
The Role of Nanosized Gold Particles in Adsorption and Oxidation of Carbon Monoxide over Au/Fe₂O₃ Catalyst

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The presence of gold is found to promote the development of weakly bonded (CO)_{ad} species over the surface of Au/Fe₂O₃ catalyst during interaction with carbon monoxide (CO) or a mixture of carbon monoxide and oxygen. The concentration of these species and the nature of the bonding depend on the gold particle size. No such species are formed for gold particles larger than ~11 nm or over gold-free iron oxide. The bulk carbonate-like species, formed in the process with the involvement of the hydroxy groups of the support, are merely side products not responsible for the low temperature activity of this catalyst.

Thermochemical measurements reveal that the oxidation of carbon monoxide on both Fe₂O₃ and Au/Fe₂O₃ occurs *via* similar redox mechanisms, involving the abstraction and replenishment of lattice oxygen, where the presence of nanosize gold particles promotes these processes. This is attributed to their capacity to adsorb carbon monoxide because of their inherent defective structural sites. It is suggested that the energy that evolves during chemisorption of CO is responsible for the surge in temperature at the Au-Fe₂O₃ interfaces, which in turn serve as sites for the accelerated reaction between CO and the support. The role of gold particle size is discussed in terms of the effect of geometry of surface metal atoms in the nanosize clusters.

The discovery by Haruta *et al* of the unexpected low temperature CO oxidation activity of supported gold (1 - 4) has opened up a new dimension in the understanding of the basics of catalysis, since gold appears to be an exception in disregarding the requirement of unfilled *d*-orbitals for a metal catalysed reaction. Gold, in this new incarnation as a catalyst, has already found application in a number of chemical reactions, such as oxidation (of CO, CH₄, CH₃OH, C₆H₆, *o*-hydroxybenzyl alcohol), epoxidation (of propylene), reduction/hydrogenation (of NO, CO, acetylene, butylene), hydrocracking, water gas shift, and isotopic exchange, etc (See recent reviews and publications 5 - 13). Some practical applications of supported gold include: gas sensors (14), regeneration of CO₂ in sealed-off cw CO₂ lasers (15, 16) and purification of air (removal of CO and VOC_s) (5). In our laboratory, we have developed a compact low-power long-life sealed-off cw CO₂ laser, where an outer jacket coated with Au/Fe₂O₃ helped in the regeneration of CO₂ from the dissociation products CO and O₂ formed during the laser discharge (15, 16). The performance of

this gold catalyst was found to be superior to that of the other noble metals dispersed on reducible oxide supports (such as Pt/SnO₂ and Pd/SnO₂), advocated earlier for this purpose (17). In most of the above-cited applications, the importance of the size of gold crystallites and the nature of the support is generally emphasized. Various issues pertaining to supported gold catalysts, however, still remain unresolved. For instance: what is the role of the gold particle size and what is the optimum size for a particular application? What is the best method of preparing supported gold? What oxidation state of gold is vital to its activity? Does an electronic bonding of the reactants occur at gold sites? What is the nature of the transient species formed in the absence and in presence of gold? Unequivocal answers to these questions are yet to be found.

While the requirement of nanosized gold particles is widely accepted, the actual role of gold as a catalyst and also that of its support in the overall performance have, however, raised many divergent views. Various factors contributing to the high activity of these catalysts are

envisaged. For instance, the study by Bocuzzi and co-workers (18, 19) on gold supported on ZnO and TiO₂ has shown the existence of two kinds of metallic gold sites, which are able to adsorb both oxygen and carbon monoxide at the same time. It has been proposed that the oxidation of carbon monoxide follows two independent pathways; a rapid direct oxidation of CO at the surface of the metallic particles and a slow induced oxidation with the surface lattice oxygen species of the supports. On the one hand, Haruta *et al* (2) proposed a reaction mechanism involving the migration of CO to the metal-support interface and the formation of bidentate carbonate species, where the decomposition of the carbonate-like species is considered to be the rate-determining step. On the other hand, Bollinger and Vannice (20) demonstrated that the deposition of TiO_x overlayers onto inactive gold particles produced a highly active catalyst. Furthermore, the bidentate and monodentate carbonates, carboxylates, and formate species formed during exposure of Au/TiO₂ to CO are thought to be just spectator species playing no role in the oxidation process (20). Knell *et al* (21), suggest that the high CO oxidation activity of Au/ZrO₂ arises due to a synergy between the zirconia and the supported gold particles. Unreduced gold species, stabilized by an interaction with the support, are proposed in some studies (22 - 24) to be more active than Au⁰.

In a recent publication, Bocuzzi and Chiorino (25) used isotopic oxygen to demonstrate that different reaction channels may operate in CO oxidation over Au/TiO₂ depending on experimental conditions, such as reaction temperature and presence of moisture. Thus, the reaction at 90 K was found to occur between preadsorbed CO molecules with nascent atomic oxygen atoms formed on activation of O₂ on gold particles, the process being promoted in the presence of water. On the other hand, a quite extensive exchange reaction occurs with the oxygen atoms of the support at room temperature (25). Tabakova *et al* (26) conclude that the catalytic activity of gold in the water gas shift depends strongly not only on the dispersion of the gold particles but also on the state and the structure of the support. In addition to the role played by the gold dispersion and the support, the importance of the morphology of gold particles has also been highlighted in some of the studies using various surface characterization techniques (27 - 31). For instance, the diffuse reflectance Fourier transform infrared study of Baiker and co-workers (31) demonstrated that the nature of gold sites depended upon the support employed. Thus, while the number of low-coordinated gold sites was much higher on TiO₂, positively polarized gold atoms existed on ZrO₂. The

better CO oxidation activity of Au/TiO₂ compared to that of Au/ZrO₂ is attributed to the gold sites of low coordination, where the weakly bound CO molecules react with oxygen via an Eley-Rideal type reaction mechanism. The shape rather than the size of crystallites is thus demonstrated to play a more important role in the catalytic activity (31).

