Correponding author.
E-mail address: f.moreau@salford.ac.uk (F. Moreau).

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variety of procedures used is responsible for the considerable range of activities reported and for the degree of importance attached to certain of the steps. Of these, calcination stands out as being of uncertain value. Some consider it to be essential [10–12]; others think it is detrimental [13].

Louis et al. [10] have shown by TEM that at 473 K gold particles present small facets with rounded edges and a large proportion of low coordinated sites, and that the negative effect of calcination above 573 K, which is generally admitted [11,12], can be explained by a change in morphology, particularly a smoothing of the surface.

The literature therefore presents a very unsatisfactory picture of the optimum procedure that should be adopted to secure high activity for carbon monoxide oxidation and is largely silent on the chemistry that takes place during the preparation. Furthermore, the influence of metal loading is unclear.

The DP method of preparing Au/TiO_2 catalysts includes the control of the following variable parameters: (i) the concentration of the $HAuCl_4$ solution; (ii) the ratio of its volume and concentration to the mass of support; (iii) the type of TiO_2 (Degussa P-25 is the most commonly chosen); (iv) the base chosen to neutralise the $HAuCl_4$ solution; (v) the temperature at which this is done; (vi) the pH, both at the time the TiO_2 is added and subsequently; (vii) the time and the temperature allowed for the deposition to occur; (viii) the method of filtration, washing, and drying; (ix) the conditions for calcination if performed; and (x) the apparent sensitivity of the precursor to light (some therefore recommend that all manipulations be performed in the dark [14]). Very careful selection and control of all of the variable parameters are therefore necessary if reproducible products are to be obtained, and an understanding of the chemical basis for this is essential for total control over the outcome. A further disturbing feature of the DP method is that the conditions used most often lead to incomplete transport of the gold to the support, with the degree of recovery (i.e., the actual gold loading obtained) varying widely, although the best specific activity is often found when the recovery is far from complete. This is clearly not ideal for the scaling up of the procedure as required for industrial or environmental applications; the recovery of gold from the filtrate adds to the production costs.

We may expect that a critical factor will be the nature of the gold species in solution at the time the support is introduced, so it is important to know how their concentrations vary with pH. Three kinds of processes appear to occur as the pH is raised (Scheme 1): (i) displacement of Cl^- from a complex anion by water, giving a neutral species (steps 1 and 3); (ii) loss of a proton from a neutral hydrated ion (steps 2 and 4); and (iii) hydrolysis by replacement of Cl^- by OH^- (steps 5 and 6) [15]. There are several reports in the literature [16–21] concerning the progress of the hydrolysis of the $AuCl_4{}^-$ ion as the pH is raised, and they are not all in good agreement (particularly at high pH). We choose to use the equilibrium constants measured by Nechayev and Nikolenko [21] as a basis for discussion; they lead to the results shown in Fig. 1. The neutral $AuCl_3 \cdot H_2O$ is the major species at about pH 3–4, and at pH 7, which is most often selected in the DP method of catalyst preparation, $AuCl(OH)_3{}^-$ is probably prevalent. At pH 10 and above, the $Au(OH)_4{}^-$ anion is the dominant species. The isoelectric point of P-25 TiO_2 is reported to be in the range of 4.5–6.3 [22], so that anionic species should adsorb by electrostatic attraction at lower pH; neutral species, of course, will not adsorb in this manner.

$$[AuCl_4]^- + H_2O \rightleftarrows AuCl_3(H_2O) + Cl^-$$
$$AuCl_3(H_2O) \rightleftarrows [AuCl_3(OH)]^- + H^+$$
$$[AuCl_3(OH)]^- + H_2O \rightleftarrows AuCl_2(H_2O)(OH) + H^+ + Cl^-$$
$$AuCl_2(H_2O)(OH) \rightleftarrows [AuCl_2(OH)_2]^- + H^+$$
$$[AuCl_2(OH)_2]^- + H_2O \rightleftarrows [AuCl(OH)_3]^- + H^+ + Cl^-$$
$$[AuCl(OH)_3]^- + H_2 \rightleftarrows [Au(OH)_4]^- + H^+ + Cl^-$$

Scheme 1. Progress of the hydrolysis of the $AuCl_4{}^-$ ion as the pH is raised.

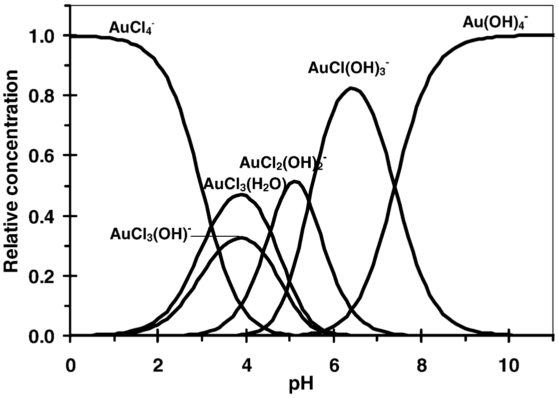


Fig. 1. Relative equilibrium concentration of gold complexes ($[Cl^-] = 2.5 \times 10^{-3}$ M) as a function of the pH of the solution, calculated with equilibrium constants reported by Nechayev et al. [15].

Given the several hundred papers and patents now published on catalysis by gold, it is curious that so little attention has been given to gold catalysts containing less than 1% gold. In contrast, the use of low loadings is common for supported metals of Group 10 when they are used for petroleum reforming and environmental control. Catalysts with 0.01–0.5% gold on various supports (SiO_2, Al_2O_3, MgO, Co_3O_4, Fe_2O_3, TiO_2) have been used for the reduction of NO, N_2O decomposition, alkene hydrogenation, and propene epoxidation [23–28]. The few studies of low-loading supported gold catalysts that concern CO oxidation are listed in Table 1; however, the use of different test conditions (temperature, contact time, CO/O_2 ratio, time on stream, etc.) makes comparison difficult [28–34]. The only paper reporting on a range of gold contents (0.5–3.1%) showed that specific activity (i.e., rate per unit mass of gold) decreased significantly, albeit somewhat irregularly, as the gold loading was lowered [34].

