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Atomic Oxygen Adsorption on Au(111) Surfaces with Defects

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We study the equilibrium structures for the adsorption of atomic oxygen on Au(111) surfaces containing defects such as vacancies and steps, using first-principles density functional theory calculations. We considered the gold−oxygen interaction as a function of surface vacancy concentration, the interaction with 1,2 and 4 gold adatoms (the latter number arranged in groups that represent 2D or 3D gold islands), the interaction at steps, and finally, the effect of strain. We find that there is an attractive interaction between oxygen atoms and vacancies on the surface, which lowers the cost to create a surface vacancy by 0.20 eV, but the interaction between oxygen and gold adatoms is repulsive. We conclude that the strength of the oxygen−gold interaction is correlated with the coordination number of the gold atom to which the oxygen is bound.

Introduction

While Au is often valued for its relative inertness, Haruta and co-workers discovered that Au nanoparticles supported on reducible metal oxides are active for the catalytic oxidation[1−3] of CO[4] and propene.[5] Supported gold nanoparticles also promote a range of other reactions, including the hydrogenation of acetylene,[6] reduction of NO_x by hydrocarbons,[7] and the oxidation of CH_4[8] and NO.[9] Au has also proven very useful in the oxidation of CO because Pt catalysts are not effective below 200 °C, resulting in the production of CO during cold start-up.[10,11]

There are several proposed explanations and factors that control the catalytic activity of gold nanoparticles on oxide supports. Studies have shown that the size of the Au nanoparticle on supported metal oxides has a substantial effect on the catalytic activity.[12−14] Other important factors impacting the catalytic activity include the nature of the metal oxide support, the oxidation state of Au, and the method by which the catalyst was prepared.[15] Recent results, however, indicate that the oxide support or nanosized gold may not be needed for the reaction. For example, unsupported bulk gold powder and nanoporous gold foams are active for CO oxidation[16−18] and CO oxidative amination.[15] Single crystal gold has also been found to be reactive for a variety of oxidation reactions.[19−21]

The mechanism for low-temperature CO oxidation is not clearly understood; undercoordinated Au could be possible sites for binding or even dissociation of O_2, which is an important step in the catalytic process.[22−24] Moreover, adsorption of CO and O is stronger on a surface where undercoordinated Au atoms exist.[12] It is therefore important to understand how undercoordinated atoms can be created on the surface and under what conditions they are stable. For example, supported gold catalysts will often deactivate over time under typical catalytic conditions, which is attributed to the agglomeration of Au particles (sintering) or the poisoning of active sites by accumulation of byproducts.[25] Understanding how gold atoms are released from a gold surface and the how islands are formed will help elucidate the mechanism of sintering.

The release of metal atoms from a surface is of deep fundamental importance to many areas of surface chemistry, especially catalysis and surface reactivity. Since changes in metal−metal bonding can have a dramatic effect on the stability of intermediates and the energies of transition states, it is important to account for the release of atoms from the surface during adsorption or reaction in theoretical models.

Herein, we investigate the effect of adsorbed oxygen atoms on the release of Au atoms from the Au(111) surface using calculations based on density functional theory, in order to address recent experimental results. Kinetically, the release of atoms from Au(111) is expected to be facile because the clean surface reconstructs to form the “herringbone” structure, which has an excess of 4.5% Au atoms compared to the bulk-terminated (111) plane. Dislocations at the “elbow” sites[26−28] form to relieve strain from lattice mismatch. Atoms at the dislocations are more weakly bound and, therefore, readily released from the surface. In fact, adsorbed species—for example, sulfur,[29,30] oxygen,[31] NO_2,[32] methanethiol,[33,34] and styrene[35]—lift (reverse) the herringbone reconstruction and release gold adatoms on the surface.[36]

Experiments show that atomic oxygen can release gold atoms from the Au(111) substrate.[31] In recent theoretical work, Shi et al. have also predicted that the energetically most favorable configuration of oxygen on Au(111) is a “surface oxide-like” structure that has gold incorporated in its structure.[37] To do so, the atomic oxygen must either have an attractive interaction with the gold adatom once it is released from the surface, or the oxygen must have an attractive interaction with the vacancy left behind after the gold atom is released from the surface site. On the basis of this assumption, we study the interaction of oxygen with gold adatoms and vacancies on the Au(111) surface and determine the energy cost for removing gold from different possible sites both with and without oxygen present. We find that atomic oxygen, at low coverages, has a repulsive interaction with adatoms and an attractive interaction with vacancies, this latter interaction being responsible for the release of gold atoms from the surface in the presence of oxygen.

