3-2003

Oxygen adsorption on Au clusters and a rough Au\(1\overline{1}1\) surface: The role of surface flatness, electron confinement, excess electrons, and band gap

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Oxygen adsorption on Au clusters and a rough Au(111) surface: The role of surface flatness, electron confinement, excess electrons, and band gap

Abstract
It has been shown recently that while bulk gold is chemically inert, small Au clusters are catalytically active. The reasons for this activity and its dramatic dependence on cluster size are not understood. We use density functional theory to study O2 binding to Au clusters and to a Au(111) surface modified by adsorption of Au clusters on it. We find that O2 does not bind to a flat face of a planar Au cluster, even though it binds well to its edge. Moreover, O2 binds to Au clusters deposited on a Au(111) surface, even though it does not bind to Au(111). This indicates that a band gap is not an essential factor in binding O2, but surface roughness is. Adding electrons to the surface of a Au(111) slab, on which one has deposited a Au cluster, increases the binding energy of O2. However, adding electrons to a flat Au surface has no effect on O2 binding energy. These observations have a simple explanation: in clusters and in the rough surface, the highest occupied molecular orbital (HOMO) is localized and its charge density sticks out in the vacuum. This facilitates charge transfer into the $\pi^*$ orbital of O2, which induces the molecule to bind to gold. A flat face of a cluster or a flat bulk surface tends to delocalize the HOMO, diminishing the ability of the surface to bind O2. The same statements are true for the LUMO orbital, which is occupied by the additional electron given to the system to charge the system negatively.

Keywords
Gold, Adsorption, Band gap, Rough surfaces, Carrier density

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Oxygen adsorption on Au clusters and a rough Au(111) surface: The role of surface flatness, electron confinement, excess electrons, and band gap

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Citation: The Journal of Chemical Physics 118, 4198 (2003); doi: 10.1063/1.1542879

View online: http://dx.doi.org/10.1063/1.1542879

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Oxygen adsorption on Au clusters and a rough Au(111) surface: The role of surface flatness, electron confinement, excess electrons, and band gap

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(Received 22 July 2002; accepted 10 December 2002)

It has been shown recently that while bulk gold is chemically inert, small Au clusters are catalytically active. The reasons for this activity and its dramatic dependence on cluster size are not understood. We use density functional theory to study O₂ binding to Au clusters and to a Au(111) surface modified by adsorption of Au clusters on it. We find that O₂ does not bind to a flat face of a planar Au cluster, even though it binds well to its edge. Moreover, O₂ binds to Au clusters deposited on a Au(111) surface, even though it does not bind to Au(111). This indicates that a band gap is not an essential factor in binding O₂, but surface roughness is. Adding electrons to the surface of a Au(111) slab, on which one has deposited a Au cluster, increases the binding energy of O₂. However, adding electrons to a flat Au surface has no effect on O₂ binding energy. These observations have a simple explanation: in clusters and in the rough surface, the highest occupied molecular orbital (HOMO) is localized and its charge density sticks out in the vacuum. This facilitates charge transfer into the π* orbital of O₂, which induces the molecule to bind to gold. A flat face of a cluster or a flat bulk surface tends to delocalize the HOMO, diminishing the ability of the surface to bind O₂. The same statements are true for the LUMO orbital, which is occupied by the additional electron given to the system to charge the system negatively. © 2003 American Institute of Physics. [DOI: 10.1063/1.1542879]

I. INTRODUCTION

Recent experiments on CO and NO oxidation,¹⁻⁸ partial oxidation of propene,⁹⁻¹¹ and partial hydrogenation of acetylene,¹² have surprised many chemists. They show that small Au clusters are good catalysts, although bulk Au is chemically inert. There is no explanation for this difference in the catalytic activity, or for its dramatic size dependence.

Here we examine four factors that may be responsible for this difference: the flatness of the surface, the band gap, the finite size, and the excess charge on Au.

