



Simplified single-step synthetic route for the preparation of a highly active gold-based catalyst for CO oxidation

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Abstract

A new single-step borohydride (SSBH) reduction technique is described for the preparation of gold-titania catalysts. The preparation method has the merit of simplicity but leads to the formation of catalysts which are among the most active Au–titania systems described to date for the oxidation of carbon monoxide and which contain gold in a highly dispersed state.

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1. Introduction

Gold-based catalysts have proved their potential activity for carbon monoxide oxidation. Extensive work has been reported by several groups for the preparation and characterisation of such catalysts. Gold nanoparticles has been deposited by various supports such as TiO₂, Al₂O₃, ZnO, Co₃O₄, MnO₂, MgO, Fe₂O₃, Zr₂O₃, etc. and has proved its prospective application for carbon monoxide oxidation. A number of methods co-precipitation [1], deposition–precipitation (DP) [1], gas-phase grafting [1], liquid-phase grafting [1], co-sputtering [2], colloidal mixing [3], aqueous impregnation [4], DP, maintaining pH (8.5–9), followed by in situ reduction [5,6], has also been used for the preparation of such type catalysts and all of them involved multi-step techniques.

Until the appearance of the work of Xu et al. [4] on the use of an aqueous impregnation approach for the preparation of highly dispersed and highly active gold on alumina, it was often accepted that the only practical route to achieve high activity and high gold dispersion involved use of the DP method [7]. The DP route is usually carried out at controlled pH (in the range 6–10) and uses H₂AuCl₄ as the gold source. The latter is often added at a carefully controlled and low rate

with vigorous stirring and with pH control, and frequently solutions are heated to ca. 60–70 °C to effect the process. A key aspect of the use of high pH appears to be associated with the removal of C lenities from the co-ordination sphere of the Au atom and to remove the chloride ions which would otherwise tend to deactivate the gold centres and also contribute to the sintering of metallic gold particles during thermal pretreatment procedures and/or during catalytic operation. Xu et al. [4] adopt essentially a two-stage approach involving first, the impregnation of alumina with the aqueous solution (acidic) of H₂AuCl₄, followed by second, a washing step carried out under basic conditions. We now wish to report that for the Au–titania system, a simple single stage method, without pH control during the contacting of the support with the gold source (an aqueous solution of H₂AuCl₄), followed by washing only with water can lead directly to highly active and stable CO oxidation catalysts. The high activity is achieved only when the contacting solution contains a suitable reducing agent, such as an aqueous solution of sodium borohydride. The synthetic approach is referred to as the single-step borohydride (SSBH) method. The catalysts prepared in this manner are among the most active reported to date and the gold dispersion is high. We believe that the SSBH approach offers distinct practical advantages over the preparative methods adopted by others [1–4,7] and previously used by our own group until recently [5,6] in that the number of variables is drastically reduced and there is no necessity to rigorously control pH during the preparative

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or washing stages. From the standpoint of furthering our attempts to understand how gold catalysis operate, it seems likely that catalyst preparation reproducibility will also be improved as a result of the simplified methodology. This could greatly aid studies attempting to reveal catalytic site genesis using various characterisation techniques.

2. Experimental

TiO₂ (P25, Degussa) was chosen as support because of its high surface area, good mechanical properties and relative inertness. HAuCl₄ (Aldrich, 99.99%) was used as the precursor of the Au nanoparticles. The target gold loading was 1.0 mass%. Analytical grade sodium borohydride (Fluka) and distilled water were used throughout our work.

In a typical experiment for the preparation of the Au–titania sample, 3 g of TiO₂ was suspended in 500 ml distilled water and vigorous stirring conditions applied. 15.2 cm³ HAuCl₄ solution (10⁻² mol dm⁻³) was added slowly with continuous stirring. After addition of HAuCl₄, the solution was kept at rest for 0.5 h and the pH of the solution was recorded as 4.0. A solution of NaBH₄ (13 cm³, 10⁻² mol dm⁻³) was added by use of an injection procedure under vigorous stirring condition. After addition of NaBH₄ the pH of the solution became 8.5. The colour of the solution changed from white to pink due to the formation of nanosized gold particles on the titania. The suspended solution containing Au–TiO₂ was aged for 20 min. After filtration, a colourless filtrate (UV-spectrophotometer monitoring) indicated that all the gold particles were incorporated into the titania and the gold content of the solid is then 1.0 mass%. The pink coloured solid mass was dried in an oven at 120 °C for 0.5 h.

