



# On the potential role of hydroxyl groups in CO oxidation over Au/Al<sub>2</sub>O<sub>3</sub>

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## Abstract

The deuterium isotope effect in the steady state CO oxidation rate over Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the presence of H<sub>2</sub> or H<sub>2</sub>O and the effect of pretreatment on an uncalcined catalyst were studied. In a reaction feed containing 1% CO, 0.5% O<sub>2</sub>, and 40.5% H<sub>2</sub> at room temperature, CO oxidation exhibited a deuterium isotope effect ( $k_H/k_D$ ) of  $1.4 \pm 0.2$ . The rate of D<sub>2</sub> oxidation was also slower than the oxidation of H<sub>2</sub>, such that the selectivity for CO oxidation was 86% in the presence of D<sub>2</sub> versus 77% in the presence of H<sub>2</sub>. In contrast, there was no deuterium isotope effect in a feed containing 1% CO, 0.5% O<sub>2</sub>, and 1.5% H<sub>2</sub>O. H<sub>2</sub> was also more effective in regenerating a CO oxidation reaction deactivated catalyst than D<sub>2</sub>, whereas H<sub>2</sub>O and D<sub>2</sub>O were equally effective. The difference was attributed to the different mechanisms with which H<sub>2</sub> or H<sub>2</sub>O prevented deactivation of the catalyst during CO oxidation. An uncalcined Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was rather inactive. It could be activated by treatment with a mixture of H<sub>2</sub> and H<sub>2</sub>O at 100 °C, although treatment by either H<sub>2</sub> or H<sub>2</sub>O alone was ineffective. The observations are consistent with the model of the active site consisting of an ensemble of metallic Au atoms and a cationic Au with a hydroxyl group.

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## 1. Introduction

The discovery of the exceptionally high activity of supported Au catalysts for low temperature CO oxidation [1] sparked tremendous interest in the study of these catalysts, and their unusual activity and selectivity for various other reactions, including the

water gas-shift reaction [2], NO reduction by H<sub>2</sub>, CO, or propene [3,4], and propene epoxidation [5], have subsequently been reported. The potential practical applications of supported Au catalysts, along with the desire to understand why these small Au nanoparticles exhibit behavior radically different than that of bulk gold, continue to fuel growth in this area of research.

Despite the increasing efforts in the investigation of supported Au catalysts for CO oxidation, the nature of the active sites and the corresponding mechanism for this reaction remain unknown. Some of the difficulty in this elucidation may be attributed to the extreme sensitivity of these catalysts to details in the preparation procedure and to the operating conditions. Such

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sensitivity may also account, in part, for the large variations in catalytic activities reported in the literature for catalysts of similar compositions [6–10]. Among the various supported Au catalysts, Au/Al<sub>2</sub>O<sub>3</sub> is perhaps one that has shown the widest variation, ranging from being very inactive [11,12] to practically as active as Au/TiO<sub>2</sub> [9,13].

Recent publications have elucidated a number of reasons that contribute to the wide variations in activities. These reasons include the residual chloride content in the catalysts, the pretreatment conditions, and the effect of water vapor in activity tests.

The detrimental effect of residual chloride in Au/Al<sub>2</sub>O<sub>3</sub> has been studied in some detail, and it was shown to affect the catalyst in two ways: it causes agglomeration of Au particles upon heating, and it poisons the active sites [14]. The Au/Al<sub>2</sub>O<sub>3</sub> could be very sensitive to the presence of chloride, and a chloride content as low as Cl/Au = 0.0006 (atom ratio) showed detectable inhibition if the chloride adsorption capacity of the alumina was first reduced by adsorbed phosphate. The inhibitive effect of chloride is somewhat reversible. A chloride-poisoned catalyst slowly regains some of its activity when the reaction mixture contains water vapor, probably due to removal of chloride from the active site by hydrolysis [14].

The pretreatment temperature of the supported Au catalysts is also important. Earlier studies concentrated on the effect of reduction and oxidation temperatures on the crystallite size of Au and the possibility of strong metal-support interaction (e.g. [15]). Recently, it was reported that for Au/TiO<sub>2</sub> [16,17], Au/iron oxide [17–19], and Au/MnOx [20] 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> [13] or Au/Y [21] can be very active. The reasons for this are not yet understood. Catalysts calcined at low temperatures generally contain small, 2–5 nm Au crystallites. However, size alone does not seem to be a sufficient factor for high activity (e.g. [13,14]).