Valden, Lai, and Goodman¹³ have suggested that the existence of a band gap is an essential factor in making small Au clusters chemically active. While the interpretation of the experiments may be open to discussion, the suggestion is interesting and deserves careful examination.

Density functional calculations by Mavrikakis, Stoltze, and Norskov¹⁴ have shown that stepped surfaces of bulk Au adsorb O₂, while the flat terraces between the steps do not. In a recent DFT study of CO binding to neutral and charged Auₙ clusters, Wu et al.¹⁵ found that CO binds to the edges, and not to the flat faces, of the clusters. They also found that charging the cluster alters the binding energy but does not alter the typical binding geometries observed, suggesting that the gold–ligand chemistry is determined more by local than by global electronic features. Furthermore, Mori and Shitani¹⁶ found that a bulk Au surface scratched by a ceramic needle adsorbs hexane, benzene, ethers, and ketones, while an unscratched Au surface does not. These findings suggest that a rough gold surface is more active than a flat one.

Gas phase measurements by Salisbury, Wallace, and Whetten¹⁷ have shown that Auₙ⁻ (n = 2,...,22) clusters having an odd number of electrons adsorb O₂, and those with an even number do not. Furthermore, a Auₙ⁻ cluster that adsorbs one O₂ molecule will not adsorb a second one. These observations suggest that oxygen binding requires the presence of an easy-to-get electron in the Au cluster. Furthermore, it seems that if such an electron is tied up by one oxygen molecule, a second O₂ molecule is unable to bind to the cluster. Density functional calculations¹⁸ agree with some, but not all, of these conclusions. They show that all small clusters (n = 1,...,7) bind O₂, in disagreement with experiment. However, the binding energy of O₂ to clusters having an odd number of electrons is much larger (by about 0.5 eV) than to electron clusters. In the calculations, all clusters bind a second molecule, but much less strongly than the first one. In the experiments the second molecule does not bind. Both calculations and experiments indicate a strong dependence of the binding energy on the parity of the number of electrons.

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in the clusters. This is true for both negative and neutral clusters. The factor controlling this behavior seems to be the ionization potential, which is smaller for clusters with an odd number of electrons; this makes one electron in such a cluster easier to transfer to the binding O₂ molecule.

The need for an easy-to-get electron may be relevant to catalysis by Au clusters supported on an oxide surface. Sanchez et al.³⁹ have noticed that the catalytic activity of a mass-selected cluster deposited on MgO depends on the state of the surface. The cluster was not active on a "perfect" surface, but it was active if oxygen vacancies were created on the MgO surface before the clusters were deposited. It is reasonable to assume that the Au clusters prefer to bind to these vacancies. Since the vacancies are negatively charged F centers, it was hypothesized that an electron is transferred from the surface to the cluster, and this electron is responsible for turning on the activity of the cluster. Density functional calculations³⁹ support this interpretation.

In this paper, we use density functional theory to show that the flatness of the surface affects very strongly oxygen adsorption on both bulk Au and Au clusters. We find that O₂ does not bind to the flat side of small Au clusters, regardless of the number of electrons in them, and in spite of the fact that the clusters have a "band gap." We conclude, therefore, that the existence of a band gap is not sufficient for turning on the chemical activity of a cluster. The next question is whether a band gap is necessary. To determine this, we have calculated the binding energy of O₂ to Au clusters deposited on the (111) face of a Au slab [we denote such a system by Auₙ/Au(111)]. We find that O₂ binds to such clusters, in spite of the fact that the system is a metal and there is no band gap. The geometry of the system and the nature of the bonds are very similar to those made with the gas phase clusters, but the binding energy is smaller. We conclude from this that the existence of a band gap is not essential to the binding of O₂ to gold, and that having a rough surface is.

As we have already mentioned, the binding energy of oxygen to a cluster oscillates with the number of electrons in the cluster: it is large if the cluster has an odd number of electrons and it is small if that number is even. This is true for both negative and neutral clusters. Our calculations do not show this effect for when O₂ binds to Auₙ/Au(111); the binding energy changes with n slightly.