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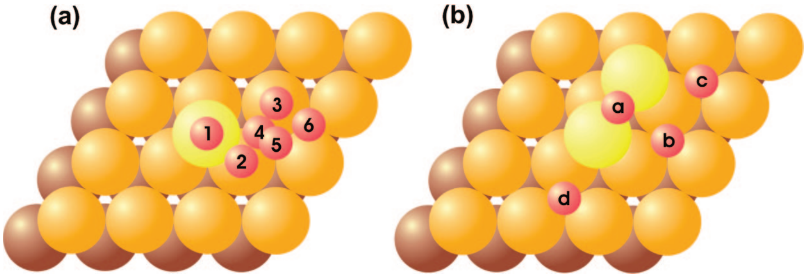

Figure 1. Starting configurations used to study the adsorption of atomic oxygen on an Au(111) surface containing one (a) and two (b) gold adatoms. The dark spheres are the underlying $p(4\times4)$ Au(111) surface, the orange spheres are the top layer of gold, and the yellow spheres are gold adatoms. The smaller red circles label the oxygen atom.

Computational Details

The computations in the work were performed with the VASP code,[38] both with the GGA-PW91[39] and the GGA-RPBE[40] exchange-correlation functionals. The RPBE functional was used because it provides a better description of the chemisorption energies for adsorbates on transition metal surfaces.[40] Ultrasoft pseudopotenitals were employed with the default plane-wave cutoffs for different elements taken from the GGA ultrasoft-pseudopotential database[41,42] and $7\times7\times1$ k-point sampling was used. The surface was modeled by a slab consisting of 4 layers in the (111) direction, with a primitive 4×4 unit cell in the lateral directions; only the two uppermost layers of the slab were allowed to relax, with the rest fixed at the ideal bulk positions. The bulk gold positions of the bottom two layers were taken from the calculated lattice constant of 4.17 Å, which is in good agreement with the experimental value 4.08 Å.[43] Spin-polarized calculations were also considered, but had no substantial effect on the reported results.

The relative energy differences on which we base our conclusions agree well when the two different exchange-correlation functionals are used, and we will quote only the results from the PW91 functional. In the few cases where there were small differences, both sets of data are presented and the differences are discussed.

Vibrational frequencies were calculated by using the force-constant approach implemented within the VASP code. To save computational cost, all vibrational results were calculated with $4\times4\times1$ Monkhorst-Pack k-point sampling. Test cases were calculated with $7\times7\times1$ k-point sampling but were found to change the resulting frequencies by no more than 1 cm^{-1}. The adsorbate and the gold atoms directly bound to the adsorbate are displaced by a step of 0.025 Å to calculate the mass-weighted dynamical (Hessian) matrix. The eigenvalues and eigenvectors of this matrix equal the vibrational frequencies and direction of each normal mode vibration, respectively.

Results and Discussion

The reference calculation used in this work is the binding of oxygen on a clean, defect-free Au(111)-(1×1) surface. All energies in the tables are reported as relative adsorption energies, with a positive relative energy indicating a weaker oxygen adsorption compared to adsorption on the (1×1) surface. All calculations were performed with a $p(4\times4)$ unit cell of Au(111), thus one adsorbed oxygen corresponds to an 1/16 ML coverage. The adsorption energy for oxygen is defined as

$$E_{\mathrm{ads}} = E_{\mathrm{O/Au}} - E_{\mathrm{Au}} - E_{\mathrm{O}}$$

where $E_{\mathrm{O/Au}}$ is the total energy of an oxygen atom bound to the gold substrate, E_{Au} is the energy of the gold substrate, and E_{O} is the energy of atomic oxygen. Oxygen prefers to bind on an FCC 3-fold hollow site and its adsorption energy is $E_{\mathrm{ads}} = -3.08$ eV (-2.69 eV) with an Au$-$O bond distance of 2.16 Å (2.17 Å) with the PW91 (RPBE) functional. This agrees well with past literature; Gajdos et al. found using the PBE functional an energy of -2.78 eV and an Au$-$O bond distance of 2.16 Å for an 1/9 ML coverage.[44] Due to the repulsive nature of atomic oxygen on the surface, our calculated adsorption energies are lower because we looked at a lower coverage (1/16 ML). The experimental Au$-$O bond length for gold coordinated to three Au atoms in bulk gold(III) oxide is 2.04 Å.[45]

TABLE 1: Relative Adsorption Energies (E_{rel}, versus 1/16 ML Coverage of Oxygen in 3-fold Sites on the Au(111)-(1×1) Surface) of Atomic Oxygen on the One (Fig. 1a) and Two (Fig. 1b) Gold Adatom Covered Surface

one Au adatom		two Au adatoms	
site	E_{rel} (eV)	site	E_{rel} (eV)
1	0.92	a	−0.07
2	0.60	b	0.08
3	0.52	c	0.23
4	0.18	d	0.18
5	0.06		
6	0.27		

Since oxygen prefers a 3-fold site and the bridge site is the second lowest energy site on the surface, diffusion of oxygen should proceed from a FCC hole (3-fold site) to a bridge site (2-fold) to an HCP hole (3-fold). The diffusion barrier for oxygen, defined as

$$E_{\mathrm{d}} = E_{\mathrm{bridge}} - E_{\mathrm{fcc}}$$

is $E_{\mathrm{d}} = 0.49$ eV. The diffusion barrier for a gold adatom through the same path is much lower, only 0.11 eV. For comparison, the calculated diffusion barrier for Au with the embedded atom method with potentials developed by Adams, Foiles, and Wolfer[46] and by Voter and Chen[47] is 0.021 and 0.038 eV, respectively.[48] It is interesting to note that the ratios between the diffusion barrier and the adsorption energy are very different for oxygen and Au adatom on Au(111): 0.160 and 0.046, respectively.