Discrepancies between reported activities may also arise from the effect of water on CO oxidation. It has been reported that the addition of H<sub>2</sub>O vapor to the CO oxidation feed has a positive effect on Au/Fe<sub>2</sub>O<sub>3</sub> [17], Au/TiO<sub>2</sub> [17,22], Au/Al<sub>2</sub>O<sub>3</sub> [17], and Au/Mg(OH)<sub>2</sub> [23], but has no effect on Au/Fe(OH)<sub>3</sub> prepared by impregnation of as-precipitated hydroxides [24] or a

negative effect on Au/TiO<sub>2</sub> [15]. Careful study of the effect of water on CO oxidation over Au/TiO<sub>2</sub> by Date and Haruta [22] showed that, depending on the partial pressure of H<sub>2</sub>O in the system, its effect could be to suppress or enhance the activity. The catalytic activity increased with increasing H<sub>2</sub>O partial pressure up to 200 ppm, then remained steady as the amount of H<sub>2</sub>O was increased to 6000 ppm. Further increase in the H<sub>2</sub>O partial pressure resulted in a suppression of activity. In a separate study, it was found that a H<sub>2</sub>O partial pressure as low as 80 ppb could affect the activity of Au/Mg(OH)<sub>2</sub> [23]. This extreme sensitivity of the CO oxidation activity of supported Au catalysts to moisture may contribute to the differences in reported catalytic activities.

While it is clear that H<sub>2</sub>O plays an important role in generating active supported Au catalysts, the exact nature of this role is not yet understood. It is possible that H<sub>2</sub>O has a direct effect on the catalytic active site. In addition to the quantum-size effect model [25], a model of the active site involving an ensemble of metallic Au atoms and Au<sup>+</sup>–OH<sup>–</sup> has been suggested [6,8,26]. There appears to be increasing support that the active site involves the perimeter of the Au particles or the Au-support interface [16,27,28,29] and for the presence of Au cations [18,19,30,31], although their role in the reaction is not accepted unequivocally [29].

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, of hydroxyl groups in the reaction. It has been found that an active Au/Al<sub>2</sub>O<sub>3</sub> catalyst could be deactivated by thermal treatment in a dry atmosphere at a temperature as low as 100 °C. The activity of a catalyst deactivated in this manner could be restored by exposure to H<sub>2</sub>O vapor at room temperature [8,26]. It is unlikely that such a mild thermal treatment can sufficiently dehydroxylate alumina, so it seems plausible that Au-hydroxyls are involved in the CO oxidation reaction. A corresponding reaction mechanism was proposed involving the insertion of CO into Au<sup>+</sup>–OH<sup>–</sup> to form Au-hydroxycarbonyl, which is oxidized to a bicarbonate. Decomposition of the bicarbonate would produce CO<sub>2</sub> and Au-hydroxyl, completing the reaction cycle (Fig. 1). Activation of oxygen could be at steps or defect sites of metallic Au atoms.

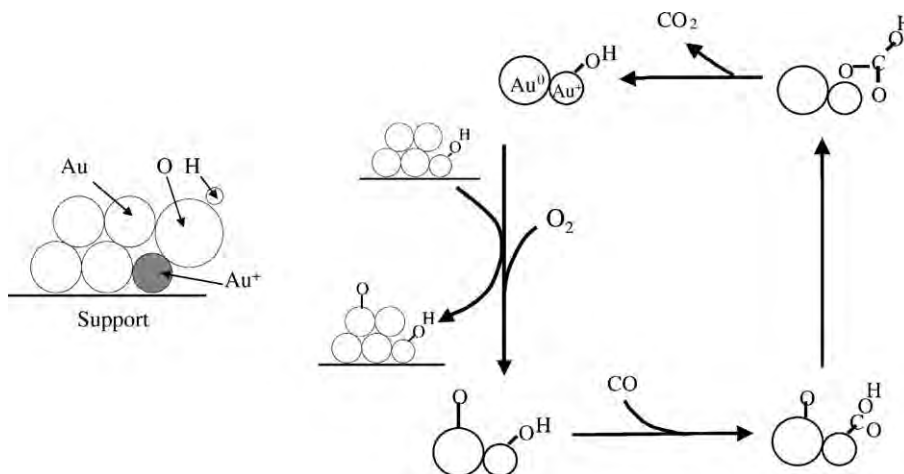


Fig. 1. Proposed model of the active site and corresponding reaction mechanism.