The current status of the catalytic properties of gold has been reviewed by Bond and Thompson (5, 32) and also by Kozlov *et al* (33). A general mechanism involving the oxidation reaction of CO at the edge of a particle containing both gold atoms and ions and involving the hydroxy groups of the support is invoked by Bond and Thompson (32).

Our motivation to take up this work was based on a realization that many of the previously reported studies, particularly those attempting to establish a structure-property relationship using surface characterization techniques, were performed under conditions different from that of actual reactions and there is therefore a lack of direct evidence. We at the same time realized that microcalorimetry is a technique sensitive to each step in a catalytic process, and the heat evolved in the reaction therefore represents the overall effect of the processes occurring on the catalyst surface at a particular time. This technique is therefore well suited for the elucidation of transient steps involved in a catalytic process, as has been amply demonstrated in our earlier publications using the catalysts consisting of noble metals on reducible metal oxides as support (34 - 37). With this in view, we measured enthalpy changes during the adsorption and reaction of CO or CO + O₂ over 5at% Au/Fe₂O₃, Fe₂O₃ and polycrystalline gold samples at different temperatures in the range 300-500 K. The 5at% gold on iron oxide catalyst is subsequently referred to as "Au/Fe₂O₃" throughout the text. The species formed over the surface of these catalysts under similar reaction conditions, and their thermal and time-dependent stability were examined using *in situ* IR spectroscopy. The highlights of these studies are presented in this article while the detailed results and the experimental procedures are given in our earlier publications (38, 39).

RESULTS AND DISCUSSION

IR Spectra of Au/Fe₂O₃ and Fe₂O₃ after Adsorption of CO

Plots a-c in Figure 1 present the IR spectra of an Au/Fe₂O₃ sample recorded as a function of time after exposure to 13.3 kPa (100 Torr) CO. As seen in this figure, the exposure of a fresh catalyst sample to CO at room temperature gave rise to a single IR band of

about 12.6 cm^{-1} width and at a frequency of $\sim 2107\text{ cm}^{-1}$. No side bands were observed. Several overlapping bands due to oxygenated species ($1100\text{--}1700\text{ cm}^{-1}$) and the IR bands in the $2300\text{--}2400\text{ cm}^{-1}$ region due to ν_3 vibrations of CO_2 , produced in the process, may also be seen in this figure. As indicated by absorbance values, given in parentheses, the intensity of the $\nu(\text{CO})$ band decreased progressively with increasing contact time while the intensity of the IR bands due to oxygenated species increased (Figure 1b, c). Also, an increase of $2\text{--}3\text{ cm}^{-1}$ in the frequency of this band was observed after about 1h (Figure 1c). While the intensity of the various bands mentioned above increased with pressure, their frequency always remained unchanged. We may mention that oxygenate species similar to those shown in Figure 1 (a-c) were also formed during exposure to CO_2 . For a comparison, curve d in Figure 1 is the IR spectrum of $\text{Au/Fe}_2\text{O}_3$ after exposure to 13.3 kPa CO_2 at room temperature. The intensity of these bands decreased progressively on increase in catalyst temperature and also on post-exposure annealing of the sample. A complete removal of these species was observed only at temperatures above 475 K (40).

The width of the $\nu(\text{CO})$ band increased considerably when an $\text{Au/Fe}_2\text{O}_3$ sample was used repeatedly for CO adsorption, pretreated each time under O_2 at 570 K and followed by evacuation at the same temperature. The shape of the band thus obtained could be resolved into at least three well-fitted

Gaussian-shaped bands having maxima at around 2090 , 2110 , and 2130 cm^{-1} , indicating the existence of some new adsorption sites (40).

Adsorption of Isotopic CO

Figure 2 gives the IR spectra of $\text{Au/Fe}_2\text{O}_3$, developed on adsorption of isotopic CO ($^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{18}\text{O}$) at 300 K . A uniform shift of all $\nu(\text{CO})$ bands was observed so that the frequency ratio ($\nu_{\text{isotopic}}/\nu_{\text{normal}}$) for an individual band was always ~ 0.977 , as was confirmed by the computer resolution of these bands. On the other hand, the individual oxygenate-region bands showed different shifts for isotopic gases. Thus the bands at 1618 , 1430 and 1410 cm^{-1} showed a red shift with $\Delta\nu$ of 46 , 35 and 20 cm^{-1} respectively, corresponding to a $^{13}\text{C}/^{12}\text{C}$ ratio of around 0.972 , 0.979 and 0.986 respectively. No shift was however observed in the 1223 cm^{-1} band (Figure 2b). Very similar behaviour was observed for the adsorption of $^{12}\text{C}^{18}\text{O}$. In this case the frequency of $\nu(\text{CO})$ band at 2107 cm^{-1} shifted to a lower frequency of 2063 cm^{-1} . The prominent oxygenate region bands at 1620 and 1430 cm^{-1} showed a red shift of about 12 and 7 cm^{-1} , respectively.

