Gold Bulletin
Volume 43 No 4 2010

Erratum

Due to the need to correct some diagrams this is a corrected reprint.

Investigation of the active site and the mode of Au/TiO_2 catalyst deactivation using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

M.C. Raphulu[1, 2,3], J. McPherson[1], E. van der Lingen[1], J.A. Anderson[2] and M.S. Scurrell[3]*

www.goldbulletin.org

Abstract

CO is a useful probe in the characterization of surface properties of both metal and metal oxide via adsorption. Adsorption of CO was used to monitor the possible active site of an Au/TiO_2 catalyst for the CO oxidation reaction. CO adsorption on the reduced catalyst results in the band at 2104 cm^{-1} indicative of Au^0. During the reaction (in the presence of both CO and O_2 present) the band is shifted to higher wave numbers indicating non-competitive adsorption on the surface of Au species. This study also reveals the relationship between the presence of CO (in the absence of oxygen) and the build-up of surface species such as bicarbonates, formates and carbonate species which decreases the activity of the catalyst. The presence of both the reduced and the cationic species of Au seem to be requirement for the activity of the catalyst.

1 Introduction

For years, gold has been considered inert and catalytically inactive. However, increasing attention has been given to Au as a catalyst since it has been reported that it can oxidize carbon monoxide at low temperatures. A CO oxidation process that is efficient at low temperatures has several technological applications such as removal of CO from automobile emissions, hydrogen gas (fuel cell applications) and CO_2 lasers. There is a global agreement on the high activity of the gold catalysts, Au nanoparticle size, and catalyst preparation methods. However, there has been a sharp dispute on the oxidation state of an active site of gold catalysts as well as the mode of catalyst deactivation [1-4].

Zanella *et al*. [1] observed an increased activity with the increasing amount of metallic gold species on Au/TiO_2 catalysts, with the highest activity being achieved with the catalyst calcined at 200°C which according to their X-ray absorption near-edge spectroscopy (XANES) results contained 100% Au^0 species. Although most of the researchers believe that active catalysts contain Au^0 species, and that Au^0 is the only species responsible for the high activity of gold catalysts, some are beginning to concede the possibility of the existence of oxidic Au species, probably in the form of $Au(OH)_3$ or Au(OH) at the perimeter interfaces at the conditions where water is present at concentration above 1 ppm, however, the role of these species the CO oxidation reaction is still disputed [2].

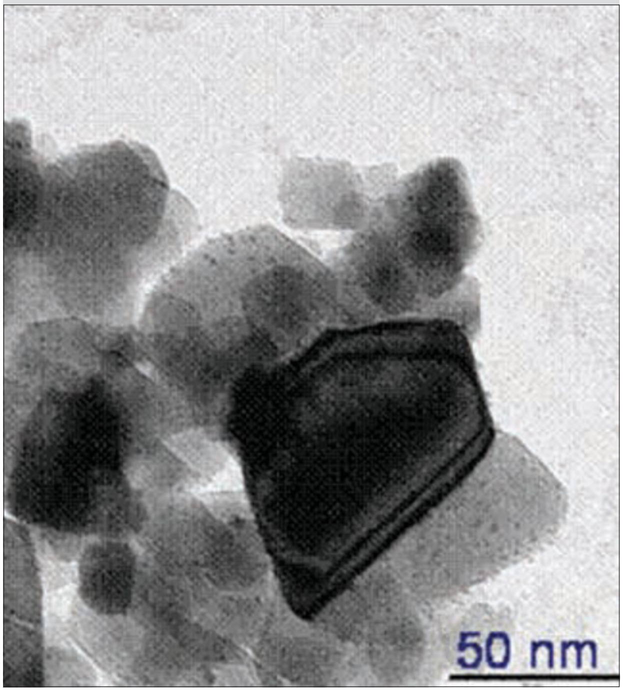
Based on the spectroscopic analysis indicating the presence of ionic gold in the most active catalysts, some researchers proposed the ionic gold to be necessary for high CO oxidation activity although there is no consensus on whether Au^{III}, Au^{I} or both, are important. However, other groups have reported that their as-prepared catalysts containing mainly

[1] *Advanced Materials Division, Private Bag X3015, Mintek, Randburg 2125; RSA*
[2] *Department of Chemistry, Kings College, University of Aberdeen, AB24 3UE. Scotland, UK*
[3] *Molecular Sciences Institute, School of Chemistry, Private Bag X3 PO Wits, 2050; RSA*

* *Corresponding author: Tel: +27 11 7176716; E-mail address: michael.scurrell@wits.ac.za*

Keywords: *DRIFTS, gold, titania, oxygen, carbon monoxide, carbonates, bicarbonates*

Figure 1



TEM image of a fresh 1% Au/TiO_2 catalyst after reductive pre-treatment

Au^{III} species were not active for CO oxidation and that activity increases with the increasing reduction of these species [1,3]. Several groups have observed the presence of ionic gold in active catalysts by Mössbauer [4,5], X-ray photoelectron spectroscopy (XPS) [6] and XANES [7] amongst others. Visco *et al*. [8] observed much larger catalytic activity with their uncalcined catalysts than with calcined ones and proposed that the oxidized Au species are the most active for low temperature CO oxidation with Au/Fe_2O_3 catalysts. Yang *et al*, [9] have used XANES to characterize the oxidation state of Au on TiO_2. These authors reported the presence of both Au^0 and Au^+ in the working catalyst. By using Secondary Ion Mass Spectrometry (SIMS), Fu *et al*. [10] found a relationship between the activity of the catalyst and the amounts of cationic Au, suggesting that higher concentrations of cationic Au result in higher activity of the catalyst.

