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Evidence of active species in CO oxidation catalyzed by highly dispersed supported gold

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Abstract

This paper is a brief review of suggested structures of catalytic sites and reaction mechanisms in CO oxidation catalyzed by highly dispersed supported gold. The review is focused on evidence of the sites, which has been determined primarily by infrared, X-ray absorption, and other spectroscopies, often combined with transmission electron microscopy; theory has also been applied to characterize supported gold catalysts. The literature gives strong evidence of the reaction of oxygen with CO adsorbed on zerovalent gold at low temperature, consistent with the role of such adsorbed CO in the catalytic reaction. There is also strong evidence of the involvement of cationic gold, even isolated single sites, in the catalysis at higher temperatures (e.g., room temperature). Because CO is only weakly adsorbed on zerovalent gold and more strongly adsorbed on cationic gold, it is suggested that the cationic gold sites may be kinetically more significant than the zerovalent gold sites under potentially practical reaction conditions.

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1. Introduction

Gold in its bulk form is known for its inertness and was long regarded as virtually inactive catalytically. However, the discovery in the late 1980s that gold, when highly dispersed on metal oxide supports, catalyzes CO oxidation at low temperatures [1] has been followed by a stream of reports of reactions catalyzed by supported gold, including epoxidation of propylene [2], synthesis of hydrogen peroxide [3] and of vinyl chloride [4], selective oxidation of alcohols [5], carbon–carbon bond coupling reactions [6], and selective reduction of nitro groups on aromatic rings in the presence of C=C bonds [7], among others [8,9].

The discoveries are continuing at an impressive pace, but reports of characterizations of supported gold catalysts in the most relevant state – while they are functioning – are still at an early stage. Most of these focus on CO oxidation, because of its potential for practical applications (e.g., in the purification of feeds to hydrogen fuel cells for automobiles, because CO poisons the fuel cell catalysts) and because CO offers advantages for fundamental understanding by being a good probe of catalyst surface structures.

The literature reflects a consensus that the preparation method and choice of support significantly influence the CO oxidation activity of supported gold [10] and, further, that this activity is affected by the presence of trace amounts of water and components such as halides [1].

But hypotheses about the nature of the active site(s) in supported gold catalysts are varied and contradictory. Catalysis has been attributed variously to supported gold nanoparticles (with the activity depending on the particle size) [11,12], and the gold has been postulated to be zerovalent [13], anionic [14], and cationic [15]. Catalytic properties have been attributed to the presence of gold atoms on the surfaces of the nanoparticles, and, specifically, to gold atoms at the gold–support interface [16] and to low-coordinated gold atoms in gold nanoparticles [17]. For each hypothesis, there is at least one reported spectroscopic or theoretical characterization that seems to provide supporting evidence.

We are thus confronted with the possibilities that (a) CO oxidation can be catalyzed by various structures of supported gold or (b) that there is essentially only one kind of active site for the reaction, and that some of the hypotheses are invalid.

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Distinguishing among the possibilities is challenging because the structures of the supported gold species are complex, non-uniform, and so small as to be difficult to characterize precisely. The typical supported gold catalyst consists of gold nanoparticles of various sizes and shapes dispersed on an amorphous support, usually a high-area metal oxide powder. Almost all the available physical characterization data point to nanoparticles of gold in the catalysts, and there are reports [18–20] of cationic gold accompanying the zerovalent gold nanoparticles in some of these catalysts.

Some researchers, in attempts to overcome the inherent structural complexity of typical supported gold catalysts, have prepared such catalysts that are simpler structurally than the typical ones and better suited to characterization. For example, some researchers have prepared catalysts with limited or controlled sizes of gold nanoclusters [21,22], and some have used planar (even single-crystal) support surfaces to facilitate investigation with ultrahigh vacuum methods [11,12]. Investigations with the latter catalysts (sometimes called model catalysts) are limited, because they lack some characteristics of potential practical catalysts, such as support hydroxyl groups and/or water.

Our goal here is to summarize the suggestions of active species and reaction intermediates in CO oxidation catalyzed by supported gold and to assess the experimental and theoretical evidence for them. We focus on the spectroscopic and theoretical investigations, especially on spectroscopic evidence of catalysts in reactive atmospheres.

2. Early proposals of active species and possible reaction mechanisms of CO oxidation catalyzed by supported gold

A substantial part of the reported research on CO oxidation catalyzed by supported gold was motivated by the goal of identifying catalyst properties that affect the activity. Two early classes of observations were important in determining the approaches used recently to investigate supported gold catalysts: (a) various preparation routes lead to catalysts with different activities [23–25], and (b) catalysts consisting of gold supported on reducible metal oxides (e.g., Fe_2O_3, CeO_2, and TiO_2) are typically more active than those supported on non-reducible metal oxides (e.g., γ-Al_2O_3, MgO, and SiO_2) [23–25]. Such observations led to wide acceptance of the inferences that the preparation method influences activity [10] and that the support plays a role in the catalysis [23–25].

Numerous results show how catalyst structures are affected by preparation methods. For example, images obtained by transmission electron microscopy (TEM) show that catalysts prepared by impregnation (which typically have relatively low catalytic activities) generally contain gold nanoparticles larger than those in catalysts prepared by coprecipitation and deposition-precipitation (which typically have relatively high activities) [23]. Such results led to hypotheses that catalytic activity is affected by the gold nanoparticle size [23]. However, because the catalysts were structurally complex, it was difficult to establish whether the nanoparticle size was a primary variable affecting the activity or, instead, whether effects such as the particle morphology or structure of the metal–support interface could have been significant.

