

# Supported Au catalysts for low temperature CO oxidation

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## Abstract

Supported Au catalysts are very active for low temperature CO oxidation. However, the reported activity from different laboratories for apparently similar catalysts can differ quite substantially. Recent progress in resolving this difficulty is summarized. Residual chloride in the sample is a very effective poison of the active site. The effect of water vapor on the catalytic activity differs depending on the support and the residual chloride content. A model of the active site, which consists of an ensemble of metallic Au atoms and Au cations with hydroxyl ligands, the reaction mechanism for CO oxidation, and the mechanism for deactivation during reaction as well as regeneration are discussed with respect to the available data.

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## 1. Introduction

The interest in studying supported Au catalysts has increased substantially since Haruta et al. discovered that these catalysts are exceptionally active for low temperature CO oxidation [1]. Compared to a highly dispersed supported Pt catalyst, Au catalysts can be an order of magnitude more active [2]. The attention arises not only from the commercial implication of this discovery, but also from the desire to answer the question of why the normally inert Au material can catalyze chemical reactions so effectively. A better understanding of the origin of the catalytic activity could lead to the discovery of other novel reactions. Already, supported Au catalysts have been shown to be active for selective reduction of NO by hydrocarbon in the presence of a high concentration of oxygen [3,4], selective oxidation of CO in a hydrogen stream [5,6], selective oxidation of hydrocarbons [7], epoxidation of propene [8], and selective hydrogenation [9,10].

Most of the studies to date have focused on the unusual low temperature CO oxidation activity. The results suggest that the activity is highly sensitive to the details in the preparation procedure and the catalytic testing conditions. Indeed, as summarized by Bond and Thompson [11] and others

(e.g., [12–14]), large variations in observed catalytic activities can be found reported in the literature over catalysts of similar compositions. This is illustrated by the data in Table 1. Among the various supported Au catalysts, Au/Al<sub>2</sub>O<sub>3</sub> is perhaps one that shows the widest variation, ranging from being very inactive [15,16] to being comparable or better than Au/TiO<sub>2</sub> [12,17]. It is important to understand the origin of the wide variations in order to eliminate them.

Ultimately, the variation in catalytic activity is due to the lack of control in the generation of the active site, either in terms of its number or its properties. Therefore, identifying the nature of the active site and the corresponding reaction mechanism would be of great value.

Significant progress has been made recently in understanding the preparation chemistry and elucidating the active site. Here, we briefly summarize the more recent results in these areas, with an emphasis on those that provide information on the underlying chemistry, and offer our view of the current state of this particular area of catalysis. Earlier work has been summarized in other reviews [11,18].

## 2. Preparation of supported Au catalysts by deposition–precipitation

Active Au catalysts can be prepared using different methods. Coprecipitation, impregnation, and deposition–precipitation are the most commonly used, and they of-

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Table 1  
Comparison of CO oxidation activities without water in the feed stream<sup>a</sup>

Catalyst	Prep. <sup>b</sup>	$D_{Au}$ (nm) <sup>c</sup>	$P_{O_2}$ (kPa)	$P_{CO}$ (kPa)	$T$ (K)	Rate <sup>d,f</sup>	TOF (s <sup>-1</sup> ) <sup>e,f</sup>	Ref.	
Au/TiO <sub>2</sub>	CP	4.5	4.9	4.9	313	2.57E-02	0.095	[19]	
	DP	1.7	20	1	273	3.41E-02	0.06	[16]	
	CVD	3.8	20	1	273	2.27E-03	0.02	[16]	
	OMD	4.7	3.67	3.67	293	2.0E-02	0.27	[13]	
	DP	2.5	20	1	300	4.0E-02	0.15	[20]	
DP	2.9	20	1	300	1.2E-01	0.62	[20]		
Au/Ti(OH) <sub>4</sub>	IAH	3	20	1	300	9.6E-03	0.05	[21]	
Au/Fe <sub>2</sub> O <sub>3</sub>	CP	3.6	20	1	203	2.6E-03	0.021	[22]	
Au/Fe(OH) <sub>3</sub>	IAH	2.6	20	1	203	6.4E-03	0.026	[23]	
Au/Al <sub>2</sub> O <sub>3</sub>	CP	3.5	20	1	273	8.0E-04	0.006	[16]	
	DP	2.4	20	1	273	5.7E-03	0.02	[16]	
	DP	3–5	2.5	1	295	3.1E-02	0.17–0.46	[12]	
	CVD	3.5	20	1	273	1.34E-03	0.01	[16]	
	DP, pH 7		4	0.5	1	298	4E-04	0.004	[14]
				20	1	298	6E-04	0.006	[14]
	DP, pH 9		< 4	0.5	1	298	9E-04	< 0.009	[14]
20				1	298	1.8E-03	< 0.018	[14]	
DP, pH 11		< 4	0.5	1	298	1.2E-03	< 0.012	[14]	
Au/SiO <sub>2</sub>	CVD	6.6	20	1	298	7.5E-04	0.02	[16]	