The deactivation of gold catalyst with time-on-stream is a crucial factor that could hamper the industrial development of gold-based catalysts. In close relation to the mechanism of CO oxidation, the mechanisms of deactivation and regeneration of supported Au catalysts are also debated. It has been demonstrated that carbonate-like species such as carbonates $(CO_3)^{2-}$; bicarbonate (HCO^-_3); and formate/carboxylate/hydroxycarbonyl groups, $(HCO_2)^-$ are formed during CO adsorption and CO reaction with oxygen [11,12, and 13] via the step $CO + OH \rightarrow HCO_2$ amongst others. These species are thought to gradually poison the periphery of the particles that contains the O_2 activation sites and deactivate the catalyst. However, not all of these surface species are considered poisons to the CO oxidation reaction. Bicarbonates [14,15], hydroxycarbonyl [3] and formates [16] for example have been reported to be the reaction intermediates, hence their formation are important for high activity of the catalyst, while the presence of carbonates [15,16] deactivates the catalysts by blocking the active sites for CO adsorption. Catalysts deactivated by these species, especially carbonates can be regenerated by the presence of water which transforms the species into less stable bicarbonates which are easily decomposed into CO_2 [14].

Here, we use diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and CO as a probe molecule for the possible oxidation state of gold during the reaction and the accumulation of surface species on the catalyst. Though our catalyst was pre-treated in 5% H_2, literature data shows that such treatment does not completely reduce the catalyst. Schwartz *et al*. [17] observed the presence of $Au^{\delta+}$ with XANES after treating 2.5% Au/TiO_2 catalyst in 4%H_2 at room temperature. The authors concluded that the degree of reduction also depends on the amount of Au on the catalyst; such treatment on the 5% and 10% Au/TiO_2 catalysts resulted in total reduction according to their XANES results. Therefore since our catalyst is only 1% Au/TiO_2 it is expected to still contain considerable amounts of cationic species.

2 Experimental procedures

Catalyst preparation

The catalyst was prepared by the deposition precipitation method. Under constant stirring, 50 gAu/l $HAuCl_4$ was added to the necessary amount of deionised water and heated to 70°C. The pH of the solution was altered to pH=7.5 over a period of 10 minutes using 0.5 M Na_2CO_3 solution. The support (Degussa, 7711 P25, TiO_2) was added into the gold bearing solution and aged with constant stirring for 1 hour at 70°C while the pH is kept constant using 0.5 M Na_2CO_3 and 2 M HNO_3. After the prescribed ageing period the material is filtered and washed using 5 ml/g_{cat} of deionised water for five minutes.

The material is then filtered with this procedure being repeated a total of five times. The catalyst is then dried at 120°C for a period of 16.5 hours in a fan assisted oven.

A reductive pre-treatment was performed, whereby the catalyst was loaded into a batch type rotary kiln and held at room temperature for a specified period of time while a speed of 7 rpm and a flow of 2 l/min of 5 mol% H_2 in N_2 were maintained at 70°C.

Brunauer-Emmett-Teller (BET) surface area

The BET surface area analysis is carried out using the Micromeritics Accelerated Surface Area Porosimetry (ASAP 2020) instrument, which uses nitrogen at -196°C at a pressure of about 2 μmHg for porosity measurements. Prior to the analysis the samples are degassed at 90°C for half an hour then at 150°C for 3 hrs while being evacuated until a pressure of less than 10 μmHg is obtained in the sample holder.

Transmission Electron Microscopy (TEM)

A solid sample was crushed and suspended in methanol and the suspension was applied to a carbon coated copper grid. After allowing the samples to dry, the grids were inserted into a LEO 912 Omega TEM operating at 120 kV. The images were photographed using a Prascan camera.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

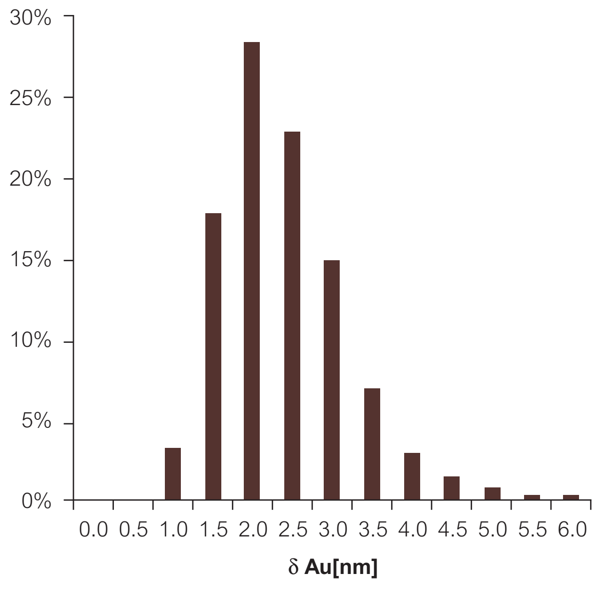
DRIFTS analysis was carried out using a Perkin-Elmer 1740 FTIR equipped with an MCT detector and a DRIFTS cell fitted with ZnSe windows. About 50 mg of the catalyst was crushed into fine powder and loaded into a DRIFTS cell and purged with air or N_2 for 1 h at 150°C, then cooled to room temperature before analysis. After this treatment, a background spectrum was taken using 128 scans and 4 cm^{-1} resolution. In some cases, gas stream leaving the DRIFTS cell was analysed using a quadrupole mass spectrometer. For the reaction a 1% CO in air mixture at 100 ml/min was used.

