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Transient studies of the mechanisms of CO oxidation over Au/TiO_2 using time-resolved FTIR spectroscopy and product analysis

Bong-Kyu Chang, Ben W. Jang [1], Sheng Dai, Steven H. Overbury [*]

Surface Chemistry and Heterogeneous Catalysis, Chemical Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Bethel Valley Road, Bldg. 4500N, MS-6201, Oak Ridge, TN 37831-6201, USA

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Abstract

Transient studies on the oxidation of CO over Au/TiO_2 have been performed at 243–363 K using a time-resolved fast-scanning Fourier transform infrared (FTIR) spectrometer coupled with a quadrupole mass spectrometer. Different CO–O_2 interactions were performed by stepping CO into a steady-state He flow, O_2 into a steady-state CO flow, CO into a steady-state O_2 flow, and CO/O_2 into an He flow. The CO oxidation reaction occurs at all temperature ranges investigated whether CO is preadsorbed or O_2 is preadsorbed, indicating that there is no competition between CO and O_2 for adsorption at a temperature range of 243–363 K (noncompetitive adsorption). It suggests that CO and O_2 adsorption occurs on two different types of sites. When there is no O_2 present in step feed (i.e., step CO into He), CO immediately builds up on the surface (rapid adsorption of CO) and desorbs slowly after cutting off CO flow. However, when O_2 is present in the step feed (i.e., step CO/O_2 into He), adsorbed CO reacts with adsorbed oxygen immediately (fast surface reaction), whereas CO_2 product desorption monitored by mass spectroscopy appears to be very slow. Slow desorption of CO_2 product is claimed to be the rate-limiting step of CO oxidation over Au/TiO_2 at a temperature range of 243–273 K.

Keywords: CO catalytic oxidation; Au/TiO_2 catalyst; FTIR; Mass spectrometry; Adsorption; Desorption; Rate-limiting step; Operando spectroscopy

1. Introduction

Since the discovery of the remarkably high activity of supported gold catalysts for CO oxidation at low temperatures [1], supported gold catalysts have been a subject of great interest [2–4]. The ability of such catalysts to oxidize CO at room temperature could be utilized in a number of practical applications, including CO detection devices, CO reduction in industrial and automotive emissions, air purification in homes and offices, and CO and O_2 recombination in orbiting, closed-cycle CO_2 lasers used for weather monitoring or other remote sensing applications [5–9]. The remarkable catalytic behavior shown by gold depends on forming it into very small particles, apparently because large particles cannot chemisorb typical reactant molecules to any useful extent [2]. The rate of CO oxidation for gold catalysts is more than one order of magnitude higher than those for similarly prepared Pt catalysts [10].

But the origin of the high catalytic activity in supported gold nanoparticles is still not well understood, with many questions remaining about the site of the reaction and the nature of the gold nanoparticle–support interaction. It has been reported that Au particles of approximately 2–3 nm diameter exhibit optimal activity [11,12]; however, it has been also reported that equal-size Au particles supported on silica are far less catalytically active than those supported on titania, suggesting that activity of Au particles is not determined by particle size alone, and that support interactions must be considered [13]. The Au–TiO_2 system is particularly interesting, because the catalysts may exhibit CO oxidation activity at temperatures as low as 90 K [14], but the preparation and pretreatment of these catalysts can profoundly affect their catalytic behavior and their deactivation rates [15–18]. The oxidation state of the active Au also has been much discussed [19–23]. X-Ray absorption studies of active Au catalysts on titania supports, some of the type used in this study, suggest that the active phase is primarily reduced Au [23], al-

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[*] Corresponding author. Fax: +1 865 576 5235.
E-mail address: overburysh@ornl.gov (S.H. Overbury).

[1] Present address: Department of Chemistry, Texas A&M University at Commerce, Commerce, TX 75429, USA.

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though recent SIMS measurements suggest that some amount of cationic Au also may be present [19].

There also appears to be uncertainty about how CO oxidation occurs on supported Au catalysts, in terms of the kinetics, the rate-determining step, competition between reactants, and products for adsorption sites. In addition, multiple pathways may occur, and the mechanism may differ from one support to another or in different temperature regimes [2,3,24]. Kinetic studies of the oxidation of CO on TiO_2-supported Au catalysts have been reported; for instance, Haruta reported zero-order kinetics for CO oxidation over Au/TiO_2 catalysts at concentration of CO and O_2 above 0.1 vol% and low apparent activation energies [3,25]. Zero-order kinetics suggest that both CO and O_2 are adsorbed to saturation and that reaction of adsorbed CO and oxygen ($O_{(a)}$ or $O_{2(a)}$) is the rate-determining step [3]. Other kinetic studies have shown partial pressure dependency of CO varying from 0.05 to 0.6, whereas the O_2 reaction order has been reported to be from 0.03 to 0.4 for reactions carried out in the 273–313 K range [9,11,16]. Vannice et al. have used kinetic modeling and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to elucidate the reaction mechanism [9,16]. A two-site model, with CO adsorbing on Au and O_2 adsorbing on TiO_2, that is consistent with Langmuir–Hinselwood kinetics for noncompetitive adsorption was found to fit the partial pressure data well and showed consistent enthalpies and entropies of adsorption [9,16]. On the other hand, it has also been reported that CO and molecular oxygen are competitively adsorbed on the gold particles at 91 K [14]. Bollinger and Vannice postulated that the reaction between adsorbed CO and O_2 is the rate-determining step. Although apparently not considered in their mechanism, they found that reversible adsorption of CO_2 may compete with CO for adsorption sites.

In an attempt to clarify such mechanistic details, CO oxidation catalyzed by Au/TiO_2 was examined at a temperature range of 243–363 K using a rapid-scanning time-resolved Fourier transform infrared (FTIR) spectroscopy coupled with dynamic analysis of gas products. By examining the time dependence of the surface species and the reaction products simultaneously under transient flow conditions, we obtained a modified view of the reaction process. In agreement with previous studies, we found noncompetitive adsorption of CO and O_2 and, surprisingly, a limiting role of CO_2 desorption in the low-temperature reaction.