<sup>a</sup> The data of Park and Lee [31] are not included because their reported rates are much higher than those of others, although the experimental conditions are similar.

<sup>b</sup> IAH, impregnation of AuPPh<sub>3</sub>NO<sub>3</sub> onto as-precipitated hydroxides; CP, coprecipitation; DP, deposition–precipitation; CVD, chemical vapor deposition; OMD, impregnation of AuPPh<sub>3</sub>NO<sub>3</sub> onto the oxide.

<sup>c</sup> Average diameter of Au particles.

<sup>d</sup> Quasi-steady state (time-on-stream > 30 min) CO oxidation rate, in mol CO (mol Au-s)<sup>-1</sup>, except for [19], which was obtained during the first 30 min.

<sup>e</sup> Turnover frequency based on surface Au atoms.

<sup>f</sup> These values are from the original reference if available. Otherwise, rates are calculated from the TOF reported, or vice versa, assuming hemispherical Au particles.

ten result in quite different catalysts as shown in Table 1. Typically, coprecipitation or deposition–precipitation methods are more desirable than impregnation, especially when chloroauric acid is used as the precursor. Various processing variables have been studied, which include pH, temperature, and concentration of the preparation solution, calcination temperature, reduction temperature, and reduction/oxidation cycling. Some of these studies have helped elucidate the underlying chemistry that causes variation in the properties of the final solid.

One of the better understood variables is pH in the deposition–precipitation procedure. In such a preparation method, HAuCl<sub>4</sub> is used as the metal precursor. The chloroauric anion hydrolyzes in solution to form Au(OH)<sub>x</sub>Cl<sub>4-x</sub><sup>-</sup>. The extent of hydrolysis depends on the pH, Au, and Cl concentrations [24]. It has been found that preparation at a pH ranging from 7 to 8 is preferable depending on the oxide support [17]. At this pH, the value of  $x$  is close to 3. At lower pH's there is less hydrolysis of the Au–Cl bond. Furthermore, at pH's below the isoelectric point of the support, the surface is positively charged and is capable of adsorbing more of the negatively charged gold species. This results in not only a larger gold loading, but also a high concentration of chloride on the surface. The presence of chloride increases the mobility of Au on the support, leading to large Au particles and some vaporization of Au from the solid upon calcination [25]. At pH's above the isoelectric point of the oxide, adsorption of the negatively charged

Au(OH)<sub>x</sub>Cl<sub>4-x</sub><sup>-</sup> complex decreases rapidly, resulting in a lower gold loading. However, there will also be less chloride at the catalyst surface, so small gold particles can be formed. Therefore, there is a narrow range of pH where sufficient Au can be deposited onto the support with minimal chloride in the Au complex. It is interesting to note that in order to obtain a high dispersion of Au in the final catalyst, it is desirable that the precursor Au complex is adsorbed as an anion. If the AuCl(OH)<sub>3</sub> precursor is added to a dilute suspension of the support while keeping the pH at 7, Au(OH)<sub>3</sub> would be the predominant species due to the low initial chloride concentration [24]. Its low solubility causes precipitation, resulting in a poor catalyst.

Recently, another effect of the pH of the solution was identified. In addition to Au(OH)<sub>x</sub>Cl<sub>4-x</sub>, Cl ions are adsorbed onto the oxide. Fig. 1 shows the chloride uptake by alumina. The amount of chloride adsorbed decreases rapidly as the isoelectric point is approached, when the oxide surface is no longer positively charged. The adsorbed Cl has two effects [25]. One effect is to cause agglomeration of Au particles during calcination, such that the average Au particle size is larger in samples with a higher residual chloride content. The adsorbed chloride can be displaced by other anions. In the earlier preparations, Mg citrate was added to the preparation solution to obtain an active catalyst [26]. We believe that the primary function of the citrate is to displace chloride from the support and possibly from the Au(OH)<sub>x</sub>Cl<sub>4-x</sub> complex [25]. Chloride can also be removed by reduction or