Table 1
Specific rates of CO oxidation for Au/TiO_2 catalysts

Au (wt%)	Temp. (K)	$10^4\ \mathrm{mol_{CO}\ s^{-1}\ g_{Au}^{-1}}$	Ref.
0.5	300	7.3	[a]
0.5	300	0.76	[33,34]
0.7	300	0.99	[33,34]
1.8	300	0.31	[33,34]
2.3	300	1.8	[33,34]
3.1	300	6.5	[33,34]
0.15	323	76	[30]
0.05–1.0	[b]	[b]	[31]
3.0	278	5.0	[9]
0.06–1.9	243	3.9	[c]
0.06–1.9	278	23	[c]
0.06–1.9	300	61	[c]
0.06–1.9	323	110	[d]

[a] The present work, 100% conversion, under mass-transport control.
[b] Reaction temperature not stated, influence of loading not discussed, turnover frequency $> 1\ s^{-1}$ reported.
[c] The present work, under kinetic control.
[d] The present work, from the extrapolation to higher temperatures of Arrhenius plots constructed from data obtained under kinetic control.

This paper reports a systematic study of the critical effect of pH during the preparation of Au/TiO_2 catalysts containing between 0.05 and 1.9 wt% gold and records observations of the influences of temperature during preparation and of calcination. A preliminary account of this work has already appeared [35].

2. Experimental

In our initial DP method, $HAuCl_4$ (Alfa-Aesar, 99.99%) solutions with concentrations between 1×10^{-4} and 5.2×10^{-3} M were first prepared. Their pH was raised to a fixed value with NaOH solution (0.1 M) added from a burette. The TiO_2 support (Degussa P-25, 55 $m^2\ g^{-1}$) was then added with stirring at room temperature (1 g per 50 ml of solution). The resulting suspension was heated to 343 K and vigorously stirred for 1 h; after cooling it was filtered and the solid was washed thoroughly with deionised water and then vacuum-dried at room temperature. The addition of TiO_2 always led to a decrease in pH, and a further decrease in pH took place during the heating to 343 K. Calcination was not usually performed, but when used it was carried out under air (30 $ml\,min^{-1}$) for 4 h at a temperature varying between 373 and 673 K.

The oxidation of CO was carried out in a plug-flow fixed-bed reactor, and the catalyst was supported on a silica wool bed near the bottom of one side of a U-shaped glass reactor. The gas flow (0.49 vol% CO in synthetic air) was introduced through a fine-control needle valve. Product analysis was performed on-line by means of a Varian 3300 GC and the use of a manual sampling valve, a CTR1 column (Alltech), TCD, and helium carrier gas. Temperatures were measured with an in situ thermocouple well. The experiments were carried out between 183 and 373 K. Subambient temperatures were achieved with a mixture of methanol and Cardice or liquid nitrogen; we obtained higher temperatures by heating the reactor in a furnace.

CO conversion was always measured as a function of the temperature. Activity was first tested at room temperature. For the most active catalysts, the reactor was then placed in a Dewar, and the temperature was lowered, after which it was allowed to rise stepwise to a final value. With less active catalysts, temperatures above ambient were used immediately. The standard test used a reactant flow of 55 $cm^3\,min^{-1}$ and 50 mg of catalyst (space velocity 17,000 h^{-1}).

We wanted to determine the activity under conditions of kinetic control, since in the region of diffusion control its value would be underestimated. For several of the more active catalysts, the reaction was therefore also carried out at a higher space velocity (flow rate 150 $cm^3\,min^{-1}$, 20 mg of catalyst, space velocity 115,000 h^{-1}). Plotting of specific rates according to the Arrhenius equation then reveals distinct regions corresponding to mass transport and kinetic control: even at the higher space velocity, mass-transport limitation starts to be apparent at conversions above 40%. The uncertainty in the conversion values is $\leqslant \pm 8\%$.

Characterisation was performed by powder XRD analysis in the region of $2\theta = 75°–85°$ (Cu-K_α, Siemens D500 diffractometer). The most useful gold peak was that at $2\theta = 77.4°$, since at this angle there is no overlap with the rutile or anatase peaks of the support. On each catalyst the percentage weight of gold deposited was determined by atomic absorption analysis; the calibration was performed with $HAuCl_4$ solutions of different concentration.

Transmission electron microscopy (TEM) images were obtained with a JEOL 200CX transmission electron microscope. Samples were finely ground in a mortar to fine particles and then dispersed on a copper mesh with a carbon micro-grid. Particle size was determined by observation of more than 100 particles.

3. Results and discussion

3.1. Effect of pH on the catalyst activity

The initial preparations were carried out by Haruta's DP method as described in the Experimental section. Several catalysts were prepared starting from the same gold concentration (1.0×10^{-3} M). The pH, initially 2.6, was raised to various values (4–11) by NaOH addition. However, to keep a constant pH between 4 and 9 was not an easy task, because its value tended to fall as OH^- ions were slowly consumed; the rates of both the hydrolysis of the various anions and their subsequent ligand exchange are slow, and it often took more than 1 h to reach equilibrium.

For each preparation the initial pH (pH_i) of the $HAuCl_4$ solution, the pH after TiO_2 addition (pH_a), and the final pH (pH_f) at the end of the preparation were noted. The way in which the pH changed during catalyst preparation is shown

Table 2
pH changes during the preparation: initial pH (pH_i), pH after TiO_2 addition (pH_a), pH at the end of the preparation (pH_f), nominal %Au = 1.0%

	Catalysts	pH_i	pH_a	pH_f
(1)	0.92 Au/TiO_2	4	3.3	2.2
(2)	0.93 Au/TiO_2	6	–	2.5
(3)	0.42 Au/TiO_2	6	5.2	3.1
(4)	1.07 Au/TiO_2	7	7	5.9
(5)	0.92 Au/TiO_2	9.1	5.8	6.4
(6)	0.89 Au/TiO_2	10.4	8.5	7.7
(7)	0.60 Au/TiO_2	11	9.4	8.5

in Table 2. Systematic pH decreases were observed just after TiO_2 addition and during the heating step; the first of these was more significant for preparations carried out at pH above 8.

The isoelectric point of TiO_2 is in the region of 4.5–6.3, and thus at higher pH the surface will be negatively charged, resulting in an electrostatic repulsion of gold-containing anions; this probably accounts for the fall in the gold content at pH above 6. Below pH 4.5, however, an attraction operates and the gold content is high.

