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The influence of metal loading and pH during preparation on the CO oxidation activity of Au/TiO$_2$ catalysts

François Moreau, Geoffrey C. Bond and Adrian O. Taylor*
Institute for Materials Research, University of Salford, Salford, Greater Manchester, UK M5 4WT.
E-mail: adrian.taylor@materials.ox.ac.uk. E-mail: f.moreau@salford.ac.uk

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Au/TiO$_2$ catalysts with gold loadings in the range 0.06–1.9 wt.%, prepared by 'deposition–precipitation' at pH 9, have a constant and high specific activity for the oxidation of CO: 3.9(± 0.4) × 10^{-4} mol$_{CO}$ s^{-1} g$_{Au}$$^{-1}$ at 243 K.

The discovery[1] that very small gold particles supported on transition metal oxides show excellent activity for CO oxidation even below room temperature has led to several hundred publications and patents relating to this[2] and other reactions,[3–4] but few describe the use of gold contents less than 0.5 wt.%. This is somewhat surprising given that economic factors favour the use of low loadings for supported precious metal catalysts. We are aware of only five papers that report on CO oxidation over low-loading supported-gold catalysts.[5–9] Unfortunately the use of different operating conditions sometimes makes activity comparisons difficult; moreover some catalysts are sufficiently active that commonly used testing conditions can result in mass-transport control, leading to a sometimes unrecognised underestimation of the activity.

With Au/TiO$_2$ (P-25) having 0.5–3.1 wt.% gold content, specific activities at 300 K were reported to be significantly lower at low loadings; the value of 6.5 × 10^{-4} mol$_{CO}$ s^{-1} g$_{Au}$$^{-1}$ for 3.1 wt.% falling by a factor of eight for 0.5 wt.%, even though the average observable gold particle size (~ 3 nm) was similar for each loading.[8] Others have reported higher activities at these loadings (Table 1), but have not discussed trends with loading. These results together with somewhat inadequate descriptions of preparation methods have led us to re-examine the preparation of Au/TiO$_2$ catalysts having ≤1.9 wt.% gold content.

Catalysts containing 0.06–1.9 wt.% gold were prepared from HAuCl$_4$.3H$_2$O (Alfa-Aesar, 99.99%) as follows. The pH of an aqueous HAuCl$_4$ solution (1 × 10^{-4}–5.2 × 10^{-3} M) was first raised to 10 using NaOH solution (0.1 M, Fischer volumetric grade). TiO$_2$ support (1 g per 50 ml solution, Degussa P-25, as received) was then added under stirring at room temperature; leading to an immediate decrease in pH, which was then raised to and held at 9 by addition of NaOH (0.1 M) as necessary. The resulting suspension was stirred for 1 h, either at room temperature or at 343 K. After cooling it was filtered and the solid washed thoroughly and then vacuum-dried at room temperature. Calcination was not only unnecessary but without significant effect on the CO oxidation activity for T_{calc} ≤ 573 K, whilst calcination at 673 K substantially reduced the activity. Preparations were also carried out at other pH values, but it proved important for high activity to keep the pH between 8.6 and 9.0 during the last 15–20 min before filtration. A consequence of using this pH range is that not all of the available gold is deposited on the support. For actual gold contents of ≤ 0.95 wt.%, 70–75% of the gold in the precursor solution is deposited, less for actual loadings of 1.4–1.9 wt.%.

Table 1 Specific rates of CO oxidation for Au/TiO$_2$ catalysts

Wt.% Au	T/K	10^4 mol$_{CO}$ s^{-1} g$_{Au}$$^{-1}$	Ref.
0.5	300	7.3	[a]
0.5	300	0.76	8
0.7	300	0.99	8
1.8	300	0.31	8
2.3	300	1.8	8
3.1	300	6.5	8
0.15	323	76	9
0.05–1.0	[b]	[b]	5
3.0	278	5.0	10
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.

We do not yet know why pH 9 is optimum, but it may be significant that there will be fewer chlorine ligands associated with the gold complex ions that adsorb on the support at these pH values.[11] The presence of chloride ions on the catalyst is known to be detrimental.[12] Since the isoelectric point of titania is in the pH range 4.5–6.3[13] the consequent negative surface charge at pH 9 may be important, perhaps favouring the deposition of neutral Au(OH)$_3$ rather than the various anionic chlorine-containing complexes present in the precursor solution. We also note that the kinetics of both the hydrolysis of chloroauric acid and the subsequent ligand exchange as pH is raised are slow: it often takes more than one hour to approach equilibrium.

This method of preparation has shown excellent repeatability. Two series of catalysts (nominally 0.14 wt.% and 1 wt.%) were each prepared three times under identical conditions. Within experimental error the same loading of gold and activity for CO oxidation was measured for the three repeats within each series. Preparations carried out either at RT or 343 K, and for batch sizes ranging from 2–20 g, led to identical deposition of gold and activities for CO oxidation. Gold loadings were assayed by AA.

Characterisation was performed by powder XRD analysis in the region 75–85° 2θ (Cu K$_\alpha$, Siemens D500 diffractometer). All catalysts gave a single, weak and very broad feature in this region, increasing in intensity with loading. This suggests that all the catalysts comprise similar gold particles, mostly of less than a few nanometres in size or amorphous in nature.