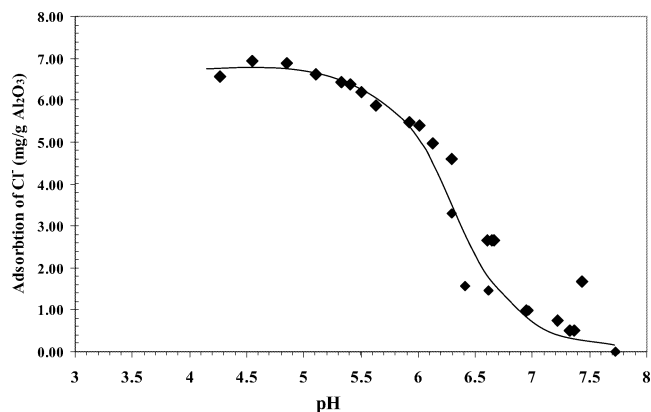


Fig. 1. Chloride uptake by alumina as a function of pH.

calcination [27,28]. However, high temperature calcination or reduction causes agglomeration of Au particles.

Residual chloride also poisons the active site. Addition of chloride to an active catalyst lowers its activity significantly. The quantitative effect depends on the sample. In general, for a 1 wt% Au/Al<sub>2</sub>O<sub>3</sub> catalyst, chloride in the amount of Cl/Au atom ratio of 0.1 would decrease the activity by approximately one half, even though most of the chloride is adsorbed on the alumina [25]. If the chloride adsorption site on the alumina is first blocked by the presence of phosphate, then a chloride content as low as 0.0006 (atomic ratio) Cl/Au exhibits a detectable inhibition effect. In the presence of moisture in the gas phase, the adsorbed chloride is mobile. Thus, the activity decreases with time-on-stream if a chloride-free catalyst is in contact with a chloride-containing solid (Fig. 2), whereas a chloride-poisoned sample regains some of its activity due to displacement of the chloride from the active site by water.

How chloride poisons the catalyst depends on the model for the active site. In the chemical model described later,

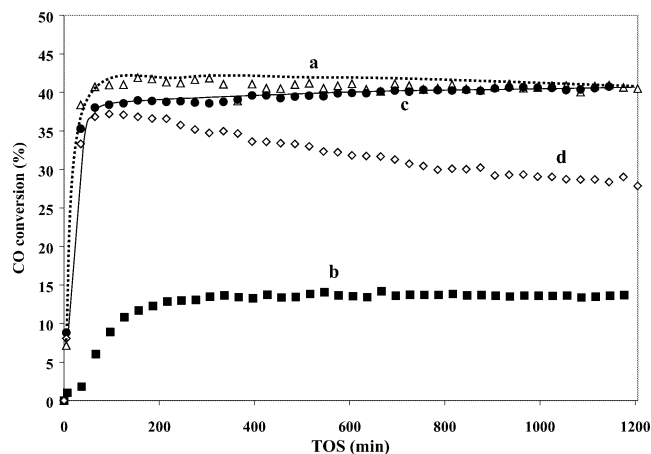


Fig. 2. Time-on-stream behavior of CO conversion Au/Al<sub>2</sub>O<sub>3</sub> prepared from Au acetate (a) as calcined, (b) with 0.3 wt% chloride added, (c) sample a mixed with 0.02 g Al<sub>2</sub>O<sub>3</sub>, (d) sample mixed with Al<sub>2</sub>O<sub>3</sub> that contained 0.15 wt% Cl. Feed composition: 1% CO, 0.5% O<sub>2</sub>, 49.5% H<sub>2</sub> in He; 100 °C (from [25]).

chloride displaces the hydroxyl from the Au cation, rendering the site inactive. This is reversible, and water can hydrolyze the Au-chloride bond to reform the hydroxyl ligand. In the quantum-size effect model [29], an adsorbed chloride on a Au particle changes its electronic property.

More recently, the attention has turned to the effect of calcination temperature. It was reported that for Au/TiO<sub>2</sub> [30,31], Au/iron oxide [31–33], and Au/MnO<sub>x</sub> [34] catalysts, calcination at a mild temperature (100–200 °C) resulted in more active catalysts than calcination at higher temperatures. There are also reports that uncalcined Au/Al<sub>2</sub>O<sub>3</sub> [17] or Au/Y [35] can be very active. The implication of these observations on the nature of the active site will be discussed later.