The catalytic activity was measured using a fixed bed flow reactor. A sample (0.2 g) was placed in the Pyrex glass

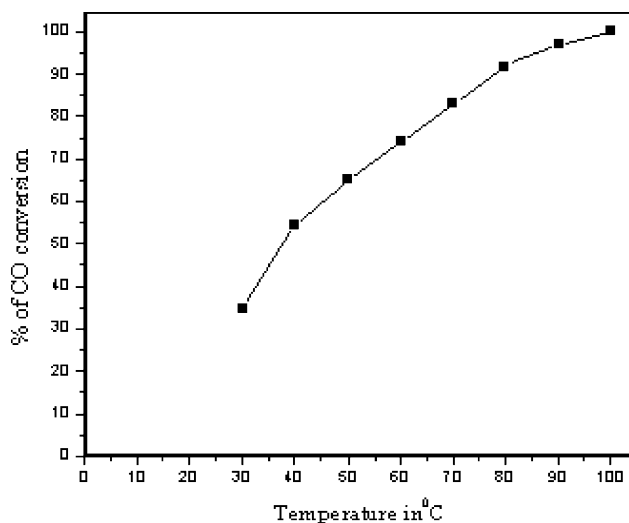


Fig. 1. CO oxidation activity at different reaction temperatures on Au–TiO₂.

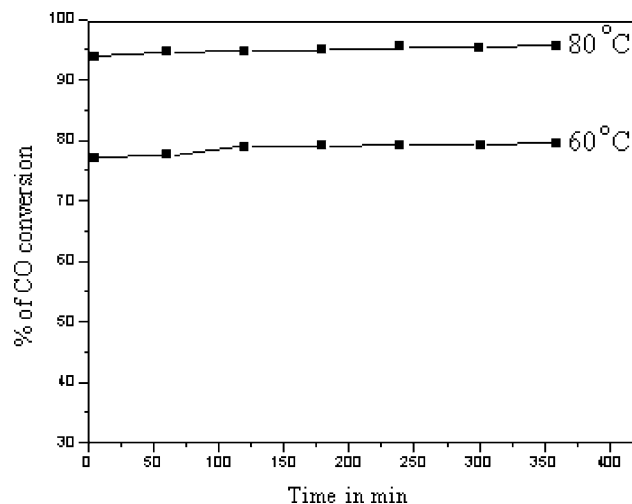


Fig. 2. CO conversion over Au–TiO₂ at different temperature as a function of time on stream.

reactor tube and heated to 200 °C for 2 h in a stream of oxygen (10% oxygen, balance He) at a flow rate of 50 cm³ min⁻¹. A mixture of oxygen and carbon monoxide (10% O₂, 20% CO, balance He) was admitted at a flow rate of 40 cm³ min⁻¹ (GHSV = 6150 h⁻¹) through the reactor while it was cooled to room temperature. The flow was controlled by a set of mass flow controllers and the exit gases from the reactor analysed by means of gas-chromatography (Shimadzu GC8A).

