

Adsorption and Dissociation of O₂ on Gold Surfaces: Effect of Steps and Strain

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The activation of dioxygen via dissociation on strained and stepped gold surfaces has been studied using periodic self-consistent (GGA-PW91) density functional theory (DFT) calculations. Although we find that molecular oxygen does not adsorb on Au(111), it does bind, albeit weakly, to an Au(111) surface stretched by 10% as well as to Au(211) surfaces both stretched and unstretched. The most stable molecular states on all three surfaces have the top–bridge–top configuration and carry about half of the magnetic moment of gas-phase O₂. On 10%-stretched Au(111), unstretched Au(211), and 10%-stretched Au(211), the binding energies of O₂ are −0.08, −0.15, and −0.26 eV, respectively, and the activation energies of O₂ dissociation are 1.37, 1.12, and 0.63 eV. Both steps and tensile strain enhance the adsorption of atomic and molecular oxygen. A comparison between unstretched and stretched Au(211) indicates that the enhancing effect of tensile strain is less pronounced on the step edge than on the flat terrace. The magnitude of the dissociation barriers, combined with the fact that the transition states lie above the gas-phase zero on all three surfaces, suggests that O₂ dissociation remains an activated process on gold. Although additional factors may be involved in O₂ activation at low temperatures on oxide-supported Au catalysts, the present work shows that steps and tensile strain substantially facilitate O₂ activation on Au surfaces.

Introduction

Gold particles the size of a few nanometers supported on various oxides have gained enormous attention in the surface science and catalysis communities in recent years. These supported gold nanoparticles possess high levels of catalytic activity and selectivity for many reactions, including the electrochemical oxidation of H₂, selective hydrogenation of acetylene,¹ epoxidation of propylene,^{2,3} reduction of NO_x by hydrocarbons,⁴ and oxidation of CH₄,^{5,6} and NO.⁷ The reaction that has generated probably the greatest amount of interest is the low-temperature oxidation of CO.^{6,8–13} Low-loading and highly dispersed gold particles supported on oxides such as TiO₂ are active at temperatures of less than 100 K and can achieve fairly high CO conversion rates around 100 °C. Some supported Au catalysts also exhibit high selectivity for preferential CO oxidation in an H₂-rich environment.^{14–16} These characteristics could greatly benefit processes that are easily poisoned by CO, one important example being fuel cells running on a variety of reformat fuels. As a result, CO oxidation on supported gold catalysts has been studied extensively experimentally. Many surface science techniques have been applied to the characterization of catalysts under a variety of conditions.^{17–19} Various aspects of this reaction have also received a theoretical treatment.^{20–25}

The mechanism of low-temperature CO oxidation, however, is under debate. The active oxygen species may be atomic oxygen (O) or molecular oxygen (O₂). Both possibilities have been demonstrated in several recent experiments of CO oxidation on TiO₂-supported gold catalysts at very low temperatures (<100 K).^{13,26,27} Using DFT calculations, Liu et al. have suggested that both atomically and molecularly adsorbed oxygen can oxidize CO, with the former having a lower activation energy.²⁴ However, Haruta and co-workers²⁸ and Kung and co-

workers^{29,30} have reasoned that CO oxidation by water-derived species such as hydroxyl is a more competitive mechanism based on the often-observed beneficial effect of moisture on reaction rates. Another important observation is that an increase in catalytic activity usually accompanies a decrease in the size of the gold particles, with the maximum activity occurring at an average particle size of 3–4 nm.^{31,32} It has therefore been suggested that steps and defects may be the active sites because their concentrations increase as the size of gold particles decreases and because both have been shown, experimentally^{33,34} and theoretically,^{20,35,36} to enhance local catalytic activity on the surfaces of transition metals. Because DFT calculations have shown that lattice strain may enhance surface reactivity³⁷ and because strain can be induced in gold particles by supports,^{38,39} it has also been suggested to explain the unusually high low-temperature CO oxidation activity of small, thin Au particles.²⁰ In addition, the type of support material has been known to affect the activity of gold particles. In particular, theoretical calculations have demonstrated that the electronic properties of thin catalytic metal particles can be substantially modified by the support.^{21,22,40} High reactivity has also been attributed to unusual features of the electronic structure of small, thin gold particles themselves.^{32,41,42} For instance, theoretical studies have confirmed that small gold clusters interact with O₂ very strongly.^{43,44} Interestingly, gold particles supported on reducible metal oxides such as Fe₂O₃ and TiO₂ are usually more reactive than those supported on neutral supports such as Al₂O₃,^{11,16} and the ability of the more reactive supports to function as oxygen reservoirs has been noted. It has been argued that the spillover of reactive oxygen from the support to the gold particles could depend on the size of the particles.⁴⁵ Finally, a very recent DFT study has demonstrated that the particle–support interface may offer particularly active sites.²⁵

These observations suggest that multiple reaction channels and therefore multiple O₂ activation mechanisms may exist. O₂ molecules may directly dissociate on the support, leaving oxygen

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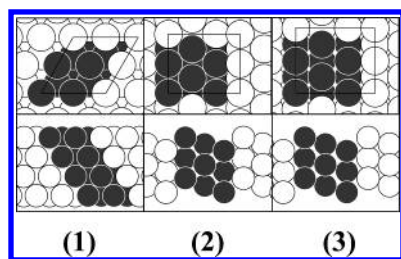


Figure 1. Slabs used to model the Au surfaces and their unit cells (shaded circles): (1) a four-layer 10%-stretched Au(111) slab with a 2×2 unit cell; (2) a nine-layer unstretched Au(211) slab with a 3×2 unit cell; and (3) a nine-layer 10%-stretched Au(211) slab with a 3×2 unit cell. The upper panels show the top view, and the lower panels show a cross-sectional view.

atoms to diffuse to the gold particles, diffuse molecularly to the gold particles and react or dissociate at the particle–support interface, or react or dissociate somewhere on the gold particles. Crucial intermediates may be atomic or molecular oxygen or some type of oxygenates. Moreover, these channels are probably not mutually exclusive, but rather, depending on the reaction conditions, the type of support, and other factors, one or a combination of them contribute more to the catalytic activity than the rest. The elucidation of such mechanisms on supported gold catalysts is important to the understanding of why these catalysts work and how they can be improved. Here we present results of periodic self-consistent DFT (GGA-PW91) calculations that we have performed to investigate the ability of gold to activate O₂. We have examined the adsorption of O and O₂ as well as the dissociation of O₂ on a flat Au surface and at an Au step edge, both with and without tensile strain. Because in a recent study of Au particles supported on TiO₂ an expansion of the gold lattice up to 12.5% has been reported,³⁸ we have investigated a tensile strain of 10%. We will first briefly describe oxygen adsorption on Au(111) and then present O₂ adsorption and dissociation on an Au(211) surface that is used as a model of steps. Then we will describe how the results change when a 10% tensile strain is introduced to both the Au(111) and Au(211) surfaces.