1. Interaction of Gold with Adatoms. The adsorption of atomic oxygen was studied on a surface containing one and two gold adatoms, Figure 1. The system was allowed to relax including all degrees of freedom of the two layers of Au(111), the gold adatom, and oxygen bound to the surface. The results are summarized in Table 1.

Oxygen is adsorbed more strongly on the clean (1×1) surface compared to adsorption next to a single gold adatom (Table 1). All of the tested configurations have a higher relative adsorption energy except for the configurations where the oxygen is placed away from the adatom. For example, in configuration 5 there is essentially no interaction between the adatom and the oxygen

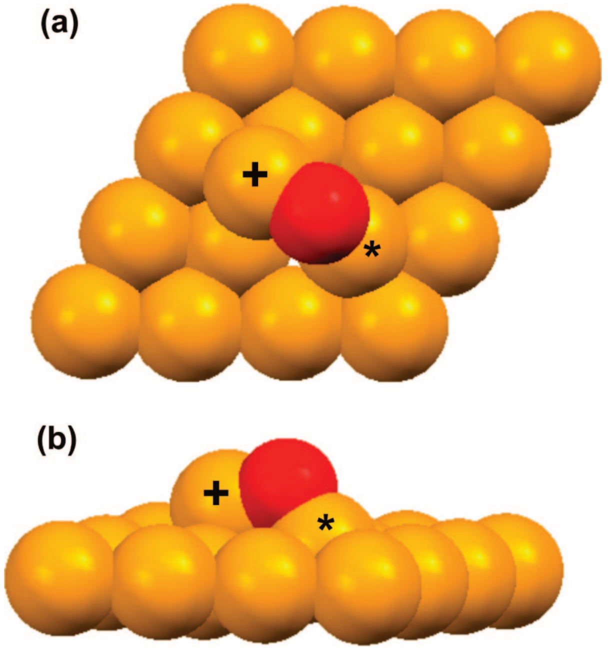

Figure 2. Top (a) and side (b) view of relaxed configuration 2. The orange spheres are gold atoms while the red sphere is oxygen. The gold atom with the plus (+) symbol is the gold adatom, while the gold atom with the asterisk (*) is pulled nearly 1 Å out of the plane of surface gold atoms. Note that only one layer underneath the adsorbed oxygen is shown; however, four layers were used in the calculation.

since the adsorption energy of oxygen is nearly equal to that of oxygen on a clean surface. When oxygen is placed in an HCP hole and relaxed (configuration 6), both the gold adatom and adsorbed oxygen stay in their 3-fold site. The relative adsorption energy of this configuration (compared to oxygen on a defect-free surface) is 0.27 eV. However, this difference is a result of the energy cost of having an oxygen atom in an HCP 3-fold site compared to the more favorable FCC 3-fold site. On a clean surface, the difference in the adsorption energies for an oxygen in an FCC compared to an HCP 3-fold site is 0.24 eV.

Given the relative calculated diffusion barriers for a gold adatom vs an adsorbed oxygen atom, we anticipate the optimization of the oxygen bonding to the surface in a system that contains both gold and oxygen adatoms. For example, when the forces were relaxed in configuration 2, the gold adatom moved away from the oxygen atom to a spot in between the neighboring 3-fold and bridge site. The oxygen atom is shared between the gold adatom and a gold atom in the surface. Interestingly, the gold atom in the first layer was pulled out of the plane of the other gold atoms in the first layer by ~1 Å (Figure 2). The distance between oxygen and both the gold adatom and gold atom that was lifted out of the surface is 2.03 Å. In configuration 3 the gold adatom was brought out of its 3-fold site toward the oxygen and the oxygen drifted slightly from the top of the Au adatom resulting in a similar $\mathrm{Au_{adatom}{-}O}$ distance of 2.04 Å.

We also studied models with two Au adatoms (Figure 1b) and found that the Au dimer also relaxes in response to the oxygen atom. For example, in configuration b, which shows the starting configuration, the two gold adatoms both moved away from the oxygen on the neighboring 3-fold site resulting in an $\mathrm{Au_{adatom}{-}O}$ distance of 4.58 Å. In configurations c and d, the Au adatoms stayed in their original configurations, resulting in a shorter distance between the oxygen and gold adatoms and a higher relative adsorption energy for oxygen.

Our calculations led us to conclude that there is generally not a favorable interaction of oxygen with gold adatoms. The adsorption energy for oxygen with a gold adatom present only becomes equal to oxygen on a clean surface when the adatom and oxygen are well-separated. Oxygen prefers the coordination of the 3-fold site and it is not energetically favorable to gain coordination from additional gold atoms. However, the adsorption of oxygen can be slightly stronger compared to the (1×1) surface if it is bound in the 2-fold site between two gold adatoms; configuration a, Figure 1b. This point is consistent with the results calculated with the RPBE functional (−0.20 eV) suggesting that oxygen indeed has a slightly favorable interaction in the 2-fold site defined by the gold adatom dimer. This result indicates that oxygen may prefer to bind with a gold atom that is missing coordination to other gold atoms. This possibility will be investigated later in this report.