3 Results and discussions

3.1 Catalyst characterization

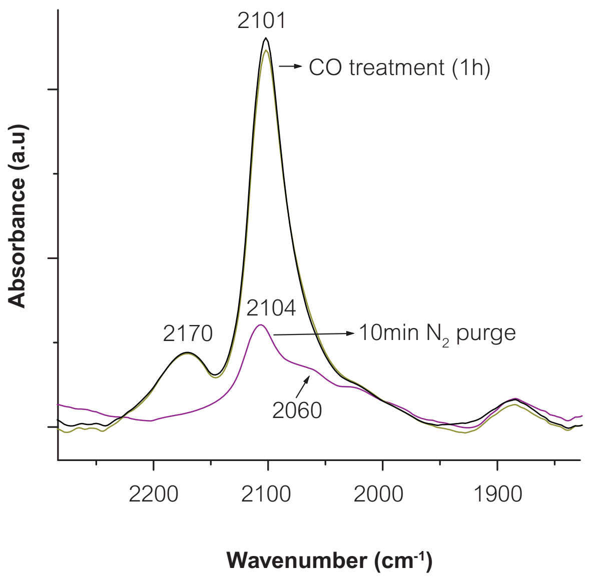
The TEM image shows that gold nanoparticles are well dispersed on the surface of the TiO_2 after both preparation and reductive pre-treatment, with average nanoparticle size of 2 nm. BET reveals that the TiO_2 support has a surface area of 45.6 m^2/g while that of an Au/TiO_2 catalyst has a surface area of 46.3 m^2/g.

Figure 2



Gold nanoparticle size distribution of 1% Au/TiO_2 catalyst as determined by TEM

Figure 3

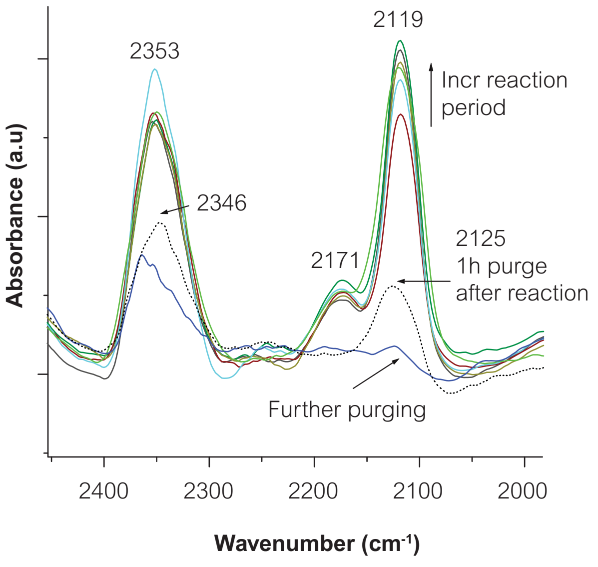


1% CO/N_2 adsorption on 1%Au/TiO_2 at 100 ml/min at room temperature

Table 1: Summary of peak positions of spectra in figure 3

Figure 3 labels	% O_2	Wavenumber (cm^{-1})
A	0	2096
B	0.1	2104
C	0.5	2113
D	1.0	2116
E	1.5	2118
F	2.0	2118
G	5.0	2120
H	10	2122
I	20	2125

Figure 4



Carbonyl section of spectra during CO oxidation (1%CO in air; 100 ml/min for 1h)

3.2 Active site

3.2.1 CO Treatment

Flowing 1%CO/N_2 results in the spectrum dominated by a sharp band at 2104 cm^{-1} and a smaller band at 2170 cm^{-1} due to interaction between CO and the Au^0 [9,18,19] and the support respectively. The CO peak observed is characteristic of high coverage, linear adsorbed CO on Au particles as has been observed previously in a single crystal Au and on Au/TiO_2. Purging the catalyst with N_2 decreases the amplitude of the sharp band to a smaller one and exposes a shoulder at *2060* cm^{-1}, which could be an indication of negatively charged Au [13].

3.2.2 CO oxidation

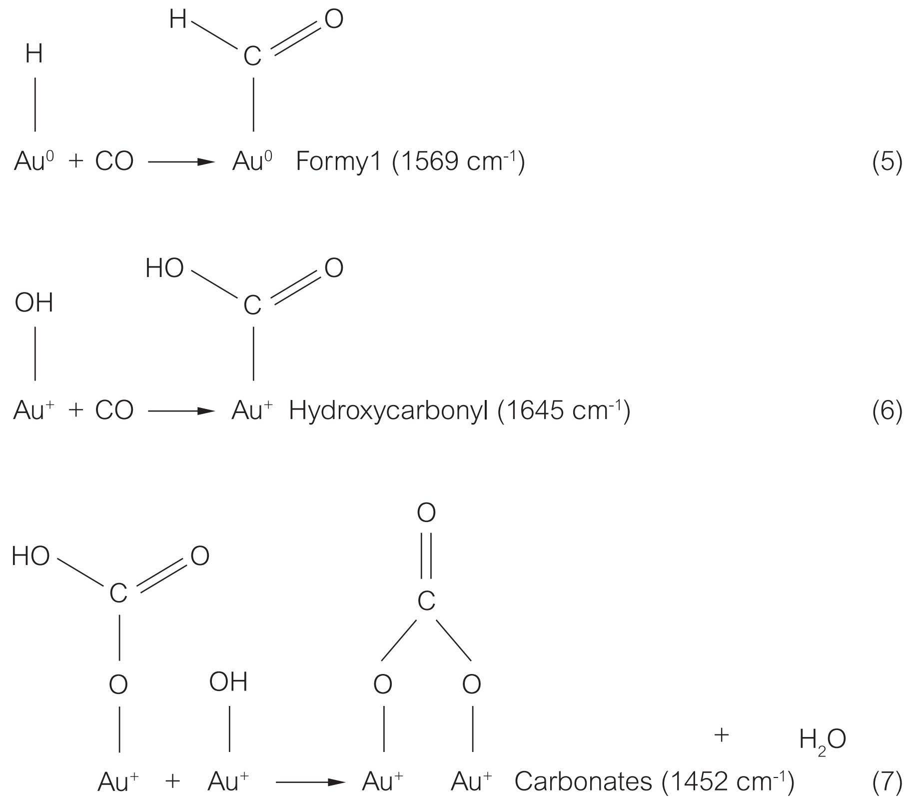
Figure 4 indicates that the catalyst exposed to both CO and oxygen consisted of positively charged (possibly just $Au^{\delta+}$) species evidenced by the band at 2119 cm^{-1} [20] and CO_2 indicated by the band at 2353 cm^{-1}. However, differences have been expressed in the literature on the assignment of the CO between 2112 and 2119 cm^{-1}. For instance, Clark *et al*, [17] reported the shift from 2102 cm^{-1} to 2114 cm^{-1} as a result of competitive adsorption on Au^0, rather than adsorption on an Au species with a different oxidation state. On the other hand, Yang *et al*, [9] and Boccuzzi *et al*, [20] described it as adsorption of CO on the Au that is associated with adsorbed oxygen. The metallic Au species observed with CO in the absence of oxygen (Figure 3) seems to have been slightly oxidized when oxygen is present (Figure 4). Switching the CO off and leaving air flowing shifts the band further to 2125 cm^{-1} owing to the presence of $Au^{\delta+}$. These species are stable even after purging for 60 minutes indicating that the interaction between CO and positively charged Au is stronger than with metallic Au. This is due to the change in the nature of bonding due to the effect of the increased σ (sigma) bonding and the synergistic increase of the π (pi) back-bond. This produces a blue shift of the CO stretching frequency and the increase in the overall $Au^{\delta+}$-CO band intensity [21].

