Catalysis Letters Vol. 109, Nos. 1–2, June 2006 (© 2006)
DOI: 10.1007/s10562-006-0064-4

The role of impurities on the low temperature CO oxidation on Au/TiO_2

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Received 3 December 2005; accepted 13 February 2006

A number of Au/TiO2 catalysts have been prepared by a variety of methods in order to assess the affect of catalysts preparation methods on performance, catalyst contamination and the interplay between them. Their activity was studied in a pulse flow microreactor and it was found that preparation methods designed to eliminate impurities lead to more active samples. The effect of chlorine is often cited to be detrimental in the literature, but we have quantified it using XPS. It was found that the activity decreased in a nearly linear fashion with an increasing amount of this element at the surface. It is generally considered that catalysts prepared by the incipient wetness (IW) technique are ineffective for CO oxidation, but we show here that, by appropriate preparation methods, high activity IW catalysts can be made.

KEY WORDS: Gold catalysis; CO oxidation; Cl poisoning; Au catalyst preparation; incipient wetness impregnation; high activity Au catalysts; low temperature catalysis.

1. Introduction

For the preparation of gold catalysts, the literature [1] refers to two different well established methods: the impregnation-incipient wetness (IW) and the deposition-precipitation (DP) method. Both of these methods lead to gold catalysts with completely different catalytic properties, the former being much less active than the later. It is known that for the generation of catalytic activity on gold catalysts, a careful control of the experimental variables is required. In particular, a washing step to eliminate impurities from catalyst preparation, is crucial for the generation of activity. In fact, the original DP method as described by Haruta *et al.* [2,3], uses this experimental step for gold catalysts preparation.

One of the most frequent impurities is chlorine because $HAuCl_4$ is the most frequent gold precursor used. Although it is stated in the literature that chlorine species might have a detrimental effect [4–7], relatively little research has been carried out to assess this. An XRF study [8] by Vanice *et al.* has shown that Cl is a poison. DFT studies by Hammer *et al.* [9] described the possible negative role of Cl on the activity of Au/MgO samples. They claimed that Cl, as an electron acceptor, makes both the adsorption of O_2 and the formation of the CO–O_2 intermediate, more difficult. A XPS study by Wan *et al.* [10], has shown that the higher the Cl/Au ratio, the less active a Au/Y-zeolite is and it also confirmed that IW samples retain much more chlorine than DP samples, consistent with lower activity. The sodium effect is usually considered to be beneficial [5] but apart from DFT studies [9], no systematic experiments were carried out to confirm this statement.

These facts motivated us to investigate the effect of impurities in more detail. Therefore, the effect of these variables on the activity of DP and IW method samples was studied in a pulse-flow microreactor. XPS study also provides insight onto the role of chlorine.

2. Experimental

For this study, several catalysts were prepared by standard methods and variants of them.

- A set of catalysts was prepared by the IW impregnation method. The pores of titania (TiO_2, 50 m^2/g, Degussa treated in air at 500 °C for 2 h) were impregnated with a suitable volume of a solution of $HAuCl_4$ (0.505 ml/gcat, in our case). The amount and concentration chosen was such in order to obtain a gold final loading of 1 wt% and achieve IW. For our study, this sample was subjected to a drying step at 120 °C for 2 h in air, to evaporate the water and another sample was additionally subjected to a pre-treatment of 400 °C.
- For the samples prepared by the DP method, TiO_2 (Degussa) was added to a solution of $HAuCl_4$ and vigorously agitated at ambient temperature in order to obtain a suspension. After that, the pH of the solution was slowly increased by means of dropwise addition of an alkaline solution (Na_2CO_3 0.1 mol L^{-1}). The principle of this method is that

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the increase of pH makes gold precipitate as $Au(OH)_3$ onto the surface of the support [11], which acts as a nucleating agent. In any case, the solution was aged at the set pH of preparation for 2 h with continuous stirring. After that it was filtered in vacuum, dried overnight in air at room temperature and dried again for 2 h in air, at 120 °C. In some cases an extra calcination step to 400 °C for 2 h in air was also performed.