Our calculations further indicate that oxygen will assume a configuration on the surface so as to achieve a coordination as close to 3 Au atoms as possible by either moving toward other gold adatoms or shortening its bond to surface gold atoms. Configurations 3 and 4 in Figure 1a illustrate this effect. In both cases, the O is coordinated to fewer than three Au centers in the (111) plane and in both cases the lowest energy configuration with the Au adatom present involves rearrangement that brings the gold adatom in closer proximity to the oxygen. The resulting $\mathrm{Au_{adatom}{-}O}$ distance was smaller when the oxygen was on a top site versus a bridge site since the oxygen on the top was missing coordination to other gold atoms.

2. Interaction of Gold with Vacancies. Oxygen *does* interact more strongly with Au vacancies compared to the (1×1) surface, in contrast to the effect of Au adatoms. To evaluate the interaction of oxygen with Au vacancies, we calculated the relative adsorption energy of the oxygen with a vacancy and the energy cost for creating n vacancies. The energy cost of creating n vacancies is defined as

$$E_{\mathrm{cost}}(n) = E_{\mathrm{vacancy}} + nE_{\mathrm{bulk}} - E_{\mathrm{full}}$$

where E_{vacancy} is the total energy of the surface with n gold atoms removed, E_{bulk} is the energy of a gold atom in the bulk crystal, and E_{full} is the energy of the surface without the removal of gold atoms used to make the vacancy.

The most striking result is that the adsorption of oxygen in 3-fold sites near the vacancy is more favorable compared to the (1×1) surface. This energy gained from oxygen bonding to this surface, however, is not sufficient to offset the cost of making the vacancy. For example, the adsorption energy for oxygen on a 3-fold site adjacent to the vacancy (site 2 in Figure 3) has an adsorption energy 0.20 eV lower than adsorption on the (1×1) surface, but the energetic cost to create the vacancy is 0.60 eV (Table 2). The oxygen does not sit exactly in the center of the 3-fold site, but rather is shifted slightly toward the vacancy. The distance between the gold atom next to the vacancy and the oxygen is 2.14 Å while the distance from the oxygen to the other gold atoms in the 3-fold site is 2.19 Å. Surprisingly, the adsorption energy of oxygen *in* the vacancy (site 3) is higher than that for O in a 3-fold site on the (1×1) surface.

3. Interaction of Oxygen with Steps and Other Structures. The prevalence of steps on extended surfaces and particle edges render them important binding sites to consider for oxygen. Previous studies by Liu et al.[49] reported that atomic oxygen is bound more strongly to the stepped Au(211) and Au(221) surface than the flat Au(111) surface by several tenths of an electron volt. The most favorable site for oxygen adsorption

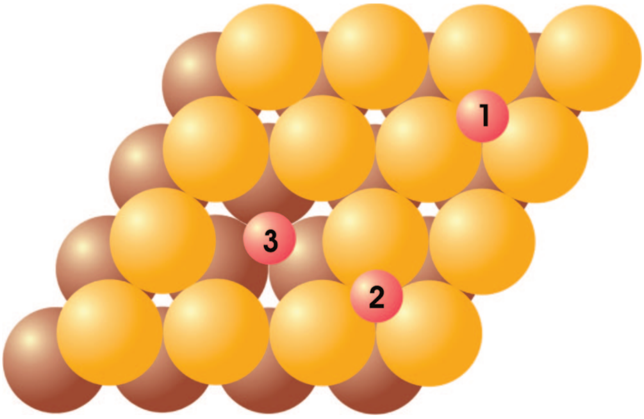

Figure 3. Adsorption sites for atomic oxygen on a Au(111) surface containing one vacancy. The orange spheres represent the top layer of gold, while dark spheres represent the second layer of gold atoms.