The absence of the band around 2100 cm^{-1} due to CO adsorbed on Au^0 is an indication that during the reaction, metallic species may be important for the activation of oxygen as suggested by the reaction mechanism proposed by Costello *et al*, [3] making Au^0-CO interaction weaker while the Au^+-CO becomes stronger.

3.2.3 Effect of increasing volume of oxygen in the gas stream on Au^0-CO band

Introducing CO on the catalyst after treatment in N_2 at 150°C results in the appearance of a band at 2096 cm^{-1} due to C-O stretching frequency (reaction scheme 1) and another one at 2352 cm^{-1} due to the formation of CO_2 (spectrum not shown). Here, CO reacts with surface/lattice oxygen to form CO_2 in the absence of gaseous O_2. However, after 1 h of CO treatment (Figure 5a), the band at 2352 cm^{-1} disappears, indicating that the oxygen from the support is depleted. Introduction and gradual increase of the amount of oxygen in the CO stream leads to the blue shift of the CO band from 2096 cm^{-1} to higher wavenumbers (Figure 3).

Scheme 5, 6, 7



$$Au^0 + CO \rightarrow Au^0\text{-}CO \quad (1)$$

$$2Au^0\text{-}CO + O_2 \rightarrow Au^0\text{-}O + {}^{\delta-}O\text{-}Au^{\delta+}\text{-}CO^{\delta-} + CO \quad (2)$$

Introduction of O_2 results in a degree of competitive adsorption between oxygen and CO leading to the decrease in the size of a CO band as some Au^0 species adsorb oxygen and activate it into two oxygen atoms one of which migrates to the nearest Au^0-CO making it slightly positively charged (δ^+) (reaction 2) [3]. This, with increased amount of oxygen shifts the 2096 cm^{-1} band to frequencies as high as 2125 cm^{-1} (Table 1). Since we do not observe gaseous CO on our spectra at this point, the displaced CO is therefore believed to migrate to the surface hydroxyls or surface oxygen to form CO_2. We have to admit though that some of the shift in the position of the absorption maximum may reflect changes taking place in the coverage of adsorbed carbon monoxide.

Catalyst deactivation

It is important to first understand the surface of the catalyst before and after hydrogen pre-treatment before further DRIFTS results discussions. The fresh as-prepared catalyst is mainly Au^{3+}, which is reduced to Au^+ (reaction 3) and Au^0 (reaction 4) during hydrogen pre-treatment as follows:

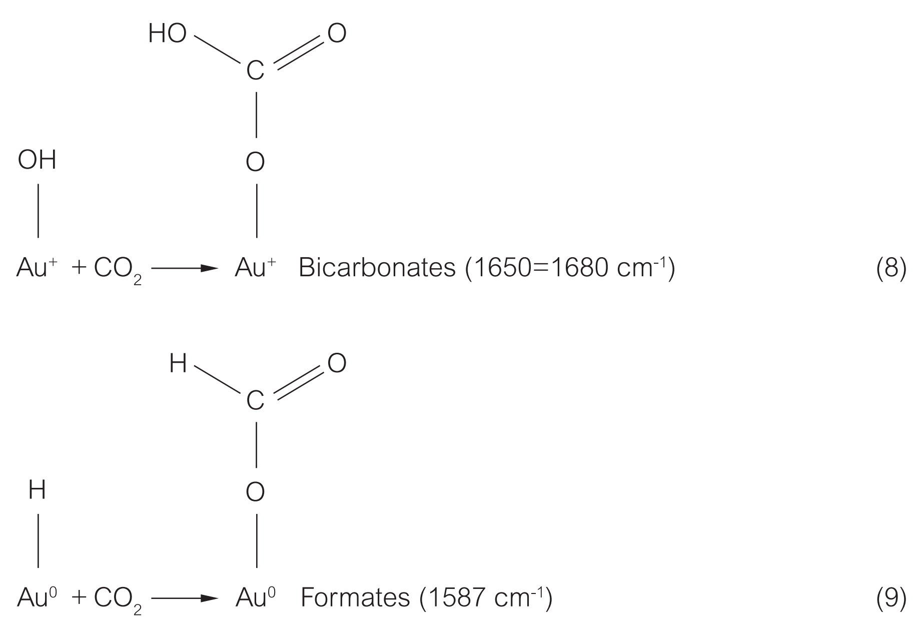
$$Au(OH)_3 + H_2 \rightarrow Au^+\text{-}OH + 2H_2O \quad (3)$$

$$Au(OH)_3 + 2H_2 \rightarrow Au^0\text{-}H + 3H_2O \quad (4)$$

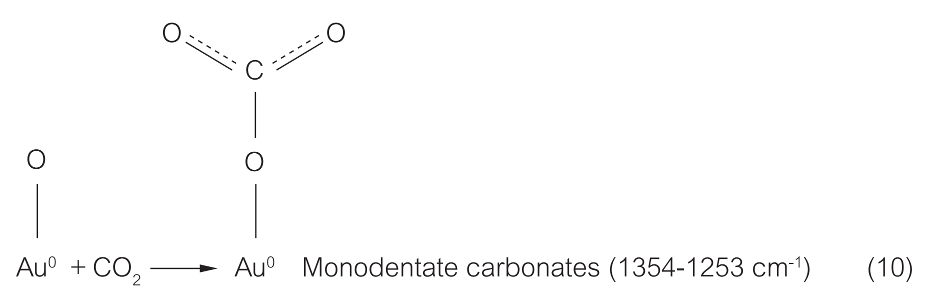
Gold monohydride species are relatively stable [22,23] and hydridic intermediates have been discussed or implicated in the context of gold catalysis [24].