Adsorption on Fe_2O_3 and Effect of Calcination

No $\nu(\text{CO})$ bands and only $\nu(\text{CO}_2)$ and carbonate region bands were observed on adsorption of CO over Fe_2O_3 irrespective of catalyst temperature or CO gas pressure. On calcination of $\text{Au/Fe}_2\text{O}_3$ at higher temperature, the intensity of the $\nu(\text{CO})$ band and that

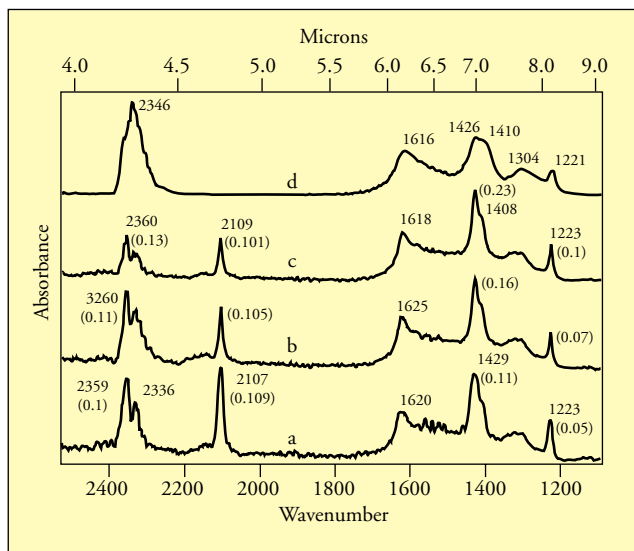


Figure 1 Development of IR spectra as a function of time on exposure of an $\text{Au/Fe}_2\text{O}_3$ catalyst to 100 Torr CO at room temperature. a) 5 min , b) 30 min , and c) 1 h . Spectrum d is for an $\text{Au/Fe}_2\text{O}_3$ sample exposed at room temperature to 100 Torr CO_2

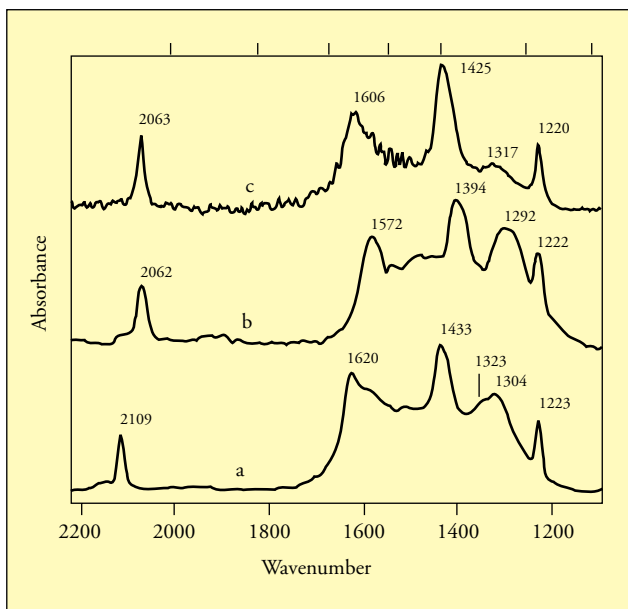


Figure 2 Development of vibrational bands on $\text{Au/Fe}_2\text{O}_3$ catalyst after exposure to a) $50\text{ Torr }^{12}\text{C}^{16}\text{O}$, b) $50\text{ Torr }^{13}\text{C}^{16}\text{O}$ and c) $20\text{ Torr }^{12}\text{C}^{18}\text{O}$

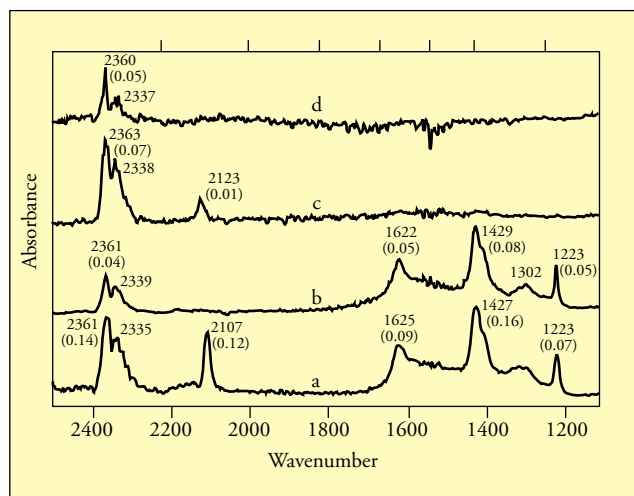


Figure 3 IR bands developed on Au/Fe₂O₃ (a) and Fe₂O₃ (b) catalysts after exposure to 100 Torr CO at 300 K. Spectra c and d are for Au/Fe₂O₃ samples calcined at 820 and 870 K, respectively. Numbers in parentheses indicate the absorbance values (Reproduced from *J. Catal.*, 1999, **187**, 332 with the permission of Academic Press)

of the IR bands due to oxygenate species and CO₂ were much lower. Figure 3 gives comparative infrared bands developed on Au/Fe₂O₃ and Fe₂O₃ samples as a function of calcination temperature. No bands were formed in the oxygenate region when CO was adsorbed at room temperature over an Au/Fe₂O₃ sample calcined at 820 or 870 K (Figure 3c, d), even though a comparable amount of CO₂ still formed (*cf* Figure 3c).

Calcination of Au/Fe₂O₃ resulted in a progressive increase in gold particle size, as evaluated by TEM (38). For a calcination temperature of 673 K, about 75% of gold particles were in the 3 - 5 nm range, while the average size was around 4.8 nm. The calcination of a sample at 873 K resulted in gold particles of 5 - 20 nm size, the average being ~11 nm.

Effect of CO Adsorption and Calcination on Hydroxyl Region Bands

The experiments performed with both Fe₂O₃ and Au/Fe₂O₃ showed that the intensity of the hydroxyl group stretching bands at 3628 and 3665 cm⁻¹ decreased considerably on adsorption of CO at room temperature. For exposures of CO at higher temperatures, OH groups were removed very quickly and no bands were detected in this region. These data are shown in Figure 4 for adsorption of CO on Fe₂O₃ at two different temperatures.

The intensity of the ν(OH) region bands was again found to decrease substantially on calcination of a sample at temperatures in range 800-900 K (40).