Methods

The spin-polarized total energy calculations were performed using DACAPO.^{35,46} The flat Au surface was modeled by an ideal bulk-truncated Au(111) slab, and Au steps were modeled by an Au(211) slab. The Au(111) slab was constructed from a (2×2) unit cell and consisted of four layers of Au atoms. Successive slabs were separated by a vacuum equivalent to six Au(111) layers. The Au(211) slab had a (3×2) unit cell (having a terrace three atoms deep and two atoms wide) and consisted of nine Au layers. Successive slabs were separated by a vacuum equivalent to 11 Au(211) layers. The model systems are shown in Figure 1. Adsorption was allowed only on one of the two sides of either slab with the electrostatic potential adjusted accordingly.⁴⁷

The surface Brillouin zone of (111) slabs was sampled at 18 special Chadi–Cohen k points, and that of (211) slabs was sampled at a set of $4 \times 4 \times 1$ Monkhorst–Pack k points. Ionic cores were described by ultrasoft pseudopotentials.⁴⁸ The Kohn–Sham one-electron valence states were expanded in a basis of plane waves below a kinetic energy of 25 Ry. The exchange–correlation energy and potential were described by the generalized gradient approximation (GGA-PW91).^{49,50} In addition to PW91, the RPBE functional was used non-self-consistently for comparison. The self-consistent PW91 density was determined

by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states ($k_B T = 0.1$ eV), and Pulay mixing of the resultant electronic density.⁵¹ All total energies were extrapolated to $k_B T = 0$ eV. The calculated equilibrium PW91 lattice constant for bulk Au was $a = 4.18$ Å, in reasonable agreement with the experimental value of $a = 4.08$ Å.⁵² The calculated PW91 bond energy and bond length of a fully relaxed gas-phase O₂ molecule were 5.64 eV and 1.24 Å, respectively, in reasonable agreement with the experimental values of 5.25 eV⁵³ and 1.21 Å.⁵⁴ The PW91 bond energy differs from the corresponding number given in ref 53 (6.20 eV) probably because the latter result was obtained with the O–O bond fixed at its experimentally determined length. We note here that our calculated gas-phase O₂ bond energy in RPBE is 5.20 eV, much closer to the experimental value (5.25 eV) than the PW91 result (5.64 eV). However, we mainly report PW91 energies below for two reasons: (i) the PW91 functional was used self-consistently and (ii) PW91 appears to describe the adsorption of O₂ on some transition metals more accurately. Nevertheless, the uncertainty in adsorption energies arising from the exchange–correlation functional approximation remains unresolved.⁵⁵

The binding energy of an adsorbed atom or molecule on a slab was calculated as $E_b = E_{\text{total}} - E_{\text{clean slab}} - E_{\text{adsorbate(g)}}$ (i.e., with respect to the adsorbate in the gas phase and the clean metal slab at infinite separation). E_{total} , $E_{\text{clean slab}}$, and $E_{\text{adsorbate(g)}}$ are, respectively, the total energies of the adsorbate–substrate system, the slab itself, and the adsorbate in the gas phase. For instance, the binding energy of an adsorbed O atom was calculated as $E_b = E_{\text{total}} - E_{\text{clean slab}} - E_{\text{O(g)}}$, and that of an O₂ precursor was calculated as $E_b = E_{\text{total}} - E_{\text{clean slab}} - E_{\text{O}_2(\text{g})}$. Binding energies, geometries, and magnetic properties of adsorbed atomic and molecular oxygen species as well as possible O₂ dissociation paths were explored on the following surfaces: unstretched and 10%-stretched Au(111) and unstretched and 10%-stretched Au(211). First these properties were calculated on the unstretched surfaces, being held static in ideal bulk-truncated configurations. The effect of surface relaxation was investigated only on unstretched Au(211) by relaxing the top four of the nine layers in the Au(211) slab. The tensile strain was modeled as an increase in the bulk lattice constant of Au by 10% (i.e., $a = 4.60$ Å) in the plane parallel to the exposed surface while preserving the thickness of the slab. This approach had been shown to yield accurate estimates of binding energies on stretched transition metals.³⁷ The various properties were then recalculated on the stretched surfaces. The convergence of the binding energies was verified with respect to the number of k points and the number of metal layers in the slab.

The climbing-image nudged elastic band (cNEB) method⁵⁶ was used in this study to determine minimum-energy paths for O₂ dissociation. cNEB is an improved version of the original NEB method.^{57,58} It was designed to search and locate the highest saddle point on the potential energy surface more rigorously. In each cNEB calculation, the minimum-energy path between an initial state (IS) and a “coadsorption” state (CA) was discretized with several intermediate images. The coadsorption state represented the intermediate product of O₂ dissociation, which yielded two O atoms per unit cell. However, when calculating the overall heat of reaction, we considered a lower coverage of atomic O (i.e., with one O atom per unit cell) to be the final state (FS). The heat of reaction was calculated as the difference between the binding energy of this atomic final state and that of the molecular initial state. The binding energies of all states in a cNEB calculation were

TABLE 2: Properties of Atomic Oxygen Adsorbed on Unstretched Au(211)^a

atomic site	E_b (eV)	z (Å)	$d_{\text{Au-O}}$ (Å)
static surface			
f0	-2.77	0.91	2.03
h1	-2.66	1.41	2.06
f2	-2.55	1.34	2.17
h3	-2.27	1.38	2.13
f4	-2.33	1.38	2.19
h5	becomes f0		
relaxed surface			
f0	-2.82	0.89	2.04
h1	-2.83	1.16	2.11
f2	-2.76	1.14	2.15
h3	-2.33	1.30	2.14
f4	-2.47	1.22	2.14
h5	becomes f0		

^a E_b is the binding energy; z is the adsorption height; and $d_{\text{Au-O}}$ is the distance between O and the nearest Au atom. z and $d_{\text{Au-O}}$ are defined in Figure 3. None of these configurations has a residual magnetic moment.

thermal energy may either cause the molecule to desorb or drive it over the barrier and become chemisorbed. A chemisorbed O₂ molecule can either desorb or dissociate. Because DFT cannot accurately capture weak interactions such as van der Waals forces, we are unable to ascertain if there is a physisorbed O₂ state on Au(111). The depth of the chemisorption well was taken by Saliba et al. to be ~ 0.2 eV below the gas-phase zero on the basis of earlier findings for Au(110) and Ag(111). Our results seem to indicate that this is an overestimation. Because DFT predicts that O₂ does not chemisorb on unstretched Au(111), the thermal dissociation of O₂ on that surface was not investigated.

