Catalysis Letters Vol. 100, Nos. 1–2, March 2005 (© 2005)
DOI: 10.1007/s10562-004-3083-z

The effect of high-temperature pre-treatment and water on the low temperature CO oxidation with Au/Fe_2O_3 catalysts

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Received 15 October 2004; accepted 15 November 2004

The low temperature activity of Au/Fe_2O_3 catalysts towards CO oxidation was examined with respect to the temperature of pre-treatment and presence of water. The activity of all the prepared catalysts decreased as a result of a high temperature treatment (HTT) at 400 °C. The inclusion of water in the gas stream significantly enhanced the oxidation of CO at room temperature. When tested under water gas shift reaction (WGSR) conditions, significantly higher temperatures were required to convert CO to CO_2, thereby excluding the possibility of the WGSR during CO oxidation in the presence of H_2O at room temperature. The loss of activity for CO oxidation is attributed to the loss of hydroxyl groups and reduction of Au^{3+} to metallic gold during HTT. The observations are consistent with the model for hydroxyl promotion of the decomposition of a carbonate intermediate by transformation to less stable bicarbonate.

KEY WORDS: CO oxidation; gold; water gas shift; active site.

1. Introduction

The studies of metal-oxide supported gold catalysts, particularly for CO oxidation and the water gas shift reaction (WGSR), have considerably increased since Haruta's early pioneering work [1,2]. It was claimed that, despite the limited adsorption properties of gold, by depositing nano-particulate gold on metal-oxide supports, high activity could be achieved for CO oxidation at low temperatures, even below 0 °C.

Since then, many groups have studied the catalytic activity of supported gold catalysts, and it has become clear that there are many variables that should be controlled in order to obtain high CO conversions. Of particular importance are the preparation method, the pre-treatment conditions, choice of support, presence of moisture in the feed, and the oxidation state of the Au in the particles (for further information see [3] and references therein).

Hutchings and co-workers [4,5] studied CO oxidation with Au/Fe_2O_3 catalysts and found that the uncalcined catalyst was most active, relative to a calcined sample. Mössbauer spectroscopy revealed the presence of both cationic Au^{3+} and metallic gold, while the support was predominantly ferrihydrite, $Fe_5HO_8{\cdot}4H_2O$. The key intermediate in the mechanism of the CO oxidation was proposed to be a carboxylate. The less active calcined sample showed the exclusive presence of metallic Au supported on haematite, α-Fe_2O_3. Wagner *et al.* [6] also studied uncalcinced Au/Fe_2O_3 catalysts with Mössbauer spectroscopy and, although they detected significant concentrations of Au^{3+}, they could not conclude if cationic gold was required for high activity. They did, however, observe an increase in activity with increasing ferrihydrite concentration.

Fe_2O_3-supported Au catalysts were studied by Gupta and Tripathi [7,8], who reported that lattice oxygen was involved in CO oxidation at low temperatures. They also reported the presence of both carbonates and bicarbonates, but dismissed these species as possible intermediates in the mechanism. In our previous work combining Mössbauer spectroscopy, FTIR, and TAP for uncalcined Au/Fe_2O_3, we proposed that the active site was an ensemble of Au^{3+} and Au^0, with hydroxyls from the cationic gold and the support promoting bicarbonate formation and decomposition to produce CO_2 (Daniells et al., submitted). The transformation of carbonates into thermally less stable bicarbonates by the presence of OH groups extends the lifetime of the catalyst, and prevents deactivation by carbonate accumulation [9–15].

Andreeva *et al.* [16–19] studied the WGSR with Au/Fe_2O_3 and reported that the key aspects of the mechanism were the dissociative adsorption of H_2O on Au particles, followed by spillover of OH to the iron oxide support and the successive reoxidation of $Fe^{2+} \rightarrow Fe^{3+}$. The Au/Fe_2O_3 catalyst prepared by co-precipitation manifested a CO conversion of less than 20% at 120 °C, and increased to approximately 50% at 200 °C

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1011-372X/05/0300–0039/0

[18]. The higher temperatures required for the WGSR, relative to CO oxidation, led Daté *et al*. [13] to exclude WGSR as the reason for increased activity for CO oxidation in the presence of H_2O.

In this letter, we report the effects of thermal pre-treatments and the inclusion of H_2O for CO oxidation on home-made Au/Fe_2O_3 catalysts, and the commercially available 4.5% Au/Fe_2O_3 supplied by the World Gold Council (WGC) [20].