Catalysts were tested between 183–343 K, measured using an *in situ* thermocouple well, in a plug-flow fixed bed reactor using 0.49 vol% CO in synthetic air. The standard test used a 55 cm^3 min^{-1} reactant flow and 50 mg of catalyst (space velocity 17 000 h^{-1}). Product analysis was by means of a Varian 3300 GC using an in-line manual sampling valve, CTR1 column (Alltech), TCD and helium carrier gas. Plotting rates according to the Arrhenius equation shows that for several of the catalysts (0.95–1.9 wt.%) the reaction was probably mass-transport controlled. To avoid this limitation, the activities of some catalysts were also determined under different test conditions (flow rates 55–150 cm^3 min^{-1}, 20–50 mg of catalyst; space velocities 17 000–115 000 h^{-1}). A short induction period was observed (up to 2 h), but results reported below are steady state values. Activation energies measured under kinetic control were ≈ 34 kJ mol^{-1}, independent of gold loading and in good agreement with the literature.[4,7,8]

Fig. 1 shows how CO conversion depends on temperature and on gold loading for uncalcined catalysts, which are usually pale lilac in

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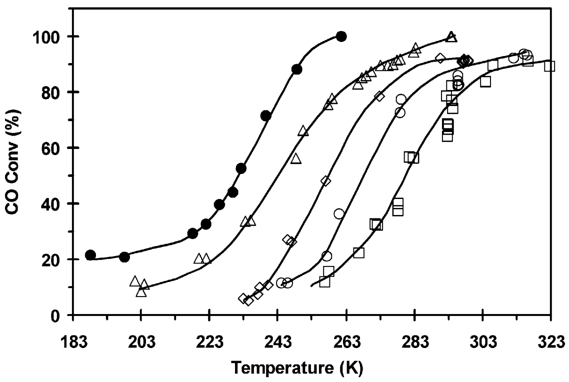

Fig. 1 CO conversion as a function of reaction temperature, for uncalcined Au/TiO_2 catalysts, standard test conditions. (wt% Au : ● 1.9, △ 0.95, ◇ 0.25, ○ 0.14, □ 0.06).[15]

colour. For 0.5–0.95 wt.% gold contents, our values of T_{50}[14] are ≈ 245 K, a substantial improvement on the previously reported values of 282–320 K for this range of loadings.[8]

Fig. 2 shows the CO oxidation rate obtained at a temperature of 243 K as a function of loading (using various space velocities to achieve kinetic control at all loadings). There is a clear linear dependence of rate per gram of catalyst on the gold loading; indicating that the specific activity (per gram of gold) is the same for all the catalysts. Its value (3.9×10^{-4} mol_{CO} s^{-1} $g_{Au}{}^{-1}$ at 243 K) indicates a higher intrinsic activity than any reported in the literature. In contrast, for Au/P25–titania, Haruta's group report an exponential decrease of specific activity with decreasing loading;[8] this difference may be due to our careful pH control during the preparation. Our result is particularly significant from a commercial point of view since it indicates that 'thrifting' is possible without losing specific activity. From an initial value of 0.90, during 100 h continuous operation the fractional conversion typically decreases by 0.003 h^{-1}.

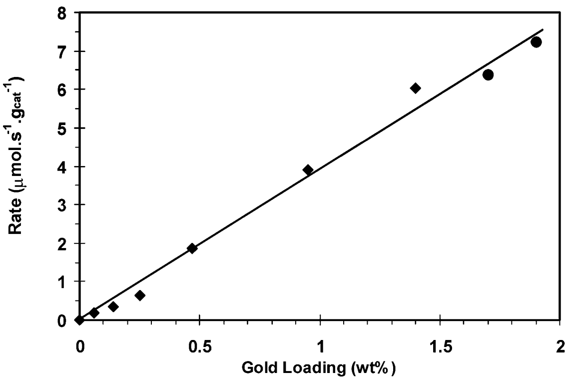

Fig. 2 Rates for CO oxidation at 243 K over uncalcined Au/TiO_2 catalysts as a function of gold loading.[15]

By extrapolating an Arrhenius plot of results obtained under kinetic control in the present work, we predict a specific activity at 323 K of 1.1×10^{-2} mol_{CO} s^{-1} $g_{Au}{}^{-1}$. If all of the gold atoms in our catalysts were surface atoms exposed to the reactants this value would equate to a turnover frequency of 2.2 molecules(CO) (gold surface atom)$^{-1}$ s^{-1}. In their study of a single loading Park and Lee reported a specific activity at 323 K of 7.6×10^{-3} mol_{CO} s^{-1} $g_{Au}{}^{-1}$ for a 0.15 wt.% Au/TiO_2 catalyst.[9]

The most straightforward explanation of the constant specific activity is that our preparation method is producing a similar distribution of gold particle sizes at all loadings, the total number of these particles simply increasing with loading. Our PXRD results are consistent with this explanation.

In addition to the obvious advantages of establishing a preparation method for the production of high activity catalysts, that is repeatable, does not require heating during deposition, or calcination, and minimises the chloride concentration adsorbed on the surface, our observation of a constant specific activity for CO oxidation may allow further benefits to be realized. In particular it enables the replacement of a higher loading catalyst with a larger amount of a lower loading catalyst in order to achieve the same conversion. The lower surface density of gold particles in the latter case may, (i) allow more effective heat transfer and control of temperature hotspots resulting from the exothermic reaction, and (ii) minimize sintering and Ostwald ripening.

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14 The temperature at which 50% conversion is observed.
15 In the figures solid circles indicate stirring at room temperature during preparation; for the other samples stirring was at 343 K.