Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Catalysis 241 (2006) 407–416

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Oxygen-exchange reactions during CO oxidation over titania- and alumina-supported Au nanoparticles

Jason T. Calla, Robert J. Davis *

Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22094-4741, USA

Received 14 March 2006; revised 16 May 2006; accepted 17 May 2006

Abstract

Gold nanoparticles supported on titania and alumina were used as catalysts for CO oxidation. The oxidation of $C^{16}O$ (2 mol%) with $^{18}O_2$ (2 mol%) in He at ambient temperature and 1.2 atm total pressure was performed in a single-pass, fixed-bed reactor. A mixture of CO_2 isotopomers was observed during oxidation over Au/TiO_2 and Au/Al_2O_3. However, no oxygen scrambling was observed in and between O_2 and CO. Moreover, no evidence for direct exchange between O_2 and CO_2 was found. Isotopic transient analysis of a switch between $C^{16}O_2$ and $C^{18}O_2$ showed that oxygen exchange occurred between the metal-oxide supports and CO_2. Therefore, the CO_2 isotopomer distribution observed during CO oxidation could not be attributed solely to the oxidation reaction on Au. Comparison of the isotopic transients from ^{13}C and ^{18}O studies suggests the primary product of $C^{16}O$ oxidation with $^{18}O_2$ is $C^{16}O^{18}O$. The presence of 0.16 mol% H_2O co-fed with the reactants significantly promoted the rate of CO oxidation by factors of 2.5 for Au/TiO_2 and 10 for Au/Al_2O_3. Despite the promotional effect of H_2O on the rate of oxidation, no significant differences in the level of oxygen exchange in the CO_2 were observed. In addition, the presence of H_2O did not result in scrambling of oxygen in O_2. Labeled oxygen found in the H_2O exiting the reactor appeared to originate from ^{18}O associated with the CO_2.

Keywords: Gold; Isotopic transient analysis; Titania; Alumina; Carbon monoxide, oxidation of; Carbon dioxide; Oxygen; Oxygen exchange; Water

1. Introduction

Although bulk gold is traditionally considered catalytically inactive, supported gold nanoparticles are effective catalysts for various reactions [1,2]. More specifically, gold particles supported on metal oxides are highly active for the oxidation of carbon monoxide at low temperature [3,4]. Despite the extensive research efforts recently focused on supported gold nanoparticles, the fundamentals of the oxidation catalysis remain a matter of speculation. Adsorption of CO directly on the Au particle is a generally accepted elementary step, but the mode of O_2 activation is still undetermined.

Researchers studying model Au/MgO systems suggest that oxygen-vacancy F-center defects anchor the Au particles and facilitate the adsorption and activation of O_2 on Au by partial charge transfer [5,6]. This is consistent with the correlation observed experimentally between the concentration of F centers on MgO and the catalytic activity of Au/MgO for CO oxidation [7].

The presence of water vapor in the reactant feed has a promotional effect on the rate of CO oxidation [8–11]. Two purposes of the H_2O are to assist in the decomposition of deactivating surface species, such as carbonates [8–11], and to promote the activation of O_2 [8]. Intermolecular interaction between O_2 and CO or H_2O has been proposed as a means to lower the barrier to cleave the dioxygen bond [8,12]. Liu et al. characterized O_2 adsorption on amorphous titania supported Au by electron spin resonance (ESR) spectroscopy and observed signals consistent with an O_2^- superoxide at oxygen vacancies on the support [13]. Using results obtained from ESR spectroscopy and oxygen exchange, they proposed an interaction between O_2^- and CO at the Au-metal oxide interface to form CO_2 and an active oxygen atom that quickly reacts with another CO molecule.

The mechanism of CO oxidation with O_2 over various Au surfaces has also been explored using density functional the-

---

* Corresponding author.
E-mail address: rjd4f@virginia.edu (R.J. Davis).

0021-9517/$ – see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2006.05.017

ory (DFT) calculations. One consistent result is that a facile oxidation path is associated with low-coordinated Au atoms [12,14–17]. Xu and Mavrikakis reported O_2 adsorption and dissociation to be more energetically favorable on strained and stepped Au surfaces relative to Au(111) [15]. Nevertheless, O_2 dissociation on Au was still an activated process. Similarly, Liu et al. investigated several possible routes for CO oxidation over different Au surfaces using DFT calculations and found the barrier for O_2 dissociative adsorption to be too high for the low temperatures at which CO oxidation is observed experimentally [16]. Thus, they also explored the direct reaction of adsorbed O_2 with adsorbed CO to yield CO_2 and a reactive oxygen atom, which readily oxidizes an adjacent CO molecule. This plausible reaction path avoids the energy costly dissociative adsorption of O_2.

Guzman et al. characterized the oxygen species on ceria-supported Au catalysts by Raman spectroscopy [18,19]. They identified several species associated with superoxide, peroxide, molecular, and lattice oxygen. However, for CO oxidation over Au supported on nanocrystalline CeO_2, only η^1 superoxide species and peroxide adspecies at the one-electron defect site were claimed to be active in the oxidation reaction.

Several research groups have monitored the exchange of oxygen over Au supported on metal oxides and hydroxides (Ti, Fe, and Zn) in an attempt to elucidate the reaction mechanism of CO oxidation. The formation of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ during the oxidation of $C^{16}O$ with $^{18}O_2$, and the absence of oxygen exchange between O_2 and CO are generally observed [10,13,20–23]. These studies lead to the suggestion that O_2 and CO do not dissociate and that the different CO_2 isotopomers observed during the reaction result solely from exchange with the oxygen of the metal oxide [10,13,20–23].

Previously, we reported the results from an investigation of CO oxidation over titania- and alumina-supported gold catalysts [24]. Steady-state isotopic transient kinetic analysis using ^{13}CO as the isotopically labeled reactant was used to explore the intrinsic turnover frequency (TOF_{intr}) and coverage of reactive carbon-containing intermediates (θ_{CO_x}) that lead to CO_2. The intrinsic TOF was found to be independent of temperature, approximately 3.4 s^{-1} for Au/TiO_2 (261–303 K) and 2.1 s^{-1} for Au/Al_2O_3 (272–343 K). This observation suggests the reaction of CO with surface oxygen is a nearly unactivated process. The coverage of carbon-containing intermediates leading to CO_2 was observed to increase with temperature. This phenomenon is contrary to that expected of θ_{CO_x} if it were determined by the equilibrium adsorption of CO, suggesting that CO adsorption may be activated. Alternatively, θ_{CO_x} could depend on the availability and subsequent activation of O_2.

In this work, ^{18}O isotopic transient analysis of CO oxidation and oxygen-exchange experiments with $^{18}O_2$ and $C^{18}O_2$ were performed in an attempt to provide insight into the activation of O_2 for CO oxidation over titania- and alumina-supported Au catalysts. Because the reducibility of a metal oxide is suspected to influence the availability of surface oxygen atoms [25,26], our study was performed with Au supported on both titania (reducible) and alumina (nonreducible). Because water is known to promote the rate of CO oxidation, we also probed the influence of added water on the extent of oxygen exchange in the system.

