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Gas-Phase Reactivity of Gold Oxide Cluster Cations with CO

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Gold oxide cluster cations, containing one to four gold atoms and between one and five oxygen atoms, were investigated employing guided-ion-beam mass spectrometry to gain insight into their reactivity with CO. Clusters with one atomically bound oxygen atom (AuO^+ , Au_2O^+ , and Au_3O^+) were found to be reactive and selective toward oxidation of one CO molecule facilitated by adsorption of a second CO. Furthermore, the mono-oxide clusters with an odd number of gold atoms (AuO^+ and Au_3O^+) were determined to be more reactive than Au_2O^+ . Species with higher oxygen content favored adsorption of one CO molecule onto the cluster accompanied by the loss of either one or two O_2 molecules, indicating that binding of O_2 molecules to positively charged gold clusters does not prevent the subsequent chemisorption of CO. Clusters with two or more gold atoms exhibited products corresponding to loss of AuO_2 when reacted with CO. Positively charged gas-phase gold clusters, therefore, may be broken apart by the exothermic adsorption of CO. Product cluster ions resulting from these O_2 and AuO_2 loss processes appear to show further reactivity for both the oxidation of CO and the adsorption of additional CO molecules. These findings provide insight into the role of positively charged centers in gold based nanocatalysis.

Introduction

Oxidation of CO to CO_2 in the presence of nanosized gold particles has been a topic of considerable research since the initial findings of Haruta and co-workers.^{1–4} Previous studies have indicated that the catalytic activity of supported gold particles results from a charge-transfer interaction between the gold catalyst and the metal–oxide support.⁵ Specifically, F-center defects present on MgO surfaces are proposed to transfer charge to the supported gold cluster. This charge then occupies the $2\pi^*$ orbital of O_2 , which activates the O–O bond, enabling enhanced oxidation reactivity with CO.⁶ Similar charging effects have also been observed for gold species supported on thin defect-free MgO surfaces supported on Mo and Ag.^{7–9} A number of recent studies, however, have uncovered the presence of positively charged gold centers in supported catalysts for CO oxidation.^{10–14} In particular, gold catalysts dispersed on MgO and Fe_2O_3 supports were determined, through XANES and XPS, to contain gold in the Au^+ oxidation state.¹⁰ Furthermore, a significant fraction of cationic gold was found to be essential for high CO oxidation efficiency over $\text{Au}/\text{Fe}_2\text{O}_3$ catalysts.¹¹ Reduction of cationic gold to zerovalent gold through exposure to CO was also observed to reduce the catalytic activity of Au/MgO catalysts.¹² Moreover, a theoretical study of small gold clusters supported on TiO_2 revealed that some of the atoms in the cluster become positively charged through interaction with the support.¹³ In addition, Au^+ and Au^{3+} were both identified in CeO_2 -supported gold catalysts.¹⁴ A fundamental question, therefore, can be raised as to how a deficiency of electron density influences the reactivity of O_2 with CO in the presence of different size gold clusters.

Gas-phase cluster experiments allow catalyst materials, such as gold, to be investigated in the absence of factors which complicate condensed-phase catalysis research.¹⁵ These studies eliminate inconsistencies which result from different catalyst

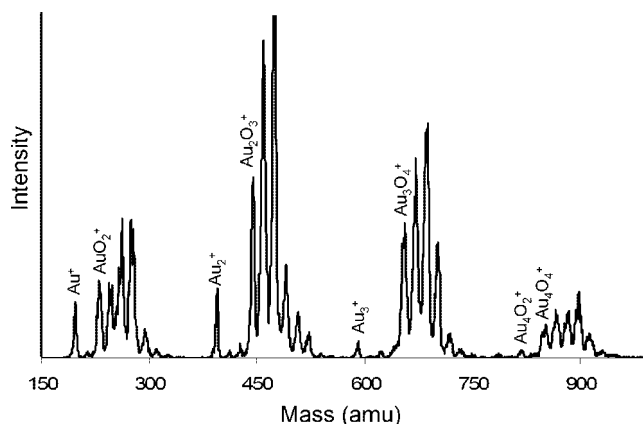


Figure 1. Typical mass distribution of gold oxide cation clusters obtained through laser vaporization.

preparation methods and allow the fundamental reactive behavior of catalyst materials to be studied with atomic level precision.¹⁶ Furthermore, it is possible to investigate the influence of factors such as size, stoichiometry, and charge state on cluster reactivity.¹⁷ Previous gas-phase studies elucidated a detailed mechanism for the oxidation of CO in the presence of anionic Au_2^- including identification of an Au_2CO_3^- metastable intermediate.¹⁸ In addition, a strong size dependence was observed in the reactivity of gold anion clusters with CO and O_2 .¹⁹ Further experiments revealed a cooperative coadsorption effect on small gold anion clusters in which adsorption of one reactant molecule was found to promote the binding of another different reactant.²⁰ The bonding of O_2 onto small gold cluster anions and neutrals was also examined, showing that the additional electron of the anion clusters results in a larger activation of the O–O bond.²¹ Furthermore, adsorption of CO onto pure gold cluster anions²² and cations²³ was investigated, revealing size-specific CO saturations and a stronger binding of CO to positively charged gold clusters.