Various hypotheses for the role of the support have been presented: (a) the support could be involved in the activation of oxygen [26], (b) defects on supports could stabilize gold nanoparticles (assumed to be the active species) [27,28], and (c) water and/or support surface hydroxyl groups might affect the catalytic activity [29,30]. When these hypotheses were advanced initially, there was a lack of spectroscopic evidence to assess them.

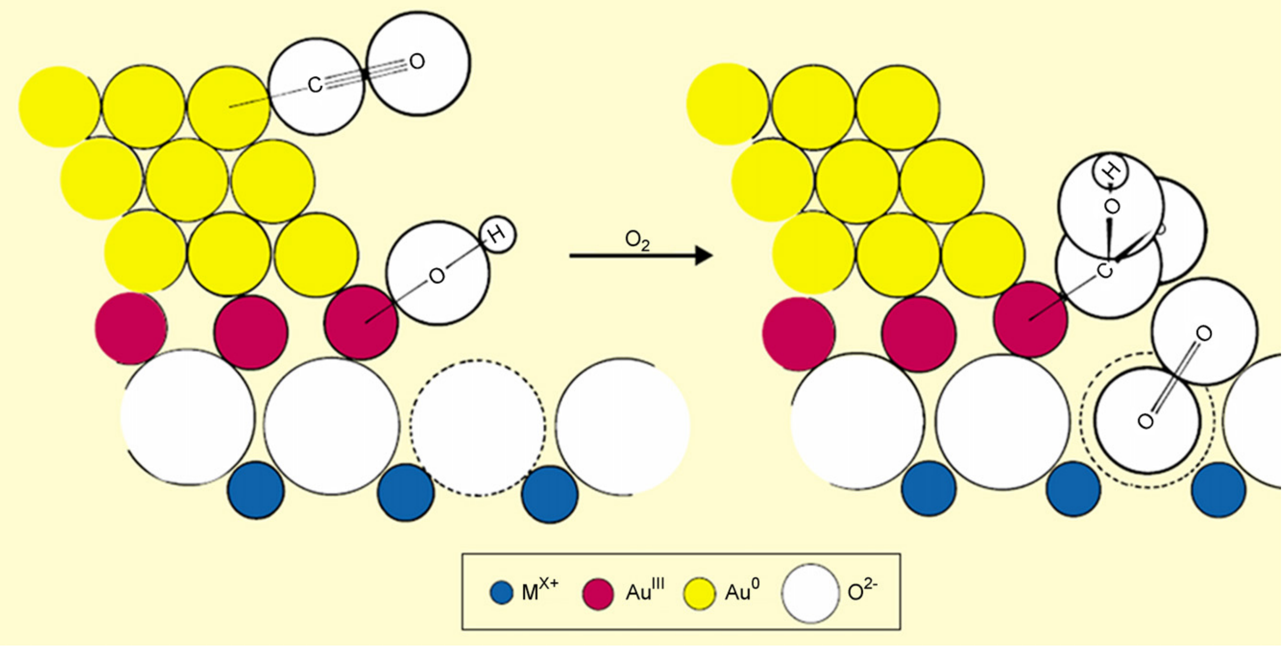

Fig. 1. Representation of an active site and possible reaction mechanism for CO oxidation catalyzed by supported gold as proposed by Bond and Thompson [24].

Bond and Thompson [24], in their review of the literature up to 2000, proposed a mechanism for CO oxidation catalyzed by supported gold that was an attempt to reconcile some apparently contradictory hypotheses (Fig. 1). Their proposed active site consists of nanoparticles incorporating both zerovalent and cationic gold, the latter positioned at the metal–support interface. Their suggestion of the presence of cationic gold was based on observations by various authors of ν_{CO} infrared IR bands characteristic of CO bonded to cationic gold, but they lacked evidence of such species in working catalysts and of their suggestion that cationic gold was a ‘‘glue’’ holding the nanoclusters to the support.

Haruta [31] presented a review of the literature in 2002 and proposed, on the basis of measurements of the kinetics of CO oxidation catalyzed by supported gold, that there are three temperature regions, with different kinetics and activation energies of the CO oxidation reaction. He suggested that at temperatures below 200 K, the reaction catalyzed by Au/TiO_2 takes place at the surfaces of small gold nanoparticles dispersed on the support, but at temperatures above 300 K, the reaction occurs at gold atoms at the perimeter sites of the supported gold nanoparticles [31].

Later, Kung and co-workers [29,32] investigated a γ-Al_2O_3-supported gold catalyst during cycles of deactivation and regeneration, observing rapid deactivation under reaction conditions and regeneration in flowing H_2 or water vapor at room temperature [29,32]. The results led the authors to propose that hydroxyl groups are part of the active sites. They suggested that the reaction occurred via the insertion of CO into Au^I–OH bonds to form hydroxycarbonyl species, which could then be oxidized to give bicarbonate species. These species were proposed to undergo decarboxylation to regenerate the Au^I–OH bonds and complete the catalytic cycle (Fig. 2). This reaction mechanism is related to Bond and Thompson’s, sharing the suggestion that cationic gold is involved, but it also includes the proposal that zerovalent gold activates O_2 [29,32]. There was no spectroscopic evidence of the presence of Au^0 or Au^I in the catalysts.

Although these early proposals lacked a strong foundation of experimental evidence of either active sites or the intermediate species, they helped to focus subsequent research.