2. Experimental

2.1. Catalyst preparation

The titania- and alumina-supported Au catalysts used in this work are the same as those studied previously with ^{13}C isotopic transient analysis of CO oxidation [24]. The samples were prepared by a deposition-precipitation procedure and thermal treatment in He. The synthesis began with 96 mL of a 9.6 mM $HAuCl_4$ (Aldrich, 99.9+%) aqueous solution at 343 K that was adjusted to pH 7 with aqueous NaOH (Mallinckrodt, 98.6%) solution. This gold solution was then added to a 150-mL aqueous suspension of 6 g of either TiO_2 (Degussa, P-25) or Al_2O_3 (Mager Scientific, AP-312) also at 343 K. This corresponds to a maximum possible Au content of 3 wt%. The mixture was stirred for 2 h, after which the solution was removed by suction filtration. The sample was then resuspended in 120 mL of distilled, deionized water at 343 K for 20 min. The process of suction filtration and resuspension in distilled, deionized water was repeated 3 more times. After the final filtration, the sample was dried in air at 310 K for 24 h. The resulting Au content was 1.22 wt% for Au/TiO_2 and 1.08 wt% for Au/Al_2O_3, as reported by Galbraith Laboratories (Knoxville, TN). The samples were treated for 4 h at 623 K under 100 mL min^{-1} He before kinetic studies. The evolution of the Au oxidation state after preparation and during thermal treatment in He was monitored using X-ray absorption spectroscopy, as reported previously [24]. On both supports, the Au was in a cationic state after the low-temperature (310 K) drying in air and was subsequently reduced to a predominantly metallic state after treatment in He at 623 K. The Au particle size distribution of the thermally treated samples was 3.3 ± 0.5 nm for Au/TiO_2 and 2.5 ± 1.1 nm for Au/Al_2O_3, as determined by scanning transmission electron microscopy [24].

2.2. Oxygen-exchange measurements

Between 0.08 and 0.17 g of catalyst (−200/+100 mesh) was mixed with 0.42–0.53 g of SiC (Universal Photonics, 120 mesh) and loaded into a quartz tubular reactor. The catalyst bed was maintained at ambient temperature (293 K). The reactant feed consisted of $C^{16}O$ (99.997%, Messer), $^{16}O_2$ (99.999%, Messer), He (99.999%, Messer, further purified by a Supelco OMI-2 filter), and Ar (99.999%, Messer, further purified by a Supelco OMI-2 filter) with a molar composition of 2:2:95.3:0.7 for CO:O_2:He:Ar, respectively, unless stated otherwise. The gas flows were regulated by mass flow controllers, and the pressure of all streams was maintained at 1.2 atm by backpressure regulators. Carbon dioxide ($C^{16}O_2$, 99.999% Messer) was co-fed with the reactants, as discussed below. All of the gases except Ar and CO_2 were also purified by passage through a silica gel trap (Davisil Grade 635, Type 60A, 60–100 mesh) held at dry ice–acetone temperature. Water vapor was introduced to the reactor feed by passing a He stream through a saturator containing distilled, deionized water at ambient temperature. A total volumetric gas flow rate of 250 mL min^{-1} was used to give space velocities of approximately 1500–3100 mL min^{-1} g_{cat}^{-1}.

A four-port valve was used to switch between O_2 isotopes in the reactor feed. A stream containing $^{16}O_2$ and Ar was exchanged with a stream containing $^{18}O_2$ (Isotec, 99.9% O_2, 99+% ^{18}O, further purified with a silica gel trap at dry ice–acetone temperature) and He. Argon was included with the $^{16}O_2$ stream as an inert gas tracer to quantify the gas-phase holdup of the reactor system. Additional experiments were performed with $^{16}O_2$ replaced with $C^{16}O_2$ and $^{18}O_2$ replaced with $C^{18}O_2$ (Cambridge Isotope Laboratories, 99.4% CO_2, 97.4% ^{18}O) to allow for a switch between $C^{16}O_2$ and $C^{18}O_2$ in the reactor feed.

The different isotopomers were monitored with a Balzers-Pfieffer Prisma 200 amu mass spectrometer. The mass spectrometer was also used to quantify the molar composition of the reactor effluent to determine the global rate of CO oxidation. Gas feeds of known molar composition were used to generate calibration factors to determine the concentration of He, O_2, CO, Ar, H_2O, and CO_2. The lines from the reactor to the mass spectrometer as well as the mass spectrometer housing were heated to approximately 443 K.

3. Results and discussion

3.1. Isotopic transient analysis and oxygen-exchange studies with $^{18}O_2$

To explore the level of oxygen incorporation into CO_2 during the oxidation of CO with O_2, $^{16}O_2$ in the reactant feed was substituted with $^{18}O_2$ during steady-state $C^{16}O$ oxidation at ambient temperature. After the switch was made, no change in the baseline $m/e = 34$ signal ($^{16}O^{18}O$) was observed, indicating no oxygen exchange in the O_2. A slight increase in the $m/e = 30$ signal was observed that might be interpreted as an increase in the $C^{18}O$ concentration. Boccuzzi et al. also observed a species with $m/e = 30$ during an investigation of the $^{18}O_2$–$C^{16}O$ interaction over Au supported on TiO_2 and ZnO [20,22]. They interpreted a peak in the Fourier transform infrared (FTIR) spectrum to be associated with $C^{18}O$ adsorbed on Au. In our work the change in the $m/e = 30$ signal appears to be the result of $C^{16}O^{18}O$ and $C^{18}O_2$ fragmentation within the mass spectrometer. This phenomenon was confirmed by tracking changes in the $m/e = 28$ signal while changing the $C^{16}O_2$ concentration in the absence of $C^{16}O$ through an empty reactor. However, the presence of a very low concentration of $C^{18}O$ cannot be excluded. The transient of O_2 was also measured during CO oxidation and was found to nearly match that of the Ar transient. Therefore, the switch of O_2 isotopomers within the reactor system does not significantly contribute to the observed CO_2 transient.

Oxygen exchange was observed in CO_2, as indicated by the change in the $m/e = 44$, 46, and 48 signals corresponding to $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$, respectively. The transients of the CO_2 isotopomers after the switch in O_2 are presented in Figs. 1a and 1b for Au/TiO_2 and Au/Al_2O_3, respectively. The ratio of ion currents recorded for each CO_2 isotopomer should be very similar to their molar ratio. The pseudo steady-state mole fractions of the different CO_2 isotopomers are included in Table 1. The steady-state ratio of $C^{16}O_2$:$C^{16}O^{18}O$:$C^{18}O_2$ was 3:6:1 for Au/TiO_2 and 4:5:1 for Au/Al_2O_3. Care should be used when comparing the values in Table 1, because the amount of catalyst used and the level of CO_2 produced were not the same between the two samples.

The average residence time of CO_2 isotopomers adsorbed on the catalyst (τ) was calculated by integrating the area between the transient of each CO_2 (F_{CO_2}) isotopomer and Ar (F_{Ar}) nor-