Fresh gold catalysts accumulate bicarbonates species during preparation, probably due to the combination of atmospheric CO_2 and surface moisture.

Scheme 8, 9



Scheme 10



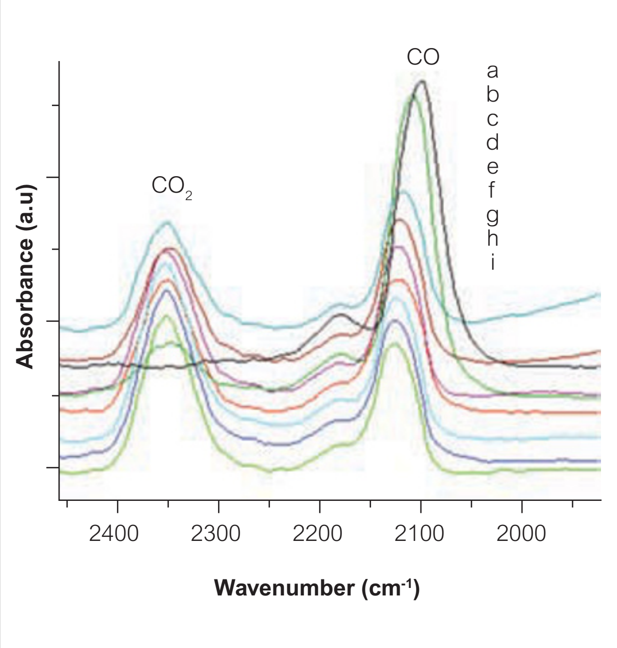
Interestingly, despite such accumulation during preparation, most gold catalysts are still highly active at the beginning of the reaction. It is therefore important to investigate the relationship between the presence of CO (in the presence and absence of oxygen) and the formation of new surface species, which probably differ from those accumulated during preparation.

3.2.4 Effect of CO exposure on surface species accumulation

The catalyst (Au/TiO_2) was dried in air at 150°C for 60 minutes, and then cooled to room temperature in N_2 before scanning the background spectrum.

A gradual increase in the amount of CO from 0.05% to 1%, results in the appearance and the increase in the band due to the interaction of CO with Au^0 at 2104 cm^{-1} together with a second band due to the interaction of CO with the support at 2170 cm^{-1}. Further increase in the CO amount up to 10% results in the formation of a species giving rise to a new band at 2051 cm^{-1} which is suspected to be due to negatively charged Au entities and a shoulder at 1986 cm^{-1} due to the bridge-bonded CO [13,19]. Purging the catalyst quickly removes the bands due to CO interaction with the support, and drastically decreases the band due to CO interaction with the Au^0. However, the band due to $Au^{\delta-}$-CO and its

Figure 5



Carbonyl section of spectra during an increase of O_2 in the 1% CO/N_2 stream. (a, 0; b, 0.1; c, 0.5; d, 1; e, 1.5; f, 2.0; g, 5.0; h, 10; I, 20%)

shoulder at 1986 cm^{-1} decrease gradually and do not completely disappear after 1 hour of nitrogen purging.

On the carbonate section of the spectrum, we observed the formation and increase in the amount of new surface species represented by the bands at 1645 cm^{-1}, 1569 cm^{-1}, and 1420 cm^{-1} due to hydroxycarbonyl, formate and carbonate species respectively (Figure 5a and reactions 5, 6 and 7). The formation of these species in the absence of oxygen shows that they result from the reaction of CO with surface/lattice oxygen. However the carbonates are considered to be formed due to the combination of Au-OH and surface bicarbonate (already present before CO introduction), though the precise final location of the observed species remains unclear. This reflects a general limitation of the infrared method.

3.2.5 Effect of Au/TiO_2 catalyst exposure to CO_2 on activity and surface species accumulation

A fresh Au/TiO_2 catalyst was treated with 1% CO_2/N_2 at room temperature for about 60 minutes then purged with N_2 for a further 30 minutes before the reaction mixture was admitted into the DRIFTS chamber.

Catalyst exposed to CO_2 does not result in the strong interaction of CO_2 with the catalyst surface. Adsorbed CO_2 is observed mainly as a product of the CO oxidation reaction (Figure 7a). The amount of adsorbed CO_2 increases sharply in the first 20 minutes, thereafter decreasing gradually with time-on-stream. Figure 7b indicates that exposure of the catalyst to CO_2 leads to the formation of bands at 1680 cm^{-1} and 1587 cm^{-1} with the latter shifting to 1650 cm^{-1} upon increased period of exposure. These are due to the formation of bicarbonate and/or hydroxycarbonyl and formate species on the surface of the catalyst as shown by reactions 8 and 9.

