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Preparation and reactivation of Au/TiO_2 catalysts

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Abstract

In the preparation of Au/TiO_2 (P-25) catalysts by the method commonly but inaccurately known as deposition–precipitation (DP), the uptake of anionic complexes in solution onto the support is maximal close to the pH of the isoelectric point (~6); below this pH, complexes are adsorbed electrostatically, but at higher pH values, especially at pH 8–9, the neutral $Au(OH)_3{\cdot}H_2O$ is reversibly adsorbed on the negatively charged surface. The specific activity (per gram of gold) peaks however at pH 8–9, because here the adsorbed complex is largely chlorine-free. The reversibility of the adsorption equilibrium is proved by alteration of the pH during the course of a single preparation through analysis of samples removed at intermediate points. This observation enables poorly dispersed precursors or sintered gold particles to be re-dispersed, and high activity restored.

Keywords: Au/TiO2; pH and temperature effect; Redsipersion

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1. Introduction

Realising the potential of gold catalysts to be superb for the oxidation of CO at low temperatures hinges on finding means of creating very small particles (<3 nm) on a supporting oxide that is capable of assisting the reaction. It is now well established that the support is preferably an oxide of a transition metal, the surface of which is able to be partially reduced by the CO during the reaction; although TiO_2, chiefly as Degussa P-25, has been widely used, other transition metal oxides show much promise [1,2]. Many ways have been explored for making gold particles of the necessary small size. Coprecipitation was initially favoured [1], but is not now much used; impregnation is not generally successful, because both it and direct anion exchange require laborious washing to eliminate chloride ion. Our attention has therefore been focussed on the method known as deposition–precipitation.

In this method the pH of a solution of $HAuCl_4$ is raised by addition of a base, to the point where the adsorption of the species then in solution can react with or be deposited on the support. The name 'deposition–precipitation' was initially applied presumably because it was thought that the support would nucleate the formation of $Au(OH)_3$ on it, but this is now thought unlikely. The method is however capable of very many variations [3,4] and the product catalyst is sensitive to small alterations to the conditions used. The objective of such work is not merely to secure the formation of small gold particles, and hence high activity for CO oxidation, but also to obtain a material showing stable activity, and to find ways in which the gold precursor is completely removed from the solution; this is vitally important if the method is ever to be considered for large-scale manufacture.

One of the most important variables is the pH at which the preparation is conducted. The principal purpose of the work to be described is to explore this parameter, and hence to understand something of the mechanism by which the catalyst precursor is formed. This understanding has allowed us to propose procedures by which poorly prepared or sintered catalysts may be reactivated.

2. Experimental

2.1. Catalyst preparation and characterisation

Procedures used have been described in detail in previous publications [3,5], and so are only briefly summarised. The pH of aqueous $HAuCl_4$ solution (10^{-3} M) was raised to the desired point by addition of NaOH at room temperature. Insertion of the P-25 support led to some decrease in the pH, which was rectified by further addition of base. The suspension was heated

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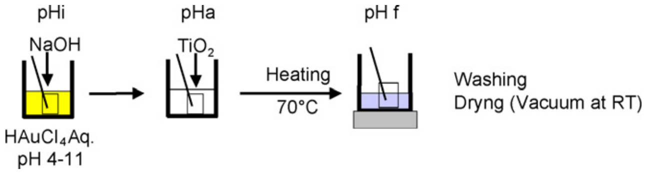

Fig. 1. Schematic of the deposition precipitation method.

at 343 K for 1 h, and more base was added as necessary; after cooling and filtration, the solid was washed and vacuum-dried at room temperature (Fig. 1). 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, it was found that the catalyst activity was directly link to the final pH of the preparation [3,5]. This procedure follows closely that described by Tsubota et al. [6]. The precursor was stored in the dark, and the preparations were made in full daylight; in our experience, confirmed by the literature [7], the discoloration of the surface caused by photochemical reduction of the precursor is not harmful to the activity. Other precursors used in this work are described in due course. Degussa P-25 was always used as support, and the target gold loading was normally 1%.