Fig. 3 shows the XRD patterns for the support and for the catalysts prepared at final pH values of 2.5, 6.4, and 8.5; the gold peak becomes more clearly defined as the final pH is decreased, indicating an increase in particle size for the crystalline gold. Later in this paper we discuss XRD patterns for a series of catalysts prepared at pH 8–9 that indicate that the broad feature in Fig. 3b in the 2θ range of 77°–80° is indeed a result of the presence of gold.

TEM pictures have confirmed the dependence of the gold particle on pH. The particle size in catalysts prepared at a final pH of 8.5 was in the range of 1.5–4 nm, and the mean diameter measured with more than 100 particles was 2 nm. Preparation at a final pH of 6 led to a heterogeneous distribution of gold particle sizes in the range of 4–20 nm and an average particle size of 10 nm.

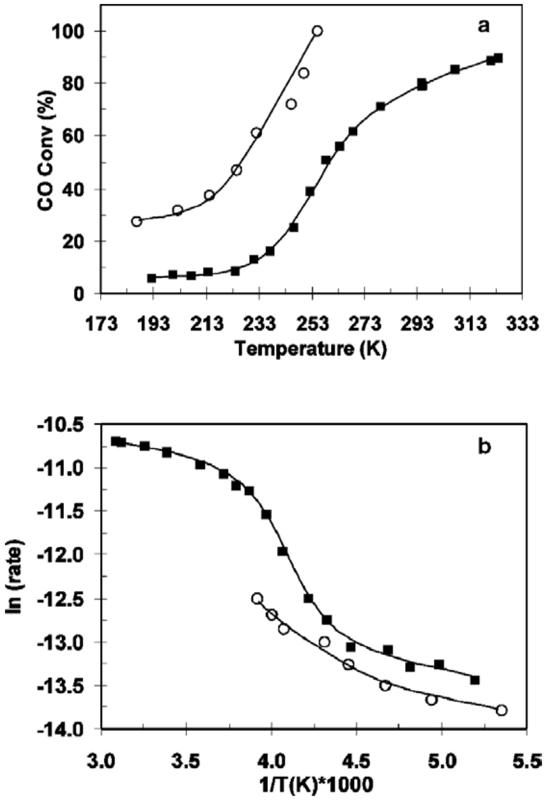


Fig. 2. CO conversion as a function of the temperature (a) and Arrhenius plot (b) for uncalcined 1.4% Au/TiO_2 catalyst, space velocity: (○) 17,000 h^{-1} (standard conditions), (■) 115,000 h^{-1}; rate in $mol_{CO}\ g_{cat}^{-1}\ s^{-1}$.

Catalysts were tested between 183 and 343 K for the oxidation of CO into CO_2. Fig. 4 shows how CO conversion depends on the temperature and on pH for uncalcined catalysts. Higher activities were obtained on catalysts prepared at pH_f 8.5 ($T_{50} = 243$ K). Despite the high deposition efficiency, a lower activity was measured for catalysts prepared

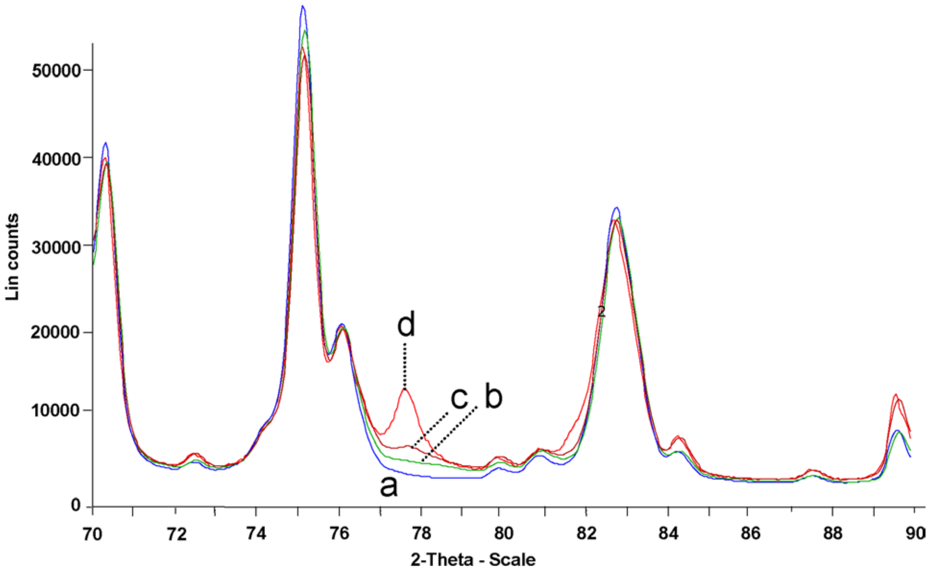


Fig. 3. XRD patterns in the region 70°–90° 2θ; (a) TiO_2, (b) 0.6 % Au/TiO_2 pH_f 8.5, (c) 0.92% Au/TiO_2 pH_f 6.4, (d) 0.93% Au/TiO_2 pH_f 2.5.

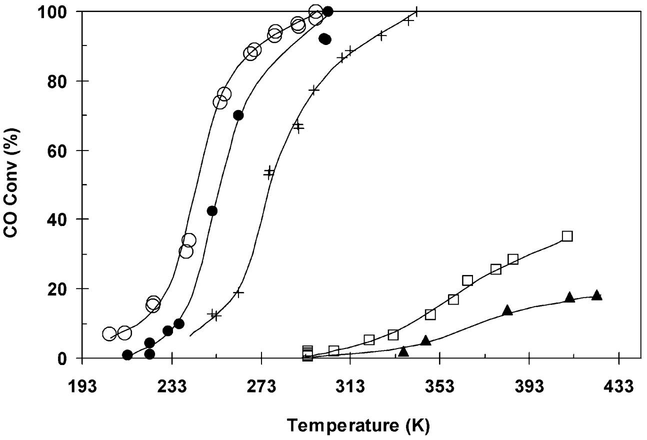


Fig. 4. CO conversion as a function of the temperature, for uncalcined catalysts, standard test conditions; (▲) 0.92% Au/TiO_2 pH_f 2.2, (☐) 0.93% Au/TiO_2 pH_f 2.5, (+) 1.07% Au/TiO_2 pH_f 5.9, (●) 0.92% Au/TiO_2 pH_f 6.4, (○) 0.60% Au/TiO_2 pH_f 8.5.

at pH_f 6.4 and 5.9, and catalysts prepared at even lower pH had very poor activity.

