

Direct Observation of Key Reaction Intermediates on Gold Clusters

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Nanosized gold clusters have attracted attention in the past decade due to their unique cluster size effects on chemical activities.^{1–17} Whereas gold has been known to be an inert material in bulk form, recent studies revealed that gold clusters smaller than 3–4 nanometers catalyze various reactions with high efficiencies even below room temperature.^{1,2}

Many experimental and theoretical studies have been devoted to unveiling the mechanism of the gold catalysts. Especially CO oxidation has been the subject of extensive studies as a model reaction;^{1–7,10–17} however, the reaction mechanism is still questionable. Analogous to the Pt-group metal catalysts,¹⁸ the reaction path of the CO oxidation on gold catalysts may involve dissociated oxygen on the surface, and the higher CO oxidation probability of smaller clusters can be attributed to the increased dissociation probability of oxygen with decreasing gold cluster size.^{1,3,4,15} An alternative CO oxidation mechanism of gold catalysts includes molecularly adsorbed oxygen such as activated peroxy-species. Haruta suggested that CO reacts with molecularly adsorbed oxygen on gold catalysts to form carbonate species (CO_3^-), which are then converted to CO_2 ,² and recent theoretical studies also supported this mechanism.^{5,6}

It is important to note that the charge transfer from supports to deposited gold clusters is crucial for enhanced catalytic activities,⁶ indicating that the free anionic gold clusters are similar to the active supported gold catalysts in terms of electronic structure. CO oxidation probabilities of free anionic Au clusters are comparable to those of gold catalysts, strongly suggesting that gas-phase Au_n^- clusters are ideal model systems for mimicking the gold catalysts consisting of gold clusters and supports.⁷

To shed light on the adsorptive behaviors of oxygen on gold catalysts, we performed experimental studies using gas-phase Au_n^- (n = number of gold atoms) clusters. Our experimental setup has been described in detail elsewhere.^{19,20} Au_n^- anions are produced with a PACIS (pulsed arc cluster ions source) and mass-selected using a reflectron time-of-flight spectrometer (mass resolution $m/\Delta m$ = 400). O_2 was inserted into the extender to generate Au_nO_2^- clusters. The vibrational temperature of the clusters is estimated to be about room temperature. A mass-selected bunch is irradiated by a UV laser pulse ($h\nu$ = 4.66 eV), and the kinetic energies of the detached electrons are measured using a “magnetic bottle”-type time-of-flight electron spectrometer. The peaks in the photoelectron spectra correspond to vertical transitions from the anionic ground state to the allowed states of the neutral species having the same geometry as the anion. The peak at the lowest binding energy corresponds to the transition into the neutral ground state, and its position is the vertical detachment energy. For example, in the case of Au_1^- , this peak is located at 2.3 eV binding energy, corresponding to the electron affinity. Vibrational fine structures of this feature can be assigned to vibrational modes of the neutral species in the geometry of the anion.

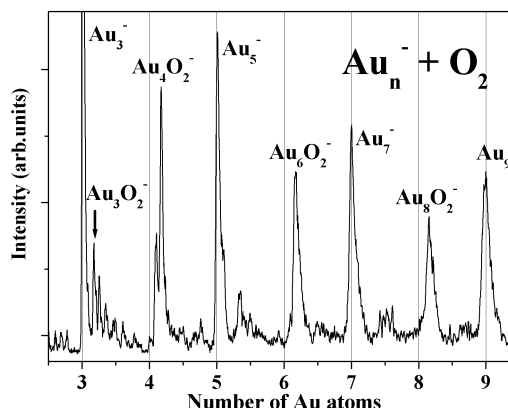


Figure 1. A magnified view of the mass spectra of Au_n^- anion clusters for the lower mass regime ($3 < n < 9$) after reaction with O_2 . The grids indicate the masses of Au_n^- clusters; thus, the peaks deviating from the grids correspond to the reacted $\text{Au}_n\text{O}_2^{2-}$ clusters.