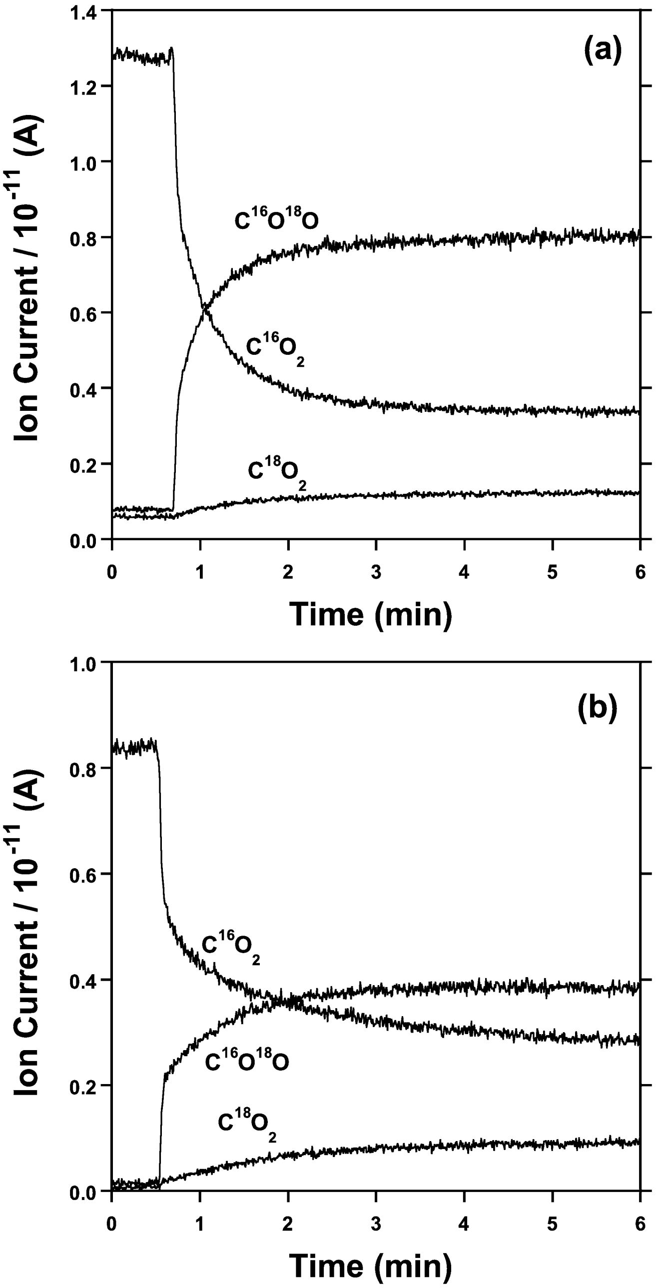


Fig. 1. Transient of CO_2 isotopomers after substitution of $^{16}O_2$ with $^{18}O_2$ during CO oxidation over (a) Au/TiO_2 and (b) Au/Al_2O_3 at ambient temperature. The steady-state signal before the switch is shown in the first half minute of the plot.

Table 1
Mole fraction[a] of CO_2 isotopomers after a switch from $^{16}O_2$ to $^{18}O_2$ during CO oxidation[b] over Au/TiO_2 and Au/Al_2O_3

	Au/TiO_2	Au/Al_2O_3
$C^{16}O_2$	0.26	0.36
$C^{16}O^{18}O$	0.63	0.51
$C^{18}O_2$	0.10	0.12
With co-fed CO_2[c]		
$C^{16}O_2$	0.30	0.38
$C^{16}O^{18}O$	0.63	0.57
$C^{18}O_2$	0.07	0.06
With co-fed H_2O		
$C^{16}O_2$	0.35	0.37
$C^{16}O^{18}O$	0.57	0.53
$C^{18}O_2$	0.08	0.09
With co-fed H_2O and CO_2[c]		
$C^{16}O_2$	0.60	0.64
$C^{16}O^{18}O$	0.36	0.32
$C^{18}O_2$	0.04	0.04

[a] Estimated error ±0.1.

[b] Conditions of CO oxidation: 293 K, 1.2 atm total pressure; $He:CO:O_2:Ar = 95.3:2:2:0.7$.

[c] Corrected for the amount of co-fed CO_2.

malized to the pseudo-steady-state values before and after the oxygen isotope switch in the reactor feed. The concentration of each CO_2 isotopomer would either increase or decrease depending on the sequence of substitution of O_2 ($^{16}O_2$ to $^{18}O_2$ or $^{18}O_2$ to $^{16}O_2$). To evaluate τ, the transients were transformed into a normalized decay curve. This was accomplished by using either F_{CO_2} or $1 - F_{CO_2}$ in Eq. (1), depending on the sequence of the isotope substitution in the reactor feed:

$$\tau = \int_0^\infty [F_{CO_2} - F_{Ar}]\,dt. \tag{1}$$

The moles of surface intermediates leading to CO_2 per mole of Au, N_{CO_x}, can be calculated using τ and the following steady-state mass balance:

$$N_{CO_x} = \tau \times R_{CO_2}, \tag{2}$$

where R_{CO_2} is the steady-state rate of CO oxidation per mole of Au atoms. The surface coverage of intermediates on the Au leading to CO_2, θ_{CO_x}, can be calculated from N_{CO_x} using the Au dispersion (29% for Au/TiO_2 and 26% for Au/Al_2O_3 [24]):

$$\theta_{CO_x} = \frac{N_{CO_x}}{\text{Au dispersion}}. \tag{3}$$

The fractional coverages estimated with Eq. (3) were well above unity ($\theta_{CO_x} > 2$), indicating that the τ values used to calculate coverages were complicated by artifacts from CO_2 readsorption and subsequent reactions, such as oxygen exchange. Therefore, the θ_{CO_x} in this case does not represent only the coverage of reactive intermediates on the Au leading to CO_2.

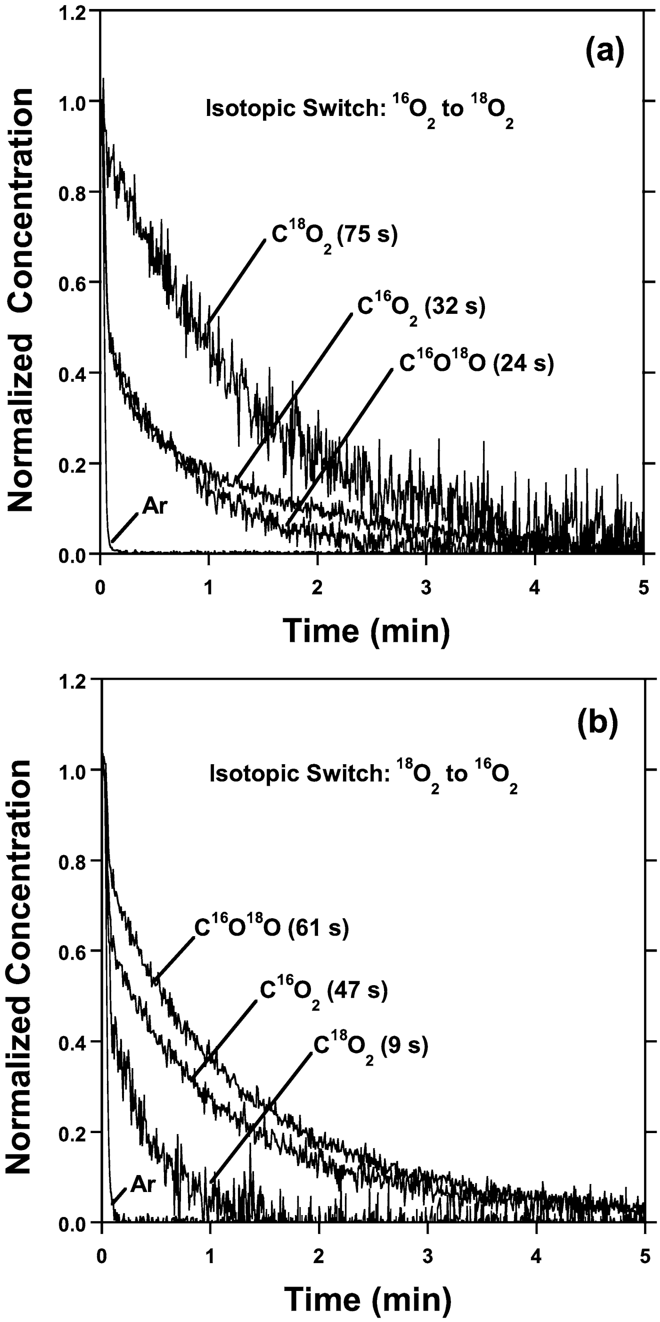


Fig. 2. Comparison of normalized CO_2 transients after a switch from (a) $^{16}O_2$ to $^{18}O_2$ and (b) $^{18}O_2$ to $^{16}O_2$ during CO oxidation over Au/Al_2O_3 at ambient temperature. Calculated τ values are noted for each transient.

The average residence time was different for each CO_2 isotopomer and depended on the order of the switch; that is, results with a switch from $^{16}O_2$ to $^{18}O_2$ were not the same as a switch from $^{18}O_2$ to $^{16}O_2$. This behavior is illustrated in Fig. 2, which includes the normalized CO_2 transients over Au/Al_2O_3. Similar behavior was observed over Au/TiO_2 (transients not shown). The calculated τ values for the switch from $^{16}O_2$ to $^{18}O_2$ and subsequently from $^{18}O_2$ back to $^{16}O_2$ are noted in Fig. 2.

