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The mechanism of low-temperature CO oxidation with Au/Fe_2O_3 catalysts: a combined Mössbauer, FT-IR, and TAP reactor study

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Abstract

The gold-catalysed oxidation of carbon monoxide was studied by Mössbauer spectroscopy, in situ FTIR, and multiple time-resolved analysis of catalytic kinetics (MultiTRACK), an advanced TAP reactor system. The active catalyst studied was 3.4% Au/Fe_2O_3, which was used without drying and/or pretreatment. Mössbauer spectroscopy analysis of this sample showed that the fresh/as-received catalyst contained mostly Au^{3+} in the form of $AuOOH \cdot xH_2O$. Based on earlier studies, the support was proposed to be predominantly ferrihydrite, $Fe_5HO_8 \cdot 4H_2O$. In situ FTIR in the presence of CO and $CO + O_2$ showed an initial increase in the bicarbonate regions, a decrease in carbonates, and a signal at 1640 cm^{-1}, attributed to consumption of OH/H_2O during the reaction. MultiTRACK analysis showed that with pulsing of CO onto a fresh catalyst sample, initially only a limited, irreversible amount of CO adsorbed. Adsorption of CO increased with increasing number of pulses, and CO_2 production and, to a lesser extent, H_2O were observed after significant surface coverage by CO. A mechanism is proposed that involves a carbonate/bicarbonate intermediate and enhancement of the rate with the presence of surface OH. The activity of the sample seems to be a function of the presence of –OH species on the support, gold, or interface sites, the rate of desorption of CO_2, or decomposition of surface carbonates.

Keywords: Gold; CO oxidation; Catalysis; TAP; Mössbauer

1. Introduction

The use of metal-oxide-supported gold catalysts has been the subject of significant study since Haruta [1,2] reported high activity of nanoparticulate Au for CO oxidation at temperatures below 0 °C. Although CO oxidation with supported gold catalysts has been extensively studied, some uncertainty and debate remain concerning its precise mechanism. It is widely agreed, however, that the size of the Au particles is critical to high activity, with an optimal particle size of 3–5 nm suggested by several groups [3–7].

The nature of the support has also been proposed to be a critical factor. “Inert” oxides such at SiO_2, MgO, and Al_2O_3 were shown to be significantly less active than oxides of reducible transition metal oxides such as Fe_2O_3 [8]. This was attributed to the ability of the “active” oxides to provide reactive oxygen and, thereby, eliminate oxygen dissociation as the rate-limiting step. Gupta and Tripathi [9,10] stated that CO oxidation occurred via a normal redox mechanism of oxygen abstraction from the Fe_2O_3 lattice for their Au/Fe_2O_3 samples. However, a TAP study by Olea et al. [11] reported that the CO_2 yield smoothly decreased with increasing delay between the O_2 “pump” pulse and the CO “probe” and, therefore, excluded a contribution from support lattice oxygen for their calcined Au/$Ti(OH)_4$ catalyst.

The methods of preparation and pretreatment have also dramatically affected the activity of the catalyst. Of particular interest is the use of calcination prior to CO oxidation, with some groups claiming promotion of catalytic activity

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after calcination [12], whereas others reported high activities for uncalcined samples [13,14]. Indeed, Hutchings and co-workers [14,15] studied Au/Fe_2O_3 catalysts by Mössbauer spectroscopy and reported that the poorly ordered uncalcined samples were more active than the calcined samples, which consisted of the "classic" 3–4-nm Au particles supported on α-Fe_2O_3. A mixed oxidation state for the Au was found and interpreted as Au^{3+} in the form $AuOOH \cdot xH_2O$ with some metallic gold, on a ferrihydrite support ($Fe_5HO_8 \cdot xH_2O$). Their results were interpreted in the context of the Bond–Thompson mechanism [4], in which Au particles are assumed to contain both Au^{x+} and Au^0. In this mechanism, CO adsorbs to Au^0 and is attacked by a hydroxyl group situated at a Au^{x+} ion, forming a carboxylate group at the gold–support interface. The carboxylate is in turn attacked by a superoxide from the support to produce CO_2, and the resulting hydroperoxide, OH_2^-, oxidises another carboxylate, forming another CO_2 and regenerating two hydroxyls at the surface [4]. Costello et al. [16,17] proposed a similar mechanism, based on deuterium isotope effect studies. In this case, a mechanism was proposed that involved the addition of CO to Au^+–OH^- to form Au–COOH, consistent with the findings of Hutchings and co-workers [14,15]. This Au-hydroxycarbonyl is then oxidised to bicarbonate, which decomposes to form CO_2 and OH^-, and the latter completes the catalytic cycle.

The role of hydroxyls in the mechanism of CO oxidation has received greater attention; Daté et al. [18] recently published a report on the enhancing effects of H_2O in the $CO + O_2$ stream for calcined samples of Au/TiO_2 and Au/Al_2O_3. Daté et al. [18] proposed a twofold role for the moisture: one was the activation of the oxygen from the support, and the second was the decomposition of the carbonate intermediate. This is in agreement with the observation of Schubert et al. [19], who studied the influence of H_2O on the activity of Au/α-Fe_2O_3. 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 [16–22]. The presence of bicarbonates has been detected by FTIR under both CO oxidation and water gas shift conditions, and assigned bands occurred at 1582, 1413, and 1220 cm^{-1} for Au/TiO_2 [23] and at 1614–1620, 1407, and 1223 cm^{-1} for Au/Fe_2O_3 [10].

It is clear that there is growing support from the literature that the addition of H_2O, even in trace amounts, can significantly enhance the rate of CO oxidation on metal-oxide-supported catalysts. The simultaneous presence of OH groups on both the Au particles and on the support, particularly on Fe_2O_3, has been reported by both Hutchings and co-workers [14,15] and Wagner et al. [13]. In both cases the catalysts were found to contain mixed Au oxidation states (assigned as Au^{3+} from Mössbauer studies) and a ferrihydrite support. On calcination at 400 °C, the activity of the samples decreased significantly, and Mössbauer analysis showed that the gold was purely metallic, whereas the support had been transformed to haematite, α-Fe_2O_3. Wagner et al. [13] reported that the activity of the catalysts increased with increasing ferrihydrite content, adding further support to the role of OH groups in CO oxidation.

This paper presents the results of ^{197}Au Mössbauer spectroscopy, FTIR, and a TAP study of CO oxidation over Au/Fe_2O_3. The focus is on the mechanism occurring on an uncalcined sample with gold loading of 3.4% Au. The essential steps of the mechanism are presented, and the role of adsorption of CO to mixed-oxidation-state gold particles, reduction of the gold, formation of carbonate, and bicarbonate-type intermediates is investigated. The role of surface hydroxyls is also considered to be a key aspect in the high activity of the sample.

2. Experimental

2.1. Catalyst preparation

Catalyst samples were prepared, and textural analyses were done by Cardiff University via the EU network Auricat. Similar samples were prepared previously by the same group; details of their preparation method have been described in Refs [14,15]. Gold loadings were determined by atomic absorption (A.A.) and BET measurements, which established the surface area of the catalysts. Prior to adsorption measurements, the samples were degassed under a vacuum of 0.667 Pa at 100 °C for 2 h. The samples were pressed and sieved to give particles with a mesh range of 212–300 nm, unless otherwise stated.

2.2. Mössbauer spectroscopy

For the ^{197}Au Mössbauer spectra, the applied ^{197}Au γ-ray sources were obtained by the irradiation of enriched platinum powder (97.4% ^{196}Pt) with thermal neutrons for 24 h in the nuclear reactor of the Interfacultair Reactor Instituut, Delft, the Netherlands [24]. This resulted in a 200-MBq Mössbauer source due to the $^{196}Pt(n, \gamma)\,^{197}Pt$ reaction. The subsequent beta decay process to the Mössbauer isotope ^{197}Au has a half-life of 18.3 h, which determines the half-life of the ^{197}Au Mössbauer source. Because of the high energy of the Mössbauer transition (77.3 keV), both the source and absorber were cooled to 4.2 K. The spectrometer was operated in transmission geometry, with the source moving according to a sinusoidal mode. The velocity scale was calibrated with the use of sodium nitroprusside, and from there the velocities were converted to absolute velocities. Therefore, the isomer shift values are given according to absolute velocities. For detection of the transmitted photons, a high-purity Ge detector was used. The data were collected in 1024 channels and were folded to remove curvature of the background. Further details of the analysis procedures are given in the corresponding figure captions.