In addition to deactivation by thermal treatment, an active Au/Al<sub>2</sub>O<sub>3</sub> catalyst also loses activity rapidly initially with time-on-stream before attaining a pseudo-steady activity [8,26]. This initial loss of activity can be prevented if H<sub>2</sub>O or H<sub>2</sub> is present in the reaction feed. Moreover, a reaction-deactivated catalyst can be regenerated by treatment with H<sub>2</sub>O vapor or H<sub>2</sub> at room temperature [8,26].

In view of the important roles of water and hydrogen in CO oxidation over Au/Al<sub>2</sub>O<sub>3</sub>, it appears that a study of the deuterium isotope effect of the effects of water and hydrogen, along with an investigation of the relationship between the regeneration process and the activation/pretreatment steps to generate an active catalyst, may provide additional insight into the role of water and hydroxyl groups in CO oxidation over supported Au catalysts. Here we report the results of such a study.

## 2. Experimental

The Au/γ-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared as described previously using a HAuCl<sub>4</sub> solution at pH 7 and 70 °C [8]. The samples were washed twice with room temperature water, then once with 50 °C water, followed by suction filtering. The resulting sample is the uncalcined sample. If the solid was then calcined in air at 350 °C for 4 h and then stored in a vial, it is the calcined sample. The Au content, as determined

by ICP, was between 0.8 and 1.1 wt.%. Unless specified, the experiments were conducted using the calcined sample.

Details of the reaction tests have been described earlier. Unless noted, the reaction tests were conducted at room temperature. Catalytic reactions were carried out in a flow system using fused silica microreactors with 20–40 mg of catalyst. For CO oxidation, the feed was 1% CO, 2.5% O<sub>2</sub>, and the balance He. It was purified by passing it through a silica trap at dry-ice temperature immediately upstream of the reactor. The CO concentration in the product stream was analyzed by FTIR using a gas phase cell and gas chromatography [8]. Water vapor, when used, was introduced by passing the feed stream through a water saturator at room temperature. The estimated water content was between 1–1.5%. For selective CO oxidation (SCO), a feed of 1% CO, 0.5% O<sub>2</sub>, 40.5% H<sub>2</sub>, and the balance He was used. The products were analyzed by gas chromatography. The catalyst was diluted with SiC [14]. Selectivity for CO oxidation was defined as the fraction of oxygen consumed that reacted with CO to form CO<sub>2</sub>. In the isotope experiments, deuterium gas was used instead of hydrogen, and D<sub>2</sub>O was used instead of H<sub>2</sub>O in the saturator.

Transmission electron microscopic examination of the catalysts was performed using a Hitachi HF-2000 TEM with field emission gun at 200 keV. The chloride contents of the catalysts were not determined, but from previous experience, they should be below the

detection limit of 0.01 wt.% Cl, or Cl/Au atomic ratio of <0.03.

### 3. Results

#### 3.1. $D_2/H_2$ isotope effects in CO oxidation

The activity of Au/Al<sub>2</sub>O<sub>3</sub> during CO oxidation decreases rapidly initially with time-on-stream, followed

by a much slower decrease once most of the initial activity is gone [8]. For example, with a flow rate of 200 ml/min over 40 mg of catalyst, the CO conversion decreased from about 50% to about 20% over 5 min and then decreased more slowly until it reached a pseudo steady-state of about 8% over the next 25 min. This pseudo steady-state activity corresponds to a turnover frequency of about  $0.26\text{ s}^{-1}$  for this catalyst, which contains Au particles about 4 nm in diameter, assuming hemispherical Au particles and