We have also performed calculations with a Auₙ/Au(111) system to which we added one electron per unit cell (to make a "negative ion"). Since, in our calculations, the unit cell for Au(111) contains 24 Au atoms with 24×1=264 valence electrons, we added one electron for 264 electrons in the slab. This is a very substantial charging and it has a detectable effect. Auₙ/Au(111) binds O₂ more strongly than does Auₙ/Au(111). Thus, our findings suggest that electrostatic charging of clusters supported on an oxide surface could affect catalytic activity substantially.

Our calculations offer a simple (hopefully, not too simple) explanation for these observations. In all calculations in which O₂ binds to Au, we find bond formation is accompanied by electron transfer from Au to the π* orbital of oxygen. Two elements play a role in a simplified description of this process: the energy of the HOMO of Au should be close to the energy of the π* orbital of oxygen; furthermore, the two orbitals must have good overlap, to give a reasonable coupling for charge transfer between them. This simple picture explains qualitatively most of our observations.

The HOMO of all small planar Auₙ clusters has a large lobe sticking out in the vacuum, at the edge of the cluster. This is where the overlap with the π* orbital of O₂ is the best and this is where O₂ binds. The same HOMO has very little charge density outside the flat (111)—like, face of a Auₙ cluster or of a Au(111) slab and O₂ does not bind there. Furthermore, disrupting surface flatness, by depositing a Auₙ cluster on the Au(111) surface, creates a localized high-energy orbital that reaches out in the vacuum and this is why O₂ binds to such roughened surfaces. The binding energy of O₂ on Auₙ/Au(111) is less than the binding energy to Auₙ (see Table I) because some of the electron density on the cluster is used to bond Auₙ to Au(111), removing thus from the cluster electron density that could be used for binding O₂. Also, the HOMO in Auₙ/Au(111) is less localized than in Auₙ.

In what follows, we present the computations on which the qualitative remarks made above are based.

### II. COMPUTATIONAL DETAILS

We use spin-polarized density functional theory with a plane wave basis set and ultrasoft pseudopotentials, as implemented in the VASP program written by Kresse, Furthmüller, and Hafner.²⁰–²³ The pseudopotentials allow us to treat the Au atom as if it has 11 "valence" electrons. In a few cases we used the projector-augmented wave function (PAW)
method,\textsuperscript{24} which includes the inner electrons as "frozen" wave functions, and obtained the same results as when we used pseudopotentials. To include correlations and exchange we used the Perdew and Wang\textsuperscript{25} functional. The convergence of the basis set was tested by performing a few calculations with a plane wave cutoff of 396 and 500 eV to show that they give nearly identical O\textsubscript{2} binding energies. The results reported here were obtained with a cutoff energy of 396 eV.

We also tested the convergence with respect to the mesh of $k$ points used to sample the Brillouin zone. We used a $2 \times 2 \times 1, 3 \times 3 \times 1,$ and $4 \times 4 \times 1$ grid, which correspond to 2, 5, and 8 irreducible $k$ points, respectively. The intermediate set offered some improvement over the smallest set (around 0.1 eV in the O\textsubscript{2} binding energy), although the trends stayed the same. The largest set did not improve the energy further. Consequently, we have used the intermediate mesh in the calculations reported, except for a few cases (the charged surfaces), where we were only interested in qualitative information, for which we considered the smallest mesh to be sufficient.

The Au(111) substrate was modeled using a two-layer-thick slab, with a $3 \times 4$ surface unit cell. The atoms in the bottom layer were held fixed in the bulk positions. We used a three-layer slab in some calculations, and found that this reduces the O\textsubscript{2} binding energy by about 0.05 eV, indicating that the results are essentially converged with only two layers. A similar observation was made by Mavrikakis et al.\textsuperscript{14} The vacuum layer between periodic images of the substrate, in the direction perpendicular to the slab surface, was 9.7 Å (four Au layer widths). For cluster calculations, the spurious electrostatic interactions between the periodic replicas were removed by using the method of Makov and Payne,\textsuperscript{26} as implemented in VASP.