Gold contents were determined by atomic absorption spectroscopy, and selected samples were subjected to XRD to obtain an estimate of mean particle size; transmission electronic microscopy was performed at the Fritz Haber Institute in Berlin.

2.2. Catalyst testing

The procedure has been described before [3,5]. Standard test conditions used 1% CO in synthetic air, 50 mg catalyst and a flow-rate of 55 ml min^{-1}. Temperature was varied in the range 183–473 K. It is particularly important that activities be measured when the reaction is under kinetic control, and not subject to mass transport limitation. Since conversions at room temperature were often near 100%, a shorter contact time was used when life-tests were conducted under this condition.

3. Results and discussion

3.1. The effect of the pH variation

Some quite complex chemistry takes place when the pH of an $HAuCl_4$ solution is raised when using the so-called DP method [4]. The concentration of the various gold species formed by the hydrolysis of the $AuCl_4^-$ ion (Table 1) is pH dependent; broadly speaking the extent of hydrolysis increases with pH, and we may use published calculations (Fig. 2 [8]) to indicate the probable species and their importance as a function of pH. Above pH 8 the fully hydrolysed $Au(OH)_4^-$ ion predominates; the extent of hydrolysis at any pH increases as the gold concentration goes down.

Table 1
Influence of the pH on the gold species in solution

$[AuCl_4]- + H_2O \rightleftarrows AuCl_3(H_2O) + Cl^- \quad K_1 = 4 \times 10^{-6}$
$AuCl_3(H_2O) \rightleftarrows [AuCl_3(OH)]^- + H^+ \quad K_2 = 2.6 \times 10^{-1}$
$[AuCl_3(OH)]^- + H_2O \rightleftarrows AuCl_2(H_2O)(OH) + Cl^- \quad K_3 = 3.6 \times 10^{-3}$
$AuCl_2(H_2O)(OH) \rightleftarrows [AuCl_2(OH)_2]^- + H^+ \quad K_4 = 2.8 \times 10^{-5}$
$[AuCl_2(OH)_2]^- + H_2O \rightleftarrows [AuCl(OH)_3]^- + H^+ + Cl^- \quad K_5 = 9.0 \times 10^{-9}$
$[AuCl(OH)_3]^- + H_2O \rightleftarrows [Au(OH)_4]^- + H^+ + Cl^- \quad K_6 = 1.0 \times 10^{-10}$

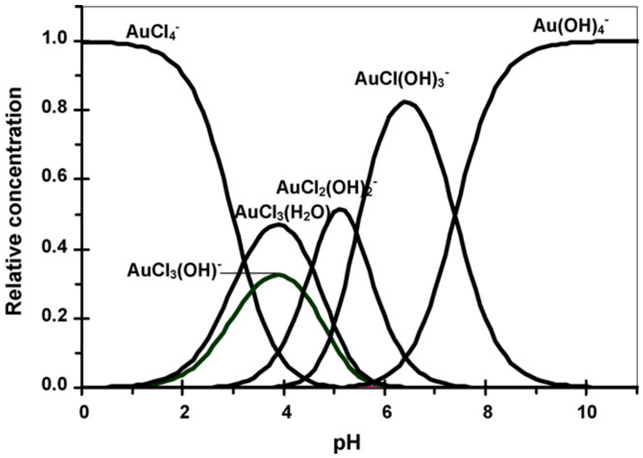

Fig. 2. Calculated dependence on pH of the concentrations of anionic gold species derived from $AuCl_4^-$ by hydrolysis, total [Au] = 4×10^{-3} M [8].

The charge on the TiO_2 surface is also pH dependent. Below the isoelectric point (pH 6 [9]) it is positive due to protonation of the surface hydroxyls; above pH 6 the charge is negative due to removal of protons from the surface hydroxyls, so the observed decrease in pH when TiO_2 is added to the $HAuCl_4$ solution (see Table 2) is due to the neutralisation of hydroxyl ions in solution by acidic surface hydroxyl groups. This means that below the IEP electrostatic adsorption of the gold anions is possible, as is direct anion exchange [10]; above the IEP some other mechanism must operate. We observe the gold uptake of gold from solution to be maximal (and almost complete) in the region of the IEP (Table 2), but it falls progressively and seriously as the pH is increased. This is unfortunate, because the specific activity (expressed per gram of gold) is low around the IEP, and only increases to its maximum value at about a final pH of 9 (Table 2) where the gold uptake is unsatisfactory.