- The DP method above was also slightly modified: *washing* steps were performed after filtering the slurry under vacuum. Three different washing procedures were tested:
  a. *Washing with Na_2CO_3* – the washing solution was chosen to have the same sodium carbonate concentration as the preparing solution. The aim was to wash the chlorine from the sample while keeping the same concentration of alkali. The washing procedure consists of five washings with a mixture of 14.3 ml of 0.1 M Na_2CO_3 and 100 ml of H_2O.
  b. *Washing with Na_2CO_3 + washing with water* – after the chlorine was washed with the sodium carbonate solution, water washing was applied to remove the alkali. A water washing procedure consists of five washings with 100 ml of H_2O.
  c. *Washing with water* – all the impurities of the catalyst were washed off with a water washing operation.
- Another modification of the DP method resulted in a method of preparation that has common features both to the IW and the DP method, so it will be called deposition-precipitation impregnation method (DPIM). In this method, the filtration step of the DP method is omitted. The sample remained in the reactive vessel and the overnight drying step was extended for longer until dryness was observed by visual inspection. The gold loading of these samples is known because since no gold can be lost in the filtration step, all the gold put in remains in the catalyst. Also, all the alkali used to increase the pH will be incorporated in the catalyst.
- A novel IW impregnation method was also used: the double impregnation method (DIM). In this case, the sample is impregnated with the gold solution to only half of the IW volume. The remaining volume of pores is impregnated with a solution of Na_2CO_3. After that, samples were subjected to Na_2CO_3 washings followed by water washings.

All the samples prepared are shown on table 1, together with the different preparation parameters.

The key to the table is as follows:

L – gold loading corresponding to the actual gold deposited from the solution onto the support, as measured by XRF [12]. When this data is not available, one knows that this value is always less than the nominal loading (NL).
NL – nominal gold loading. This is the theoretical gold loading corresponding to 100% deposition of the gold contained in the preparing solution onto the support. $NL = (100 \cdot m_{Au})/(m_{Au} + m_s)$

m_{Au} (mass of gold) = $(M_{Au}/M_p).\ m_p$
m_p = mass of $HAuCl_4 \cdot 3H_2O$
m_s = mass of TiO_2
M_{Au} = atomic mass of gold
M_p = molecular mass of $HAuCl_4 \cdot 3H_2O$
T_c = temperature of pre-treatment
pH = is the final equilibrium pH of the preparative solution
$\dot{V}$ = normalised volume of solution = $(V + V_{pH})/m_s$
V = volume of water used in the beaker initially
V_{pH} = volume of Na_2CO_3 solution used to increase the pH.

Table 1
Studied samples: Preparation parameters

Code	L/NL (wt%)	Tc (°C)	pH	$\dot{V}$(ml/g)	Washing method[a]	Filtration
IW1	1.0/1.0	120	~ 2.5	0.5	None	No
IW2	1.0/1.0	400	~ 2.5	0.5	None	No
DP1	0.5/1.0	120	8	405	None	Yes
DP2	0.5/1.0	400	8	405	None	Yes
DP3	[a]/1.0	120	8	24	None	Yes
DP4	[a]/1	120	8	24	Na_2CO_3	Yes
DP5	[a]/1	120	8	24	Na_2CO_3 + Water	Yes
DP6	[a]/1	120	8	24	Water	Yes
DP7	[a]/1	120	8	405	Water	Yes
DP8	[a]/1	400	8	405	Water	Yes
DPIM1	1.0/1.0	120	8	24	None	No
DIM1	1.0/1.0	120	$2.5 < pH < 8$	0.5	Na_2CO_3 + Water	Yes
DIM2	1.0/1.0	400	$2.5 < pH < 8$	0.5	Na_2CO_3 + Water	Yes

[a] The Au loading (L) is unknown for these samples but it is always less than the nominal loading (NL).

All of the catalyst samples were subjected to the same preparation procedure prior to use in the reactor: 1 g of catalyst was grounded, pressed into pellets, crushed and sieved to give a particle size range of 600 μm $< d <$ 850 μm. The performance of the catalysts was studied in a pulse flow reactor (PFR) in which the gases involved in the reaction are continually analysed by a quadrupole mass spectrometer. In this manner, the PFR enables us to obtain in a straightforward manner conversions/yields versus temperature together with detailed kinetic information from pulse line shape analysis. Explanation of its mode of operation can be found in previous articles [12,13].