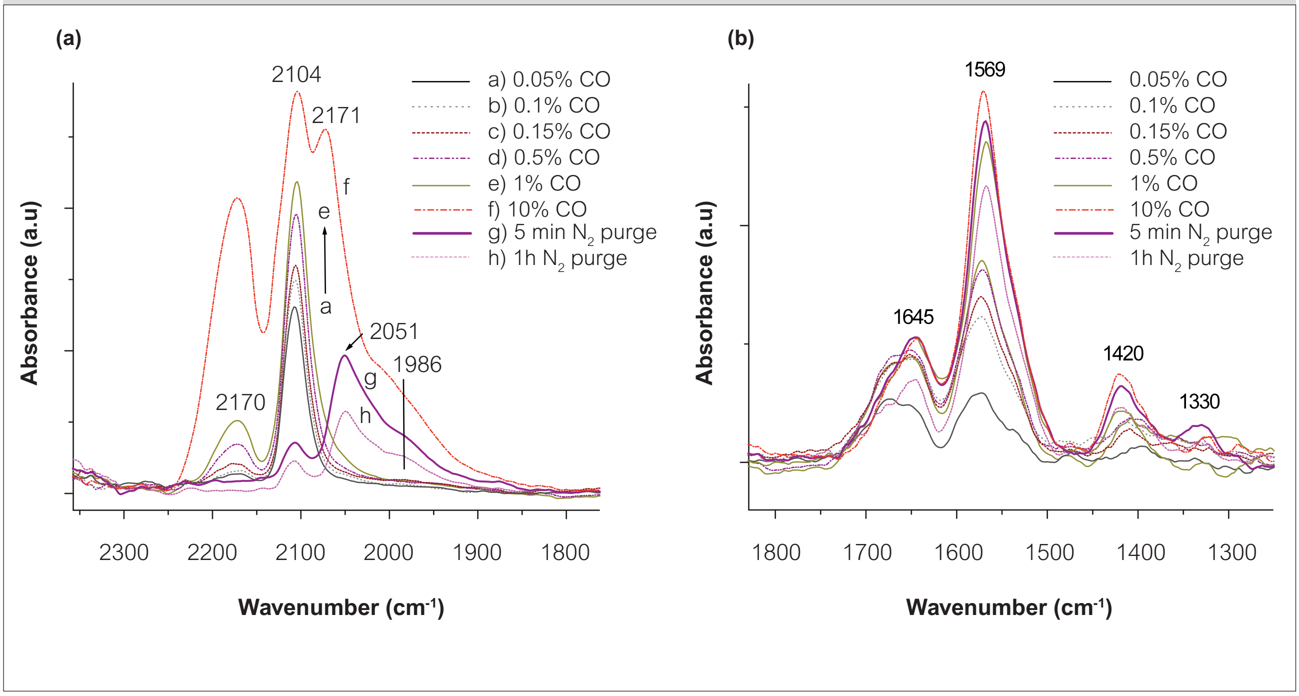
When the reaction mixture is introduced onto the catalyst, new bands due to carbonate species at 1452 cm^{-1} (bidentate bridging, [25]22]), 1354 cm^{-1} (monodentate, [26,27] 23,24]), and 1253 cm^{-1} [16 and references therein] are formed while those that previously existed (1677 cm^{-1}, 1599 cm^{-1}), are much more pronounced and blue-shifted. During the reaction, the surface species population increase sharply in the first 20 minutes as was seen with the amount of surface CO_2 in the carbonyl region, decreasing slightly and become constant with further time-on-stream.

Bicarbonate and formate species form on the surface of the catalyst as shown in the reaction schemes 8 and 9.

During CO oxidation, the catalyst consists of Au^0-O species when an O_2 molecule is activated as shown in reaction 2. The bicarbonates and the available OH groups accumulate as shown in reaction 7 to form carbonate species (1452 cm^{-1}). In addition, CO_2 was produced as a reaction product adsorbed on Au^0-O sites to form different kinds of carbonate species (1354 cm^{-1}) as shown in reaction 10 [18].

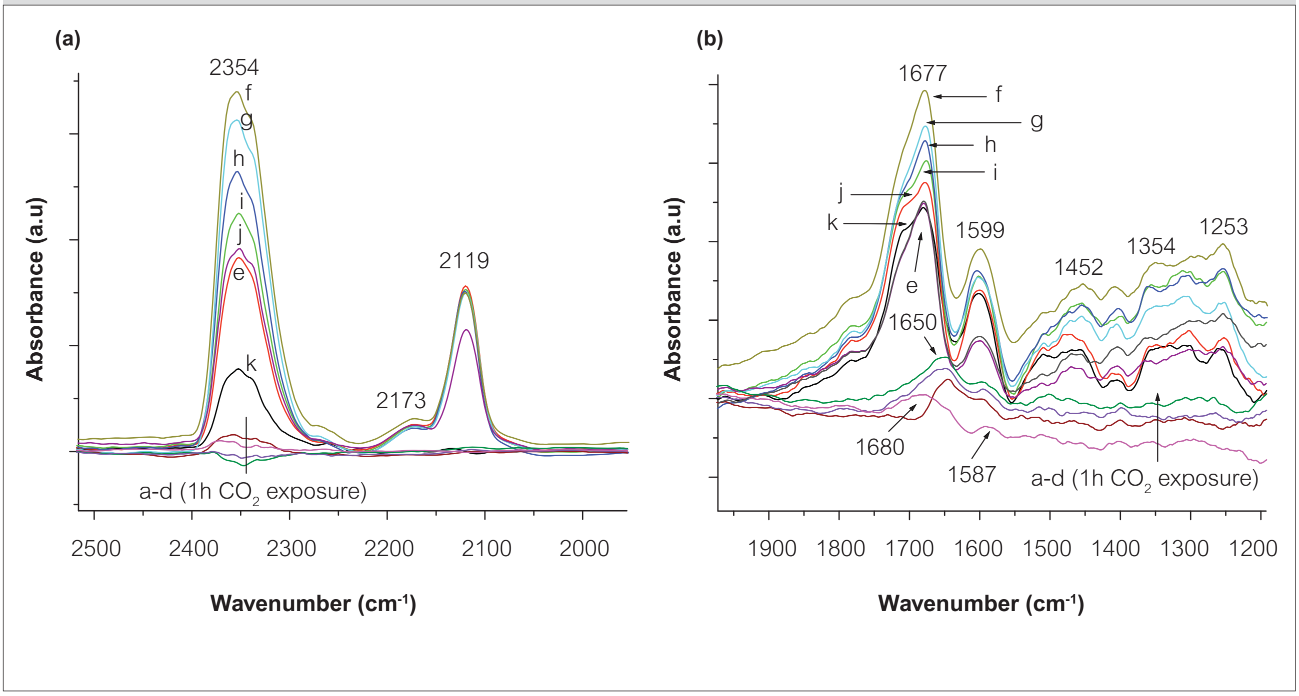
Again, we speculate that these species are formed on gold sites, but their precise final location, given that a support surface is also available, remains unclear. CO was allowed to flow through the catalyst, for the first 30 minutes, after which oxygen was introduced into the gas stream resulting in the rapid decrease in the amount of CO and an increase in the amount of CO_2. Three minutes after the reaction started the amount of CO started to slowly increase indicating the deactivation of the catalyst. However, the amount of CO_2 was still increasing in the gas phase for the following 20 minutes after the start of reaction.

