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High activity supported gold catalysts by incipient wetness impregnation[☆]

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Abstract

It is generally thought that catalysts produced by incipient wetness impregnation (IW) are very poor for low temperature CO oxidation, and that it is necessary to use methods such as deposition–precipitation (DP) to make high activity materials. The former is true, indeed such IW catalysts are poor, and we present reactor data, XPS and TEM analysis which show that this is due to the very negative effect of the chloride anion involved in the preparation, which results in poisoning and excessive sintering of the Au particles. With the DP method, the chloride is largely removed during the preparation and so poisoning and sintering are avoided.

However, we show here that, contrary to previous considerations, high activity catalysts can indeed be prepared by the incipient wetness method, if care is taken to remove the chloride ion during the process. This is achieved by using the double impregnation method (DIM). In this a double impregnation of chloroauric acid and a base are made to precipitate out gold hydroxide *within the pores* of the catalyst, followed by limited washing. This results in a much more active catalyst, which is active for CO oxidation at ambient temperature. The results for DIM and DP are compared, and it is proposed that the DIM method may represent an environmentally and economically more favorable route to high activity gold catalyst production.

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1. Introduction

In the past 20 years there has been an ever-expanding effort in the field of catalysis by gold, ever since the reports of Haruta et al. [1,2] and Hutchings et al. [3] on high gold activity for certain reactions under low temperature conditions. From these first reports it was evident that the method of preparation of such catalysts was a crucial factor in determining the efficiency of these materials for, for example, the CO oxidation reaction. It was shown that one of the best catalysts for the latter reaction was Au/TiO_2 and that this could successfully convert CO below ambient temperature [4,5], but such activity was only achieved when using the method of deposition–precipitation (DP). Catalysts produced using the incipient wetness (IW) method were shown to have poor activity, only giving significant conversion at $T > 100\,^{\circ}C$ [6,7]. The deposition–precipitation method involves increasing the pH of a dilute slurry containing the support (e.g. TiO_2 P25), usually using ammonia, NaOH or Na_2CO_3 to a pH > PZC of support (PZC = point of zero charge). For P25 TiO_2, the PZC is 4–6 [8]. At this point $Au(OH)_3$ is precipitated from solution onto the surface of the support. In contrast, incipient wetness involves impregnating a gold salt, usually chloroauric acid in aqueous solution into the pores of the catalyst, with very little volume of liquid used. The purpose of this brief report is to show that, in contrast to the general view, it is indeed possible, by careful preparation, to make highly active Au catalysts by IW methods.

2. Experimental

Catalysts were prepared by the deposition–precipitation method described in detail elsewhere [4,5,9] and also by incipient wetness. The source of Au in all cases was chloroauric acid supplied by Acros Organics. The new method used (the double impregnation method, DIM) is described in more detail below. The reactivity of the catalysts was measured using a pulsed flow microreactor outlined elsewhere [7,10]. CO was regularly pulsed into a continuous flow of 10% oxygen in

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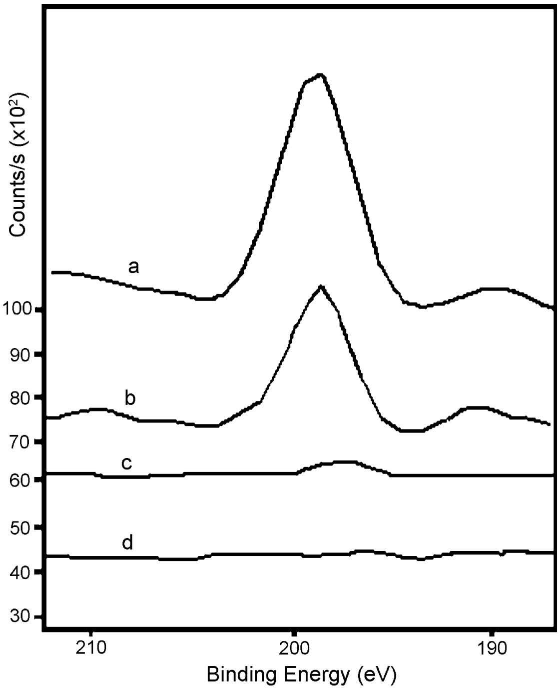

Fig. 1. XPS Cl_{2p} binding energy. 5 wt% Au/TiO_2 catalyst prepared by the IW method: (a) pre-treatment 120 °C; (b) pre-treatment 400 °C. 1.6 wt% Au/TiO_2 catalyst prepared by the DP method: (c) pre-treatment 120 °C; (d) pre-treatment 400 °C.

helium. Products were measured using a quadrupole mass spectrometer (Hiden HAL 201) positioned after the catalyst bed and separated from it by a capillary tube. The mass spectrometer only samples part of the reactor stream. Most bypasses the mass spectrometer. XPS measurements were made using an VSW HAC 100 system.