2.3. Catalytic performance

These experiments were performed in a 6-flow reactor setup, which has been described in detail elsewhere [25]. Fifty-milligram 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 the temperature, and the reactor furnace was controlled with 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. A typical GSHV of 50,000 h^{-1} was applied. CO, O_2, and CO_2 were analysed with a gas chromatograph (Chrompack CP 9001) equipped with a thermal conductivity detector, with the use of a Poraplot Q column and a Molsieve 5 A column. Results refer to either the fresh/as-received sample with no treatment or the sample subjected to a high-temperature treatment (HTT) at 400 °C in flowing He for 30 min prior to cooling to reaction temperature. Gas compositions were typically 2% CO, 2% O_2 balanced with He, unless otherwise stated.

2.4. Infrared spectroscopy

IR studies were performed with a Thermo Nicolet Nexus IR with corresponding OMNIC software. The flow of CO (20.0% in Ar) was diluted with a Brooks 5850 E Mass Flow Controller to give 0.5% CO/Ar. The experiments were performed at room temperature and pressure. The catalyst sample was compared with KBr and exposed to CO at atmospheric pressure.

2.5. Temporal analysis of products

Transient studies were performed in an advanced TAP reactor system [26,27], MultiTRACK (multiple time-resolved analysis of catalytic kinetics). The system has been described elsewhere [28]; however, the main points are summarised here. The reactor (inner diameter 7 mm, bed height 10 mm) is located in an ultra-high-vacuum chamber into which gas pulses on the order of 10^{15} to 10^{17} molecules can be introduced. Pulse valve 1 was used for the O_2/Ar and $^{18}O_2$ pulsing, and pulse valve 2 was always used for CO/Ar and CO_2 pulsing. Samples of Fe_2O_3 and Au/Fe_2O_3 (3.4% Au loading) with a mesh range of 212–300 µm were held between SiC plugs (212–300 µm, 300–425 µm). 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 for α-Fe_2O_3 of 0.5 nm [29] and 0.05-g samples, the total number of surface sites available was 4.1×10^{19}, with approximately 8×10^{17} Au 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.); they were used without further purification. Reactants and products were recorded at the reactor outlet with three PC-interfaced Balzers QMA 124 quadrupole mass spectrometers (QMS), one after the other. 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

3.1. Catalyst characterisation

The Au contents of the fresh/as-received and HTT Au/Fe_2O_3 catalysts as determined by AA were 3.4 and 4.1 wt%, respectively. The surface area as determined by BET analysis was also altered as a result of the high-temperature treatment. The initial surface area of the highly active 3.4% Au/Fe_2O_3 decreased from 203 to 45 m^2/g after HTT.

3.2. Catalytic performance

Fig. 1 shows the effect of pretreatment on the activity of 3.4% Au/Fe_2O_3 samples for CO oxidation at 25 °C. It is clear that the fresh/as-received 3.4% Au/Fe_2O_3 sample was highly active and showed only slight deactivation after 20 h on-line. Pretreating the sample at 400 °C in flowing He for 30 min and cooling to room temperature significantly altered catalyst activity. The initial activity was 85% CO conversion at 25 °C, with rapid deactivation to approximately 45% CO conversion after 20 h on-line.

3.3. Mössbauer spectroscopy

Fig. 2 shows ^{197}Au Mössbauer spectra for fresh, CO-treated, and HTT 3.4% Au/Fe_2O_3 catalyst. The spectra are similar to the spectra presented by Hutchings and co-workers [15]. For the calcined sample a single absorption peak was observed, with an isomer shift (IS) of ca. -1.18 mm/s. This component is typical for metallic gold. The fresh/as-received sample and the CO-treated samples have similar asymmetrical lineshapes, probably resulting from a distribution of Au sites. To model this distribution, the spectra were fitted with two doublets. In addition, a singlet line with spectral parameters that correspond to Au metal was included in the fit. The spectral contribution of this singlet line is more or less the same in the two cases and amounts to ca. 10%. The doublets with positive isomer shifts have been assigned to a Au(III) oxyhydroxide species, $AuOOH \cdot xH_2O$, in line with assignments made by Wagner et al. [13] and Hutchings and co-workers [14,15]. The adsorption of CO to the Au/Fe_2O_3 catalyst has a small effect on the lineshape, indicating some changes in the chemical environment of the Au(III) species. Table 1 shows all of the spectral parameters for the samples studied.

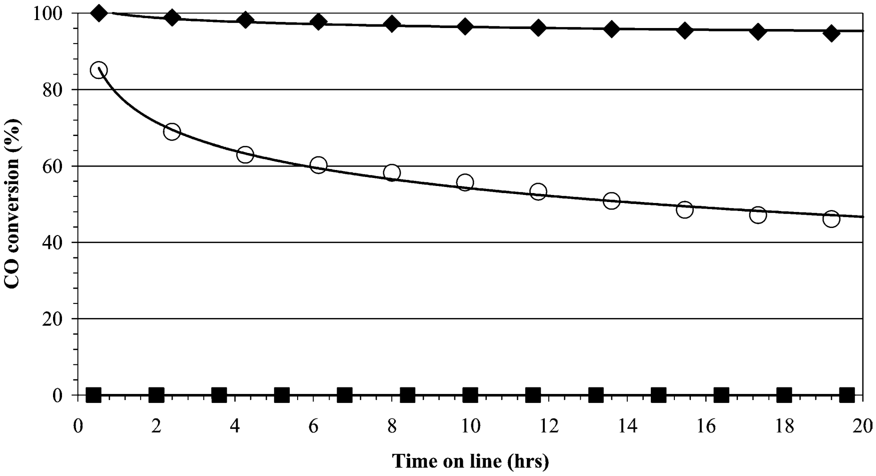

Fig. 1. CO conversion (%) at 25 °C as a function of time-on-line for Fe_2O_3 (■), fresh 3.4% Au/Fe_2O_3 (♦), and HTT 3.4% Au/Fe_2O_3 (○). Conditions: 2% CO, 2% O_2, balance He. GSHV of 50,000 h^{-1}.

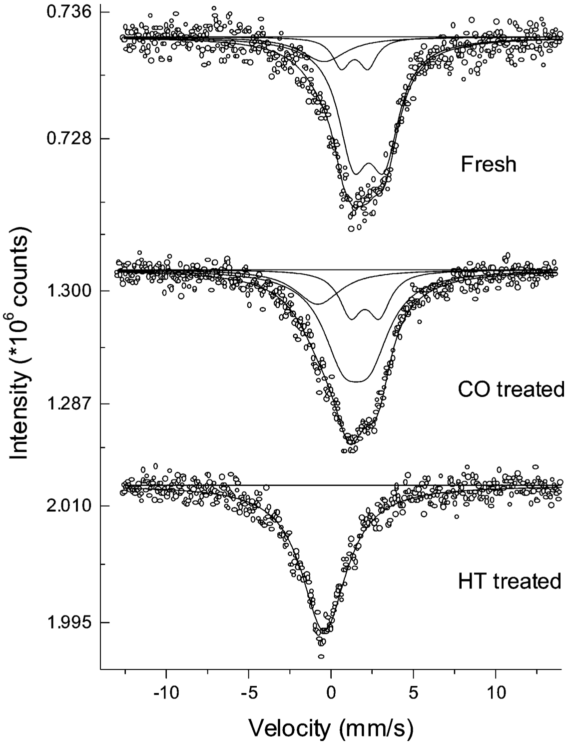

Fig. 2. ^{197}Au Mössbauer absorption spectra (MAS) of Au/Fe_2O_3: (a) fresh/as-received, (b) after exposure to a flow of CO for 20 min at room temperature, and (c) after a high temperature treatment (400 °C, flowing Ar, 30 min). The fresh catalyst had an Au loading of 3.4%. The spectra were recorded at 4.2 K and have been fitted with three gold contributions and one gold contribution for spectra (a and b), and c, respectively. The spectra are vertically shifted in the same intensity scale.