3. Microscopic and spectroscopic evidence of possible active species and reaction mechanisms of CO oxidation catalyzed by supported gold

Although microscopic and spectroscopic methods for the characterization of solids have developed rapidly in recent decades, characterization of supported metal catalysts remains challenging. Thus, for example, although high-resolution TEM provides images of individual gold nanoparticles on supports, it is usually limited by the need for vacuum (although recent developments allow imaging of catalysts at low pressures).

In contrast, a number of spectroscopic techniques allow characterization of catalysts under realistic reaction conditions, but they give only average structural information. Because the structures are complex, spectroscopic results are generally limited by the possibility that only a small minority of the surface species—which may not be indicated by the spectra or images—actually catalyze a reaction, with most of the sample being catalytically inactive spectator species.

Because of these limitations of the available techniques, it is often most fruitful to characterize catalysts by multiple, complementary methods. For example, TEM and extended X-ray absorption fine structure (EXAFS) spectroscopy together are especially useful in determining the sizes of supported metal clusters or particles [33]. TEM provides evidence of individual metal clusters or particles, and EXAFS spectroscopy allows investigation of catalysts in reactive atmospheres (and most effectively at low temperatures—the fact that some supported gold catalysts are active at room temperature and lower temperatures is a strong advantage in the application of this method).

In general, because the structures of supported metal catalysts can be affected by reactive atmospheres, methods that can be applied to functioning catalysts are among the most

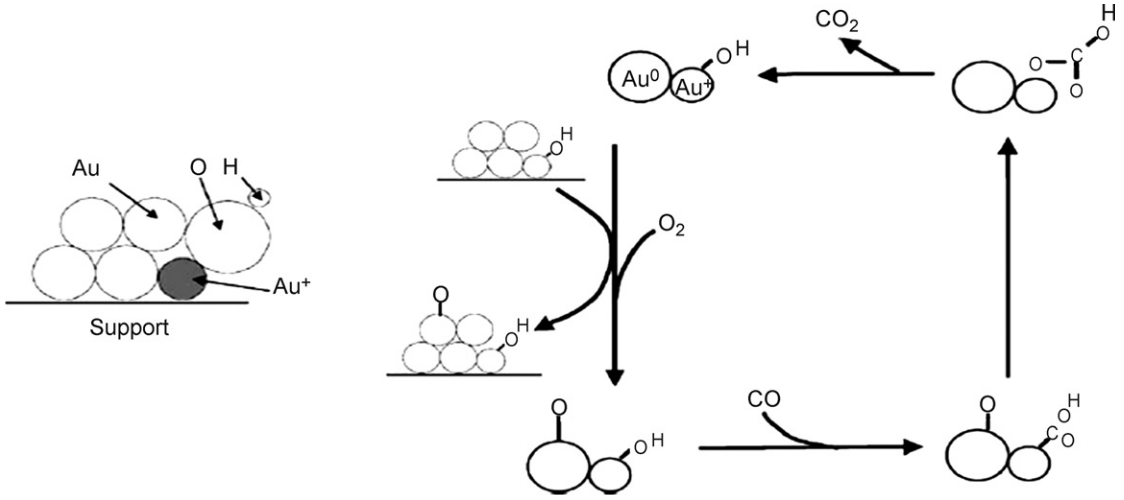

Fig. 2. Representation of an active site and possible reaction mechanism for CO oxidation catalyzed by γ-Al_2O_3-supported gold as proposed by Costello et al. [29].

informative. A principal goal of an investigation of a functioning catalyst is often identification of reactant- and product-derived ligands on the metal, which could be reactive intermediates in the catalysis. This approach has been helpful for understanding the activation of CO and O_2 on supported gold catalysts for CO oxidation. Specifics follow.

3.1. Activation of CO

IR spectroscopy has been the most widely used technique for investigations of the activation of CO on supported gold catalysts. The technique is especially valuable because spectra can be recorded under reaction conditions and because CO, besides being a reactant in CO oxidation, is an informative probe molecule. Although the positions of the ν_{CO} bands are often taken as evidence of a given oxidation state of supported gold, we emphasize that the frequencies of these bands are also affected by the coordination of the gold and the structures containing gold [34].

One of the complications of using CO as a probe for the structure of supported gold is that it can relatively easily reduce gold cations [34], possibly leading to aggregation of supported gold [35]. Furthermore, although IR spectroscopy has been used extensively to characterize supported gold catalysts, the assignments of ν_{CO} bands are varied and even contradictory in some cases, as summarized in Table 1. Table 1A is a summary of what were considered in recent publications to be the most appropriate assignments by the group of Hadjiivanov and co-workers [36], and Table 1B is a collection of recent assignments from the literature [37–46].

For example, Boccuzzi et al. [44] measured IR spectra at 298 K of various ZrO_2-supported gold samples prepared by deposition-precipitation before and after use as CO oxidation catalysts. Spectra in the ν_{CO} region characterizing the samples in the presence of CO before catalysis showed a band at 2108 cm^{-1}, which the authors assigned to CO bonded to Au^{0} (assumed to be present on the surfaces of gold nanoparticles). In contrast, spectra recorded with the samples in the presence of CO, after they had been used for catalysis, included a band at 2140 cm^{-1}, which the authors assigned to CO bonded to positively charged gold nanoparticles. Because the sample became less active for catalysis during operation, the authors suggested that the presence of positively charged gold in the deactivated samples was evidence of the lack of catalytic activity of electron-deficient gold, and they proposed that zerovalent gold nanoparticles were necessary for catalysis.