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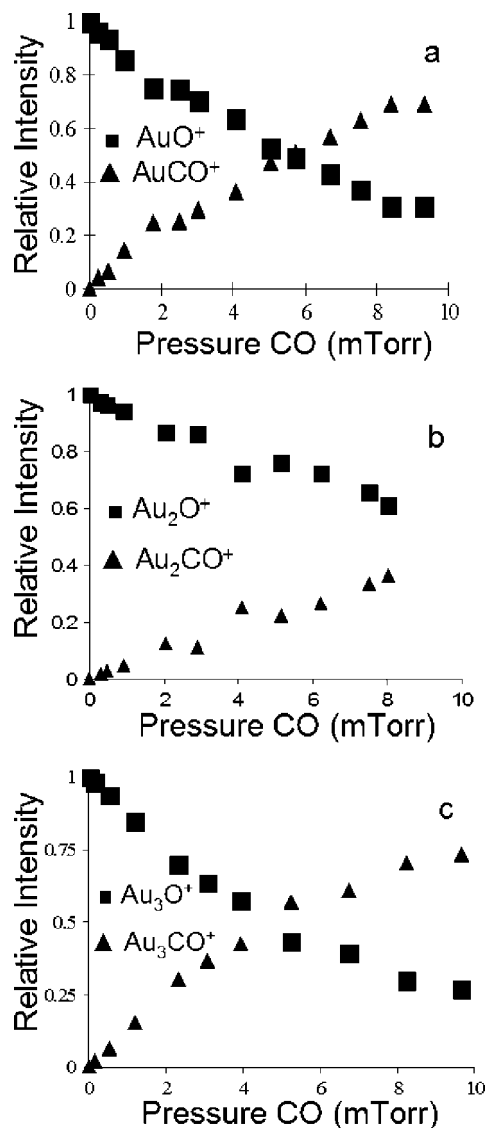


Figure 2. Relative ion intensity of (a) AuO^+ , (b) Au_2O^+ , and (c) Au_3O^+ with increasing pressure of CO. Note the decrease in the reactant ion intensity and increase in the product corresponding to oxidation of one CO molecule and adsorption of a second CO. The relative ion intensity is plotted on the y axis.

Previous research in our laboratory focused on the reactivity of atomic gold anions²⁴ and anionic oxide clusters containing two and three²⁵ and four²⁶ gold atoms with CO. For the gold oxide anion clusters an atomically bound peripheral oxygen atom was found to be the active site for CO oxidation which occurs according to a general charge-transfer mechanism.^{24,25} Furthermore, it was established that the presence of an atomically bound oxygen atom, where O_2 activation has already occurred, is not always sufficient to enable oxidation of CO.²⁵ We also discovered that gold oxide cluster anions with energetically low-lying lowest unoccupied molecular orbital (LUMO) levels bind CO more strongly because they serve as an efficient acceptor of the lone pair electrons of CO.²⁵ Finally, in a recent publication we described how ionic charge state influences the mechanism of CO oxidation on small gold clusters (AuO^\pm and Au_2O^\pm).²⁷

In this publication, we describe the reactivity of gold oxide cation clusters containing one to four gold atoms and between one and five oxygen atoms. We demonstrate that gold oxide cation clusters with one atomically bound oxygen atom (AuO^+ , Au_2O^+ , and Au_3O^+) are reactive and selective toward oxidation

of one CO molecule facilitated by adsorption of a second CO. In contrast, species with higher oxygen content favor adsorption of CO onto the cluster accompanied by loss of either one or two O_2 molecules. Clusters with two or more gold atoms also exhibit products corresponding to loss of AuO_2 subunits when reacted with CO. The cationic clusters resulting from these O_2 and AuO_2 loss processes appear to show further reactivity for both the oxidation of CO and the adsorption of additional CO molecules. These findings provide insight into the influence of positively charged gold centers in CO oxidation catalysis, an important reaction for atmospheric pollution abatement.

Experimental Section

The reactivity of gold oxide cation clusters with CO was studied using a guided-ion-beam mass spectrometer described in detail in a previous publication.²⁹ Briefly, gold oxide cation clusters were produced in a laser vaporization (LaVa) cluster source by pulsing oxygen seeded in helium (20%) into the plasma formed by ablating a gold rod with the second harmonic (532 nm) of a Nd:YAG laser. The clusters exit the source region through a 55 mm long conical expansion nozzle and are cooled through supersonic expansion into vacuum. The clusters pass through a 3 mm skimmer forming a collimated molecular beam and are directed into a quadrupole mass filter employing a set of electrostatic lenses. The quadrupole mass filter isolates clusters of a desired mass which are then passed into an octopole collision cell. The entrance lens to the octopole collision cell is grounded to ensure that no additional kinetic energy is added to the cluster ions in excess of that imparted by the supersonic expansion. Variable pressures of CO are introduced into the octopole collision cell employing a low-flow leak valve. The gas pressure is monitored using a MKS Baratron capacitance manometer. Product ions formed in the collision cell are mass analyzed by a second-quadrupole mass spectrometer. Finally, the ions are detected with a channeltron electron multiplier connected to a multichannel scalar card.

The experimental branching ratios presented in the Results section illustrate the change in normalized ion intensity with increasing pressure of CO reactant gas. At higher gas pressure, therefore, the ratio of reactant ion intensity to total ion intensity becomes smaller while the ratio of product ion intensity to total ion intensity becomes larger. This behavior is observed because the collision frequency between cluster ions and CO reactant gas molecules increases with higher gas pressure, resulting in a larger yield of product ions. We present the data as pressure-dependent normalized ion intensities because the absolute intensity of different mass-selected reactant ions varies substantially between species. Product mass spectra at a specific CO pressure would indicate the absolute intensity of both reactant and product ions for a given reaction but would not allow for a comparison of the relative reactivity of different cluster ions.