3. Results and discussion

The essential difference between the DP and IW methods is that for the former, Au is deposited as the hydroxide and Cl largely remains in solution. In contrast, for IW catalysts, XRF and XPS studies have been used to show that the Cl remains in the catalyst and reaction correlations suggest that it is connected with their lower activity [11–13]. Despite that, information on the role of chlorine is scarce. Fig. 1 shows XPS data for the Cl_{2p} signal and confirms that high levels of Cl are present in the IW samples, whereas there is almost none in the DP samples. Cl probably results both in some poisoning of the active sites of the catalyst, but also in enhanced sintering of the Au nanoparticles. Small particle size is important for this reaction, and this is achieved for the DP catalysts, the usual size range being ~2–8 nm [5,13,14] (see the example TEM image in Fig. 2) whereas IW catalysts can have small numbers of very large particles, often larger than 30 nm diameter [15].

In the new method of IW preparation for gold catalysts that we are reporting here, we use a somewhat more sophisticated approach to make the catalyst, in which we aim to deposit gold hydroxide within the pores of the titania and to remove chloride from the sample. We do this by using a double impregnation method (DIM) as follows. Five grams of Degussa P25 titania was impregnated with 1.25 ml of 0.08 g/ml $HAuCl_4{\cdot}3H_2O$ solution while gently stirring the powder; note that this is insufficient liquid to fill the pores. Subsequently, 1.43 ml of Na_2CO_3 1 M solution was then added while continuing to stir the paste. This total volume of liquid was then just sufficient to fill the pores of the powder to the incipient wetness point. The mixture was next washed on a vacuum filter with 14 ml of the sodium carbonate solution in 100 ml of water and this was repeated five times, followed by five washings with 100 ml of water. The paste was left to dry overnight in air at ambient temperature and was further dried at 120 °C in air for 2 h. Some samples were used directly in this form, others were further calcined to 400 °C in air for 2 h. The amount of gold added in the catalyst preparation was equivalent to 1 wt% of Au.

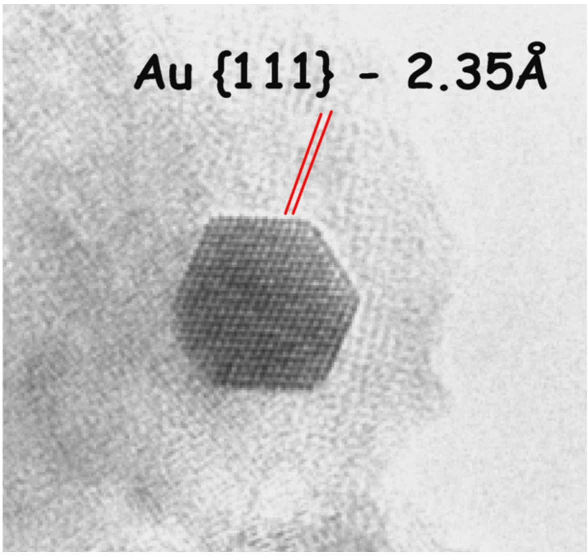

Fig. 2. TEM image of a Au nanoparticle on the DP catalyst.

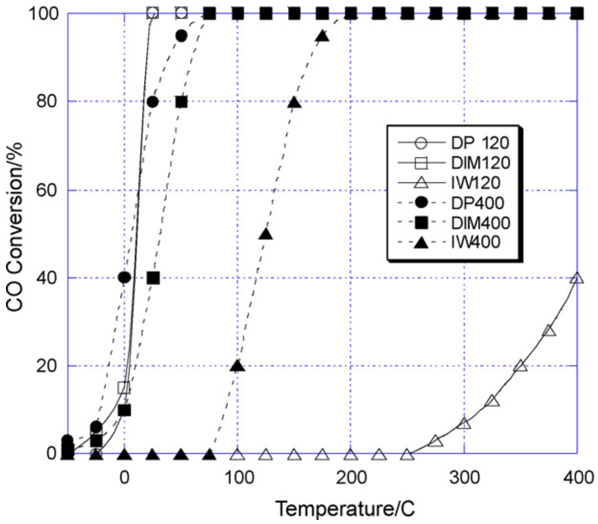

Fig. 3. CO conversion as a function of reaction temperature for a variety of Au/TiO_2 catalysts, showing the high activity of DP and DIM catalysts. The two sets of data are for catalysts pre-calcined in air at 120 °C or at 400 °C and are results for CO pulsing into a 10% O_2/He stream.