The most straightforward explanation of this variation in activity is that the pH decrease favours the formation of larger gold particles, which are well known to be less active for the transformation of CO into CO_2.

It now seemed important to decide on the preparation stage at which the pH is decisive in determining the size, shape, site, chemical nature, and, hence, activity of the gold particles. Is it before the support addition, after it, or at the end of the preparation? To answer this question, two catalysts were prepared: with the first, the initial pH (pH_i) of the gold solution was raised to 4 by NaOH addition; the pH was slightly affected by TiO_2 addition (pH 3.8), and it was then fixed at 9 until the end of the experiment. We prepared a second catalyst by raising the initial gold solution to pH 9, and this pH was maintained until the end of the preparation. Identical gold percentages, XRD patterns, and activities for CO oxidation (Fig. 5) were obtained on both catalysts, proving that the decisive pH was that used during the later stages of the preparation. It has proved important for high activity to keep the pH between 8.6 and 9.0 during the last minutes before filtration.

3.2. Dependence of activity on Au content using a modified DP method

The literature presents a less than clear description of the optimum deposition-precipitation preparation procedure and is largely silent on the chemistry that takes place during the preparation. This lack of precision in the preparation and particularly in the pH development during the preparation led us to reexamine attentively the preparation of Au/TiO_2 catalysts.

Based on the results described above, we decided to maintain the pH of the solution at 9 throughout the preparation. To allow for a pH decrease after the addition of TiO_2, the pH of the $HAuCl_4$ solution was raised initially to 10.4 by the addition of NaOH. The TiO_2 was then added, and the suspension was heated to 343 K; some experiments were also carried out at room temperature. The suspensions were then filtered, washed, and dried. With this method a range of Au/TiO_2 catalysts were prepared with gold loadings between 0.06 and 1.9 wt%. Typically they were pale lilac in colour.

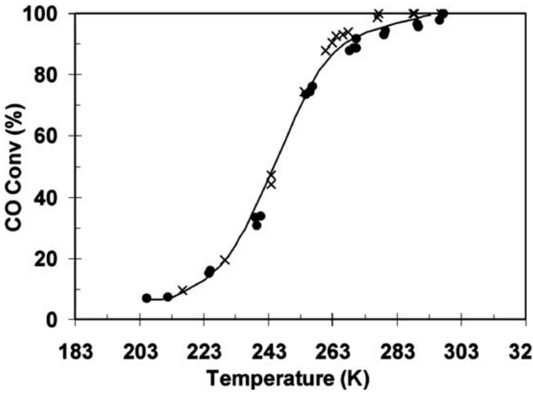


Fig. 5. CO conversion as a function of the temperature for uncalcined catalysts, standard test conditions: (×) 0.47% Au/TiO_2 (pH_i 4 and pH_f 9) and (●) 0.55% Au/TiO_2 (pH_i 11 and pH_f 8.5).

Three of the XRD patterns are shown in Fig. 6; the intensity at $2\theta \sim 78^\circ$ remained broad, but it increased with gold content. The fraction of gold in the initial solution that was deposited on the support was fairly constant (0.70–0.75) up to a nominal content of 0.95 wt% but decreased somewhat for 1.4 wt%.

Fig. 7 shows that the activity of uncalcined catalysts increases with the gold loading. For a loading of 0.95 wt%, we obtained a T_{50} of 243 K, indicating a substantial improvement on the previously reported values of 282–320 K for this loading at a similar space velocity [33,34]. Arrhenius plots showed, however, that for 0.95–1.9 wt% Au/TiO_2 catalysts the reaction was under mass-transport control over most of the range of conversion covered when our standard space velocity was used. Specific rates for the most highly loaded catalysts (0.95, 1.4, and 1.9 wt%) were therefore determined at the higher space velocity. Activation energies determined from data measured under kinetic control were $\approx 35\ \mathrm{kJ\,mol^{-1}}$, independently of gold loading, and in good agreement with the literature [3].

Very active catalysts, that is those containing more than about 1% gold, allowed measurements to be made in the range of 173–223 K, where the conversion fell only slowly as the temperature was lowered (see Fig. 2a for an example). The activation energy here was 0–5 $\mathrm{kJ\,mol^{-1}}$ (Fig. 2b). It seems possible that the reaction in this range involves an unstable but highly active oxygen species adsorbed on the gold, such as O or $O_2{}^-$; such species have been postulated to occur on other sp metals such as zinc and magnesium [36,37]. Because of its instability the concentration of such a species

