

Coadsorption of CO and O₂ on Selected Gold Clusters: Evidence for Efficient Room-Temperature CO₂ Generation

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Abstract: Spurred by the recent demonstrations of the size- and support-dependent reactivity of supported gold clusters, here we present results on the coadsorption of CO and O₂ on selected anionic gold clusters, Au_N⁻, in the gas phase. O₂ adsorbs in a binary (0,1) fashion as a one-electron acceptor on the Au_N⁻ clusters, with even-*N* clusters showing varying reactivity toward O₂ adsorption, while odd-*N* clusters show no evidence of reactivity. CO shows a highly size-dependent reactivity for Au_N⁻ sizes from *N* = 4 to 19, but no adsorption on the gold dimer or trimer. When the gold clusters are exposed to both reactants, either simultaneously or sequentially, interesting effects have been observed. While the same rules pertaining to individual O₂ or CO adsorption continue to apply, the preadsorption of one reactant on a cluster may lead to the increased reactivity of the cluster to the other reactant. Thus, the adsorbates are not competing for bonding sites (competitive coadsorption), but, instead, aid in the adsorption of one another (cooperative coadsorption). New peaks also arise in the mass spectrum of Au₆⁻ under CO and O₂ coadsorption conditions, which can be attributed to the loss of a CO₂ molecule (or molecules). By studying the relative amount of reaction, and relating it to the reaction time, it is found that the gas-phase Au₆⁻ anion is capable of oxidizing CO at a rate 100 times that reported for commercial or model gold catalysts.

Introduction

Due to its largely nonreactive nature, gold has long been considered a “noble” metal, undergoing few of the reactions of its transition metal counterparts. Therefore, much of its use has been as a support material for self-assembled monolayers or as a null reaction system. However, early gas-phase studies on charged gold clusters indicated that adsorption activity was both strongly size- and charge-state dependent.^{1,2} Even more interesting was the fact that the reaction gases used (H₂, CH₄, O₂) showed measurable adsorption activity, which is remarkable considering that these gases do not adsorb on extended gold surfaces at room temperature. The demonstration by Haruta and co-workers that gold clusters prepared on oxide supports showed a pronounced size- and support-dependency in their low-temperature catalytic activity has led to an increasing number of studies on model gold catalysts.^{3–5} These studies have led us to undertake the study of the size- and electronic-structure-dependent reactivity of gas-phase gold clusters with various reactants, namely CO and O₂. Preliminary results indicated that the adsorption of one of these gases affected subsequent adsorption, encouraging the further investigation of the exact nature of this effect.

Experimental Section

Studies of the coadsorption of CO and O₂ on gold cluster anions were performed by using pulsed-helium flow-reactor techniques at room temperature as described previously.^{6,7} Briefly, charged clusters were formed and equilibrated by laser vaporization of a rotating and translating target rod in a high-pressure helium flow stream, produced using a pulsed valve with a stagnation pressure of approximately 5 atm. The highly diluted clusters are then exposed to reactants and detected by time-of-flight mass spectrometry, using perpendicular pulsed extraction fields. A view of the cluster source is shown in Figure 1.

Two methods were used for introducing the two reactants. The first method uses a secondary pulsed valve (stagnation pressure of approximately 1.5 atm) to introduce the reactants into the system following cluster growth and cooling. An alternate method is to introduce a reactant gas directly into the metal vaporization zone by seeding the helium buffer gas. The latter method allows the greatest possible reaction between the gold clusters and the reactant gas, favoring the establishment of chemical equilibrium conditions. In our previous studies,^{6,7} it was found that introduction of the reactant gas into the vaporization zone would lead to the same product compositions as if the reactant gas was introduced into the reactor region of the experimental apparatus. Under our experimental conditions, it is impossible to determine whether the structures of the cluster–adduct species are the same when the reactants are introduced in the two different areas. We assume, though, given the nature and strength of bonding in the Au_N⁻:reactant species described here, that equilibration to the same temperature and pressure yields the same structures.

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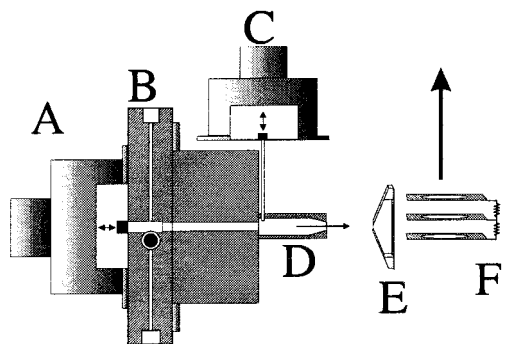
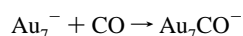


Figure 1. A view of the cluster source, reactor, and extraction region of the time-of-flight mass spectrometer. (A) The primary pulsed-gas valve, in which room-temperature He is normally used as a buffer gas. However, for “upstream” addition of reactants, the He gas may be seeded with the reactant gas. For pressures used, see the text. (B) The vaporization block and expansion region, in which Au clusters are formed by laser vaporization of a Au rod and cooled in a He flowstream provided by (A). (C) The secondary pulsed-gas valve, where room-temperature reactant:He mixtures can be added into (D) a 2.5 cm reaction region. (E) A skimmer that collimates the beam of clusters and cluster:reaction products for entry into (F) the perpendicular extraction region of a time-of-flight mass spectrometer.