### 3. Nature of the active site and reaction mechanism

The nature of the active site for CO oxidation on supported Au catalysts and the reaction mechanism are also subjects of great research interest. Although active catalysts commonly contain small, 2–5 nm Au crystallites, size alone does not seem to be a sufficient factor for high activity (e.g., [17,19,25]). There have been a number of proposals of the active site, which include gold-support interface [36,37], small Au clusters that possess nonmetallic electronic properties due to a quantum-size effect [29], and surface step and strain defects [38]. A chemical model that involves an ensemble of metallic Au atoms and Au cations with hydroxyl ligands has been suggested [11,12,39] (Fig. 3). The Au cation must be stable in a reducing environment and also in the neighborhood of metallic gold. It seems more likely that Au(I) would be able to satisfy these requirements than Au(III). Therefore, Au(I)–OH has been proposed as the cationic Au component.

There appears to be increasing support that the active site involves the perimeter of the Au particles or the Au-support interface [7,19,30,37,40] and for the presence of Au cations in the active catalysts [32,33,41,42] although their role in the reaction is not yet accepted unequivocally [40]. In the study of Au/Mg(OH)<sub>2</sub> catalyst with <sup>197</sup>Au Mössbauer spectroscopy, the most active catalyst was found to contain the highest concentration of Au(I) [43].

While there is spectroscopic evidence of the presence of Au cations in an active catalyst, there is only inferential evidence of the presence, and particularly the participation,

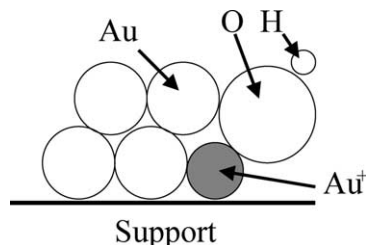


Fig. 3. Model of active site for CO oxidation (from [12]).

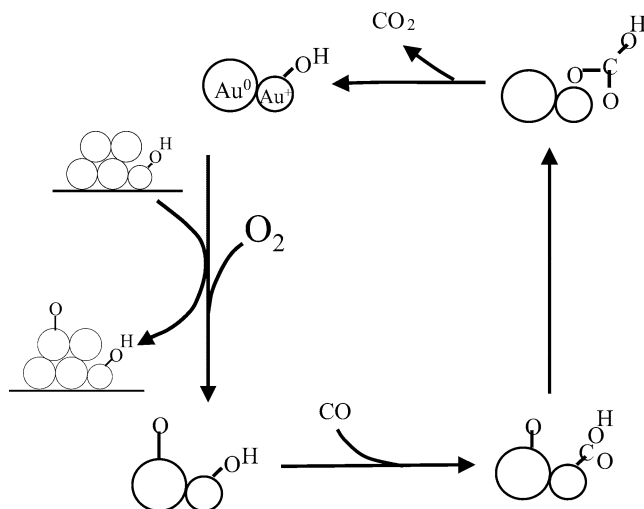


Fig. 4. Mechanism of CO oxidation on Au catalysts.

of hydroxyl groups in the reaction. The effect of water in the CO reaction and the fact that water regenerates a CO-reaction deactivated catalyst are supporting evidence for the involvement of hydroxyl groups [12,39]. A reaction mechanism that is consistent with these observations is shown in Fig. 4 [12]. In this mechanism, the reaction proceeds by insertion of an adsorbed CO into an Au–OH bond to form a hydroxycarbonyl. Stable hydroxycarbonyl complexes of many group VIII metals have been prepared [44], and their formation from the CO and OH<sup>−</sup> ligands is enhanced by lower electron density at the metal [45]. The hydroxycarbonyl is oxidized to a bicarbonate, which is then decarboxylated to Au–OH and CO<sub>2</sub>. The decarboxylation step is likely similar to a step in the water–gas shift reaction, which is catalyzed effectively by supported Au catalysts [46]. This proposed cycle does not involve participation by OH radical-like species [47] or superoxide [36] or direct participation of the support [48], as suggested by others. While there is evidence for the superoxide species for Au/TiO<sub>2</sub> [49,50], there is no indication that such species are present on Al<sub>2</sub>O<sub>3</sub>. Therefore, we have suggested that O<sub>2</sub> is dissociatively adsorbed on Au, a process which has been found to be thermoneutral at Au step sites by DFT calculations [38]. Furthermore, these latter mechanisms are less likely because they should be quite dependent on the nature of the support. Yet the observations suggest that when properly prepared, the catalytic activity does not have a strong dependence on the support. The relatively minor differences on different supports can be explained by other factors, especially the effect of water as discussed later.