Effect of the Step Edge. Au steps are modeled by an Au(211) surface in this study. As identified in Figure 2b, a greater variety of adsorption sites exist on Au(211) than on Au(111). Threefold sites are labeled sequentially from the edge inward as either the “f” (fcc) or the “h” (hcp) sites, two-fold sites labeled as the “b” (bridge) sites, and atop sites are labeled as the “t” sites. The site designated f0 in Figure 2b, which is located on the edge of the upper terrace, would be a three-fold fcc site if the terrace did not terminate there, so we group it with the other three-fold sites. The h5 site is located at the foot of the step (i.e., on the lower terrace). During energy minimization, the O atom is allowed to move in all directions. Overall, the three-fold sites are energetically more favorable, with those closer to the step binding O atoms more strongly. Bridge and top sites are less favorable, and most of them are not stable, where an adsorbed oxygen atom would eventually slide off into an adjacent three-fold site. Therefore, only binding energies in the three-fold sites are shown (Table 2). The best site for O adsorption on the static surface, f0, has a binding energy of -2.77 eV/O. We tried placing an O atom in h5 only to find it climbing up the step to occupy f0 instead. This is similar to Feibelman et al.’s finding that O prefers to occupy fcc-like edge-bridging sites on Pt steps so that it “hangs off” the step edge.⁷⁷ They have argued that the passivation of the least-coordinated step-edge Pt atoms is the key driving force. The preference of the f0 site over the h5 site suggests that the edge of the step (on the upper terrace) is more reactive than the foot of the step (on the lower terrace). Surface relaxation results in a gain of 0.05 eV/O in binding energy for atomic oxygen.

Molecular oxygen is able to adsorb on Au(211). The best adsorption configuration is a di- σ -type top-bridge-top (henceforth abbreviated to t-b-t; see Figure 2b) state located on and

TABLE 3: Summary of O₂ Dissociation on Unstretched Au(211)^a

	state	E_b (eV)	$d_{\text{O-O}}$ (Å)
static surface	IS (t-b-t)	-0.15	1.29
	TS	0.97	1.89
	CA (f4+f0)	0.62	3.12
	FS (2 × f0)	0.08	
relaxed surface	IS (t-b-t)	-0.15	1.30
	TS	0.80	1.87
	CA (f4 + f0)	0.43	3.23
	FS (2 × f0)	0.01	

^a E_b is the binding energy, and $d_{\text{O-O}}$ is the O-O bond length. $d_{\text{O-O}}$ is defined in Figure 3. The activation energy for O₂ dissociation is therefore 1.12 eV on the static surface and 0.95 eV on the relaxed surface. IS, TS, CA, and FS stand for initial, transition, coadsorption, and final atomic states, respectively.

along the step edge. We find no other stable molecular states along the edge and none at the foot of the step. The t-b-t state itself has only a modest binding energy of -0.15 eV/O₂. Surface relaxation does not change its binding energy or adsorption geometry. Its short O-O bond length (1.29 Å) and significant residual magnetic moment are characteristics of weak interaction between O₂ and Au(211). Our findings agree with those of Mavrikakis et al. that the adsorption of both O and O₂ was enhanced at Au step edges.²⁰

Next we turn our attention to the O₂ dissociation process on Au(211). The cNEB method was applied to construct a dissociation path leading from the t-b-t molecular precursor state to the coadsorption of two oxygen atoms in the unit cell. It was not immediately obvious, however, which combination would produce the most favorable O₂ dissociation path. Therefore, we performed cNEB calculations for several possible final states. Without obtaining full convergence for all of them, we were able to determine that the path that ended in f4 + f0 (Figure 2b) would most likely yield the lowest dissociation barrier. We believe this approach to be sound because we have observed in a number of cNEB calculations^{61,78} that, although the forces on the intermediate images and thus their geometric structures tend to converge slowly, the energy converges much faster to the final result. After it was chosen, the f4 + f0 path was then allowed to converge fully.

cNEB calculations have been carried out both on a static and on a relaxed Au(211) surface. The results are summarized in Table 3, and the minimum-energy paths are shown in Figure 4. The geometric features of the two paths look very similar. (See Figure 5 for snapshots of selected states on the relaxed Au(211) surface.) First the O₂ molecule rotates away from the t-b-t position and falls off the step edge toward the terrace beneath. In image 3 (panel 3 of Figure 5), the precursor has completed the rotation and is about to fall onto the lower terrace. Up to this stage, the O-O bond length is less than 1.3 Å, indicating that the precursor is moving as a molecule. Image 4 (panel 4 of Figure 5) depicts the bond-breaking event (i.e., the transition state) in which the O₂ molecule forms a complex bridging the step edge and the lower terrace. This transition-state configuration is also seen in the DFT studies of the dissociation of diatomic molecules on several other fcc(211) surfaces.⁷⁹ After the O-O bond is broken, one of the O atoms occupies the f4 site, and the other occupies the f0 site (CA state, Table 3). By diffusing away from each other, the two O atoms can gain more energy until they each reach an f0 site (FS state, Table 3).