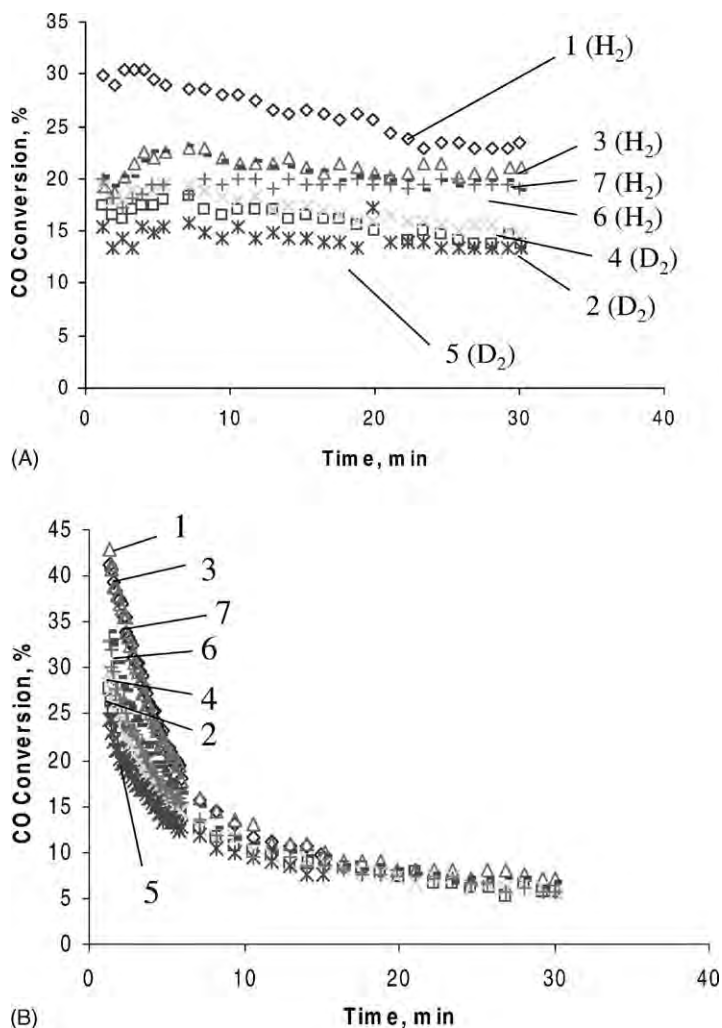


Fig. 2. (A) Selective catalytic oxidation of CO in H<sub>2</sub> or D<sub>2</sub> at 22 °C over 0.04 g of 1.1 wt.% Au/γ-Al<sub>2</sub>O<sub>3</sub>. Numbers indicate the sequence of the reactions. (B) CO oxidation at 22 °C over 0.04 g 1.1 wt.% Au/γ-Al<sub>2</sub>O<sub>3</sub> after regeneration by selective CO oxidation in H<sub>2</sub> or D<sub>2</sub>. The numbers indicate the sequence of reactions. 1, 3, 6, and 7 correspond to CO oxidation after SCO with H<sub>2</sub>; 2, 4, and 5 to CO oxidation after SCO with D<sub>2</sub>.

that all surface Au atoms are active. The turnover frequency (TOF) corresponding to the initial activity was about  $1.6 \text{ s}^{-1}$  at 50% conversion. When  $\text{H}_2$  was present in the reaction mixture with CO and  $\text{O}_2$ , as in SCO, no deactivation was observed over hours of testing. For the data in Fig. 2A, the TOF for CO at 30 min time-on-stream was about  $0.72 \text{ s}^{-1}$ . Replacing  $\text{H}_2$  with  $\text{D}_2$  was also effective in preventing deactivation (Fig. 2A). However, the rate of CO oxidation in the presence of  $\text{D}_2$  was only about 70% of that in  $\text{H}_2$ , which corresponded to an isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) of  $1.4 \pm 0.2$ . The rate of  $\text{D}_2$  oxidation was also much slower than the oxidation of  $\text{H}_2$ , resulting in a selectivity for CO oxidation of 86% in the presence of  $\text{D}_2$  versus 77% in the presence of  $\text{H}_2$ .

It was shown previously [8,26] that a  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  catalyst deactivated by CO oxidation can be regenerated by exposure to a SCO reaction feed. Consequently, the effectiveness of regeneration using a deuterium-containing SCO feed was investigated. The results are shown in Fig. 2B. In this figure, the curves are labeled according to the order of the experiment. The catalyst was first exposed to a flow of the SCO feed. Then the feed was stopped, and the system was purged with He for 15 min. After purging, a premixed CO oxidation feed was introduced, and the conversion of CO to  $\text{CO}_2$  was monitored. The CO conversion decreased with time-on-stream, indicating deactivation of the catalyst. After 30 min, the system was purged with He, and then a SCO feed was introduced. In cy-

cles 2, 4, and 5, deuterium was used in the SCO feed, whereas in cycles 1, 3, 6, and 7, hydrogen was used. The results showed that the deuterium-containing SCO feed could regenerate the catalyst, but less effectively than the feed containing  $\text{H}_2$ . On the average, a deuterium-SCO feed could only recover 65% of the activity that a hydrogen-SCO feed could. Interestingly, the deuterium effect was completely reversible. Subsequent exposure to a hydrogen-SCO feed returned the catalyst close to the state at the beginning of the experiment.