Experiments were also conducted with the same pressure of inert N_2 as CO to verify that the products observed with CO are the result of a chemical reaction and not the products of collisional fragmentation. The kinetic energy imparted to the cluster ions by the supersonic expansion was determined, employing a retarding potential analysis,²⁹ to be approximately 1.0 eV in the laboratory energy frame. Ideally, all clusters exiting the supersonic expansion source have the same initial kinetic energy. Using eq 1

$$E_{\text{CM}} = E_{\text{LAB}} \frac{\text{mass}[\text{CO}]}{\text{mass}[\text{cluster}] + \text{mass}[\text{CO}]} \quad (1)$$

the initial center-of-mass collision energy was calculated for clusters containing one, two, three, and four gold atoms to be

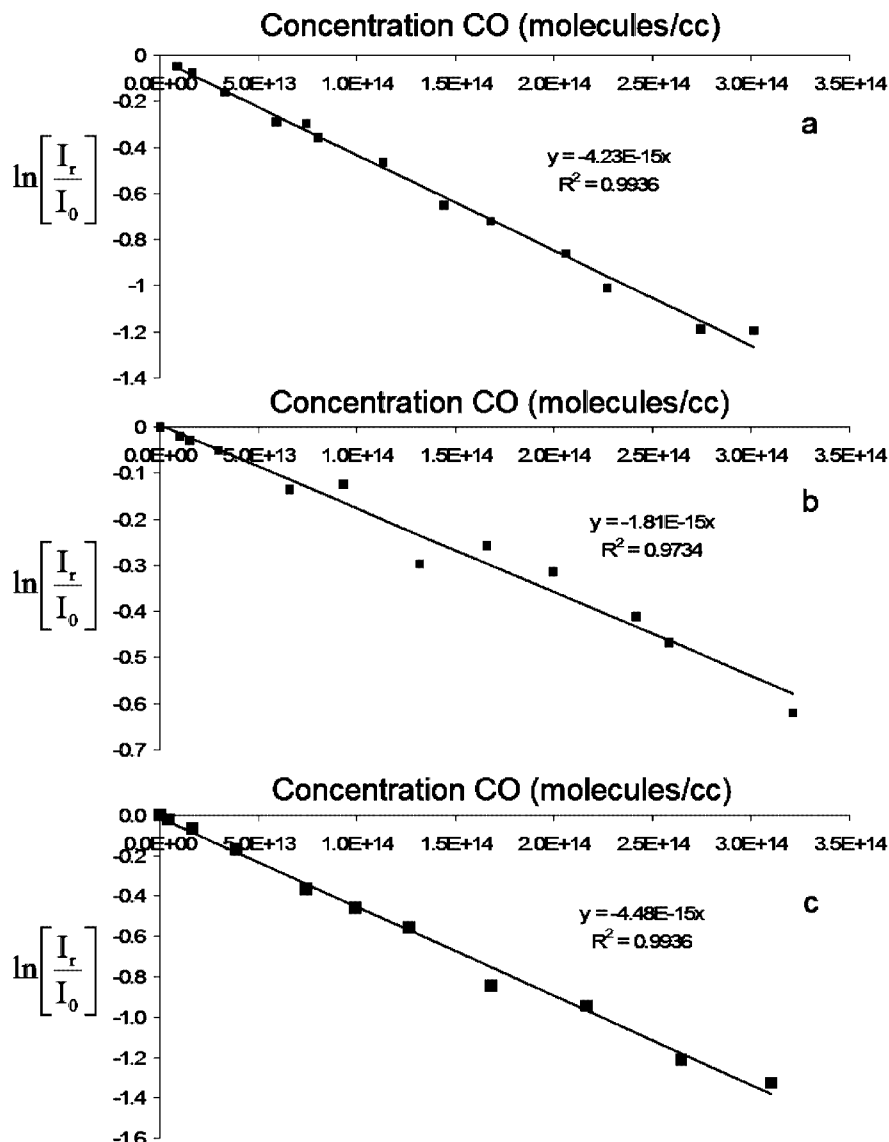


Figure 3. Plot of the logarithm of the ratio of reactant ion intensity with and without CO reactant gas $\ln[I_r/I_0]$ as a function of the concentration of CO for (a) AuO^+ , (b) Au_2O^+ , and (c) Au_3O^+ . Note the larger value of $-kt$ for AuO^+ and Au_3O^+ compared to Au_2O^+ .

approximately 0.12, 0.07, 0.05, and 0.03 eV, respectively. Using the impulsive collision model proposed by Jarrold and co-workers³⁰ the fraction of kinetic energy converted into internal energy of the clusters per collision (F_{ic}) was determined employing eq 2

$$F_{ic} = \frac{(n-1)(1-c)}{2n} \quad (2)$$

In eq 2, n is the number of atoms in the cluster and c is defined by eq 3

$$c = \frac{m_{\text{Au}} - m_{\text{CO}}}{m_{\text{Au}} + m_{\text{CO}}} \quad (3)$$

The fraction of kinetic energy converted into internal energy for clusters containing one, two, three, and four gold atoms was determined to be approximately 0.00, 0.06, 0.08, and 0.09, respectively. It should be noted that this impulsive collision model significantly overestimates the values of F_{ic} .³⁰ On the basis of the pressure of CO gas in the reaction cell, length of the collision cell (12.9 cm), and velocity of the cluster ions, it was determined that an average of approximately 77 collisions occur between clusters containing four gold atoms and CO at

the maximum reactant gas pressure of 10 mTorr CO. Assuming that each collision is as energetic as the first collision, a maximum of 0.25 eV would be converted into internal energy for clusters containing four gold atoms. The four gold atom clusters are the most massive and, consequently, lowest velocity species that were investigated. Due to their lower velocity in comparison to the lighter clusters, these species spend the most time in the collision cell and, consequently, experience the largest number of collisions. The internal energy value reported above, therefore, serves to establish an upper limit on the amount of kinetic energy that is converted into internal energy of the clusters. In fact, each collision is expected to dissipate the initial energy of a given cluster. Hence, these calculations indicate that there is not likely to be heating of the clusters in excess of 0.25 eV due to multiple collisions in the reaction cell.