The (111) surface of Au reconstructs with a very large surface unit cell. Since the reconstruction affects the local structure of the surface very little, we have worked with an unreconstructed Au(111) surface.

### III. RESULTS

#### A. The systems studied

We have calculated the energy of the bond between O\textsubscript{2} and various forms of Au. We have looked at (1) O\textsubscript{2} binding to the flat, (111)-like faces and to the edges of Au\textsubscript{n} (neutral and anionic) and Au\textsubscript{n}\textsuperscript{-} (neutral and anionic) clusters; (2) O\textsubscript{2} binding to the flat, unreconstructed, (111) surface of bulk gold; (3) O\textsubscript{2} binding to Au\textsubscript{n}/Au(111), for $n=1, 2,$ and 3; (4) O\textsubscript{2} binding to a row of Au atoms forming a one-dimensional "wire" on Au(111); (5) O\textsubscript{2} binding to a Au(111) surface or a Au\textsubscript{n}/Au(111) surface that has an excess of one electron per unit cell. Each system was chosen so as to illuminate a specific point about oxygen binding.

#### B. O\textsubscript{2} binding to (111)-like facets and to the edges of Au\textsubscript{n}: The role of flatness

For all clusters we have studied (Au\textsubscript{n} and Au\textsubscript{n}\textsuperscript{-} with $n=1\text{--}7$), O\textsubscript{2} binds to the edges of the cluster, with binding energies shown in Table I. We note that several binding sites are possible along the edge of the clusters and they have quite different binding energies; here we give the results for the most stable bonds. The clusters with an odd number of electrons bind oxygen more strongly than those with an even number of electrons (in our calculations each Au atom has 11 electrons). This is true for both negative\textsuperscript{17,18} and neutral clusters.\textsuperscript{18}

The clusters Au\textsubscript{5}, Au\textsubscript{6}, Au\textsubscript{5}\textsuperscript{-}, and Au\textsubscript{6}\textsuperscript{-} are planar and their flat faces have a (111)-like structure (see Figs. 1 and 2, which show the optimized structures of Au\textsubscript{6} and Au\textsubscript{5}O\textsubscript{2}). The positions of Au in Au\textsubscript{5}\textsuperscript{-} and Au\textsubscript{6}\textsuperscript{-} are very similar to those in Au\textsubscript{5} and Au\textsubscript{6}, respectively. Our calculations show that the binding energy of O\textsubscript{2} to the flat faces of Au\textsubscript{5}, Au\textsubscript{6}, Au\textsubscript{5}\textsuperscript{-}, and Au\textsubscript{6}\textsuperscript{-}, or to the (111) surface of a Au slab, is negligible. In spite of the fact that the Au(111) slab is a metal (it has no band gap) and the Au\textsubscript{n} clusters are not, they have a common feature: O\textsubscript{2} does not bind to their flat faces. This property is independent of the number of electrons or the charge of the system.

A possible explanation for this behavior is provided below. We have shown that it is very likely\textsuperscript{18} that chemisorption of O\textsubscript{2} to Au clusters involves the formation of a negative species, similar to O\textsubscript{2}\textsuperscript{-}, by electron transfer to the empty $\pi^*$ orbital of O\textsubscript{2}. This suggestion is supported by plots of charge displacement during bond formation and by the fact that the bond length of the chemisorbed O\textsubscript{2} molecule is comparable to that of the O\textsubscript{2}\textsuperscript{-} molecule and is substantially longer than...
that of O\textsubscript{2} (see Table I). If this scenario is true, then the O\textsubscript{2} molecule ought to bind at sites where the HOMO of the Au system overlaps well with the $\pi^*$ orbital of O\textsubscript{2}. This turns out to occur in all cases we have examined ($\text{Au}_n$ and $\text{Au}_n^+$ with $n$ from 1–7). One example is shown in Fig. 3, where we plot the charge density in the HOMO of a Au\textsubscript{5} cluster. Note the large lobe, on top of the two Au atoms, in the upper part of the figure. This is where O\textsubscript{2} binds most strongly. The charge densities in the HOMOs of Au\textsubscript{5}, Au\textsubscript{6}, and Au\textsubscript{6} have similar features.