With respect to the discussion about the presence or absence of Au(I), the spectral parameters that we find for the nonmetallic Au species are typical for Au(III) compounds [30]. The spectral windows discussed in [30] are typical for the different forms of Au: metallic Au(0), Au(I), and Au(III). Comparison with our spectra indicated that we were dealing with Au(III) rather than Au(I).

Table 1
Spectral parameters of analyses of ^{197}Au Mössbauer spectra

Samples	I.S. (mm/s)	Q.S. (mm/s)	S.C. (%)
Fresh	−1.18	–	12.4
	0.91	1.76	10.1
	1.87	2.09	77.5
CO-treated	−1.18		16.4
	1.15	1.61	63.0
	1.68	1.73	20.6
HT-treated	−1.18	–	100

3.4. FT-IR spectroscopy

In situ FTIR studies were performed to investigate surface species under both CO oxidation conditions and CO in the absence of O_2. Both spectra also confirmed the presence of a band at 1640 cm^{-1}, indicative of the OH stretch of H_2O [23]. Fig. 3 shows the carbonate region (1800–1200 cm^{-1}) for fresh 3.4% Au/Fe_2O_3 during CO oxidation at 22 °C. It is clear that the fresh sample already contained a significant concentration of surface carbonate-type species and a large peak at 1640 cm^{-1}. These bands were also observed for fresh Fe_2O_3, indicating that the support contained significant quantities of carbonate-like species and H_2O, as was also shown by the earlier work of Hutchings and co-workers [14,15]. Exposure of the sample to $CO + O_2$ led to initial increased absorptions at approximately 1626, 1420, and 1221 cm^{-1}, which have previously been assigned to bicarbonates [10,23,31]. Corresponding decreases in the signals at 1640 and 3600 cm^{-1} were also observed. With increasing time on-line, the peaks at 1500 and 1360 cm^{-1} and at 1620, 1410, and 1220 cm^{-1} decreased steadily.

Fig. 4 shows the carbonate region for 3.4% Au/Fe_2O_3 during exposure to CO in the absence of O_2. As was observed with the $CO + O_2$ system, there is an increase in peaks at approximately 1500 and 1360 cm^{-1}. The decrease was less pronounced with increasing time on-line. However,

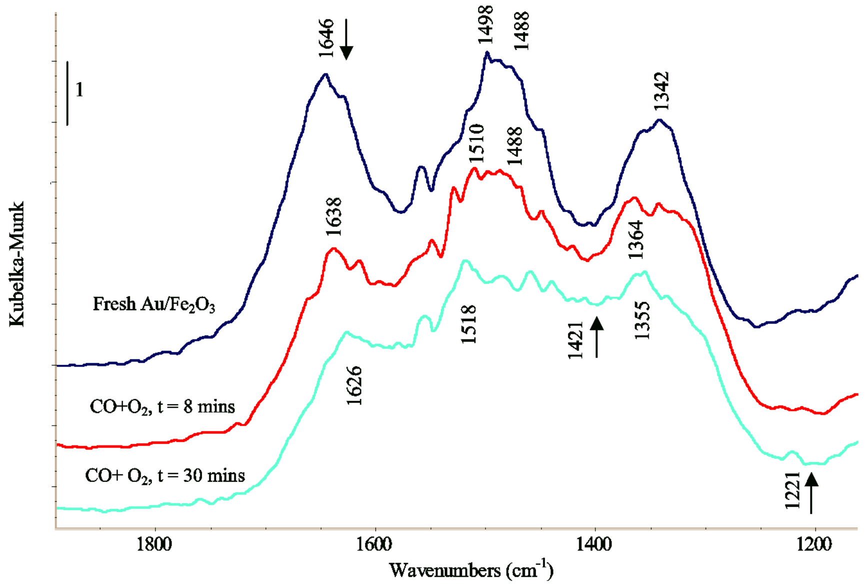

Fig. 3. FTIR spectra of fresh 3.4% Au/Fe_2O_3 in the carbonate region obtained during CO oxidation at room temperature. The arrows indicate peaks that increase or decrease over the course of the experiment. 1% CO, 1% O_2, balance Ar, flow rate = 60 cm^3/min.

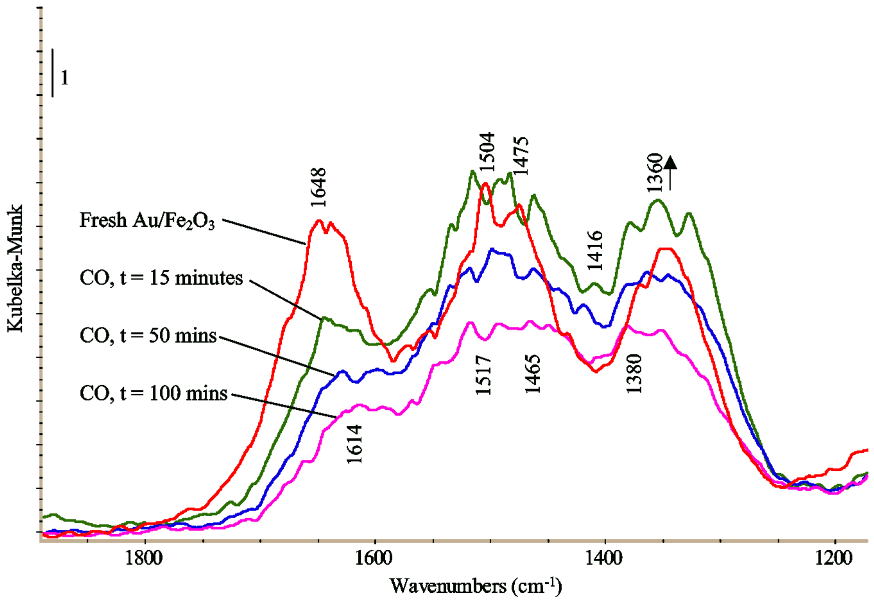

Fig. 4. FTIR spectra of fresh 3.4% Au/Fe_2O_3 in the carbonate region obtained during CO exposure at room temperature. 0.5% CO, balance Ar, flow rate = 60 cm^3/min.

decomposition of the carbonate-type species does appear to have occurred. The bands at intermediate wavenumbers (1620 and 1410 cm^{-1}) were also observed in the CO-only system, indicating the formation of bicarbonates. This is in contrast to the work of Boccuzzi et al. [31], who proposed that the formation of carbonate-like species was promoted only in the presence of gas-phase oxygen for calcined samples.

The FTIR spectra of the carbonyl region for the CO-only and CO + O_2 systems are shown in Figs 5a and 5b, respectively. An initial appearance of bands indicative of CO in the gas phase was recorded (2176 and 2111 cm^{-1}); these subsequently decreased to zero with increasing time on-line, suggesting that there is an initial activation period of the catalyst in the presence of CO. With increasing time on-line of the sample for the CO-only systems, the bands that appeared at approximately 2085 and 2040 cm^{-1} were assigned to CO adsorbed to Au^0 and CO bridge-bonded to metallic Au (Au^0), respectively [23]. No such bands were observed in the presence of O_2 (Fig. 5b). Apparently, a partial reduction of Au^{3+} to Au^0 is observed as a function of the CO-only pretreatment.