2. Experimental

2.1. Catalysts

The calcined Au/TiO_2 catalyst was provided by the World Gold Council (lot no. 02-5), as was the following detailed information on the catalyst. The catalyst was prepared by deposition–precipitation onto a P25-TiO_2 support, followed by calcination at 300 °C. Elemental analysis by inductively coupled plasma spectroscopy indicated 1.5 wt% Au, and the average diameter of Au particles was 3.7 nm as measured by transmission electron microscopy. This catalyst was used as provided without further treatment. Experiments were also performed on P25-TiO_2 obtained from Alfa-Aesar along with the Au catalysts.

2.2. Time-resolved in situ infrared spectroscopy and product analysis

Infrared (IR) spectroscopy was conducted in a home-made brass IR cell fitted with CaF_2 windows in a Nicolet Nexus 670 FTIR spectrometer using an MCT/A detector with a KBr beamsplitter. All results described here were obtained using 5-s intervals and summing 16 scans in each spectrum with a spectral resolution of 16 cm^{-1}. Before initiation of a gas-switching protocol, a background FTIR spectrum was run (256 scans summed) at otherwise identical conditions. The background spectrum was subtracted automatically from subsequent spectra, so the difference spectra reported below are with respect to the starting ($t = 0$) conditions. The temperature of the IR cell was controlled by circulating an ethylene glycol (EG)–water mixture (1:1 by volume) controlled by a ThermoNESLAB RTE refrigerated bath/circulator. A controlling thermocouple was embedded in the body of the cell at a position near the sample to detect the temperature. In this way, the temperature of the catalyst could be controlled in the 243–363 K range.

Approximately 55 mg of catalyst was pressed to make a self-supporting pellet for IR measurements. Two opposing CaF_2 rods were inserted through sliding O-ring seals and pushed directly against the sample pellet. By design, the dead volume of the IR cell reactor was negligible (theoretically $<0.1\ cm^3$). Thus the gas in the cell could be changed abruptly using a gas flow of 25 mL/min. In addition, the path length of the IR beam was determined only by the pellet thickness, essentially eliminating gas-phase contribution. Premixed gases used in this study were 2% CO/2% Ar/He, 2% O_2/He, and 1% CO 1% O_2/He, in addition to pure He (Air Liquide). The effluent of the IR cell was analyzed by quadrupole mass spectrometry (QMS) using an OmniStar Pfeiffer vacuum instrument with a gas sampling system based on a heated 1-m stainless steel capillary with a tip positioned in the effluent stream.

2.3. Transient reaction studies

The step transient technique was used to examine the dynamic behavior of adsorbates. Gas-switching protocols were performed by switching from a background gas to a reactant gas (switch on) and holding for 60 s and then back again (switch off). For example, switching to CO (2% CO/He, 25 mL/min) from a steady-state He flow (25 mL/min) and back again is referred to as “switching CO into He.” Similarly O_2 (2% O_2/He, 25 mL/min) was switched into CO (2% CO/He, 25 mL/min), CO (2% CO/He, 25 mL/min) was switched into O_2 (2% O_2/He, 25 mL/min), a mixture CO/O_2 (1% CO/1% O_2/He, 25 mL/min) was switched into He flow (25 mL/min), and CO_2 (1% CO_2/He, 25 mL/min) was switched into He (25 mL/min). On activation of the switching valve, there was a delay of approximately 15 s while the altered flow reached the catalysts (IR cell) and another 15 s while it reached the QMS system. Blank experiments demonstrated that switching through the empty