Table 1A
Broad grouping of assignments of ν_{CO} bands in IR spectra of supported gold samples, taken from Refs. [36,42]

ν_{CO} (cm^{-1})	Assignment
2101–2115	CO bonded to metallic Au
2130, 2143	Au$^{(\delta)+}$–CO/on Au^{0} clusters
2168	Au^{+}–CO
>2170	Au^{3+}–CO
>2200	Au^{3+}–CO in zeolite cation site

Table 1B
Assignments of ν_{CO} bands in IR spectra of supported gold samples

Sample	ν_{CO} (cm^{-1})	Assignment	Reference
Au/TiO_2	2140–2160	CO on Au^{I}	[37]
	<2130	CO on low coordinated Au^{0}	[37]
	2155	CO interacting by hydrogen-bonding with hydroxyl groups on TiO_2	[38]
	2090	CO adsorbed on Au^{0}	[39]
	2112	CO adsorbed on electron-deficient gold	[39]
Au/zeolite	2111–2122	CO linearly adsorbed on Au^{0}	[40]
	2169, 2172	CO adsorbed on oxidized gold	[40]
	2138–2142	CO linearly adsorbed on Au$^{\delta+}$	[40]
Au/NaY zeolite	2169	CO adsorbed on Au^{III}	[19]
	2133	CO adsorbed on Au^{I}	[19]
	2192	CO adsorbed on Au^{I}	[41]
	2128	CO adsorbed on Au^{0}	[41]
	2207	CO adsorbed on Au^{III}	[42]
	2205	Dicarbonyls of Au^{III}	[42]
	2000, 2033 and 2070	Tricarbonyls of Au^{0}	[43]
Au/ZrO_2	2108	CO adsorbed on Au^{0}	[44]
	2140	CO adsorbed on positively charged gold clusters	[44]
Au/SiO_2	2112	CO adsorbed on Au^{0}	[45]
Au/γ-Al_2O_3	2167	CO adsorbed on Au^{I}	[46]
	2112, 2105	CO adsorbed on Au^{0}	[46]

Recently, Henao et al. [39] reported IR spectra characterizing a TiO_2-supported gold catalyst prepared by deposition-precipitation; data were recorded at 213 K. In transient experiments, the authors found that CO adsorbed on Au^{0}, characterized by a ν_{CO} band present at 2090 cm^{-1}, reacts stoichiometrically with O_2 (giving CO_2), as evidenced by the decrease in the intensity of the 2090 cm^{-1} band. The authors estimated the rate of stoichiometric oxidation reaction from the decrease in intensity of the 2090 cm^{-1} band and found that it agreed approximately with the rate of CO oxidation catalysis at steady state at the same temperature. Although the authors also observed a ν_{CO} band at 2112 cm^{-1}, which had been assigned to CO adsorbed on electron-deficient gold, this band disappeared only relatively slowly in the presence of flowing O_2. Thus, the authors concluded that CO absorbed on Au^{0} is important for CO oxidation catalyzed by TiO_2-supported gold, in contrast to CO adsorbed on cationic gold, at least at 213 K. Note that there is a significant difference between the band assigned by Henao et al. to Au^{0}–CO species and that observed by Boccuzzi et al. [44] and that the band at 2112 cm^{-1}, which was assigned to CO bonded to electron-deficient gold, appears at a frequency that is low relative to those of bands that have been assigned to these species by other authors (Table 1B).

Venkov et al. [46] investigated the catalytic activities and structures of γ-Al_2O_3-supported gold samples prepared by deposition-precipitation, before and after various treatments, finding that the activity for CO oxidation of untreated samples increased with increasing temperature and was always higher at temperatures between 330 and 620 K than that of a sample calcined at 773 K. IR spectra in the ν_{CO} region recorded in the presence of a mixture of CO and O_2, and characterizing the initially prepared sample after if had been evacuated at 473 K, included a band at 2167 cm^{-1}, which the authors assigned to CO bonded to Au^I species present in gold nanoparticles; no bands characteristic of CO bonded to Au^0 were detected. In contrast, ν_{CO} spectra characterizing a sample that had been evacuated at 573 K include bands at 2112 and 2105 cm^{-1}, which the authors assigned to CO bonded to two types of Au^0–CO species [46]. On the basis of these results, the authors suggested that a Au^I/Au^0 redox couple was in play during catalysis. This suggestion is contrasted with the aforementioned inferences of Boccuzzi et al. [44] and Henao et al. [39] that cationic gold is not kinetically significant for CO oxidation catalysis under their conditions. However, we emphasize that the supports in the various catalysts were different, as well as the conditions of the CO treatments and the preparation of the samples.

Although the proposals for the activation of CO are controversial and the ν_{CO} assignments seem to be contradictory, the results of these investigations of various catalysts indicate that CO can be adsorbed on a number of supported gold species, including zerovalent and cationic gold. We cannot rule out the possibility that several of these species are important for catalysis, nor can we rule out the possibility that only one of them is catalytically active, with the others being spectators.

The various possibilities regarding sites for CO adsorption have led to an increasing interest in determining which species are involved in catalysis, with a focus on investigations intended to elucidate the oxidation state of gold in the active sites.

3.2. Role of oxidation state(s) of supported gold for CO oxidation catalyzed by supported gold

Although the early proposals of active species suggested that the oxidation state(s) of supported gold played a role on the activity of CO oxidation catalysts, spectroscopic results characterizing various catalysts [37–46] have seemingly been contradictory and added to the controversy. However, it is necessary to consider that the interpretation of spectroscopic data is affected by the complexity of the structures of the catalysts, and species that are identified spectroscopically might not necessarily be part of the active sites, especially when spectra are recorded under non-catalytic conditions.