The reason for this becomes evident when catalysts are characterised. X-ray diffraction shows that the peak at $2\theta = 77.5$ °C decreases and finally disappears as the pH is

Table 2
Effect of final pH (pH_f) on gold content and activity

Au (wt%)	pH_f	T_{50} (K)	$r_{sp} \times 10^4$ (mol $_{CO}$ s^{-1} $g^{-1}$$_{Au}$)
0.92	2.2	>433	0.03
0.93	2.5	463	0.016
1	5.9	273	0.25
0.89	7.7	253	1.1
0.60	8.5	246	2.7
0.65	9	243	3.7
0.16	11.5	293	2.0
0.06	12.5	373	0.01

Column headings: Au weight percentage (Au wt%), pH at the end of the preparation (pH_f), temperature at 50% conversion (T_{50}), specific activity at 243 *K* (r_{sp}).

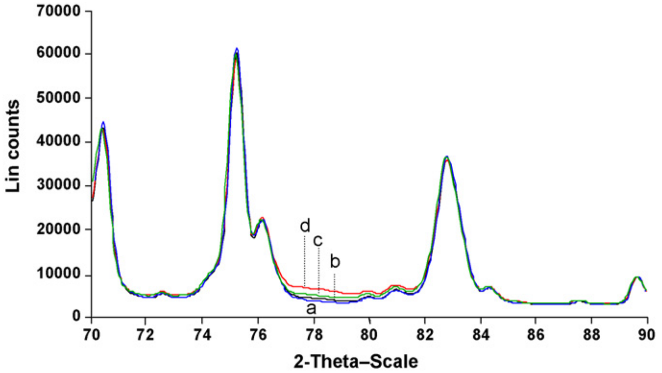

Fig. 3. XRD patterns in the region 70–90° 2θ: (a) TiO_2, (b) 0.6% Au/TiO_2, pH_f 8.5, (c) 0.92% Au/TiO_2, pH_f 6.4, and (d) 0.93% Au/TiO_2, pH_f 2.5.

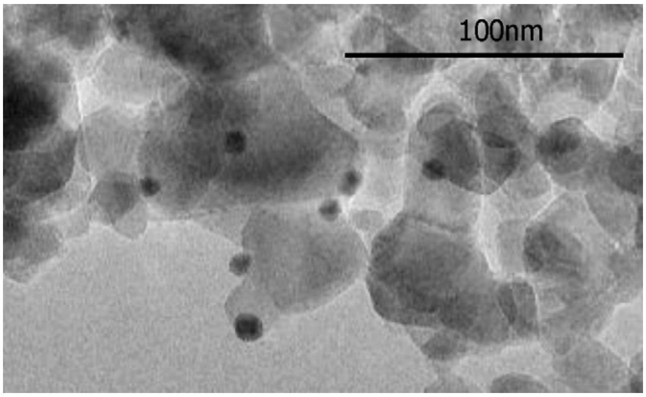

Fig. 4. Electron micrographs of 1% Au/TiO_2 prepared at pH 6, particles 4–20 nm, d_{av} 10 nm.