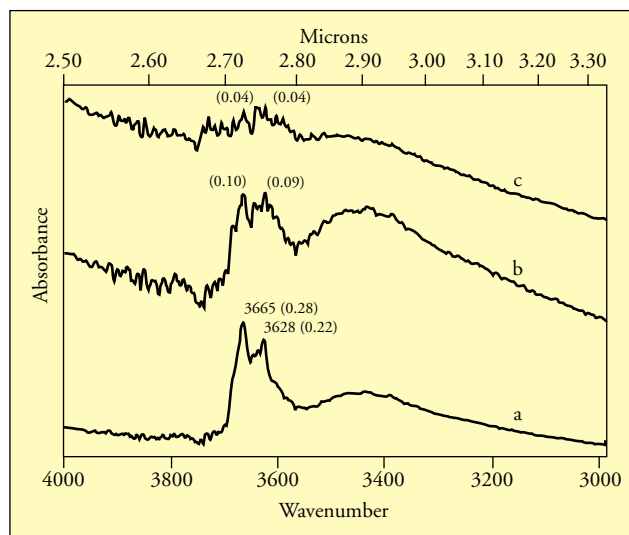


Figure 4 Hydroxyl region bands of Fe₂O₃ after adsorption of 100 Torr CO at different temperatures. a) no CO, b) 300 K and c) 370 K. Numbers in parentheses indicate the absorbance values

Adsorption of CO + O₂

Behaviour similar to that of ν(CO), ν(CO₂) and oxygenate region bands shown in Figures 1, 2 and 3 was also observed for exposures of CO + O₂, even though their intensities varied marginally. These data are included in an earlier publication (38).

Catalytic Activity

The Au/Fe₂O₃ catalyst calcined in air at 673 K showed considerable activity at 273 K for the CO oxidation reaction, the percentage conversion of CO to CO₂ being around 50% when a reaction mixture consisting of CO + O₂ + He (2:1:17) was employed at a flow rate of 1.2 Lh⁻¹g⁻¹. 100% conversion was observed during the reaction at room temperature or above (Figure 5a). The catalytic activity remained unchanged during 40 h on stream.

Both Fe₂O₃ and polycrystalline gold powder showed poor activity as compared with Au/Fe₂O₃ and the reaction onset temperature in these cases was more than 373 K. In the case of Fe₂O₃, 100% conversion of CO was observed only at temperatures above 473 K under identical reaction conditions. Curves b and c in Figure 5 show the temperature-dependent catalytic activity of Fe₂O₃ and polycrystalline gold samples.

Calcination of Au/Fe₂O₃ at temperatures above 850 K resulted in a steady decrease in catalytic activity. Curves d and e in Figure 5 indicate typical activity data for samples calcined at 870 and 970 K, respectively.

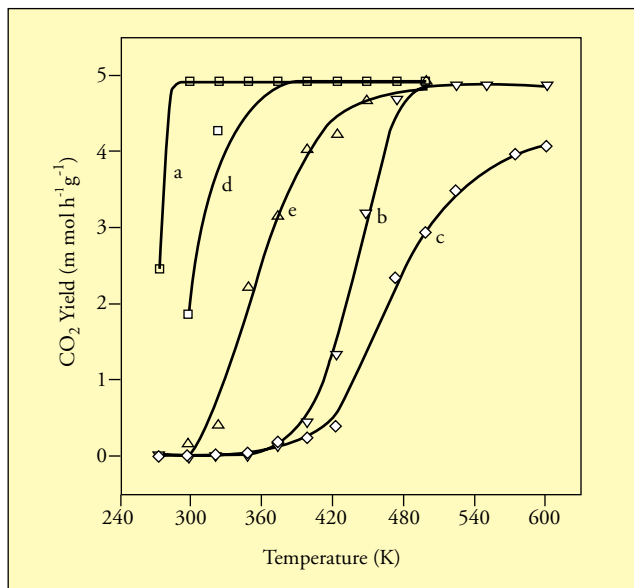


Figure 5 CO oxidation activity at different reaction temperatures of Au/Fe₂O₃ (a), Fe₂O₃ (b) and polycrystalline gold (c) calcined at 670 K. Curves d and e show corresponding data for an Au/Fe₂O₃ sample calcined at 870 and 970 K, respectively

THERMOCHEMICAL DATA

Adsorption of CO and O₂ from a CO + O₂ pulse

Data given in Figure 6 show the fraction of CO and O₂ adsorbed/reacted (average value from 5 to 6 successive pulse exposures) when an Au/Fe₂O₃ sample was exposed to a 4.1 μmol pulse of CO + O₂ (2:1) at different temperatures. At 300 and 330 K the amount of CO adsorbed/reacted was marginally higher than that of O₂. Thus, the fractions of CO and O₂ adsorbed from a pulse were about 60 and 51% respectively at a reaction temperature of 300 K. This gap decreased progressively with increasing temperature, and at temperatures above 330 K almost identical fractions of CO and O₂ were adsorbed/reacted from a pulse (Figure 6a, b).

CO₂ yield

The amount of CO₂ produced from a pulse also increased progressively with a rise in catalyst temperature as shown by data in Figure 6c. Thus, while about 70% of CO adsorbed from a pulse was converted to CO₂ at 470 K, the yield of CO₂ from CO_{ad} was negligibly small at room temperature.

Enthalpy Changes

Curve d in Figure 6 presents the temperature dependence of the amount of heat evolved per mol (Q_{molar}) when a

CO + O₂ pulse was dosed over a catalyst sample. A Q_{molar} value of ~ 175 kJ mol⁻¹ was observed for the exposure of 4.1 μmol CO + O₂ at room temperature. The value increased marginally to 210 kJ mol⁻¹ for an experiment at 330 K and then decreased again with further increase in catalyst temperature (Figure 6d).