Results and Discussion

Figure 1 displays a typical distribution of gold oxide cation clusters obtained by laser vaporization. Species with one to four gold atoms and between one and five oxygen atoms were reacted with CO to determine the influence of size and stoichiometry on cluster reactivity. Oxygen-rich clusters with more than five

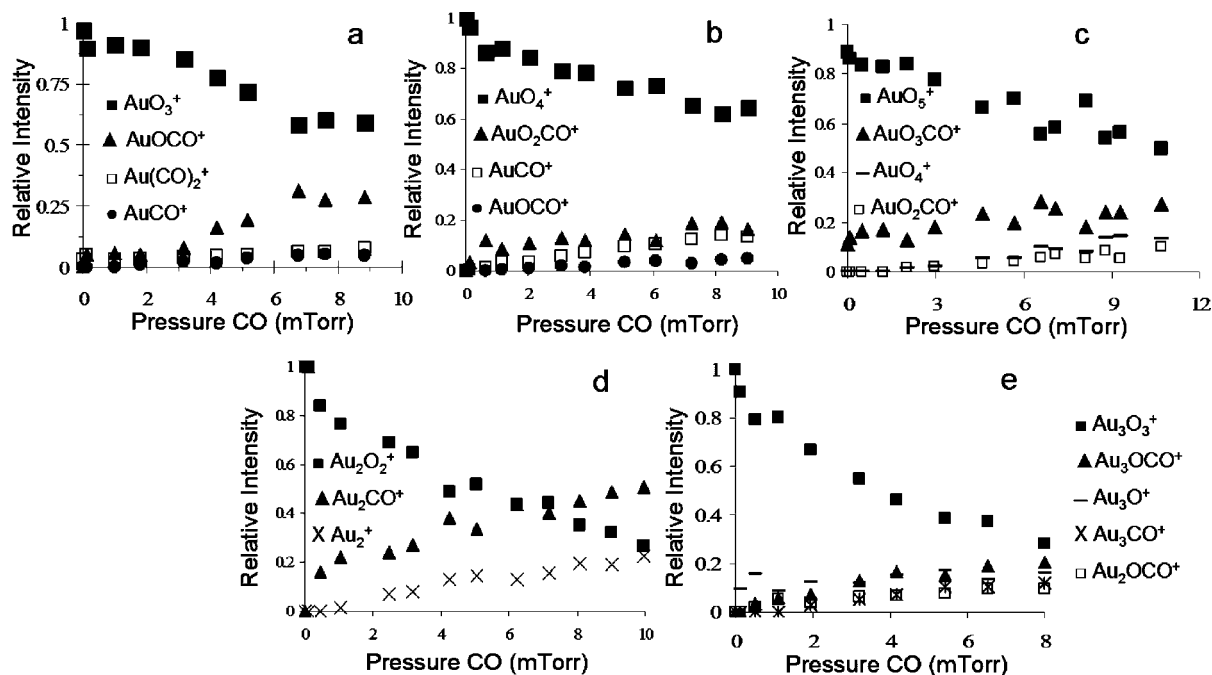
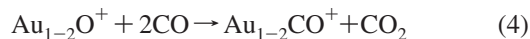


Figure 4. Relative ion intensity of (a) AuO_3^+ , (b) AuO_4^+ , (c) AuO_5^+ , (d) Au_2O_2^+ , and (e) Au_3O_3^+ with increasing pressure of CO. Note the decrease in the reactant ion intensity and increase in the product corresponding to adsorption of CO and loss of O_2 . The relative ion intensity is plotted on the y axis.

oxygen atoms were not reacted with CO because fragmentation studies with inert N_2 revealed intense collisional O_2 loss products from these species. The additional oxygen, therefore, is very weakly adsorbed onto the surface of these clusters and not activated to a superoxide-like state.³¹ An important feature of the distribution is that clusters containing both even and odd numbers of oxygen atoms are present, allowing the study of species with both atomically and molecularly bound oxygen.

Clusters with one atomically bound oxygen atom (AuO^+ , Au_2O^+ , and Au_3O^+) were found to be reactive and selective toward loss of one oxygen atom and adsorption of CO as displayed in Figure 2. In a recent publication²⁷ we attributed this product to oxidation of one CO molecule promoted by adsorption of a second CO onto the cluster according to eq 4



For AuO^+ and Au_2O^+ we demonstrated that oxidation of CO can occur by mechanisms analogous to both the Eley–Rideal and Langmuir–Hinshelwood processes that are observed on infinite surfaces.²⁷ The Langmuir–Hinshelwood-like mechanism is facilitated by the high adsorption energy of two CO molecules onto the positively charged clusters.²⁷ As the same product was observed experimentally for the reaction of Au_3O^+ with CO, it is reasonable to conclude that these mechanisms are also feasible for CO oxidation on the three gold atom cluster. In a previous study employing a fast-flow reactor mass spectrometer²⁸ both AuO^+ and Au_2O^+ were observed to decrease in intensity with increasing pressures of CO. Furthermore, the product ions AuCO^+ and Au_2CO^+ were found to increase in intensity with the initial introduction of CO but decrease in intensity at higher CO pressures. This behavior is in disagreement with the findings of the current study (Figure 2) where increasing yields of AuCO^+ and Au_2CO^+ are observed with higher pressures of CO. We attribute this difference in reactivity to the high pressure of helium bath gas present in the previous experiments which would efficiently remove the energy gained by the clusters through adsorption of the first CO. This would make further

reaction with a second CO molecule according to eq 4 less favorable. Indeed, in the previous study the intensity of the AuOCO^+ intermediate was observed to increase with higher CO pressure while the intensity of Au_2OCO^+ only decreased slowly.²⁸