In general, due to the fact that the actual partial pressure of the reactant is not measured in the experiments, only relative reactivities or equilibrium constants can be obtained. However, for initial reactivity results, the absolute bimolecular rate constant for the room-temperature reaction,



measured by Lee and Ervin,⁸ which yields a reaction cross-section of $\sim 5 \text{ \AA}^2$ as the high pressure limit is approached, can be used as an internal reference. Using a 1% CO:He mixture, these methods lead to reactant partial pressures of approximately 0.01 (reactor) and 1 Torr (source). In both cases, the total helium pressure in the reactor is estimated to approach 100 Torr, which yields approximately 1 ns between buffer gas collisions for Au_7^- .

For these experiments, several combinations were used to introduce the reactants. In one series of trials, O_2 was seeded into the buffer gas, while CO was subsequently introduced in the reactor. For another series, the order of reactant introduction was reversed. This allows one to study the effect that a particular adsorbate may have on the subsequent adsorption of another type. Finally, the reactants were mixed in various concentrations and introduced into the reactor by using the second pulsed valve. In all cases, the mass spectra were observed to be stable for the duration of the experiments. Finally, to determine that decomposition reactions make a negligible contribution to our reaction systems, we have accounted for all peak intensity, as described earlier,⁶ to check whether mass-spectral intensity has been lost or gained across cluster sizes, N .

Results and Discussion

Experiments on the adsorption activity of molecular oxygen with gold cluster anions at ambient temperature have led to results that have been recently presented.⁶ Essentially, O_2 is seen to adsorb molecularly on gold clusters in a binary fashion, i.e., either zero or one O_2 molecule is adsorbed, and no evidence of single O-atom adsorption is seen. There is no evidence of secondary adsorption seen in the results, either by pulsing pure O_2 into the reactor region or by introducing O_2 directly into the metal vaporization zone of the cluster source. Another extremely striking result is seen in the selective nature of O_2 adsorption.

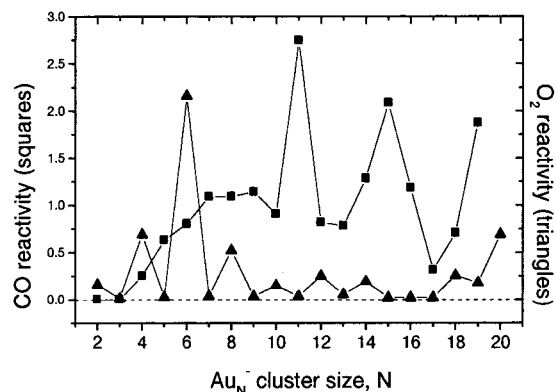


Figure 2. Size (N) variations in the reactivities of CO (squares) and O_2 (triangles) toward gold cluster anions, Au_N^- , when a 20% reactant gas:He mixture is pulsed into the flow-tube reactor. Note that none of the odd- N clusters or Au_{16}^- bind O_2 , and Au_{10}^- is less reactive toward O_2 than the other even- N clusters.

In short, *no* adsorption is seen for odd- N gold clusters, nor for $N = 16$, and the relative reactivity of O_2 toward even- N clusters is observed to vary from size to size. The relative reactivities of the small- N clusters ($N = 2-7$) correlate well with the low-pressure (< 1 Torr) guided-ion beam studies of Lee and Ervin,⁸ who measured the bimolecular and termolecular rate coefficients of the $\text{Au}_N^- + \text{O}_2$ reaction. Their relative bimolecular rate coefficients show an even-odd effect with the coefficients of the even- N clusters increasing from $N = 2$ to 6. The earlier studies of Cox et al.^{1,2} also reported relative reactivities for gold clusters in the size range of $N = 3-20$ and showed reasonable agreement with our results in both a qualitative and quantitative manner. However, those studies did not discuss saturation coverages, especially to the extent of restricting that coverage to 0 or 1 molecule adsorbing. Also, the authors attributed the pattern of reactivity to activated dissociative adsorption of O_2 onto the cluster, as had been seen in other transition metal clusters,⁹⁻¹² but this is not consistent with the recent results of Sanchez et al.⁴ on supported gold clusters.