Monochromated XPS measurements were performed by Dr. Matt Hall (Chemistry Department – Cardiff University) on the NCESS (National Centre for Experimental Surface Science) facilities in Daresbury. The instrument was a Scienta ESCA 300 equiped with a high power rotating anode and a monochromatised Mg/Al X-ray source. The detection system consists of a 300 mm hemispherical analyser and a multi-channel detector. The data were collected at a constant pass energy of 150 eV for the survey scan and 50 eV for the regions. For the non-monochromated work an Al K_α X-ray source was used. Analysis of the XPS data was performed with the aid of Marco Cristofolini (Chemistry Department – Cardiff University). The Cl_{2p} signal of some of the samples was scanned and the peak areas, which are known to be proportional to the amount of chlorine in the surface region, were integrated. The Ti^{4+} $2p_{3/2}$ peak of the underlying TiO_2 was used as a reference state to correct for charging effects.

3. Results and discussion

The first set of samples studied was prepared by the DP method at high concentration of the preparative solution. Therefore they were not the most active samples. Figure 1A and B show the effect of several washing methods on the activity of these samples.

In both cases, for dried 120 °C (figure 1A) samples and for samples treated to 400 °C (figure 1B), the order of activity is: Washed with H_2O ~ Washed with Na_2CO_3 + H_2O > Washed with Na_2CO_3 > No washing > No filtration. This effect is more noticeable for samples treated to 400 °C. From above, it is clear that activity is enhanced by filtering the solution with pecipitate. If the sample is subsequently subjected to washings with a solution of Na_2CO_3, this will wash the remaining Cl off and even though sodium carbonate will be present, the activity increases anyway. This procedure will also make the sample much more resistant to deactivation (figure 1A and B). It appears, then, that the chlorine presence makes the catalyst prone to deactivation upon high temperature treatment. If the Na_2CO_3 is subsequently washed out with water, the activity is further increased, though if a DP sample is simply washed with water, similar results are obtained. In the second run (after the samples had been heated to 400 °C), samples were deactivated. However the more the sample is washed, the less it deactivates.

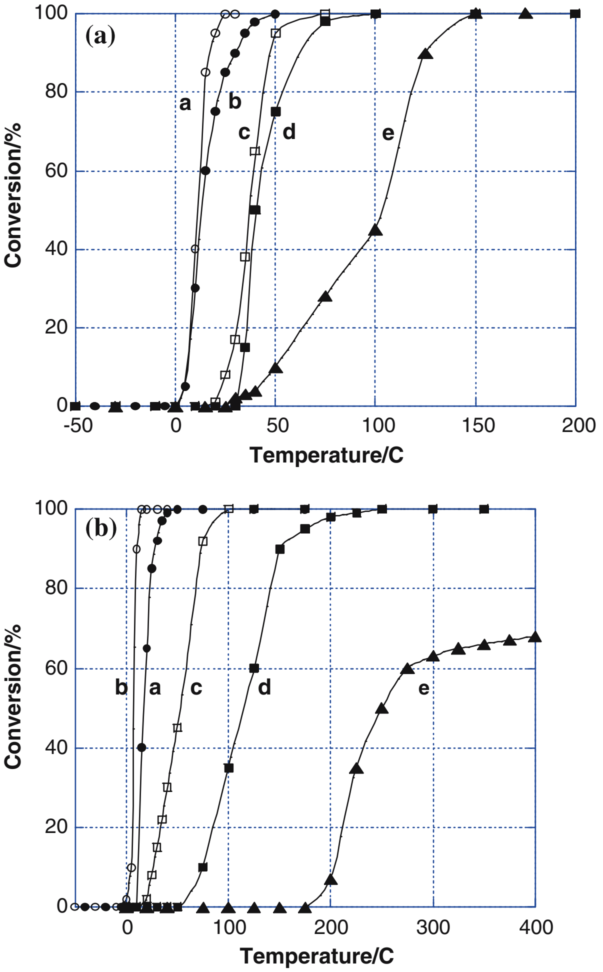

Figure 1. Temperature Programmed reaction–Pulsing CO in 10%O_2/He–Au/TiO_2 prepared by the DP method, dried 120 °C. Studying the effect of washing. Samples (a) DP6, (b) DP5, (c) DP4, (d) DP3, (e) DPIM1. (A) 1st run – as prepared samples. (B) 2nd run – after samples were heated in situ to ~400 °C.