The barrier to O₂ dissociation is 1.12 eV/O₂ on the static Au(211) surface and 0.95 eV/O₂ on the relaxed surface. The

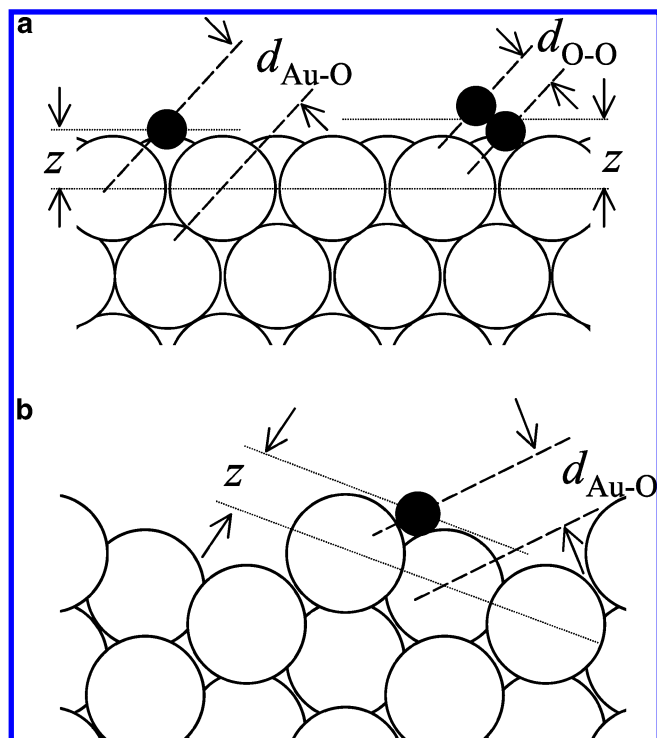


Figure 3. Schematics showing the definitions of the adsorption height, z , the distance to the nearest Au atom, $d_{\text{Au-O}}$, and the O-O bond length, $d_{\text{O-O}}$, (a) on Au(111) and (b) on Au(211) as referred to in the Tables. Open circles denote Au atoms, and filled circles denote O atoms. z is the distance measured from the plane of the centers of mass of the top-layer [Au(111)] or top-terrace [Au(211)] gold nuclei (fixed bulk-truncated positions) to the center of mass of the O atom or the O₂ molecule.

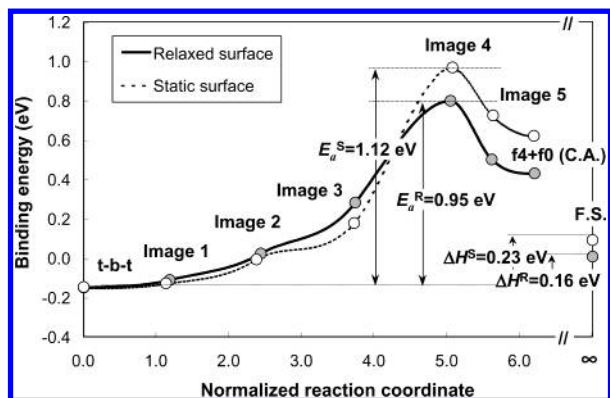


Figure 4. Minimum-energy path determined by cNEB calculations for O₂ dissociation on static and relaxed unstretched Au(211) surfaces. The seven circles on each line indicate the positions of the end states (from t-b-t to f4 + f0) and five intermediate images in the cNEB calculations. The last points, located on the right vertical axis, represent the atomic final states. The calculated dissociation barrier (E_a) and heat of reaction (ΔH) associated with each path are shown.

latter value is in good agreement with the value calculated by Liu et al.²⁴ Here surface relaxation, unlike that for the initial t-b-t state, stabilizes the transition state by ~ 0.2 eV. Measured against the atomic final state of $2 \times \text{f0}$ (FS), the O₂ dissociation process is endothermic by 0.23 eV/O₂ on the static Au(211) surface and by 0.16 eV/O₂ on the relaxed Au(211) surface.

Chesters et al. reported observing no difference in oxidation characteristics between the (111) and stepped Au surfaces.⁶⁶ The LEED patterns and oxidation rates that they obtained were essentially identical. They therefore concluded that the chemisorption of oxygen was structure-insensitive on Au. This, they noted, was in contrast to marked differences in oxygen chemi-

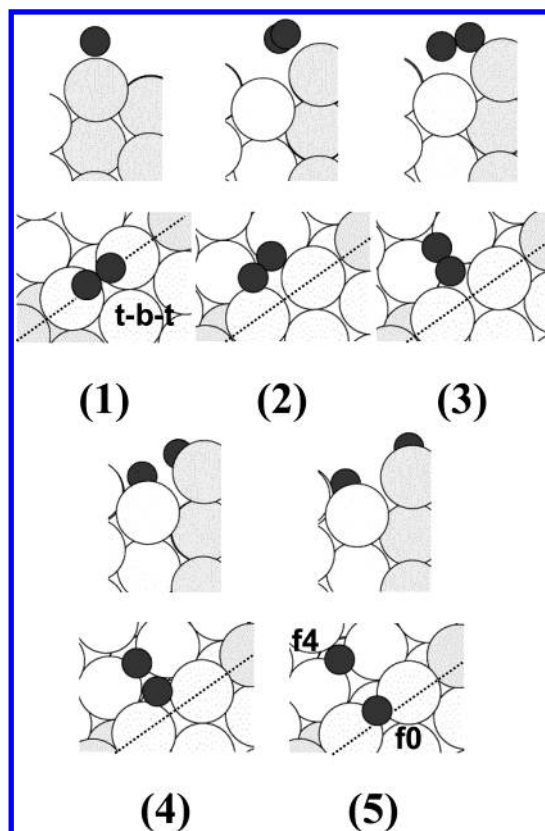


Figure 5. Cross section and top views of selected states along the O₂ dissociation path from t-b-t to f4 + f0 on the relaxed Au(211) surface (see Figure 4): (1) the initial state (t-b-t), (2) the second, (3) third, and (4) fourth intermediate images, and (5) the coadsorption state (f4 + f0). For clarity, only one O₂ molecule is shown in each panel. The dashed lines indicate the step edge. The fourth image (panel 4) is the transition state.

sorption behavior between Pt(111) and Pt steps. They hypothesized that the activation energy for O₂ dissociative adsorption likely remained high at stepped Au surfaces, with the net result being that stepped Au surfaces do not behave much differently from Au(111) under UHV conditions. Barring an anomalously high preexponential factor, the sizes of the O₂ dissociation barriers combined with the weak binding of O₂ that we have found at Au steps lead to conclusions similar to theirs.