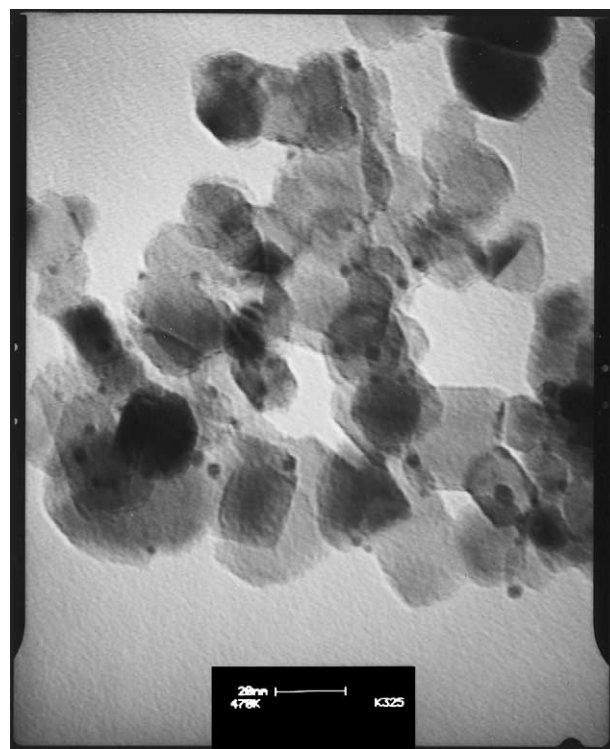


Fig. 3. High resolution TEM images of Au nanoparticles, prepared by in situ reduction using the SSBH treatment with sodium borohydride. The Cu signal arises from the sample grid used.

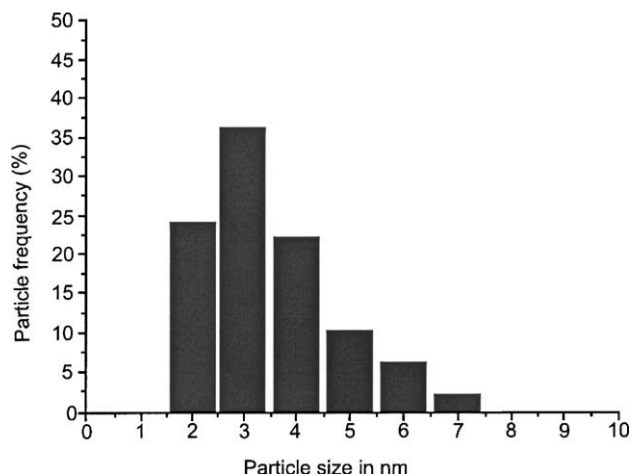


Fig. 4. Particle size distribution revealed by the TEM analysis.

3. Results and discussion

Fig. 1, shows the CO conversion with temperature and Fig. 2, shows the conversion behaviour as a function of time on stream at 60 and 80 °C. From Fig. 2 it is clear that there was no indication of deactivation taking place during the period investigated. The TEM image (Fig. 3) and particle size analysis (Fig. 4) shows that the particle diameters of the gold are in the range 2–5 nm. EDS analysis (Fig. 5) confirms that no residual sodium or boron containing species are present in the vicinity of the gold particles on these catalysts.

The turnover frequency (TOF) calculated from the observed average gold particle size and assuming spherical or cubic crystallite geometry for the dispersed gold was estimated as 0.4 s^{-1} at 30 °C and 1.1 s^{-1} at 80 °C, from the observed conversion levels. Since detailed kinetic analyses are not yet available no allowance was made for the impact of reactant consumption on observed rates, which means that the TOF value particularly at 80 °C is likely to be underestimated by our approach. Values of TOF for CO oxidation, reported by others, as summarised recently by Costello et al. [8], with re-calculations being carried out where necessary using the specific reaction rates quoted [8], for Au–titania produced by various preparative methods are: 0.02 s^{-1} (chemical vapour deposition) for CO oxidation at 0 °C, 0.03 s^{-1} (deposition–precipitation) for reaction at 0 °C and 0.1 s^{-1} (co-precipitation) for CO reaction at 40 °C. In our other recent studies, using sodium borohydride treatment [5,6], but applying the reductive step subsequent to the incorporation of gold into titania using the DP technique, we have found TOF values of ca. 0.3 s^{-1} for CO oxidation at 80 °C. We therefore conclude that the SSBH approach now described leads to catalysts which are more active by a factor of at least three to four times.

