Oxygen chemisorption on Au nanoparticles

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Abstract

Oxygen molecules do not adsorb on flat gold surfaces at room temperature, but recent experimental results have demonstrated adsorption of oxygen on small, negatively charged gold nanoparticles. Here we report first-principles density functional calculations of oxygen adsorption on neutral and charged Au n nanoparticles. We find that: (i) Oxygen molecules chemisorb on Au n clusters, with typical binding energies of 0.5–1.5 eV; the binding energy is larger for negatively charged clusters. (ii) In the most stable configurations, the two oxygen atoms are spatially separated and form a linear O–Au–O bridge. The results establish a correlation between the experimental reactivity of gold clusters and the oxygen binding energy.

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Platinum and platinum-group metals (such as palladium and rhodium) are excellent catalysts and have enjoyed widespread applications in the oil, chemical, and automotive industry for many years. On the other hand, the catalytic properties of gold are much more elusive, as only a few reports of gold-based catalysis have been published during most of the 20th century [1]. A breakthrough came in the late 1980s when Haruta [2] observed room-temperature catalytic activity in nanometer-sized gold particles adsorbed on TiO2, Fe2O3, and Co3O4 substrates. This discovery has spurred an intense research effort aimed at developing gold-based catalysts for industrial applications. From a fundamental point of view, however, the origin of the catalytic activity in gold nanoparticles is still not well understood. In particular, it is not clear whether the reactivity of gold nanoparticles is an intrinsic quantum-size effect, or it is associated with the interface between the gold particles and the substrate [3]. The inability of large, macroscopic gold particles to catalyze common chemical reactions, such as CO oxidation, has been attributed to the negative enthalpy of chemisorption of oxygen on gold surfaces [4], which, in turn, can be traced back to the chemical instability of bulk gold oxides. For example, Au2O3 has a positive enthalpy of formation \( \Delta H_f = +192.3 \text{ kJ mol}^{-1} \) [1]. Thus, the question arises whether oxygen molecules can chemisorb on nanometer-sized gold particles, as their catalytic activity seems to indicate, and whether the
chemisorption is dissociative or molecular in nature. Indeed, recent experimental work [5,6] has suggested that oxygen molecules do in fact adsorb on negatively charged gold clusters, although the adsorption probability appears to be strongly size dependent.

Previous first-principles calculations have focused primarily on the stability and structure of bare gold clusters [7–10]. Okamura et al. [11] and Häkkinen and Landman [12] reported calculations of the electronic structure of the AuO2 and Au2O2 molecules, respectively. They found that in the lowest-energy configuration the O2 molecule attaches to the gold atoms in an end-bonded, bent configuration. They reported a binding energy of 8.13 kcal/mol for AuO2 [11] and 1.39 eV for Au2O2 [12]. More recently, Mills et al. [13] have investigated the adsorption of O2 molecules on neutral and charged Au_n clusters (with n = 1–5), finding that the binding energy is larger (smaller) if the number of electrons in the gold cluster is odd (even). The adsorption of molecular oxygen on Au_9, Au_10, and Au_11 neutral and charged clusters was studied by Wells et al. [14]. For the Au_10 cluster they found an oxygen binding energy of 23 kcal/mol, while for the Au_5 and Au_11 clusters they reported a binding energy of 8 and 9 kcal/mol, respectively.

In this Letter, we report first-principles calculations of the stability of oxidized gold clusters Au_nO_2 (with n = 3–6), both neutral and negatively charged. We search a large number of structures to determine the low-energy configurations. We consider both molecular chemisorption, where the O–O molecular bond is preserved, and dissociative chemisorption, where the two O atoms do not form a direct bond. We find that: (i) Oxygen molecules chemisorb on Au_n clusters, with typical binding energies of 0.5–1.5 eV. The binding energy is larger for negatively charged clusters than for neutral clusters. (ii) With the exception of the neutral Au_3O_2 and Au_5O_2 clusters, in the lowest-energy configuration the oxygen molecule dissociates into two O atoms, forming a nearly linear O–Au–O bridge. Molecular adsorption occurs with smaller binding energy. For example, for the negatively charged Au_4 cluster, we find a binding energy of 1.69 eV for dissociative adsorption and 1.16 eV for molecular adsorption. (iii) The oxygen binding energy of negatively charged Au_n clusters shows characteristic odd–even oscillations as a function of n. The binding energy is larger (in magnitude) for even-n clusters, in agreement with recent experimental observations.