Effect of Strain. It has been shown that small metal particles deposited on a substrate consisting of another substance tend to contract to less than their equilibrium lattice constants and that the smaller the particles the more pronounced the contraction.^{80,81} However, isotropic lattice dilation has been observed in systems such as Pd/MgO.⁸² Similarly, in small Au particles supported on TiO₂, the Au lattice prefers to become strongly distorted so as to adopt the lattice dimensions of the substrate. An expansion of 12.5% with respect to the Au equilibrium lattice constant has thus been measured in one crystalline direction for Au/TiO₂.³⁸ Because lattice expansion has been shown theoretically to increase the reactivity of many transition-metal surfaces,³⁷ we have also investigated the adsorption of atomic and molecular oxygen on a 10%-stretched Au(111) surface to determine whether tensile strain could account for the observed enhancement of the activity of small supported Au particles. Calculated binding energies are listed in Table 1. It can be seen that both atomic and molecular oxygen are stabilized. Atomic O gains a substantial 0.6 eV, or more than 20%, in binding energy. The O atom now burrows 0.3 Å more deeply into the fcc site compared to the unstretched Au(111) surface. Molecular oxygen can adsorb on the 10%-stretched Au(111) surface, albeit

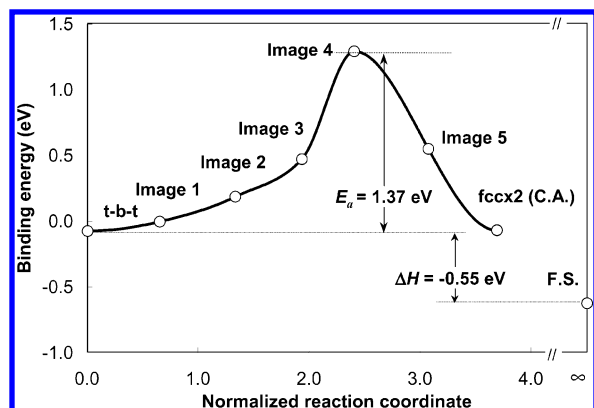


Figure 6. Minimum-energy path determined by cNEB calculations for O₂ dissociation on a 10%-stretched Au(111) slab (from t-b-t to fcc × 2). The seven circles indicate the positions of the initial, intermediate, and coadsorption states. The last point, located on the right vertical axis, represents the atomic final state. The calculated dissociation barrier (E_a) and heat of reaction (ΔH) are shown.

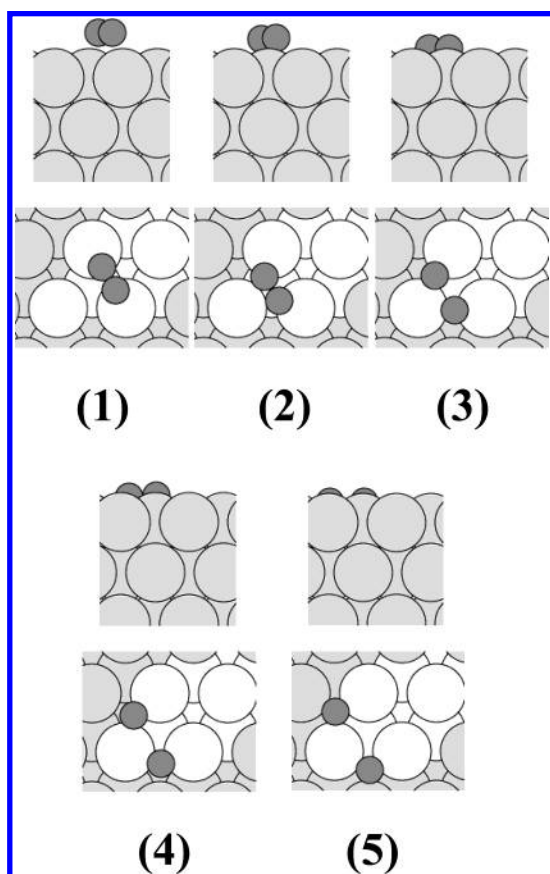


Figure 7. Cross-section and top views of selected states along the O₂ dissociation path from t-b-t to fcc × 2 on a 10%-stretched Au(111) slab (see Figure 6): (1) initial state (t-b-t), (2) the second, (3) the fourth, and (4) the fifth intermediate images, and (5) the coadsorption state (fcc × 2). For clarity, only one O₂ molecule is shown in each panel. The fourth image (panel 3) is the transition state.

very weakly (-0.08 eV/O₂), in the t-b-t state. Because O₂ adsorbs on the 10%-stretched Au(111) surface, we have performed a cNEB calculation to find a minimum-energy dissociation path from the t-b-t precursor to the fcc × 2 coadsorption state (i.e., two O atoms occupying two adjacent fcc sites). The interpolated path is shown in Figure 6, and the snapshots of selected states along the dissociation coordinate are shown in Figure 7. The dissociation barrier is calculated to be 1.37 eV/O₂. The O₂ precursor slides off the t-b-t site as a molecule,

TABLE 4: Properties of Adsorbed Atomic Oxygen and Summary of O₂ Dissociation on a Static 10%-Stretched Au(211) Surface^a

Atomic Oxygen			
site	E_b (eV)	z (Å)	d_{Au-O} (Å)
f0	-2.99	0.90	2.03
h1	-2.99	1.09	2.12
f2	-3.07	1.06	2.13
h3	-2.85	1.09	2.14
f4	-2.99	1.05	2.13
h5	becomes f0		
O ₂ Dissociation			
state	E_b (eV)	d_{O-O} (Å)	
IS (t-b-t)	-0.26	1.30	
TS	0.37	1.88	
CA (f4 + f0)	-0.38	3.40	
FS (2 × f2)	-0.49		

^a E_b is the binding energy; z is the adsorption height; d_{Au-O} is the distance between O and the nearest Au atom; and d_{O-O} is the O-O bond length. z , d_{Au-O} , and d_{O-O} are defined in Figure 3. None of the atomic configurations has a residual magnetic moment. The activation energy for O₂ dissociation is 0.63 eV. IS, TS, CA, and FS stand for initial, transition, coadsorption, and final atomic states, respectively.

and the bond-breaking event occurs in what may be described as a bridge-bridge position, similar to what is found in our previous study of O₂ dissociation on the Cu(111) surface,⁶⁰ although in contrast to Cu(111) there is no stable bridge-bridge molecular state on this surface. At the transition state (panel 3 of Figure 7), the O-O bond has a length of 1.90 Å. Contrary to our findings on unstretched Au(211) where O₂ dissociation was determined to be endothermic, the dissociation of O₂ on 10%-stretched Au(111) is exothermic by 0.55 eV/O₂ when measured against the atomic final state (FS) of two oxygen atoms adsorbed in fcc sites at $1/4$ ML ($2 \times$ fcc).