Analysing further our own recent work [5,6] together with the results of the study now reported, we find that the gold particle sizes and size distributions are not greatly different for the samples prepared by a two-step DP-borohydride method and the SSBH approach. The reasons for the higher activity must be sought in characterisation studies now underway. However, a few comments may be appropriate at

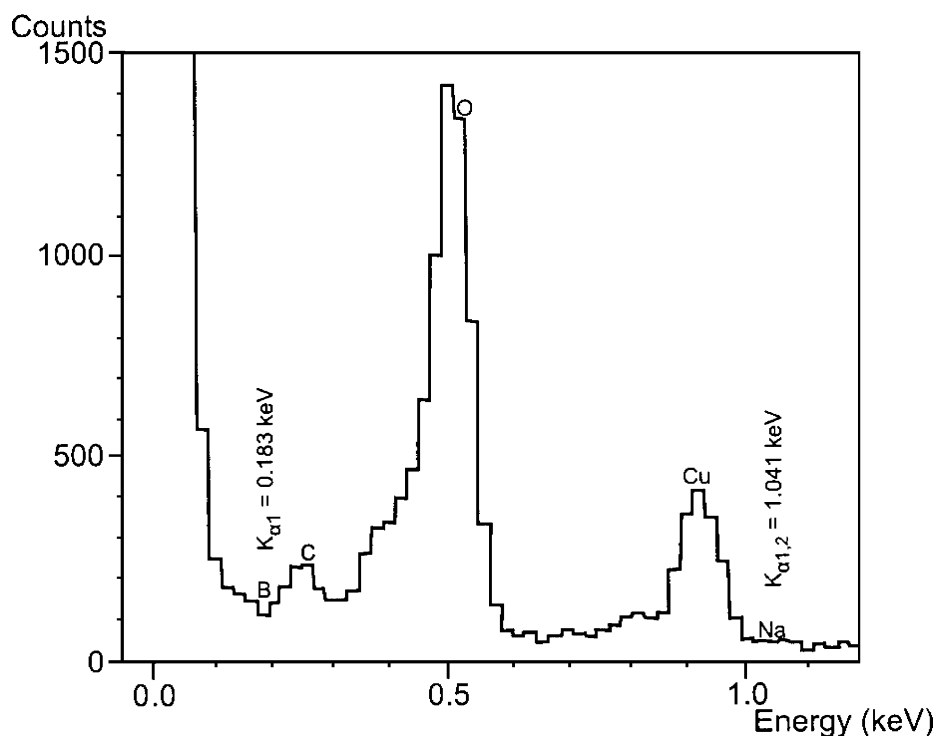


Fig. 5. EDS analysis confirms the absence of boron and sodium species on the catalyst surface.

this stage of our investigations concerning the need for, or beneficial effect of reductive pretreatments such as those now described. That the treatment with sodium borohydride is beneficial seems to be beyond doubt. Elsewhere [9], we have shown such a beneficial effect on the activity of gold-ferric oxide catalysts as revealed by their activities in the water–gas-shift (WGS) reaction. Yet it is difficult to conclude that the sole reason for the treatment is in order to produce metallic gold. For the Au–ferric oxide system in the WGS reaction we have proposed that either no reduction or, alternatively, over-reduction are associated with lower activities and it appears that a partial reduction is therefore desirable. It is clear from infrared spectroscopic studies carried out by us on Au–titania that the majority of CO chemisorption sites comprise metallic gold [5,6]. But, a minority (partially) ionic gold species is also present and able to chemisorb CO [5,6], so that the formation of metallic gold may not be the sole reason why reductive pretreatments are of benefit. In this connection we note the proposals made by others [8,10,11] that ensembles of $\text{Au}^+ - \text{OH}^-$ and metallic gold atoms may constitute the active sites in supported gold catalysts for CO oxidation and related reactions. Metallic gold is perhaps required but its presence is not a sufficient condition for high catalytic activity to be developed.

In the SSBH method, we have used an excess of sodium borohydride of some 125% calculated on the basis of the reductive stoichiometry of sodium borohydride undergoing conversion to sodium metaborate and all the gold in HAuCl_4 being reduced to the zero-valent state, so that on this basis alone, the complete reduction of gold in our system is possible. Further, we emphasise that the pH of the system under borohydride treatment rises to over eight and so the beneficial effects of an alkaline medium on chloride removal from the co-ordination sphere of the gold may still be

relevant to the SSBH technique. Preliminary work on using a single-step synthesis approach using non-reductive but high pH conditions, such as employing sodium hydroxide, rather than sodium borohydride [12] do not however lead to high activity catalysts for CO oxidation, so that the reductive aspect of the SSBH step seems to be a key requirement.

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