Treatment by flowing  $\text{H}_2$  over a CO reaction-deactivated catalyst at room temperature could also regenerate the catalytic activity [8,26]. However, compared to regeneration by the SCO feed, regeneration with  $\text{H}_2$  was much slower. An exposure to a  $\text{H}_2$  stream for at least 2 h at room temperature was needed to fully regenerate the catalyst, while an exposure for 1 h restored about 80% of the activity. Regeneration by  $\text{D}_2$  was much less effective; the extent of recovery was, on the average, 70% of that achieved using  $\text{H}_2$  (Fig. 3).

### 3.2. $\text{D}_2\text{O}/\text{H}_2\text{O}$ isotope effect in CO oxidation

Similar to  $\text{H}_2$ , the presence of 1.5%  $\text{H}_2\text{O}$  in a feed stream of CO and  $\text{O}_2$  prevented deactivation [8]. Interestingly, the steady activity observed for CO oxidation was independent of whether  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  was used (Fig. 4). The TOF corresponding to the data in the figure was  $1.6 \text{ s}^{-1}$ . Treating a catalyst deactivated by

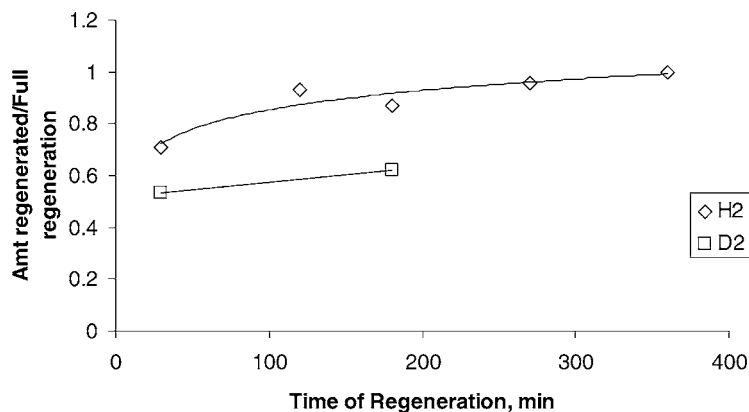


Fig. 3. Fraction of catalytic activity for CO oxidation restored by treatment in a flow of 100 ml/min  $\text{H}_2$  or  $\text{D}_2$  as a function of time of treatment. The fraction regenerated is the ratio of the initial CO oxidation rate after the indicated treatment time to the initial CO oxidation rate after 6 h treatment in  $\text{H}_2$ . All CO oxidation reactions were carried out at  $22^\circ \text{C}$  with 0.04 g of 1.1 wt.%  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ .

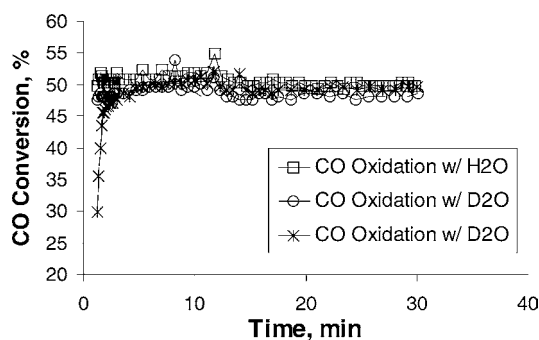


Fig. 4. CO oxidation in the presence of 1.5% H<sub>2</sub>O or D<sub>2</sub>O over 0.04 g 1.1 wt.% Au/γ-Al<sub>2</sub>O<sub>3</sub> at 22 °C.

CO oxidation in a flow of water vapor in He at room temperature was highly effective in restoring catalyst activity. Complete regeneration could be achieved by a stream of 1.5% H<sub>2</sub>O in 20–40 min. D<sub>2</sub>O was equally effective; there was little difference in the subsequent CO oxidation activity after regeneration using H<sub>2</sub>O versus regeneration using D<sub>2</sub>O (Fig. 5).

It was shown previously [8,26] that a Au/γ-Al<sub>2</sub>O<sub>3</sub> catalyst could be deactivated by thermal treatment at 100 °C in a stream of dried He or at 350 °C in a stream of dried O<sub>2</sub> or He. A catalyst deactivated in this manner could be regenerated by exposure to water vapor at room temperature. Similar to the results obtained for regeneration of a reaction-deactivated catalyst, there

was little difference in the subsequent CO oxidation activity whether H<sub>2</sub>O or D<sub>2</sub>O was used to regenerate a thermally-deactivated catalyst.