Since a simple washing procedure was one of the best ways to activate a catalyst and protect it against thermal deactivation, this same treatment was also applied to another DP sample (sample DP1) prepared with different experimental conditions (higher dilution of the preparing solution). For the dried samples the extra dilution had little effect (figure 2). However for the calcined sample, higher activity was obtained for the washed sample (figure 2) consistent with the previous results. The small change in activity with washing for this particular sample by comparing with the previous example is perhaps due to the fact that one should expect less concentration of impurities due to a higher volume of water used in the initial preparation (compare for instance samples DP1 and DP3 on table 1). That is, by using more water in the reactor vessel, the sample is

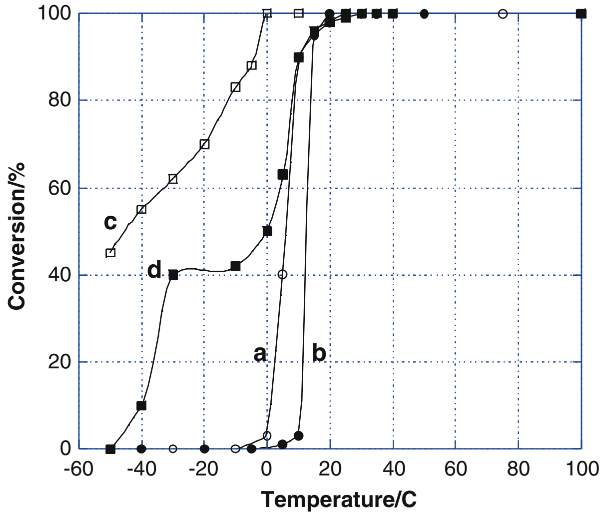

Figure 2. Temperature Programmed reaction–Pulsing CO in 10%O$_2$/He–Au/TiO$_2$ prepared by the best DP method. Studying the effect of washing. Pre-treatment: 120 °C–Samples DP1 (a, unwashed) and DP7 (b, washed). Pre-treatment: 400 °C–Samples DP8 (c, washed) and DP2 (d, unwashed).

as if it was already washed because impurities were much more diluted in the first place. Upon filtration the solution that remains in the pores of the titania, will have less concentration of impurities. In this set of samples, calcination actually improves activity, especially in the sub-ambient regime. The reproducibility of the data for the same catalyst run several times below ambient temperature is somewhat worse than that above ambient. The conversion varies by about 20% of the conversion value, and so the shape of the conversion-temperature curve varies a little. The reason for the enhancement of activity after calcination might be that the particle size of gold is smaller for these highly active catalysts, and calcination perhaps induces a better physical/chemical interaction with the TiO$_2$, an interaction which is important for activity. This could be a process analogous to the one described by Haruta *et al.* [2,3], for gold catalyst samples prepared by the colloidal method. Here it was observed that a change in gold morphology from spherical to hemispherical led to higher activities. Even though the mean particle size will increase, the interfacial length, where the reaction is assumed to take place, will also increase. Additionally, it is discussed by Thompson and Bond [1], that calcinations may be beneficial in certain cases because it can create porosity and access to buried Au in the gold catalysts. Also it can induce the anion vacancies ideal for O$_2$ adsorption on the oxide component.

Since a washing step improves the activity for DP samples, it was decided to study this experimental technique applied to the IW samples. Therefore, samples were subjected to Na$_2$CO$_3$ washings followed by water washings and this is the basis of the DIM method described in the experimental section. One can observe that the effect of chlorine and sodium on activity is also present for these samples (figure 3). In the case of the dried samples, the change in activity is extraordinary. A normal dried IW catalyst is only *catalytically* active at temperatures well above 300 °C whereas an IW catalyst with washing (DIM sample) becomes nearly as active as our best DP catalyst (figure 2). The CO$_2$ production on the temperature range before 300 °C, for sample IW1, refer to non-catalytic CO$_2$ production as studied by us on [12].

If the samples are calcined to 400 °C (figure 3), the activity of the DIM samples remains substantially higher than the non-washed IW samples. A calcination step slightly deactivates the DIM sample. However it greatly enhances the activity of the IW sample. The $T_{1/2}$ for the DIM sample is now only 40–50 °C and the $T_{1/2}$ for the calcined IW sample is now 120 °C.