Figure 2 suggests that the mono-oxide cluster containing an even number of gold atoms, Au_2O^+ , is less reactive than the clusters with an odd number of gold atoms, AuO^+ and Au_3O^+ . To further analyze the difference in reactivity between AuO^+ , Au_2O^+ , and Au_3O^+ the reaction rate constant was calculated for each cluster assuming pseudo-first-order kinetics according to eq 5

$$\ln\left[\frac{I_r}{I_0}\right] = k[R]t \quad (5)$$

In eq 5, I_r is the normalized reactant ion intensity with addition of CO, I_0 is the normalized reactant ion intensity without CO, k is the rate constant, R is the concentration of CO reactant gas, and t is the time it takes the reactant ion to pass through the octopole reaction cell. The reaction time may be calculated based on the length of the reaction cell (12.9 cm) and velocity of the ions resulting from the supersonic expansion.^{32,33} The plots of $\ln[I_r/I_0]$ as a function of CO concentration are displayed in Figure 3. Assuming pseudo-first-order kinetics, the slopes of the plots are equal to $-kt$. The values of the slopes presented in Figure 3, when divided by reaction time, reveal rate constants on the order of $7.93 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for AuO^+ , $2.42 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for Au_2O^+ , and $4.98 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for Au_3O^+ . Higher rate constants for AuO^+ and Au_3O^+ in comparison to Au_2O^+ , therefore, indicate that at the same pressure of CO, the reaction rates for AuO^+ and Au_3O^+ are larger than for Au_2O^+ . The rate constant also takes into account the larger amount of time spent in the reaction cell by heavier clusters due to their lower velocity. Comparison of the rate constants, therefore, allows the relative reactivity of different clusters to be compared with a higher degree of accuracy than can be obtained from the relative ion intensities in Figure 2. This kinetic analysis,

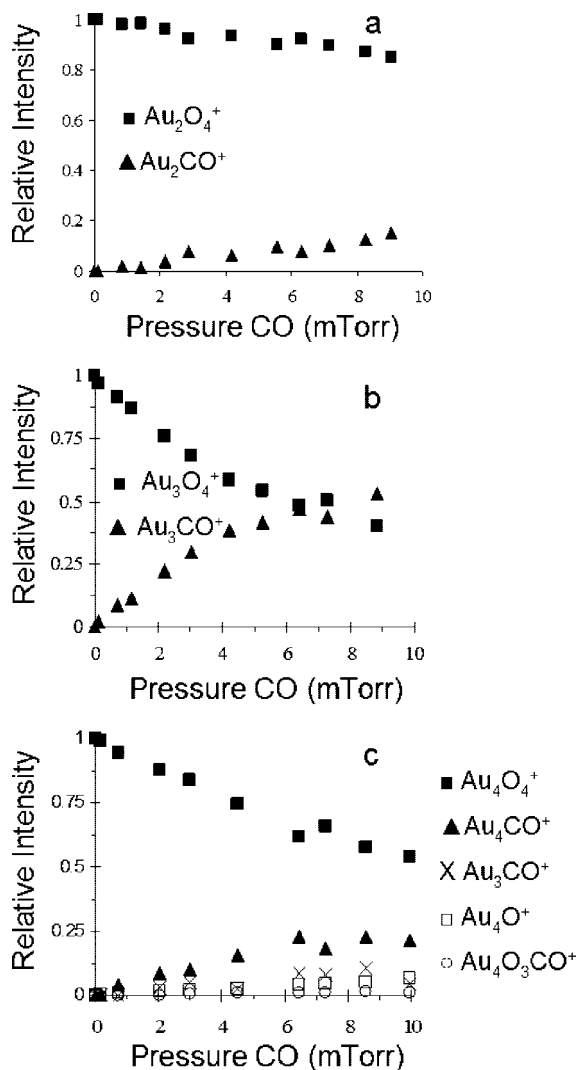


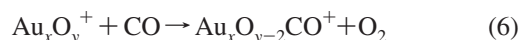
Figure 5. Relative ion intensity of (a) Au_2O_4^+ , (b) Au_3O_4^+ , and (c) Au_4O_4^+ with increasing pressure of CO. Note the decrease in the reactant ion intensity and increase in the product corresponding to adsorption of CO and loss of two O_2 molecules. The relative ion intensity is plotted on the y axis.

therefore, confirms that AuO^+ is the most reactive species, followed by Au_3O^+ and last Au_2O^+ . Unfortunately, we were unable to produce a sufficient intensity of the Au_4O^+ cluster to further examine this trend.

Previous studies of the adsorption of O_2 onto gold anion clusters revealed that clusters with an even number of gold atoms are reactive, while odd-numbered clusters are inert.¹⁶ This behavior was attributed to the open-shell electronic configuration of the even-numbered anion clusters and the closed-shell configuration of the odd-numbered anion clusters. A similar effect may underlie the difference in reactivity between AuO^+ , Au_2O^+ , and Au_3O^+ . With increasing size, two additional factors are expected to influence the reactivity of cationic gold oxide clusters with CO. First, as the size of the cluster increases, the single positive charge of the cation becomes distributed over a larger number of gold atoms.³⁴ This results in a smaller partial positive charge at each gold center. Correspondingly, the adsorption energy of CO onto the cluster is expected to decrease because the gold centers become less efficient acceptors of the lone pair electrons of CO. Second, in a larger cluster, the CO adsorption energy will be distributed throughout an increased number of internal modes. It is less probable, therefore, that

sufficient energy will partition into the mode corresponding to the reaction coordinate leading to oxidation. This will cause the Langmuir–Hinshelwood-like mechanism for CO oxidation, which relies on the structural fluxionality of the cluster, to become less favorable with increasing cluster size. Nevertheless, positively charged gold clusters with between one and three gold atoms and a single atomically bound oxygen atom are active and selective toward oxidation of CO.

As displayed in Figure 4, clusters with higher oxygen saturation (AuO_3^+ , AuO_4^+ , AuO_5^+ , Au_2O_2^+ , and Au_3O_3^+) exhibited dominant products corresponding to adsorption of one CO accompanied by the loss of a single O_2 according to eq 6



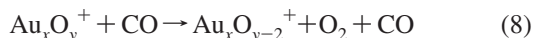
Close inspection of Figure 4 reveals that for certain clusters there is a noticeable product yield at zero pressure of CO. This is likely due to small residual background pressures of CO outside of the octopole collision cell that were not completely pumped away between subsequent experiments. The ligand-exchange reaction described by eq 6 has been observed previously for gold oxide anion clusters containing three gold atoms.²⁵ It is anticipated that cation clusters would show a stronger preference for this reaction than anions as molecular oxygen is less strongly bound and, therefore, less activated at positively charged gold centers.²¹ Indeed, separate experiments, employing N_2 gas, revealed less intense O_2 loss products than with CO, indicating that O_2 is weakly bound to these clusters but that there is some enhancement in O_2 loss by CO due to reactivity effects. Furthermore, CO is known to bind more strongly to positively charged gold clusters than to negatively charged species,^{27,34} and because all of the adsorption energy is retained by the gas-phase cluster, it is reasonable that loss of the weakly bound O_2 molecule would occur. Previous studies of the reactivity of CO and O_2 with gold anion clusters revealed that the presence of one reactant on the cluster can facilitate the binding of the second molecule in a cooperative coadsorption process.²⁰ In the case of gold cation clusters, however, the large adsorption energy of CO results in displacement of O_2 .