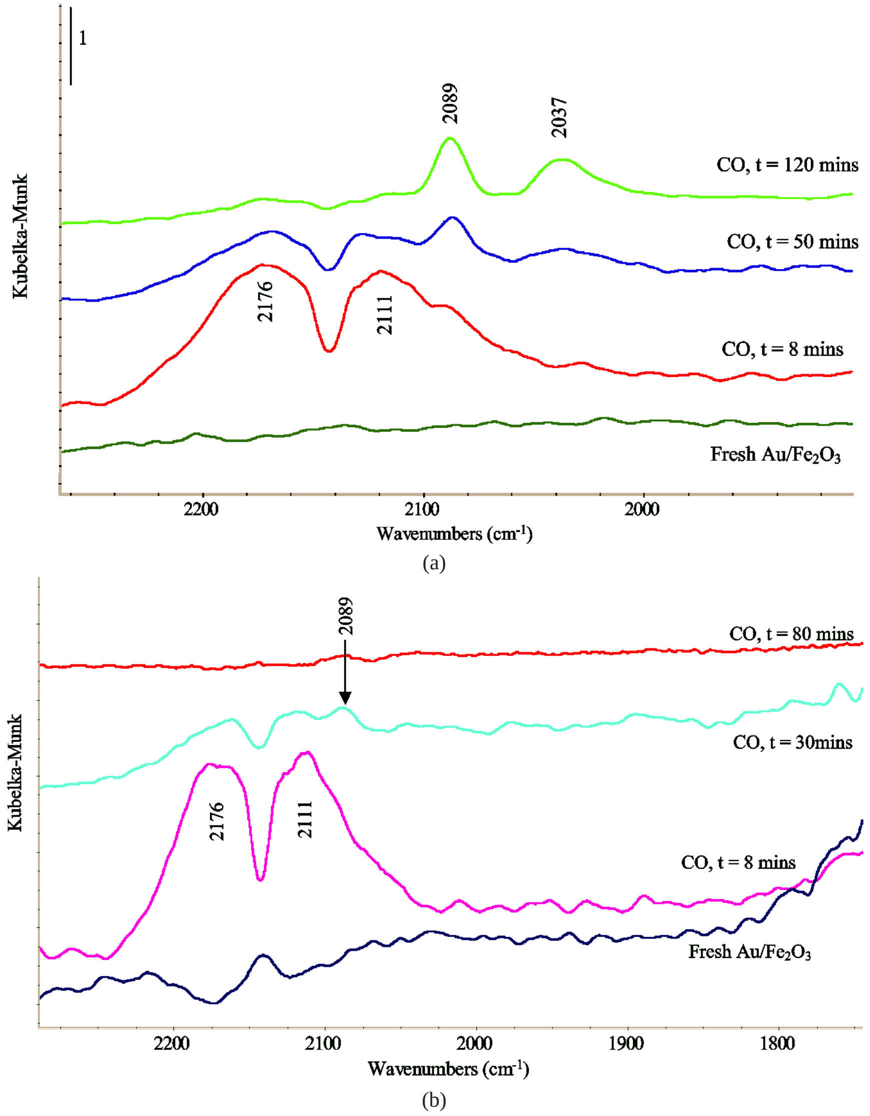

Fig. 5. FTIR spectra of the carbonyl region obtained during (a) CO flowing and (b) CO + O_2 over fresh 3.4% Au/Fe_2O_3 at room temperature. 0.5% CO/Ar or 0.5% CO, 10% O_2/Ar, flow rate = 60 cm^3/min.

3.5. *Transient studies using an advanced TAP reactor*

Pulsing of O_2 onto a fresh sample of 3.4% Au/Fe_2O_3 is shown in Fig. 6. It is clear that all of the Mass 32 signals overlap for all of the pulses selected. There is also no deviation of pulse shape when compared with the Ar signal (result not shown). This indicated that the fresh sample of Au/Fe_2O_3 did not have any oxygen vacancies or oxygen adsorption sites present. This result was supported by pulsing of $^{18}O_2$ over a fresh sample of 3.4% Au/Fe_2O_3 (Fig. 7). The responses once again indicated no adsorption of O_2. The signals for mixed-label O_2 ($^{18}O^{16}O$) and AMU 32 ($^{16}O_2$) are shown as insets (a) and (b), respectively. In neither case was measurable isotopic scrambling observed.

Fig. 8 shows the results of pulsing CO over a fresh sample of 3.4% Au/Fe_2O_3 at room temperature. No pretreatment was performed on the catalyst prior to pulsing. The shapes of the initial pulses are approximately the same as that of an Ar pulse, indicating that there is negligible reversible CO adsorption on the fresh catalyst. The peak height decreases with increasing number of pulses, and the overall shape of the pulse relative to the Ar standard broadens. This suggests that the 3.4% Au/Fe_2O_3 surface is changing, allowing reversible adsorption of CO. No such adsorption was observed for pulsing of CO over pure Fe_2O_3 (results not shown). The decrease and broadening in the CO response with increasing number of pulses indicated that CO was adsorbing both reversibly and irreversibly.

Adsorption of CO increased with increasing pulse number for approximately 1400 pulses, after which considerable CO_2 production was observed. This result indicated that oxygen species from the Fe_2O_3 support were participating in CO oxidation, as was also reported by Gupta and Tripathi for their Au/Fe_2O_3 catalysts [10]. This result is also consistent with the FTIR study that showed an initial “activation period” prior to CO oxidation.

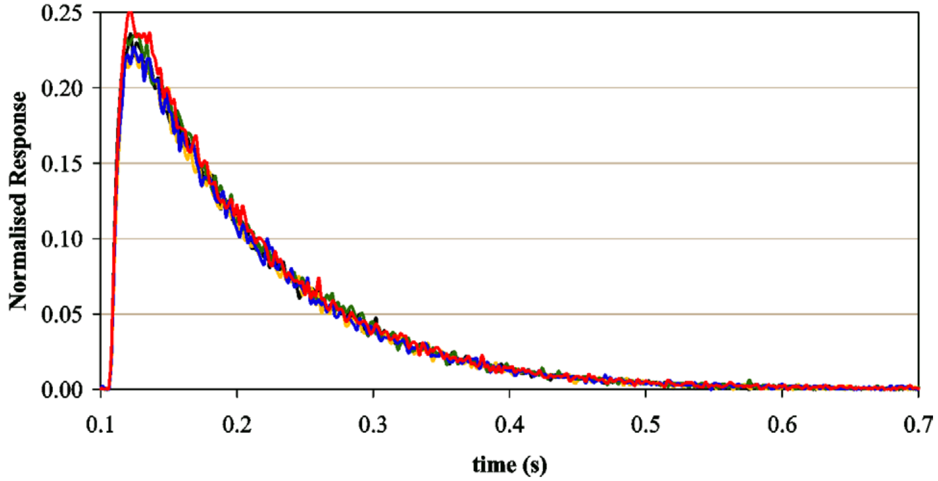

Fig. 6. MultiTRACK profiles for AMU 32 during pulsing of O_2 over fresh/as-received 3.4% Au/Fe_2O_3. The O_2 response for pulse 5, 50, 200, 500, 750 are shown. Responses are normalised with respect to the Ar pulse, not shown for clarity. Conditions: 20% O_2/Ar, pressure $= 1.2 \times 10^{-3}$ Pa. Average pulse size $= 2 \times 10^{16}$ molecules.

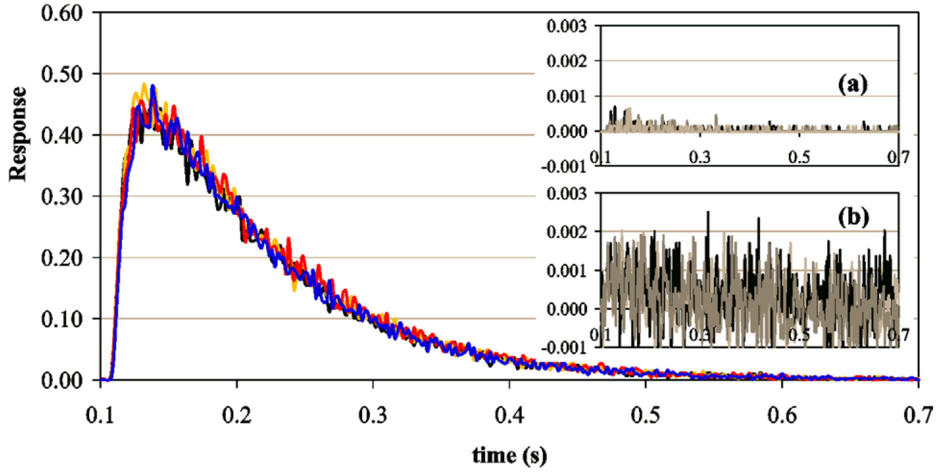

Fig. 7. MultiTRACK profiles for AMU 36 during pulsing of $^{18}O_2$ over fresh/as-received 3.4% Au/Fe_2O_3. The $^{18}O_2$ response for pulse 20, 100, 250, 400 are shown. The $^{18}O^{16}O$ (AMU 34) and $^{16}O_2$ (AMU 32) responses are shown in (a) and (b), respectively. Conditions: 100% $^{18}O_2$, pressure $= 1.2 \times 10^{-3}$ Pa. Average pulse size $= 2 \times 10^{16}$ molecules.