The oxygen binding energy of a cluster of n gold atoms having total charge q is defined as

$$\Delta E_n^q = E(Au_nO_2)^q - E(Au_n)^q - E(O_2),$$

where E is the ground-state total energy of the cluster. In this notation, the oxygen binding energy is negative when the oxidized cluster is stable against dissociation into a gold cluster and an O2 molecule. Total energies are calculated here using density functional theory in the spin-polarized generalized gradient approximation. Ultrasoft pseudopotentials are used to describe electron–ion interactions, and the wave functions are expanded in a plane-wave basis set with an energy cutoff of 30 Ry. Plane wave calculations for finite systems require a periodically repeated supercell, such that the cluster is surrounded by a sufficiently large region of vacuum. We use a cubic supercell with a typical size of 13 Å. In addition, the total energy is corrected for the spurious electrostatic interactions between the cluster and its periodic images. The calculations of the total energies of the bare and oxidized clusters, as well as the O2 molecule, are performed using the same plane-wave cutoff, the same supercell size, and the same real-space grid, so that systematic errors cancel out in Eq. (1). The atomic positions are relaxed until the quantum-mechanical forces acting on atoms are smaller than 0.02 eV/Å.

The most time consuming part of the calculation is by far evaluating the ground-state geometries of the bare and oxidized clusters, as the number of possible configurations increases exponentially with the number of atoms in the cluster. Several approaches to this problem have been proposed in the literature, including simulated annealing and genetic algorithms [15]. Here we find more convenient to start from a randomly selected ensemble of candidate configurations, and relax the atomic positions of each configuration to obtain the lowest-energy structure. Since the relaxation is performed using a conjugate-gradients
algorithm, different initial configurations lead, in principle, to different relaxed structures. Unlike simulated annealing and genetic algorithm approaches, where it can be difficult to gather information about the excited states, our approach allows us to obtain a number of low-energy configurations for each cluster.

The calculated ground-state geometries of the neutral and negatively charged Au\(_n\) clusters (with \(n = 3\)–6) are shown in the first column of Figs. 1a,b, respectively. Several first-principles calculations of the structure of bare gold clusters (no oxygen) have been reported in the literature [7–9,13,16,17]. The ground-state geometries obtained here are in agreement with those of [7,8,13,16]. In particular we find that small gold clusters have a planar structure. In [9], it was found that the lowest-energy structure of the Au\(_3\) cluster is a triangle with equal sides. In our calculations, this structure is \(~30\) meV higher in energy than the ground-state structure shown in Fig. 1a; this energy difference is small compared to the estimated numerical error. Similarly, [9] and [17] reported a zig-zag geometry for the ground-state structure of the Au\(_3\) cluster. We find that this structure is almost degenerate with the Y-shaped structure of Fig. 1b.

The second column of Figs. 1a,b shows the lowest-energy configurations of the oxidized Au\(_n\)O\(_2\) and Au\(_n\)O\(_2^-\) clusters in the case of dissociative chemisorption, where the molecular O–O bond is broken. Also shown are the oxygen binding energies, as defined in Eq. (1).

Finally, the last column of Figs. 1a,b shows the lowest-energy configurations of the oxidized clusters in the case of molecular chemisorption, where the O–O molecular bond is preserved. The lowest-energy structures for molecular adsorption of oxygen on Au\(_n\) clusters, with \(n = 2\)–5, have been recently calculated by Mills et al. [13] using a similar approach. Both the binding energies and the cluster geometries of [13] are in agreement with our results.