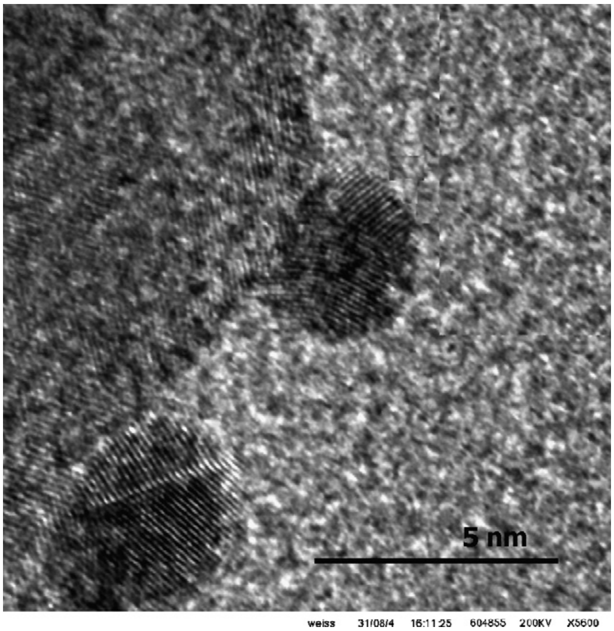

Fig. 5. Electron micrographs of 2.3% Au/TiO_2 prepared at pH 9, particles 1.5–4 nm, d_{av} 2 nm.

raised (Fig. 3), and high resolution TEM (Figs. 4 and 5) demonstrates very clearly that at pH 9 the gold particles are exceedingly small (~2 nm) compared to those formed at pH 6 (~10 nm). The main reason for the larger size at the lower pH is thought to be the retention of chlorine in the gold complex ions that exist in solution at this pH (Fig. 2) and that are attached to the surface in some way or other; such species are apparently more mobile than those at higher pH that are devoid of chlorine. They seem to aggregate into larger clusters during drying, and so when reduced either by calcination or by CO in reaction; they form quite big particles of metallic Au.

The mechanism by which the Au species in solution are affixed to the TiO_2 surface in the pH range above the IEP needs some explanation. It cannot be by electrostatic force or ion exchange; it is probably best described simply as "adsorption", but because solution species are anionic the adsorbing species may be the neutral $Au(OH)_3{\cdot}H_2O$, which is in equilibrium with $Au(OH)_4{}^-$:

$$Au(OH)_4{}^- + H_2O \leftrightarrows Au(OH)_3{\cdot}H_2O + OH^-$$

We may the describe the adsorption as for example [5]:

$$Au(OH)_3{\cdot}H_2O + 2TiO^- \leftrightarrows [Au(OH)_2{\cdot}(OTi)_2]^- + OH^- + H_2O$$

The high dispersion obtained when reduction takes place is a consequence of the strength with which the gold species are held, and their wide distribution over the surface. We show elsewhere [2] that the sites at which this reaction can occur are limited in number, and are perhaps only 15% of the total. The lesser dispersion found in the lower pH range is therefore seen as a consequence of either (i) weaker (electrostatic) bonding of the complex ions, and/or (ii) more limited opportunity for forming Au–OTi bonds because of the presence of coordinated chloride. Weaker bonding allows migration and aggregation during drying, as noted above.

The specific activity however does decrease when the final pH is greater that about 9 (Table 2). We may speculate that this is because the particle size has actually fallen below the optimum; this fall is associated with a marked decrease in the gold loading (Table 2), so that the adsorbed complexes are very widely separated and hence are unlikely to aggregate much on reduction. The decrease in loading follows from the reversal of the adsorption equilibrium. Similar effects of pH on gold uptake and activity (T_{50}) have been reported by other workers [7,11].

Careful control of the pH at all stages of the preparation has allowed us to make a series of catalysts with gold contents between 0.06 and 2.4 wt%, none of which show particles large enough to give a visible XRD peak, and the activity of which is exactly proportional to the gold content, i.e. the specific rate at 243 K is constant at 3.7×10^{-4} $mol_{CO}\, s^{-1}\, g^{-1}{}_{Au}$ (Figs. 6 and 7). Of particular interest is the conversion versus the temperature plot for the 1.9% Au/TiO_2 (Fig. 6); below about 220 K the temperature coefficient becomes very low, and the conversion is still 20% at 183 K. We do not know why this only happens with the higher gold loading, but think it may arise from a particularly reactive form of adsorbed oxygen stable only at low temperature [3], and hence noticed only when there is sufficient metal present to make this condition accessible.