2. Experimental

2.1. Catalyst preparation

Catalyst samples were prepared using the co-precipitation method and partially characterised at Cardiff University, and transferred *via* the EU network *Auricat* (Contract Number: HPRN-CT-2002-00174). The samples were not calcined prior to transfer. Similar samples were prepared previously by the same group and details of their preparation method have been described in references [4,5]. The Au/Fe_2O_3 reference catalyst from the WGC was prepared by co-precipitation and obtained with full characterisation. The Au/Fe_2O_3 (WGC) was calcined after preparation at 400 °C. The average Au particle size was 3.7 nm and actual gold loading determined by ICP was 4.5 wt%.

2.2. Catalytic performance

These experiments were performed in a 6-flow reactor set-up, which has been described in detail elsewhere [21]. About 50 mg samples were placed in quartz reactors (i.d. 4.0 mm) and secured between two quartz wool plugs. A thermocouple was positioned in each of the catalyst beds to monitor temperature, and the reactor furnace was controlled using a Eurotherm 2604 controller. The reactant gases, He (100%), CO (100%), and O_2 (100%) were used without further purification and were fed from independent Bronkhorst F-201C mass-flow controllers. H_2O was fed using a Bronkhorst liquid MFC. A typical GSHV of 50,000 L/L h was applied. CO, O_2, CO_2, and H_2O were analysed using Gas Chromatography (Chrompack CP 9001) equipped with a thermal conductivity detector, using a Poraplot Q column and a Molsieve 5 A column. Results refer to catalysts after either no treatment or a high temperature treatment (HTT) at 400 °C in flowing He for 30 min prior to cooling to reaction temperature. Gas compositions typically used 0.5% CO, 10% O_2, and 2.5% H_2O, and were balanced with He, unless otherwise stated.

2.3. Temporal analysis of products

Transient studies were performed in an advanced TAP reactor system [22,23], MultiTRACK (**Multi**ple **T**ime **R**esolved **A**nalysis of **C**atalytic **K**inetics). The system has been described elsewhere [24], however, the main points are summarised here. The reactor (7 mm inner diameter, 10 mm bed height) is located in an ultra-high vacuum-chamber to which gas pulses in the order of 10^{16}–10^{17} molecules can be introduced.

Samples of Fe_2O_3 and Au/Fe_2O_3 (1% and 3.4% Au loading) with particle size 212–300 μm were held between SiC plugs (212–300 μm, 300–425 μm). The catalysts were either used without any pre-treatment or heated to 400 °C under vacuum for 20 min prior to cooling to the experimental temperature. The surface area of the fresh (as-received) 3.4% Au/Fe_2O_3 calculated from BET theory was 203 m^2/g. Assuming a lattice constant of α-Fe_2O_3 of 0.5 nm [25], and 0.05 g samples, the total number of surface sites available was 4.1×10^{19}, with approximately 8×10^{17} Au gold sites. The total bulk molecule amount was calculated to be 1.5×10^{20}.

The gases (Hoek Loos Gases) used for the experiments were O_2 (20.2% in Ar), CO (20.0% in Ar), CO (100%), CO_2 (100%), and $^{18}O_2$ (100%, 99.2% Isotopic purity, Isotec Inc.), and were used without further purification. Reactants and products were recorded at the reactor outlet by three PC interfaced Balzers QMA 124 quadrupole mass spectrometers (QMS) in line. A fourth mass spectrometer was positioned above the exit point of the reactor to continuously monitor the product stream. Standard fragmentation patterns and sensitivity factors were used to extract the variation in each reactant from the output of the QMS.

3. Results and discussion

3.1. The effect of pretreatment on CO oxidation

Figure 1 shows the effects of thermal pre-treatment on the CO oxidation reaction at 25 °C. Both 1% Au/Fe_2O_3 and 3.4% Au/Fe_2O_3 samples showed decreased CO conversion after HTT at 400 °C. The 3.4% Au/Fe_2O_3 sample was sensitive to HTT and rapidly deactivated with increasing time-on-stream. The BET surface area also decreased dramatically after HTT, falling from 203 to 45 m^2/g. Conversely, the 4.5% Au/Fe_2O_3 reference catalyst from WGC showed increased CO conversion at the HTT. The extent of deactivation of the HTT sample was greater than that for the fresh catalyst (Table 1).

This result is consistent with the work of Hutchings and co-workers [4,5] who reported that the activity of their Au/Fe_2O_3 catalysts, prepared using the same methodology as the samples in this study, decreased as a result of a high temperature treatment. Mössbauer studies in our laboratory (Daniells *et al*., submitted) for the 3.4% Au/Fe_2O_3 showed that the fresh (uncalcined) catalyst was predominantly Au^{3+} (88%) with some Au^0 (12%). The support was proposed to be ferrihydrite, $Fe_5HO_8{\cdot}4H_2O$. The low loading Au sample (1.15% in the study of Hutchings and co-workers [4]) showed relative spectral areas of Au^{3+} and Au^0 of 14 and 86,

