

The Important Role of Hydroxyl on Oxidation Catalysis by Gold Nanoparticles

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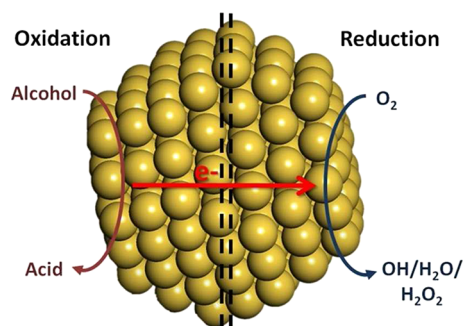
CONSPECTUS

Although gold is generally considered to be a relatively inert metal, supported gold nanoparticles have demonstrated exceptionally high catalytic activity for the oxidation of carbon monoxide and alcohols at modest temperatures. In both cases, the presence of hydroxyl groups substantially promotes the reaction rate, presumably by participating in the reaction.

Direct comparisons of CO oxidation to alcohol oxidation over gold catalysts have been difficult for scientists to explain. The former reaction is usually performed with gas phase reagents, whereas the latter reaction is often performed in the condensed phase. In this Account, we discuss the important role of hydroxyl for these two oxidation reactions catalyzed by gold, in terms of its influence on the turnover frequency.

During CO oxidation over gold, a hydroxyl can directly react with CO to form COOH, which eventually decomposes to CO₂. The gas phase CO oxidation reaction likely occurs at the gold–support interface, where adsorbed hydroxyl groups can be found after the addition of water to the feed. When we perform CO oxidation in liquid water, increasing the pH substantially promotes the reaction rate by providing an external source of hydroxyl. Likewise, we can also promote alcohol oxidations over gold catalysts in aqueous media by increasing the pH of the system. Since the hydroxyl groups are supplied through the reaction medium instead of on the support surface, the gold–support interface is much less important in the aqueous phase reactions. Even bulk gold powder becomes an active oxidation catalyst in alkaline water.

The role of O₂ in both CO and alcohol oxidation in aqueous media is to remove electrons from the gold surface that are deposited during oxidation, maintaining electroneutrality. Thus, the oxidation of CO and alcohols in water at high pH is analogous to the electrochemical oxidation reactions performed on gold electrodes. As the field of chemistry continues to encourage the development of sustainable chemical processes utilizing environmentally benign reaction conditions, the use of water as a “green” solvent becomes an attractive choice. In general, however, heterogeneous catalysts that scientists have developed over the last century for the petrochemical industry have not been optimized for use in aqueous media. Given the active role of water in oxidation reactions catalyzed by gold, additional research is needed to understand how water affects other catalytic transformations on traditional transition metal catalysts.



1. Introduction

Catalysis by gold has attracted the attention of researchers worldwide after the exciting reports by the Haruta group more than two decades ago describing the exceptional performance of Au nanoparticles as catalysts for CO oxidation and H₂ oxidation with molecular oxygen when the particles were supported on titanium dioxide or iron oxide.^{1,2} Since Au nanoparticles on silica or alumina were much less catalytically active for CO oxidation than those supported on titania or iron oxide, the nature of the latter two supports was

thought to be a critical factor in the unusual performance of the catalysts.³ The remarkable activity of gold for CO oxidation at temperatures as low as 203 K was perplexing, because the reaction rate depended on Au particle size yet was nearly independent of the partial pressure of CO and O₂. In addition, bulk gold metal and small gold particles are inactive for molecular oxygen dissociation at low temperatures, although adsorption of CO still occurs.

Subsequent work by Daté and Haruta involved cofeeding H₂O with CO and O₂ to explore the effect of moisture on

CO oxidation activity over Au/TiO₂.⁴ Great care was taken to remove all moisture from the dry feed gas of CO and O₂. Interestingly, the rate of CO oxidation increased by an order of magnitude when the water concentration was increased from 0.1 to 3 ppm and doubled again upon further increasing the concentration to 200 ppm. Despite an order of magnitude increase in CO oxidation activity by increasing the moisture content from 0.1 to 3 ppm, the apparent activation energy was unaffected by water, which suggests that the mechanism was unaltered by the addition of water. Earlier work by Cunningham and Haruta showed a similar promotional effect of water on CO oxidation over Au/Mg(OH)₂.⁵ In that study, the rate of CO oxidation was significantly lowered when the residual moisture level of 10 ppm present in the feed gas was decreased to 0.08 ppm. Recent work by Karwacki et al. determined that the rate of CO oxidation was higher at 25% relative humidity compared with dry conditions and that decreasing the concentration of surface hydroxyl groups on the support decreased the TOF over Au/ZrO₂.⁶ All of these studies propose that a water derived species, such as OH, was involved in CO oxidation. Addition of H₂ also accelerates the CO oxidation reaction on Au, presumably by the formation of low levels of water by the oxidation of H₂.⁷