Combined Effect of Steps and Strain. Because strain can also be present in a stepped surface, we investigate a 10%-stretched Au(211) surface next, which combines the effect of step edge and strain. The binding energies of O atoms in the f and h sites on this surface as well as results for O₂ dissociation are listed in Table 4. Tensile strain (10%) has clearly enhanced the adsorption of atomic oxygen on the stepped surface (see Table 1 for comparison), and as on the flat surface, the O atom burrows more deeply into the terrace by ~ 0.3 Å, with the exception of f0. Note that the differences among the binding energies of atomic oxygen at the various three-fold sites on unstretched Au(211) have been greatly diminished on 10%-stretched Au(211). The most stable site for atomic oxygen on 10%-stretched Au(211) is f2 with a binding energy of -3.07 eV/O, whereas the f0 site is the best on unstretched Au(211) with a binding energy of -2.77 eV/O. The h5 site is unstable, as before. Compared to unstretched Au(211), the binding of O₂ is also enhanced, but the t-b-t state at the step edge remains the only state in which O₂ adsorption is exothermic. Although the binding of O₂ on the stretched Au(211) surface is the strongest found in this study, it is still much weaker than on other transition metals such as Cu,⁶⁰ Pt,⁵⁹ and Ir.⁶¹ The dissociation path with the lowest barrier is determined to be that connecting t-b-t and f4 + f0, as on unstretched Au(211). It can be seen in Figure 8 that the later, more atom-like states on the path are more stabilized than the earlier, more molecule-like states. Whereas the t-b-t precursor gains 0.11 eV/O₂ in binding energy because of 10%-tensile strain, the transition state gains 0.60 eV/O₂, and f4 + f0 (CA) gains an even greater 1.00

TABLE 5: Summary of Energetic Properties of Key States along the O₂ Dissociation Coordinate on Several Static Au Surfaces^a

	PW91				RPBE				ϵ_d	σ
	E_b^O	E_b^{IS}	E_b^{TS}	E_a	E_b^O	E_b^{IS}	E_b^{TS}	E_a		
(111) unstretched	-2.54	n/a	n/a	n/a	-1.99	n/a	n/a	n/a	-3.3	4.4
(111) 10%-stretched	-3.14	-0.08	1.29	1.37	-2.54	0.29	1.90	1.62	-2.8	3.2
(211) unstretched	-2.77	-0.15	0.97	1.12	-2.27	0.20	1.65	1.44	-3.1	3.9
(211) 10%-stretched	-3.07	-0.26	0.37	0.63	-2.47	0.12	1.08	0.96	-2.6	2.9

^a E_b^O , E_b^{IS} , and E_b^{TS} are the binding energies of the best atomic oxygen state, the initial (molecular) state, and the transition state, respectively. E_a is the activation energy of O₂ dissociation; ϵ_d is the center of the d band; and σ is the spread of the d band. E_b , E_a , and ϵ_d have units of eV. ϵ_d and σ are those of the clean surfaces. ϵ_d and σ of the (211) surfaces are those found at the edge of the step.

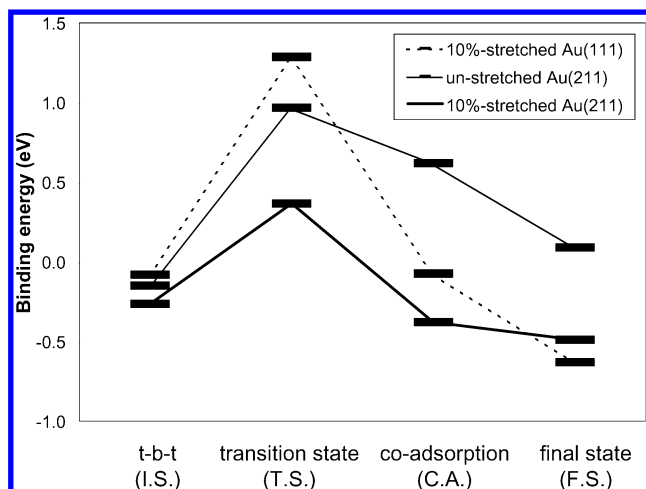


Figure 8. Comparison of the O₂ dissociation processes on 10%-stretched Au(111), unstretched Au(211), and 10%-stretched Au(211) (all static surfaces). Only the binding energies of the key states (IS, TS, CA, and FS) in each process are shown.

eV/O₂. The dissociation barrier thus drops to 0.63 eV, the lowest of all systems considered in this study. The overall reaction on the 10%-stretched Au(211) surface is exothermic by 0.23 eV/O₂ when measured against the atomic final state of $2 \times f_2$.

Next we turn our attention to possible effects of steps and strain on the CO oxidation mechanism on Au catalysts. The increased binding energy of O₂ at stretched Au steps would translate into a longer residence time than possible on an Au terrace for O₂ molecules. This, coupled with a lowered dissociation barrier, may allow an appreciable amount of atomic oxygen to be generated when operating under high oxygen partial pressure. Once adsorbed, oxygen atoms are moderately stable as shown by several TPD studies^{64,70} and could be present on the surface long enough to oxidize CO directly. Alternatively, the longer residence time of O₂ molecules at stretched steps may give them the opportunity to oxidize CO via a two-step mechanism that was proposed by Liu et al.²⁴ to be dominant on unstretched Au steps (i.e., $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$ followed by $\text{CO} + \text{O} \rightarrow \text{CO}_2$). Separate experiments conducted by Manzoli and co-workers²⁷ and Mullins and co-workers¹³ to investigate CO oxidation on Au particles supported on TiO₂ at cryogenic temperatures (<100 K) have provided tantalizing evidence. O₂ appears to have a strong affinity for the step sites so that preadsorption of O₂ inhibits CO adsorption and almost completely shuts off CO₂ formation.²⁷ Because CO can readily react with atomic oxygen directly dosed onto Au surfaces,¹³ this indirectly suggests that O₂ does not dissociate at such temperatures. Nevertheless, particle-size dependence is observed when the source of oxygen is gas-phase O₂²⁷ but not when predissociated oxygen is used,¹³ which underscores the effect of steps on O₂ and CO adsorption and on the barriers in the oxidation mechanism. Interestingly, Lopez et al. calculated that

O₂ dissociation and O₂ oxidation of CO can occur with equal facility on a neutral Au₁₀ cluster.²³

As mentioned earlier, we have calculated energies non-self-consistently using the RPBE functional. Table 5 compares the RPBE energies for key oxygen states with those obtained using the PW91 functional on unstretched and stretched Au(111) and Au(211). We find that RPBE yields an upshifted 1D potential energy surface compared to PW91, with the average upshift being 0.5 eV. This finding is in agreement with previous reports that indicate that RPBE predicts decreased binding energies for various adsorbates on a number of transition-metal surfaces.⁴⁶ Because the difference in the initial-state energy is not identical to the difference in the transition-state energy, the activation energies of O₂ dissociation are also affected by the choice of the exchange-correlation functional. The activation energies calculated in RPBE are greater by ~ 0.3 eV.