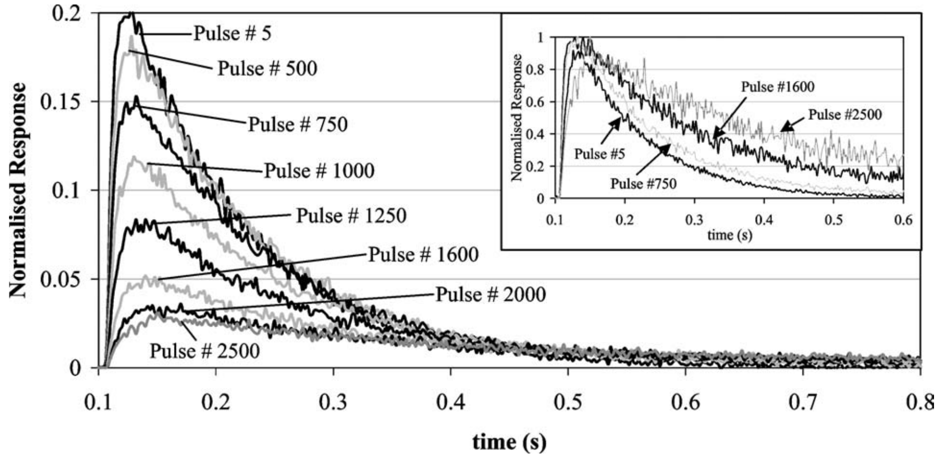

Fig. 8. MultiTRACK profiles for AMU 28 during pulsing of CO over fresh/as-received 3.4% Au/Fe_2O_3. Insert shows the responses for selected pulse normalised with respect to themselves, allowing comparison of pulse shape. Conditions: 20% CO/Ar, pressure $= 1.2 \times 10^{-3}$ Pa. Average pulse size $= 2 \times 10^{16}$ molecules.

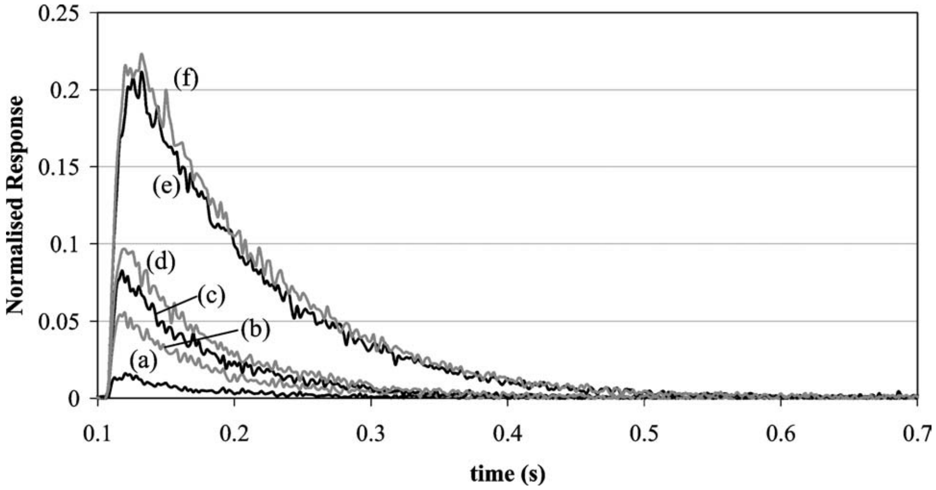

Fig. 9. MultiTRACK profiles for AMU 32 during pulsing of O_2 over 3.4% Au/Fe_2O_3 after exposure to 2500 pulses of CO. O_2 after (a) 10 pulses, (b) 50 pulses, (c) 75 pulses, (d) 100 pulses, (e) 250 pulses, and (f) 1000 pulses. Responses are normalised with respect to the Ar pulse, not shown for clarity. Conditions: 20% O_2/Ar, pressure $= 1.2 \times 10^{-3}$ Pa. Average pulse size $= 2 \times 10^{16}$ molecules.

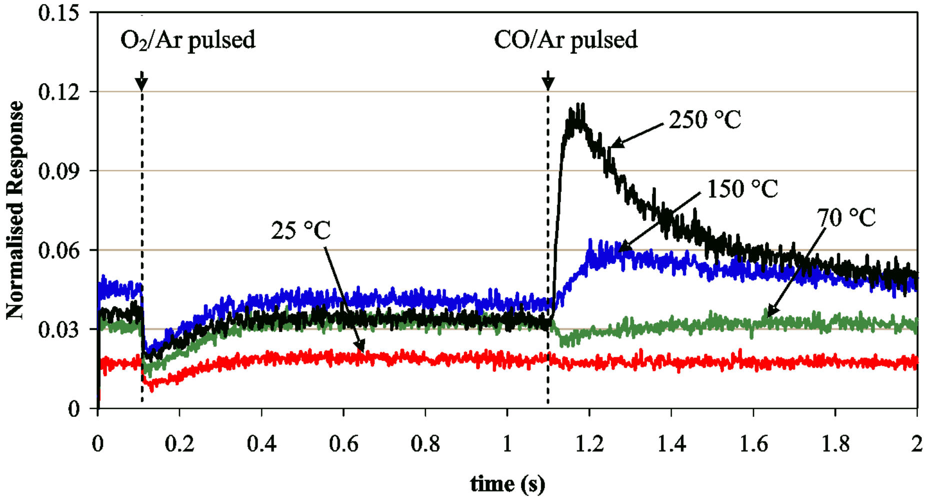

Fig. 10. Steady-state MultiTRACK profile of CO_2 during CO + O_2 pulsing at different temperatures with fresh 3.4% Au/Fe_2O_3. The responses are normalised with respect to Ar, not shown for clarity. The decrease at 0.1 s is due to introduction of the O_2/Ar pulse, which dilutes the CO_2 response. Average pulse size $= 2 \times 10^{16}$ molecules.

At the onset of deactivation (after approximately 2500 pulses of CO/Ar) the CO pulse was switched for O_2/Ar. Fig. 9 shows the O_2 response for selected pulses. It is clear that irreversible adsorption of O_2 occurred and decreased with increasing number of pulses. This was to be expected, since the concentration of oxygen vacancies created by O-extraction from the support during CO pulsing would be decreasing with increasing O_2 pulse number.

Desorption of CO_2 was slow relative to the Ar pulse, and accurate quantification of the CO_2 production was not possible. Fig. 10 shows the response for CO_2 during sequential pulsing of O_2 and CO as a function of temperature. At 25 °C and 70 °C, the production of CO_2 is observed merely as an increase in the baseline. At higher temperatures (150 and 250 °C) the desorption is more marked. However, the increasing baseline was still present and indicated either slow desorption of CO_2 from the surface or slow decomposition of a (meta-stable) intermediate species.

Pulsing of CO_2 over fresh/as-received Au/Fe_2O_3 is shown in Fig. 11. When compared with the Ar inert pulse, it is clear that CO_2 does adsorb reversibly to the catalyst, albeit to a limited extent.

Extended sequential CO and O_2 pulsing over fresh/as-received Au/Fe_2O_3 is shown in Fig. 12. The CO response was similar to that observed during CO pulsing (Fig. 8), with some irreversible CO adsorption over the initial 500 pulses, followed by increasing CO conversion and CO_2 production. The O_2 response also decreased with increasing pulse number, indicating that O_2 was being consumed during the reaction. However, the area of the O_2 response was always greater than the corresponding CO pulse, suggesting that O_2 was merely replenishing vacancies on the catalyst that had been created during CO_2 production.