In the conventional IW method, gold is deposited as gold chloride. By the DIM method, by adding sodium carbonate to the porous structure, a very active catalyst is obtained. It is likely that this is due to a transformation in the pores of the titania of the gold chloride into Au(OH)$_3$,a kind of DP directly within the pores. As a result, the Cl is either left in solution, or is not associated with the Au, and is removed from the catalyst by washing. Galvagno *et al.* claim that washing with hot water hydrolyses HAuCl$_4$ to Au–O like species [14]. An interesting feature of the samples prepared by this new IW method with washing steps (DIM samples) is that their colour (mauve/light blue for 120 °C treated samples and violet for 400 °C samples) look much more similar to the DP samples rather than the IW ones (yellow for 120 °C treated samples and blue for 400 °C

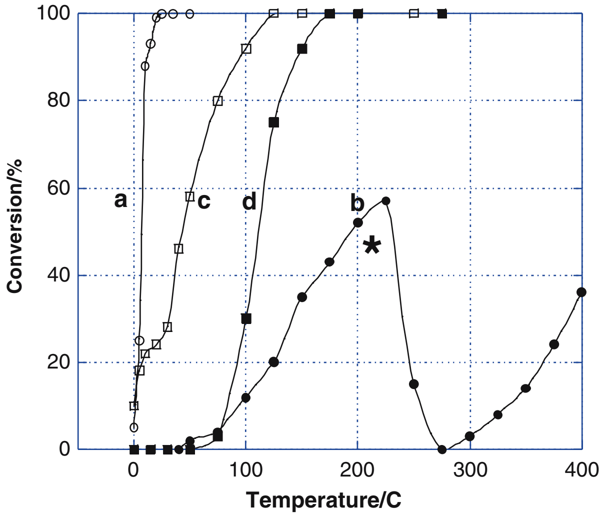

Figure 3. Temperature Programmed reaction – Pulsing CO in 10%O$_2$/He – comparing Au/TiO$_2$ prepared by the IW and DIM methods. Pre-treatment to only 120 °C. Samples DIM1(a) and IW1(b). Pre-treatment to 400 °C. Samples DIM2(c) and IW2(d). The (*) indicates CO2 production from non-catalytic processes (for details see ref [12]), whereas that above 280 °C is truly catalytic.

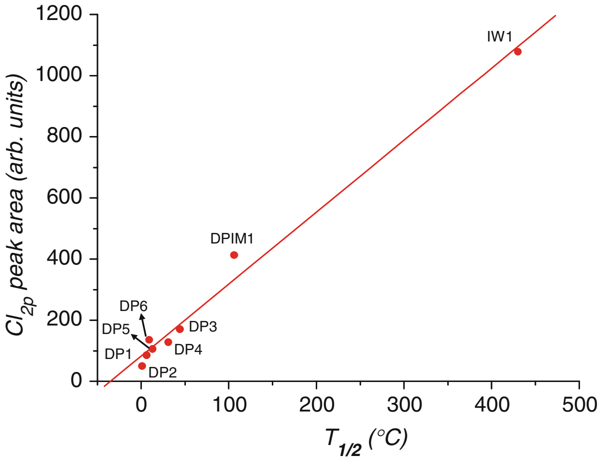

Figure 4. XPS – Cl$_{2p}$ binding energy versus the temperature of half conversion for CO oxidation for different catalyst samples.

samples). This is also consistent with the higher activity, these samples have. Although exhibiting 100% conversion of CO to CO$_2$ at room temperature, the DIM sample is prone to some deactivation upon high temperature pre-treatment. An explanation for this is that the highly concentrated gold precursor solution (table 1) results in a bigger particle size and a less intimate contact between gold/support, which in turn promotes sintering, or the possibility of Au^{n+} conversion to Au^0.

The DIM method is original, but various methods of impregnation preparation can be found in the recent literature, although impregnation is not by the IW method. Datye *et al.* [15] prepared active catalysts by mixing a solution of HAuCl$_4$ with Al$_2$O$_3$. The solution was then decanted and the solid washed with water. The solid was then put in contact with NH$_3$ until no change in pH. The mixture was washed with water, dried 100 °C + calcined 400 °C. These samples lead to a high dispersion of gold (d = 2.4 nm) and they were highly active and stable against hydrothermal sintering. Gavriilidis and Lee [16] also used successfully another modified IM method. He found that an intermediate pH in the preparation phase is required for best maximum CO conversion. V. Pitchon *et al.* [17] pointed out that an ammonia washing step removes chlorine and promotes anchoring of Au to support (on either Au/Al$_2$O$_3$ or Au/CeO$_2$). This results on samples resistant to sintering and thermal ageing. None of these methods involves truly IW impregnation and they use big volumes of solution like samples prepared by the DP method. With the DIM method it is therefore also possible, after heating, to obtain gold highly interacting with the support probably in the form of nanoparticles that are reported in literature [1] to be essential for high area, concentration of interfacial sites and activity.