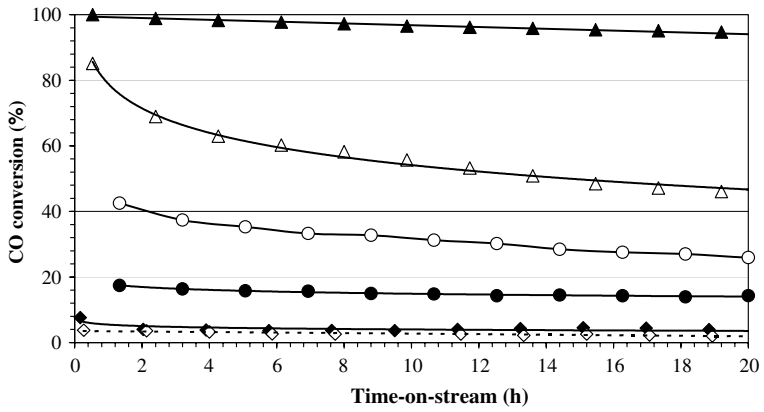

Figure 1. CO conversion during CO oxidation at 25 °C with fresh/as-received Fe_2O_3 supported Au catalysts as a function of time-on-stream for thermal pre-treatments: (◆) 1% Au/Fe_2O_3, (▲) 3.4% Au/Fe_2O_3, and (●) 4.5% Au/Fe_2O_3 (WGC). Closed symbols: fresh/as-received catalyst. Open symbols: After HTT at 400 °C in flowing He. 2% CO, 2% O_2, balance He. GSHV of 50,000 L/L h.

Table 1
Sample BET surface area and Au loadings for Fe_2O_3 and Au/Fe_2O_3 samples

Sample	Au loading (wt%)	BET (m^2/g)	
		Fresh sample	HTT sample
Fe_2O_3	0	172	51
Au/Fe_2O_3	1.0	176	44
Au/Fe_2O_3	3.4	203	45
Au/Fe_2O_3 (WGC)	4.5	38.7*	38.7

HTT refers to the high temperature treatment of 400 °C in He for 30 min.
*High temperature treatment applied during production.

respectively. Therefore, the significant difference between these two fresh (non-thermal pre-treatment) samples observed in the oxidation of CO at 25 °C may be due to the higher concentration of Au^{3+} in the higher loading sample.

When treated at 400 °C, the catalysts were found to be exclusively metallic gold supported on haematite, α-Fe_2O_3 [4, Daniells *et al.*, submitted]. Treatment of the catalyst at high temperature led to complete reduction of the Au^{3+} to Au^0, and a phase transition of ferrihydrite to haematite. During TPD analysis, significant quantities of H_2O were recorded during the heating process, thereby indicating the loss of surface OH/H_2O. The loss of activity for the 3.4% Au/Fe_2O_3 catalyst is greater than for the 1% Au/Fe_2O_3. In the latter catalyst, there exists only a minority of Au^{3+} in the fresh sample, whereas the relative spectral area of Au^{3+} in the higher loading sample is greater than 80%. This loss of Au^{3+} in the 3.4% Au/Fe_2O_3 is consistent with the proposal that a higher concentration of Au^{3+} in the sample enhanced the activity. The HTT samples would have considerably less OH and H_2O present on the surface and this might be reflected in the decrease in the oxidation of CO. The increase in the activity of the WGC reference catalyst after HTT may be simply due to the decomposition of carbonate-type species as were evidenced on the fresh samples by FTIR and TPD (Daniells et al., submitted). For the other catalysts, 1% Au and 3.4% Au/Fe_2O_3, the presence of hydroxyls enhances the conversion of CO. However, after HTT at 400 °C, the surface is predominantly clear of OH/H_2O, the surface area has decreased, and the catalyst is a much more ordered Au/α-Fe_2O_3 [4,5,7,8]. All catalysts were prepared using the co-precipitation technique [4,5]. However, different sources of the Fe_2O_3 and Au-precursor would undoubtedly affect the final catalyst. Therefore, it is proposed that direct comparison between the 1% and 3.4% Au/Fe_2O_3 catalysts and the 4.5% Au/Fe_2O_3 WGC reference catalyst based mainly only on Au gold loading is not accurate.