Recently, Willneff et al. [47] used synchrotron X-ray photoelectron spectroscopy (XPS) to investigate TiO_2-supported gold catalysts during CO oxidation catalysis. The XP spectra show two components in the Au4f region. The value of the binding energy (BE) of one component is similar to that characterizing zerovalent gold, whereas the BE of the other component is shifted by $+0.9 \pm 0.1$ eV with respect to that of metallic gold, indicating changes in the electronic structure of gold as a result of the imposition of the reactive atmosphere. These changes are suggestive of changes in the gold oxidation state. The contrast between the spectra recorded under reaction conditions and those recorded in the absence of reactants emphasizes the importance of characterizing functioning catalysts; however, one must consider that the partial pressures of CO and O_2 (0.1 mbar, each) were significantly lower than those used under potentially practical catalytic conditions.

X-ray absorption near edge structure (XANES) spectroscopy is another technique that provides information about the local electronic structure of supported metals and can be used as a basis for estimation of the gold oxidation state(s)—and XANES data can be recorded under potentially practical reaction conditions (simultaneously with EXAFS spectra). Au L_{III}-edge XANES peak locations and intensities characterizing reference materials containing gold in various oxidation states [48–50] provide a basis for interpretation of XANES spectra of supported gold catalysts, but, as for IR spectroscopy of adsorbed CO, we emphasize that the spectra depend on the surroundings of the Au atoms and not just their oxidation states.

XANES data characterizing complexes containing Au^{III} typically show a prominent feature (white line) in the Au L_{III} near-edge region, centered at an energy 4 eV higher than that of the edge. This absorption peak is missing from the spectra of metallic gold because of the complete occupancy of the *d* states (the gold ground state electron configuration is $[Xe]4f^{14}5d^{10}6s^1$). Furthermore, the XANES spectrum of Au^{III} includes a shoulder at an energy 15 eV beyond the absorption edge and a broad shoulder at 50 eV beyond the edge, whereas the spectrum of Au^0 includes a shoulder at 15 eV and intense peaks at 25 and 50 eV beyond the Au L_{III} edge [48–50].

XANES provides essentially qualitative information, which can be complemented with quantitative information from temperature-programmed methods such as temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) [35]. Guzman and Gates [18] used these methods in an investigation of the oxidation states of gold in MgO-supported gold catalysts during CO oxidation catalysis. The catalysts contained gold nanoparticles of approximately 30 Å in average diameter, as shown by EXAFS spectroscopy. XANES spectra were recorded at steady state for catalysts with various activities in a flow reactor; the activities were changed by changing the CO:O_2 ratio in the feed. The spectra show features characteristic of mixtures of Au^I and Au^0. The relative quantities of cationic and zerovalent gold were determined in TPR and in TPO experiments (which were consistent with each other), with the results showing an increase in catalytic activity with an increasing fraction of the gold that was cationic. The data indicate a role of cationic gold in the catalytic sites, but they do not determine whether zerovalent gold plays a role (Fig. 3).

Recently, Hutchings et al. [20] investigated the oxidation states of gold in α-Fe_2O_3-supported gold catalysts for CO oxidation. Iron oxide-supported gold catalysts are among the most active for CO oxidation [23]. The authors used a set of complementary characterization methods, including X-ray photoelectron, X-ray absorption, and Mössbauer effect spectroscopies, combined with TEM, comparing the structures of active and almost inactive catalysts and finding that the most active catalysts contained cationic gold (with small amounts of

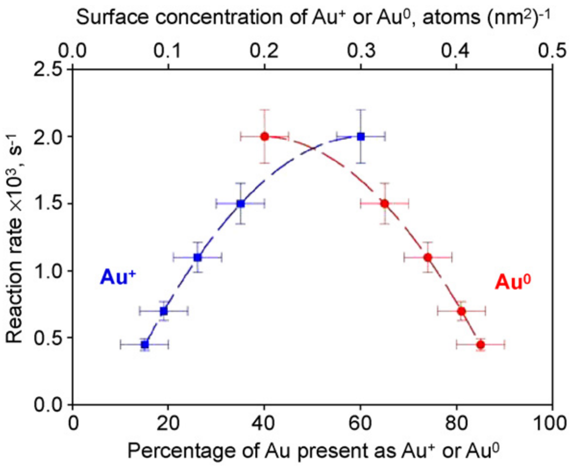

Fig. 3. Correlation of the activity of functioning MgO-supported gold catalysts with the percentage of gold that was cationic; the ratio of cationic to zerovalent gold was regulated by the ratio of O_2 to CO in the feed [18].

zerovalent gold), whereas no evidence of cationic gold was found in the almost inactive catalysts. These results are consistent with those of Guzman and Gates [18] and demonstrate that cationic gold plays a role in CO oxidation catalysis. However, because a few gold nanoparticles (5–7 nm in average diameter) were present even in the most active catalysts, a possible role of Au^0 could not be entirely ruled out.