We believe this is a novel approach to making these kinds of catalysts, which is certainly not yet optimised. For instance, there is no guarantee that the weight loading of Au which was used here is the optimum amount, improved catalysts may be made with 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$_2$O$_3$. There may be several advantages of this kind of approach to preparing these catalysts, such as simplicity compared with the DP method and the likely avoidance loss of Au in the preparation which is reported elsewhere [18,19]. Another advantage is the possibility of using reduced volumes of the tanks that are required for large-scale production.

The catalyst preparation and microreactor activity studies above gave us insight into the role of impurities on the activity of careful designed gold catalysts for low temperature CO oxidation. Because chlorine is the impurity most likely to be present, we decided to perform XPS studies to test our assumptions on the detrimental effect of chlorine. A selection of the prepared samples with different chlorine levels was investigated. A plot of the Cl$_{2p}$ peak areas was obtained versus the temperature of half conversion for CO oxidation and the results are summarised on figure 4. It is striking how a fairly good linear correlation between the amount of chlorine and activity is obtained. However, the straight line shown in the graph is meant exclusively to guide the eye. It is sufficient to say that activity increases with decreasing amount of chlorine and this shows the effect of chlorine as a poison. The expected amount of gold on each sample should be roughly the same, since the NL was the same in all samples analysed (table 1). However it can be argued that some of the gold might be lost during the preparation. The correlation remains valid if the sets (DP3, DP4, DP5 and DP6); (DPIM1, IW1) or (DP1, DP2) are taken separately, because within each set, the true gold loading is expected to be similar in all cases due to similarities in the preparation procedure. It can also be argued that the particle size might play a role on activity for these samples. However samples IW1, DP1 and DP2 have gold particle sizes in the same range has shown by TEM [12,20]. Also the samples DPIM1, DP3, DP4, DP5 and DP6 were prepared in the same precipitating conditions that is same pH and gold concentration of the preparing solution (see table 1). This should result in similar gold particle size and the only difference between these samples would be the degree of washing. In either of the above cases, the correlation remains valid. This rules out the possibility of the effect of the dilution of the solution and possibly the effect of particle size for these experiments.

The fact that the set of samples (DP1, DP2) contained less chlorine than the set (DP3, DP4, DP5 and DP6), agrees with our proposal that samples prepared at higher dilutions of the preparing solution will result in fewer impurities than those prepared at higher concentrations. This technique seems as effective in the prevention of impurities as a washing procedure.

4. Conclusions

In this article the effect of catalyst preparation on the activity of these samples was investigated and this helped to understand that:

- The generation of activity and resistance to deactivation by heating is associated with preparation methods that *avoid impurities* such as chlorine and sodium carbonate from the preparation. The first step in the preparation of active catalysts must be the generation of the right gold species devoid of chlorine. To do that, it is first necessary to convert the precursor $HAuCl_4$ into $Au(OH)_3$ by means of addition of an alkali (sodium carbonate in our case). This results in a considerable improvement of the activity of the resulting catalysts, but they are very prone to high temperature deactivation. This is due to the fact that impurities remain in the catalyst. To prevent this, impurities must be removed and this can be accomplished by using a low concentration the prepared solution and by washing of the samples. It was found that for the *DP samples*, these techniques *improve activity* and *resistance to deactivation* on heating.
- By using the previous principles, it was found for the first time that highly active samples could be prepared by IW methods *by using the DIM*.
- Finally a clear correlation between the chlorine amount on the samples as determined by XPS and the activity for low temperature CO oxidation was obtained.

Washing was shown to greatly enhance activity whatever the preparation method chosen (IW or DP method). It looks almost certain from these experiments, that the presence of Na and Cl has a detrimental effect on activity. Nevertheless, the avoidance of contamination is not the only requirement for a Au/TiO$_2$ sample to be active. In fact it still can be argued that the gold particle size changes when one performs the washings. To remove any doubts of the explanation of this striking washing effect, information on particle size, Na, Cl content and gold loading is required to tell which of these variables play the major roles in the activity. In the case of the determination of sodium in the sample, XPS is not ideal because of interference of secondary peaks in the titania signal. A good alternative could be AAS or ICP.

We think these results are important to point out the importance of acquiring relevant information on the chlorine and other impurities content prior to drawing any meaningful conclusion on the relation of the activity of catalysts to other parameters such as the gold particle size.

Acknowledgments

We thank the Portuguese government for funding J. Soares under grant SFRH/BD/831/2000 and the Universities of Cardiff and Reading for the provision of reactor facilities and analysis equipment.

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