A measurable promotional effect of water for CO oxidation over gold particles was also observed with supports that were known to be less active than titania. For example, Daté et al. explored the influence of H₂O on the rate of CO oxidation over Au/Al₂O₃ and Au/SiO₂ at 273 K.⁸ An increase in water concentration from 0.3 to 200 ppm increased the CO oxidation rate by 2 orders of magnitude for Au/SiO₂ and an order of magnitude for Au/Al₂O₃. While Au/TiO₂ always had a rate that was an order of magnitude larger than Au/Al₂O₃ and Au/SiO₂, the apparent activation energy was similar regardless of the support. Park et al. observed similar results, with Au/Fe₂O₃ and Au/TiO₂ being more active than Au/Al₂O₃ for CO oxidation, regardless of whether the reaction was performed wet or dry.⁹ All three supported gold catalysts were promoted upon the addition of water vapor. Daté et al. suggested that water played an important role in the activation of molecular oxygen and that oxide supports with redox properties have higher mobility of adsorbed hydroxyl groups or oxygen atoms at the interface between gold and the support.

Other authors have characterized the promotional effect of water on CO oxidation over Au as the prevention of catalyst deactivation. Costello et al. determined that the rate of CO oxidation over Au/Al₂O₃ in rigorously dry conditions

decreased by an order of magnitude after 30 min at 295 K but that exposure of the catalyst to 1.5% water vapor completely regenerated the catalyst.^{10,11} Kung et al. proposed not only that hydroxyl groups play a key role in CO oxidation but that deactivation was due to removal of hydroxyl groups from the support.¹² The activity for CO oxidation and deactivation behavior would therefore depend on both the Au–support interface and the type of oxide support.

In this Account, we discuss the mechanistic role of the hydroxyl on catalysis by gold nanoparticles for the selective oxidation of both CO and alcohols with molecular oxygen as the oxidant. The importance of water in the vapor and liquid phase for CO oxidation and in the liquid phase for alcohol oxidation is discussed. Finally, a comparison of liquid phase oxidation and electro-oxidation will address the similarities between the two processes over gold supported catalysts.

2. Catalysis by Gold and Oxidation Activity

2.1. CO Oxidation in the Gas Phase. The selective oxidation of CO has been studied extensively in both the gas and liquid phase in the presence of water. Remarkably, the rates of reaction for CO oxidation are similar over gold nanoparticles regardless of the phase. Calla et al. investigated the effect of gold loading on the turnover frequency (TOF) of gas phase CO oxidation by leaching Au/Al₂O₃ with various concentrations of NaCN.¹³ The turnover frequency is defined as the number of CO molecules reacted per surface Au atom in the reactor per time. The TOF of CO oxidation with cofed water was within a factor of 2 regardless of the gold loading, between approximately 0.2 and 0.4 s⁻¹ at 298 K.

The steady-state isotopic transient kinetic analysis (SSITKA) of gas phase CO oxidation with water vapor over the same highly dispersed Au/Al₂O₃ catalyst revealed a TOF of approximately 0.25 s⁻¹ at 296 K but an intrinsic TOF of 2.0 s⁻¹.¹⁴ While the TOF is based on the conversion of CO normalized by all surface Au atoms (inactive and active) and is therefore a lower bound on the rate, the intrinsic TOF is based on the rate of turnover of intermediate species that actually form product. Although in dry conditions the measured TOF was an order of magnitude lower than in the presence of water, the intrinsic TOF was still 1.6 s⁻¹, which was similar to that measured with water vapor. Further SSITKA experiments with Au/TiO₂ and Au/Al₂O₃ in dry conditions determined that the intrinsic TOFs at 293 K were 3.1 and 2.0 s⁻¹, respectively, showing that the reaction rate is nearly independent of the support used even without water.¹⁵ Even though the overall rate of reaction, or TOF,

was significantly affected by the nature of the support and the relative humidity of the reaction, the intrinsic TOF for CO oxidation over metal-oxide supported gold is between 2 and 4 s⁻¹ at room temperature.

Further investigation of the effect of water vapor on the gas phase CO oxidation rate over Au/Al₂O₃ determined that water affected the orders of reaction with respect to CO and O₂.⁷ The O₂ order increased from 0.36 to 0.48 in the presence of water and the CO order decreased from 0.32 to 0.18. Despite the promotional effect of water, no incorporation of labeled oxygen from H₂¹⁸O was observed in product CO₂.¹⁶ However, labeled oxygen was observed in CO₂ during dry CO oxidation with ¹⁸O₂ over both Au/TiO₂ and Au/Al₂O₃. While the exact role of both O₂ and H₂O is not clear, both are required for the high TOFs observed for CO oxidation in the vapor phase.