It so happens that the HOMOs of the four clusters just mentioned have little charge density along the flat face of the clusters. This is why the O\textsubscript{2} molecule does not bind there. The same is true for the HOMO of Au\textsubscript{(111)} (see Fig. 4); the orbital is delocalized and the charge density at possible binding sites is small. We infer from this that a flat Au surface, of a cluster or of the bulk, favors the spreading (delocalization) of the HOMO over many sites, which is unfavorable to the coupling with the $\pi^*$ orbital of O\textsubscript{2}. Since such coupling is required for the electron transfer that facilitates bonding, the binding energy is small.

Of course, other orbital interactions are likely to contribute to bonding, but we assume here that the effect of the two orbitals invoked is dominant. Such an assumption is justified only by the qualitative agreement with the results of the full calculation.

C. Metallic (bulk) Au adsorbs O\textsubscript{2} if its surface is not flat: Binding to Au\textsubscript{n}/Au(111)

The opinions expressed above suggest the following “computer experiment.” If we deposit on the Au(111) surface a Au\textsubscript{n} cluster, to break the monotony of the flat surface, O\textsubscript{2} should bind to it, if the HOMO of Au\textsubscript{n}/Au(111) is localized around the cluster and protrudes into the vacuum. To test the "prediction," we have calculated the binding energy of O\textsubscript{2} to Au\textsubscript{n}/Au(111), for $n=1,2,3$ (see Table I). O\textsubscript{2} binds to the "supported cluster," but the binding energy is less than the binding to the same cluster in the gas phase (see Table I). The charge density in the HOMOs of Au\textsubscript{1}/Au(111) and Au\textsubscript{2}/Au(111) are shown in Figs. 5 and 6. These orbitals are localized around the cluster and have a lobe pointing toward the vacuum, and we expect the O\textsubscript{2} to bind there. Indeed it does, as can be seen in Figs. 7 and 8, which show the binding geometry corresponding to the minimum energy. We also show, in Fig. 9, the geometry of O\textsubscript{2} bound to Au\textsubscript{3}/Au(111). This too follows the rule mentioned above.

To better understand how the electron density changes upon bond formation, we have performed a number of electron density subtractions, whose results we present next. We subtract from the charge density of O\textsubscript{2}/Au\textsubscript{1}/Au(111), the charge density of O\textsubscript{2} and that of Au\textsubscript{1}/Au(111). The charge densities of the last two systems have been computed at the geometry they have in the O\textsubscript{2}/Au\textsubscript{1}/Au(111) compounds. This calculation shows how the electron density changes when the bond of O\textsubscript{2} with the Au\textsubscript{1}/Au(111) is formed. The positive
values of this charge density difference are shown in Fig. 10(a); they indicate regions where the electron density increases when the oxygen–gold bond is formed. In Fig. 10(b), we plot the negative values of the difference, which show the regions where charge is lost during the formation of the same bond. Note the gain of electrons in the $\pi^*$ orbital of O$_2$, some gain on the Au atom, and very little change around three of the atoms of the Au$_{111}$ surface. The electron density is lost by the O$_2$ molecule and the Au atoms of the cluster. There is charge transfer into the $\pi^*$ orbital of O$_2$, but also a charge rearrangement on O$_2$ and the Au atom.