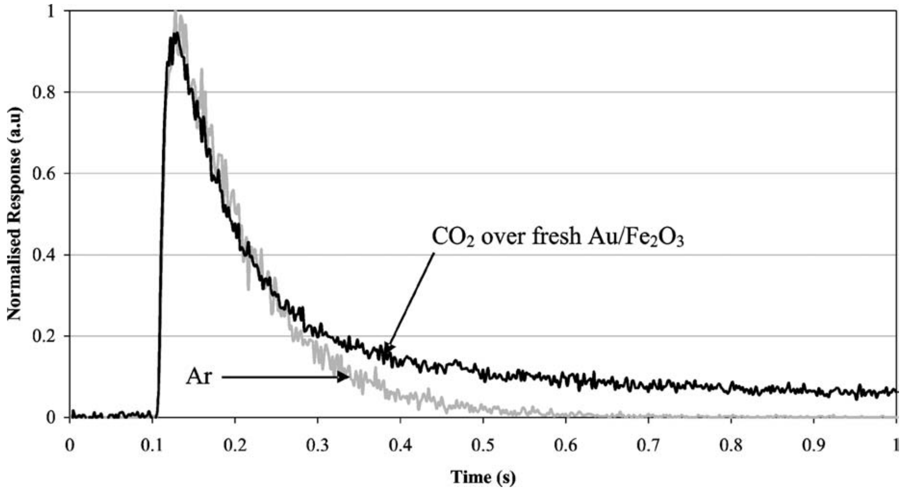

Fig. 11. The interaction of CO_2 with fresh 3.4% Au/Fe_2O_3 during CO_2 pulsing at room temperature. An inert Ar pulse is shown for comparison. Average pulse size $= 2 \times 10^{16}$ molecules.

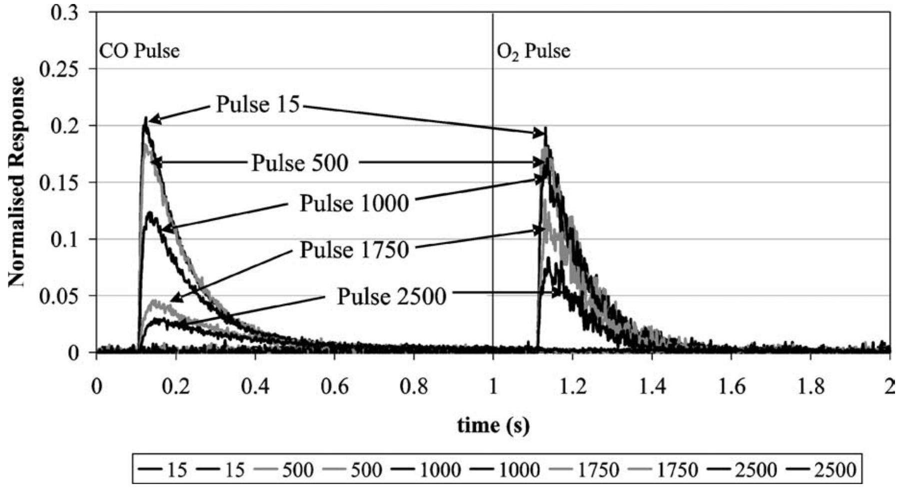

Fig. 12. MultiTRACK profiles of CO and O_2 during 'pump-probe' CO oxidation with fresh/as-received 3.4% Au/Fe_2O_3 at room temperature. The responses are normalised with respect to Ar, not shown for clarity. 'Pump': 20% CO/Ar pulsed at 0.1 s. 'Probe': 20% O_2/Ar pulsed at 1.1 s. Average pulse size $= 2 \times 10^{16}$ molecules.

The production of CO_2 during CO oxidation was monitored with a continuously sampling mass spectrometer situated within the MultiTRACK but not configured to monitor a pulse. Fig. 13 shows the responses of AMU 18 and AMU 44 during CO oxidation. Neither CO_2 nor H_2O was observed initially, showing that an initial "activation period" for the catalyst was required. The production of CO_2 reached a maximum after approximately 3000 $CO + O_2$ pulses and then began to decrease with increasing $CO + O_2$ pulsing. The response for H_2O also increased and decreased, following the trend of CO_2 production.

4. Discussion

To facilitate the discussion of these results, it is useful to provide a summary of the key observations:

- Characterisation by Mössbauer spectroscopy showed that the fresh sample of 3.4% Au/Fe_2O_3 was predominantly in the Au^{3+} oxidation state, which was present as $AuOOH \cdot xH_2O$. The support was characterised by the results of Hutchings and co-workers [14,15] and assumed to be predominantly ferrihydrite, $Fe_5HO_8 \cdot 4H_2O$. High-temperature treatment (HTT) at 400 °C in flowing He produced a sample that was exclusively metallic gold, Au^0, and the support most likely consists of haematite, α-Fe_2O_3 [14,15]. This agreed with previous results for similar catalysts by Wagner et al. [13].[1]
- The activity of the catalyst was significantly affected by the pretreatment. Fresh catalyst converted 100% of the

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[1] No ^{57}Fe Mössbauer studies were performed as part of our study, and the assignment of the phase of the Fe support is based on the work of Hutchings and co-workers, who provided the samples for this study using the same preparative method as described in [14,15].

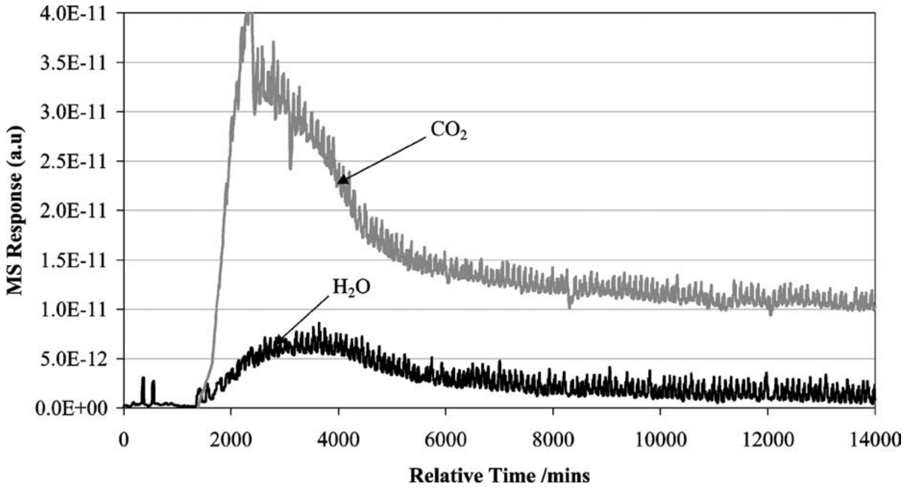

Fig. 13. MS Response for AMU 44 (CO_2) and AMU 18 (H_2O) during pulsing of $CO + O_2$ over fresh/as-received 3.4% Au/Fe_2O_3. Conditions: 20% CO, 20% O_2/Ar, pressure $= 1.2 \times 10^{-3}$ Pa. Average pulse size $= 2 \times 10^{16}$ molecules. Pulsing commenced at $t = 0$ min.

CO, and only slight deactivation was observed after 20 h on-line. The HTT sample yielded an initial CO conversion of 70% and rapidly deactivated with increasing time on-line, under the conditions used.

- In situ FTIR study of the sample under CO oxidation conditions showed an initial increase in the bicarbonate regions, with a corresponding decrease in the carbonate region, and a –OH signal at 3600 and 1640 cm^{-1}. The carbonyl region showed an initial presence of CO in the gas phase, which decreased with increasing time on-line. This indicated an "activation period" for the catalyst. After significant time on-line of the CO-only system, bands at approximately 2085 and 2040 cm^{-1} appeared and were assigned to CO on Au^0 and bridge-bonded CO, respectively.
- CO pulsing over the fresh catalyst in an advanced TAP reactor showed gradual irreversible adsorption of CO. This adsorption increased after significant uptake of CO, and CO_2 and H_2O production was eventually recorded. CO pulses were stopped and O_2 was introduced. Irreversible adsorption of the O_2 occurred, indicating the creation of oxygen vacancies in the sample.
- Pulsing of both $^{16}O_2$ and $^{18}O_2$ over fresh/as-received 3.4% Au/Fe_2O_3 indicated no adsorption to and/or reaction with the surface. No scrambling of isotopic oxygen was recorded.
- Desorption of the product CO_2 was extremely slow, as indicated by a gradual increase in the baseline during CO oxidation at room temperature. At higher temperatures the desorption of CO_2 was significantly quicker. CO_2 pulsing showed only slight reversible adsorption on the fresh/as-received sample.