As had been noted earlier,^{1,2} the size-dependent reactivities of the gold clusters toward O_2 adsorption, as shown by the triangles in Figure 2, showed a strong correlation to the measured electron affinities, an effect that had previously been described as the filling of electron shells and subshells.¹³ In fact, the more recent results show an even stronger correlation than those of Cox et al.,^{1,2} in that Au_{18}^- shows a very high activity, as great as that of Au_{14}^- , and almost as large as that of Au_{20}^- . In order that both the observed saturation behavior, as seen in the gray bars of Figure 3, and the even-odd alternation in the activity of gold cluster anions toward O_2 are satisfied, a mechanism was proposed involving the adsorption of O_2 as a one-electron acceptor. In this mechanism, the easily activated superoxide form of O_2 is generated and the gold clusters attempt to gain a closed electronic level. Although the simultaneous adsorption of two O_2 molecules by an odd- N gold

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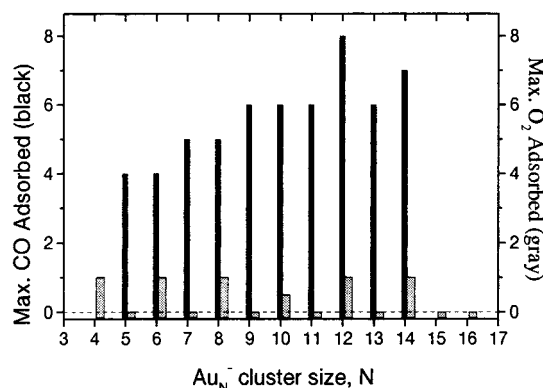


Figure 3. A bar graph representation of the maximum number of CO (black) and O₂ (gray) molecules found to bind on gold cluster anions when the reactant gas is seeded into the buffer gas of the primary pulsed valve.

cluster would also allow a closed level to be maintained, the probability of this process occurring is statistically insignificant. Therefore, the proposed mechanism provides a consistent explanation for the observed experimental results, which otherwise cannot be accounted for by other adsorption models.

The adsorption activity of carbon monoxide (CO) on gold clusters also raises interesting questions,⁷ considering that CO adsorption has been cited¹⁴ as the most extensively studied chemisorption process on extended gold surfaces. This is although CO has a vanishing sticking probability on those same surfaces at room temperature. Even so, CO adsorption characteristics can provide important information regarding the size, shape, and electronic property dependence of nanometer-sized supported gold particles and provide incentive for performing adsorption studies in the gas phase. In the same study mentioned above,⁸ Lee and Ervin measured the rate of initial CO adsorption on Au_N⁻ ($N = 2-7$). They found that the rate of reaction started to increase with Au₅⁻ and continued to increase to Au₇⁻. Only Au₇⁻ seemed to approach the high-pressure limit of bimolecular reactions, and their limited pressure range did not allow them to make any determinations of saturation coverages. In our studies, when introducing the reactant gas following cluster growth and in small partial pressures, adsorption of CO (as a two-electron donor) tends to favor such compositions as to achieve electronic (sub)shell closings. Such (N, M) compositions are displayed by peaks in the mass spectra at (5,1), (11,1), (15,1), and (15,2), where N represents the number of gold atoms and M the number of adsorbed carbon monoxide molecules, which correspond to shell and subshell closings at 8, 14, 18, and 20 electrons. By increasing the partial pressure of CO in the reaction zone or by introducing the reactant into the carrier gas, evidence of apparent CO saturation is obtained, i.e., conversion of each cluster to some composition, (N, M_{\max}). Such compositions show a definite size dependence, as can be seen by the variation in the maximum number of adsorbate molecules, which is shown by the black bars in Figure 3. It must be noted that the probability of reaction does not continue to increase with an increase in cluster size. On the contrary, as can be seen from the reactivity plotted with squares in Figure 2, the probability of adsorption decreases dramatically with Au₁₂⁻ and shows a slight decrease following Au₁₅⁻. The most significant conclusion that can be drawn from the apparent saturation results is that,

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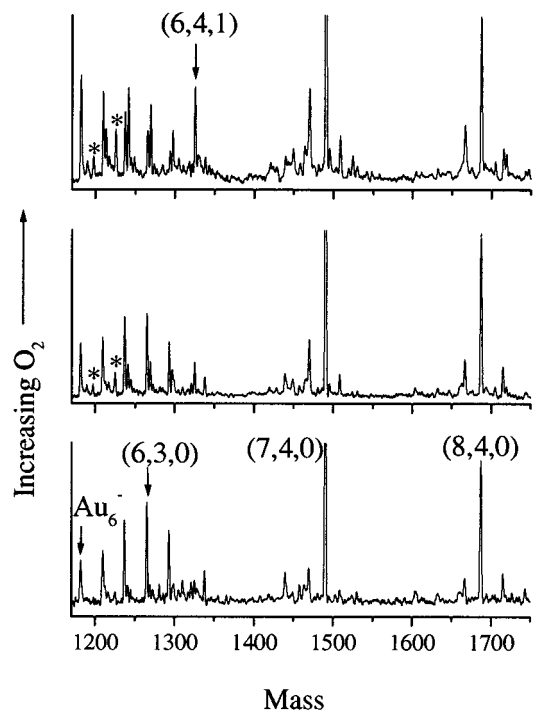


Figure 4. A series of spectra resulting from increasing the partial pressure of O₂ in the reactor region in which the bottom frame represents Au_N⁻ ($N = 6-8$) saturated with CO, without the introduction of any O₂. Increasing O₂ causes additional peaks to appear, mostly belonging to the addition of an O₂ molecule to a cluster already possessing M CO adsorbates, most notably exhibited by the growth of a peak corresponding to Au₆(CO)₄O₂⁻ and which is marked in the top frame. The constant intensity of Au₇(CO)₄⁻ represents stable conditions for the duration of the experiments. The peaks marked with asterisks correspond to CO₂-loss peaks arising from processes 3 and 4 (see text).