Analyses of Electronic Structures. Table 5 also shows the first and second moments of the projected density of the Au d bands, namely, their center (ϵ_d) and the spread (σ), of the surfaces studied. It can be seen that 10% tensile strain makes a greater difference in the electronic structures of Au surfaces than the step edge does. The difference in ϵ_d is +0.2 eV between the unstretched terrace (-3.3 eV) and the unstretched step edge (-3.1 eV) and between the stretched terrace (-2.8 eV) and the stretched step edge (-2.6 eV) compared to +0.5 eV that accompanies the introduction of 10% tensile strain. The upshift of ϵ_d due to steps or strain agrees with the observed increase in surface reactivity. Similarly, σ decreases by ~ 0.4 when going from the flat surface to the step edge, but the effect due to 10% tensile strain is a much larger decrease of ~ 1.1 . The differences among the spreads of the d band of the different surfaces can also be seen in Figure 9, where the projected densities of the Au d states and the O s and p states in the O₂ dissociation processes are shown. Figure 9 also furnishes a view of how the density of states evolves along the dissociation coordinate. The discrete states of the gas-phase O₂ molecule are somewhat broadened and shifted to lower energies in the initial states. As O₂ dissociates, its various states continue to broaden and form two major peaks that correspond to the bonding (lower in energy) and antibonding (higher in energy) states, and progressively more of the antibonding states are occupied.

Because molecular O₂ fails to adsorb on unstretched Au(111), according to our calculations several data are not available, which prevents a systematic comparison of the effects of strain and step edges on the binding energies. Nonetheless, it is clear that both 10% tensile strain and step edges enhance the adsorption of atomic and molecular oxygen on gold. However, whereas the adsorption of molecular oxygen is indeed most enhanced and O₂ dissociation becomes the easiest at the stretched step edge, the effects of step edges and tensile strain do not always appear to be additive: the best binding energy of atomic oxygen on the stretched Au(211) surface is actually somewhat less than that on the stretched Au(111)

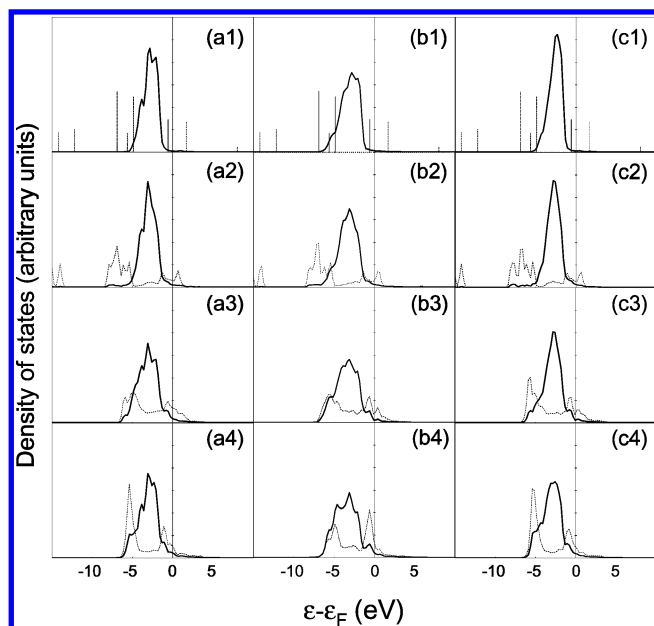


Figure 9. Evolution of the density of states in the O₂ dissociation process on static Au surfaces. ϵ_F denotes the energy of the Fermi level. Panels a1–a4 correspond to the 10%-stretched Au(111) surface, b1–b4 correspond to the unstretched Au(211) surface, and c1–c4 correspond to the 10%-stretched Au(211) surface. Dashed lines represent local s- and p-DOS projected onto an O atom, and solid lines represent local d-DOS projected onto an Au atom that is bound to that O atom. The first row (a1–c1) represents the clean surface and gas-phase O₂ (discrete states) and serves as a reference. The second row (a2–c2) corresponds to the initial state (t–b–t), the third row (a3–c3) corresponds to the transition state, and the last row (a4–c4) corresponds to the atomic final state (FS). In panel a3, the Au atom bound to both O atoms is chosen (refer to panel 3 of Figure 7). In panels b3 and c3, the O atom located on the step edge is chosen (refer to panel 4 of Figure 5). In panel c4, a second-row Au atom is chosen (refer to Figure 2b).

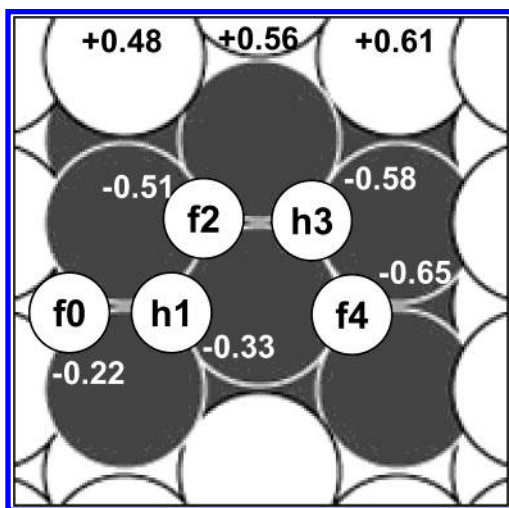


Figure 10. Changes in the binding energies of atomic oxygen and in the d-band centers of surface Au atoms due to 10% tensile strain on Au(211). The white numbers are the differences in binding energy (in eV) at the respective sites, calculated as $\Delta E = E_b^{O(\text{stretched } (211))} - E_b^{O(211)}$, and the black numbers are the amounts by which the d-band centers of Au atoms (in eV) in the respective rows on the clean surface have shifted upward, calculated as $\Delta \epsilon_d = \epsilon_d^{\text{stretched } (211)} - \epsilon_d^{(211)}$.

surface (Table 1), as opposed to a further stabilization that may have been expected. This anomaly may be the result of two opposing trends: (i) An analysis of the Au d-band distribution of a clean unstretched Au(211) terrace indicates that the d-band center drops lower beneath the Fermi level the farther away a