Fig. 3 shows pulsed flow reactor results for CO oxidation on these catalysts and for standard DP and IW samples. The details of the methodology for carrying out these rate measurements are given elsewhere [7,16], but in this case 0.5 ml pulses of CO were injected every minute into a continuous flow of 10%O_2 in He at a flow rate of 21 ml min^{-1}. For the dried samples the figure clearly shows the poor activity of the IW catalysts which only begins converting CO at ~300 °C. In contrast, the standard DP catalyst gives 100% conversion at ~7 °C, which is very comparable with the conversion found for the standard Au/TiO_2 catalyst supplied by the World Gold Council [17] under these reaction conditions. However, the catalyst produced by the new DIM method is as good as the DP material. For the calcined samples shown in Fig. 3, a similar trend is observed, though the detailed effects are different. The DP catalyst reactivity profile is little changed—there is some evidence of lower temperature activity, and 100% conversion is to somewhat higher temperature (40 °C). Similarly the DIM catalyst is deactivated, achieving 100% conversion by ~70 °C. It is notable that the standard IW catalyst improves in activity, presumably due to the fact that some Cl is lost during heating (HCl is seen as a product in TPD [15] and see Fig. 1b); 100% conversion is achieved by ~150 °C. Of course, calcination to 400 °C may be an inappropriately high temperature for calcinations of the DP and DIM catalysts, as also suggested elsewhere [18], and so such heating is unnecessary, indeed detrimental, for such catalysts, which are only designed to operate at low temperature anyway.

The main reason for this enhanced activity of such incipient wetness catalysts is that the double impregnation has resulted in the deposition of Au in the pores of the titania as $Au(OH)_3$, not as gold chloride, which is what usually forms in IW methods. As a result the Cl is either left in solution in the pores, or is not associated with the Au, and is removed from the catalyst by washing. In this way, after heating, it is possible to obtain the kind of small nanoparticles which interact well with the support, and which are reported in the literature [19] to be essential for high area, for a high concentration of interfacial sites and therefore for activity. In contrast, conventional IW catalysts have highly chlorided gold species, as is evident from the XPS above, which are prone to sintering upon calcination. Additionally, the chlorine may poison reaction sites in the catalyst. There appears to be a very good correlation between the level of Cl measured by XPS for our various catalysts and the activity, as shown in Fig. 4.

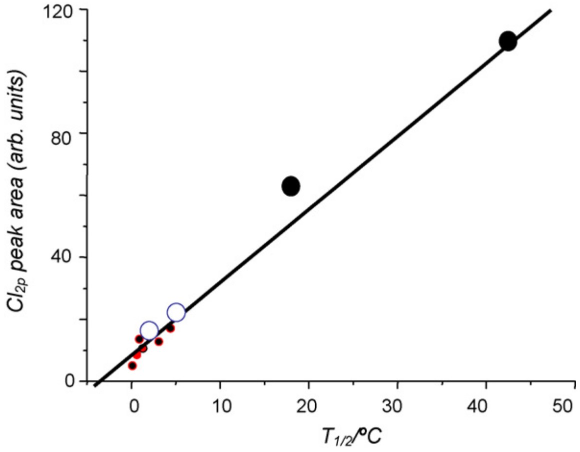

Fig. 4. The relationship between Cl XPS intensity and conversion (in terms of the temperature required for 50% conversion) for a variety of catalysts: large black circles, IW catalysts; small black circles, DP catalyst; open circles, DIM catalysts.

We believe that this is a novel approach to making these kinds of catalysts, and it is an approach which is certainly not yet optimised. For instance, there is no guarantee that the weight loading of Au which we have used here is the optimum amount, and it is likely that improved catalysts may be made by use of other routes to raise the pH in the pores (e.g. ammonia solution), and better catalysts may be produced with other oxidic supports such as Fe_2O_3. We look forward to other groups producing even more active catalysts using this DIM method than we have reported here.

There may be several advantages of this kind of approach for preparing these catalysts, such as the likely avoidance of loss of Au in the preparation which is reported elsewhere [9,20]. Since all the Au is precipitated in the pores before the washing procedure, the weight loading can be accurately determined without external analysis. Another advantage could be the possibility of using reduced volumes of the tanks of slurry that would be required for large-scale production of Au catalysts by the DP method.

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