2.2. CO Oxidation in the Liquid Phase. The rate of CO oxidation in the presence of water vapor can be directly compared with CO oxidation in aqueous solution. The Dumesic group showed that gold nanotube membranes catalyzed the oxidation of CO in liquid water.¹⁷ Upon the addition of base to increase the pH of the liquid to 13, the rate increased by a factor of 5 compared with that in neutral solution. The enhancement of rate at a basic pH suggests that the hydroxyl groups in the solution interacted with the gold surface and either facilitated the activation of O₂ or directly participated in the reaction with CO. Interestingly, the authors mentioned the presence of small quantities of hydrogen peroxide in solution. When H₂O₂ was used as the oxidant instead of O₂, the rate of CO oxidation was an order of magnitude faster. This might be due to the ease of O–O cleavage of H₂O₂ as compared with O₂.

The promotional effect of base on aqueous CO oxidation over supported gold catalysts was further investigated by Ketchie et al.¹⁸ The vapor phase oxidation of CO over Au/TiO₂ had a TOF of 0.34 s⁻¹ at 300 K, similar to that discussed above for other oxide-supported gold catalysts, while the aqueous phase oxidation had a TOF of 0.11 s⁻¹ at a pH of 7 at 300 K.^{7,14,15} The reaction orders with respect to CO and O₂ in the aqueous phase were 0.35 and 0.25, respectively, which are very close to the reaction orders determined in the gas phase in the presence of water vapor over Au/Al₂O₃, implying that there is no change in the reaction mechanism.⁷ When the solution was acidic (pH = 0.3), the TOF of CO oxidation was 0.15 s⁻¹, which is close to that measured at neutral conditions. However, when the solution was basic (pH = 14), the TOF increased by an order of magnitude to 1.8 s⁻¹. Likewise, the TOFs of CO oxidation over Au

nanoparticles on two different carbon supports were 5.3 and 5.4 s⁻¹ at a pH of 14, which were an order of magnitude greater than those measured at acidic conditions. Evidently, the role of support was negligible compared with the role of solution pH. The availability of OH⁻ in solution greatly accelerated the rate of CO oxidation.

The TOF for aqueous-phase CO oxidation over Au/TiO₂ at high pH (1.8 s⁻¹ at 300 K) was within a factor of 2 of the intrinsic turnover rate of CO oxidation over Au/TiO₂ evaluated by isotopic transient analysis in the vapor phase (3.1 s⁻¹ at 293 K). The comparison of the TOF in aqueous solution to the intrinsic TOF in the vapor phase evaluated by SSITKA can be reconciled by assuming all available surface gold sites can adsorb a hydroxyl from solution, while in the vapor phase reaction, water activation to form an adsorbed hydroxyl is promoted only at the gold–oxide interface.

2.3. Alcohol Oxidation in the Liquid Phase at Basic Conditions. Alcohol oxidation to an acid with molecular oxygen as the oxidant under basic conditions can also be catalyzed by supported gold nanoparticles. Gold particles supported on carbon and alumina were demonstrated to be highly active for liquid phase alcohol oxidation under basic conditions¹⁹ but were relatively inactive under neutral to acidic conditions at 333 K.²⁰ Alcohol oxidation over Au occurs under acidic conditions at elevated temperatures (>373 K), but the rates were orders of magnitude lower than those under basic conditions. Carrettin et al. determined that the use of NaOH as the added base achieved a slightly higher glycerol conversion than CsOH and LiOH and double the conversion compared with KOH, RbOH, and NaNO₃.²¹ Ketchie et al. also investigated the oxidation of glycerol at a basic pH to produce a variety of products as depicted in Figure 1.^{18,22} The TOF of glycerol oxidation over Au/TiO₂ at 308 K was 1.7 s⁻¹ and is quite similar to the TOF of 1.8 s⁻¹ measured at 300 K for aqueous-phase CO oxidation under basic conditions. It should be emphasized that basic solution alone is not adequate to oxidize alcohols or CO over Au, since neither reaction proceeds without O₂.