Combination of the Mössbauer spectroscopy study and the catalytic performance shows that the more ordered HTT sample contained exclusively metallic gold and haematite support. These were significantly less active than the fresh/as-received samples, which were characterised as containing both Au^{3+} and Au^0, and the support, which was characterised as ferrihydrite [13–15]. The concentration of surface –OH/H_2O significantly decreased as a result of the high-temperature treatment. Hutchings and co-workers [14,15] were the first to propose gold oxyhydroxide as the active phase for CO oxidation, and Wagner et al. [13] reported increased CO conversion with high ferrihydrite content of the support. Table 1 showed that 77% of the Au^{3+} was AuOOH, which is equal to approximately 1.2×10^{18} atoms of O and molecules of OH, in total.

It is apparent from the Mössbauer spectroscopy study that the fresh/as-received 3.4% Au/Fe_2O_3 catalyst was comparable to the earlier samples prepared by Hutchings and co-workers [14,15] and contained Au of mixed oxidation state. After a high-temperature treatment (HTT) of the catalyst at 400 °C the activity of the catalyst was significantly less. The BET surface area also decreased markedly as a result of the HTT, and the catalyst was shown to be exclusively metallic gold.

The presence of a combination of metallic and ionic gold has also been proposed by Costello et al. [16,17,21] and by Bond and Thompson [4]. The former [17,21] proposed a model with Au(I)–OH at the interface stabilised by Au^0, supported by the ^{197}Au Mössbauer study of Au/$Mg(OH)_2$, where the most active catalyst contained the highest concentration of Au(I) [32]. However, the Bond–Thompson model proposes a Au particle with a Au^{3+} layer at the interface; the cations act as a "chemical glue" between the metallic Au particle above and the support beneath [4]. Although the current work cannot rule out the Bond–Thompson model for "chemical glue," the possibility of Au(I) as the active phase does not seem plausible, since no Au(I) was observed with Mössbauer spectroscopy. It appears that the active centre for gold catalysts may be an ensemble of Au^{3+} (with hydroxyl groups) and Au^0. Indeed, the active phase may be different for every Au-catalysed reaction, as ^{197}Au Mössbauer spectroscopy and XPS studies for propene epoxidation by Zwijnenburg et al. [24] had indicated that the active phase in gold/titania catalysts was metallic gold.

FTIR study of CO dosing and CO + O_2 reaction on the catalyst clearly showed an initial decrease in the carbonate, region with an accompanied increase in bicarbonates region. The initial peak at 1640 cm^{-1}, assigned to OH/H_2O, also supported the conclusions for Au-oxyhydroxide from the Mössbauer study. Prolonged exposure to CO produced a decrease in both the signal at 1640 cm^{-1} and the carbonate-region signals (1620, 1410, and 1220 cm^{-1} for bicarbonates, and 1500 and 1360 cm^{-1} for carbonates), suggesting possible OH participation in hydroxycarbonyl and bicarbonate formation. Gupta and Tripathi [10] reported that the presence of OH groups was important for the formation of oxygenates. However, they specified that oxygenates were formed after the reaction of CO_2 with OH, rather than bicarbonate decomposition to *yield* CO_2. The transformation of carbonates into less thermally stable bicarbonates has been proposed previously [18,19].

A previous TAP study of CO oxidation using Au catalysts was presented by Olea et al. [11] for calcined $Au/Ti(OH)_4$. CO adsorption was shown to be reversible on their catalyst, which differs from our result. However, CO pulsing over HTT Au/Fe_2O_3 did show reversible adsorption of CO [33], consistent with the result of Olea et al. [11]. The response of the CO_2 product of Olea et al. [11] for CO oxidation at 25 °C differs significantly from the product response of our CO oxidation experiments. In the report of Olea et al. [11] the CO_2 response is sharp and indicative of a “typical” TAP response for fast production and some reversible adsorption. This result, when combined with additional isotopic experiments, led the authors to the conclusion that CO_2 was produced by a reaction with molecular oxygen and that the lattice oxygen atoms were active in oxygen exchange only with CO_2 after its formation [11]. However, Figs. 6 and 7 clearly showed that no oxygen was adsorbed to the fresh/as-received 3.4% Au/Fe_2O_3 at 25 °C, and no oxygen exchange occurred. Pulsing of only CO produced only limited, irreversible adsorption of CO and negligible CO_2 production (Fig. 8). Continued pulsing of CO eventually produced CO_2, thereby indicating the participation of lattice oxygen atoms or OH groups present on the Au and the support in the formation of CO_2. The response for CO_2 production at room temperature in our experiments was very slow (Fig. 10), whereas pulsing of CO_2 over fresh Au/Fe_2O_3 produced a CO_2 response similar to that observed by Olea et al. [11] (Fig. 11). We conclude that some CO_2 may be involved in oxygen exchange with the catalyst, but the vastly different shapes of CO_2 product and pulsed CO_2 indicated that the rate-limiting step was more likely the decomposition of a relatively stable intermediate.

Adsorption of oxygen was observed only after CO_2 production was detected during CO + O_2 pulsing (Fig. 12). This supports the view that, under the conditions of our study, the extraction of an oxygen species from the support oxidises CO on Fe_2O_3-supported catalysts [9,10]. Indeed, quantification of CO uptake during the initial stages of the reaction (Fig. 8) when no CO_2 was observed showed that the CO uptake (approximately 2×10^{18} molecules of CO [2]) was significantly greater than the quantity of O/OH present on the Au species ($\sim 1 \times 10^{18}$ O species). This indicated that once the CO had reacted with the O/OH on the Au during a noncatalytic reaction, extraction of O from the support (and subsequent replenishment from the gas phase) signaled the start of the catalytic cycle. The participation of lattice oxygen is consistent with the observations of Gupta and Tripathi for uncalcined Au/Fe_2O_3 catalysts.

The production of H_2O during CO oxidation with fresh Au/Fe_2O_3 was observed during the MultiTRACK experiments (Fig. 13). H_2O production during CO oxidation was also reported by Costello et al. [16,17,21] from the study of CO oxidation in the presence of H_2O over Au/Al_2O_3 catalysts. It was proposed that deactivation in CO oxidation is probably due to deprotonation of bicarbonate to a carbonate, which would poison the active site at the interface [16,17,21]:

$$\text{Au–CO}_3\text{H} + \text{Al–OH} \rightarrow \text{Au–CO}_3\text{–Al} + \text{H}_2\text{O}.$$

This would explain both the production of H_2O observed in Fig. 13 and the apparent deactivation of the catalyst after a decrease in the concentration of surface OH/H_2O.

Incorporation of all the presented results allows elucidation of a consistent mechanism for CO oxidation with fresh/as-received Au/Fe_2O_3 samples. Mössbauer spectroscopy showed that the catalyst contained an initial ratio of Au^{3+}:Au^0 that is unsuitable for CO oxidation. An initial “activation period” as indicated by the MultiTRACK and FTIR studies shows that this ratio changed before CO_2 production was observed. The Mössbauer spectrum of Au/Fe_2O_3 exposed to CO remains predominantly that of cationic Au; the environment of the Au^{3+}, however, appears to have changed (Fig. 2).