As presented in Figure 5, another series of clusters (Au_2O_4^+ , Au_3O_4^+ , and Au_4O_4^+) showed dominant products corresponding to adsorption of CO accompanied by loss of two O_2 molecules according to eq 7



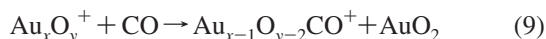
Again, it is proposed that this reaction is favorable due to the weak binding of O_2 and the strong binding of CO to cationic gold centers. Collisional studies with N_2 revealed loss of O_2 from Au_2O_4^+ and loss of both O_2 and 2O_2 from Au_3O_4^+ and Au_4O_4^+ , albeit with lower intensities than with CO. The energy gained through adsorption of CO onto these clusters, therefore, is enough to facilitate loss of two O_2 units. This finding has potential ramifications for gold-based nanocatalysis. Ideally, there is an optimum binding energy for reactant molecules to catalyst particles.³⁵ Reactant molecules, such as O_2 , must bind strongly enough to become activated but not so strongly as to poison the catalyst.³⁶ The results presented above indicate that binding of oxygen molecules to small positively charged gold centers does not prevent subsequent chemisorption of CO. Indeed, one CO can displace twice as many O_2 molecules.

Figure 6 displays the reactivity of another set of clusters (Au_2O_3^+ , Au_2O_5^+ , Au_3O_2^+ , Au_3O_5^+ , Au_4O_2^+ , and Au_4O_3^+) which exhibits collisional fragmentation products corresponding to loss of O_2 without CO adsorption according to eq 8



All of these clusters except Au_2O_5^+ exhibit steadily increasing product yields with higher pressures of CO reactant gas. Au_2O_5^+ , in contrast, does not show significant product ion intensity until a CO pressure of approximately 8 mTorr of CO. We attribute this reactive behavior to the need for approximately 60 collisions with CO to observe products. The reaction described by eq 8 is attributed to collisional O_2 loss due to the fact that the same products are also observed in separate fragmentation studies with inert N_2 . These clusters, therefore, contain very weakly bound O_2 molecules associated onto a more stable core cluster.

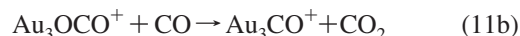
Products resulting from adsorption of CO accompanied by the loss of AuO_2 according to eq 9



were observed for Au_2O_3^+ , Au_3O_3^+ , Au_4O_2^+ , and Au_4O_3^+ , as displayed in Figures 4 and 6. Evidently, the energy gained through adsorption of CO onto these clusters is sufficient to dissociate both Au–O and Au–Au bonds. These results also have implications for gold-based nanocatalysis. Specifically, if CO adsorption is exothermic enough to break apart small gold clusters, this may cause the destruction of active sites and,

ultimately, reduced catalytic activity. Furthermore, the CO adsorption energy may be sufficient to break positively charged gold centers free from the catalyst–support material, resulting in surface migration and agglomeration into larger, less active particles. On an actual catalyst surface, however, the adsorption energy would be dissipated throughout the bulk material, making these effects less pronounced than in the gas phase.

In several instances the product ions resulting from the O_2 and AuO_2 loss processes described above appear to exhibit further reactivity with CO. For instance, AuOCO^+ and Au_3OCO^+ , which result from adsorption of CO onto and loss of O_2 from Au_3O_3^+ and Au_3O_5^+ , respectively, appear to be active for oxidation of CO according to eqs 10a, 10b, 11a, and 11b



We propose that the AuOCO^+ and Au_3OCO^+ intermediates may react with another CO to produce CO_2 . Similar species are