Fe₂O₃ Catalyst

Similar but much smaller fractions of CO or O₂ were adsorbed/reacted when CO + O₂ (2:1) pulses (4.1 μmol each) were dosed over an Fe₂O₃ sample at different temperatures. Thus, only ~5 to 6% of CO and 3 to 4% of O₂ were adsorbed/reacted for exposures at temperatures of 300 or 330 K. These values increased progressively with the rise in sample temperature, the adsorbed fraction being ~55% at a reaction temperature of 470 K. Curves a and b in Figure 7 indicate the average amount of CO and O₂ adsorbed/reacted from 5 - 6 successive pulse exposures at different sample temperatures. Correspondingly, a negligible amount of CO₂ was formed at temperatures below 400 K (Figure 7c), whereas at higher reaction temperatures the yield of CO₂ was almost similar to that shown in Figure 6c.

While low Q_{molar} values (~125 kJ mol⁻¹) were observed for reaction at 330 and 370 K, the average

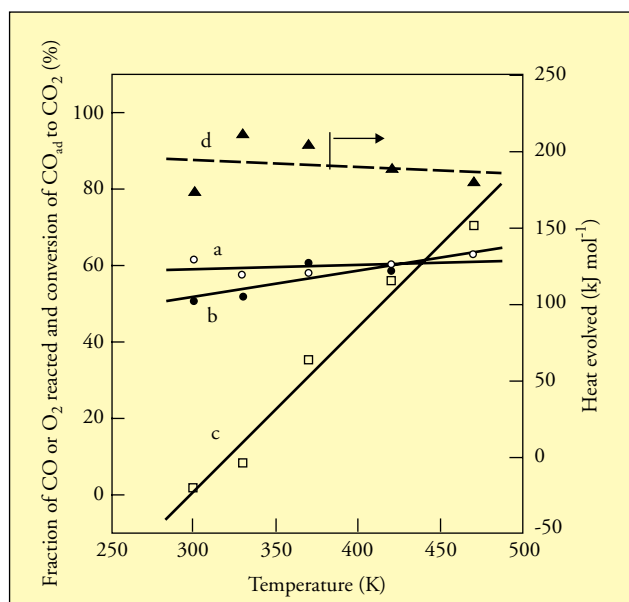


Figure 6 Average fraction of CO (a) and O₂ (b) adsorbed/reacted when 4.1 μmol CO + O₂ (2:1) pulses were dosed over Au/Fe₂O₃ catalyst at different temperatures. Curve (c) shows the conversion of CO_{ad} to CO₂ and curve d presents the data on the heat evolved in the process. (Reproduced from *J. Catal.*, 1999, **187**, 332 with the permission of Academic Press)

values were around 200 and 190 kJ mol⁻¹ for the interaction of CO + O₂ at 420 and 470 K, respectively (Figure 7d).

Gold Catalyst

No measurable amount of CO or O₂ was adsorbed/reacted when a polycrystalline gold powder was exposed to CO + O₂ pulses at temperatures below 370 K. Even at the higher reaction temperatures of this study, smaller fractions of both CO and O₂ were adsorbed as compared with the Au/Fe₂O₃ catalysts, as is shown in the data of Figures 8a, b. Correspondingly, no CO₂ was formed at reaction temperatures below 370 K, whereas at temperatures above 400 K a complete transformation of CO_{ad} to CO₂ was observed (Figure 8c).

Curve d in Figure 8 presents the average Q_{molar} values for adsorption of CO + O₂ over a gold sample at different temperatures. A negligible amount of heat was evolved for reaction temperatures below 370 K, commensurate with the amounts of CO/O₂ adsorbed. Also, the Q_{molar} values for gold (Figure 8d) are comparatively lower than the corresponding data in Figures 6 and 7.

Rise of Catalyst Bed Temperature During CO + O₂ Reaction

Precise measurements indicated that the bulk temperature of Au/Fe₂O₃ catalyst increased almost

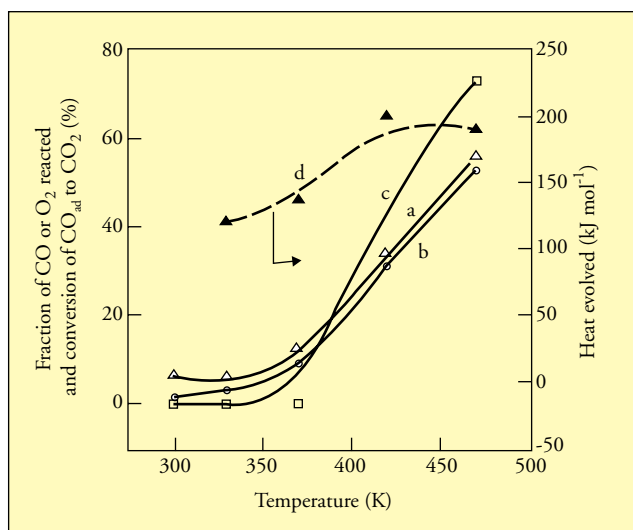


Figure 7 Average fraction of CO (a) and O₂ (b) adsorbed/reacted and conversion of CO_{ad} to O₂ (curve c) when 4.1 μmol pulses of CO + O₂ (2:1) were injected over Fe₂O₃ catalyst at different temperatures. Curve (d) gives the heat evolved in the process. (Reproduced from *J. Catal.*, 1999, **187**, 332 with the permission of Academic Press)