If the CO_2 isotopomers were the product of the same surface reaction, then their normalized transients would be superimposable when switching from $^{16}O_2$ to $^{18}O_2$ and when switching from $^{18}O_2$ to $^{16}O_2$. Most notable is the τ associated with the $C^{18}O_2$ transient, which is considerably longer than the other CO_2 isotopomers when switching from $^{16}O_2$ to $^{18}O_2$, but shorter when switching from $^{18}O_2$ to $^{16}O_2$. This behavior suggests that processes other than the surface oxidation reaction contribute to the transient behavior of the CO_2 isotopomers. Therefore, it was necessary to determine whether readsorption and oxygen exchange were occurring with CO_2. These secondary processes would contribute to a longer calculated τ, as well as an overestimation of the mean residence time and the number of adsorbed intermediates leading to CO_2, as discussed earlier.

Carbon dioxide is known to absorb on TiO_2 and Al_2O_3 [27,28]. To reduce the contribution of CO_2 readsorption in our previous study using ^{13}CO, isotopically unlabeled CO_2 ($^{12}CO_2$) was co-fed to the system to compete for adsorption sites with the CO_2 produced catalytically ($^{13}CO_2$). Although introduction of $^{12}CO_2$ reduced the contribution of readsorption, it did not completely eliminate it. Similarly, co-fed $C^{16}O_2$ was introduced in this work to reduce the interaction between the CO_2 produced catalytically and the catalyst surface.

After correcting for the amount of $C^{16}O_2$ co-fed, we found that introduction of additional $C^{16}O_2$ to compete for oxide surface sites on the catalysts did not significantly influence the exchange of oxygen (Table 1, transients not shown). Therefore, additional experiments were required to identify the CO_2 isotopomers formed in the oxidation reaction.

To explore the possibility of oxygen exchange between CO_2 and gas-phase O_2, $^{16}O_2$ was again switched to $^{18}O_2$ in the presence of only $C^{16}O_2$. No scrambling of O_2 was observed, and no ^{18}O was incorporated into CO_2 (transients not shown). These observations suggest that O_2 does not exchange with CO_2. Another possible source of the different CO_2 isotopomers is oxygen scrambling within O_2 before reaction with CO. This possibility was explored by feeding equal molar concentrations (1 mol% each) of $^{16}O_2$ and $^{18}O_2$ over the catalysts. No change in the $m/e = 34$ signal corresponding to $^{16}O^{18}O$ was observed. The absence of $^{16}O^{18}O$ does not rule out the dissociation of O_2 because $^{16}O^{18}O$ would be observed only if subsequent associative desorption of dioxygen occurred after dissociation. Therefore, O_2 does not dissociatively adsorb *and* associatively desorb over these catalysts. Temperature-programmed desorption of oxygen atoms from Au islands (1.3 to >6 atomic layers) on $TiO_2(110)$ demonstrated that associative desorption of dioxygen does not occur below about 500 K [29]. No change in the $m/e = 34$ signal from the background indicates that O_2 does not exchange with the lattice oxygen of the metal-oxide supports. The lack of oxygen exchange between O_2 isotopomers, between O_2 and CO_2, and between O_2 and lattice oxygen of the metal oxides is consistent with previous oxygen-exchange studies [10,13,20–22,28,30].

3.2. Oxygen-exchange studies with $C^{18}O_2$

To clarify the source of oxygen during exchange reactions with CO_2, studies using $C^{18}O_2$ were performed. A 0.2 mol% feed of $C^{16}O_2$ was substituted with $C^{18}O_2$ while feeding 2 mol% $^{16}O_2$ (and no $C^{16}O$) over Au/TiO_2 and Au/Al_2O_3. The results of the isotopic switch over Au/Al_2O_3 are presented in Fig. 3a, and similar trends were observed over Au/TiO_2. The pseudo-steady-state mole fractions of the different CO_2 isotopomers are included in Table 2.

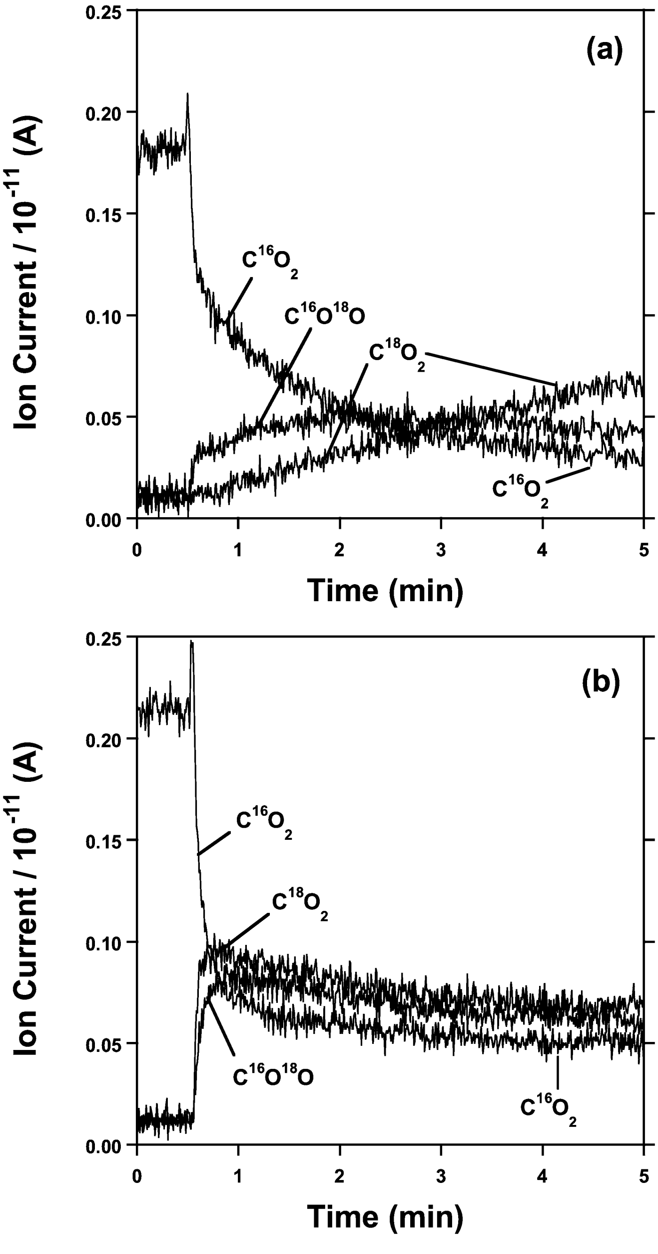


Fig. 3. Transient of CO_2 isotopomers after substitution of $C^{16}O_2$ with $C^{18}O_2$ in the presence of $^{16}O_2$ over Au/Al_2O_3 at ambient temperature in the (a) absence and (b) presence of co-fed H_2O. The steady-state signal before the switch is shown in the first half minute of the plot.

The $C^{18}O_2$ exchanged oxygen to form a new pseudo-steady-state concentration of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ over both metal-oxide-supported catalysts. Because O_2 and CO_2 do not exchange oxygen with each other, the source of ^{16}O is the oxygen associated with the metal oxide. The critical observation here is the ratio of CO_2 isotopomers observed during the oxidation of $C^{16}O$ with $^{18}O_2$ is not directly related to CO oxidation, but is instead influenced by oxygen exchange with the metal-oxide support *after* CO_2 formation.