It should be noted that the dominant CO oxidation reaction pathway may be dependent on the reaction temperature, time-on-stream, and the moisture content. Based on a study of the activation energy for CO oxidation over Au/TiO<sub>2</sub>, Haruta [51] has suggested that there are three different pathways for CO oxidation. At temperatures below 200 K, the reaction takes place only at step, edge, and corner sites on the Au particles. The reaction cannot proceed on TiO<sub>2</sub> or at

the perimeter interface between Au and TiO<sub>2</sub> because they are covered with carbonate species produced by surface reactions between CO and TiO<sub>2</sub>. Between 200 and 300 K, the reaction proceeds at the perimeter interface. As the temperature increases, the amount of carbonate at the interface decreases, and at 300 K, there is relatively little carbonate left. The reaction continues to proceed at the perimeter interface with an activation energy of nearly zero as the temperature is increased further. The model of the active site presented here is intended to represent the CO oxidation pathway at room temperature in a wet reaction feed for Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The reaction pathway may also depend on moisture content. For example, the changes in activation energy observed by Haruta could also be attributed to changes in the amount of H<sub>2</sub>O adsorbed on the catalyst surface. The activity of supported Au catalysts is extremely sensitive to the presence of moisture, and it is important to take this into account when the reaction data are analyzed.

It is additionally possible that there are several simultaneous pathways by which CO oxidation occurs. Our proposed mechanism is intended to apply to the dominant pathway that is responsible for the high initial activity observed in CO oxidation over Au/Al<sub>2</sub>O<sub>3</sub> and the high steady-state activity in the presence of H<sub>2</sub>O vapor (or H<sub>2</sub>) in the feed.

#### 4. Catalytic activity, deactivation, and effect of water vapor

As mentioned earlier, the activity of a catalyst depends not only on its method of preparation, but also on the manner that it is tested. The rate at which a catalyst attains a steady-state activity during CO oxidation depends on the catalyst. In a feed of 1% CO and 2.5% O<sub>2</sub> in He that was purified by passing through a silica trap at dry-ice temperature, we found that a Au/TiO<sub>2</sub> catalyst can maintain relatively stable activity. On the other hand, a Au/Al<sub>2</sub>O<sub>3</sub> catalyst loses its activity rapidly. If the feed stream is first passed through a water saturator at 25 °C, then the initial high activity could be maintained (Fig. 5) [12]. Therefore, when CO oxidation activities are compared, especially among different research groups, it is necessary to exercise caution because of the sensitivity to water partial pressure. Date and Haruta reported strong dependence of the activity of Au/TiO<sub>2</sub> on water content over a wide range of concentrations commonly encountered but often uncontrolled in laboratory experiments [52]. Depending on the water partial pressure, its effect could be to enhance or suppress the activity. In the literature, the effect of water includes enhancement [31,53], suppression [19], and no effect [54].

The apparently complex effect of water may be due to its multiple roles in the reaction. As described earlier, water can remove chloride poison by hydrolyzing the Au–Cl bond. Water also prevents deactivation during CO oxidation as shown in Fig. 5. Finally, in the chemical model of the active

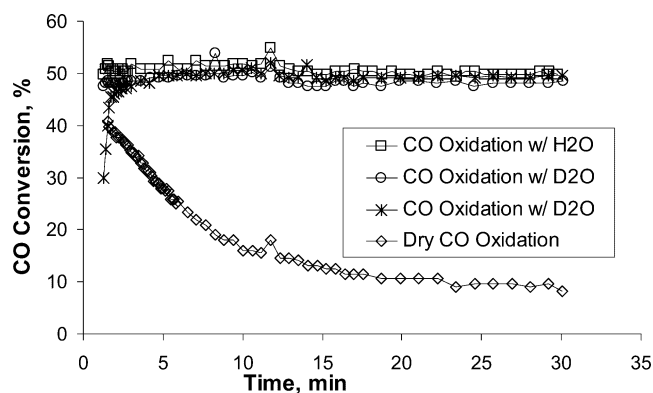


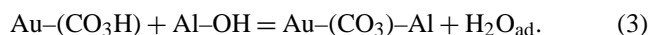
Fig. 5. Effect of water vapor in CO oxidation over Au/Al<sub>2</sub>O<sub>3</sub>.