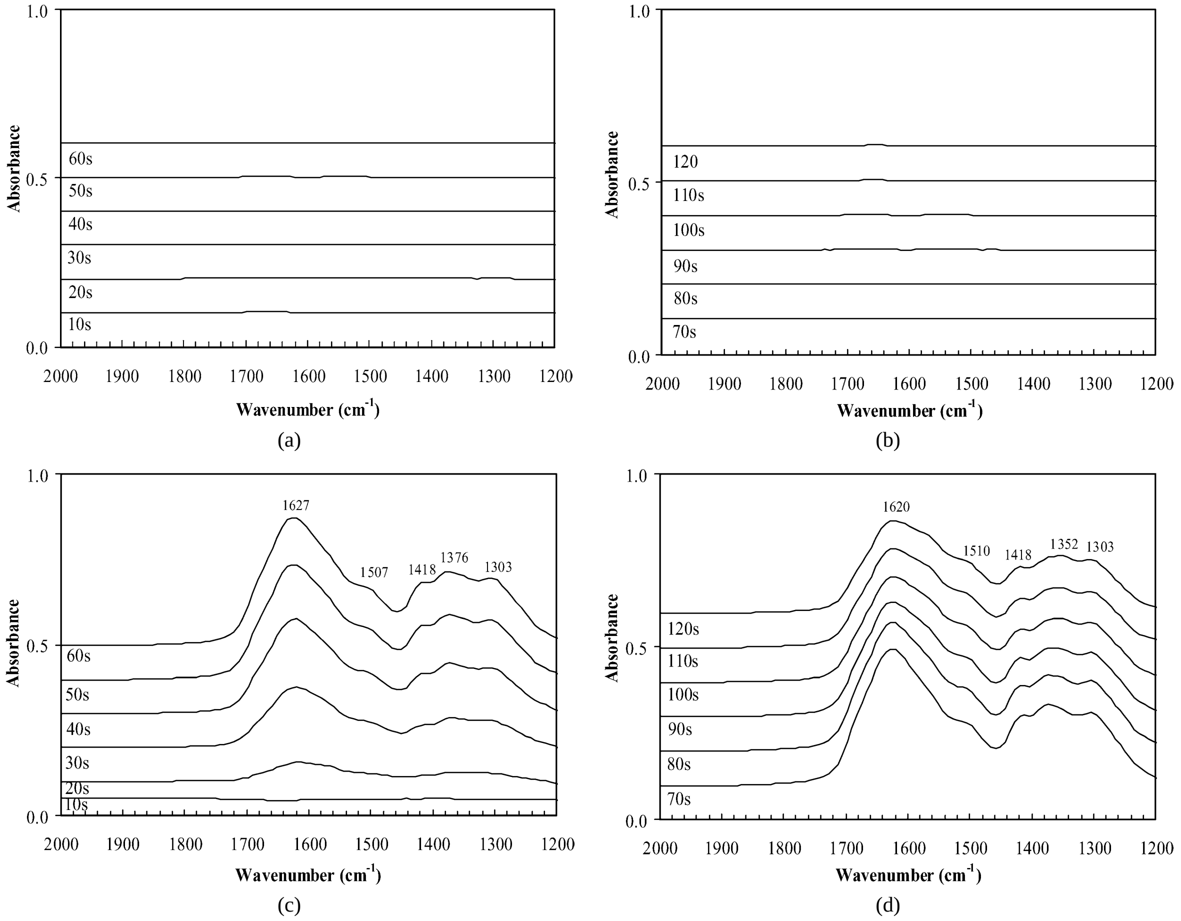


Fig. 1. IR spectra obtained from a TiO_2 support (no Au) at $T = 283$ K are shown as a function of time, t, upon (a) switching-on CO/O_2 into a steady-state He flow at $t = 0$ and (b) switching off CO/O_2 and returning to He flow at $t = 60$ s. Results of identical experiments performed on Au/TiO_2 catalyst are shown in (c) and (d). A 15 s delay is required for the flow to reach the IR cell. Note: IR spectra offset vertically for viewing purposes.

reactor (i.e., no catalyst) resulted in abrupt changes in downstream gas compositions.

3. Results and discussion

3.1. Transient studies of the formation of carbonate species

Switching mixed CO/O_2 into He was conducted at temperatures of 243–363 K to investigate CO adsorption and subsequent formation of carbonate species on TiO_2 (P25) support in the absence of Au. FTIR spectra obtained throughout this switch at 283 K are shown in Figs. 1a and 1b. Only weak IR features grew during the switch at 1600–1700 cm^{-1}, indicating that very little CO adsorption or formation of carbonate species was detected by IR on the TiO_2 support. Although not shown in Figs. 1a and 1b, no features were observed in the range of 2000 to 2400 cm^{-1} that could be indicative of adsorbed CO or CO_2, demonstrating that no reaction occurs on the bare TiO_2 (i.e., no gold). The results demonstrate that CO does not readily interact directly with the TiO_2 support. Carbonate species were not detected at other temperatures investigated between 273 and 363 K (data not shown) or on switching CO (i.e., without O_2) into He.

Corresponding IR spectra from the Au/TiO_2 catalysts obtained on switching CO/O_2 into He are shown in Figs. 1c and 1d. Strong IR absorption bands were observed on Au/TiO_2, compared with undetectable IR bands on the TiO_2 support in the absence of Au. These results suggest that Au is necessary for facile adsorption of CO and subsequent formation of carbonate species on either Au or TiO_2 support. Similar bands were obtained by switching CO alone into He, suggesting that the presence of O_2 is not necessary for carbonate formation.

It has been reported that the bands observed in the 1700–1000 cm^{-1} range can be assigned to carbonate-like species adsorbed on the TiO_2 support [26]. Peaks near 1620 cm^{-1} have been previously assigned to bidentate carbonate species on anatase [9,27] and to carbonate-like species in Au/TiO_2 samples [28]. The peak near 1500 cm^{-1} could be due to a carboxylate species or a bidentate carbonate species bound to a single Ti atom [29]. Monodentate carbonate species may also be present, because they have peak positions typically around 1530–1470 and 1370–1300 cm^{-1} [29]. The major contributions are tentatively assigned to bidentate carbonate and carboxylate ions, with monodentate carbonate and free carbonate species possibly present as well [9]. Published isotopic substitution studies of $^{12}CO–^{16}O_2$ and $^{12}CO–^{18}O_2$ interactions have

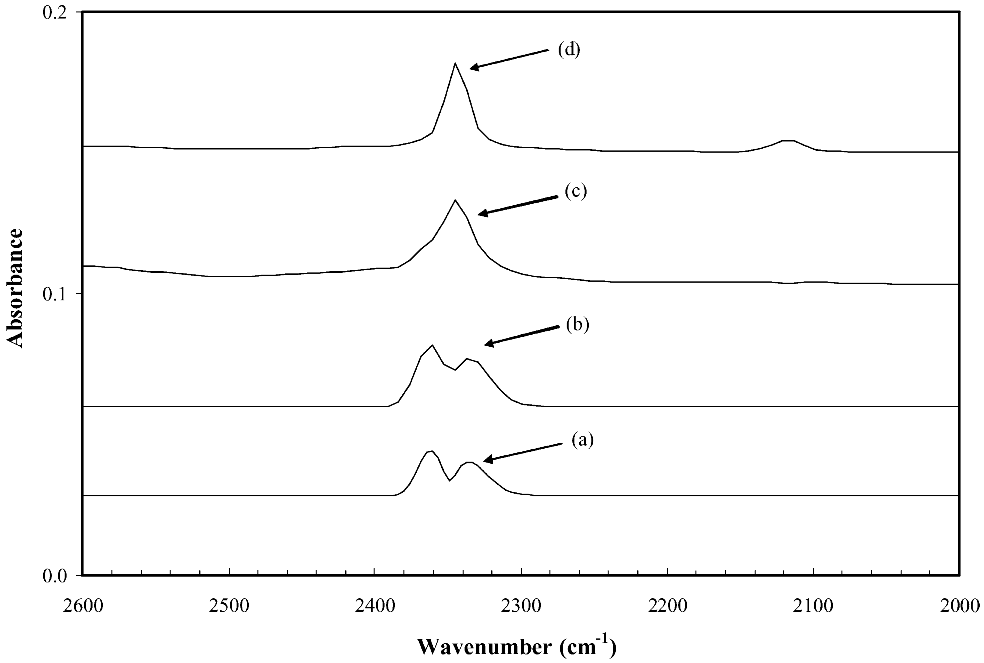


Fig. 2. IR spectra obtained at 273 K by switching CO_2 into He through an empty IR cell (curve a), through the TiO_2 support (curve b), through Au/TiO_2 catalyst (curve c), and also by switching CO/O_2 through Au/TiO_2 sample (curve d). Spectra are obtained at time part-way between switch on and switch off. Note: IR spectra offset vertically for viewing purposes.