Figure 2 shows the results of CO oxidation at 25 °C as a function of CO and O_2 partial pressure. It is clear from the figure that the 3.4% Au/Fe_2O_3 catalyst was the most active and demonstrated only limited deactivation after 20 h-on-stream at the higher CO partial pressure. A marked decrease in activity for the 4.5% Au/Fe_2O_3 (WGC) reference catalyst was observed, with an initial CO conversion of 85% for 0.5% CO, 20% O_2, and only approximately 20% CO conversion for 2% CO, 2% O_2. This result suggests that CO oxidation is 1st order with respect to CO for the WGC sample since the CO conversion is proportional to the relative CO concentration. Decreasing the O_2 concentration from 10% to 2% does not appear to have such a marked affect, suggesting that the reaction is zero-order, with respect to O_2. The 1% Au/Fe_2O_3 sample also demonstrated a decrease in CO conversion, with a steady-state conversion of 15% and 5% for the 0.5% CO, 20% O_2 and 2% CO, 2% O_2 conditions, respectively. Fe_2O_3 (predominantly in the form of ferrihydrite [4]) showed no activity for CO oxidation at 25 °C for both sets of conditions.

Multiple **T**ime **R**esolved **A**nalysis of **C**atalytic **K**inetics (MultiTRACK), an advanced TAP reactor system, was used to study the CO and O_2 adsorption under

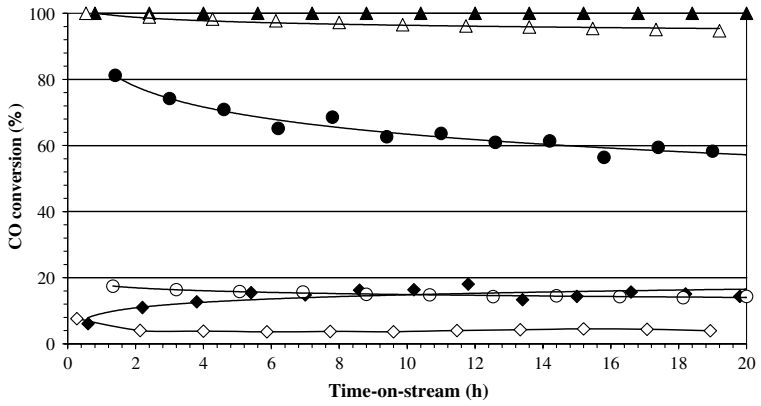

Figure 2. CO conversion during CO oxidation at 25 °C with fresh/as-received Fe_2O_3 supported Au catalysts as a function of time-on-line for different CO and O_2 partial pressures: (◆) 1% Au/Fe_2O_3, (▲) 3.4% Au/Fe_2O_3, and (●) 4.5% Au/Fe_2O_3 (WGC). Closed symbols: 0.5% CO, 10% O_2, Balance He. Open symbols: 2% CO, 2% O_2, balance He. GSHV of 50,000 L/L h.

transient conditions. The effects of the HTT for CO pulsing over Fe_2O_3 at 25 °C are shown in figure 3. The shape of the CO response over the fresh (as-received) Fe_2O_3 was exactly the same as the Ar pulse, indicating that no reaction or adsorption occurred. Broadening of the CO response for the HTT Fe_2O_3 sample indicated significant reversible adsorption of CO at 25 °C. CO_2, however, was never recorded and the CO appeared to merely adsorb and desorb with no reaction.

In our previous paper (Daniells *et al*., submitted) we reported that CO irreversibly adsorbed on fresh (as-received) Au/Fe_2O_3 with no initial CO_2 production. After a surface build-up of carbon-surface species, CO_2, and to a lesser extent H_2O, production was recorded. Figure 4 clearly shows that pulsing of CO over a HTT sample of Fe_2O_3, 1% Au/Fe_2O_3, and 3.4% Au/Fe_2O_3 is reversible in all cases. The size of the CO response decreased with increasing gold loading indicating that CO oxidation was occurring due to the presence of Au at room temperature. The insert shows that the unreacted CO observed in each case, when normalised so that the maxima of the respective pulses equals 1, clearly overlap each other. This suggests that the CO is reversibly adsorbing to similar sites on the catalyst, which can only be the Fe_2O_3 support. Such reversible adsorption was not observed when pulsing CO over fresh (untreated) Fe_2O_3, 1% Au/Fe_2O_3 or 3.4% Au/Fe_2O_3 at room temperature (Daniells *et al*., submitted). This reversible adsorption of CO on Fe_2O_3-supported gold catalysts after a HTT is consistent with reports in the literature [8,26,27].

The results of pulsing CO_2 over fresh and HTT 3.4% Au/Fe_2O_3 are shown in figure 5. It is clear that the degree of reversible adsorption is increased for the HTT catalyst. This suggested that, like the CO pulsing of fresh and HTT catalyst, the Fe_2O_3 support became active for CO/CO_2 adsorption after HTT. This may be due to removal of H_2O and carbonate-type species during the temperature treatment, allowing increased CO/CO_2 interaction, or phase-transition of the support during HTT, or both. During CO oxidation, desorption of CO_2 was slow from the surface, and the CO_2 production from the 3.4% Au/Fe_2O_3 at different temperatures is shown in figure 6. The increasing baseline for the