site, the Au–OH groups participate in the reaction. These hydroxyl groups can be removed thermally rather easily. For example, an active Au/Al<sub>2</sub>O<sub>3</sub> catalyst can be severely deactivated by thermal treatment in a dry gas stream at 100 °C. The deactivated catalyst can be fully regenerated by exposure to water vapor at room temperature [12,39]. The low temperature at which the catalyst is deactivated and the regeneration by water suggest the involvement of hydroxyl groups associated with Au. We propose that thermal deactivation is due to condensation of Au–OH either with a hydroxyl group of the support (Eq. (1)) or with another Au–OH (Eq. (2)). Deactivation by Eq. (1) would suggest dependence on the nature of the support. This needs to be investigated. Mixing the catalyst with SiC in reaction tests also slows down deactivation. SiC removes heat effectively and thus can minimize local heating. It also may contain adsorbed water. Both of these factors would help prevent OH group removal during reaction.



The two ways to deactivate a Au/Al<sub>2</sub>O<sub>3</sub> catalyst, thermal treatment or CO oxidation, involve different chemistries. Therefore, methods to regenerate the catalyst also differ. Water is effective in regenerating catalysts deactivated by either method. However, treatment with hydrogen at room temperature is effective only for catalysts deactivated by the CO oxidation reaction. Exposing a CO oxidation-deactivated catalyst to a mixture of CO, O<sub>2</sub>, and H<sub>2</sub> also regenerates the catalyst [12,39]. In this case, both the hydrogen present in the feed and the water formed in the reaction participate in the regeneration.

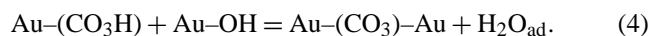
Based on the mechanism in Fig. 4, deactivation during CO oxidation may occur by the transformation of the bicarbonate intermediate into a relatively inactive carbonate at the active site by dehydration, as shown in Eq. (3). This reaction also involves a hydroxyl group of the support.



The ability of water to reverse the carbonate formation explains why its presence can keep the catalyst from deacti-

vation. The different reactivities and stabilities of the support hydroxyl groups and the bridging carbonate may explain the different sensitivity to water and different rates of deactivation for Au catalysts on different supports.

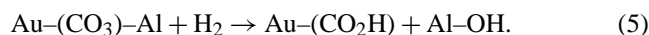
An alternative to Eq. (3) is reaction of carbonate with another Au–OH:



This is less likely than Eq. (3) because it would imply a weaker dependence of the rate of deactivation or sensitivity to water vapor on the nature of the support than that observed experimentally (e.g., compare the data on Au/Al<sub>2</sub>O<sub>3</sub> [12] with those on Au/TiO<sub>2</sub> [52]).

Regeneration of a CO oxidation-deactivated catalyst by treatment with water vapor is achieved by reversing Eq. (3) (or Eq. (4)). The reverse reaction, hydrolysis of the carbonate, involves a nucleophilic attack of water on the metal-carbonate bond, a step that would not exhibit any significant deuterium isotope effect. Indeed, when D<sub>2</sub>O is used instead of H<sub>2</sub>O during the CO oxidation reaction, there is no observable deuterium isotope effect (Fig. 5). Similarly, D<sub>2</sub>O can regenerate a CO oxidation-deactivated catalyst as effectively as H<sub>2</sub>O [55].

A CO oxidation reaction-deactivated catalyst can also be regenerated in a flow of hydrogen at room temperature. Hydrogen regeneration proceeds by a different mechanism. A possibility is that hydrogen hydrogenates the carbonate to a formate or hydroxycarbonyl, returning the site to the catalytic cycle (Eq. (5))