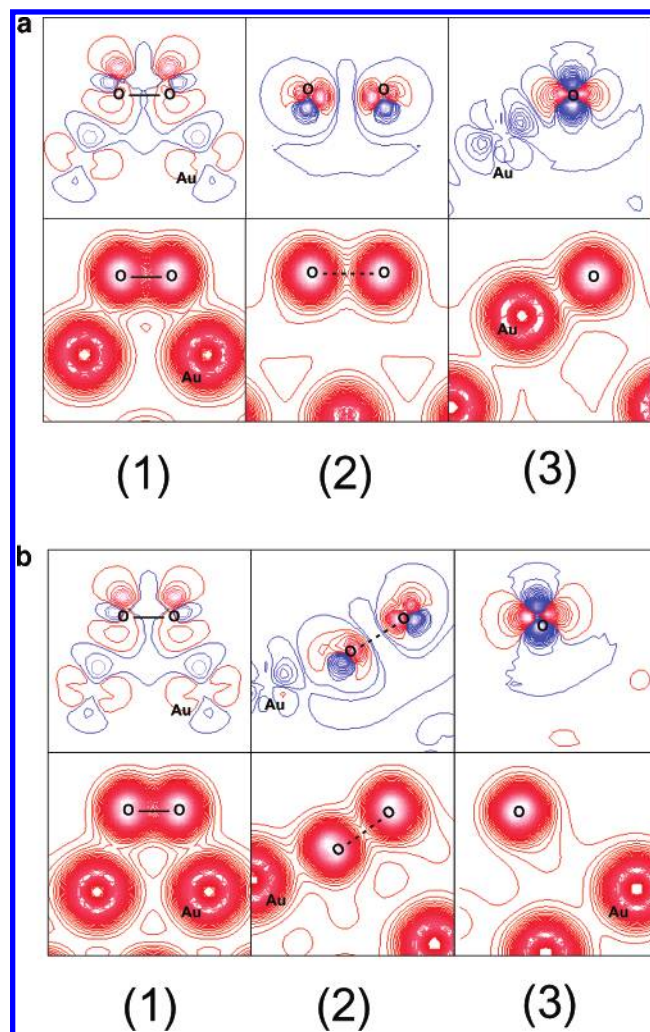


Figure 11. Contour diagrams of electron density distributions for the initial, transition, and atomic final states in the O₂ dissociation process (a) on the 10%-stretched Au(111) surface and (b) on the unstretched Au(211) surface. The upper row of images in a and b shows density differences. The red and blue contours adjacent to each other have the lowest absolute values and correspond to +0.01 (density increase) and −0.01 (density depletion) $e/\text{\AA}^3$, respectively. The lower row shows total densities, where the outermost red contour in each image has the lowest value (0.01 $e/\text{\AA}^3$). Contours with greater absolute values are increasingly lighter. Two successive contours of the same color differ by 0.05 $e/\text{\AA}^3$. Each system is sliced in a different plane to expose regions in space of greatest interest, such as where the O–O bond occurs.

surface Au atom is from the step edge. This pattern agrees with the decreasing binding energies of atomic oxygen in the f and h sites shown in Table 2. (ii) However, Figure 10 shows that the effect of tensile strain on the surface electronic structure is such that the d-band center is more upshifted the farther away a surface Au atom is from the step edge. The differences in binding energy are therefore evened out among the three-fold sites on the stretched Au(211) surface. The f0 site, located right on the step edge, thus benefits the least from the tensile strain. As a result, the binding energy for atomic oxygen is actually greater on the 10%-stretched Au(111) surface than on the 10%-stretched Au(211) surface (Figure 8).

To further elucidate possible differences in the adsorption of molecular and atomic oxygen on the different surfaces, we have plotted the total electron densities (n_{total}) and the electron density differences (defined as $\Delta n = n_{\text{total}} - n_{\text{clean slab}} - n_{\text{adsorbate}}$, where $n_{\text{clean slab}}$ is the electron density of the substrate alone and $n_{\text{adsorbate}}$ is that of the adsorbate in the gas phase) of the initial (t–b–t),

transition, and atomic final states in O₂ dissociation on the 10%-stretched Au(111) surface and unstretched Au(211) surface (Figure 11). The two difference plots for the t-b-t precursors have similar features: The σ orbitals along the O-O axis are weakened, whereas the π^* orbitals of O₂ are substantially enhanced compared to those of O_{2(g)}. The precursor interacts with the Au atoms to which it is bound through the Au d orbitals. The d_{z²} orbital, which has the greatest overlap with the oxygen π^* orbitals, suffers a loss in electron density, whereas the d_{xz} and d_{yz} orbitals, which do not have the correct symmetry to bond to the O atoms, gain electron density. The total density plot for the transition state shows a weak residual O-O interaction. In the difference plots, it is clear that around the transition states (middle columns, Figure 11a and b) the O atoms begin to take on features of the final atomic state. In the final state, the O atom suffers a significant loss of electron density in its perpendicular p_z orbital but gains electron density in a donut-shaped region around it and parallel to the surface. As the dissociation process progresses on each surface, the range of density difference broadens, confirming that atomic oxygen interacts much more strongly with the surface than the molecular precursors do.

Conclusions

A 10% tensile strain enhances the adsorption of atomic and molecular oxygen on Au surfaces. On a 10%-stretched Au(111) surface, the binding energy of atomic oxygen is increased from -2.54 eV/O on the unstretched surface to -3.14 eV/O, the adsorption of molecular O₂ becomes marginally exothermic with -0.08 eV/O₂, and the barrier to O₂ dissociation is calculated to be 1.37 eV. On Au(211), a 10% tensile strain increases the binding energy of atomic oxygen from -2.77 to -3.07 eV/O and increases that of molecular O₂ from -0.15 to -0.26 eV/O₂ while lowering the barrier to O₂ dissociation from 1.12 to 0.63 eV, the lowest found in this study. Step edge and tensile strain therefore both enhance oxygen adsorption and O₂ dissociation, although the effect of strain is less pronounced at step edges. We conclude that stretched step edges can be the sites for O₂ adsorption and activation on Au nanoparticles. Without excluding other possible factors influencing low-temperature reactivity, we propose that the greater activity of smaller Au nanoparticles observed in many experiments may originate both from a higher step density and from a greater amount of surface strain that can be present in smaller Au particles.

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