regardless of whether adsorption probability is dependent on electron counting methods (accounting for the preferential initial adsorption products) or simply on the number of possible “active” sites on the surface of the cluster, the coverage achieved is much less than would be expected under simple “geometric” considerations. By way of illustration, 38-atom nickel and platinum clusters have both been produced which adsorb 36 and 44 CO molecules, respectively.^{15,16} However, even on the extended surface of Au, it has been shown that CO chemisorption saturation occurs at low coverages (approximately 17% of geometrical coverage).¹⁷

With this picture of CO and O₂ adsorption established, turn now to the question of their effects on the adsorption of each other. When CO was first introduced “upstream” (in the source valve), and O₂ was introduced “downstream” (in the secondary valve), an example of the types of spectra obtained from these experiments is shown in Figure 4. As can be seen, the bottom frame represents Au_N⁻ ($N = 6-8$) saturated with CO, without the introduction of any O₂. As the amount of O₂ is increased, additional peaks begin to appear in the spectra, corresponding to the addition of an O₂ molecule to a cluster already possessing M CO adsorbates (note the presence of the peak corresponding to Au₇(CO)₄⁻ whose intensity remains constant throughout the

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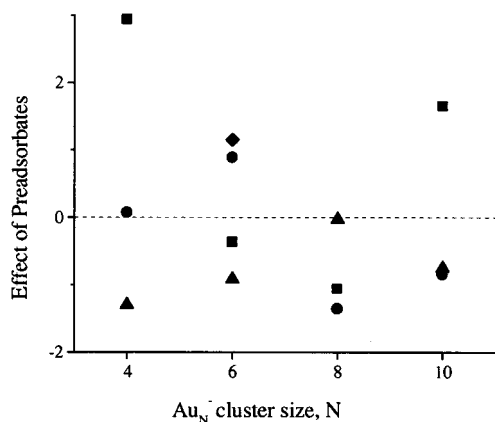


Figure 5. A series of log plots of the change in equilibrium constants with the presence of a preadsorbate on several even- N clusters. Cooperative coadsorption would be defined by a ratio of equilibrium constants (on a log scale) greater than 0, while competitive coadsorption would have a ratio of less than 0. The black squares represent the effect of a single preadsorbate on the subsequent adsorption of another molecule. The triangles and circles represent the effect of two and three initial preadsorbates, respectively. The effect of four preadsorbates on the subsequent adsorption of another molecule on Au_6^- has also been plotted as a diamond. A dotted line has been placed at a ratio of 0 (no effect) to differentiate between the competitive and cooperative processes. Cooperative coadsorption at low adsorbate coverages can be seen for Au_4^- and Au_{10}^- , with Au_6^- showing the effects of cooperative coadsorption at higher coverages.

experiment, representing stable conditions). This is most notably exhibited by the appearance and growth of a post-CO saturation peak corresponding to $\text{Au}_6(\text{CO})_4\text{O}_2^-$ and which is marked in the top frame. These new peaks can provide an opportunity to ascertain the exact nature of coadsorption between these molecules, whether it is competitive, noncompetitive, or cooperative. By studying the mass spectra and determining the relative equilibrium constants (as described in refs 6 and 7), an interesting and quite unexpected answer to that particular question arises. While the normal view of coadsorption on surfaces may assume that adsorbates will compete for binding sites, it is not necessarily the case. As can be seen in Figure 5, by studying the relative effects of a preadsorbate on the equilibrium constants of a series of even- N cluster peaks, it is found that the presence of adsorbed CO (O_2) may actually enhance the subsequent adsorption of O_2 (CO) on the cluster. For example, the presence of a preadsorbate on the Au_4^- cluster enhances the binding probability of the second adsorbate by a factor of approximately 18:1. Likewise, a dramatic increase in adsorption efficiency can be seen for the Au_{10}^- anion. When O_2 is preadsorbed on Au_{10}^- , the equilibrium constant for subsequent CO adsorption is greater than 5, as opposed to a value of ~ 0.7 for CO adsorption on bare Au_{10}^- . The effect of cooperative coadsorption is even more dramatic in the case of Au_2^- (not shown in the figure). On this size cluster, *no* isolated adsorption of CO is seen, even under conditions that lead to saturation of the larger cluster anions. However, when O_2 is preadsorbed on the cluster, a CO molecule is seen to adsorb with a relative equilibrium constant of ~ 0.27 . While, for instance, the presence of two preadsorbate molecules may cause the coadsorption process to show no effect or to become competitive, it must be noted that the probability of cooperative coadsorption does not simply continue to decrease with added preadsorbates. On the contrary, Au_6^- shows an increase in cooperative coadsorption with increasing numbers of preadsorbates. This type of cooperative adsorption could help to explain how, on the supported