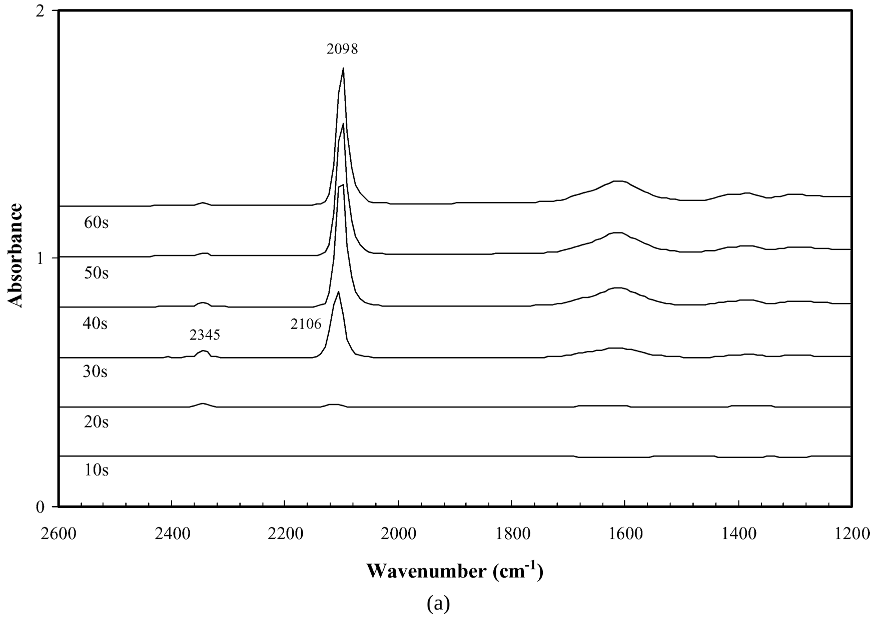
suggested that gas-phase oxygen does not participate in the formation of carbonate-like species, and thus the oxygen involved in the formation of carbonate-like species is from the oxide support, not from gas-phase oxygen ($^{16}O_2$ or $^{18}O_2$) [26]. Comparing IR spectra obtained from TiO_2 support without Au and those from Au/TiO_2 samples leads us to propose that Au enhances CO adsorption and subsequent formation of carbonate species on either the Au–TiO_2 interface or TiO_2. CO adsorbs on Au and may be transferred to TiO_2, where it forms carbonate on TiO_2 support. A model has been proposed in which a bidentate carbonate species is a reaction intermediate reacting with CO adsorbed on Au near the TiO_2 interface to form CO_2 [9, 11,30]. IR intensities of all species (bidentate, carboxylate, and monocarbonate) observed in the present study grew together immediately after “switch on” and evolved little except for a slow uniform decrease in all peaks after switch off. This suggests that these species are spectators and are not involved in the surface reaction.

3.2. Gas-phase CO_2 versus surface-adsorbed CO_2

Fig. 2 compares the IR spectra obtained at 273 K by switching CO_2 into He through (a) an empty IR cell, (b) the TiO_2 support, and (c) Au/TiO_2 catalyst and (d) by switching CO/O_2 through the Au/TiO_2 sample. Switching through either the empty cell (curve a) or the TiO_2 alone (curve b) leads only to the broad P and R bands typical of gas-phase CO_2. These bands appear abruptly during switch on and disappear abruptly after switch off, consistent with gas-phase species. In contrast, a singlet IR peak (2345 cm^{-1}) was observed on identical stepping of CO_2 over a Au/TiO_2 sample (curve c) assigned to an adsorbate form, $CO_{2(a)}$. Broadening the wings of the peak may indicate a trace of gas-phase CO_2. Gas-phase CO_2 was absent or only barely visible because of the very short gas-phase path length for the IR beam coupled with the adsorption of CO_2 onto the Au/TiO_2 sample. A similar singlet peak was obtained by switching CO/O_2 over Au/TiO_2 (curve d), indicating formation of the adsorbate $CO_{2(a)}$ by reaction. Unreacted, linearly adsorbed CO was also observed in this spectrum (at 2100 cm^{-1}). The failure to form adsorbate $CO_{2(a)}$ on the TiO_2 sample (curve b) indicates that CO_2 does not interact directly with the TiO_2 support without Au.

3.3. Noncompetitive adsorption of CO and O_2

Fig. 3 shows typical time evolution of the IR spectrum during switching of CO into O_2 at 243 K. The difference spectra (referenced to $t = 0$) exhibit a rapid increase in the linear $CO_{(a)}$ feature after switch on and a subsequent decrease in intensity after switch off. As mentioned in the discussion of the spectra in Fig. 2, the gas-phase species (CO) is not seen, primarily because of the short gas-phase path length. Collecting peak intensities from such spectra, Fig. 4 shows the intensity of linearly adsorbed CO on Au/TiO_2 during four different switching protocols extracted from such spectra at 243 K. On switching of CO into He (curve a), the IR peak intensity at 2100 cm^{-1} builds up immediately, indicating rapid adsorption of CO to form linear $CO_{(a)}$. Actually, the curve suggests a two-stage adsorption, with an initial fast adsorption followed by a slower approach to saturation. Desorption of $CO_{(a)}$ is slow, as indicated by gradual decrease after switch off (after 75 s). However, on switching off of CO into O_2 (curve b, starting at 75 s), the amount of $CO_{(a)}$ decreased more rapidly, indicating that incoming O_2 adsorbs and reacts with preadsorbed $CO_{(a)}$. The decrease was rapid com-