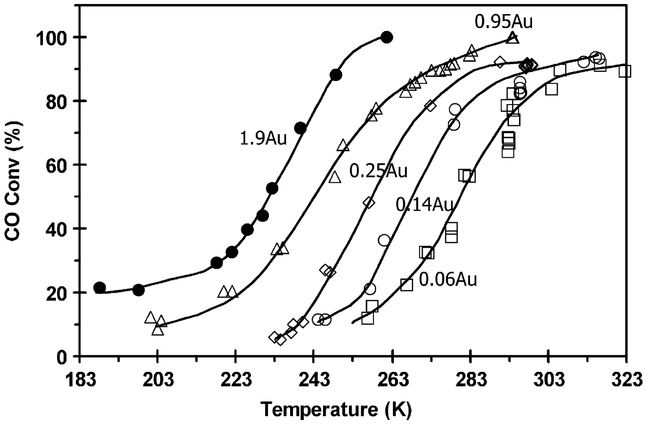

Fig. 6. Conversion–temperature plots for Au/TiO_2 catalysts having 0.06–1.9%Au.

3.2. Use of different temperature profiles

The method of preparation used in the work so far described entailed heating the suspension after adjusting the pH to 343 K for 1 h. While this follows the first described preparation [4,5], the need for and purpose of this heating has never been explained, nor has the detailed chemistry taking place been elucidated. In fact the heating is unnecessary [5]; carrying out the whole preparation at 293 K and pH 9 gives an excellent catalyst (80% gold uptake, $T_{50} = 255$ K). We have also performed the $AuCl_4^-$ hydrolysis at 343 K before adding the P-25 as other authors have done [6], using various pH values [5]; this turned out to be advantageous because complete uptake of gold was found at pH 5.6 together with a very satisfactory activity ($T_{50} = 248$ K). We conclude (i) that the gold species in solution at 293 K and pH 9 are readily adsorbed on the P-25 in 1 h, and (ii) that more extensive hydrolysis of the $AuCl_4^-$ ion occurs at 343 K and gives about the same solution concentrations as pH 9 and 293 K. The product of the standard method is therefore liable to variation depending on the heating rate, as adsorption will occur continuously as the temperature is raised. Unthinking imitation of the literature method is not always the best thing to do.

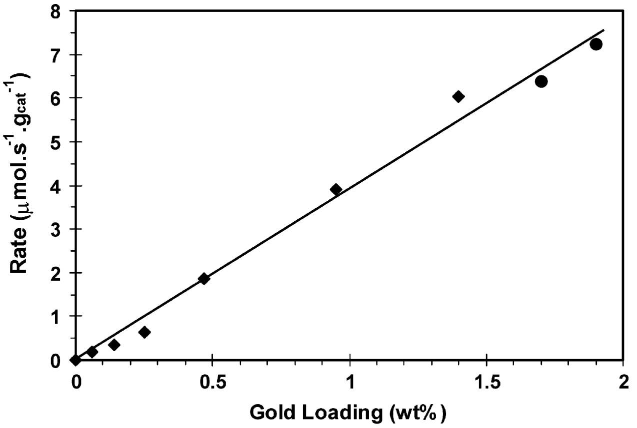

Fig. 7. Dependence of rate at 243 K per g_{Au} on gold content; specific rate = 3.7×10^{-4} mol_{CO} s^{-1} $g^{-1}{}_{Au}$.

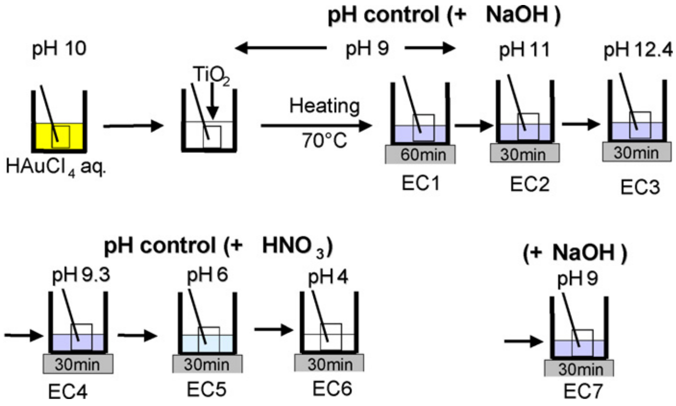

Fig. 8. Schematic of the procedure used in the pH reversal experiment.