### 3.3. Catalytic activity of uncalcined Au/Al<sub>2</sub>O<sub>3</sub>

The above results indicated the importance of water in the feed stream in the CO oxidation reaction on Au/Al<sub>2</sub>O<sub>3</sub>. In view of this, investigation was conducted to examine the effect of adsorbed water using an uncalcined sample, which should have a higher water content than a sample calcined at 350 °C. Table 1 shows the various pretreatments investigated and the corresponding activity of the sample. Catalytic activity could be obtained after treatment with H<sub>2</sub> and H<sub>2</sub>O simultaneously at 100 °C, but not by treatment at 100 °C in He, H<sub>2</sub>, or water vapor.

The SCO activity of the uncalcined sample was also tested. Starting at 25 °C, the reactor was heated to 40, 75, and 100 °C in steps, maintaining at each step for 1 h. No CO conversion was observed at 25 or 40 °C, but CO and H<sub>2</sub> conversion were observed at both 75 and 100 °C. At 100 °C, the activity was about as high for this sample as a calcined sample (Table 2). Interestingly, the selectivity for CO oxidation was similar. After the 100 °C experiment, the reactor was cooled to 25 °C, and the catalyst had become more active, showing about 4% conversion of CO. An

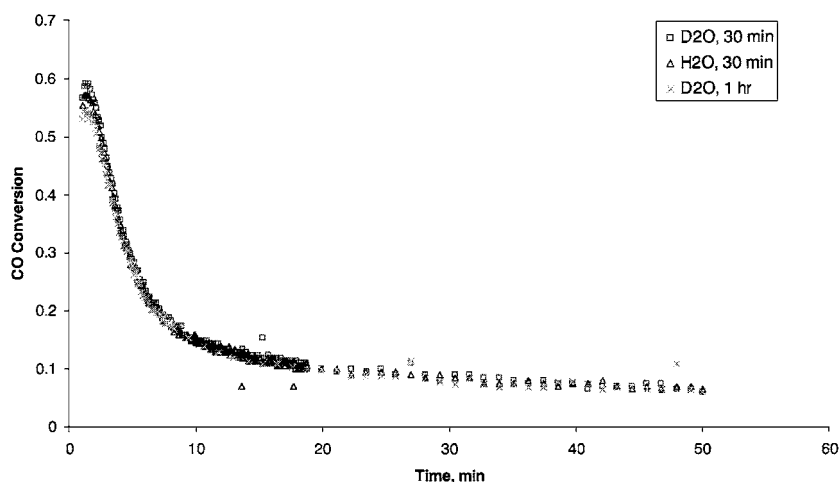


Fig. 5. CO oxidation at 22 °C over 0.04 g of 1.1 wt.% Au/γ-Al<sub>2</sub>O<sub>3</sub> after regeneration with ~1.5% H<sub>2</sub>O or D<sub>2</sub>O in He. After the regeneration procedure, the system was purged with He for 30 min.

Table 1  
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
He at 25 °C, 30 min	No
H <sub>2</sub> at 25 °C, 1 h	No
H <sub>2</sub> at 100 °C, 15 min	No
1% CO + 2.5% O <sub>2</sub> + 1.5% H <sub>2</sub> O at 25 °C, 1 h	No
H <sub>2</sub> O at 100 °C, 30 min	No
H <sub>2</sub> at 100 °C, 25 min, then 1.5% H <sub>2</sub> O at 25 °C, 20 min	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 25 °C, 1 h	No
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 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%.

Table 2  
Selective CO oxidation over an uncalcined Au/Al<sub>2</sub>O<sub>3</sub> at 100 °C

Catalyst	Flow rate (ml/min)	Cat. wt.(mg)	CO conv. (%)	CO <sub>2</sub> select. (%)
Uncalcined	200	6.5	29	55
Calcined	200	11.8	27	55

uncalcined catalyst activated by the SCO reaction at 100 °C was also active for CO oxidation (Table 1, last entry), whereas exposure to the SCO mixture at 25 °C did not result in an active catalyst.