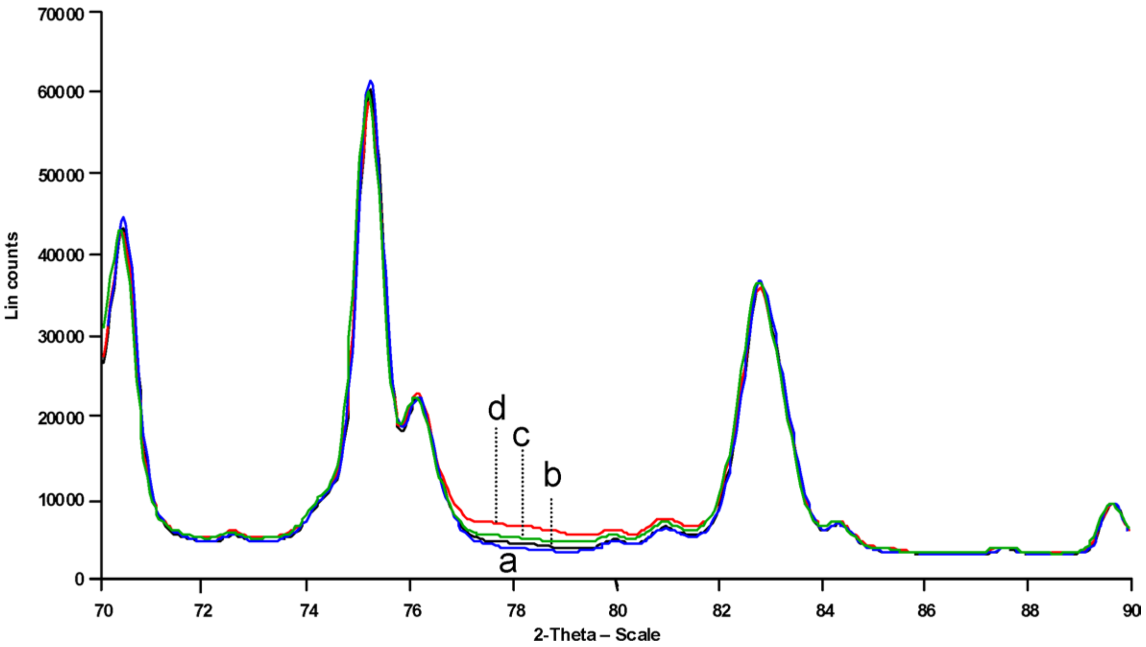


Fig. 6. XRD pattern in the region 70°–90° 2θ of: (a) TiO_2, (b) 0.14% Au/TiO_2, (c) 0.77% Au/TiO_2, (d) 1.4% Au/TiO_2 prepared at a final pH of 9.

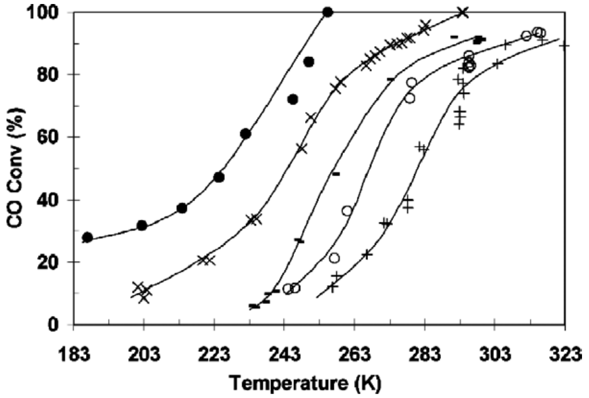


Fig. 7. CO conversion as a function of the temperature for uncalcined catalysts, standard test conditions; (●) 1.4% Au/TiO_2, (×) 0.95% Au/TiO_2, (−) 0.25% Au/TiO_2, (○) 0.14% Au/TiO_2, (+) 0.06% Au/TiO_2.

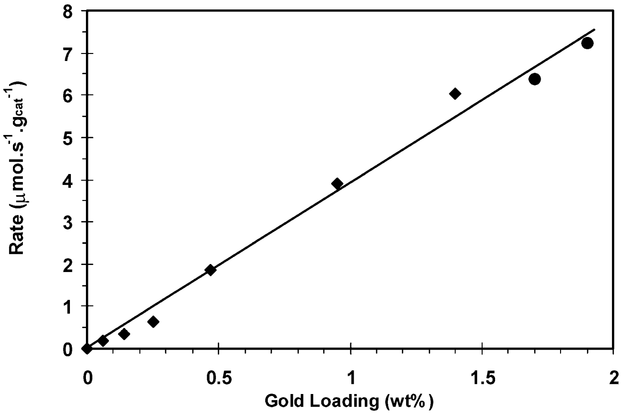


Fig. 8. Rates for uncalcined Au/TiO_2 catalysts as a function of gold wt% at 243 K, (◆) preparation at 298 K, (●) preparation at 343 K.

Table 3
Reproducibility tests for low loading Au/TiO_2 catalysts prepared under identical condition (final pH 9, $[HAuCl_4] = 4 \times 10^{-4}$ M); gold deposited (Au wt%), gold deposition efficiency (%*DP*), temperature at 50% conversion (T_{50}), specific activity (r_{sp}), and activation energy (E_a)

Catalyst	T (K)	Au (wt%)	%*DP*	T_{50} (K)	$r_{sp} \times 10^4$ ($mol_{CO}\,s^{-1}\,g_{Au}^{-1}$)	E_a ($kJ\,mol^{-1}$)
1	343	0.14	70	266	3.1	34
2	343	0.12	60	273	2.6	35
3	293	0.14	70	268	3.0	34
4	293	0.15	70	263	4.0	37

would fall quickly as its temperature is raised, causing the apparent activation energy to be very low or even zero.

Fig. 8 shows rates obtained at 243 K (under kinetic control at all loadings). They increase linearly with the gold loading; consequently the specific activity (per unit mass of gold) is the same for all of the catalysts, and its value of $3.9(\pm 0.4) \times 10^{-4}\ mol_{CO}\,s^{-1}\,g_{Au}^{-1}$ is higher than those reported in the literature (Table 1).

The most logical explanation for this constant specific activity is that our preparation method produces a similar distribution of gold particle sizes at all loadings, and hence the number of active sites just increases in simple proportion to the gold content.

The preparation method also has the advantage of being very reproducible; catalysts prepared in batches ranging from 3 to 30 g gave similar gold weight percentages (0.15 wt% Au/TiO_2) and activities for CO oxidation (Table 3). Two preparations were also carried out wholly at room temperature, without affecting catalyst properties. From an initial value of 0.90, during 100 h of continuous

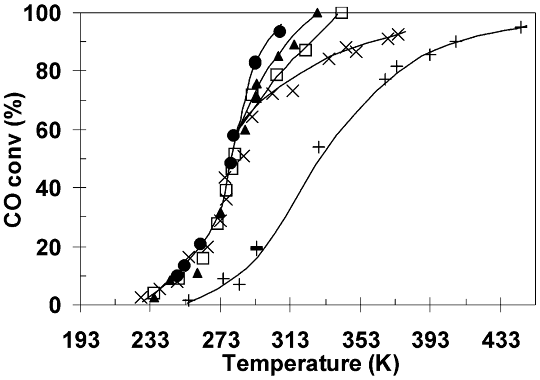


Fig. 9. CO conversion as a function of the temperature for 0.14% Au/TiO_2 prepared at final pH 9, standard test conditions; (●) uncalcined; calcination: (□) 373 K, (▲) 473 K, (×) 573 K, and (+) 673 K.