We find several interesting properties of the oxidized clusters: (i) With the exception of the neutral Au\(_3\) and Au\(_5\) clusters, in the lowest-energy configuration the two O atoms are spatially separated. Thus, in most cases, the structures found by Mills et al. are not the lowest-energy structures of the Au\(_n\)O\(_2\) clusters. (ii) The topology of the Au\(_n\) cluster is preserved upon oxidation. We point out that this is not an artifact of the calculations, given that our choice of initial configurations includes several randomly generated structures. Rather, it indicates that oxidation does not break Au–Au bonds. This finding is consistent with the well-known fact that bulk gold does not oxidize at normal ambient conditions. (iii) In the case of
dissociative adsorption, the two oxygen atoms are arranged to form an almost linear O–Au–O bridge configuration. If the two oxygen atoms do not share a common Au atom, the total energy is higher. For example, in the case of the Au$_4$O$_2$ cluster, if the two O atoms reside on opposite sides of the Au$_4$ rhombus the energy increases by $\sim$1.3 eV with respect to the ground-state configuration. (iv) In the case of molecular adsorption, the most common low-energy configurations are the ‘end bonded’ configuration (e.g., Au$_4$O$_2$), where the O$_2$ molecule is attached to a single Au atom, and the ‘bridge’ configuration (e.g., Au$_3$O$_2$), where the O$_2$ molecules forms a bridge between two Au atoms. (v) Like the bare Au clusters, the oxidized clusters have a planar geometry in the lowest-energy configuration. This is true for both neutral and negatively charged clusters. Häkkinen and Landman [12] found that in the ground-state geometry of the Au$_2$O$_2$ molecule the O atoms are molecularly bonded to the Au atoms, in an end-bonded configuration. Our calculations suggest that this result does not extend to larger Au$_n$ clusters.

The oxygen binding energies of neutral and negatively charged clusters are plotted in Fig. 2 as a function of the number of gold atoms. We see from Fig. 2 that: (i) The oxygen binding energy is always negative, indicating the formation of a stable gold–oxygen compound. (ii) The binding energy is larger (in magnitude) for negatively charged clusters than for neutral clusters. (iii) In the case of negatively charged clusters, the binding energy shows characteristic even–odd oscillation. The binding energy is larger (in magnitude) when $n$ is even. This is true both for molecular adsorption and dissociative adsorption. (iv) In the case of neutral cluster we find odd–even oscillations only in the case of molecular adsorption, with the binding energy being larger for odd-$n$ clusters.

Recently, the reactivity of gold clusters to oxygen was measured by Salisbury et al. [6]. In that work, negatively charged gold clusters were exposed to molecular oxygen, and the reactivity $R = [\text{Au}_nO_2]/[\text{Au}_n] + [\text{Au}_nO_2]$ was measured as a function of $n$ by time-of-flight mass spectroscopy. It was found that odd-$n$ clusters have negligible reactivity, while even-$n$ clusters have a significant reactivity, suggesting that molecular oxygen binds only to even-$n$ negatively charged clusters. This was explained [6,13] by the fact that the O$_2$ molecule acts as a one-electron acceptor, thus favoring configurations where the negatively charged Au$_n$ cluster has an unpaired electron (odd number of electrons). Our results support this explanation, although we find, in agreement with [13], that odd-$n$ clusters also bind an oxygen molecule.

We have also calculated the binding energy of a single oxygen atom, defined as

\[
\Delta E_n = E(\text{Au}_nO_1) - E(\text{Au}_n) - 1/2E(O_2),
\]

for some of the clusters of Fig. 1. For example, in the case of the Au$_4$ cluster we find a negligible binding energy of less than 0.02 eV. This indicates that in the ground state configuration of the Au$_4$O$_2$ cluster (see Fig. 1a) the two O atoms, although spatially separated, interact strongly with each other via the intermediate Au atom, and that the resulting interaction energy can be approximately identified with the oxygen binding energy of 0.85 eV.

In conclusion, we have shown by ab initio density functional calculations that oxygen molecules chemisorb on gold nanoparticles. The binding energy is larger for negatively charged clusters than for neutral clusters. In most cases, oxygen chemisorption is dissociative in nature, with the
two O atoms forming a nearly linear O–Au–O bridge.

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