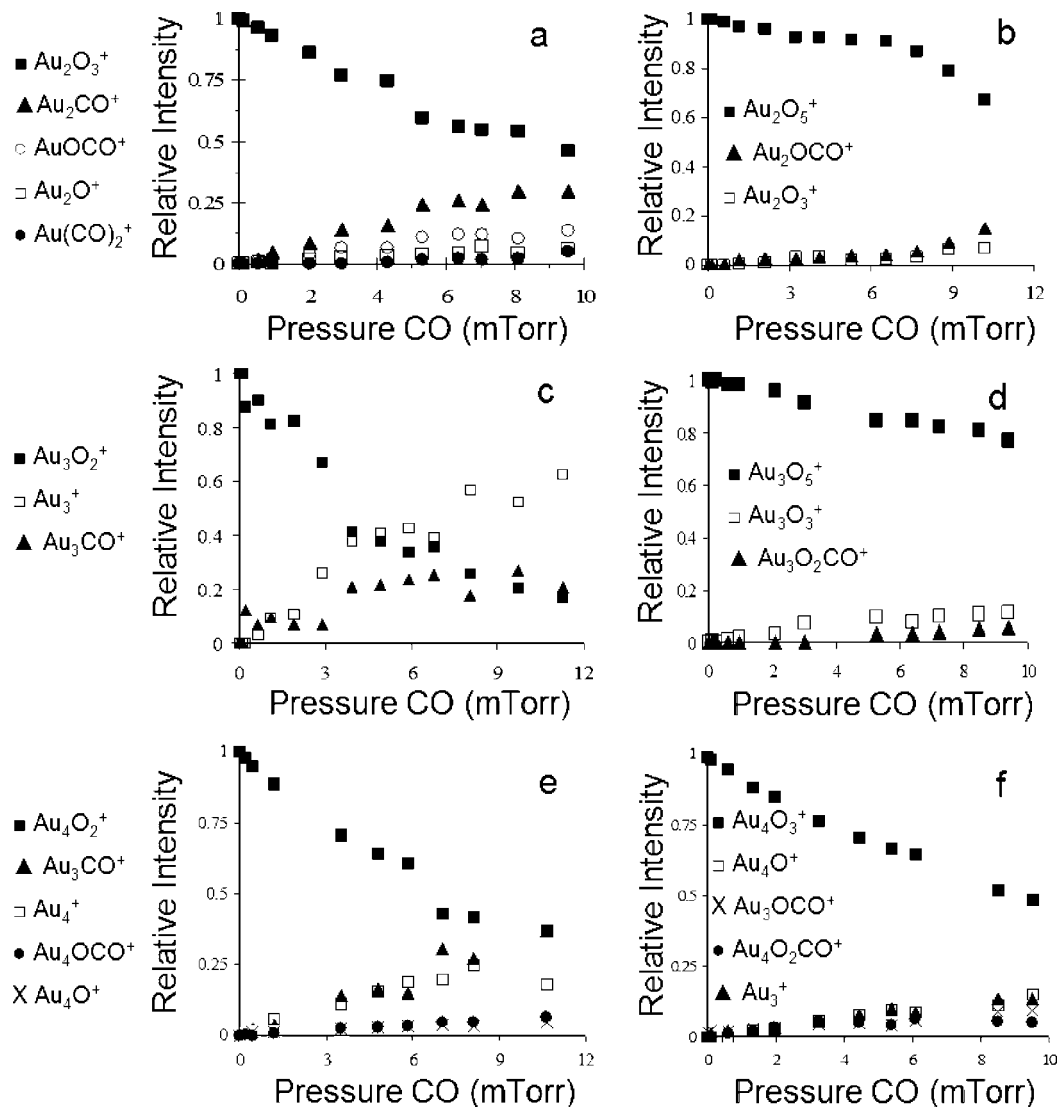


Figure 6. Relative ion intensity of (a) Au_2O_3^+ , (b) Au_2O_5^+ , (c) Au_3O_2^+ , (d) Au_3O_5^+ , (e) Au_4O_2^+ , and (f) Au_4O_3^+ with increasing pressure of CO. Note the decrease in the reactant ion intensity and increase in the product corresponding to collisional loss of O_2 . The relative ion intensity is plotted on the y axis.

theoretically predicted as intermediates in the reaction of AuO^+ and Au_2O^+ with CO according to eq 4.²⁷ Close inspection of Figure 4a reveals that the intensity of the AuOCO^+ intermediate begins to plateau at a pressure of around 7 mTorr of CO. At this pressure the AuCO^+ product also begins to become pronounced. This suggests that the AuOCO^+ intermediate is feeding the final AuCO^+ product. A similar trend cannot be definitively established for Au_3O_3^+ (Figure 4e) but also cannot be excluded.

Adsorption of a second CO molecule onto the product ions resulting from loss of O_2 and AuO_2 from larger clusters such as AuO_3^+ and Au_2O_3^+ was also observed. This indicates that while the binding of CO to positive gold centers is strong enough to displace O_2 and in some cases AuO_2 it does not necessarily result in a complete loss of reactivity with additional CO molecules.

The gas-phase findings presented herein demonstrate that CO binds more strongly to positively charged gold oxide clusters than to negatively charged species. This observation is consistent with the molecular orbital picture of how CO binds to metal centers. Bonding occurs through a combination of electron donation from the sp^* orbitals of CO to the lowest unoccupied molecular orbital (LUMO) of the cluster and π backdonation from the d orbitals of the metal cluster into the $\text{p}\pi^*$ orbitals of CO.³⁷ The contribution of σ donation to the bonding of CO to cationic clusters should be dominant because positively charged metal centers will act as efficient acceptors of the lone pair electrons of CO. For gold cation clusters with one atomically bound oxygen, the energy gained from the binding of CO to the cluster is sufficient to overcome any subsequent barriers to CO oxidation. Molecular oxygen, in contrast, is not activated when bound to positively charged gold centers and, therefore, unable to participate in the oxidation of CO. In fact, based on molecular orbital arguments, it is expected that binding of O_2 to positively charged metal centers will result in the transfer of an electron from the π_g^* molecular orbital of O_2 to the cluster resulting in a shorter, stronger O—O bond. Indeed, such a phenomenon has been observed for binding of molecular oxygen to positively charged silver clusters.³⁸ Concerning heterogeneous oxidation catalysis, it is reasonable to propose, based on these gas-phase findings, that positively charged gold particles serve to efficiently bind CO to the catalyst surface. Negatively charged gold particles, in contrast, preferentially bind and activate O_2 . Therefore, a mixture of both positively and negatively charged sites in close proximity is probably necessary to ensure that a sufficient amount of both CO and activated O_2 is present on the catalyst surface to allow reasonable oxidation efficiency.

Conclusion

The gas-phase findings presented herein demonstrate that cationic gold oxide clusters with one atomically bound oxygen atom (AuO^+ , Au_2O^+ , and Au_3O^+) are active and selective for oxidation of CO to CO_2 . Clusters with higher oxygen saturation exhibit products corresponding to adsorption of CO accompanied by loss of either one or two O_2 molecules. CO adsorption onto oxide clusters containing two or more gold atoms is also shown to result in loss of AuO_2 subunits. The clusters produced by O_2 and AuO_2 loss appear to exhibit further reactivity for the oxidation and adsorption of CO. These results are relevant to the interaction of CO with O_2 at positively charged gold centers that are known to exist in supported gold catalysts.