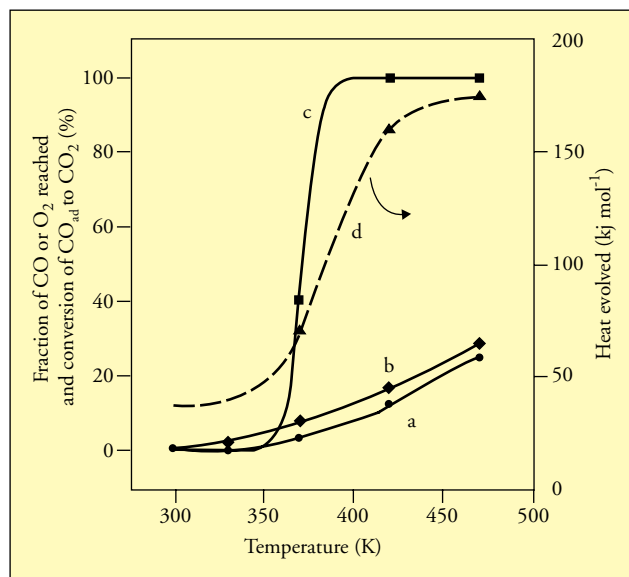


Figure 8 Average fraction of CO (a) and O₂ (b) adsorbed/reacted and conversion of CO_{ad} to CO₂ (curve c) when 4.1 μmol pulses of CO + O₂ (2:1) were injected over polycrystalline gold powder at different temperatures. Curve (d) gives the heat evolved in the process. (Reproduced from *J. Catal.*, 1999, **187**, 332 with the permission of Academic Press)

instantly when the catalyst maintained at room temperature was exposed to a CO + O₂ flow and the extent of this rise depended on the calcination temperature to which the catalyst was subjected before the CO + O₂ flow commenced. Thus, a rise of ~12 K in catalyst bulk temperature was observed for the sample calcined below 700 K. The corresponding rise was about 10 and 5 K for the samples pretreated at 773 and 873 K respectively. Furthermore, no rise in catalyst bulk temperature was observed when a sample calcined at 973 K was exposed to CO + O₂ flow at 298 K. Also, no measurable temperature rise was detected for the experiments performed at higher reaction temperatures and also for the CO + O₂ reaction over Fe₂O₃ or gold powder at the reaction temperatures used in this study. The temperature rise, as mentioned above, remained unchanged during a run time of 5 to 6 h. These data are given in Table 1.

We interpret our results as follows:

- 1 The adsorption of CO is facilitated by the presence of gold (Figures 1 - 3). However, the isotopic shift of -0.977 in the ν(CO) bands (Figure 3) corresponds to the shift expected for gaseous CO as per the Redlich-Teller rule, and therefore indicates only a weak Au-CO bonding where bonded carbon monoxide retained its gaseous

Table 1 Temperature Rise of a 5at%Au/Fe₂O₃ Catalyst Bulk, Subjected to Calcination at Different Temperatures and Exposed at 298 K to a CO + O₂ + He (2:1:17) Stream (50 ml min⁻¹)

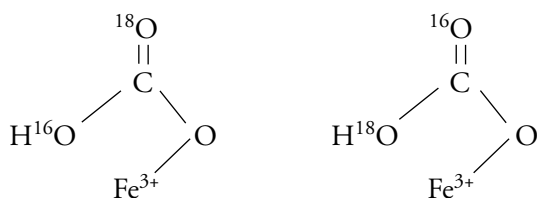
	Calcination Temperature, K	Initial Temperature Rise, K (within 2-5 min)	Equilibrium Temperature Rise after 5 h Test Run, K
1	673	12	10
2	773	10	8
3	873	5	5
4	973	0	0

character. This observation finds support from a study of Grunwaldt *et al* (31), who demonstrated that CO adsorption was reversible on supported gold catalysts and the weaker CO bonding led to a more active catalyst. Also, the presence of weak side bands (Figure 1) particularly on samples used repeatedly for CO oxidation, reveals the formation of a small number of Au(CO)O species. Since the oxidative pretreatments of supported catalysts are known to improve the metal dispersion further (41 - 43), it is likely that such co-adsorbed species are formed only over very small gold particles.

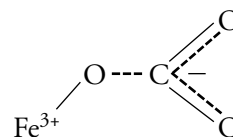
2 Figure 3 (c, d) shows that no carbonate-type species were formed by interaction with the CO (or CO + O₂) in the case of calcined Au/Fe₂O₃ or Fe₂O₃ samples that are devoid of hydroxy groups (Figure 4), even though the formation of CO₂ occurred. It is thus apparent that the OH groups are important for the formation of oxygenates through reaction with product CO₂, rather than in the CO + O₂ reaction as envisaged by some authors (32). This is in agreement with the observed formation of identical carbonate-like species during interaction of CO₂ with Au/Fe₂O₃ (Figure 1d) and also with Fe₂O₃ (40) at different temperatures in range 295 - 475 K.

3 Based on the results for adsorption of isotopic gases (Figure 2), the CO or CO₂ formed during its oxidation give rise to formation of the following bulk oxygenate species (44):

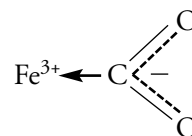
- (i) Bicarbonate species (1614 - 1620, 1407 and 1223 cm⁻¹ bands) - formed at room temperature and below:



- (ii) Monodentate carbonate (1430, 1300 - 1320 cm⁻¹) - formed at room temperature and below:



- (iii) Bidentate carbonates or adsorbed CO₂ species (1510, 1340 cm⁻¹) - formed only at elevated temperatures (>350 K):



The temperature-dependent variation in intensity has demonstrated that the species (i) and (ii) shown earlier are fairly stable below 450 K, both under ambient pressure and under pumping conditions (38, 40). In agreement with the study of Vannice *et al* (20) we may therefore infer that such species may not play an important role in CO₂ formation, particularly at low reaction temperatures.