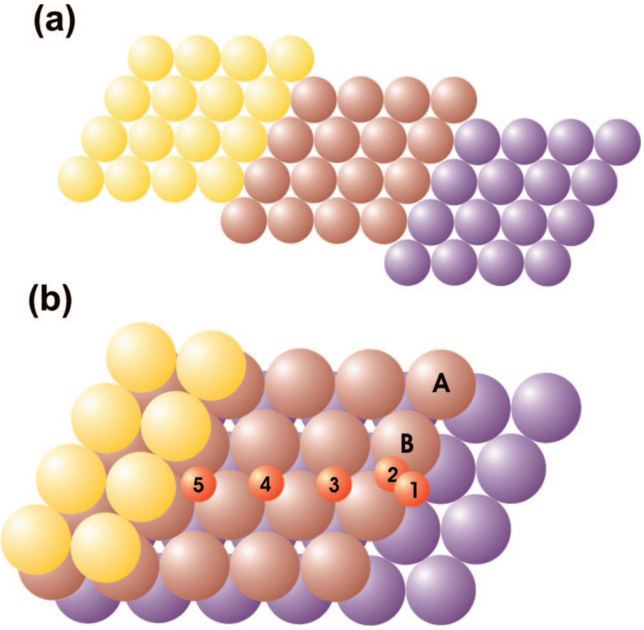

Figure 4. Model of stepped ⟨100⟩/{100} Au(533) surface, where ⟨100⟩ is the direction along the step edge and {100} is the plane of the step edge: (a) side view of the step and (b) top view. Yellow spheres are gold atoms that make up the upper step, the dark spheres comprise the middle terrace, and the blue spheres are the gold layer of the lower step. The red numbered circles represent different binding sites of oxygen. The gold atoms with capital letters are removed to create a step vacancy.

TABLE 2: Relative Oxygen Adsorption Energy (E_{rel}) and Energy Cost To Create a Gold Vacancy (E_{cost}) for Different Adsorption Sites on the Vacancy Covered Surface As Shown in Figure 3

site	E_{rel} (eV)	E_{cost} (eV)
no oxygen		0.60
1	−0.02	0.58
2	−0.20	0.41
3	0.21	0.81

TABLE 3: Relative Oxygen Adsorption Energy (E_{rel}) and Energy Cost To Create a Gold Vacancy (E_{cost}) for Oxygen Bound on the Stepped Surface As Shown in Figure 4[a]

	E_{rel} (eV)			E_{cost} (eV)	
site	PW91	RPBE	site	PW91	RPBE
1	0.09	0.00	no oxygen	0.19	0.16
2	0.08	0.00	2a	0.31	0.25
3	0.12	0.07	3a	0.03	0.01
4	0.26	0.23	3b	0.23	0.23
5	0.35	0.35			

[a] The number indicates the location of the oxygen, while the letter represents which gold atom was removed to create a vacancy (Figure 4b). Calculations were done with both the PW91 and RPBE functional.

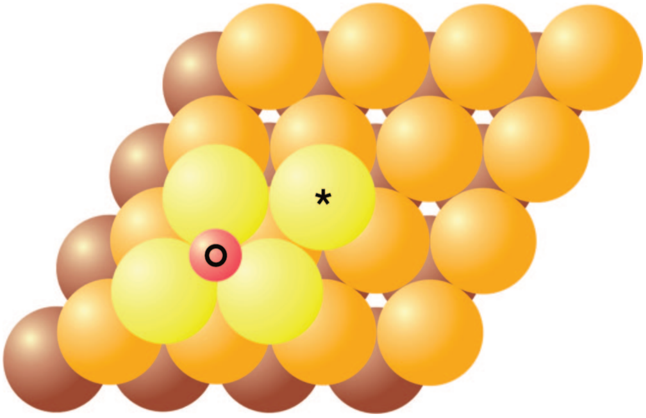

Figure 5. Diagram of 2D-island. Dark spheres represent the underlying Au(111) surface, orange spheres are the top layer of gold, and yellow spheres are adatoms that make up the 2D-island. The oxygen is adsorbed on an fcc 3-fold site of the gold adatoms and is labeled by a red sphere with an O. The cost to remove a gold adatom was calculated for the atom labeled with an asterisk.

was reported to be the bridge site at the edge of the step (site 2 in Figure 4b) using the GGA-PBE functional. Xu and Mavrikakis[50] also found that atomic oxygen is more strongly bound to an Au(211) surface; however, they found that the most favorable adsorption site is a hanging fcc site at the edge of a step (site 1 in Figure 4b) using the GGA-PW91 functional. Our objective was to isolate the effect of the step by using a bigger unit cell, Au(533), and to specifically investigate the ability of oxygen to remove gold atoms from the step.

In our work, the stability of the oxygen decreased as the adsorption site moves away from undercoordinated gold atoms at the step edge and toward a site with a coordination greater than three against the ledge of a step (configurations 1 and 5, Figure 4b, Table 3). This conclusion is based on a comparison of the binding energy of oxygen at various positions relative to the step edge (Figure 4, Table 3). We found that oxygen was essentially equally stable at the "hanging fcc" site at the edge of a step (site 1), bridge site (site 2), and the fcc site at the edge of the step (site 3). The oxygen that started on the bridge site (site 2), relaxed toward (but not completely) the hanging fcc site (site 1). With the PW91 functional, however, the adsorption of oxygen at the step is not stronger than oxygen adsorption on the (1 × 1) surface, as was found in the literature with the PBE functional. Our results indicate that adsorption in the middle of the terrace is weaker than that at the edge of the step, but because of the small size of the terrace in our step calculations and contradiction with previous work that used a different exchange-correlation functional, we cannot conclude convincingly that the adsorption of oxygen is stronger on a step edge. As a comparison, the same set of calculations were done with use of the RPBE functional. Nearly the same trends and values were found.