Because exchange of oxygen in CO_2 occurs after CO_2 formation and our previous ^{13}CO isotopic transient analysis [24]

Table 2
Mole fraction[a] of CO_2 isotopomers after a switch from $C^{16}O_2$ to $C^{18}O_2$ over Au/TiO_2 and Au/Al_2O_3

	Au/TiO_2	Au/Al_2O_3
$C^{16}O_2$	0.17	0.20
$C^{16}O^{18}O$	0.28	0.29
$C^{18}O_2$	0.55	0.51
With co-fed CO_2[b]		
$C^{16}O_2$	0.30	0.16
$C^{16}O^{18}O$	0.40	0.72
$C^{18}O_2$	0.29	0.12
With co-fed H_2O		
$C^{16}O_2$	0.16	0.28
$C^{16}O^{18}O$	0.24	0.34
$C^{18}O_2$	0.60	0.38
With co-fed H_2O and CO_2[b]		
$C^{16}O_2$	0.41	0.43
$C^{16}O^{18}O$	0.20	0.28
$C^{18}O_2$	0.38	0.29

[a] Estimated error ±0.1.

[b] Corrected for the amount of co-fed CO_2.

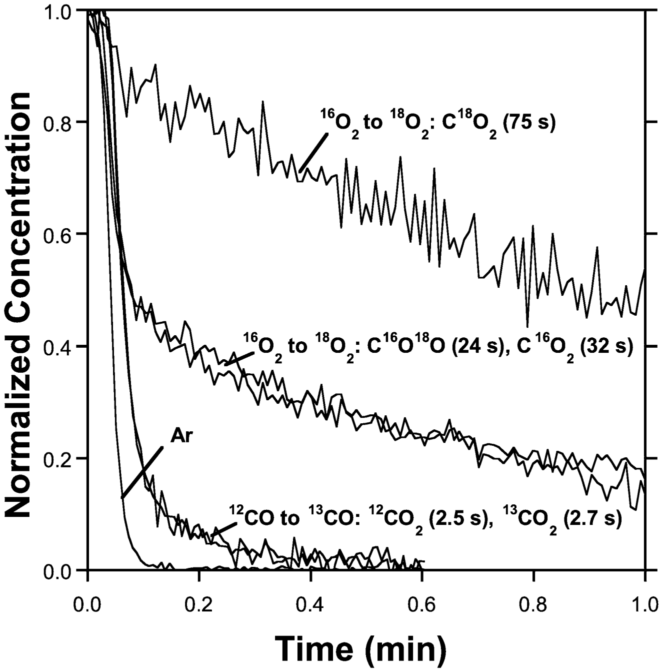


Fig. 4. Comparison of normalized CO_2 transients after a switch from ^{12}CO to ^{13}CO ($^{12}CO_2$ and $^{13}CO_2$) and $^{16}O_2$ to $^{18}O_2$ ($C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$) during CO oxidation over Au/Al_2O_3 at ambient temperature. Calculated τ values are noted for each transient.

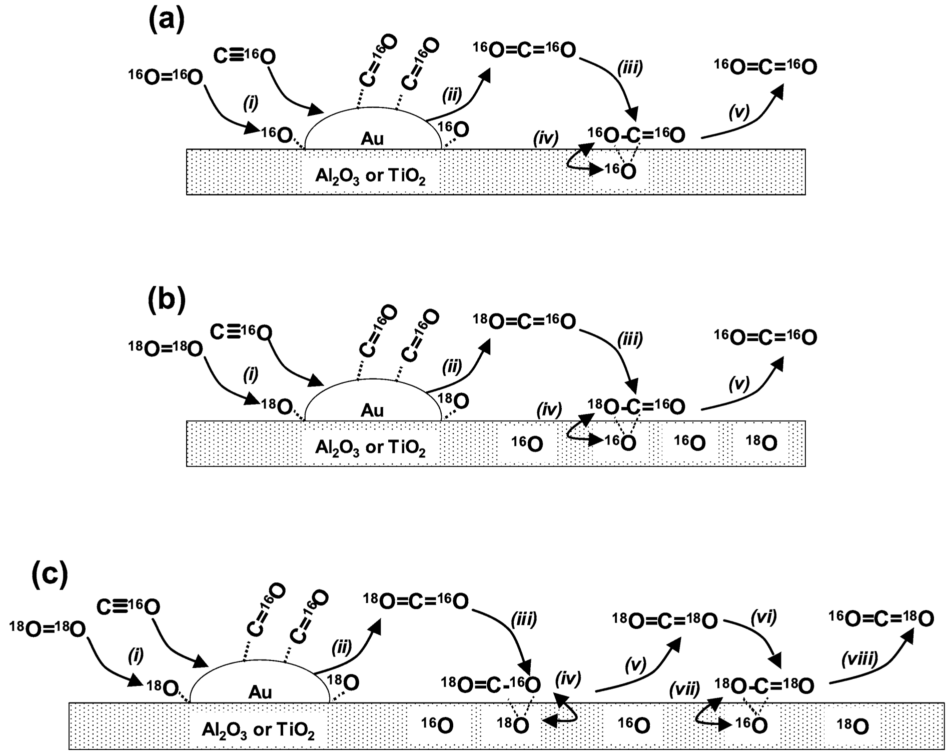
was not complicated by oxygen exchange, we compared the results of the ^{18}O and ^{13}C isotopic transient analyses to deconvolve the CO_2 isotopomers that are the product of the oxidation reaction. The temperature, flow rate, reactor feed concentration, and catalyst loading were similar for the two experiments. Fig. 4 shows the normalized transients of the different isotopically labeled CO_2 products observed during the isotopic transient analysis of CO oxidation over Au/Al_2O_3 using ^{13}CO and $^{18}O_2$ as the isotopically labeled reactants. Similar results were observed over Au/TiO_2 (transients not shown).

Because isotopically labeled oxygen species were not used during the experiments with ^{13}CO, the oxygen-exchange process could not be monitored. This condition is depicted in Fig. 5a. Therefore, when substituting ^{12}CO with ^{13}CO, the normalized transients of the decay of $^{12}CO_2$ and the growth of $^{13}CO_2$ superimpose each other (Fig. 4). Oxygen exchange between CO_2 and oxygen associated with the metal oxide supports still occurred, but its contribution to the observed τ was not as significant as that observed in $^{18}O_2$ isotopic transient analysis.

The considerably longer CO_2 transients observed with isotopically labeled O_2 (Fig. 4; $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$) can be explained by tracking the labeled atomic oxygen as depicted in Figs. 5b and 5c.

As shown in Fig. 5b, after a switch from $^{16}O_2$ to $^{18}O_2$, the ^{18}O from the $C^{16}O^{18}O$ resulting from the oxidation reaction (step (ii)) can exchange with the ^{16}O of the metal oxide (step (iv)). This results in ^{18}O incorporation into the metal oxide. The ^{18}O now on the metal oxide can subsequently exchange with another CO_2, as shown in Fig. 5c, step (iv). The accumulation of ^{18}O on the surface of the metal oxide is responsible for the longer τ observed during $^{18}O_2$ isotopic transient analysis. The actual exchange between CO_2 and support oxygen (steps (iv) and (vii)) must be relatively rapid, because the τ observed during ^{12}CO–^{13}CO transient analysis is on the order of seconds. Therefore, comparison of the normalized CO_2 transients observed during the ^{13}CO and $^{18}O_2$ isotopic transient analyses at short times should provide an indication of the CO_2 isotopomers produced directly by the oxidation of $C^{16}O$ with $^{18}O_2$. As shown in Fig. 4, the transients of $^{12}CO_2$ and $^{13}CO_2$ using ^{13}CO, as well as the transients of $C^{16}O_2$ and $C^{16}O^{18}O$ using $^{18}O_2$, are similar at very short times. Because the decay of the $^{12}CO_2$ and $C^{16}O_2$ transients and the growth of $^{13}CO_2$ and $C^{16}O^{18}O$ transients are superimposable at these short times, $C^{16}O^{18}O$ appears to be the sole product of the oxidation of $C^{16}O$ with $^{18}O_2$. This is consistent with the work of Schubert et al., in which $C^{16}O^{18}O$ was reported to be the only product of $C^{16}O$ oxidation with $^{18}O_2$ over Au/α-Fe_2O_3 at 348 K in a temporal analysis of products reactor system [25]. The gradual growth of the $C^{18}O_2$ transient relative to that of $^{13}CO_2$ (Fig. 4) indicates that double ^{18}O-labeled CO_2 is formed only through oxygen exchange on the surface of the metal oxide, as depicted in Fig. 5c, step (iv).