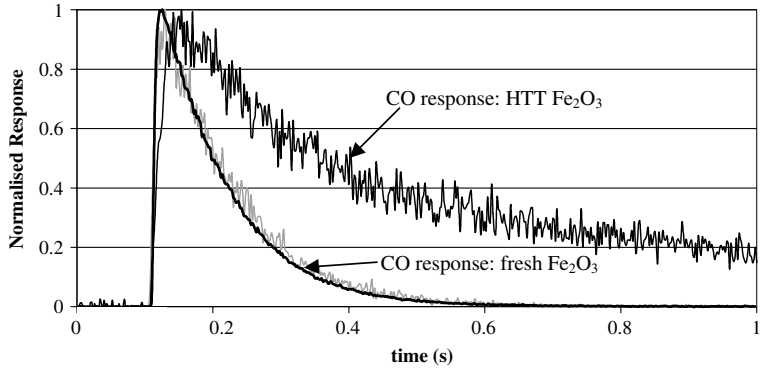

Figure 3. Qualitative results for the interaction of CO with fresh Fe_2O_3 and HTT Fe_2O_3 during CO pulsing at room temperature. All the responses are normalised so that the respective maximum = 1. An inert Ar pulse (grey signal) is shown for comparison. Average pulse size: 2×10^{16} molecules.

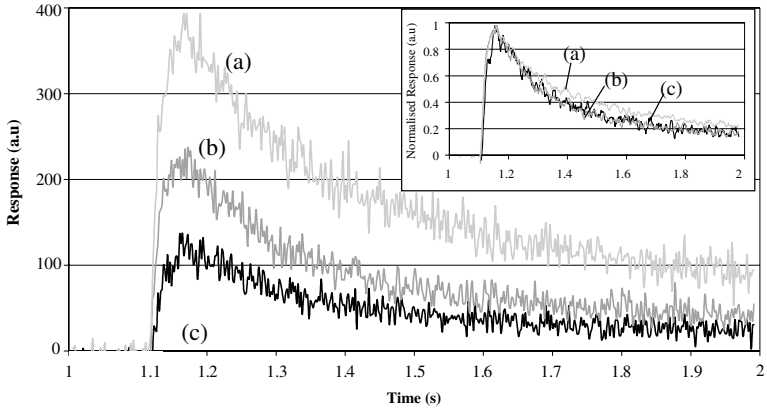

Figure 4. MultiTRACK profiles for AMU 28 during pulsing of CO over (a) HTT Fe_2O_3, (b) HTT 1% Au/Fe_2O_3, and (c) HTT 3.4% Au/Fe_2O_3. Conditions: 100% CO, pressure = 9×10^{-6} Torr. Average pulse size = 2×10^{16} molecules. Insert is the responses normalised so that the maximum for each = 1, allowing comparison of peak shapes.

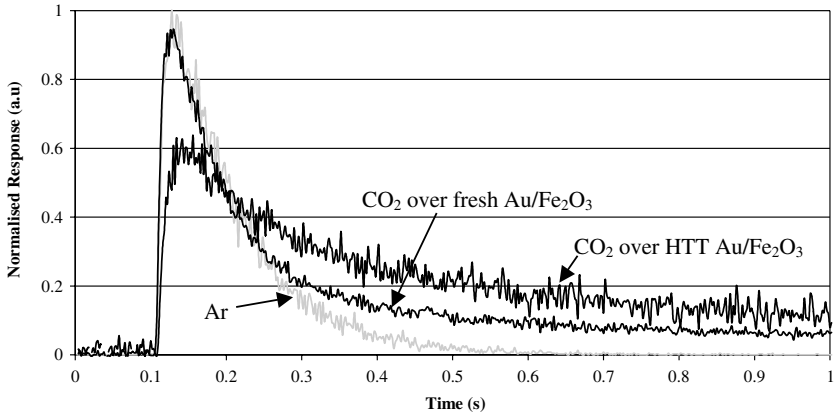

Figure 5. The interaction of CO_2 with fresh 3.4% Au/Fe_2O_3 and HTT 3.4% Au/Fe_2O_3 during CO_2 pulsing at room temperature. An inert Ar pulse is shown for comparison. Average pulse size: 2×10^{16} molecules.