Whereas small gold nanoparticles are needed to produce an active catalyst for gas phase CO oxidation,³ the influence of gold particle size on aqueous phase glycerol oxidation at high pH was less significant.²³ The TOF of 5 nm Au particles supported on carbon for CO oxidation was 5.4 s⁻¹ at a pH of 14, while 45 nm Au nanoparticles on carbon had a TOF an entire magnitude lower at 0.48 s⁻¹ and even gold powder in solution had a TOF of 0.36 s⁻¹ at 300 K. Similarly, over dispersed Au/C the TOF of glycerol oxidation was 17 s⁻¹, and over 20 and 45 nm gold nanoparticles on

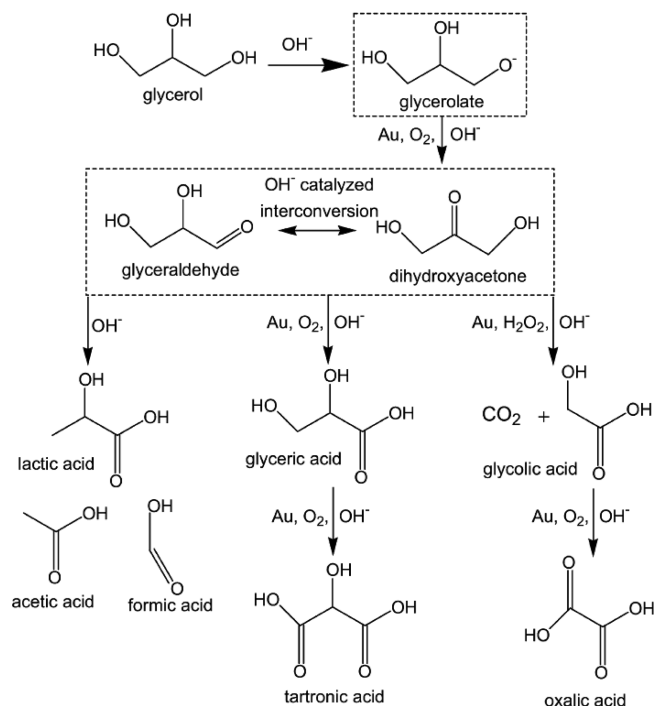


FIGURE 1. Suggested reaction network for the aqueous-phase oxidation of glycerol over Au catalysts under basic conditions. Proposed intermediates are shown in dotted boxes. Reprinted with permission from ref 22. Copyright 2007 Elsevier Inc.

carbon, the TOF was 2.3 and 2.2 s^{-1} , respectively, at 333 K. Even the gold powder in solution had a TOF of 2.5 s^{-1} , suggesting that large Au particles (>20 nm) behave similarly to bulk gold. While the rates of CO oxidation and alcohol oxidation appear to moderately depend on particle size, both oxidation reactions require the presence of a basic solution and dioxygen to achieve high rates of reaction in the liquid phase. The hydroxyl group appears to play an important role in the reaction mechanism for both oxidation reactions over gold catalysts.

3. Mechanism of Selective Oxidation over Gold Catalysts

3.1. Alcohol Oxidation with Adsorbed Hydroxide on Gold. The similar turnover rate for CO and alcohol oxidation over gold supported catalysts based on the total number of surface gold atoms is not likely a coincidence but is suggestive of common elements in the reaction mechanisms. As mentioned above, hydroxide ions and dioxygen are both required for lower temperature alcohol oxidation in aqueous solution over supported gold. To explore the mechanism of the reaction, isotopic-labeling experiments were performed with glycerol, ethanol, and 5-hydroxymethylfurfural over supported gold catalysts at high pH to determine

the source of oxygen inserted into the acid product. When $^{18}\text{O}_2$ was used as the oxidant for glycerol oxidation in H_2^{16}O solution over Au/C and Au/TiO₂ at 333 K and high pH, no ^{18}O was observed in the glyceric acid product.²⁴ Identical experiments carried out over Pt/C and Pd/C catalysts also failed to show ^{18}O in the glyceric acid product. In contrast, when H_2^{18}O was used for glycerol oxidation over both Au/C and Au/TiO₂, up to four ^{18}O atoms were incorporated into the glyceric acid product. Additional experiments with ethanol oxidation to acetic acid and 5-hydroxymethylfurfural oxidation to 2,5-furandicarboxylic acid over supported gold catalysts also confirmed that oxygen atoms incorporated into the acid products originated exclusively from the water solvent.^{17,25}

Although dioxygen was not the source of the oxygen atoms that were incorporated into the acid products, molecular oxygen was required for all of the above-mentioned reactions to proceed. Kinetic studies revealed that at high enough oxygen pressures (>5 atm), the rate of 5-hydroxymethylfurfural oxidation over Au/TiO₂ at 295 K was fairly independent of O₂ pressure.²⁶ To explain the isotopic labeling results during alcohol oxidation, Zope et al. proposed that O₂ played an indirect role in the mechanism by removing electrons from the metal surface generated by alcohol oxidation.²⁴ The evidence of hydrogen peroxide formation in solution suggests that O₂ is sequentially reduced to a peroxide intermediate and eventually to hydroxide. Thus, O₂ closes the catalytic cycle by serving as an electron scavenger and regenerating hydroxide ions that are consumed in the reaction to produce aldehyde intermediates and acid products. Further work by Zope et al. supports this reaction sequence because the number of OH⁻ moles consumed per mole of glycerol oxidized to glyceric acid over Au/TiO₂ was about 2, whereas consumption of 4 OH⁻ moles is predicted by the electrochemical balance.²⁷ The partial regeneration of hydroxide via the reduction of molecular oxygen may account for the difference.