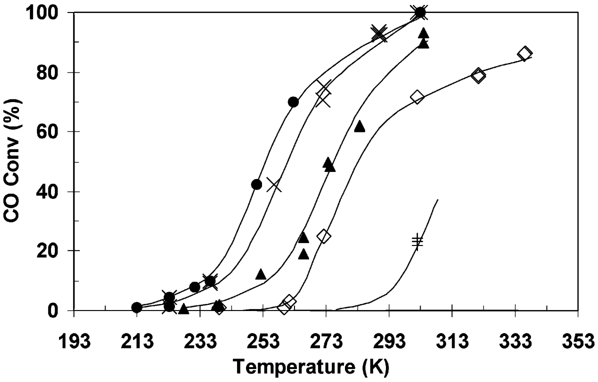


Fig. 10. CO conversion as a function of the temperature for 0.92 wt% Au/TiO_2 prepared at final pH 6, standard test conditions; (●) uncalcined; calcination: (×) 373 K, (▲) 473 K, (◇) 573 K, and (+) 673 K.

operation, the fractional conversion typically decreased by 0.003 h^{-1}.

As mentioned earlier, low-loading gold catalysts have been studied by only a few authors, and Haruta and his colleagues have reported an exponential decrease in the CO oxidation rate with decreasing gold content (Table 1) [33,34]. A series of catalysts with loading in the range of 0.5–3.1 wt%, with fairly similar average particle sizes, had significantly lower specific activity (per unit mass of gold) at the low loadings; for some reason it would appear that a gold particle on the order of 3 nm in diameter is less active when present at low loading. However, it is difficult to explain the anomalous drop in specific activity observed on the 1.8 wt% Au/TiO_2 catalyst (Table 1).

The difference between our results and those of Haruta might be explained by the careful pH control performed in the present work. In addition to the advantages of reproducibility of preparation and high activity, the fact that this method results in a constant specific activity allows the replacement of a high gold loading catalyst with a larger quantity of low-loading catalyst, potentially leading to a better control of heat transfer and temperature hot spots resulting from the exothermic reaction. Moreover, the lower surface density of gold on the support probably limits sintering and Ostwald ripening. These factors therefore ought to encourage the use of catalysts with low gold contents for CO oxidation.

3.3. Dependence of activity on calcination temperatures

Calcination was performed at 373, 473, 573, and 673 K, for catalyst series prepared with final pH values of both 6.4 and 9. XRD patterns for calcined and uncalcined catalysts within each series were identical, indicating that calcination to 673 K does not significantly affect the size of the crystalline gold particles.

As seen in Fig. 9, for catalysts prepared at pH 9, for conditions resulting in kinetic control, the activity was essentially unchanged by calcination up to 573 K, but when catalyst were calcined at 673 K, a substantial loss in activity was observed, in agreement with the literature [9–11]. At conversions greater than 70%, where diffusion control dominates, the activity is slightly affected by calcination. In contrast, on the series prepared at a final pH of 6.4, the activity decreased progressively with increasing calcination temperature; as seen in Fig. 10, calcination at just 473 K causes substantial loss of activity. There are two possible factors that contribute to this: (i) At pH 6.4 the gold ions in solution are still rich in chlorine, and if retained by the support they would have a detrimental effect, perhaps assisting the mobility of gold atoms during calcination and affecting the particle morphology. At pH 9 there would be fewer chlorine ligands associated with the gold complex adsorbed on the support and the chloride ions probably would be more easily eliminated by washing. (ii) As discussed earlier, there is also a difference in the particle size. At pH 6.4 some large particles are created and probably some small ones as well, whereas at pH 9 large crystalline particles are absent. The existence of a mixture of sizes in the former case provides a driving force for Ostwald ripening, which does not exist when the particles are uniformly small.

The greater effect of heating on conversion in the regime of diffusion limitation (Fig. 9) is not easily explained; there may be some physical aggregation of the titania particles as their surface is dehydroxylated (starting at about 423 K), inhibiting mass transport at high conversion.

3.4. Analysis performed at various stages of interrupted preparations

A clearer understanding of the way in which pH at various stages of the preparation affects the properties of the finished catalyst has been obtained by withdrawing samples for analysis at critical points in an experiment in which the pH is systematically varied during a single preparation. The protocol used is shown in Fig. 11, together with the coding used to identify each sample. The experiment was carried out with 10 g of TiO_2, corresponding to an initial volume of 500 ml of chloroauric acid solution. For each critical point,

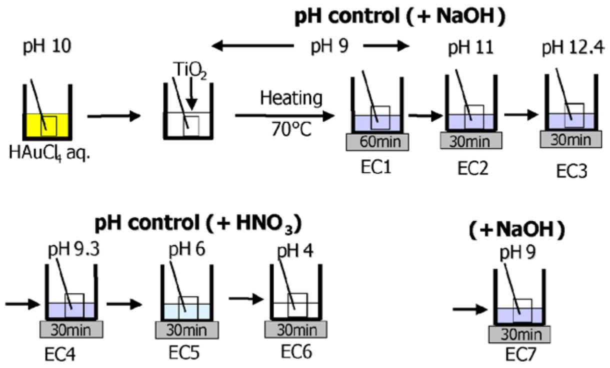


Fig. 11. Sequential withdrawal of samples for analysis: schematic to illustrate protocol.

Table 4
Time, final pH of the preparation (pH_f), gold deposited (Au wt%), gold deposition efficiency (*%DP*), temperature at 50% conversion (T_{50}), specific activity (r_{sp}), and activation energy (E_a) of the EC1–EC7 catalysts

Catalyst	Time (min)	pH_f	Au (wt%)	*%DP*	T_{50} (K)	$r_{sp} \times 10^4$ ($mol_{CO}\, s^{-1}\, g_{Au}^{-1}$)	E_a ($kJ\, mol^{-1}$)
EC1	90	9	0.75	60	248	1.7	26
EC2	120	11	0.50	40	260	1.0	35
EC3	150	12.4	0.35	28	291	0.8	24
EC4	180	9.3	0.90	72	243	1.6	25
EC5	210	6	1.23	98	260	0.5	27
EC6	240	4	1.25	100	403	0.0022	33
EC7	270	9.3	0.97	78	248	1.9	29

EC1–EC6, 25-ml aliquots were recovered with a syringe without interruption of the preparation.