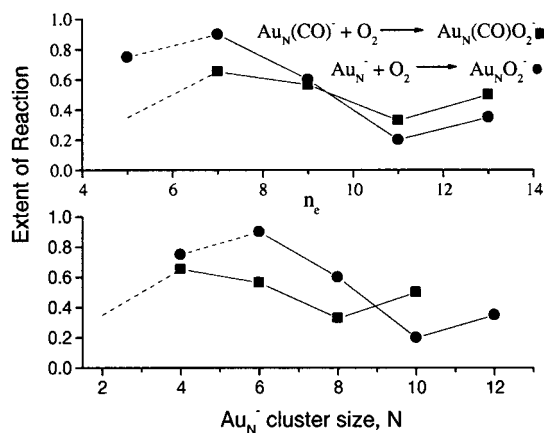


Figure 6. A comparison of O_2 adsorption activity on bare clusters (circles) and those possessing a preadsorbed CO molecule (squares). The bottom frame shows the extent of O_2 adsorption plotted versus cluster size, N . The top frame presents the extent of reaction plotted against the number of valence electrons of the cluster or cluster: CO complex, as defined by (1) and (2). The addition of two electrons from a preadsorbed CO molecule causes an approaching O_2 molecule to treat a $\text{Au}_M(\text{CO})^-$ cluster as if it were Au_{M+2}^- .

gold clusters, large rates of CO_2 production can be seen when neither of the reactant molecules is known to readily adsorb on bulk gold surfaces. However, though the effects of preadsorbed CO may lead to high probability of O_2 binding on a cluster (or O_2 enhancing subsequent CO adsorption), they do not relax the forbidden nature of an odd- N cluster gaining an O_2 adsorbate or for a second O_2 molecule adsorbing on an even- N cluster.

A possible explanation for this coadsorption activity is that the first adsorbate affects the electronic structure of the cluster, causing it to appear electronically different to the second approaching molecule. A recent theoretical study of the gas-phase catalytic oxidation of CO by Au_2^- provides some insight into this possibility.¹⁸ CO binds much more tightly to neutral Au_2 than to the anion (1.60 eV versus 0.96 eV). Assuming that this also applies to the larger cluster sizes, a Au cluster anion with a preadsorbed O_2 will appear to be neutral to the approaching CO molecule due to the charge transfer that takes place from the Au_N^- cluster to the O_2 . Another test of the effect of an adsorbate on the electronic structure of the cluster is to compare the reactivity of a second adsorbate on both the bare cluster and a cluster with a preadsorbate. For instance, the extent of reaction for O_2 adsorption on Au_N^- may be different than adsorption on $\text{Au}_M(\text{CO})^-$. Figure 6 provides an analysis of this question. In the bottom frame, O_2 adsorption on Au_N^- (circles) and on $\text{Au}_M(\text{CO})^-$ (squares) is plotted as a function of cluster size. In the top frame, the extent of reaction is plotted again, but as a function of the number of valence electrons:

$$n_e = N + 1 \quad (1)$$

for bare Au_N^- clusters or

$$n_e = N + 3 \quad (2)$$

for Au_N^- clusters with a preadsorbed CO molecule (acting as a two-electron donor). As can be seen, the extent of reaction of O_2 changes with the presence of a preadsorbed CO . In fact, the addition of two electrons from the CO causes the adsorption

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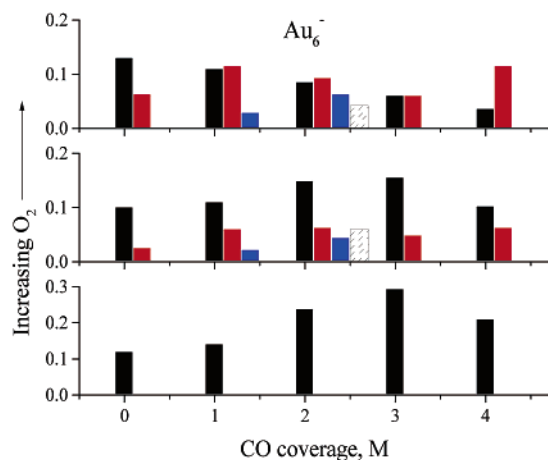
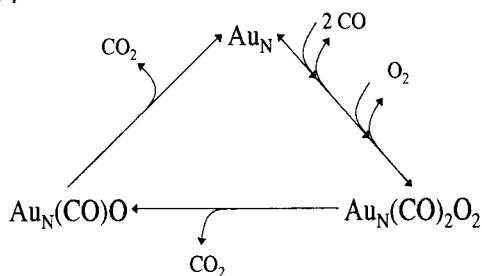


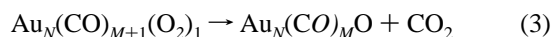
Figure 7. Results from coadsorption experiments with preadsorption of CO and variable amounts of O₂ introduced downstream. Relative abundances, or probabilities, of detecting various Au₆X⁻ species are grouped according to their CO coverage, and plotted as bar graphs. *Lower frame:* from a reference mass-spectrum with no O₂ introduced, showing only the distribution of CO coverage, *M*, Au₆(CO)_{*M*}⁻, as black bars. *Middle (upper) frames:* for O₂ present at lower (higher) concentration, such that ~20% (33%) conversion of Au₆⁻ to Au₆O₂⁻ is obtained. Red bars indicate coadsorption species, Au₆(CO)_{*M*}O₂⁻, or equivalently, Au₆(CO)_{*M*-1}CO₃⁻, eliminating CO₂, which gives primary reaction products Au₆(CO)_{*M*-1}O⁻, represented by blue bars. This species, which may also be denoted Au₆(CO)_{*M*-2}CO₂⁻, may eliminate a second CO₂ to give the secondary product Au₆(CO)_{*M*-2}⁻, an estimate of which is represented by the crosshatched bars.