Supporting evidence from density functional theory (DFT) calculations for ethanol oxidation on Au not only confirms that the reduction of dioxygen to hydroxide is energetically feasible but also suggests an alcohol reaction mechanism over gold, as shown in Figure 2. The DFT calculations (Table 1) for the deprotonation of ethanol to form an adsorbed alkoxide on Au(111) in water solvent showed that the presence of a coadsorbed hydroxide on the surface lowered the activation barrier by an order of magnitude to 22 kJ mol⁻¹ compared with that associated with a bare gold surface (204 kJ mol⁻¹).²⁴ A coadsorbed hydroxide on the

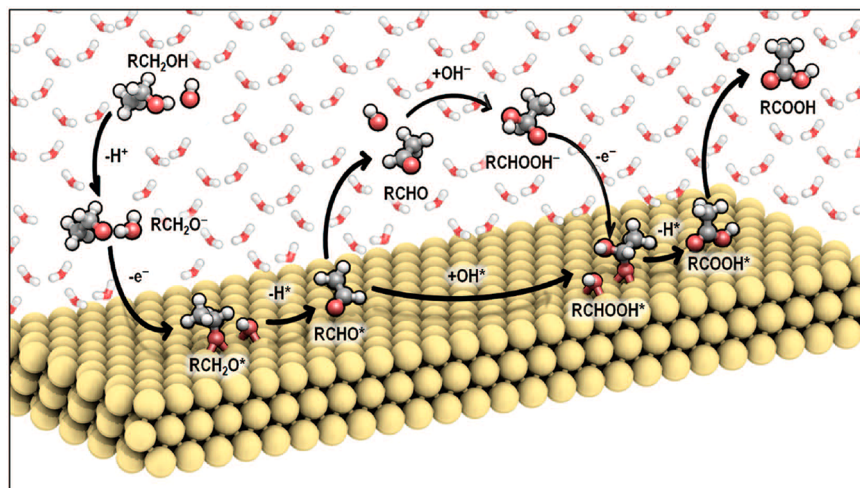


FIGURE 2. Reaction scheme for the aqueous-phase oxidation of an alcohol to an acid over Au at basic conditions. From ref 24. Reprinted with permission from AAAS. Copyright 2010 Science.

TABLE 1. DFT Results for Reaction Energies (kJ mol^{-1}) and Activation Energies (kJ mol^{-1}) for the Oxidation of Ethanol and Reduction of Oxygen on Au(111) in a Water Solvent²⁴

reaction	ΔH_{RXN}	E_{ACT}
$\text{CH}_3\text{CH}_2\text{OH}^* + * \rightarrow \text{CH}_3\text{CH}_2\text{O}^* + \text{H}^*$	196	204
$\text{CH}_3\text{CH}_2\text{OH}^* + \text{OH}^* \rightarrow \text{CH}_3\text{CH}_2\text{O}^* + \text{H}_2\text{O}^*$	13	22
$\text{CH}_3\text{CH}_2\text{O}^* + * \rightarrow \text{CH}_3\text{CHO}^* + \text{H}^*$	-40	46
$\text{CH}_3\text{CH}_2\text{O}^* + \text{OH}^* \rightarrow \text{CH}_3\text{CHO}^* + \text{H}_2\text{O}^*$	-222	12
$\text{CH}_3\text{CHO}^* + \text{OH}^* \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{O}^* + *$	-33	5
$\text{CH}_3\text{CH}(\text{OH})\text{O}^* + * \rightarrow \text{CH}_3\text{COOH}^* + \text{H}^*$	-151	21
$\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^* + *$	-183	39
$\text{O}_2^* + * \rightarrow \text{O}^* + \text{O}^*$	41	105
$\text{O}_2^* + \text{H}^* \rightarrow \text{OOH}^* + *$	-161	25
$\text{O}_2^* + \text{H}_2\text{O}^* \rightarrow \text{OOH}^* + \text{OH}^*$	-4	16
$\text{OOH}^* + \text{H}^* \rightarrow \text{HOOH}^* + *$	-146	19
$\text{OOH}^* + \text{H}_2\text{O}^* \rightarrow \text{HOOH}^* + \text{OH}^*$	37	48
$\text{HOOH}^* + * \rightarrow \text{OH}^* + \text{OH}^*$	-86	71