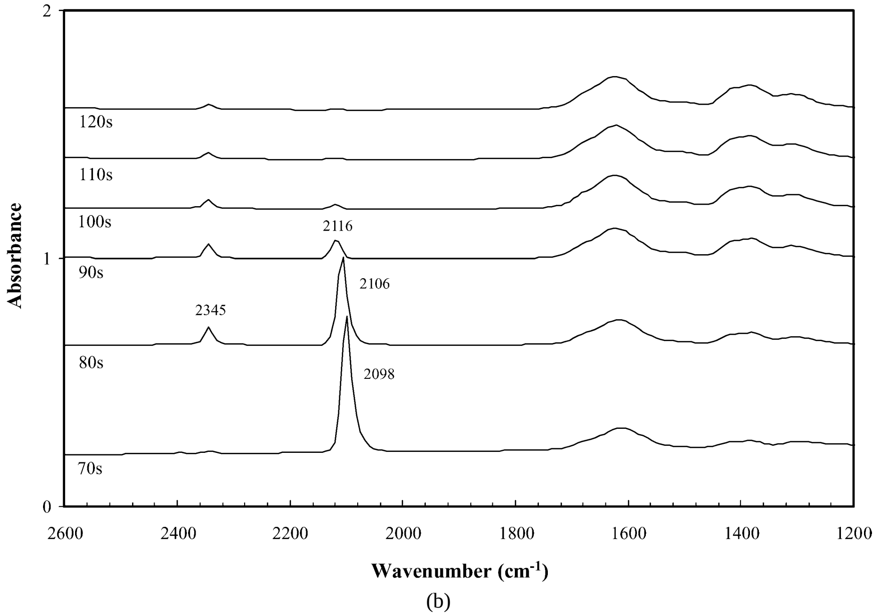


Fig. 3. IR spectra obtained from Au/TiO_2 at $T = 243$ K are shown as a function of time, t, upon (a) switching CO into O_2 at $t = 0$ and (b) switching off CO at $t = 60$ s and flowing O_2 only. Note: IR spectra offset vertically for viewing purposes.

pared with the desorption of CO after switching off of CO into He (curve a). These two results suggest that adsorbed $CO_{(a)}$ does not hinder O_2 adsorption and subsequent rapid reaction at this temperature. Further evidence that CO does not hinder O_2 adsorption is also apparent in the switching on of O_2 into CO. A rapid decrease in $CO_{(a)os}$ is observed (curve c, after 15 s) relative to the sample saturated in CO before the switch. In this case, surface $CO_{(a)}$ also decreased rapidly due to reaction with oxygen.

The above experiments indicate that preadsorbed CO does not inhibit rapid adsorption and reaction with O_2. Similarly, the results in Figs. 3 and 4 also indicate that preadsorbed oxygen (whether atomic or molecular) does not inhibit rapid CO adsorption. This is evident in both the switching on of CO into O_2 (curve b, after 15 s) and the switching off of O_2 into CO (curve c, after 75 s). Neither the preadsorbed nor the transient O_2 exposure inhibited subsequent rapid CO adsorption. Although adsorbed oxygen is not detected by FTIR, its presence is inferred by the observed, transient CO_2 reaction product detected by the QMS (data not shown) after switching from O_2 to CO (or from CO to O_2).

Fig. 3 shows another feature besides $CO_{(a)}$, due to adsorbed $CO_{2(a)}$. It exhibits a rapid increase after switching on of CO into O_2 due to the rapid surface reaction of $CO_{(a)}$ with preadsorbed oxygen, but then slowly decreases due to CO_2 desorption and depletion of surface oxygen, which prevents further $CO_{2(a)}$ production. After switching off of CO and flowing O_2, the $CO_{2(a)}$ band rapidly increases through surface reactions of oxygen with preadsorbed $CO_{(a)}$, but then slowly decreases due to CO_2 desorption and depletion of surface $CO_{(a)}$. Therefore, the behavior of the $CO_{2(a)}$ feature is also consistent with rapid formation of CO_2 and noncompetitive adsorption of CO and O_2.

Similar experiments were performed at 273, 303, 333, and 363 K (supplemental data Figs. S-1 to S-4). The overall IR intensity decreases with increasing temperature mainly due to enhanced desorption. However, the same general tendency was observed, that is, neither pre-adsorbed $CO_{(a)}$ nor $O_{(a)}$ blocks reaction by impeding subsequent O_2 or CO adsorption, respectively. Therefore, it can be concluded that there is no competition between CO and O_2 for adsorption suggesting that CO and O_2 adsorb on different surface sites leading to rapid surface reaction.

In previous work, an FTIR study of CO adsorption and oxidation on Au/TiO_2 catalysts showed that at 90 K, CO and O_2 are molecularly and competitively adsorbed on Au step sites [31]. Boccuzzi et al. used IR spectroscopy and isotopic scrambling to study the nature of Au/ZnO and Au/TiO_2 catalysts for CO oxidation and concluded that Au metal particles adsorb both CO and O_2 simultaneously, leading to rapid reaction [28]. Metallic Au has been proposed to be the active site, with some proponents advocating the view that the greatest activity occurred when two layers of Au atoms were deposited on a TiO_2 surface [32–34]. It was also proposed that special Au–TiO_2 interfacial sites are the most likely explanation for the high activity in Au–TiO_2 systems [9]. A Langmuir–Hinshelwood model invoking CO adsorbed on Au that reacts with oxygen activated at the Au–TiO_x interface was proposed, and it was assumed that CO and O_2 adsorption occurs on two different types of sites [9].