4 A comparison between the data in Figures 6 and 7 shows that the presence of gold resulted in the augmented adsorption/reaction of both CO and O₂ and in the higher conversion of adsorbed CO to CO₂, particularly at reaction temperatures lower than 450 K. The enthalpy data of our study suggest the preponderance of a normal redox mechanism, *ie* via lattice oxygen abstraction, for both the Fe₂O₃ and Au/Fe₂O₃ catalysts. Thus, the Q_{molar} value of 175 to 200 kJ mol⁻¹ in Figure 6 can be attributed to the simultaneous occurrence of reactions IV and V (Table 2), where Step IV may play a greater role because of larger CO adsorption. In the case of the Fe₂O₃ sample, almost the same Q_{molar} values are observed at reaction temperatures above 400 K (Figure 7). At lower reaction temperatures, the

amount of CO adsorbed is marginally higher than that of O₂ and therefore a lower Q_{molar} (~120 - 130 kJ mol⁻¹) value at temperatures below 400 K (Figure 7) may be ascribed to a greater role for reaction Step IV (Table 2). Our thermochemical data show that, contrary to prevailing views, a Langmuir-Hinshelwood type mechanism involving CO_(ad) + O_(ad) reaction may not play an important role with the supported gold catalyst (see Table 2), at least at room temperature and above. The heat values observed for the polycrystalline gold sample, on the other hand, suggest that the reaction mechanism in the case of CO oxidation over pure gold depends upon the catalyst temperature. Thus, while at lower reaction temperature CO_{ad} + O_{ad} (Reaction III, Table 2) governs the CO oxidation explaining the lower Q_{molar} values, the value of Q_{molar} ~200 kJ mol⁻¹ at higher temperatures corresponds to CO_(g) + O_(ad) process (Reaction II, Table 2).

The above points thus clearly indicate that the reaction mechanism of CO oxidation on Au/Fe₂O₃ catalyst is quite different from that on metallic gold. A comparison of data in Figures 6 and 7 shows that the presence of gold-promoted adsorption of CO and O₂ to an almost equal extent lowers the reaction temperature for the CO oxidation reaction.

As has been brought out in detail in our earlier publications (38, 39), gold may augment the CO oxidation activity of Fe₂O₃ (Figure 5) in the following two possible ways:

i) CO or O₂ molecules on activation at Au sites may

spill over to adjacent Fe₂O₃ sites leading to higher activity, and

ii) The energy released in the chemisorption of CO or O₂ molecules over Au sites may give rise to a localized energy surge and hence to a temperature rise in the neighbouring lattice regions where the Fe₂O₃ + CO reaction may occur at an accelerated rate.

The concept of localized thermal surge at metal/support interfaces as advocated in reference 38, is in complete harmony with the observations of the present study. This is in accordance with the data in Table 1 showing that the temperature of the catalyst bed increased by ~10 - 15 K when a CO + O₂ (2:1) gas stream was passed over Au/Fe₂O₃ catalyst at room temperature in the flow through mode. The actual temperature rise at the metal/support interfaces may be still higher, and that would result in accelerated CO + O₂ reaction at these specific sites.

CONCLUSIONS

We thus suggest that a possible explanation for the synergistic catalytic activity of Au/Fe₂O₃ for the CO oxidation reaction is the transfer of chemisorption energy from the metal particle to the support thus leading to a localized temperature surge at the metal/support interface, which may act as the sites of higher CO oxidation activity. Being restricted to metal/support interfaces at microscopic level, the bulk temperature of the catalyst may be affected only marginally, as has been observed in our study.

Table 2 Estimated Values of Heat Evolution for the Possible Reactions Occurring on the Au/Fe₂O₃ Catalyst Surface During CO Oxidation Reaction: see reference 38

I. Direct reaction of CO and O at gold sites	
CO _(g) + 1/2 O _{2(g)} = CO _{2(g)}	ΔH = -280 kJ mol ⁻¹ ----- (I)
CO _(g) + O _{2(ad)} = CO _{2(g)}	ΔH = -230 kJ mol ⁻¹ at 300 K & -200 kJ mol ⁻¹ at 470 K ----- (II)
CO _(ad) + O _{2(ad)} = CO _{2(g)}	ΔH = -150 kJ mol ⁻¹ at 300 K ----- (III)
CO _(ad) and O _(ad) represent adsorption at gold sites	
2. Redox mechanism involving lattice oxygen of support	
CO _(g) + 3Fe ₂ O ₃ = 2 Fe ₃ O ₄ + CO _{2(g)}	ΔH = -48.3 kJ mol ⁻¹ ----- (IV)
4Fe ₃ O ₄ + O ₂ = 6Fe ₂ O ₃	ΔH = -465 kJ mol ⁻¹ ----- (V)
3. Secondary Reactions	
CO ₂ + Fe ₂ O ₃ → Carbonate-like species, such as carbonates, bicarbonates, formates etc	
	ΔH = -75 kJ mol ⁻¹ at 300 K and -90 kJ mol ⁻¹ at 470 K ----- (VI)

The data in Figures 1 and 3 clearly reveal that the mode of CO chemisorption depended on the size of gold particles, which in turn is sensitive to the pretreatment conditions used for a sample. Our X-ray photoelectron spectroscopy studies (40) showed that no ionic gold species may exist to a significant extent, both prior to and after using an Au/Fe₂O₃ catalyst for CO oxidation. Several other studies have reported similar observations (31, 45, 46). The particle size effect in the catalytic properties of gold may therefore have its origin in the effects of geometry controlled by crystallographic characteristics of the faces exposed (47) rather than in the modified electronic properties of gold. The concentration and the nature of geometric defects are known to be dependent on particle size and these in turn are known to control the catalytic properties (48).