A second role of oxygen bonding at step edges is that it facilitates the removal of Au from the step edge. In particular, oxygen adsorbed on a 3-fold site at the edge of a step (site 3,

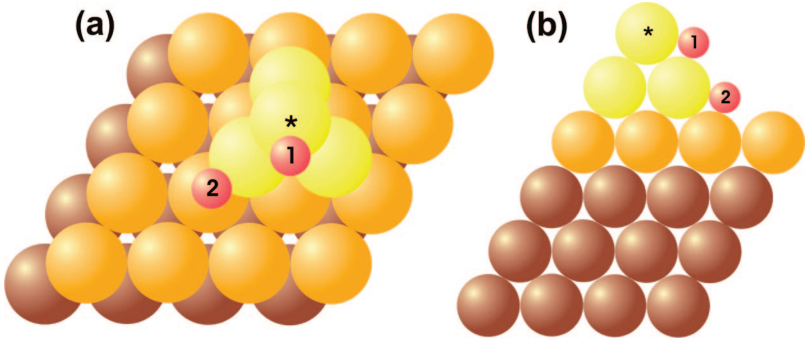

Figure 6. Top (a) and side (b) diagram of a 3D-island. Dark spheres represent the underlying Au(111) surface, orange spheres are the top layer of gold, and yellow spheres are adatoms that make up the 3D-island. The location of the adsorbed oxygen atom is labeled with a smaller red sphere. The gold atom on top of the pyramid with the asterisk is removed to create the vacancy.

Figure 4) lowered the cost of removing a gold atom from the step (Table 3).

The adsorption for oxygen in a 3-fold site is stronger on a small 2D-island of Au (by −0.21 eV) than a flat (1×1) surface. This effect is illustrated by our study of four gold adatoms forming a cluster adsorbed on top of the Au(111) surface (Figure 5). Furthermore, the presence of oxygen lowers the cost to remove the fourth adatom in the 2D-island by 0.10 eV.

In contrast to the 2-D island, oxygen's interaction with 3-D islands (Figure 6) is weaker compared to that of the (1×1) surface. The 3-D island consists of 4 gold adatoms that form a pyramid on top of the Au(111) surface. While it is an unphysical system, it can serve as a model to understand the interaction of oxygen to different gold species. Two different adsorption sites for oxygen were tested, one is a 3-fold site on the side of the 3-D island (labeled as site 1 in Figure 6) and the second is on the side of the bottom layer of the 3-D island (labeled as site 2). In both cases, oxygen is more weakly bound than in the case of oxygen on a flat surface, and the relative adsorption energy for sites 1 and 2 is 0.63 and 0.32 eV, respectively.

The energy cost to remove the gold atom on top of the 3-D island without any oxygen present is −0.48 eV. If the oxygen from site 1 is allowed to "roll" into the 3-fold site as in the 2D-island, the energy cost becomes −1.42 eV, which is a gain in energy of almost 1 eV. Since the adsorption of atomic oxygen on a 3D-island is weak, the energetic gain for destroying the 3D-island is large.

4. Oxygen Adsorption on a Strained Surface. Previous studies have suggested that surface strain plays an important role in the reactivity of Au catalysts. For example, it was found that strain is induced in gold particles by interaction with the MgO support.[51] The DFT studies of Xu and Mavrikakis[52] also found that Au(111) and Au(211) surfaces with elongated Au−Au bond lengths led to an increase in the adsorption energy of both atomic oxygen and molecular oxygen. Accordingly, we investigated the effect of stretching and compressing Au−Au bonds on the bonding of atomic oxygen. All the layers of the gold were held fixed in these calculations to avoid buckling of the surface. The results are summarized in Figure 7.

The adsorption of oxygen on the 3-fold site becomes stronger as the gold surface is stretched. As the gold substrate is stretched, the effective coordination of each gold atom is lowered. The stronger adsorption of oxygen on the stretched surface is consistent with our other results that showed stronger oxygen binding in a site adjacent to a gold vacancy and at an edge of a step. On the other hand, compression of the Au−Au lattice destabilizes the O−Au bonding in the 3-fold site, again agreeing with the trend that oxygen does not prefer a higher coordination of gold. This illustrates an important correlation between the strength of the binding of oxygen with the coordination of the gold atoms to which the oxygen is bound too.

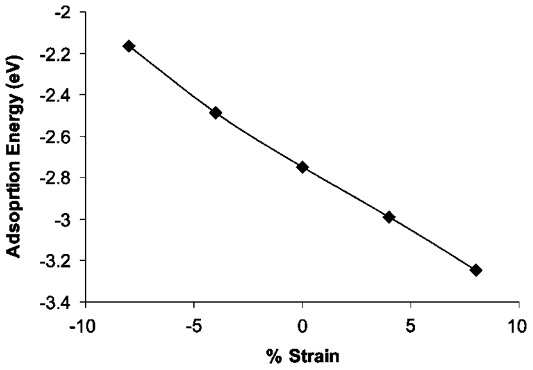

Figure 7. Adsorption energy of atomic oxygen on the strained surface versus the percent of strain. The percent of strain is the percent change in the unit cell vectors, where 0% represents the ideal unit cell lengths of the gold surface.