In an attempt to determine whether cationic gold alone is catalytically active for CO oxidation, Fierro-Gonzalez et al. [19,51] synthesized CO oxidation catalysts containing cationic gold in the absence of detectable zerovalent gold. For example, they synthesized a catalyst from $Au^{III}(CH_3)_2(C_5H_7O_2)$, initially physisorbed in zeolite NaY [19]. This catalyst was initially active for CO oxidation in a flow reactor, but its activity decayed, and when a steady state was attained the activity was an order of magnitude less than that observed initially. EXAFS spectra characterizing the functioning catalyst at steady state showed that the gold was present essentially as mononuclear species, as evidenced by the lack of detectable Au–Au contributions in the spectra [19]. IR spectra of the functioning catalyst showed that carbonyls of Au^{III} were present initially, being converted into carbonyls of Au^I as the activity declined. XANES spectra of the functioning catalyst measured at steady state include features characteristic of Au^I; consistent with the EXAFS results, no XANES features characteristic of Au^0 were detected in the spectrum of the functioning catalyst. Thus, these data indicate catalytic activity of isolated Au^{III} sites and of isolated Au^I sites in the zeolite, with the latter having an order-of-magnitude-lower activity than the former (Fig. 4).

Simple as this mononuclear zeolite-supported catalyst is in structure, it offered a good opportunity for characterization of structural changes in real time as the environment changed. Time-resolved EXAFS spectroscopy was used to follow changes in the coordination sphere of the gold, as evidenced by changes in Au–O contributions in the spectra [52]. Exposure of an initially prepared sample to a mixture of CO and O_2 (with excess O_2) led to the rapid formation of cationic gold complexes, each bonded to approximately two O atoms of the zeolite support [52]. Further exposure to the CO + O_2 mixture led to the breaking of one Au–O bond, as evidenced by a decrease in the Au–O coordination number from approximately 2 to approximately 1 [52]. This change, however, was not attributed to reduction or aggregation of the supported complexes, because (a) no evidence of Au–Au contributions was found in the EXAFS data, (b) XANES spectra recorded simultaneously do not show any features characteristic of zerovalent gold, and (c) ν_{CO} bands characteristic of CO bonded to Au^{III} and ν_{CH} bands (inferred to represent methyl groups on cationic gold) were evident in IR spectra measured separately under the same conditions [52]. The lack of reduction of the gold was explained by the inference that, as Au–O bonds were broken, new ligands, such as carbonyls and formates, were bonded to the gold [52]. Furthermore, when the flow of CO and O_2 was replaced by flow of He, the Au–O coordination number increased back to approximately 2, evidently without changes in the oxidation state of the gold in the supported complexes. These results show that, under some conditions, it is possible to avoid reduction of supported gold during CO oxidation catalysis, even as the coordination sphere of the gold is modified in the presence of reactive ligands. The results demonstrate the opportunities for determining details of reactive species on catalyst surfaces by spectroscopic methods when the catalysts are structurally simple (Fig. 5).

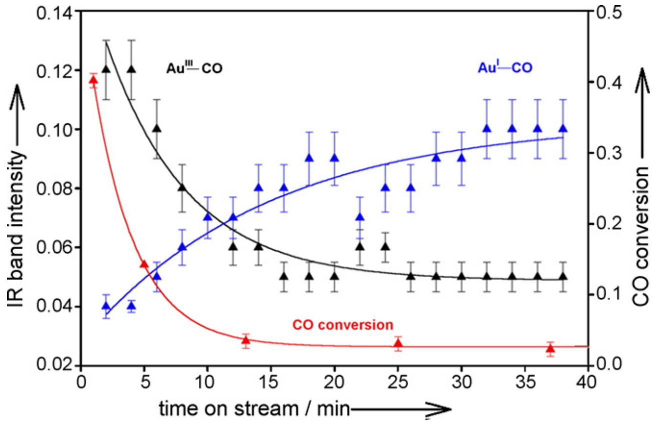

Fig. 4. Dependence of CO conversion and the reduction of Au^{III} to Au^I during CO oxidation catalyzed by zeolite NaY-supported gold complexes [19].

Although the zeolite-supported gold complex catalyst has provided information about the reactivity and, by inference, the catalytic properties, of cationic gold, one might question whether the results get to the heart of the matter about the catalytic activity of supported gold, because this zeolite-supported catalyst is much less active than some others. Table 2 provides a comparison of the activities at steady state of various catalysts (the comparison is not optimal because of the various conditions used by various authors). Note that the zeolite-supported complexes are roughly an order of magnitude less active than the most active supported gold catalysts under the conditions represented in the table.

Consequently, efforts were made to prepare analogous mononuclear Au^{III} complexes on a support that would give catalysts with activities comparable to those of the most active

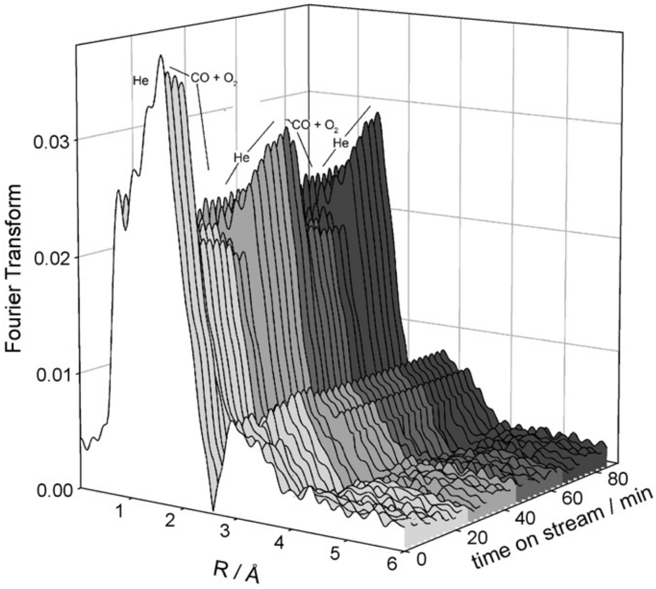

Fig. 5. Radial distributions of time-resolved EXAFS spectra recorded as Au^{III} complexes bonded to zeolite NaY were successively exposed to He (no shading, gray, darker gray) and a catalytically reacting mixture of CO and O_2 (light gray, dark gray) [52].