The mechanism of oxygen exchange between CO_2 and the oxygen of the metal-oxide supports could involve the formation and decomposition of surface carbonate species. Carbonate species have been observed by FTIR spectroscopy during CO oxidation over Au/metal oxide catalysts [10,11,20,22,31,32]. Boccuzzi et al. monitored the absorption bands assigned to carbonate-like species over Au supported on ZnO and TiO_2 at ambient temperature and observed no change in frequency with the substitution of gas-phase $^{16}O_2$ with $^{18}O_2$ [20]. Therefore, they suggested that the carbonates are formed from support oxygen atoms and are not intermediates in the oxidation reaction.



i. Adsorption of CO and O_2
ii. Surface reaction of CO + O = CO_2 followed by CO_2 desorption
iii. Re-adsorption of CO_2 on metal oxide
iv. Oxygen exchange between CO_2 and support oxygen
v. Desorption of CO_2
vi. Re-adsorption of CO_2 on metal oxide
vii. Oxygen exchange between CO_2 and support oxygen
viii. Desorption of CO_2

Fig. 5. Schematic representation of CO oxidation and oxygen-exchange processes between CO_2 and support oxygen of the Al_2O_3 or TiO_2. (a) Oxygen-exchange process without isotopically labeled O_2 during CO oxidation. (b) and (c) oxygen-exchange processes after a switch from $^{16}O_2$ to $^{18}O_2$ during CO oxidation.

3.3. Influence of H_2O on the exchange of oxygen

The presence of co-fed water vapor in the reactant feed resulted in a significant increase in the global rate of CO oxidation. The rate of CO_2 formation over Au/TiO_2 at 293 K was 0.19 $\mathrm{mol_{CO_2}\,mol_{Au}^{-1}\,s^{-1}}$ in the absence of co-fed H_2O, but increased to 0.51 $\mathrm{mol_{CO_2}\,mol_{Au}^{-1}\,s^{-1}}$ in the presence of 0.16 mol% H_2O. Similarly, the rate of reaction over Au/Al_2O_3 at 293 K was 0.04 $\mathrm{mol_{CO_2}\,mol_{Au}^{-1}\,s^{-1}}$ with a dry feed, but increased to 0.37 $\mathrm{mol_{CO_2}\,mol_{Au}^{-1}\,s^{-1}}$ in the presence of 0.16 mol% H_2O. No CO_2 was observed in the presence of CO and H_2O without O_2. Therefore, the promotional effect of water cannot be attributed to the water–gas shift reaction.

Despite the significant promotional effect of co-fed H_2O on the rate of CO oxidation, minimal differences (relative to a dry feed) were observed in the steady-state levels of oxygen exchange evaluated by switching from $^{16}O_2$ to $^{18}O_2$ during $C^{16}O$ oxidation at 293 K. The resulting CO_2 isotopomer compositions, with and without co-fed $C^{16}O_2$, are given in Table 1 (transients not shown). The only change observed in the CO_2 isotopomers with the addition of $H^{16}O_2$ was observed in the presence of co-fed $C^{16}O_2$. A higher proportion of $C^{16}O_2$ was observed compared with the dry conditions, with and without co-fed $C^{16}O_2$. The higher proportion of $C^{16}O_2$ could be the result of $C^{16}O^{18}O$ exchanging ^{18}O with H_2O, as discussed below.

Similar to the case with a dry feed stream, neither oxygen scrambling in O_2 nor oxygen exchange between O_2 and CO was observed in the presence of water. This lack of exchange in the presence of H_2O was also verified by feeding an equal molar concentration of $^{16}O_2$ and $^{18}O_2$ (1 mol% each) over both catalysts during CO oxidation. Again, no oxygen exchange was observed in O_2 or CO. To explore the possibility that atomic oxygen formed in the presence of CO would react rapidly to CO_2 and thus not associatively desorb as $^{16}O^{18}O$, equal molar concentrations of $^{16}O_2$ and $^{18}O_2$ (1 mol% each) were fed over both catalysts in the absence of CO with 0.16 mol% co-fed H_2O. Again, no change in the $m/e = 34$ signal was observed, indicating a lack of $^{16}O^{18}O$ formation.

Although the presence of H_2O did not facilitate oxygen exchange between O_2 and CO, oxygen exchange with H_2O was observed. The $H_2{}^{18}O$ ($m/e = 20$) concentration increased during CO oxidation after switching from $^{16}O_2$ to $^{18}O_2$ in the

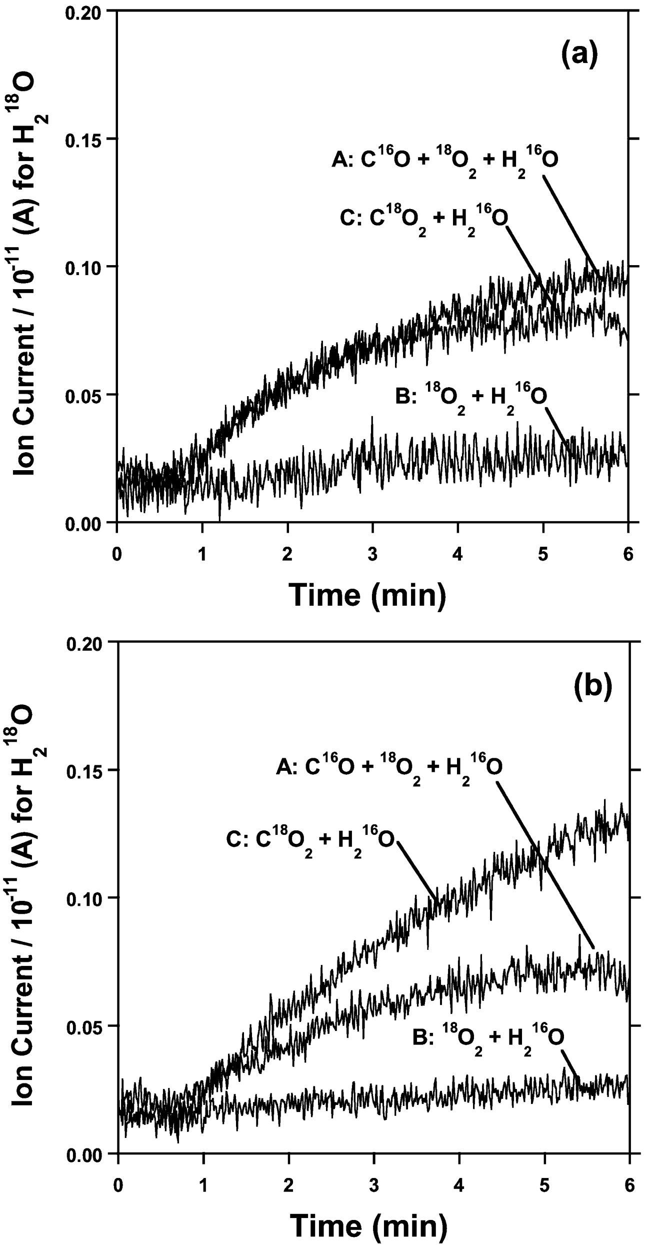


Fig. 6. Transient of $H_2{}^{18}O$ over (a) Au/TiO_2 and (b) Au/Al_2O_3. Curve A, after a switch from ${}^{16}O_2$ to ${}^{18}O_2$ during $C^{16}O$ oxidation with co-fed $H_2{}^{16}O$; curve B, after a switch from ${}^{16}O_2$ to ${}^{18}O_2$ without CO, with co-fed $H_2{}^{16}O$; curve C, after a switch from $C^{16}O_2$ to $C^{18}O_2$ without CO or O_2, with co-fed $H_2{}^{16}O$. The steady-state signal before the switch is shown in the first half minute of the plot.

presence of 0.16 mol% H_2O, as shown by curve A of Figs. 6a and 6b for Au/TiO_2 and Au/Al_2O_3, respectively.