Scheme 1



behavior of O₂ toward the cluster to mirror that of a bare cluster two atoms larger.

Under coadsorption conditions, evidence for CO₂ elimination depends on the appearance of peaks of the type, Au_{*N*}(CO)_{*M*}O₁⁻, which is attributed to the process (the reaction “cycle” under low-coverage conditions is shown in Scheme 1):



as well as to the recovery enhancement of Au_{*N*}(CO)_{*M*-1}⁻ peaks, from



Figure 7 presents the results of coadsorption experiments on Au₆⁻, organized for convenient viewing, when CO and O₂ are introduced sequentially. As can be seen, the cluster is first saturated with CO, giving a relatively flat distribution of Au₆(CO)_{*M*}⁻ complexes. As O₂ is introduced in the secondary reactor, the initial peaks that appear are due to CO:O₂ coadsorption products. However, with increasing amounts of O₂ being introduced, peaks begin to appear at irregular intervals. Upon closer inspection, the mass of these peaks corresponds to that which would be expected if a CO₂ molecule were lost from

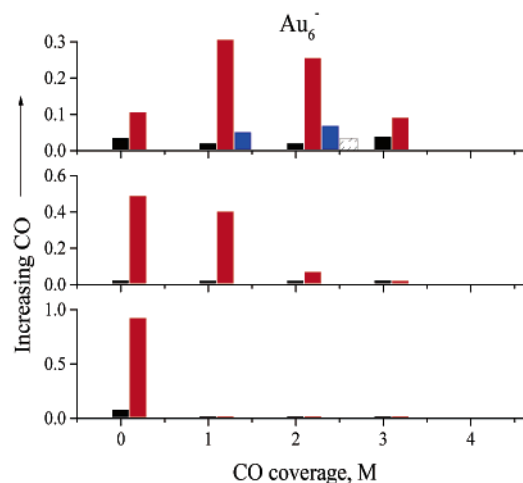


Figure 8. Results from coadsorption experiments with preadsorption of O₂ and variable amounts of CO introduced downstream. Relative abundances, or probabilities, of detecting various Au₆X⁻ species are grouped according to their CO coverage, and plotted as bar graphs. *Lower frame:* no CO introduced, showing as a reference only the nearly complete upstream conversion of Au₆⁻ to Au₆O₂⁻ (main red bar). *Middle (upper) frames:* for CO present at lower (higher) concentration, such that ~40% (70%) conversion of Au₆O₂⁻ to Au₆(CO)₁O₂⁻ occurs. The format of the bars is the same as that given in Figure 7.

the cluster. Similarly, in Figure 8, it can be seen that reversing the method of reactant introduction continues to lead to the appearance of CO₂-loss peaks. These peaks are also marked with asterisks in Figure 4.

The information gained on the adsorption of CO and O₂, as well as that presented here for the case of coadsorption, provides an opportunity to propose a mechanism for the gold cluster-catalyzed oxidation of CO, which, while exothermic, is marked by a sizable activation barrier under noncatalyzed conditions. One proposal, based on detected species in our experiment and illustrated for low-coverage conditions, is shown in Figure 9: The bare Au₆⁻ cluster (I), in its calculated equilibrium structure,¹⁹ adsorbs O₂ in the superoxo form (II). Upon subsequent adsorption of a CO molecule, providing a cluster complex with a mass corresponding to Au₆(CO)₁O₂⁻ (III), a rearrangement occurs to form a stable CO₃⁻ intermediate (IV). The presence of this stable form can be inferred from the lack of a metastable decay species in the mass spectrum arising from the loss of CO in the free-flight region of the mass spectrometer, which has been seen in previous work.^{7,20} Studying the higher CO-coverage complexes, evidence of metastable decay can be seen from the coadsorbate complexes, indicating that a single CO is being stabilized by an interaction with the coadsorbed O₂ molecule. Following the loss of a CO₂ molecule, a Au₆O⁻ complex (V) is detected, as in process 3. The adsorption of a second CO molecule leads to a complex possessing the Au₆(CO)₂⁻ mass (VI), which may desorb a second CO₂ molecule and return the bare Au₆⁻.