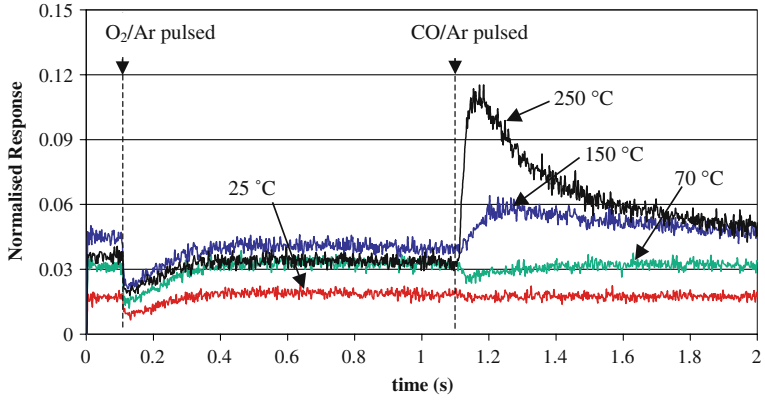

Figure 6. MultiTRACK profile of CO_2 during steady-state CO oxidation at different temperatures for fresh (as-received) 3.4% Au/Fe_2O_3. The responses are normalised with respect to Ar, not shown for clarity. The decrease at 0.1 s is due to introduction of the O_2/Ar pulse, which dilutes the CO_2 response. Average pulse size: 2×10^{16} molecules.

AMU 44 (ascribed to CO_2) is the only indication of CO oxidation at low temperature (25 °C and 70 °C). The slow production of CO_2 may be due to the slow decomposition of a stable (carbonate) intermediate, or due to a strong interaction of CO_2 with the catalyst surface. At higher temperatures the response for CO_2 is

considerably sharper. The increased temperature may be increasing the slow desorption step, or increasing the rate of decomposition of the intermediate. Another possibility, which demands serious consideration, is that above 100 °C ,the Fe_2O_3 support becomes active towards CO oxidation [8]. At 250 °C, it appears probable that two CO oxidation mechanisms may be complementing each other (see figure 7): CO oxidation at the Au–support interface (as observed at low temperature), and CO oxidation by the Fe_2O_3 support at higher temperatures:

$$CO_{(ads)} + 3Fe_2O_3 \rightarrow CO_2 + 2Fe_3O_4 \qquad (1)$$

3.2. CO oxidation in the presence of H_2O

Inclusion of water in the feed gases (0.5% CO, 10% O_2) increased the conversion of the 1% Au/Fe_2O_3 catalyst to a steady-state conversion of ~55%, while the 4.5% Au/Fe_2O_3 reference catalyst from the WGC gave 100% CO conversion at 25 °C in the presence of 2.5% H_2O. Similar results purporting to the enhancement of CO oxidation by moisture were presented by Daté *et al.* [13] for SiO_2, Al_2O_3, and TiO_2-supported Au catalysts.

3.3. Water gas shift reaction

When tested under conditions of the WGSR all the fresh/as-received catalysts required temperatures greater than 120 °C before significant activity was manifested, figure 8. Once again, the 3.4% Au/Fe_2O_3 sample was most active. However, no sample attained 100% CO conversion under the conditions and temperature range studied. This indicated that the increased oxidation of CO during CO + O_2 + H_2O at room temperature was not due to a complementary WGS reaction. Haruta and co-workers [13] noted that neither H_2O nor OH were significantly consumed during their CO + O_2 + H_2O studies, but they did contribute to increase the rate.

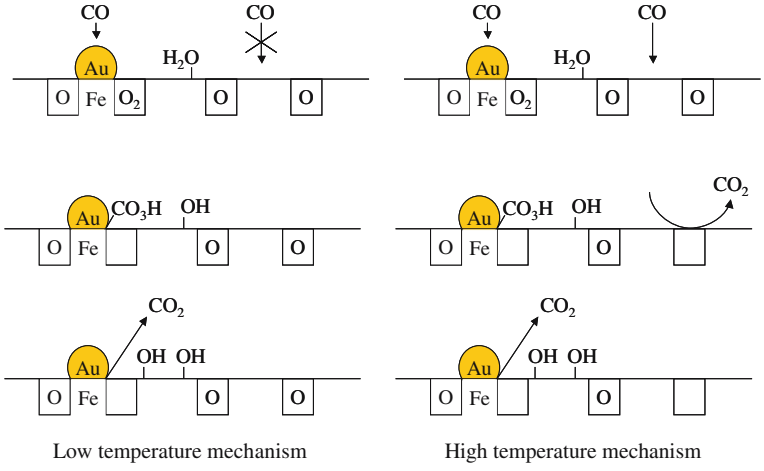

Figure 7. Schematic of proposed mechanisms of CO oxidation at low and high temperatures. At low temperatures (mechanism on right hand side) CO oxidation only occurs at the Au–support interface. At higher temperatures (mechanism on left hand side) the interface mechanism is complemented by CO oxidation on the Fe_2O_3 support.