gold surface acts as a Brønsted base to assist in the deprotonation of ethanol to form the adsorbed alkoxide. Another coadsorbed hydroxide on the gold surface can also participate in the subsequent C–H activation of the adsorbed alkoxide to produce an adsorbed aldehyde, with an activation barrier of 12 kJ mol^{-1} compared with the bare surface with a barrier of 46 kJ mol^{-1} . Once an aldehyde is formed from the alcohol, subsequent base-catalyzed formation of a gem-diol and dehydrogenation results in the formation of an acid product. Thus, the hydroxide is involved in alcohol deprotonation, dehydrogenation to the aldehyde, hydration of the aldehyde, and dehydrogenation of the diol to the acid. The critical role of O_2 is to remove the electrons that must be deposited into the metal throughout the alcohol oxidation, thus partially regenerating hydroxide.

It should be noted that supported Au catalysts for glycerol oxidation in high pH solution slowly deactivate.²⁸ Although

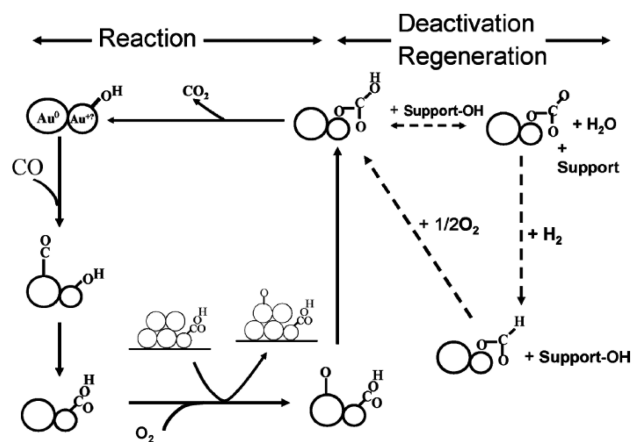


FIGURE 3. Proposed reaction and regeneration/deactivation pathway for CO oxidation involving cationic gold. Reprinted with permission from ref 29. Copyright 2007 American Chemical Society.

carboxylic acids do not strongly compete with the substrate, products of secondary reactions that produce ketones or enones adsorb strongly to the Au surface.

3.2. CO Oxidation with Water Vapor over Gold. A kinetic model for CO oxidation also suggests that the role of hydroxide is vital to the mechanism. Figure 3 illustrates a suggested reaction path for CO oxidation over gold supported catalysts as proposed by Kung et al. involving a cationic gold species.²⁹ The importance of water is highlighted because an initial hydroxide on a cationic gold species in close proximity to the support reacts with weakly adsorbed carbon monoxide on a neighboring gold atom. The reaction forms a hydroxycarbonyl that eventually decomposes to the products CO_2 and OH . For vapor phase CO oxidation with Au, the origin of the adsorbed hydroxide

and involvement of H₂O and O₂ in the reaction mechanism has been further investigated by kinetic modeling and isotopic labeling studies.

A detailed kinetic study of CO oxidation in the presence of water was undertaken by Ojeda and Iglesia over Au/Al₂O₃ at room temperature in an attempt to further elucidate the mechanism.³⁰ One kinetic model that fit their experimental observations involved an equilibrium reaction between dioxygen and water to produce adsorbed hydroxide and a hydroperoxy (OOH) species. The peroxide can then react with CO to produce CO₂ and OH in a kinetically relevant step. An isotopic study comparing H₂O and D₂O measured a kinetic isotope effect of 1.21 at room temperature, which is a relatively small effect. Evidently, activation of the O–H bond was not kinetically relevant. Since exchange between ¹⁶O₂ and ¹⁸O₂ and between H₂¹⁸O and ¹⁶O₂ was not observed over the Au/Al₂O₃ catalyst at 300 K, the researchers concluded that the direct dissociation of O₂ was not involved in the mechanism of CO oxidation.³⁰

Surface science experiments performed by Kim et al. for CO oxidation on Au(111) at 77 K determined that there was exchange of atomic oxygen in the presence of coadsorbed water.³¹ More specifically, when a Au surface that was precovered in ¹⁶O and H₂¹⁸O was exposed to CO, both CO¹⁶O and CO¹⁸O were produced. While slightly more CO¹⁸O was produced, the authors also showed scrambling between the atomic oxygen and water, complicating the final analysis. Apparently, if there is a mechanism for the production of atomic oxygen on Au, the resulting oxygen is reactive with both CO and H₂O. However, Schubert et al. determined that for CO oxidation with ¹⁸O₂ over an iron oxide supported gold catalyst only CO¹⁸O was observed.^{32,33} In conclusion, the influence of water on gas phase CO oxidation may be attributed to atomic oxygen and/or hydroxyl depending on the steady state coverages formed during the reaction. However, in the liquid phase at high pH, we suspect that hydroxyl would be the dominant species on the surface of the catalyst.

