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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.

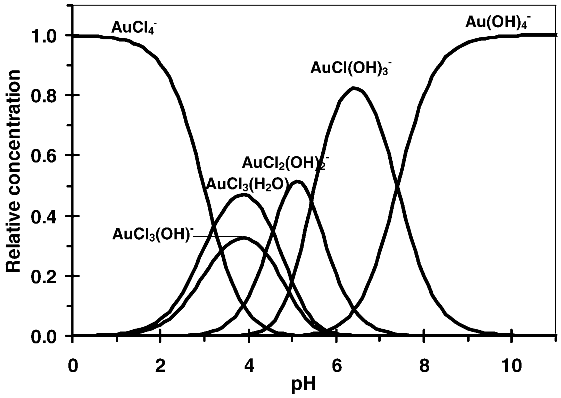

Fig. 1. Relative equilibrium concentration of gold complexes ($[Cl^-] = 2.5 \times 10^{-3}$ M) as a function of the pH of the solution, calculated with equilibrium constants reported by Nechayev et al. [15].

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].