gold catalysts operating at room temperature. With $Au(CH_3)_2$(acac) again used as the precursor, cationic gold species were bonded to the surface of high-area porous (nanostructured) La_2O_3 [51]. This sample was found to be almost as active as the most active supported gold catalysts under the conditions investigated (Table 2) [23], and the activity was maintained for more than 50 h on stream in a flow reactor operated at steady state. Again, EXAFS spectra characterizing the functioning catalyst at steady state indicated the lack of detectable Au–Au contributions, consistent with the presence of mononuclear gold complexes, and XANES spectra recorded simultaneously show features characteristic of Au^{III} complexes. Although it could be argued that the suggested presence of Au^{III} is not consistent with the intensity of the white line in the XANES spectra characterizing this sample (this intensity is not the same as that observed in the XANES spectra of many Au^{III} complexes), the intensity of the white line is not a direct measure of the oxidation state of a metal, also being affected by the nature of ligands bonded to the metal [48–50] and, by inference, the support, as shown by FEFF8 calculations done for zeolite-supported platinum clusters [53].

The differences in activities and stabilities of the mononuclear gold complexes in zeolite NaY and on La_2O_3 are in line with the suggestion that both the support and ligands on the metal influence the catalytic properties. It was reported recently that gold supported on rare-earth metal oxides, such as CeO_{2-x} [54] and Y_2O_3 [55], is highly active for CO oxidation. The CeO_{2-x}-supported gold catalyst contained gold nanoparticles with an average diameter of 3–4 nm, and XANES spectra characterizing the functioning catalyst at steady state provided evidence of mixtures of cationic gold as well as zerovalent gold nanoparticles [54]. Furthermore, EXAFS spectra characterizing the functioning catalysts indicate the presence of oxygen atoms near gold atoms, characterized by a relatively long Au–O distance, 3.5 Å (this average distance is too long to be a bonding distance). Such Au–O contributions were also found in EXAFS spectra characterizing the functioning La_2O_3-supported gold complexes [51], suggesting that similar oxygen species on the support might play a role in the catalysis (these species are discussed below).

3.3. Activation of O_2

Raman spectra characterizing the functioning CeO_{2-x}-supported gold catalysts gave evidence of oxygen species in the form of peroxides and superoxides. Raman spectra of the catalyst incorporating these surface species showed that they reacted stoichiometrically with CO to give CO_2, consistent with the inference that they were reactive intermediates that resulted from the activation of oxygen on the surface of the nanocrystalline support [54]. Such oxygen species are known to be formed and stabilized on redox-active supports such as CeO_2 [56], but this observation leaves open the question of how O_2 may be activated on gold supported on non reducible metal oxides.

Thus, the activation of oxygen in CO oxidation catalyzed by supported gold remains a matter of controversy. Some authors [57,58] have proposed that oxygen is adsorbed molecularly, whereas others [59] have suggested that dissociative adsorption of oxygen is necessary, and some [29,32] have claimed that support hydroxyl groups can be considered as reactive oxygen species.

Table 2
Comparison of activities of supported gold catalysts for CO oxidation [48]

Catalyst	Average Au cluster diameter (nm)	T (K)	TOF (s^{-1})	Time on stream in flow reactor (h)	Reference
Au/La_2O_3	[a]	298	1×10^{-2}	50	[51]
Au/zeolite NaY	[a]	298	3×10^{-3}	1	[19]
Au/γ-Al_2O_3	2.4	273	2×10^{-2}	>0.5	[32]
Au/Fe_2O_3	<1[c]	293	[d]	10	[66]
Au/CeO_{2-x}	4	278	[b]	10	[54]

[a] No gold clusters detected in sample; gold inferred to be present as mononuclear complexes, as evidenced by the lack of detectable Au–Au contributions in the EXAFS spectra [48].

[b] The authors did not report a TOF, but instead reported specific reaction rates >0.4 $mol_{CO}\,h^{-1}\,g_{Au}^{-1}$.

[c] Inferred, as the authors [66] did not observe any gold nanoparticles by TEM.

[d] TOF indeterminate because CO conversion was 100% under reported reaction conditions [66].

Stiehl et al. [57] investigated the adsorption of oxygen on gold clusters deposited on TiO_2 (110). The adsorption experiments were performed in an ultrahigh vacuum molecular beam surface scattering apparatus at 77 K [57]. Oxygen was dosed via a supersonic, radio-frequency generated plasma-jet source. Thermal desorption spectra indicated that exposure to oxygen had led to both molecularly and dissociatively adsorbed oxygen on the gold [57]. Later, Stiehl et al. [58] observed that adsorption of oxygen on their Au/TiO_2-(110) samples followed by CO exposure led to CO_2 production. Because more CO_2 formed when the treated samples contained more molecular oxygen than when only dissociated oxygen was present, the authors suggested that molecularly adsorbed oxygen on supported gold participates in CO oxidation catalysis [58].

In contrast, Deng et al. [59] recently reported that that the dissociation probability of oxygen on Au (111) increases when the surface has been pre-covered with atomic oxygen. The authors concluded that their results have implications for CO oxidation catalyzed by supported gold, suggesting that the activity of the catalysts might be the result of enhanced oxygen dissociation on low-coordinated gold atoms [59].

In summary, there are experimental results providing evidence of various routes to activation of oxygen on gold catalysts, and more work is needed to winnow the possibilities and generalize the results.