Figure 6 a, b



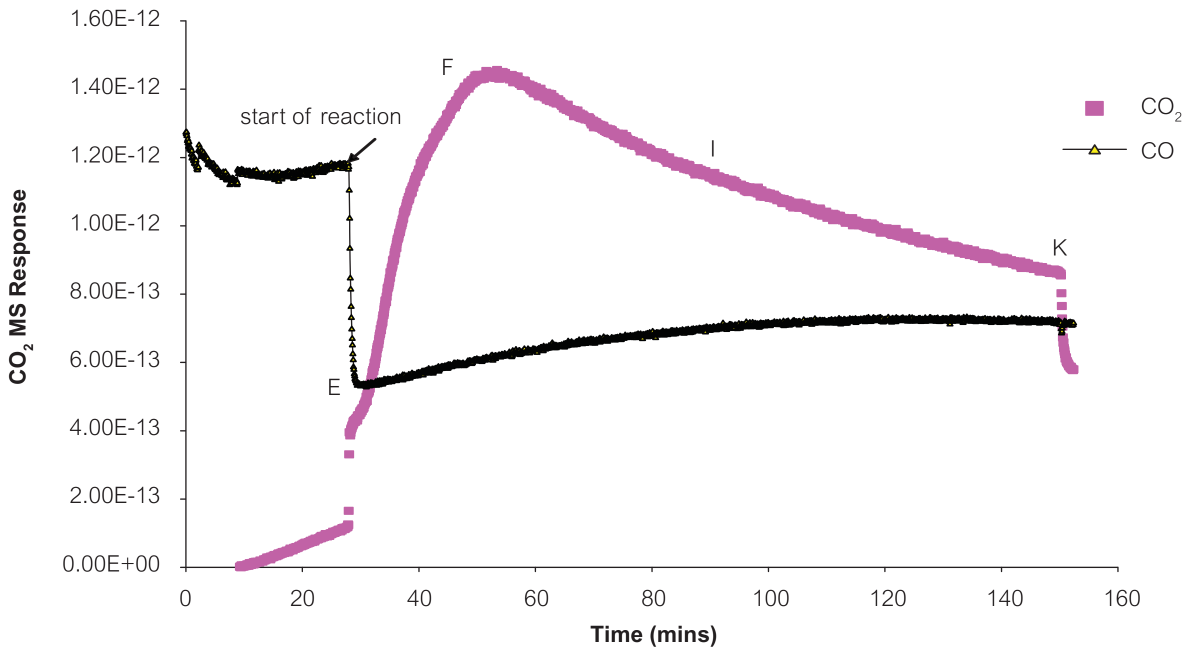
Effect of increasing CO on accumulation of surface species: (a) carbonyl section, (b) carbonate section

Figure 7 a, b



Effect of increasing CO on accumulation of surface species: (a) carbonyl section, (b) carbonate section

Figure 8



Mass spectrometer profile of CO oxidation with 1% CO in air at room temperature; where labeled points relate to DRIFTS spectrum in figure 5

This increase is accompanied by the formation of bicarbonate species during the first 20 minutes of the reaction as shown in Figure 7b. However, after 20 minutes the amount of CO_2 produced begin to decrease accompanied by a decrease in the amount of bicarbonate species and the increase in the formation of the carbonate species.

Conclusions

On a reduced catalyst, CO is weakly adsorbed on Au^0 species. In the presence of oxygen, the Au^0-CO band shifts to higher wavenumber indicating the adsorption of CO on the Au particle associated with oxygen. Metallic Au particles are believed to be activating an oxygen molecule into two oxygen atoms. This shows a synergy between positively charged and metallic gold nanoparticles. It is recognized that the precise location of carbonate and bicarbonate entities is not revealed by the use of infrared spectroscopy [28] alone. The suggestion has been made by others [28] that extensive work is needed with blank runs using the support alone, possibly in conjunction with other techniques. However, in practice, blank runs themselves may have a limited use, since it is clear that the presence of gold seriously disrupts the surface and the bulk properties of the support [29,30]. Sites present on the gold-free support may be greatly modified by the gold, and this may apply even at relatively large distances from the gold centres. This seriously hampers the use of blank runs.

CO adsorption in the absence of oxygen results mainly in the formation of formate species while bicarbonates and carbonate species are minimal. The presence of oxygen however results in the formation of more carbonates and bicarbonates on the surface of the catalyst, and deactivation of the catalyst. There seem to be more ways of carbonate formation on the surface of the catalyst as shown in reactions 7 and 10. Catalyst deactivation is the result of the formation of carbonate species on the surface of the catalyst. These species form gradually during the reaction and prevent the activation of oxygen on Au^0 species and the adsorbtion of both oxygen and CO to form CO_2.

Acknowledgements

This work was facilitated by the award of a Postdoctoral Fellowship (to MCR) from the Royal Society, London, administered by the University of the Witwatersrand. Mintek is thanked for granting leave to MCR as well as providing gold catalysts. Project AuTEK (Mintek and Anglogold-Ashanti) is thanked for the permission to publish the results.