#### 4. Discussion

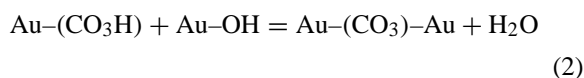
There is a deuterium isotope effect when H<sub>2</sub> or D<sub>2</sub> is used either in the reaction mixture with CO and O<sub>2</sub>, as in SCO, or as a means of regenerating a CO reaction-deactivated catalyst. However, there is no discernable deuterium isotope effect between H<sub>2</sub>O and D<sub>2</sub>O both in the CO oxidation reaction and in the regeneration of deactivated samples. Furthermore, regeneration of a CO reaction-deactivated catalyst by H<sub>2</sub> is much less effective than regeneration by H<sub>2</sub>O. The possibility that H<sub>2</sub> regeneration is actually a consequence of H<sub>2</sub>O formed from air leak into the system can be excluded by the following experiment. After

deactivating the catalyst by the CO oxidation reaction and purging the system, a stream of 50% H<sub>2</sub> in He was passed over the catalyst. Pulses of O<sub>2</sub> (1 cm<sup>3</sup>, 5% O<sub>2</sub> in H<sub>2</sub>) were injected into the H<sub>2</sub> stream. Afterward, the system was purged with He, and the CO oxidation activity was tested. It was found that even after 20 pulses of O<sub>2</sub>, which is equivalent to an O<sub>2</sub>/Au atomic ratio of 8, there was no detectable difference between regeneration with H<sub>2</sub> alone and regeneration with H<sub>2</sub> combined with O<sub>2</sub> pulses. The amount of O<sub>2</sub> introduced in this experiment was substantially more than the amount that would have leaked in, which was determined separately by trapping the catalyst bed at liquid nitrogen temperature. Therefore, it appears that H<sub>2</sub> and H<sub>2</sub>O regenerate the catalyst by different mechanisms. It was suggested previously [8,26] that the rapid deactivation observed during CO oxidation results from the formation of a relatively inactive carbonate at the active site by dehydration of the surface bicarbonate intermediate and an adjacent hydroxyl. A possible reaction for deactivation is shown in Eq. (1), which also involves a hydroxyl group of the support.



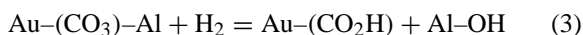
This reaction removes an active site from the catalytic cycle. Water vapor can reverse this reaction, resulting in regeneration of the catalyst. The reverse reaction, hydrolysis of Au-carbonate, involves nucleophilic attack of water on the Au-carbonate bond. One would expect a weak deuterium isotope effect for this reaction, that is, a weak isotope effect on the regeneration by water, as observed experimentally.

The ability of water to reverse carbonate formation also explains why its presence in the reaction mixture can prevent catalyst deactivation with time-on-stream. It may also be the reason for the different sensitivity to water and different rates of deactivation for Au on different supports. These differences are a result of the different reactivities and stabilities of the support hydroxyl groups and the bridging carbonate, which control the rate of formation and removal of the carbonate responsible for catalyst deactivation. An alternative to Eq. (1) is the formation of carbonate by reaction of the bicarbonate with another Au-OH:



Although the data obtained cannot exclude this possibility, this pathway seems less likely because one would not expect as strong a dependence of the rate of deactivation or the sensitivity to water vapor on the nature of the support as observed experimentally. For example, compare the data presented here for Au/Al<sub>2</sub>O<sub>3</sub> with those on Au/TiO<sub>2</sub> in [22].

Hydrogen regeneration of a CO oxidation-deactivated sample proceeds by a different mechanism. It is plausible that it occurs by hydrogenolysis of the carbonate to a formate or hydroxycarbonyl and a hydroxyl, returning the site to the catalytic cycle (Eq. (3)).



This reaction involves activation of hydrogen and hydrogenation of the carbonate, steps that are expected to exhibit deuterium isotope effects. This corresponds with the obtained experimental results. Regeneration with D<sub>2</sub> is slower than regeneration with H<sub>2</sub>, and this slower regeneration leads to a lower steady state concentration of active sites during SCO in D<sub>2</sub> and the observed kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) of 1.4. Interestingly, the selectivity for CO oxidation during SCO is higher in the presence of D<sub>2</sub> than in H<sub>2</sub>. This implies that deuterium has a larger effect on the rate of reaction of hydrogen with oxygen to form H<sub>2</sub>O than on the rate of the CO oxidation reaction. This can be explained if Eqs. (1) and (3) determine the kinetics of the regeneration reaction, whereas either the hydrogen activation step or the reaction between hydrogen and oxygen determines the kinetics of hydrogen oxidation.

The importance of hydroxyl groups on the catalyst is illustrated by Eqs. (1) and (2). This is consistent with Haruta's observation that water on the catalyst is more important than water in the vapor phase [22]. However, a Au–OH group alone is insufficient for catalytic activity. Consequently, it has been proposed that the active site consists of an ensemble of metallic Au atoms and Au–OH [8,26], wherein metallic Au atoms are responsible for the activation of oxygen. This is supported by density functional theory calculations, which indicated that O<sub>2</sub> dissociation is thermoneutral on Au step sites [30]. It is therefore expected that there exists a catalyst pretreatment condition that provides optimal reduction of the Au precursor.