3.3. Reversal of the pH

The foregoing model for the interaction of the $AuCl_4^-$ ion and species derived from it by hydrolysis at various pH values with the P-25 surface implies two or perhaps more modes of retention, and it was unclear whether it was the initial or final pH that mattered and whether the modes were reversible as the pH was changed. To examine these matters further, a series of measurements was made, starting with 20 g of P-25, and making progressive alterations in the pH at 343 K before taking a small sample (1–2 g) for analysis (Fig. 8) [5]. Specifically, starting with pH 9 (EC1) the pH was further raised by NaOH addition to 11 (EC2) and then to 12.4 (EC3); it was then lowered to 9.3 by adding HNO_3 (EC4) and further to 6 (EC5) and then 4 (EC6); finally it was again raised to 9.3 by NaOH (EC7). The results are shown in Table 3, from which it is clear that the interactions are readily reversible; very similar catalysts are obtained at pH 9 irrespective of the previous history of the system. Moreover the results obtained are essentially the same as those found earlier when only single pH was used (Fig. 9). What is happening is that at pH values above the IEP the position of adsorption equilibrium moves progressively to the solution side, that at pH 12 only about 10% of the gold is adsorbed (Fig. 9). Lowering the pH (from 12.4 → 9.3 → 6 → 4) causes the adsorption to be again favoured, complete uptake being achieved by electrostatic means at pH 4.

Table 3
Results of the pH reversal experiment

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

Column headings: catalysts, time, final pH of the preparation (pH_f), gold deposited (Au wt%), gold deposition efficiency (%DP), temperature at 50% conversion (T_{50}) and specific activity (r_{sp}).

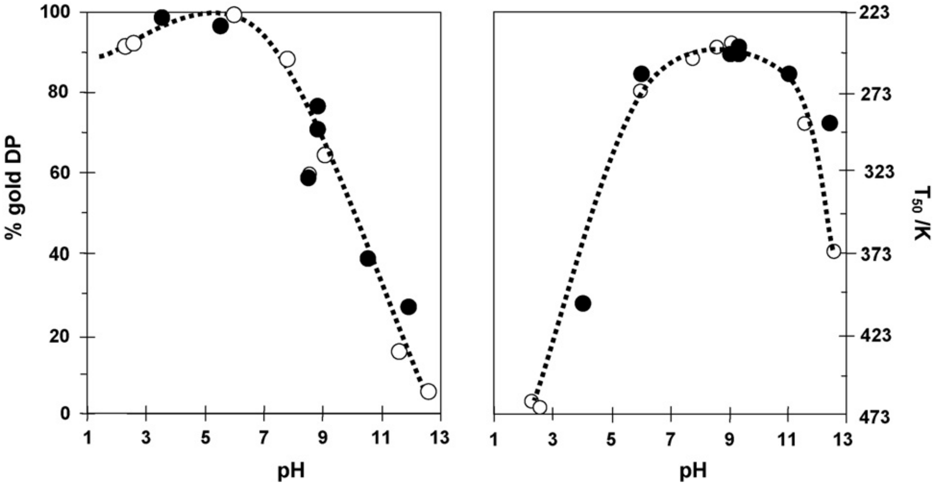

Fig. 9. Gold uptakes (% gold DP) and activities (T_{50}) as a function of pH; comparison of use of a single pH (●) and of pH reversal (○).

3.4. Redispersion and reactivation

The easy reversal of the adsorption processes opens the way to devising procedures for the redispersion of catalyst precursors prepared at the wrong pH, and for the reactivation of catalysts in which large gold particles have arisen through sintering.