Adsorption of CO occurs on the Au particles, as no CO adsorption was observed with Fe_2O_3 by either MultiTRACK or FTIR. The (OH) groups present on the Au particles, as indicated by Mössbauer spectroscopy, react with the CO to form a hydroxycarbonyl, which is consistent with the proposal of Costello et al. [16]. We propose that spillover of these species to the Au–support interface allows the path to CO_2 production to commence. The Au–COOH at the interface could be oxidised to bicarbonate by oxygen from the support (Fig. 14). After this initial conversion of Au-hydroxyls, a different mechanism involving carbonate formation via reaction of CO and lattice oxygen and subse-

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[2] Average pulse size = 2×10^{16} molecules. 20% CO/Ar gas mixture used, giving 4×10^{15} molecules of CO per pulse. Uptake increased with increasing pulse number. CO uptake quantified using the number of CO pulses required before CO_2 “break-through” (approximately 1500 pulses). Desorption pattern of CO_2 prevented accurate quantification beyond this point.

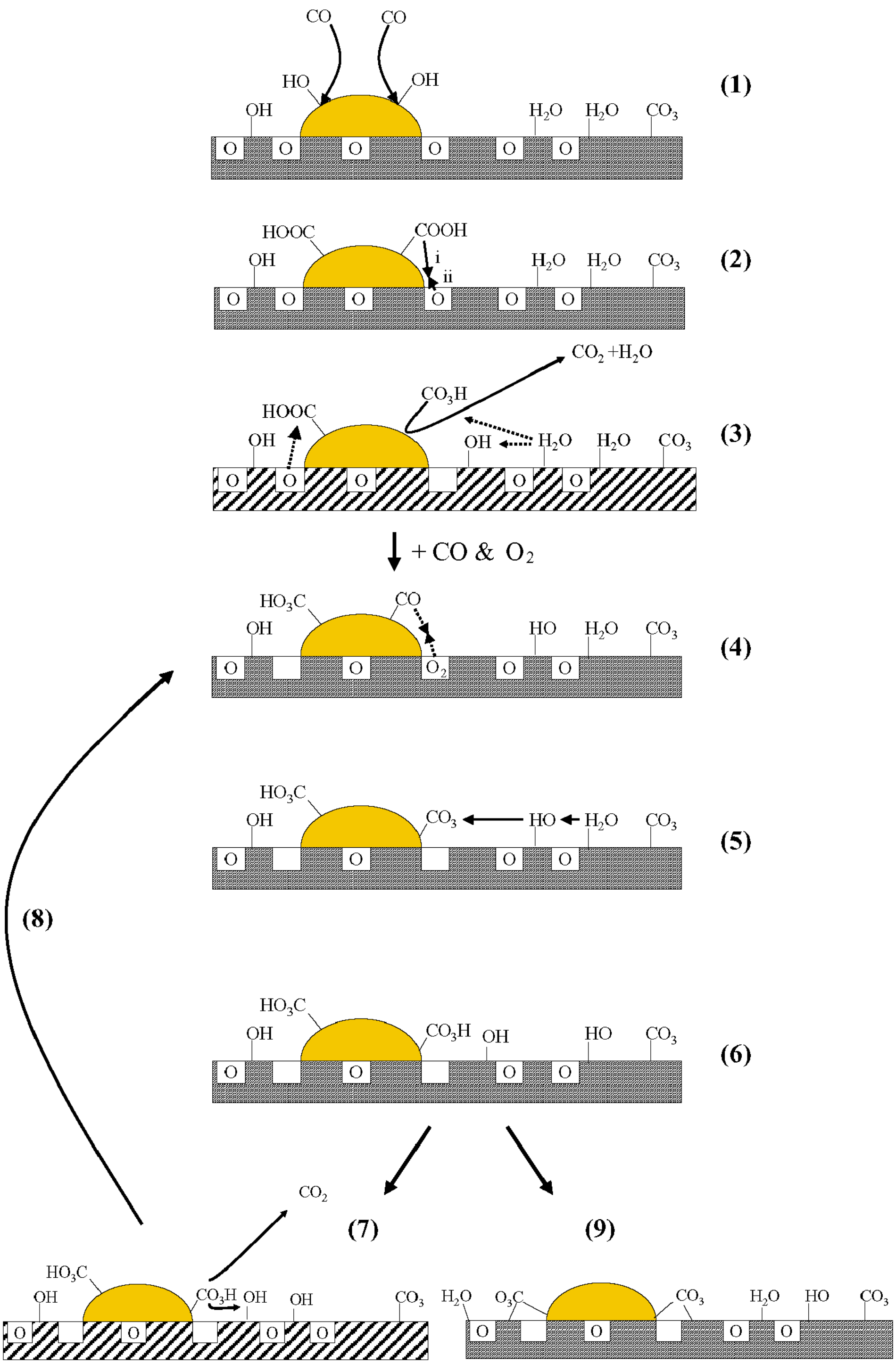

Fig. 14. Schematic model of CO oxidation with fresh Au/Fe_2O_3: (1) adsorption of CO onto hydrated Au particle, (2) formation of hydroxycarbonyl, spillover to Au–support interface (i), and oxidation to bicarbonate by lattice oxygen (ii), (3) decomposition of the bicarbonate to produce CO_2 and H_2O, (4) further CO adsorption on Au particle and O_2 adsorption in oxygen vacancy of the Fe_2O_3, (5) H_2O attack of carbonate at interface for further bicarbonate formation (6). (7) Decomposition of bicarbonate yields CO_2, and recycles OH to continue the catalytic cycle (8). Step (9) shows reaction of bicarbonate with OH to form H_2O and stable carbonate at interface.

quent bicarbonate formation may then occur [18]. Pulsing of oxygen after considerable CO_2 production (Fig. 9) showed irreversible adsorption of O_2, which did not occur for the fresh catalyst. This suggested that oxygen vacancies had been created in the support as a direct result of CO oxidation. Costello et al. [16,17,21] claimed that there was no direct participation of the support for CO oxidation when Au/Al_2O_3 was used. It is important to note that we propose that the oxygen is adsorbed associatively in the form of a superoxide species (O_2^-), based on the work of Schubert et al. [8]. However, no clear discrimination between associative or dissociative adsorption of O_2 can be made from our results at this stage. Schubert et al. [8] also clearly showed that reducible metal oxides such as Fe_2O_3 were more active than the so-called inert oxides such as Al_2O_3 and SiO_2 because of the ability of the “active” oxides to provide reactive oxygen [9,10].

Since CO did not adsorb to or react on fresh Fe_2O_3 at 25 °C, it can be concluded that the adsorbed CO observed in Fig. 8 was on the Au particles. Evidence of potential spillover from the Au particles is obtained after consideration of the available Au sites and number of CO molecules pulsed prior to CO_2 production. When we calculated the number of gold sites available, we made an estimation of 15% Au dispersion (based on 4-nm particles, as is typically observed on Fe_2O_3 supports) [34]. Based on this, it can be calculated that the number of adsorbed CO molecules is slightly greater than the available number of Au adsorption sites. Therefore, spillover of carbonates onto the support may have occurred. Without subsequent transformation into bicarbonates by the presence of hydroxyls, carbonate ion migration would cover the surface of the catalyst [22]. Daté et al. [18] recently proposed that hydroxyl radicals may act by activating oxygen or by promoting the decomposition of a carbonate, and this pathway cannot be excluded at present. The response of CO_2 from the MultiTRACK experiments suggests that the decomposition of an intermediate is slower than the simple desorption of CO_2, thereby supporting the growing school of thought of a (bi-)carbonate-type intermediate at the interface [35,36]. Deactivation occurs as the interface active sites are gradually covered by the accumulation of inert carbonate and surface hydroxyls are depleted [16–18,37].

5. Conclusions

Mössbauer spectroscopy, in situ FTIR, and MultiTRACK (an advanced TAP reactor) were used to study low-temperature CO oxidation with Au/Fe_2O_3. Mössbauer spectroscopy revealed the presence of gold in mixed-oxidation states, which was consistent with previous reports of similar catalysts. The iron oxide support was proposed to be in the form of a poorly crystallised ferrihydrite, $Fe_5HO_8 \cdot 4H_2O$. MultiTRACK studies showed that O_2 did not adsorb to the fresh catalyst, and no oxygen exchange was observed during $^{18}O_2$ pulsing. CO adsorbed irreversibly during the initial stages of the reaction, and CO_2 production was negligible. A mechanism involving a bicarbonate intermediate is proposed as the main pathway for CO oxidation on this uncalcined catalyst.

Acknowledgments

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