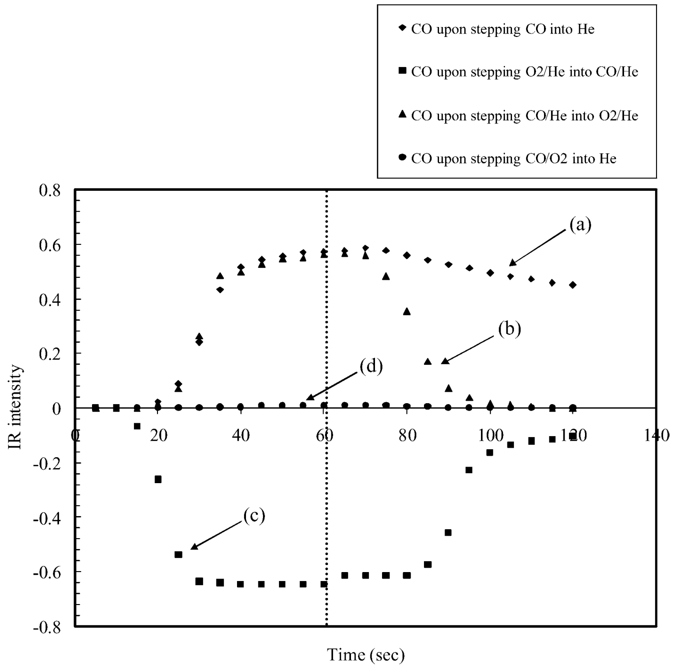


Fig. 4. Intensity of $CO_{(a)}$ IR species (2100 cm^{-1}) on Au/TiO_2 at 243 K for different switching protocols. Reactant gas is switched on at $t = 0$ and off again at $t = 60$ s. It takes 15 s for the flow to reach the IR cell after switch.

3.4. CO_2 desorption as rate-limiting step

The effect of CO_2 was examined in an attempt to better understand the kinetics of CO oxidation on Au/TiO_2. On switching of CO/O_2 into He at 243 K (Fig. 4, curve d; FTIR spectra in supplemental Fig. S-5), surface-adsorbed $CO_{(a)}$ does not build up appreciably. This is in marked contrast to switching on CO alone into He, in which case $CO_{(a)}$ builds up rapidly to more than 50 times higher intensity (cf. curves a and d in Fig. 4). However, rapid buildup of $CO_{2(a)}$ product was clearly observed at 2345 cm^{-1}. Together these observations demonstrate fast surface CO oxidation with high conversion on adsorption. After switch off, $CO_{2(a)}$ desorption is very slow, and $CO_{2(a)}$ remains

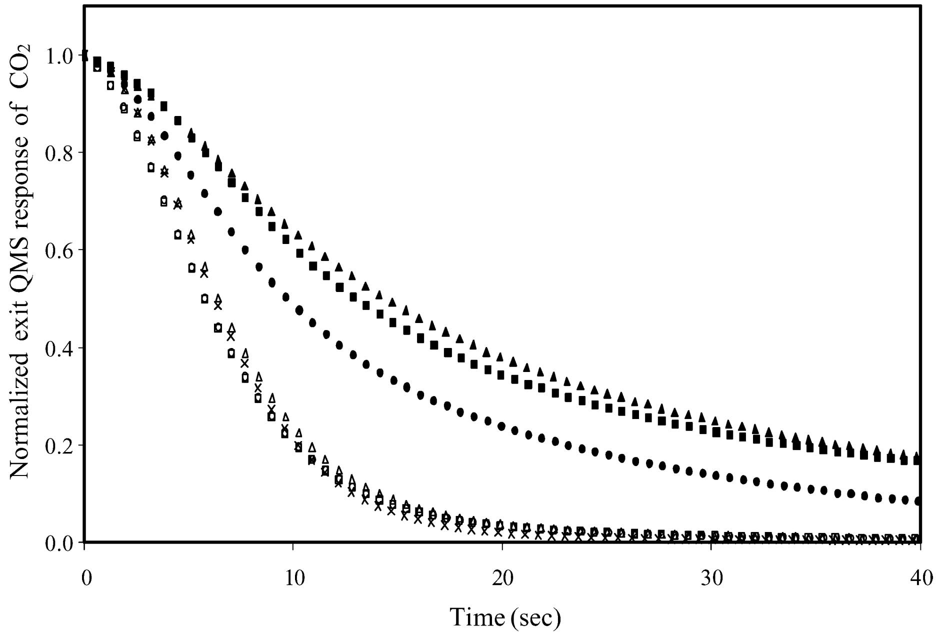
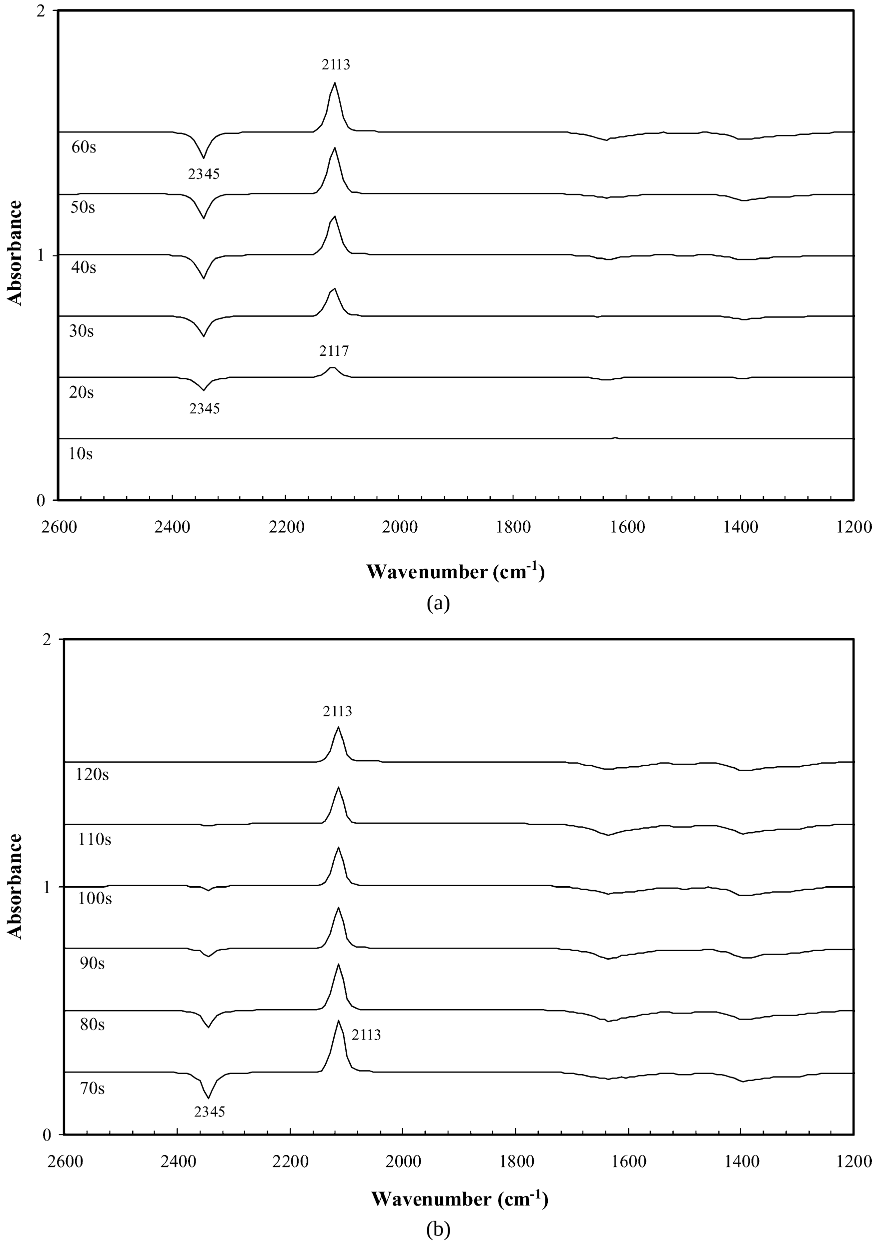