There are several points in this process at which obstacles could possibly arise. Inefficient adsorption and coadsorption of CO and O₂ on the cluster would not allow the reactants to be held long enough for the reaction to occur. Second, a large barrier to diffusion will not allow the reactants to find each other on the surface of the cluster. Once the O₂ and CO molecules

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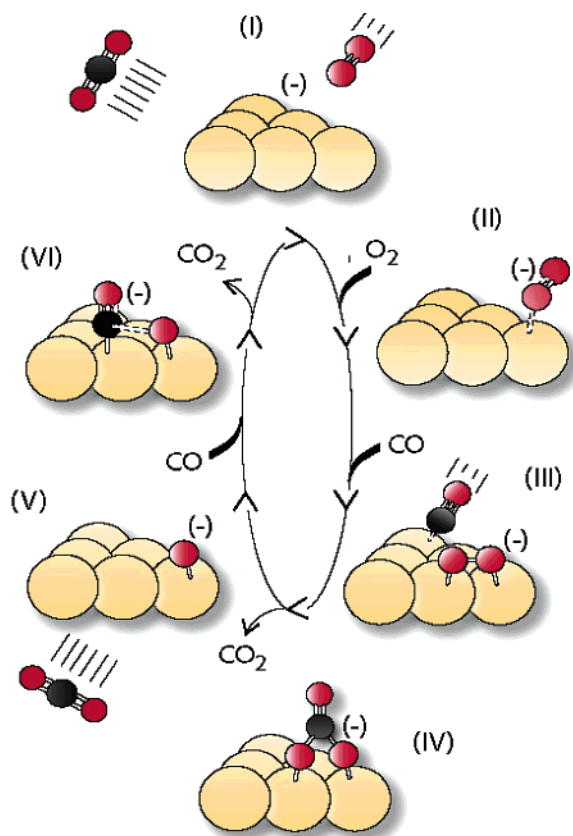


Figure 9. Schematic illustration of one of the coadsorption and catalytic combustion cycles, corresponding to the species detected at lowest coverage. Proceeding clockwise from top, (I) the bare hexaauride (Au_6^-), in its calculated equilibrium structure, adsorbs molecular oxygen, in the superoxo form (II). Subsequent coadsorption of CO may initially yield an Au_6CO_3^- species (III), which rearranges to produce the very stable CO_3^- adsorbate (IV). Elimination of CO_2 yields the Au_6O^- form (V). Adsorption of a second CO yields the Au_6CO_2^- mass (VI), which may desorb a second CO_2 and return the Au_6^- catalyst. (For ease of viewing, the Au_6 structure is depicted as retaining the same structure throughout.)

have interacted, too large a barrier to reaction will not allow the production of CO_2 . Also, in order for the reaction products to be seen, there must not be a large interaction between the CO_2 and the cluster. Otherwise, the barrier of reaction for desorption of CO_2 will be too large to overcome. Finally, side reactions and destructive processes must be avoided. For instance, besides being highly active, the cluster must have a high selectivity for CO_2 production as opposed to other reactions. One such reaction is the poisoning of the cluster by impurities. Each of these obstacles must be avoided for each CO_2 production process on a cluster, whether an impinging CO encounters an O_2 on the surface or it encounters an O atom left behind following the earlier production of a CO_2 . The final, and perhaps most pressing point, though, is whether the high exothermicity of the reaction could lead to the cluster being destroyed. This is obviously a valid concern, considering that, in the case of Au_6^- , the energy required to dissociate a single gold atom¹⁹ is very nearly the same as that released from CO oxidation (~ 2.8 eV). As mentioned above, though, a summation of the intensities of parent and product peaks involved in our experiments shows no loss of ion signal due to cluster dissociation. The excess energy released from the reaction must be dissipated by the desorption of a “hot” CO_2 molecule or

through collisions with the He buffer gas, which occur at a frequency of 10^9 collisions per second (at a He pressure of 100 Torr).

Previously, Shi and Ervin presented results indicating that platinum cluster anions are capable of catalytically oxidizing carbon monoxide.²¹ While this work is exciting in its own right, several questions arise. First, the lack of coadsorption species in the mass spectra lead to the question as to whether the CO is ever adsorbed on the cluster in this reaction process. Second, the fact that the order of reactant addition can lead to cluster fragmentation and much lower product yields indicates that these cluster “catalysts” could be easily poisoned or even destroyed. Finally, the low reactant coverages studied do not allow the effect of adsorbate saturation on the catalytic activity to be determined. In contrast, the results presented here show that, under reactant saturation conditions, easily identifiable coadsorption and product peaks are found for anionic gold clusters and that the order of reactant introduction does not lead to either cluster fragmentation or loss of catalytic ability.

While the results of O_2 and CO adsorption alone present a favorable avenue for discussion of the relevance of gas-phase cluster reactions to those carried out on supported clusters, the appearance of the CO_2 elimination peaks due to processes 3 and 4 provides several opportunities. These consist of the opportunity to gain a more detailed understanding of the role of the support material, as well as to compare the relative rate of CO_2 elimination on the gas-phase clusters with those achieved on the model systems and the actual supported-gold catalysts. In the work of Sanchez et al.⁴ on size-selected gold clusters supported on MgO, it was noted that, if the F-center (oxygen vacancy) defects on the surface were removed, the CO oxidation activity was almost nonexistent. As these surface defects provide a large amount of localized electron density, it was suggested that charge transfer from the surface to the cluster was responsible for the activation of O_2 , the rate-limiting step in CO oxidation. The present results reinforce this explanation in that O_2 adsorption is seen from the gold anions, while it was previously reported that gold cations, with the exception of Au_{10}^+ , did not show any O_2 adsorption activity.¹ The excess electron clearly is necessary for the reaction to occur, and the neutral supported clusters acquire the electron via charge transfer from the surface. The results of Sanchez et al. also noted a tendency toward an even–odd N dependency for CO_2 oxidation activity, in agreement with our results for O_2 adsorption. The only contradiction with our gas-phase results is the fact that the smallest supported cluster to show significant activity was Au_8 , while we found Au_6^- to show extremely high activity.