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REFERENCES

- M. Haruta, T. Kobayashi, H. Sano and N. Yamada, *Chem. Lett.*, 1987, 405
- M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301
- S. Tsubota, D.A.H. Cunningham, Y. Bando and M. Haruta, in 'Preparation of Catalysts VI', ed. G. Poncelet *et al.*, Elsevier, Amsterdam, 1995, p. 227
- M. Haruta, S. Tsubota, T. Kobayashi, M. Kageyama, M.J. Genet and B. Delmon, *J. Catal.*, 1993, **144**, 175
- G.C. Bond and D.T. Thompson, *Catal. Rev. -Sci. Eng.*, 1999, **41**, 319
- 'The Abilities and Potential of Gold as a Catalyst' - Report of the Osaka National Research Institute (ONRI) No.393, August, 1999
- M.J. Kahlich, H.A. Gasteiger and R.J. Behm, *J. Catal.*, 1999, **182**, 430
- J.Jia, K. Haraki, J.N. Kondo, K. Domen and K. Tamaru, *J. Phys. Chem. B*, 2000, **104**, 11153
- C. Milone, R. Ingoglia, G. Neri, A. Pistone and S. Galvagno, *Appl. Catal. A : General*, 2001, **211**, 251
- S. Miao and Y. Deng, *Appl. Catal. B: Environmental*, 2001, **31**, L1-L4
- M. Bonarowska, A. Malinowski, W. Juszczyk and Z. Karpinski, *Appl. Catalysis B: Environmental*, 2001, **30**, 187
- R.J.H. Grisel and B.E. Nieuwenhuys, *J. Catal.*, 2001, **199**, 48
- D. Andreeva, T. Tabakova, L. Ilieva, A. Naydenov, D. Mehanjiev and M.V. Abrashev, *Appl. Catal. A : General*, 2001, **209**, 291
- C. Baratto, G. Sberveglieri, E. Comini, G. Faglia, G. Benussi, V. La Ferrara, L. Quercia, G. Di Francia, V. Guidi, D. Vincenzi, D. Boscarino and V. Rigato, *Sensors and Actuators B*, 2001, **68**, 74
- A.K. Tripathi, N.M. Gupta, U.K. Chatterjee and D.D. Bhawalkar, *Rev. Sci. Instrum.*, 1994, **65**, 3853
- A.K. Tripathi, N.M. Gupta, U.K. Chatterjee and R.M. Iyer, *Ind. J. Technol.*, 1992, **30**, 107
- S.D. Gardner, G.B. Hoflund, D.R. Schryer, J. Schryer, B.T. Upchurch and D.R. Brown, in 'Low Temperature CO Oxidation Catalysts for Long-Life CO₂ lasers', ed., D.R. Schryer and G.B. Hoflund, NASA Conference Publication No. 3076, 1990, p.123
- F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, *J. Phys. Chem.*, 1996, **100**, 3625
- F. Boccuzzi, A. Chiorino, S. Tsubota and M. Haruta, *Catal. Lett.*, 1994, **29**, 225
- M.A. Bollinger and M.A. Vannice, *Appl. Catal. (B)*, 1996, **8**, 417
- A. Knell, P. Barnickel, A. Baiker and A. Wokaun, *J. Catal.*, 1992, **137**, 306
- A.M. Visco, A. Donato, C. Milone and S. Galvagno, *React. Kinet. Catal. Lett.*, 1997, **61**, 219
- T.M. Salama, T. Shido, H. Minagawa, and M. Ichikawa, *J. Catal.*, 1995, **152**, 322
- D.A.H. Cunningham, W. Vogel, H. Kageyama, S. Tsubota and M. Haruta, *J. Catal.*, 1998, **177**, 1
- F. Boccuzzi and A. Chiorino, *J. Phys. Chem. B*, 2000, **104**, 5414
- T. Tabakova, V. Idakiev, D. Andreeva and I. Mitov, *Appl. Catal.*, 2000, **202**, 91
- Y. -S. Su, M. -Y. Lee and A.D. Lin, *Catal. Lett.*, 1999, **57**, 49
- M. Haruta, *Catal. Today*, 1997, **36**, 153
- W. Valden, X. Lai and D.W. Goodman, *Science*, 1998, **281**, 1647.
- L. Guzzi, D. Horváth, Z. Pászti, L. Tóth, Z.E. Horváth, A. Karacs and G. Pető, *J. Phys. Chem. B*, 2000, **104**, 3183
- J.-D. Grunwaldt, M. Maciejewski, O.S. Becker, P. Fabrizioli and A. Baiker, *J. Catal.*, 1999, **186**, 458
- G.C. Bond and D.T. Thompson, *Gold Bull.* 2000, **33**, 41
- A.I. Kozlov, A.P. Kozlova, H. Liu and Y. Iwasawa, *Appl. Catal. A. Gen.*, 1999, **182**, 9
- N.D. Gangal, N.M. Gupta and R.M. Iyer, *J. Catal.*, 1990, **126**, 13
- N.D. Gangal, N.M. Gupta and R.M. Iyer, *J. Catal.*, 1993, **140**, 443
- A.K. Tripathi and N.M. Gupta, *J. Catal.*, 1995, **153**, 208
- V.P. Londhe and N.M. Gupta, *J. Catal.*, 1997, **169**, 415
- A.K. Tripathi, V.S. Kamble and N.M. Gupta, *J. Catal.*, 1999, **187**, 332
- N.M. Gupta and A.K. Tripathi, *J. Catal.*, 1999, **187**, 343
- A.K. Tripathi, Ph.D. Thesis, Mumbai University, 1999
- V.P. Londhe, V.S. Kamble and N.M. Gupta, *J. Mol. Catal. A : Chemical*, 1997, **121**, 33
- N.M. Gupta, V.S. Kamble, V.B. Kartha, R.M. Iyer, K.R. Thampi and M. Gratzel, *J. Catal.*, 1994, **146**, 173
- F. Solymosi and J. Rasko, *J. Catal.*, 1989, **115**, 107
- N.M. Gupta and A.K. Tripathi, unpublished work
- W.S. Epling, G.B. Hoflund, J.F. Weaver, S. Tsubota and M. Haruta, *J. Phys. Chem.*, 1996, **100**, 9929
- D. Horváth, L. Tóth and L. Guzzi, *Catal. Lett.*, 2000, **67**, 117
- M. Che and C.O. Bennett, in *Advances in Catalysis*, ed., D.D. Eley, H. Pines and P.B. Weisz, Vol.36, p.76, Acad. Press, San Diego, CA, 1989
- G.A. Somorjai in 'Introduction to Surface Chemistry and Catalysis', John Wiley, New York, 1994, p. 442