The pH of an $HAuCl_4$ solution (sufficient to give a nominal gold loading of 1.25%) was raised to 10.4, and TiO_2 was added. The pH was raised to 9 by the addition of NaOH (0.5 M), and the first sample was recovered after 1 h of mixing (EC1); this stage of the preparation corresponded to our DP method (reference catalyst). The pH of the solution was then raised and maintained for 30 min at 11 (EC2), and then raised again to 12.5 (EC3). After each pH change the suspension was stirred for 30 min. The addition of nitric acid (0.5 M) led to a progressive pH decrease, during which further samples were taken at pH 9 (EC4), pH 6 (EC5), and pH 4 (EC6), and finally the pH was raised again to 9 by NaOH addition. This latter suspension provided catalyst EC7. All samples were filtered, washed, and dried.

The results are summarised in Table 4. Gold uptakes at pH 9–9.3 were about the same (60–78%), regardless of the point at which this pH was attained, and they varied with pH much as was found earlier (Table 2), with low values found at high pH. In this experiment uptakes close to 100% occurred at pH 4 and 6, which is the range in which the isoelectric point of the support occurs. Results for XRD characterisation are shown in Fig. 12. The catalyst prepared at pH 9 (sample EC1) corresponds to our standard DP procedure, and as before showed only a broad signal at $2\theta = 77°–78°$, whereas changing the pH to and then 4 gave products (EC 5 and 6) that showed both greater intensity and a more clearly defined peak in this region, indicating as before the presence of larger particles. The most important observation was that finally increasing the pH back to ~ 9 (EC7) again resulted in a catalyst without large crystalline particles. This shows that the form of the precursor, which must determine the ultimate gold particle size, is reversible by a change in the pH; that is, the form observed at, say, pH 4 is altered to that found at pH 9, probably by dissolution and re-precipitation.

Fig. 13 shows conversion-temperature plots for each uncalcined catalyst; the harmful effects of using high and low pH values are clearly indicated. The final reversal of the pH to 9 restored high activity. Table 4 gives the specific rates at 243 K, as well as values of T_{50} and activation energies obtained under kinetic control. Specific rates for samples obtained at pH ~ 9 are almost constant ($r_{sp} \times 10^4 = 1.6$–

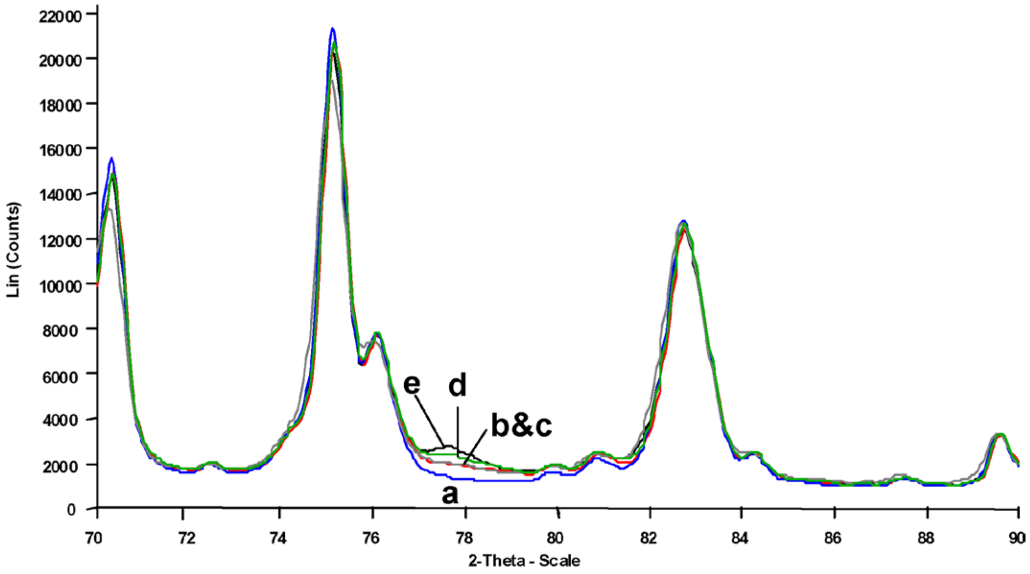


Fig. 12. XRD patterns in the region 70°–90° 2θ of: (a) TiO_2, (b) and (c) EC2 and EC8 pH_f 9, (d) EC6 pH_f 6 and (e) EC7 pH_f 4.

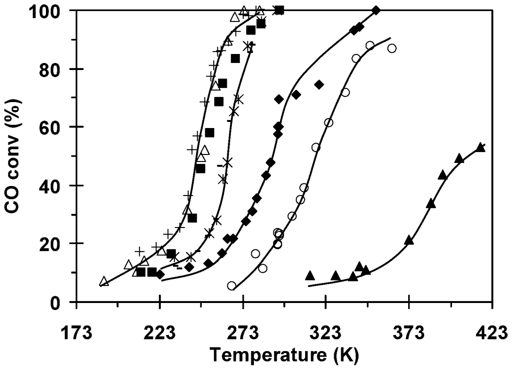


Fig. 13. Effect of pH at various stages of an interrupted preparation on CO conversion as a function of the temperature for uncalcined EC (Au/TiO_2) catalysts, standard test conditions, ((□) EC1, (−) EC2, (◆) EC3, (△) EC4, (○) EC5, (▲) EC6, (+) EC7). See text and Table 4 for further details.

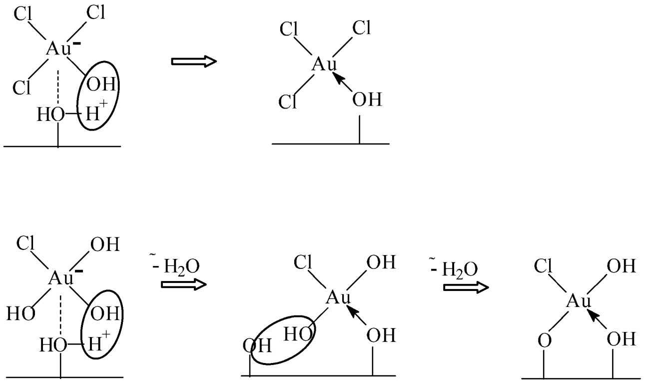
Table 5
pH final of the preparation (pH_f), gold deposited (Au wt%), temperature at 50% conversion (T_{50}), specific activity (r_{sp}) at 243 K, and activation energy (E_a) of the catalysts before (A, B) and after recovery process (A_R, B_R)

Catalyst	Au (wt%)	pH_f	T_{50}	$r_{sp} \times 10^4$ ($mol_{CO}\,s^{-1}\,g_{Au}^{-1}$)	E_a ($kJ\,mol^{-1}$)
A	0.92	3.3	> 433	0.013	26
A_R	0.46	9	256	2	39
B	0.86	2.2	473	0.013	22
B_R	0.42	9	268	1.5	26

1.9 $mol_{CO}\,s^{-1}\,g_{Au}^{-1}$), and except for the low rate found at pH 4, all of the rest give $r_{sp} \times 10^4$ in the range of 0.5–1.9 $mol_{CO}\,s^{-1}\,g_{Au}^{-1}$, showing that the low activity at high pH is due chiefly to the lower gold content. We have already suggested that the low activity at pH 4 could be due to a larger particle size, higher chloride content, or both.