Though the results presented for the size-selected supported clusters provide important information as to the reaction mechanism taking place for CO oxidation, they provided no information as to the rate of CO_2 production, only stating that 1–2 CO_2 molecules were seen in the range of 8 to 20 Au atoms. The turnover frequency (tof) of these supported clusters is important if they are ever to be used as improved catalysts. The initial studies of Haruta³ showed a tof of ~ 0.2 CO_2 per exposed Au atom per second for supported gold particles under 2 nm in diameter. Further studies on model gold cluster catalysts by Valden et al.⁵ showed a tof of approximately 2 CO_2 molecules per total gold atoms per second on two-atom thick clusters of

(21) Shi, Y.; Ervin, K. M. *J. Chem. Phys.* **1998**, *108*, 1757–1760.

approximately 2–2.5 nm. In both cases, the gold catalysts were exposed to CO:O₂ mixtures, and the resulting CO₂ production was measured. By noting that the reaction time (t) in our experiments is 100–200 μ s (transit time through the reactor region) and determining the fraction of Au_N clusters (f_r) detected in a form due to processes 3 and 4, a rough estimate of the gas-phase turnover frequency can be formed:

$$\text{turnover frequency} = (f_r/N)t$$

Assuming a reactive fraction of 10% from a ten-atom gold cluster, this formula estimates a turnover frequency of \sim 100 CO₂ per Au atom per second, 2 orders of magnitude *greater* than that seen for the present commercial gold catalysts. It must be noted, though, that the gold cluster anions have undergone only a single reaction cycle at most, while the model catalysts of Goodman⁵ and the commercial catalysts of Haruta have been exposed to many cycles. Indeed, the efficiency of a real catalyst must be measured as an average over thousands of reaction cycles. Even with the concerns over the ability of the gold clusters to undergo multiple reaction cycles and to dissipate the excess energy produced in the reaction, these estimates of τ show the possible capabilities of small gold clusters and provide an incentive for further study to improve the efficiency of supported gold cluster catalysts.

While the present results are interesting, further studies will continue to provide more information as to the exact nature of the interaction of O₂ and CO, together and separately, with gold clusters. For instance, the recent development²² of electron diffraction of mass-selected clusters provides an opportunity to study the structural characteristics of the Au_M(CO)_M[−] system at each stage of adsorption and reaction with O₂. Furthermore, infrared spectroscopy has been used with success on the supported gold cluster systems²³ to distinguish between different forms of CO binding, and the use of recently improved methods of infrared absorption–dissociation on a mass selected cluster beam could provide important information as to the bonding characteristics of the CO and O₂ adsorbates and their reaction products. Combined with the information on reactivity, these types of techniques could aid in understanding reaction mechanisms on a step-by-step basis.

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Conclusion

In conclusion, the coadsorption properties of CO and O₂ on selected anionic gold clusters have been studied under ambient conditions by using pulsed flow reactor and mass spectrometric techniques. By comparing the relative adsorption activity of a reactant on a cluster in which another reactant is preadsorbed with the adsorption activity on bare gold clusters, interesting effects appear. In several cases, instead of competing for adsorption sites (competitive coadsorption), the adsorption activity of CO or O₂ is actually *increased* when the cluster already possesses the other molecule (cooperative coadsorption). In addition, the coadsorption of CO and O₂ on Au₆[−] leads to new peaks in the mass spectrum which can be attributed to the loss of a CO₂ molecule. By studying the relative amount of reaction that occurs in the defined reaction zone, it is found that, under coadsorption conditions, Au₆[−] is capable of oxidizing CO at a rate 100 times greater than previously reported for model or commercial gold cluster-based catalysts.

Note Added in Proof. After this research had been completed, we have learned of the report of Hagen et al.²⁴ on the coadsorption of carbon monoxide and molecular oxygen on smaller gold-cluster anions, namely the dimer and trimer, at cryogenic temperatures, $T = 100$ K. Among their results, they have also found that coadsorption is cooperative, agreeing with the statements above concerning cooperativity on the dimer anion, and also reporting that preadsorption of CO is essential to adsorption of molecular oxygen on the trimer anion, whereas our room-temperature conditions precluded measurable adsorption of either gas on this small cluster. Besides the difference in temperature, their ion-trap method operates at a pressure of 1 Pa (\sim 0.01 Torr) of thermalization gas (He), well below the He pressure in our reactor (approaching 100 Torr), as required for high-pressure-limit kinetics.

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