The geometry of the O$_2$/Au$_1$/Au$_{111}$ complex is similar to that of O$_2$ bound to Au$_5$ (in the gas phase) and so the electron density difference plots (see Ref. 18). This suggests that O$_2$ binding to Au$_1$/Au$_{111}$ involves mainly two of the surface atoms.

In Figs. 11(a) and 11(b), we show the result of a subtraction of the charge of Au$_1$O$_2$ and that of Au$_{111}$ [both having the same geometry as in O$_2$/Au$_1$/Au$_{111}$] from that of O$_2$/Au$_1$/Au$_{111}$. This difference describes electron migration upon the formation of the bond between Au$_1$O$_2$ and Au$_{111}$. One can clearly see a substantial charge transfer into the region between the Au adatom and Au$_{111}$. Upon bond formation, electrons from the adsorbed Au atom and three surface Au atoms move into the region between the adsorbed Au atom and the Au surface. Some electron density rearrangement takes place on the O$_2$ molecule. The removal of electronic charge from the protruding Au atom is the reason why the oxygen binding energy in O$_2$/Au$_1$/Au$_{111}$ is less than that of oxygen binding in O$_2$Au$_1$.

It is interesting to see that bonding of either Au$_1$O$_2$ to Au$_{111}$ or that of O$_2$ to Au$_1$/Au$_{111}$ affects only a very few Au atoms in the slab. This is probably due to the high mobility of the electrons in the system, which screen efficiently the disruption of the electron density caused by bonding.

Similar things can be said about O$_2$/Au$_2$/Au$_{111}$ and O$_2$/Au$_3$/Au$_{111}$. In both cases the geometry of O$_2$ bound to the supported cluster is similar to that of binding to Au$_5$. The electron density shifts caused by the binding of O$_2$ to Au$_2$/Au$_{111}$ are shown in Fig. 12; the density shifts upon the formation of O$_2$/Au$_3$/Au$_{111}$ look very similar.

Only a few atoms in the Au$_{111}$ surface participate in the HOMO of the Au$_n$ (111) or in the bonding of oxygen. In a limited sense the Au$_n$/Au$_{111}$ behaves like a small cluster. There are, however, differences. The binding energy of O$_2$ to the supported Au$_n$ cluster is less than that of binding to the Au$_n$ cluster in the gas phase. We attribute this to a confinement effect: the HOMO of the gas phase cluster is more localized than that of the supported cluster. Moreover, some of the electrons in the supported clusters are engaged in bonding to the Au$_{111}$ surface and are not available for O$_2$ bonding to the cluster.
D. The role of the parity of the number of electrons

The binding energy of O\textsubscript{2} to gas-phase Au\textsubscript{n} and Au\textsubscript{n}\textsuperscript{2} depends strongly on the parity of the number of electrons. If the number of electrons is odd, the binding energy is large (see Table I); if it is even, it is small (see Table I). This alternation correlates with an alternation in the ionization potential of the cluster: if the number of electrons in the gold cluster is odd, the ionization potential is small. This facilitates electron transfer to O\textsubscript{2} and strengthens the O\textsubscript{2}–Au bond. Thus, a gas-phase cluster behaves as if the highest-energy electrons in the cluster are not as willing to leave the cluster and help O\textsubscript{2} bond to it, if they are paired.

The concepts advanced here suggest that the bond of O\textsubscript{2} with Au\textsubscript{n}/Au(111) is different and that there should be no alternation of the bonding energy with \(n\); the work function of Au\textsubscript{n}/Au(111) changes very little with \(n\) and therefore the ionization potential is roughly independent of \(n\). Calculations support this statement: for O\textsubscript{2}/Au\textsubscript{n}/Au(111), the binding energy is not large for odd \(n\) and small for even \(n\), as in the gas phase. The variation of binding energy with \(n\) (Table I) is probably due to changes in the geometry of the binding site.