5. Adsorption Dependence on Number of Vacancies. There are two important factors that determine the binding energy of oxygen to gold: (1) the number of gold atoms the oxygen is bound to and (2) the coordination of the gold atoms to which the oxygen is bound. On the (1×1) surface it is clear that atomic oxygen prefers to be bound to three gold atoms, while two and one gold atoms become increasingly less favorable. There can be favorable 2-fold coordination of oxygen to gold but the gold must have a different coordination to other gold atoms. Examples include the ability of oxygen to bind on a bridge site at a step edge or on two gold adatoms.

To further understand how the coordination of gold can affect the adsorption energy of oxygen, a systematic study was done to calculate the adsorption energy with respect to the number of vacancies on the surface. Atomic oxygen was bound on a 3-fold site and different gold atoms were removed to create vacancies on the surface (Figure 8).

The results show that the adsorption energy of oxygen on the surface can be decreased with the presence of vacancies, but interestingly, there is a minimum of this energy at three vacancies. Furthermore, oxygen lowers the cost to creating vacancies on the surface. Figure 9 shows the cost of creating vacancies as a function of the number of vacancies. Throughout the entire range of vacancies, the cost of creating a vacancy is always lower when oxygen is present. The cost is lowered from 0.20 eV (for 1 vacancy) to up to 0.56 eV (for 3 vacancies).

6. Vibrational Spectra. To compare our results with experimental data for oxygen bound to Au(111), we calculated the vibrational frequencies of several bonding configurations.

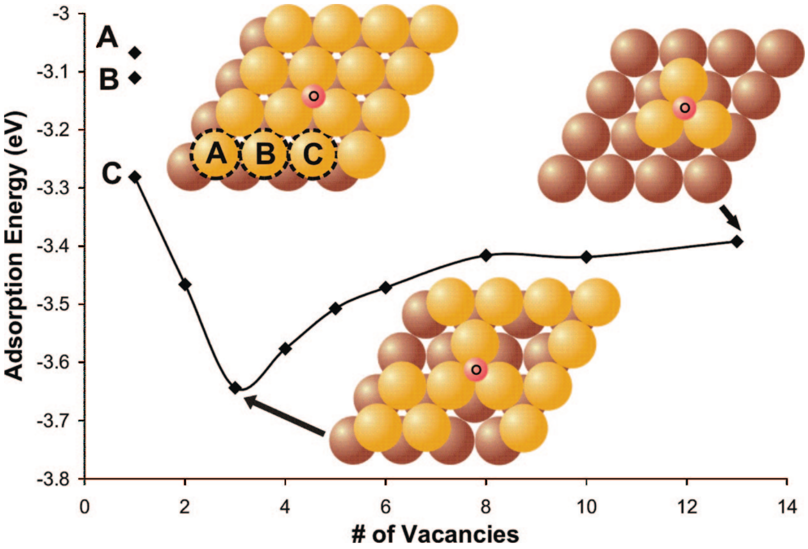

Figure 8. Adsorption energy of atomic oxygen as a function of the number of vacancies on Au(111). With only one vacancy there are three different configurations tested. The gold atom removed to create the vacancy is labeled A, B, or C on the model in the figure and its corresponding data point is also labeled. Models also show the atoms removed to create three vacancies and the final configuration with the maximum number of vacancies. Lighter yellow and darker brown large circles represent the top and second layer of gold, respectively.

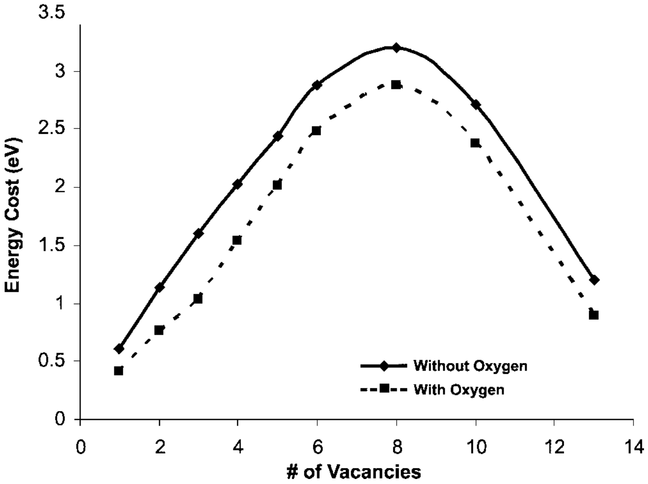

Figure 9. Energetic cost to create Au vacancies as a function of the number of vacancies. The solid top line is the cost without oxygen and the dotted line is that with oxygen.