The results obtained by interruption of the course of the preparation by this intermediate raising and lowering of the pH are broadly similar to those reported earlier, where the pH was moved immediately to its final value. Specific rates are slightly lower than those given earlier, because, as suggested by the values of the activation energies, the rates may not always have been entirely free of mass-transport limitation. The reversible changes produced by alteration of pH may be of value in the preparation of gold catalysts on an industrial scale.

The results described above led to a further experiment in which the recovery of activity was attempted for unused, dried catalysts prepared at non-optimum pH. Two catalysts (A and B) were chosen for their low activity and significant gold content (Table 5). Both batches were prepared at a final pH of 3; they showed a sharp and intense XRD signal at $2\theta = 77°–78°$, indicating the presence of large gold particles, and their activity for CO oxidation was low, giving $T_{50} > 433$ K.



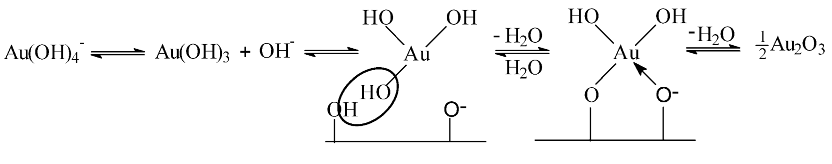
Scheme 2. Adsorption of gold anions at positively charged TiO_2 surface and possible subsequent reaction.

Unused samples of the catalysts were dispersed in deionised water (50 ml per g of catalyst), and the pH of the solution was raised and then maintained throughout at 9 by NaOH addition. The resulting suspension was heated to 343 K and vigorously stirred for 1 h; after cooling it was filtered, washed with deionised water, and dried under vacuum.

On the recovered catalysts, A_R and B_R, respectively 0.42 and 0.46 wt% gold was retained (Table 5). The gold peak at $2\theta = 77°–78°$ became broader, indicative of a diminishing gold particle size; however, the band is slightly sharper than the signal obtained with a catalyst prepared directly at pH 9 and containing a similar gold percentage, probably indicating the presence of a few larger gold particles.

The catalysts were tested between 183 and 293 K for CO conversion into CO_2. The recovery attempt led to a substantial improvement in activity; T_{50} values of 265 K and 260 K were obtained for A_R and B_R, respectively. The activity at 243 K of 2×10^{-4} $mol_{CO}\,s^{-1}\,g_{Au}^{-1}$ is, however, slightly lower than those obtained for catalysts prepared directly at pH 9; the difference is probably due to the presence of the larger particles mentioned above.

We must keep in mind that the recovery has been demonstrated for uncalcined, virgin catalysts, that were never in contact with CO and consequently not chemically altered, sintered, or otherwise modified under calcination or reaction conditions. In these fresh catalysts the gold is probably partly present in an oxidised form, which may, for example, be transformed into a metallic form during the reaction. It remains to be seen whether the recovery process described here can also assist in the reactivation of a used catalyst.



Scheme 3. Adsorption of $Au(OH)_3$ on negatively charged TiO_2 surface and possible subsequent reactions.

3.5. *Mechanism of pH effect*

In the pH region where the TiO_2 surface is positively charged ($\lesssim 4.5$–6.3) and is populated by protonated hydroxyl groups (H_2O^+–), the gold species in solution comprise anions $AuCl_x(OH)_{4-x}{}^-$ ($x = 1$–4) and, between pH 2 and 5, the neutral $AuCl_3 \cdot H_2O$ (Fig. 1). We may therefore suppose that much of the initial adsorption is electrostatic in character; each anion may be attracted to a single positive centre, but other formulations involving two or more centres are possible. Spectroscopic studies are needed to resolve this. The only uncertainty concerns the pH 2–5 region, where adsorption of anions may disturb the solution equilibrium and cause ionisation of the neutral complex. Alternatively, the low gold uptake observed at pH 3.1 (Table 2) may reflect the reluctance of this species to interact with the positively charged surface. On filtration and drying, further changes may be expected; these are outlined speculatively in Scheme 2.

When the surface is definitely negatively charged (pH $\gtrsim$ 6) because of deprotonation of surface hydroxyls, the predominant species in solution is probably $AuCl(OH)_3{}^-$ and/or $Au(OH)_4{}^-$ and simple electrostatic attraction cannot operate; some other mechanism is required. A neutral $Au(OH)_3 \cdot H_2O$ may exist in solution in equilibrium with the anion, and this may interact with the surface as suggested in Scheme 3. Gold uptake decreases progressively as the final pH is raised above 8 (Table 4), so clearly there is a mobile equilibrium between the adsorbed species and those in solution, in which the solution side is more favoured as the pH is increased.

The effect of abrupt changes to the pH of the suspension as in the interrupted experiment may be to directly change the nature of the adsorbed species or may lead to their dissolution and re-adsorption in a modified form.

The irony of this method of catalyst preparation is that in the pH range where gold uptake from solution is very high, somewhat large gold particles are formed, and activities are correspondingly low, and per contra best size and activity are observed where the uptake is far from complete. It may be that during the stages leading to the formation of metallic gold from the precursor, below pH 6–7 the support surface and/or the adsorbed complexes still retain some chloride ion, and this encourages mobility and aggregation. Above pH ~ 8 the adsorbed precursor is substantially chlorine-free, the adsorption of chloride ions is less favourable, and excessive particle growth does not occur.

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