3.3. Alkali Promotion of Gold for Gas Phase CO Oxidation. In summary, the adsorbed hydroxide appears to participate in the fast reaction path for CO oxidation. Thus, one might suspect that supported gold catalysts modified with alkali metals might also promote the rate of CO oxidation. Qian et al. showed that the addition of NaOH to a Au/SiO₂ catalyst improved its catalytic oxidation activity.³⁴ While the Au/SiO₂ catalyst was inert at room temperature, the addition of a 6:1 sodium/gold molar ratio increased the rate of gas phase CO oxidation to 0.0866 mol g⁻¹ h⁻¹ without the presence of added water. Similarly, Gluhio et al. observed

that the addition of Rb₂O and BaO to a Au/Al₂O₃ catalyst decreased the temperature that achieved 95% conversion of CO from 385 to 351 and 298 K, respectively, at dry conditions.³⁵ The recent patent literature also contains a few examples of base promotion of CO oxidation by gold supported catalysts. For example, Brey et al. determined that the addition of Ba(NO₃)₂ to a Au/Al₂O₃ increased the amount of CO converted from 800 to 1500 ppm at 85% relative humidity and room temperature.³⁶ Similarly, Brady et al. determined that the addition of KOH to a Au/TiO₂ catalyst slightly increased CO conversion at 90% relative humidity and approximately 303 K.³⁷

4. Analogy to Electrochemistry

Electrocatalysis simply divides the oxidation and reduction reactions into two different reaction zones, whereas both reactions happen simultaneously at the same location in heterogeneous catalysis. For example, in electrocatalysis, oxidation of substrates such as H₂, CO, or alcohols generates electrons at the anode, whereas reduction of O₂ consumes the electrons at the cathode. For heterogeneous catalysis by gold nanoparticles, the oxidation of substrate and reduction of O₂ occur on a single gold particle. Whereas the electrical potential in an electrochemical cell provides the major driving force for reaction, the chemical potential is important in catalysis. The analogy between electrochemical oxidation and catalytic oxidation is quite informative and has been reviewed recently by Wieckowski and Neurock.³⁸ The implications of the electrochemical analogy for CO oxidation and alcohol oxidation are discussed briefly below.

The electrocatalytic oxidation of CO over Au electrodes is thought to proceed similarly to that of the vapor and liquid phase catalytic oxidation. Figure 4 shows the reaction scheme for catalytic CO oxidation in basic aqueous solution on a bulk Au(111) surface.³⁸ The reaction proceeds via the coupling of adsorbed CO and OH species whereby the cleavage of the formed adsorbed bicarbonate produces CO₂ and H₃O⁺. The reaction pathway depicted in Figure 4 has been shown to be energetically reasonable by DFT theory calculations with an overall reaction energy of –231 kJ mol⁻¹.³⁸ While CO oxidation can proceed in acidic media, higher potentials are required to produce adsorbed hydroxide on the gold surface and the rate of oxidation is much greater in alkaline media. Hayden et al. observed that small Au particles supported on a TiO_x electrode oxidized CO to CO₂ at much lower potentials than a polycrystalline Au electrode suggesting a strong influence of gold particle size

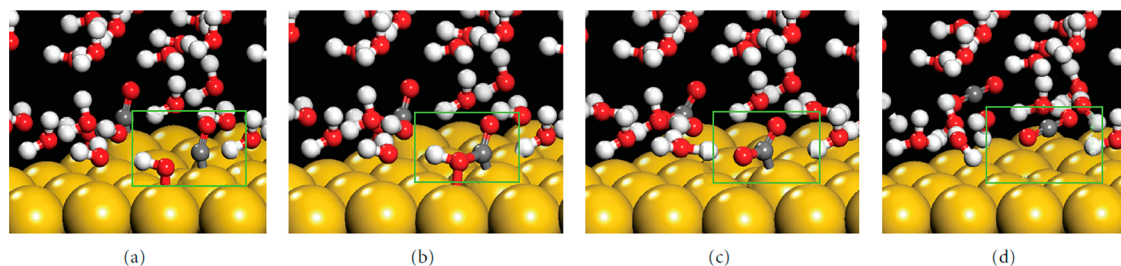


FIGURE 4. DFT calculations for the reaction coordination of CO oxidation. The reaction scheme is (a) adsorption of CO* and OH*, (b) nucleophilic addition of OH* to CO* to form COOH**, (c) cleavage of O–H bond, and (d) formation of CO₂ and H₃O⁺. Reprinted with permission from ref 38.