The adsorption of atomic oxygen following ozone decomposition on Au(111) results in several oxygen species that have been studied with a variety of techniques.[19,53] Min et al. identified two prominent species on the surface as chemisorbed oxygen and gold oxide. Chemisorbed oxygen was observed in XPS at low oxygen coverages for ozone decomposition at 200 K, and oxidic oxygen is prevalent at higher coverages, >0.5 ML, or when ozone is dosed on the surface at 400 K resulting in an ordered oxide. Both the work of Saliba et al.[53] and that in our laboratory (unpublished) clearly observe at least two peaks with high resolution electron energy loss spectra (HREELS): one at ~380 cm^{-1} and the other ~580 cm^{-1}. In our experimental work, we attribute the lower frequency peak at ~380 cm^{-1} to chemisorbed oxygen; however, the experiments are not able to determine the specific binding sites populated.

The calculated vibrational frequencies are in a range consistent with the experimental measurements for the "chemisorbed" oxygen formed on Au(111) and associated with a very defective surface (Table 4). Specifically, the calculated frequency for oxygen adsorption on a fcc site on the (1×1) surface is 405 cm^{-1}. Bonding in a site adjacent to a single vacancy shifts the stretch frequency to 370 cm^{-1} while binding to a 2-D island shifts the frequency up to 422 cm^{-1}. Surface strain also leads to shifts: compression leads to an upshift of ~20 cm^{-1} whereas elongation leads to very little change.

TABLE 4: Calculated Vibrational Frequencies for Various Systems[a]

system	ν (cm^{-1})
FCC	405.5
top of a single adatom (Figure *1*a, site 1)	674.9
FCC on a 2D-island (Figure *5*)	421.9
edge of the step (Figure *4*b, site 1)	452.5
next to one vacancy (Figure *3*, site 2)	370.3
bridge on 2 Au adatoms (Figure *1*b, site a)	491.9
FCC on Au strained −8%	442.5
FCC on Au strained 8%	405.9

[a] Only the highest frequency is listed because lower frequencies were significantly lower in intensity than the highest frequency and are generally at too low of a frequency to be resolved with most experimental HREELS systems. The motion corresponding to these frequencies is typically of the oxygen atom vibrating normal to the surface.

The most significant change in frequency was calculated for oxygen bound atop a single adatom. The vibrational frequency is significantly higher than either of the major vibrational peaks observed experimentally; however, there is some intensity in this region of the spectrum, suggesting that there may be a minor amount of O−Au adatom bonding. Notably, none of the models described herein are consistent with the peak associated with the "2-D oxide", which forms at higher coverage and has an ordered structure. This result indicates that the oxide is fundamentally different in its bonding than the low-coverage structures studied herein, which is consistent with experimental studies showing that the "oxide" is much less reactive than the lower coverage structures.[19]

Conclusions

It is known experimentally that atomic oxygen will release gold atoms from the Au(111) surface.[31] The cause for the evolution of this release of atoms is unknown. Our DFT calculations have shown that oxygen prefers to bind on 3-fold sites on the Au(111)-(1×1)

TABLE 5: Summary of the Cost of Creating a Gold Vacancy in Various Configurations Both with and without Oxygen Adsorbed

Au(111)	E_{cost} (eV) no oxygen	E_{cost} (eV) oxygen	Δ in E_{cost} (eV)
terrace (one vacancy)	0.61	0.41	−0.20
terrace (three vacancies)	1.60	1.03	−0.57
step	0.19	0.03	−0.16
2D-island	−0.21	−0.31	−0.10

surface and will not interact with single gold adatoms. The number of gold atoms to which the oxygen is bound to has a significant effect on its stability. The fact that the oxygen prefers a 3-fold coordination is consistent with the noble nature of gold. There is only one known crystal of a stable gold oxide, Au_2O_3, and its synthesis is extremely difficult, requiring hydrothermal conditions with pressures of several 1000 atm.[54]

The coordination of the gold atoms to which oxygen is bound to is an important factor in the energetics of oxygen adsorption. Oxygen interacts favorably with semiundercoordinated gold in the form of terrace vacancies, steps, and 2D-islands but not with single adatoms or 3D-islands. This result suggests that atomic oxygen could break up bigger islands leaving just oxygen bound to 2D-islands with three atoms, since oxygen bound to a 3-fold site is more stable. This agrees well with the experimental STM observation that the adsorption of oxygen results in a roughened gold surface.[31]

Our calculations also show that oxygen can lower the thermodynamic cost for creating a vacancy by stabilizing (by at least 0.14 eV) the resulting vacancy left behind after the gold is released, in agreement with experimental results.[55] Table 5 summarizes the different systems and the cost for creating the vacancy with and without oxygen. This gain in energy could drive the release of gold atoms on Au(111) upon the adsorption of atomic oxygen.

Deciphering how adsorbates interact and release gold atoms that lead to a rough surface on Au(111) is crucial in understanding its catalytic properties. The interaction of oxygen with Au is critical for all oxidative catalysis. In general electronegative atoms and molecules can convert lattice Au atoms to Au adatoms. Generally understanding electronegative atoms on gold is not just important for atomic oxygen but other atoms including chlorine, which has been shown to enhance the selectivity toward olefin epoxidation on Au(111).[56] Future work in this direction will attempt to resolve issues related to the process by which gold is released, such as the energy barrier for this release, and the interaction of gold vacancies and adatoms with other electronegative species.

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