This reaction is expected to exhibit a noticeable deuterium isotope effect because of the steps of activation of hydrogen and/or hydrogenation of the carbonate. Indeed, regeneration by deuterium is slower, about 70% of that by hydrogen. The slower regeneration by deuterium also leads to a lower steady-state CO oxidation rate under the selective CO oxidation reaction conditions (using a feed containing 1% CO, 0.5% O<sub>2</sub>, and 40.5% H<sub>2</sub> or D<sub>2</sub>). In such a feed, the formation and hydrogenation of carbonate occur simultaneously, but its steady-state concentration would be higher in deuterium than in hydrogen. A kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) of 1.4 is observed for the oxidation of CO in such a mixture [56]. Interestingly, the selectivity for CO oxidation in the presence of D<sub>2</sub> is higher than in H<sub>2</sub>. This implies that the reaction of deuterium with oxygen to form D<sub>2</sub>O has a larger kinetic isotope effect than the CO oxidation reaction. This is expected, since the hydrogen oxidation reaction involves activation of H<sub>2</sub> and reaction of hydrogen with oxygen. It should exhibit a larger deuterium isotope effect. On the other hand, the CO oxidation reaction proceeds by a different mechanism, and H<sub>2</sub> is involved only in the regeneration of the active site by Eq. (5), which is a minor part of the overall reaction.

Eqs. (1)–(4) illustrate the importance of water on the catalyst. This is consistent with Haruta's observation that water

on the catalyst is more important than water in the vapor phase [52]. However, an Au–OH group alone is insufficient for catalytic activity. The active site is an ensemble of metallic Au atoms and Au–OH [12,39]. Metallic Au atoms are responsible for activation of oxygen, perhaps at steps or corner sites. Therefore, one expects that there would be an optimal catalyst pretreatment for the most active catalyst.

### 5. Catalytic activity of uncalcined catalysts

The dependence of catalytic activity of supported gold catalysts on the calcination temperature is a surprisingly complex issue. There are several reports that uncalcined samples or samples calcined at relatively mild temperatures are more active than those calcined at higher temperatures [17,30–35,55], but there is no explanation for these observations that has been accepted unequivocally.

For Au/TiO<sub>2</sub> and Au/Co<sub>3</sub>O<sub>4</sub>, Wolf and Schuth [17] reported that the highest activity was obtained with catalysts calcined at 200 °C compared to samples calcined at 300, 400, and 500 °C. The activity decreased with increasing calcination temperature, and the authors attribute this to the corresponding increase in gold particle size. They note also that the reason for the decrease in catalytic activity could be the change of oxidic gold to metallic gold that occurs with increasing calcination temperature. However, they argue that after 400 °C all the gold should be metallic, yet these samples still exhibit activity for CO oxidation, implying that metallic gold is the active species.

Similar results were obtained by Park and Lee [31], who observed that for both Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> the activity decreased with increasing calcination temperature. The highest activity was observed for catalysts calcined at 100 °C. Investigation by XPS showed that these samples contained the largest amount of oxidic gold and that the ratio of oxidic to metallic Au decreased with increasing calcination temperature, indicating that oxidic gold is responsible for high CO oxidation activity. This agrees with the results of other research groups [32,33,35] who also found that the catalysts exhibiting the highest activity were those containing the largest ratio of oxidic to metallic gold.

Somewhat different results were obtained by Haruta et al. [30,55] for Au/TiO<sub>2</sub>. After comparing the activity of catalysts calcined at 200, 300, 400, and 600 °C, they found that the samples calcined at 300 °C were the most active. Again, it was observed that the Au particle size increased with increasing calcination temperature, and the higher activity of the sample calcined at 300 °C could be attributed to its small Au particle size, which offers the largest number of steps, edges, and corners where the reaction can occur. The particle size of the sample calcined at 200 °C was nearly identical to that of the samples calcined at 300 °C, yet it still had lower activity, indicating that small Au particle size is not the only necessary requirement for CO oxidation activity. The authors noted that this sample was gray, as opposed

to the samples calcined at higher temperatures, which were purple. However, when this sample was kept in a glass reactor for approximately 12 days, its activity increased considerably, then decreased but still remained higher than the initial activity and was more active than the catalysts calcined at higher temperatures. Additionally, its color gradually changed from gray to purple, which is indicative of the decomposition of oxidic gold to metallic gold. No structural changes in this catalyst could be observed by TEM, and the authors attribute the increase in activity to the increase in the amount of metallic gold in the sample. However, it seems that the presence of metallic gold cannot wholly explain the higher activity of the catalyst calcined at 200 °C and exposed to ambient conditions for several days because it had a higher activity than the catalyst calcined at 300 °C, which should have had a larger amount of metallic gold. This suggests that there may be an optimal ratio of ionic to metallic gold that corresponds to the highest activity for CO oxidation. The sample calcined at 200 °C might have reached this ratio after storage at ambient conditions, but the sample calcined at 300 °C had already too much metallic gold.