3.4. Proposals of active species based on theory

Theory is gaining importance in the arsenal of catalyst characterization tools, and a number of stimulating theoretical contributions to the field of catalysis by supported gold have emerged in the preceding few years. Theoretical results are valuable in complementing the aforementioned experimental characterization methods by predicting the stabilities of supported gold species. Theoretical characterization of supported gold catalysts has been limited to structurally simplified catalysts, and only in 2006 have there been contributions that begin to account for conditions approaching catalytic conditions. For example, most of the reported theoretical models fail to include species that are present in real catalysts and likely to influence the catalytic activity, such as hydroxyl groups on supports and adsorbed water.

Theory has been used to determine how CO could be activated for catalysis on supported gold, and the calculations predict that cationic [60], zerovalent [61], and anionic gold [62] are capable of adsorbing CO. The predictions are broadly in agreement with the experimental results presented above regarding the oxidation state(s) of gold in the active sites for CO oxidation catalysis, but recent reports [63,64] indicate that accounting for changes in external conditions, such as partial pressures of the reactants and temperature, significantly affects the predictions based on density functional theory (DFT) and *ab initio* methods.

For example, Wang and Hammer [63] reported calculations at the DF level of the adhesion and catalytic activity of Au_7 clusters on TiO_2 (110). Their calculations predict a strong adhesion of the gold clusters to TiO_2 (110) surfaces containing terminal OH groups (oxidized TiO_2 (110)). The adsorbed clusters become cationic as Au–O bonds form between gold atoms in the clusters and oxygen atoms of the support. This prediction is in broad agreement with reported EXAFS results (of various authors [19,20,33,35,50–53]), which consistently give evidence of such bonds—and with XANES spectra indicating the presence of cationic gold. The inference of cationic gold present at metal–support interfaces might be general, as EXAFS spectra characterizing many supported metals indicate the presence of similar metal–oxygen bonding distances [33].

Rösch's and co-workers [65] used DFT to investigate small supported metal clusters that might, to a first approximation at least, be considered prototypical of supported group-8 metal clusters, namely, zeolite-supported Rh_6; the calculated Mulliken charges indicate that the rhodium atoms at the rhodium–support interface are positively charged, essentially in agreement with expectations for what would be referred to formally as Rh^{I} [65].

According to the calculations of Wang and Hammer [63], their TiO_2-supported cationic gold clusters are able to adsorb both molecular and atomic oxygen, which can then react with CO with relatively small energy barriers to form CO_2. These authors referred to Au^{I} when describing the Au atoms bonded to the support. In contrast, their calculations carried out for models in which the support was a model of TiO_2 (110) containing bridging OH groups (reduced TiO_2 (110)) did not indicate strong adhesion of the gold clusters. Because a reduced TiO_2 (110) surface is less similar to a realistic high-area TiO_2 support than the oxidized TiO_2 (110) surface, the results of Wang and Hammer characterizing the models reported for the oxidized TiO_2 (110) surface were considered by them to be more relevant to practical catalysts than the others—and to be broadly consistent with the experimental results demonstrating a role of cationic gold.

Recently, Laursen and Linic [64] reported DFT and *ab initio* thermodynamic calculations showing differences in the electronic structure of gold on various metal oxide supports. Their calculations show that the oxidation state(s) of supported gold are affected by the presence of reactants, with gold predicted to be cationic when the oxygen chemical potential is chosen to imitate practical reaction conditions [64].

Taken together, these results show that, like spectroscopy, theory is most informative when models are chosen to take account of the influence of reactants and conditions that approach catalytic reaction conditions.

4. Summary and outlook

Supported gold catalysts for CO oxidation have attracted wide attention because of their potential use for practical applications. Although these catalysts have been investigated extensively, consensus has not been reached regarding the nature of the active site(s) and the reaction mechanism(s). Most of the reported research attempting to clarify these matters has been focused on supported gold species that were formed initially or formed by treatments with reactants CO or O_2 or products formed in CO oxidation catalysis. Spectroscopic data have provided evidence of various sites for CO adsorption, including anionic, zerovalent, and cationic gold.

The weight of evidence, in our judgment, now points clearly to the involvement of cationic gold in the active sites of numerous supported gold catalysts, including site-isolated mononuclear gold cations on supports. There is also convincing evidence of catalysis by zerovalent gold at low temperatures. Thus we consider it likely that more than one reaction channel is operative in CO oxidation catalysis by supported gold. Because IR data, among others, indicate that CO is only weakly adsorbed on zerovalent CO (and more strongly adsorbed on cationic gold), we hypothesize that coverages of the zerovalent gold by CO in supported gold catalysts at temperatures higher than about room temperature may be small, and thus that reaction channels involving CO bonded to cationic gold may be the more significant kinetically under such conditions. Recent theoretical work, cited above, supports this hypothesis. We suggest that this statement might be of help in guiding future research on gold-catalyzed reactions.

We emphasize that the issues of oxygen activation on supported gold catalysts also need resolution, as the existing proposals are contradictory, invoking involvement of either molecular or dissociated oxygen in catalysis. Water, hydroxyl groups, and peroxide species on supports are plausible candidates for activated oxygen species.

The rapid growth in interest in catalysis by highly dispersed supported gold, an emerging focus on understanding of the phenomena rather than discovery of new catalytic reactions, and the expected merging of theoretical and experimental approaches lead us be optimistic that understanding of these fascinating catalysts will develop rapidly and that it will increasingly help in the prediction of new catalytic properties of highly dispersed gold.

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