This requirement of intimate contact between metallic Au atoms and Au–OH may explain the results obtained for the uncalcined Au/Al<sub>2</sub>O<sub>3</sub> catalyst.

The catalysts used in this study were prepared from a HAuCl<sub>4</sub> precursor. At the preparation condition of pH 7, the predominant species would be Au(OH)<sub>4–x</sub>Cl<sub>x</sub><sup>–</sup>, which was adsorbed on alumina. The value of x should be close to unity. Further hydrolysis of the Au–Cl bond could occur during washing. Upon drying at room temperature, the Au cations are expected to remain in the cationic form. The reaction results presented in Table 1 show that, in this form, the catalyst is inactive. It is plausible that this is a consequence of the complete absence of metallic Au atoms. Indeed, Au particles could not be detected on a fresh, uncalcined sample upon examination by high resolution electron microscopy, even though this technique could detect Au particles as small as 3 nm on other Au/Al<sub>2</sub>O<sub>3</sub> samples. Treating the catalyst in H<sub>2</sub> at 25 °C is insufficient to reduce the Au cations, so the catalyst remains inactive. Likewise, treating the sample in H<sub>2</sub>O vapor at 100 °C could not activate the sample. In earlier preparations, the Au catalysts were calcined to 350 °C before use [8,14,26]. At this high temperature, Au hydroxide and Au oxide are unstable, and metallic Au particles can be detected readily in the calcined sample. It is possible that the reduction to metallic Au is incomplete, and a small amount of Au cations remain at the Au particle–support interface. Recently, there is reported spectroscopic evidence of the presence of cationic Au in the active catalysts [18,19,31,32]. In one report, the most active catalyst was found to contain the highest concentration of Au(I) [31].

The uncalcined catalyst could be activated only in the simultaneous presence of H<sub>2</sub> and H<sub>2</sub>O at elevated temperatures. This was accomplished either by subjecting the catalyst to the SCO feed at 75 or 100 °C, wherein H<sub>2</sub>O is generated by H<sub>2</sub> oxidation, or by treating it with a flow of H<sub>2</sub>O in H<sub>2</sub> at 100 °C. This suggests that at least some of the Au cations are reduced to metallic Au atoms at these temperatures. High resolution electron microscopy showed the presence of a few Au particles about 5 nm in size on the activated sample. However, the density of the particles is much lower than that on a 350 °C calcined sample. Once the metallic Au atoms are formed, the catalyst is active even at 25 °C. However, metallic Au atoms alone are insufficient for activity, since treatment with H<sub>2</sub> at 100 °C could not activate the sample.

It is interesting to note that H<sub>2</sub> and H<sub>2</sub>O must be present simultaneously in order to activate the



uncalcined catalysts. Supplying them sequentially is not sufficient to generate activity. The reason for this is not yet understood. It is possible that their simultaneous presence facilitates close contact between the metallic Au atoms and Au–OH groups or maintains an appropriate oxidation potential to avoid over-reduction of the Au. This requirement should depend on the support in a way that parallels the effect of adsorbed water on the catalytic activity. That is, a titania-supported catalyst might require a lower partial pressure (of hydrogen) for activation than an alumina-supported sample.

The specific requirements of the active site based on this model, the consequent thermal stability, and the sensitivity to chloride poisoning are among the reasons why there are wide variations in the activity of catalysts in the literature. The Au cations are relatively easy to reduce, so the details in the preparation procedure could cause variation in the activity of the catalyst also. For example, if some of the Au cations are photo-reduced by room light or reduced by air-borne reductants during preparation or storage, an uncalcined catalyst could become active without the pre-treatment outlined here. In our experience in preparing Au/TiO<sub>2</sub>, Au/Al<sub>2</sub>O<sub>3</sub>, and Au/Y catalysts using a similar deposition/precipitation procedure, the color of the uncalcined sample could vary depending on the drying time in the suction filter and exposure to light, presumably indicative of different degrees of reduction of Au.

In conclusion, the results reported here provide additional evidence in support of an active site model that consists of an ensemble of metallic Au atoms and Au–OH groups. The reaction mechanism for CO oxidation previously proposed [8] can be used to explain the deactivation and regeneration phenomena and the deuterium isotope effects. The results also provide insight into the reported effect of water vapor on the reaction, as well as suggest a reason for the large variations in the activities of catalysts of similar compositions.

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