About the authors

Dr Mpfunzeni Raphulu is a Senior Scientist at Mintek, in Randburg, South Africa. Having obtained a PhD in catalysis from the University of Witwatersrand in 2004, his main interests are the deactivation of gold catalysts and surface characterisation.

Mr Jason McPherson heads up the Scale-up and Commercialisation Unit of Project AuTEK's Catalysis Programme (Mintek, South Africa) and as such is actively involved in the production, marketing and application of AuTEK's AUROlite^{TM} range of gold catalysts. He is highly active in application areas such as CO oxidation, preferential oxidation, liquid phase oxidations (e.g. glucose, glycerol), and selective hydrogenation.

Dr Elma van der Lingen is Manager of the Advanced Materials Division at Mintek, in which Project AuTEK (programme on new industrial uses for gold) is hosted. She is involved in research and development projects in the fields of catalysis, corrosion, electrochemistry, coatings, powder metallurgy, catalysis, nanotechnology and alloy development.

Jim Anderson hold a 6th Century Chair in chemistry at the University of Aberdeen. He is currently chairman of the UK catalysis society (SURCAT) and secretary of EFCATS. His research interests include the use of vibrational spectroscopy to study selectivity effects over supported metals and for site quantification.

Mike Scurrell holds the Chair of Physical Chemistry at the University of the Witwatersrand, Johannesburg and his research interests are associated with surface chemistry and heterogeneous catalysis.

References

1 R. Zanella, S. Giorgio, C.-H. Shin, C.R. Henry, C. Louis, *J. Catal*. **222** (2004) 357
2 M. Haruta, *Chem. Record*. **3** (2003) 75
3 C.K. Costello, M.C. Kung, H.-S. Oh, Y. Wang, H.H. Kung, *Appl. Catal. A*: **232** (2002) 159
4 J.M.C. Soares, P. Morrall, A. Crossley, P. Harris, M. Bowker, *J. Catal*. **219** (2003) 17
5 R.M. Finch, N.A. Hodge, G.J. Hutchings, A. Meagher, Q.A. Pankhurst, M. Rafiq, H. Siddiqui, F.E. Wagner, R. Whyman, *PCCP. 1* (1999) 485
6 E.D. Park and J.S.Lee, *J. Catal*. **186** (1999) 1
7 J. Guzman and B. Gates, *J. Phys. Chem. B*: **106** (2002) 7659
8 A. Visco, A. Donato, C. Milone, S. Galvagno, *Reac. Kinet. Catal. Lett*. **61** (1997) 219
9 J. Yang, J. Henao, M.C. Raphulu, Y. Wang, T. Caputo, A. Groszek, M.C. Kung, M.S. Scurrell, T.J. Miller, H. Kung, *J. Phys. Chem. B*. **109** (2005) 10319
10 L. Fu, N. Wu, J. Yang, F. Qu, D. Johnson, M.C. Kung, H. Kung, and V. Dravid, *J. Phys. Chem. B*. **109** (2005) 3704
11 P. Konova, A. Naydenov, D. Venkov, D. Mehandjiev, D. Andreeva, T. Tabakova, *J. Mol. Catal. A* **213** (2004) 235
12 M. Manzoli, A. Chiorino, F. Boccuzzi, *Appl. Catal. B*. **52** (2004) 259
13 B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R. Behm, *J. Catal*. **224** (2004) 449
14 M. Schubert, A. Venugopal, M. Kahlich, V. Plzak, R. Behm, *J. Catal*. **22** (2004) 32
15 S. Daniells, A. Overweg, M. Makkee, J. Moulijn, *J. Catal*. **230** (2005) 52
16 Y. Denkwitz, A. Karpenko, V. Plazk, R. Leppelt, B. Schumacher, R.Behm, *J. Catal*., **246** (2007) 74

17 V. Schwartz, D. Mullins, W. Yan, B. Chen, S. Dai, S. Overbury, *J. Phys Chem B* **108** (2004) 15782

18 J.C. Clark, S. Dai, H. Overbury, *Catal. Today* **126** (2006) 135

19 F. Boccuzzi, A. Chiorino, M. Manzoli, *Surf. Sci.* **942** (2000) 454

20 F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, *J. Catal.* **202** (2001) 256

21 M. Manzoli, F. Boccuzzi, A. Chiorino, F. Vindigni, W. Deng, M. Flytzani-Stephanopoulos, *J. Catal.*, **245** (2007) 306

22 P. Pyykkö, *Chem. Rev.*, **88** (1988) 563

23 P. Schwendtfeger, W.H.E. Schwarz, G.A. Bowmaker, P.D.W. Boyd, *J. Chem. Phys.*, **91** (1989) 1752

24 G.C. Bond, C. Louis, D.T. Thompson, *Catalysis by Gold, Catalytic Sceince Series*, vol. 6, Imperial College Press, London, 2006, pp. 150-152

25 M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, *J. Catal.*, **144** (1993) 175

26 B-K. Chang, B. Jang, S. Dai, S. Overbury, *J. Catal.* **236** (2005) 392

27 A. Karpenko, R. Leppelt, V. Plzak, J. Cai, A. Chuvilin, B. Schumacher, U. Kaiser, R.J. Behm, *Top. Catal.* **44** (2007) 183

28 Y. Hao, M. Mihaylov, E. Ivanova, K. Hadjiivanov, H. Knözinger, B.C. Gates, *J. Catal.* **261** (2009) 137

29 A. Debeila, M.C. Raphulu, E. Mokoena, M. Avalos, V. Petronovskii, N.J. Coville, M.S. Scurrell, *Mater. Sci. Engng A* **396** (2005) 61

30 A. Debeila, M.C. Raphulu, E. Mokoena, M. Avalos, V. Petronovskii, N.J. Coville, M.S. Scurrell, *Mater. Sci. Engng A* **396** (2005) 70