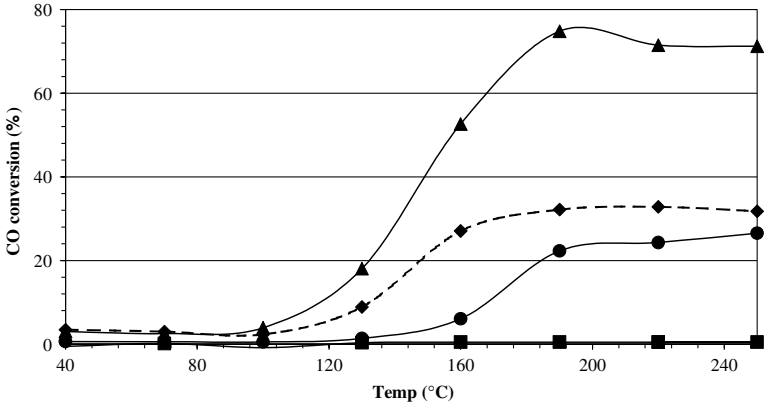

Figure 8. CO conversion during WGS reaction with fresh (untreated) Au/Fe_2O_3 catalysts as a function of temperature: (■) Fe_2O_3, (◆) 1% Au/Fe_2O_3, (▲) 3.4% Au/Fe_2O_3, and (●) 4.5% Au/Fe_2O_3 (WGC). 0.5% CO, 2.5% H_2O, Balance He. GSHV of 50,000 L/L h.

The stability test for the WGSR at 200 °C illustrated in figure 9 clearly shows that an activation period for each catalyst is required, with maximum CO conversion achieved after 10–15 h-on-stream. After this point the conversion decreases markedly, indicating the deactivation of the catalyst. Carbon deposition [28], agglomeration of Au particles [29], and carbonate formation [30] have all been proposed as the cause of deactivation during WGS reaction. However, gold agglomeration can be ruled out since no sintering was observed after a high temperature treatment at 400 °C. It is unclear if either of the two other processes is occurring in our case, and further study would be required.

3.4. General discussion

In our previous paper, it was clearly shown that the fresh/uncalcined 3.4% Au/Fe_2O_3 catalyst could oxidise CO in the absence of O_2 (Daniells et al., submitted). This indicated that lattice oxygen from the support was involved in CO oxidation. As could be expected the activity was short-lived in the absence of O_2. Addition of oxygen to the gas feed enabled the replenishment of the oxygen vacancies in the support and CO oxidation at room temperature continued with high steady-state activity.

The role of hydroxyls has been proposed to aid decomposition of inert carbonates. Indeed, many groups choose to perform CO oxidation in the presence of air, without drying of the gas feed. Daté *et al.* [13] showed that the presence of 1 ppm of H_2O could significantly enhance the activity of a Au/SiO_2 catalyst at room temperature. The commercial gas cylinder used by Daté *et al.* [13] contained approximately 3 ppm H_2O, which was dried and then moistened accordingly. Since their experiments showed that 1 ppm of H_2O could promote CO oxidation by 40% at 25 °C for a calcined Au/SiO_2 catalyst, the presence of moisture in our gas cylinders may have enhanced the activity of our catalysts that were supported on the more active Fe_2O_3 support. Costello *et al.* [9,10], and Bond and Thompson [3] consider hydroxyl participation as a key factor in the prolonging of CO oxidation activity. The results of density functional theory calculations by Gong *et al.* [31] on Pt surfaces showed that the barrier for CO oxidation could be substantially reduced in the presence of H_2O.

The mechanism we proposed previously (Daniells *et al.*, submitted) is consistent with these further results. The initial stages of the reaction are *non-catalytic* and involve adsorption of CO onto the Au particle, followed by reaction with a hydroxyl on a neighbouring Au^{3+} ion. This results in the formation of a hydroxycarbonyl, which is further oxidized by lattice oxygen to form a bicarbonate. Subsequent decomposition of $-CO_3H$ yields CO_2 and –OH. The *catalytic* cycle begins after removal of the OH groups on the Au and creation of an oxygen vacancy in the support. O_2 fills the vacancy and reacts with CO adsorbed on the gold particle, forming a carbonate at the Au–support interface. In accordance with the proposal of Daté *et al.* [13], H_2O from the support reacts with CO_3 at the interface to produce a less stable bicarbonate, which can decompose to yield CO_2 and OH.

In accordance with the proposed loss of hydroxyls by Costello *et al.* [9,10], reaction of a bicarbonate with a hydroxyl would produce H_2O and an inert carbonate adsorbed at the Au–support interface. Deactivation of the catalyst may occur due to depletion of –OH groups on the catalyst surface, reduction of Au^{3+} to Au^0, and accumulation of carbonates at the active site.