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References and Notes

- (1) Haruta, M. *Catal. Today* **1997**, *36*, 153.
- (2) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301.
- (3) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.
- (4) Daté, M.; Haruta, M. *J. Catal.* **2001**, *201*, 221.
- (5) Sanchez, A.; Abbet, S.; Heiz, U.; Schneider, W. D.; Häkkinen, H.; Barnett, R. N.; Landman, U. *J. Phys. Chem. A* **1999**, *103*, 9573.
- (6) Yoon, B.; Häkkinen, H.; Landman, U.; Worz, A. S.; Antonietti, J. M.; Abbet, S.; Judai, K.; Heiz, U. *Science* **2005**, *307*, 403.
- (7) Zhang, C.; Yoon, B.; Landman, U. *J. Am. Chem. Soc.* **2007**, *129*, 2228.
- (8) Sterrer, M.; Risse, T.; Pozzoni, U.; Giordano, L.; Heyde, M.; Rust, H.; Pacchioni, G.; Freund, H. *Phys. Rev. Lett.* **2007**, *98*, 096107.
- (9) Honkala, K.; Häkkinen, H. *J. Phys. Chem. C* **2007**, *111*, 4319.
- (10) Fierro-Gonzales, J. C.; Guzman, J.; Gates, B. C. *Top. Catal.* **2007**, *44*, 103.
- (11) Hutchings, G. J.; Hall, M. S.; Carley, A. F.; Landon, P.; Solsona, B. E.; Kiely, C. J.; Herzing, A.; Makkee, M.; Moulijn, J. A.; Overweg, A.; Fierro-Gonzales, J. C.; Guzman, J.; Gates, B. C. *J. Catal.* **2006**, *242*, 71.
- (12) Guzman, J.; Gates, B. C. *J. Am. Chem. Soc.* **2004**, *126*, 2672.
- (13) Wang, J. G.; Hammer, B. *Top. Catal.* **2007**, *44*, 49.
- (14) Concepcion, P.; Carrettin, S.; Corma, A. *Appl. Catal., A* **2006**, *307*, 42.
- (15) Böhme, D. K.; Schwarz, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 2336.
- (16) Kim, Y. D. *Int. J. Mass. Spectrom.* **2004**, *238*, 17.
- (17) Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. *J. Phys. Chem. B* **2002**, *106*, 6136.
- (18) Socaciu, L. D.; Hagen, J.; Bernhardt, T. M.; Woste, L.; Heiz, U.; Häkkinen, H.; Landman, U. *J. Am. Chem. Soc.* **2003**, *125*, 10437.
- (19) Bernhardt, T. M.; Socaciu-Siebert, L. D.; Hagen, J.; Woste, L. *Appl. Catal., A* **2005**, *291*, 170.
- (20) Wallace, W. T.; Whetten, R. L. *J. Am. Chem. Soc.* **2002**, *124*, 7499.
- (21) Sun, Q.; Jena, P.; Kim, Y. D.; Fischer, M.; Ganteför, G. *J. Chem. Phys.* **2004**, *120*, 6510.
- (22) Fielicke, A.; von Helden, G.; Meijer, G.; Simard, B.; Rayner, D. M. *J. Phys. Chem. B* **2005**, *109*, 23935.
- (23) Fielicke, A.; von Helden, G.; Meijer, G.; Pedersen, D. B.; Simard, B.; Rayner, D. M. *J. Am. Chem. Soc.* **2005**, *127*, 8416.
- (24) Kimble, M. L.; Castleman, A. W., Jr.; Mitrić, R.; Bürgel, C.; Bonačić-Koutecký, V. *J. Am. Chem. Soc.* **2004**, *126*, 2526.
- (25) Kimble, M. L.; Moore, N. A.; Johnson, G. E.; Castleman, A. W., Jr.; Bürgel, C.; Mitrić, R.; Bonačić-Koutecký, V. *J. Chem. Phys.* **2006**, *125*, 204311.
- (26) Kimble, M. L.; Castleman, A. W., Jr.; Bürgel, C.; Bonačić-Koutecký, V. *Int. J. Mass Spectrom.* **2006**, *254*, 163.
- (27) Bürgel, C.; Reilly, N. M.; Johnson, G. E.; Mitrić, R.; Kimble, M. L.; Castleman, A. W., Jr.; Bonačić-Koutecký, V. *J. Am. Chem. Soc.* **2008**, *130*, 1694.
- (28) Kimble, M. L.; Castleman, A. W., Jr. *Int. J. Mass. Spectrom.* **2004**, *233*, 99.
- (29) Bell, R. C.; Zemski, K. A.; Justes, D. R.; Castleman, A. W., Jr. *J. Chem. Phys.* **2001**, *114*, 798.
- (30) Jarrold, M. F.; Honea, E. C. *J. Phys. Chem.* **1991**, *95*, 9181.
- (31) Huang, X.; Zhai, H. J.; Waters, T.; Li, J.; Wang, L. S. *Angew. Chem., Int. Ed.* **2006**, *45*, 657.
- (32) Anderson, J. B.; Fenn, J. B. *Phys. Fluids* **1965**, *8*, 780.
- (33) Moore, N. A.; Mitrić, R.; Justes, D. R.; Bonačić-Koutecký, V.; Castleman, A. W., Jr. *J. Phys. Chem. B* **2006**, *110*, 3015.
- (34) Neumaier, M.; Weigend, F.; Hampe, O.; Kappes, M. M. *J. Chem. Phys.* **2005**, *122*, 104702.
- (35) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.
- (36) van Santen, R. A.; Neurock, M. *Molecular Heterogeneous Catalysis*; Wiley-VCH: Weinheim, Germany, 2006.
- (37) Bernhardt, T. *Int. J. Mass. Spectrom.* **2005**, *243*, 1–29.
- (38) Manard, M. J.; Kemper, P. R.; Bowers, M. T. *Int. J. Mass. Spectrom.* **2003**, *228*, 865–877.