Water has been proposed to influence the oxidation of CO over metal-oxide-supported Au through two mechanisms: intermolecular activation of O_2 either as H_2O or species derived from H_2O [8,9] and enhanced decomposition of site-blocking carbonate species [9–11]. Daté et al. proposed O_2 activation by H_2O through the formation of surface hydroxyl groups [8]. However, Boccuzzi et al. observed only the formation of $C^{16}O^{18}O$ during the oxidation of $C^{16}O$ in the presence of ${}^{18}O_2$ and $H_2{}^{16}O$ at 90 K over Au/TiO_2, suggesting that O_2 is the sole oxygen supply for the oxidation reaction [22]. A recent DFT study of O_2 adsorption on titania(110) indicated that surface hydroxyl groups enhance both O_2 adsorption and diffusion on the oxide surface, which may account for the promotion of CO oxidation on TiO_2-supported Au particles in the presence of co-fed H_2O [33].

To focus on O_2–H_2O interactions without potential contributions from interaction with CO_2, ${}^{16}O_2$ was substituted with ${}^{18}O_2$ over the catalysts in the presence of 0.16 mol% $H_2{}^{16}O$ without CO or CO_2. A slight increase in the $m/e = 20$ signal (Fig. 6, curve B) was observed that was significantly less than that observed during CO oxidation in the presence of H_2O (curve A). Therefore, the $m/e = 20$ signals observed during CO oxidation do not appear to result from interaction between O_2 and H_2O. This does not rule out the possibility of O_2 activation with H_2O, because either associative desorption of dioxygen or dehydration of the surface would be required to observe oxygen scrambling in O_2 or exchange with H_2O. Muggli and Falconer also studied exchange reactions with O_2 and H_2O over TiO_2, but observed oxygen exchange only on exposure of the sample to ultraviolet light [30].

To explore the possibility of H_2O interaction with CO_2, $C^{16}O_2$ was substituted with $C^{18}O_2$ over both catalysts in the presence of 0.16 mol% $H_2{}^{16}O$ without O_2 or CO. A concentration of 0.8 mol% CO_2 was used while co-feeding H_2O to better represent the higher CO_2 concentration observed during CO oxidation in the presence of H_2O. The response of the $m/e = 20$ (corresponding to $H_2{}^{18}O$) signal after the switch in CO_2 isotopomers is included in Fig. 6, curve C. Comparison of the $m/e = 20$ transients in Fig. 6 during CO oxidation with co-fed H_2O (curve A) and in the presence of only CO_2 and H_2O (curve C) reveals similar growth of the signal with time. The exchange of oxygen in H_2O during CO oxidation appears to be the result of interaction between H_2O and CO_2 or species derived from CO_2 such as carbonates. This is consistent with a report of oxygen exchange between H_2O and CO_2 over TiO_2 by Muggli and Falconer [30]. Differences in the magnitude of exchange can be attributed to the different amounts of ${}^{18}O$ in the CO_2 for each condition. During the switch from $C^{16}O_2$ to $C^{18}O_2$, the total concentration of CO_2 was 0.8 mol%, whereas during CO oxidation, the total concentration of CO_2 was 1.48 mol% over Au/TiO_2 and 1.22 mol% over Au/Al_2O_3 with a molar ratio of 4:5:1 for $C^{16}O_2$:$C^{16}O^{18}O$:$C^{18}O_2$ for both samples.

A role of carbonates is suspected in the exchange of oxygen between H_2O and CO_2. Behm and co-workers used diffuse reflectance infrared spectroscopy to monitor carbonate species over TiO_2- and Fe_2O_3-supported Au catalysts during CO oxidation [10,11] The presence of H_2O appeared to facilitate decomposition of the carbonates, which correlated with an increase in catalytic activity. Therefore, oxygen exchange could be facilitated by H_2O-assisted decomposition of carbonates. A potential mechanism for the decomposition of carbonates via the less stable bicarbonate has been proposed by Costello et al. [9] and is represented by

$$CO_3^{2-} + H_2O \rightarrow CO_3H^- + OH^-, \tag{4a}$$

$$CO_3H^- \rightarrow CO_2 + OH^-. \tag{4b}$$

However, we cannot rule out the possibility of indirect exchange of CO_2 and H_2O via the support oxygen. For example, CO_2 could exchange with oxygen of the support, which could subsequently exchange with the H_2O. Exchange of oxygen between H_2O and oxygen on TiO_2 is suspected to occur at ambient temperature [30]. Because oxygen exchange was not observed between gas-phase O_2 and the oxygen of the metal oxides, oxygen exchange observed in the H_2O is not likely through exchange between O_2 and support oxygen.

The influence of water vapor on the exchange of oxygen using $C^{18}O_2$ was also explored. As with our previous work using $C^{18}O_2$, a 0.2 mol% feed of $C^{16}O_2$ was substituted with $C^{18}O_2$ while 2 mol% $^{16}O_2$ and no $C^{16}O$ was fed over both alumina- and titania-supported gold catalysts. The result of the isotopic switch over Au/Al_2O_3 is presented in Fig. 3(b). Similar behavior was observed over Au/TiO_2 (transients not shown). The pseudo-steady-state mole fractions of the different CO_2 isotopomers are included in Table 2.

In these experiments, the presence of H_2O had an effect on the time constants of the CO_2 isotopomers. A new steady-state concentration of CO_2 isotopomers was reached much quicker after the substitution of $C^{16}O_2$ with $C^{18}O_2$ in the presence of H_2O (Fig. 3b) compared with that observed in the corresponding experiment without H_2O (Fig. 3a). However, the pseudo-steady-state mole fractions of CO_2 isotopomers were not significantly different than those observed in the absence of H_2O. One possible explanation of this finding is that H_2O adsorbs on the titania and alumina and competes with CO_2 adsorption, and thus fewer carbonates are formed. Another possibility is that H_2O simply facilitates the decomposition of carbonates on the surface of the metal oxides. It is difficult to conclude which of these mechanisms is occurring without characterization of the surface carbonates.

As previously noted, the lack of observable oxygen exchange between O_2 and H_2O does not eliminate the possibility of water-enhanced activation of O_2. In principle, isotopic transient analysis can discriminate between enhancement of the pseudo-first-order rate constant for reaction of surface species and creation of additional reactive intermediates in the presence of H_2O. In an earlier study, we introduced 0.18 mol% H_2O during CO oxidation over Au/Al_2O_3 at ambient temperature and observed an increase in the global rate of about a factor of 6 [34]. The rate constant, also known as the intrinsic TOF, determined by a ^{13}CO transient analysis in the presence of H_2O was $2.0\ s^{-1}$, whereas it was $1.1\ s^{-1}$ in dry conditions. Because the global rate increased by a factor of 6 and the pseudo-first-order rate constant only doubled, the surface coverage of carbon-containing intermediates leading to CO_2 apparently increased by about a factor of three. These results indicate that H_2O both enhances the pseudo-first-order rate constant and increases the coverage of carbon-containing species leading to CO_2. It should be emphasized that the pseudo-first-order rate constant for CO surface reaction contains both a surface rate constant and the coverage of reactive oxygen species. Therefore, the increase in the observed pseudo-first-order rate constant due to water might be attributed to greater availability of reactive oxygen and/or an enhanced surface rate constant.