on the rate of reaction, which is consistent with results in gas phase CO oxidation over Au/TiO₂.³⁹

Similar to the electro-oxidation of CO over Au, oxidation of alcohols occurs in acidic media but requires very high potentials to generate adsorbed hydroxyl on the surface, and the rate is greatly enhanced in alkaline conditions. The mechanism of alcohol electro-oxidation is believed to proceed either by a four or six electron process. For example, the four electron path for alcohol electro-oxidation is selective to the acid product, whereas the six electron path overoxidizes the alcohol to produce CO and CO₂. Although the latter path is desired for maximum production of electrons in a fuel cell, it is difficult to completely oxidize ethanol and larger alcohols because of the high activation barrier of C–C bond breaking over Au.⁴⁰ The mechanism for selective electrochemical oxidation of ethanol to acetic acid involves activation of the O–H and C–H bonds by adsorbed hydroxide on the gold surface, which is identical to that proposed for the selective catalytic oxidation of ethanol.

Kwon et al. studied the electro-oxidation of glycerol and other alcohols in basic solution and proposed that a significant portion of the chemistry was carried out in the alkaline solution.⁴¹ They suggest that the initial deprotonation of glycerol (or other alcohols) was base-catalyzed, but the subsequent dehydrogenation of the alkoxide to form glyceraldehyde occurred on the Au electrode. The researchers then argued that the final products of selective glycerol oxidation were primarily those resulting from the decomposition of glyceraldehyde in basic solution, without the need for the Au. It should be noted that glyceraldehyde decomposition at high pH also produced lactic acid and glyceraldehyde dimers, which are not frequently observed in the presence of a gold catalyst.

Although gold is generally inert toward O₂, it becomes an active electrode for the O₂ reduction reaction (ORR) in alkaline media.⁴² The reduction of molecular oxygen in water by four electrons generates four hydroxide ions, similar to that

suggested for the mechanism of dioxygen reduction during Au-catalyzed selective oxidation of alcohols, as discussed above. The incomplete electroreduction of dioxygen in acidic conditions on Au electrodes produces a peroxide intermediate, which explains why small quantities of peroxide were observed during catalytic alcohol oxidation reactions over gold.⁴³ Ab initio quantum chemical calculations show that the reaction of molecular oxygen and water as well as the reduction of OOH is energetically feasible on Au(111) surface.⁴⁰

These examples illustrate the useful analogy between selective oxidation reactions on supported Au nanoparticles and electro-oxidation reactions on Au electrodes. In both cases, the role of hydroxyl is critical for rapid oxidation rates on Au surface at modest temperatures.

5. Conclusions and Outlook

In conclusion, the important mechanistic role that adsorbed hydroxyl plays in the catalysis by gold nanoparticles for both CO and alcohol oxidation with molecular oxygen and water has been described. The intrinsic turnover frequency of gas phase CO oxidation over titania supported gold nanoparticles determined by an isotopic transient method was similar to both CO and glycerol oxidation rates in aqueous solution. Evidently, the role of the hydroxyl is important for oxidizing both substrates, whereby during alcohol oxidation an adsorbed hydroxyl activates O–H and C–H bonds, while during CO oxidation the adsorbed hydroxyl may directly react with CO to perhaps form COOH, which decomposes to CO₂. The observed particle size dependence for gas-phase oxidation reactions over gold nanoparticles is most likely related to the optimum number of metal–support interfacial sites, which may contain hydroxyl groups. If hydroxyl groups are supplied through the solution medium, the metal–support interface is much less important so that even bulk gold becomes an active catalyst. Since selective oxidation reactions in the liquid phase can also be performed in an

electrochemical cell, results from electrochemistry have provided important mechanistic insights on the role of hydroxyl. As the demand by the chemical community for environmentally benign reaction conditions and so-called “green” solvents increases, researchers must pay careful attention to water as an active participant in catalysis.

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BIOGRAPHICAL INFORMATION

Matthew S. Ide received his B.S. in chemical engineering from Lafayette College in 2008 and his M.S. in chemical engineering from the University of Virginia in 2011. He is currently a Ph.D. candidate in chemical engineering in the laboratory of Professor Robert J. Davis at the University of Virginia. His doctoral research focuses on alcohol oxidation by supported metal catalysts.

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FOOTNOTES

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