The mass spectra of Au_n^- clusters for $n = 1–27$ taken after being exposed to O_2 show that Au_n^- clusters with even numbers of gold atoms easily react with oxygen up to $n = 20$ with an exception of Au_{16}^- , whereas the odd-numbered clusters are generally inert (Figure 1). For odd-numbered clusters, exceptions are Au_1^- and Au_3^- clusters, which can react with O_2 to some extent. Au_n^- clusters with $n > 20$ do not react with oxygen. The correlation between the size-dependent variation of oxygen adsorption reactivity and electron affinity of gold clusters for $n < 20$ has been well-established previously;⁸ that is, a lower electron affinity results in a higher free energy of the $\text{Au}_n^- - \text{O}_2$ bond, because the oxygen adsorption takes place via the charge transfer from the gold clusters to the antibonding π^* orbitals of O_2 . In the absence of an additional barrier for O_2 adsorption,⁸ a larger $\text{Au}_n^- - \text{O}_2$ bond free energy results in a higher oxygen adsorption reactivity. The inert characteristics of Au_n^- for $n > 20$ can also be explained along this charge transfer model, considering the higher electron affinities of these larger clusters.²¹

In Figure 2, photoelectron spectra of Au_nO_2^- ($n = 1, 2, 4$) clusters are presented. First, we focus on the clusters with $n = 2, 4$. The photoelectron spectra for Au_2O_2^- and Au_4O_2^- clusters show vibrational fine structures, corresponding to 179 and 152 meV, respectively. These values are higher than those known for the chemisorbed di-oxygen species on metal single-crystal surfaces. Note that the superoxo- (O_2^- , O–O bond order = 1.5) and peroxy-like species (O_2^{2-} , the O–O bond order = 1) on various metal surfaces can be identified by the O–O stretching frequencies of 80–120 and 135–150 meV, respectively.^{22,23} It should be recalled that the vibrational fine structures in the photoelectron spectroscopy correspond to those of the final states, that is, the neutral cluster with an anionic geometry. On the basis of a simple assumption that the additional electron in the anion state occupies the antibonding π^* orbital of $\text{O}_2(\text{ad})$, the O–O formal bond order of the

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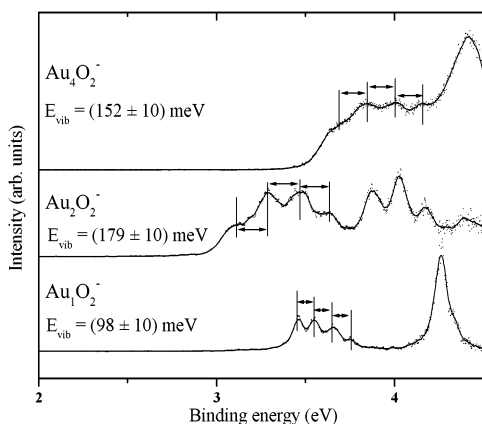


Figure 2. Photoelectron spectra for Au_nO_2^- clusters ($n = 1, 2, 4$). Fine structures correspond to the vibrational frequencies of the neutral state in the geometry of the anion.

anionic clusters decreases by 0.5 with respect to the neutral ones, which corresponds to the reduction of about 50 meV in the O–O stretching frequencies.^{22–24} The vibrational frequencies of oxygen molecules bound to the Au_2^- and Au_4^- clusters should then become quite close to those of the superoxo- and peroxy-like species on the surface, respectively, in line with recent theoretical calculations.^{5,9}

The vibrational frequency of the Au_1O_2^- cluster (98 meV) can be assigned either to atomic (Au–O stretching) or to molecular oxygen (O–O stretching); thus, our data do not provide direct evidence for the chemical states of oxygen. If dissociation of oxygen takes place on the gold monomer anions, we can conclude that the interaction between O_2 and Au_1^- is stronger than those of larger gold clusters. The same conclusion holds for the formation of di-oxygen species bound to Au_1^- , because the much lower vibrational frequency for the Au_1O_2^- clusters (98 meV) is evidence for a weaker O–O bonding, or stronger $\text{O}_2\text{–Au}_1^-$ bonding. It is important to mention that the electron affinity of Au_1^- is higher than that of Au_2^- ,^{21,25} and therefore the stronger bonding between O_2 and Au_1^- is not explained in terms of the electron affinity and the charge transfer model.

To acquire more detailed information on the structures of Au_nO_2^- ($n = 1, 2, 4$), first principle calculations are carried out for the equilibrium geometries and total energies corresponding to the ground state as well as the vertical and adiabatic electron affinities based on density functional theory with generalized gradient correction for exchange and correlation potential (Gaussian 98 software). In the case of gold monomer, the ground-state structure is a linear chain with dissociated oxygen atoms, whereas oxygen binds in the molecular form on gold dimer and tetramer. While the details of these results will be published elsewhere, the calculated vibrational frequencies and electron affinities agree very well with experiments, providing proof of the accuracy of the calculated geometries.