Table 3
Mole fraction[a] of CO_2 isotopomers after a switch from $C^{16}O_2$ to $C^{18}O_2$ over Au-free TiO_2 and Al_2O_3

	TiO_2	Al_2O_3
$C^{16}O_2$	0.16	0.16
$C^{16}O^{18}O$	0.27	0.24
$C^{18}O_2$	0.57	0.60
With co-fed CO_2[b]		
$C^{16}O_2$	0.34	0.10
$C^{16}O^{18}O$	0.36	0.77
$C^{18}O_2$	0.30	0.13
With co-fed H_2O		
$C^{16}O_2$	0.15	0.24
$C^{16}O^{18}O$	0.22	0.35
$C^{18}O_2$	0.63	0.41
With co-fed H_2O and CO_2[b]		
$C^{16}O_2$	0.42	0.47
$C^{16}O^{18}O$	0.19	0.26
$C^{18}O_2$	0.39	0.27

[a] Estimated error ±0.1.

[b] Corrected for the amount of co-fed CO_2.

3.4. Oxygen-exchange studies over Au-free TiO_2 and Al_2O_3

Results of our study suggest that oxygen exchange in CO_2 occurs only through the oxygen associated with the catalyst surface. Thus, we explored the isotopic switch of $C^{16}O_2$ with $C^{18}O_2$ over TiO_2 and Al_2O_3 without any gold particles. A 0.2 mol% feed of $C^{16}O_2$ was substituted with $C^{18}O_2$ while feeding 2 mol% $^{16}O_2$ (and no $C^{16}O$) over Au-free TiO_2 and Al_2O_3 diluted with SiC. The amounts of metal oxide and SiC were similar to those used during the study of the Au-containing samples. The pseudo-steady-state mole fractions of CO_2 isotopomers are included in Table 3 (transients not shown).

There were no significant differences in oxygen exchange of $C^{18}O_2$ over the TiO_2 or Al_2O_3 with or without the presence of Au. Control experiments involving switches between $C^{16}O_2$ and $C^{18}O_2$ over SiC and an empty reactor confirmed that no oxygen exchange occurred without the metal oxide supports.

4. Conclusion

1. Scrambling of O_2 and exchange of O_2 and CO were not observed over Au/TiO_2 and Au/Al_2O_3 at 293 K. These results indicate that dissociative adsorption of O_2 is not reversible on these catalysts. In addition, the oxygen of the titania and alumina did not exchange with O_2 at our conditions.
2. Comparison of isotopic transients during $^{18}O_2$ and ^{13}CO switches in the feed indicates that $C^{16}O^{18}O$ was the primary product of $C^{16}O$ oxidation with $^{18}O_2$.
3. Oxygen exchange was observed in CO_2 produced by the oxidation of $C^{16}O$ with $^{18}O_2$ over titania- and alumina-supported Au nanoparticles at ambient temperature. However, the CO_2 isotopomer distribution during CO oxidation was not the direct result of the oxidation reaction, but was determined by subsequent exchange with oxygen atoms associated with the supports. Both the reducible (titania) and

nonreducible (alumina) supports readily exchanged oxygen with CO_2.

4. Despite a promotional effect of H_2O on the rate of CO oxidation, there was no exchange of labeled oxygen within O_2 or CO. Although labeled oxygen was incorporated into H_2O when CO_2 was present in the product stream, there was no incorporation in the absence of CO_2.

Acknowledgment

This work was supported by the National Science Foundation (grant CTS-0121619).

References

[1] G.C. Bond, D.T. Thompson, Catal. Rev.-Sci. Eng. 41 (1999) 319.
[2] M. Haruta, M. Date, Appl. Catal. A 222 (2001) 427.
[3] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 115 (1989) 301.
[4] H.H. Kung, M.C. Kung, C.K. Costello, J. Catal. 216 (2003) 425.
[5] H. Hakkinen, W. Abbet, A. Sanchez, U. Heiz, U. Landman, Angew. Chem. Int. Ed. 42 (2003) 1297.
[6] B. Yoon, H. Hakkinen, U. Landman, A.S. Worz, J.M. Antonietti, S. Abbet, K. Judai, U. Heiz, Science 307 (2005) 403.
[7] Z. Yan, S. Chinta, A.A. Mohamed, J.P. Fackler, D.W. Goodman, J. Am. Chem. Soc. 127 (2005) 1604.
[8] M. Date, M. Okumura, S. Tsubota, M. Haruta, Angew. Chem. Int. Ed. 43 (2004) 2129.
[9] C.K. Costello, J.H. Yang, H.Y. Law, Y. Wang, J.N. Lin, L.D. Marks, M.C. Kung, H.H. Kung, Appl. Catal. A 243 (2003) 15.
[10] B. Schumacher, Y. Denkwitz, V. Plzak, M. Kinne, R.J. Behm, J. Catal. 224 (2004) 449.
[11] M.M. Schubert, A. Venugopal, M.J. Kahlich, V. Plzak, R.J. Behm, J. Catal. 222 (2004) 32.
[12] L.M. Molina, B. Hammer, Appl. Catal. A 291 (2005) 21.
[13] H. Liu, A.I. Kozlov, A.P. Kozlova, T. Shido, K. Asakura, Y. Iwasawa, J. Catal. 185 (1999) 252.
[14] N. Lopez, T.V.W. Janssens, B.S. Clausen, Y. Xu, M. Mavrikakis, T. Bligaard, J.K. Norskov, J. Catal. 223 (2004) 232.
[15] Y. Xu, M. Mavrikakis, J. Phys. Chem. B 107 (2003) 9298.
[16] Z.P. Liu, P. Hu, A. Alavi, J. Am. Chem. Soc. 124 (2002) 14770.
[17] I.N. Remediakis, N. Lopez, J.K. Norskov, Appl. Catal. A 291 (2005) 13.
[18] J. Guzman, S. Carrettin, A. Corma, J. Am. Chem. Soc. 127 (2005) 3286.
[19] J. Guzman, S. Carrettin, J.C. Fierro-Gonzalez, Y.L. Hao, B.C. Gates, A. Corma, Angew. Chem. Int. Ed. 44 (2005) 4778.
[20] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, J. Phys. Chem. 100 (1996) 3625.
[21] H.C. Liu, A.I. Kozlov, A.P. Kozlova, T. Shido, Y. Iwasawa, Phys. Chem. Chem. Phys. 1 (1999) 2851.
[22] F. Boccuzzi, A. Chiorino, M. Manzoli, P. Lu, T. Akita, S. Ichikawa, M. Haruta, J. Catal. 202 (2001) 256.
[23] S.T. Daniells, A.R. Overweg, M. Makkee, J.A. Moulijn, J. Catal. 230 (2005) 52.
[24] J.T. Calla, M.T. Bore, A.K. Datye, R.J. Davis, J. Catal. 238 (2006) 458.
[25] M.M. Schubert, S. Hackenberg, A.C. van Veen, M. Muhler, V. Plzak, R.J. Behm, J. Catal. 197 (2001) 113.
[26] A.K. Tripathi, V.S. Kamble, N.M. Gupta, J. Catal. 187 (1999) 332.
[27] S.V. Bordawekar, E.J. Doskocil, R.J. Davis, Langmuir 14 (1998) 1734.
[28] D. Martin, D. Duprez, J. Phys. Chem. 100 (1996) 9429.
[29] V.A. Bondzie, S.C. Parker, C.T. Campbell, Catal. Lett. 63 (1999) 143.
[30] D.S. Muggli, J.L. Falconer, J. Catal. 181 (1999) 155.
[31] P. Konova, A. Naydenov, C. Venkov, D. Mehandjiev, D. Andreeva, T. Tabakova, J. Mol. Catal. A 213 (2004) 235.
[32] B.K. Chang, B.W. Jang, S. Dai, S.H. Overbury, J. Catal. 236 (2005) 392.
[33] L.M. Liu, B. McAllister, H.Q. Ye, P. Hu, J. Am. Chem. Soc. (2006), published on Web.
[34] J.T. Calla, R.J. Davis, J. Phys. Chem. B 109 (2005) 2307.