We have investigated an uncalcined Au/Al<sub>2</sub>O<sub>3</sub> in an attempt to better understand the observations reported in the literature. When tested for CO oxidation at 25 °C, it showed no activity. High resolution electron microscopy did not detect any Au particles larger than 1–2 nm, which is the limit of our technique. This suggests that cationic species alone do not possess activity for CO oxidation. However, when the sample was exposed to a flow of 1% CO, 0.5% O<sub>2</sub>, and 40.5% H<sub>2</sub> in He at 100 °C, it was active for oxidation of both CO and H<sub>2</sub>. In fact, it was almost twice as active (per weight of catalyst) as a sample calcined to 350 °C (Costello et al., submitted for publication). Further tests showed that a fresh uncalcined sample could be activated in this reaction mixture at about 75 °C and higher. Moreover, after treatment in this reaction feed, the catalyst was active for CO oxidation at room temperature.

The need to activate the sample in a CO–O<sub>2</sub>–H<sub>2</sub> mixture at a moderate temperature suggests that, perhaps, reduction of Au or exposure to water is needed for activity. Thus, the effect of treatment with these gases was tested separately, and the results are presented in Table 2. Interestingly, neither treating the sample in H<sub>2</sub> or in water vapor at 100 °C resulted

Table 2  
Catalytic activity for CO conversion over an uncalcined Au/Al<sub>2</sub>O<sub>3</sub>

Pretreatment <sup>a</sup>	CO conversion <sup>b</sup>
None	No
H <sub>2</sub> at 100 °C, 20 min, then 1.5% H <sub>2</sub> O at 100 °C, 20 min	No
H <sub>2</sub> and 1.5% H <sub>2</sub> O at 100 °C, 30 min	35%
1% CO + 0.5% O <sub>2</sub> + 40.5% H <sub>2</sub> at 100 °C, 1 h	35%

<sup>a</sup> The reactor was purged with He after each treatment for 30 min and before the reaction test. For treatment in H<sub>2</sub>O, the sample was cooled to 25 °C in the wet stream before purging with He.

<sup>b</sup> No conversion means below 1%.

in any activity. In fact, hydrogen treatment followed by water treatment did not activate the sample either. To activate the catalyst, it was necessary to expose the sample to a mixture of H<sub>2</sub> and H<sub>2</sub>O at 100 °C. Electron microscopy of this uncalcined but activated sample detected a few Au particles approximately 5 nm in diameter, but the density of these particles was much lower than that on a calcined sample.

These observations are consistent with the active site model described earlier. They suggest that a combination of metallic and ionic gold is needed for CO oxidation activity. If metallic gold alone were sufficient, then treatment with H<sub>2</sub> should have activated the sample. However, it is still not clear why the simultaneous presence of H<sub>2</sub> and H<sub>2</sub>O is needed for activation. It is possible that this facilitates close contact between the metallic Au atoms and Au–OH groups or maintains an appropriate oxidation potential to avoid over-reduction of Au in order to generate the optimal ratio of ionic to metallic gold. Further study of the effect of calcination temperature on catalytic activity and characterization of the samples needs to be carried out in order to elucidate the nature of the gold species that are responsible for CO oxidation.

## 6. Conclusion

The specific requirements of the active site according to the active site model and the sensitivity to chloride poisoning and moisture are among the reasons there are wide variations of reported activities of catalysts of similar compositions in the literature. It is important to interpret experimental results with respect to the amount of residual chloride that may be present in the catalyst or the moisture content of the catalyst and in the reaction test system. However, it still remains to obtain direct evidence of the active site and reaction mechanism, such as conclusive data for the mode of activation of oxygen and spectroscopic evidence for the reaction intermediates. Are the active sites and reaction mechanism different depending on the support? To this end, computational chemistry will be instrumental in testing the feasibility of the proposed active sites and reaction mechanisms.

Being able to reproducibly prepare catalysts of high activities should greatly facilitate progress in these areas. Thus, a clear understanding of changes in the catalysts upon storage and consequent to various pretreatment and preparation conditions is critical. Along with our model of the active sites, it would be desirable to understand how Au cations can be stabilized, such that stable samples containing a high density of active sites can be prepared and rational modification of the catalyst can be carried out.

This new catalyst system has substantial potential in advancing our knowledge in catalysis and for commercial applications. But to realize these potentials, various challenges, such as those described above, need to be met.

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