E. The role of electron localization: O\textsubscript{2} binding to a one-dimensional wire of Au atoms on Au(111)

We have pointed out that the HOMO in the Au\textsubscript{n}/Au(111) compounds is localized around the cluster, and this facilitates oxygen binding. To better understand this effect we decided to study O\textsubscript{2} binding to a one-dimensional row of atoms deposited on a Au(111) surface, whose structure is shown in Fig. 13. Making such a wire is likely to delocalize the HOMO along the wire. This means that the binding energy of O\textsubscript{2} to the supported wire will be lower than the binding to a supported Au\textsubscript{2} cluster, which can be thought of as being formed by removing every third atom from the wire (see Fig. 13). This removal will help localize the electron on the Au\textsubscript{2} cluster and increase oxygen bonding to it.

The calculations bear out this expectation: the binding energy of O\textsubscript{2} to a wire of Au atoms on Au(111) is less than that to a Au\textsubscript{2} supported cluster (see Table I). In both systems, O\textsubscript{2} prefers to bind parallel with two Au adatoms. This allows us to compare the binding energies directly. In Fig. 14 we show the electron density shifts caused by bringing together O\textsubscript{2} with the wire/Au(111). This figure shows that the third Au adatom (in the unit cell), which is missing in the Au\textsubscript{2}/Au(111) system, is also involved in the charge transfer and thus in the bonding.

FIG. 11. The same as Fig. 10, for forming O\textsubscript{2}/Au\textsubscript{1}/Au(111) from Au\textsubscript{1}O\textsubscript{2} and Au(111). (a) Electron density gain; (b) electron density loss.

FIG. 12. The same as Fig. 10, for forming O\textsubscript{2}/Au\textsubscript{2}/Au(111) from O\textsubscript{2} and Au\textsubscript{2}/Au(111). (a) Electron density gain; (b) electron density loss.

FIG. 13. (a) The geometry of the Au\textsubscript{2}/Au(111) system. (b) The geometry of Au wire/Au(111). In (a), we show how a rotation of the gold atom and the addition of one Au atom per unit cell (dashed line) transforms Au\textsubscript{2}/Au(111) into Au wire/Au(111).
roughness to mean any deviation from “flatness.” Oxygen does not bind to a flat facet of gold, no matter whether the facet is that of a small cluster or of a bulk surface. Roughening a Au(111) surface, by putting Au₃ clusters on it, leads to binding. Roughness acts by localizing of the HOMO of Au to provide a higher electron density at the site where O₂ binds. This facilitates electronic charge transfer to the π* orbital of O₂, which leads to bonding.

One reason for the activity of small Au clusters, is that it is impossible to avoid having a large number of “rough” atoms; they must have isolated clusters on a facet, many edges between facets, kinks, steps, etc. On very large clusters the fraction of rough centers is diminished by faceting. The mobility of adsorbed Au atoms and adsorbed clusters tends to make large surfaces smoother; protruding atoms or adsorbed small islands congregate to make large islands or migrate to the steps.

In all cases we have studied, roughness acts by localizing the HOMO of Au, thus creating small regions with high HOMO-electron density, where O₂ can bind. We see this along the rough edges of a planar Au₃ cluster as well as in the case of the Au₃/Au(111) system. Another illuminating example is that of the one-dimensional Au wire on a Au(111) surface. Placing the wire on the surface creates roughness and this increases the binding energy of O₂, as compared to binding to the flat surface. The HOMO is, however, delocalized along the wire. We can roughen the wire by removing every third atom in it. This creates dimers separated by a Au atom vacancy in the wire. This localizes the electron in the HOMO on the Au dimers and increases the binding energy of oxygen.

The binding energy of oxygen to Au₃ or Au₃⁻ depends on the parity of the number of electrons in the cluster. Binding is strong when the number of electrons is odd. This occurs because clusters with an odd number of electrons have a small ionization potential and this makes the electron in the HOMO more readily available. No such dependence is seen in Au₃/Au(111), where the system is metallic and the ionization potential (i.e., the work function) is roughly independent of n.