Fig. 5. Normalized exit QMS response after switching off gas-phase CO_2 flowing through TiO_2 support (open symbols) and after switching off CO/O_2 flowing through Au/TiO_2 (filled symbols) are shown at three different temperatures (△ and ▲ at 263 K, □ and ■ at 273 K, and ○ and ● at 283 K).



(a)

(b)

Fig. 6. IR spectra obtained at 243 K by (a) switching CO/O_2 into CO_2 at $t = 0$ and (b) switching off CO/O_2 at $t = 60$ s and flowing CO_2 only over Au/TiO_2. Note: IR spectra offset vertically for viewing purposes.

on the surface even 60 s after switching off of CO/O_2 (supplemental Fig. S-5). Slow CO_2 desorption was also seen after switching off of CO into O_2 (Fig. 3b). These observations suggest that slow desorption of $CO_{2(a)}$ is the rate-limiting step.

More experimental results supporting this conclusion are given in Fig. 5, which shows the downstream CO_2 pressure response in the effluent stream as measured by QMS. The normalized gas-phase CO_2 effluent pressure is compared for switching off gas-phase CO_2 across nonreactive TiO_2 versus switching off CO/O_2 across reactive Au/TiO_2. In the latter case, most of the signal must originate from production of CO_2 over the Au catalysts, because measurements of the $CO + O_2$ stream bypassing the reactor show CO_2 levels (from impurity or production at QMS filaments) of less than about 5% of catalytically produced CO_2. The comparison indicates a much slower evolution of CO_2 from the Au/TiO_2 catalyst compared with gas-phase CO_2 diffusion through the support alone. The sluggish evolution of CO_2 produced over the Au catalyst must be due to either slow surface reaction or slow desorption. Because the foregoing IR data indicate that $CO_{2(a)}$ formation is rapid, the evolution thus must be limited by desorption of product $CO_{2(a)}$.

Further evidence supporting our conclusion that CO_2 desorption is the rate-limiting step can be found in Fig. 6, which demonstrates that the presence of $CO_{2(a)}$ inhibits the CO oxidation rate. Fig. 6 shows IR spectra obtained on switching of CO/O_2 into CO_2 over Au/TiO_2 at 243 K. During switch on, preadsorbed $CO_{2(a)}$ decreases while adsorbed $CO_{(a)}$ increases. Apparently CO is capable of displacing $CO_{2(a)}$ or else it adsorbs at sites vacated by slowly desorbing $CO_{2(a)}$. It was shown earlier that without preadsorbed $CO_{2(a)}$ (i.e., switching of CO/O_2

into He, shown in Fig. 4, curve d), very little surface $CO_{(a)}$ was detected by IR due to immediate oxidation of $CO_{(a)}$ after noncompetitive rapid adsorption. Therefore, both the buildup of $CO_{(a)}$ and the decrease of $CO_{2(a)}$ observed in Fig. 6 suggest an inhibition of CO oxidation compared with the case of no CO_2 preadsorption on the surface. Such an inhibition would be consistent with the reaction kinetics of negative order in CO_2. As temperature increases above 273 K, however, differentiating the rate-limiting step by only IR and QMS becomes difficult.

Surprisingly, the literature does not contain many articles discussing the effect of CO_2 on the CO oxidation reaction on supported Au nanoparticles. An adsorption band near 2350 cm^{-1} has been reported for CO_2 on TiO_2 [9,27,35]. Our results suggest, however, that the adsorption band at 2345 cm^{-1} (Fig. 2) would be more appropriate to assign to CO_2 on Au or at the interface of Au and the TiO_2 support. The evidence is that the IR feature of surface $CO_{2(a)}$ was observed only in the presence of Au and competes with $CO_{(a)}$, which is generally accepted to be on the Au. Bollinger and Vannice [9] found a decreased amount of chemisorbed CO during reaction compared with the amount present when only CO is flowing, a finding in agreement with the present observations. They concluded that the most likely explanation for this is competitive adsorption between CO and CO_2, which decreases the surface coverage of CO. That interpretation differs slightly from our conclusion that decreased $CO_{(a)}$ is observed during reaction because of its rapid consumption. It has also been reported that addition of CO_2 to the feed in kinetic experiments causes a reversible inhibition of CO oxidation rate [36], in agreement with our conclusions.