The mechanism of the WGSR is clearly different. Fu *et al.* [32] and Vengupol *et al.* [33] showed that the presence of oxidised gold was required for a good WGS rate. Indeed, the XPS data of the active catalyst from the study of Fu *et al.* [32] suggested Au^+ was more responsible for the high activity than Au^{3+}. In our fresh/uncalcined 3.4% Au/Fe_2O_3, the gold is predominantly in the form of Au^{3+}. The stability test (figure 9) showed that an initial activation period was required at 200 °C. This may be due to the gradual

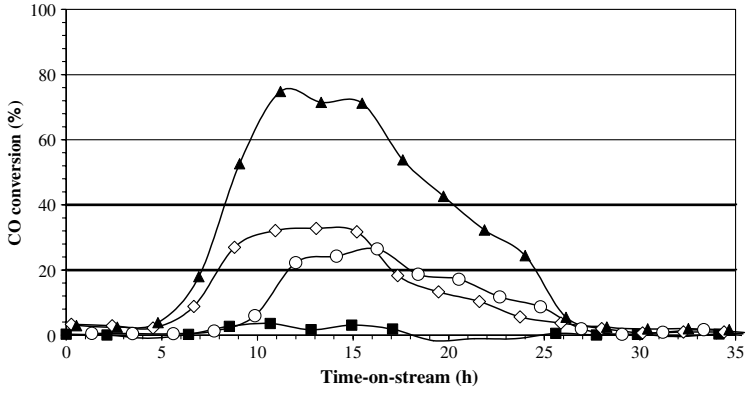

Figure 9. CO conversion during WGS reaction with fresh (untreated) Au/Fe_2O_3 catalysts as a function of time-on-stream at 200 °C: (■) Fe_2O_3, (◇) 1% Au/Fe_2O_3, (▲) 3.4% Au/Fe_2O_3, and (◯) 4.5% Au/Fe_2O_3 (WGC). 0.5% CO, 2.5% H_2O, Balance He. GSHV of 50,000 L/L h.

reduction of Au^{3+} to the more active Au^0. Au^+ was not observed by Mössbauer Spectroscopy by our laboratory for a Au/Fe_2O_3 sample exposed to a flow of CO [9], or by the work of Hutchings and co-workers [4,5]. The nature of the support may also significantly affect the activity for WGS. Andreeva and co-workers [19,34] reported that the active phase of the iron oxide support was magnetite, Fe_3O_4. The transition of haematite to magnetite was reported to occur at 140 °C in the presence of Au. However, for our 1% and 3.4% Au/Fe_2O_3 catalysts, the support is the form of ferrihydrite. The lower activity of the 4.5% Au/Fe_2O_3 reference catalyst from the World Gold Council may be due to the lack of oxidic Au in the catalyst. The need for higher temperatures is proposed to be required for H_2O dissociation on Au particles.

The present results provide additional evidence in support of the active site model that consists of both cationic and metallic gold, and the enhancing effects of OH/H_2O on the Au and support. The active site for the water gas shift reaction is proposed to be different to that of CO oxidation.

5. Conclusions

The activity of Fe_2O_3-supported Au catalysts was studied for both CO oxidation and WGSR. It was found that the fresh/as-received sample with a gold loading of 3.4% Au had the greatest activity for CO oxidation at room temperature. The sample converted 100% of the CO and no deactivation was observed over 20 h-on-stream. Loss of activity may be due to the reduction of Au^{3+} to Au^0, and the depletion of –OH groups from the catalyst surface. In the presence of water vapour the CO conversion of less active catalysts increased significantly, indicating that water had a positive effect on the CO oxidation mechanism. When tested under WGSR conditions, the conversion of CO was considerably less than for $CO + O_2$, or $CO + O_2 + H_2O$ conditions. This indicated that the increased conversion of CO during the CO oxidation in the presence of water was not due to the WGSR. It was proposed that dissociation of H_2O is the rate-limiting step for WGSR.

Mechanistic studies using an advanced TAP reactor showed that the method of pretreatment was critical in the activity of the catalyst. High-temperature treatment produced less active samples as a result of the removal of –OH groups, and reduction of Au^{3+} to Au^0. A mechanism involving carbonate formation and decomposition *via* a bicarbonate in the presence of H_2O/-OH was proposed.

Acknowledgments

We acknowledge the EU Training Network 'Catalysis by Gold' (Auricat) for funding (http://www.cf.ac.uk/chemy/staff/willock/Welcome.html). We are grateful to Dr. B. Solsona at Cardiff University for providing the Au/Fe_2O_3 catalysts and the corresponding BET and AA results. The authors wish to thank Ing. Bart van der Linden and Dr. Ignacio Melian-Cabrera for assistance with the MultiTRACK and 6-flow reactors, respectively. The World Gold Council (WGC) is acknowledged for the provision of the 4.5% Au/Fe_2O_3 reference catalyst, and Dr. Silvio Carrettin (Universidad Politécnica de Valencia, *Auricat* Partner University) is gratefully acknowledged for providing the BET surface area result of the WGC catalyst.

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