The finite size of small clusters leads to better binding because the HOMO is more localized. The HOMO of Au₃/Au(111) is more spread out than that of Au₃, and for this reason the bond to Au₃ is stronger. We like to call this a confinement effect: the finite size of the cluster prevents the delocalization of the HOMO.

The binding to Au₃ clusters is different from that on Au₃⁻, suggesting that charging a supported cluster increases its chemical activity with respect to oxygen. Calculations show that the binding energy of O₂ to Au(111) is affected very little by adding electrons to the system. However, adding electrons to the Au₃/Au(111) system leads to an increase in the binding energy of O₂. This difference in behavior is explained by the fact that in the case of Au(111), the additional electrons go into a delocalized orbital while in the case of Au₃/Au(111) that orbital is localized around the cluster and overlaps with the π* orbital of O₂.

These findings have some implications for catalysis by Au clusters supported on an oxide surface. Unlike the case of

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F. The effect of charging the Au substrate

The addition of one electron to a gas-phase Auₙ cluster has a very strong effect on the binding energy of O₂ (see Table I). To see whether this is also true for Auₙ/Au(111) or for Au(111) we have performed a computer experiment in which we added an electron in each unit cell of these systems. Since the substrate has 24 atoms per unit cell, which are periodically repeated, this amounts to a rather large charging (we added one electron for each 24×11 electrons of the neutral system). The electrostatic interaction between repeated images in the z direction (i.e., across the vacuum layer) has been cancelled by using the method of Makov and Payne.²⁶ There is a discernible increase in the binding energy of O₂ to Auₙ/Au(111) when an electron is added to the system (see Table I). This occurs because the additional electrons go into the LUMO of Auₙ/Au(111) and this orbital is localized and has a lobe sticking out into the vacuum, where the O₂ binds.

Finally, we mention a last “computer experiment.” Since the availability of electrons seems to be essential in binding O₂ to a gold surface, we have added an electron per supercell to the slab simulating Au(111), to see if this will tempt O₂ to bind to the flat surface. The O₂ binding energy rises from 0.1 eV on a neutral surface to 0.2 eV (see Table I). Neither value should be taken too seriously, as DFT may have difficulty describing these very weak bonds. The O₂ is located at about 4 Å away far from the Au(111) surface, and its bond length is close to that of the gas phase O₂ molecule. The charged surface does not induce O₂ to chemisorb, because the additional electron goes into a delocalized orbital and this does not facilitate oxygen binding. Thus, even when electrons are added to the surface, roughness is essential for making the additional electron help oxygen bind to gold.

IV. SUMMARY

Throughout this article we have advocated that oxygen binding to Au requires some electron transfer from Au to the π* orbital of O₂. Two elements control this process: the HOMO of Au and the π* orbital of O₂ must overlap well and their energies must be close to each other. The difference between the activity of Au clusters and that of bulk Au can be explained in terms of these simple concepts.

The calculations show that roughness is a very important factor controlling oxygen binding. Here we use the word...
Au$_n$/Au(111) the cluster supported on a perfect oxide surface does not interact very strongly with the substrate. The properties of the supported clusters are expected to be, to a first order, very close to those of the gas-phase clusters. Thus, the chemistry taking place on clusters of different sizes will be different. Furthermore, coarsening (ripening), which changes the cluster size, will have a conspicuous effect on catalytic chemistry, moreso than in those cases where coarsening changes only the total surface area of the clusters but not the chemistry taking place on them.

In the case of a surface with oxygen vacancies, it is likely that the clusters will be bound to the defect sites and make use of the electron located in the dangling bond formed by the departure of oxygen. Since the addition of one electron to the cluster can change is properties, we expect the activity of clusters supported on defective surfaces to differ from that taking place on the perfect ones. Such effects would be best detected in work with mass-selected clusters, of the kind pioneered by Heiz et al.$^{27}$

ACKNOWLEDGMENT

This work was supported by the AFOSR through a DURINT grant.