4. Conclusion

Transient studies on the oxidation of CO over Au/TiO_2 have demonstrated the following:

- Au catalyzes the formation of several carbon oxide species (i.e., bidentate and monodentate carbonate, carboxylate) on the surface of Au/TiO_2 catalysts, but these appear to be only spectators of the fast CO oxidation reaction.
- CO oxidation reaction occurs under the switching conditions at all temperatures investigated if either CO or O_2 is preadsorbed.
- CO and O_2 are noncompetitively adsorbed during reaction conditions at all temperatures studied, suggesting different adsorption sites for the two reactants.
- Under reaction conditions, CO adsorption is rapid and CO desorption is slow, but rapid oxidation prevents buildup of $CO_{(a)}$ under reaction conditions.
- Adsorbed CO_2 species, $CO_{2(a)}$, is rapidly formed and is the reaction intermediate leading to CO_2 evolution, but its desorption from the catalyst bed appears to be rate-limiting step at 243 K and 273 K, suggesting negative-order reaction kinetics for the product CO_2.

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Supplemental data

The online version of this article contains additional supplemental data.

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References

[1] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, Chem. Lett. (1987) 405.
[2] G.C. Bond, D.T. Thompson, Catal. Rev.-Sci. Eng. 41 (1999) 319.
[3] M. Haruta, CatTech 6 (2002) 102.
[4] M. Haruta, M. Date, Appl. Catal. A: Gen. 222 (2001) 427.
[5] T. Kobayashi, M. Haruta, S. Tsubota, H. Sano, B. Delmon, Sens. Actuators B 1 (1988) 399.
[6] T. Kobayashi, M. Haruta, S. Tsubota, H. Sano, B. Delmon, Sens. Actuators B 1 (1990) 222.
[7] S.D. Gardner, G.B. Hoflund, D.R. Schryer, J. Schryer, B.T. Upchurch, E.J. Kielin, Langmuir 7 (1991) 2135.
[8] S.D. Gardner, G.B. Hoflund, B.T. Upchurch, D.R. Schryer, E.J. Kielin, J. Schryer, J. Catal. 129 (1991) 114.
[9] M.A. Bollinger, M.A. Vannice, Appl. Catal. B 8 (1996) 417.
[10] G.R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, Catal. Lett. 44 (1997) 83.
[11] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175.
[12] M. Valden, S. Pak, X. Lai, D.W. Goodman, Catal. Lett. 56 (1998) 7.
[13] S.H. Overbury, L. Ortiz-Soto, H. Zhu, B. Lee, M.D. Amiridis, S. Dai, Catal. Lett. 95 (2004) 99.
[14] F. Boccuzzi, A. Chiorino, J. Phys. Chem. B 104 (2000) 5414.
[15] D. Cunningham, S. Tsubota, N. Kamijo, M. Haruta, Res. Chem. Intermed. 19 (1993) 1.
[16] S. Lin, M. Bollinger, M.A. Vannice, Catal. Lett. 17 (1993) 245.
[17] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda, Y. Nakahara, Stud. Surf. Sci. Catal. 63 (1991) 695.
[18] W. Yan, B. Chen, S.M. Mahurin, V. Schwartz, D.R. Mullins, A.R. Lupini, S.J. Pennycook, S. Dai, S.H. Overbury, J. Phys. Chem. B 109 (2005) 10676.
[19] L. Fu, N.Q. Wu, J.H. Yang, F. Qu, D.L. Johnson, M.C. Kung, H.H. Kung, V.P. Dravid, J. Phys. Chem. B 109 (2005) 3704.
[20] C.K. Costello, M.C. Kung, H.-S. Oh, Y. Wang, H.H. Kung, Appl. Catal. A Gen. 232 (2002) 159–168.
[21] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, Science 301 (2003) 935–938.
[22] J. Guzman, B.C. Gates, J. Am. Chem. Soc. 126 (2004) 2672–2673.
[23] V. Schwartz, D.R. Mullins, W.F. Yan, B. Chen, S. Dai, S.H. Overbury, J. Phys. Chem. B 108 (2004) 15782–15790.
[24] R. Meyer, C. Lemire, K. Shaikhutdinov, H.J. Freund, Gold Bull. 37 (2004) 72.
[25] M. Haruta, J. New Mat. Electrochem. Syst. 7 (2004) 163.
[26] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, J. Phys. Chem. 100 (1996) 3625.
[27] K. Tanaka, J.M. White, J. Phys. Chem. 86 (1982) 4708.

[28] F. Boccuzzi, S. Tsubota, M. Haruta, J. Electron. Spectrosc. Relat. Phenom. 64–65 (1993) 241.
[29] A.A. Davydov, C.H. Rochester (Eds.), Infrared Spectroscopy on the Surface of Transition Metal Oxides, Wiley, Chichester, 1984.
[30] M. Haruta, S. Tsubota, A. Kobayashi, A. Ueda, H. Sakurai, M. Ando, Stud. Surf. Sci. Catal. 75 (1993) 2657.
[31] F. Boccuzzi, A. Chiorino, M. Manzoli, Mater. Sci. Eng. C 15 (2001) 215.
[32] J.H. Yang, J.D. Henao, M.C. Raphulu, Y. Wang, T. Caputo, A.J. Groszek, M.C. Kung, M.S. Scurrell, J.T. Miller, H.H. Kung, J. Phys. Chem. B 109 (2005) 10319.
[33] M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647.
[34] M.S. Chen, D.W. Goodman, Science 306 (2004) 5694.
[35] P. Jackson, G.D. Parfitt, J. Chem. Soc., Faraday Trans. 68 (1972) 896.
[36] M.A. Bollinger, MSc. Thesis, Penn. State Univ., 1994.