An uncalcined catalyst (0.92 wt% Au/TiO_2) prepared at a final pH of 2.2 was tested, and confirmed to have low activity (Table 4); this was because the mean particle size was large (∼40 nm). It was then dispersed in water and the pH raised to 8.5–9 with heating for 1 h (Fig. 10), and after the usual processing its specific rate increased to a normal value (Table 4). The least satisfactory feature of this procedure was that the final gold content was only 0.47%, but no doubt this could be raised by optimisation of the conditions used. Even so, the extent of the improvement is very marked (Fig. 11).

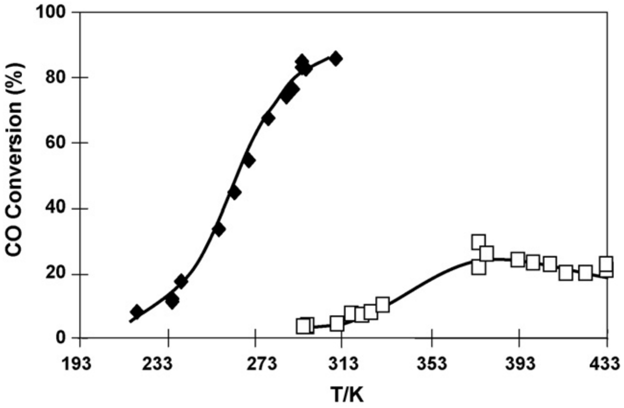

Fig. 11. Effect of the redispersion of the precursor on activity as a function of temperature: initial material, 0.92% Au/TiO_2, reactivated material 0.42% Au/TiO_2.

Table 4

Au (wt%)	pH_f	T_{50} (K)	$r_{sp} \times 10^4$ (mol $_{CO}$ s^{-1} g^{-1}$_{Au}$)
0.92	2.2	433	0.03
0.42	9.0	263	1.5

Column headings: Au weight percentage (Au wt%), pH at the end of the preparation (pH_f), temperature at 50% conversion (T_{50}), specific activity at 243 K (r_{sp}).

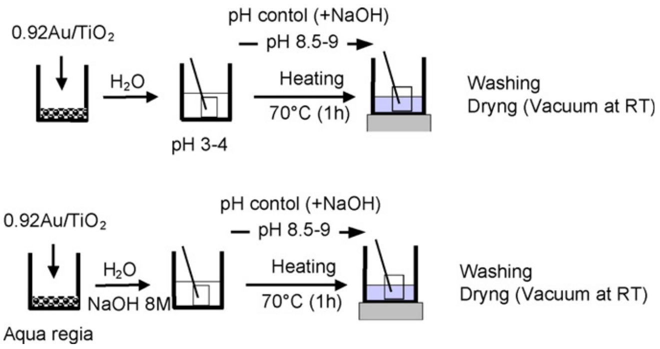

Fig. 10. Schematic of the procedure used for precursor redispersion.

Another part of the same preparation was calcined at 673 K, and its activity was further lowered ($T_{50} > 473$ K). We presumed that the gold was reduced, so the catalyst was suspended in aqua regia, and after dilution the pH was increased in the usual way (Fig. 10); normal proceeding afforded a catalyst of excellent specific activity (Table 4) and 0.55%Au. This level of gold uptake from solution (60%) is typical of what is found at pH 9.

4. Conclusion

The interaction of the anionic gold species in solution at pH values below the IEP of TiO_2 (6), where the surface is positively charged, is probably electrostatic in character, but above pH the adsorption of neutral species becomes important, and at pH > 8 it is chiefly $Au(OH)_3{\cdot}H_2O$ that is adsorbed. Thus, while the extent of gold uptake from solution passes though a maximum close to the IEP, the specific activity is maximal at higher pH (8–9) because here the adsorbed complex retains little if any chlorine. It can be re-dissolved by reaction with hydroxyl ion since the adsorption equilibrium is easily reversible, and re-adsorption at the most favourable pH provides a way of redispersion a poorly dispersed precursor. Similarly large gold particles may be dissolved in aqua regia, and the gold precursor again deposited at the best pH; heavily sintered catalysts are thereby reactivated.

Acknowledgments

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