We compare the CO oxidation mechanism on Pt-group bulk metals with that on gold nanoclusters. On Pt-group metal surfaces,

O_2 spontaneously dissociates above room temperature, forming relatively strong metal–O bondings, and CO oxidation on these metal surfaces can take place via CO adsorption on the surface, followed by its diffusion on the surfaces and reaction with a thermally activated atomic oxygen on the surface.¹⁸ On gold clusters, in contrast, di-oxygen species are first stabilized, and CO further activates the O–O bonding to yield $\text{CO}_2(\text{g})$ and $\text{O}(\text{ad})$.^{2,5,7}

In conclusion, we provided direct evidence for the existence of oxygen molecularly bound to free Au_2^- and Au_4^- clusters at room temperature, indicating that the CO oxidation mechanism on the small gold clusters involves di-oxygen species rather than atomic oxygen. The stabilization of the di-oxygen on gold clusters is most likely not only responsible for the high activity toward CO oxidation but also other reactions such as partial oxidation of propylene. We also show that experiments using free gas-phase clusters can provide crucial information for obtaining a molecular-level understanding of catalysts consisting of nanomaterials.

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References

- (1) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *281*, 1647–1650.
- (2) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175–192.
- (3) Bondzie, V. A.; Parker, S. C.; Campbell, C. T. *J. Vac. Sci. Technol., A* **1999**, *17*, 1717–1720.
- (4) Bocuzzi, F.; Chiorino, A. *J. Phys. Chem. B* **2000**, *104*, 5414–5416.
- (5) Häkkinen, H.; Landman, U. *J. Am. Chem. Soc.* **2001**, *123*, 9704–9705.
- (6) Sanchez, A.; Abbet, S.; Heiz, U.; Schneider, W.-D.; Häkkinen, H.; Barnett, R. N.; Landman, U. *J. Phys. Chem. A* **1999**, *103*, 9573–9578.
- (7) Wallace, W. T.; Whetten, R. W. *J. Am. Chem. Soc.* **2002**, *124*, 7499–7505.
- (8) Salisbury, B. E.; Wallace, W. T.; Whetten, R. L. *Chem. Phys.* **2000**, *262*, 131–141.
- (9) Mills, G.; Gordon, M. Y.; Metiu, H. *Chem. Phys. Lett.* **2002**, *359*, 493–499.
- (10) Hagen, J.; Socaciu, L. D.; Elijazyfer, M.; Heiz, U.; Bernhardt, T. M.; Wöste, L. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1707–1709.
- (11) Grunwaldt, J.-D.; Maciejewski, M.; Becker, O. S.; Fabrizioli, P.; Baiker, A. *J. Catal.* **1999**, *186*, 458–469.
- (12) Bocuzzi, F.; Chiorino, A.; Manzoli, M. *Surf. Sci.* **2000**, *454–456*, 942–946.
- (13) Iizuka, Y.; Fujiki, H.; Yamauchi, N.; Chijiwa, T.; Arai, S.; Tsubota, S.; Haruta, M. *Catal. Today* **1997**, *36*, 115–123.
- (14) Iizuka, Y.; Tode, T.; Takao, T.; Yatsu, K.; Takeuchi, T.; Tsubota, S.; Haruta, M. *J. Catal.* **1999**, *187*, 50–58.
- (15) Lopez, N.; Norskov, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 11262–11263.
- (16) Liu, H.; Kozlov, A. I.; Kozlova, A. P.; Shido, T.; Asakura, K.; Iwasawa, Y. *J. Catal.* **1999**, *185*, 252–264.
- (17) Okumura, M.; Coronado, J. M.; Soria, J.; Haruta, M.; Conesa, J. C. *J. Catal.* **2001**, *203*, 168–174.
- (18) Engel, T.; Ertl, G. *Adv. Catal.* **1979**, *28*, 1.
- (19) Cha, C.-Y.; Ganteför, G.; Eberhardt, W. *Rev. Sci. Instrum.* **1992**, *63*, 5661.
- (20) Ganteför, G.; Sieckmann, H. R.; Lutz, H. O.; Meiwes-Broer, K.-H. *Chem. Phys. Lett.* **1990**, *165*, 293.
- (21) Taylor, K. J.; Pettiette-Hall, C. L.; Cheshnovsky, O.; Smalley, R. E. *J. Chem. Phys.* **1992**, *96*, 3319–3327.
- (22) Steiniger, H.; Lehwald, S.; Ibach, H. *Surf. Sci.* **1982**, *123*, 1–17.
- (23) Shinn, S. D.; Madey, T. E. *Surf. Sci.* **1986**, *176*, 635–652.
- (24) There is a linear relationship between the formal bond orders of di-oxygen species and its stretching frequencies, which allows direct conversion of the bond order to the vibrational frequency. For more details, see refs 22 and 23.
- (25) Handschuh, H.; Ganteför, G.; Bechtold, P. S.; Eberhardt, W. *J. Chem. Phys.* **1994**, *100*, 7093–7100.

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