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Making gold less noble

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Self-consistent density functional calculations for the adsorption of O and CO on flat and stepped Au(111) surfaces are used to investigate effects which may increase the reactivity of Au. We find that the adsorption energy does not depend on the number of Au layers if there are more than two layers. Steps are found to bind considerably stronger than the (111) terraces, and an expansive strain has the same effect. On this basis we suggest that the unusually large catalytic activity of highly-dispersed Au particles may in part be due to high step densities on the small particles and/or strain effects due to the mismatch at the Au–support interface.

Keywords: gold, CO oxidation, catalysis, particle-size effect, steps, DFT, supported metal clusters

Gold is usually quite inert. Even reactive molecules like O_2 and H_2 do not adsorb on gold surfaces [1,2], and gold is therefore not expected to be a good catalyst for oxidation or hydrogenation processes which require adsorption of the reactants. Nonetheless, there is now a growing number of reports that nanometer-size gold particles on various oxide supports can serve as very efficient catalysts for, e.g., the CO oxidation process [3–5] at low temperatures. Several possible explanations for this effect have been suggested. Some authors point to the special role of sites at the metal/support interface [6,7], others to the degree of coordinative unsaturation of the surface atoms [8], whereas most recently Goodman and coworkers [9] suggested that the anomalously high reactivity of small gold particles is due to quantum–size effects. Using scanning tunneling microscopy (STM) they showed that gold particles form disc-like structures on a TiO_2 surface and that the reactivity depends strongly on the disc height, reaching its maximum for a two-layer structure.

In the present letter we investigate the question of the particle-size-dependent gold reactivity in more detail on the basis of a set of self-consistent density functional theory (DFT) calculations. In particular, we address the question whether a considerably more reactive form of gold exists. We do that by considering the adsorption of O, CO and O_2 on Au(111) slabs with one to six layers of Au with varying lattice constants, and on an Au(211) slab. The latter is chosen because it consists of (111) facets separated by steps. We find that there is little variation in the chemical activity of Au(111) with the slab thickness except for the one-layer slab which is substantially less reactive than thicker Au(111) slabs. An array of small Au particles was also considered and found to be even less reactive. We find two effects which can increase the ability of Au to bond to simple adsorbates significantly. One is the presence of steps, as found on the Au(211) slab. Whereas dissociative oxygen adsorption is endothermic on the flat Au(111) surfaces, it is essentially thermo-neutral at the steps. Similarly, CO binds much more strongly at the steps than on the flat Au(111) surfaces. The other effect is the introduction of strain parallel to the Au surface. An increase in the Au lattice constant parallel to the surface of only 1.5% is enough to make O_2 dissociation thermo-neutral. On this basis, we identify two effects which may both contribute to the unusual catalytic properties of nanometer-size gold particles. One is related to the fact that the relative concentration of *steps* and other surface *defects* increase with decreasing particle size. The other is related to the fact that interactions at the Au–support interface may induce a *strain* which will affect the reactivity of surface Au atoms for the smallest particles.

In the DFT calculations [10], we used three different models of an Au surface: (a) An Au(111) slab with between one and six layers periodically repeated in a super cell geometry with nine to four equivalent layers of vacuum between any two successive metal slabs, respectively. (b) An Au(211) slab with nine atomic layers of metal separated from the next metal slab by 14 equivalent layers of vacuum. The results reported here for the Au(211) surface were found to be unchanged when the corresponding calculations were performed by using a 12-layer thick metal slab. (c) An array of two-layer thick clusters containing 18 Au atoms each. The three types of model systems are shown in figure 1.

To probe the reactivity of the different Au surfaces, we consider here the adsorption energy for O, CO, and O_2. This is a measure of the ability of the surface to interact with adsorbates, but may also more generally be a measure of the barriers for surface reactions, since it is often found that there is a close correlation between bond energies and activation energies for surface reactions [11]. In addition, since Au surfaces bind atoms and molecules too weakly, it

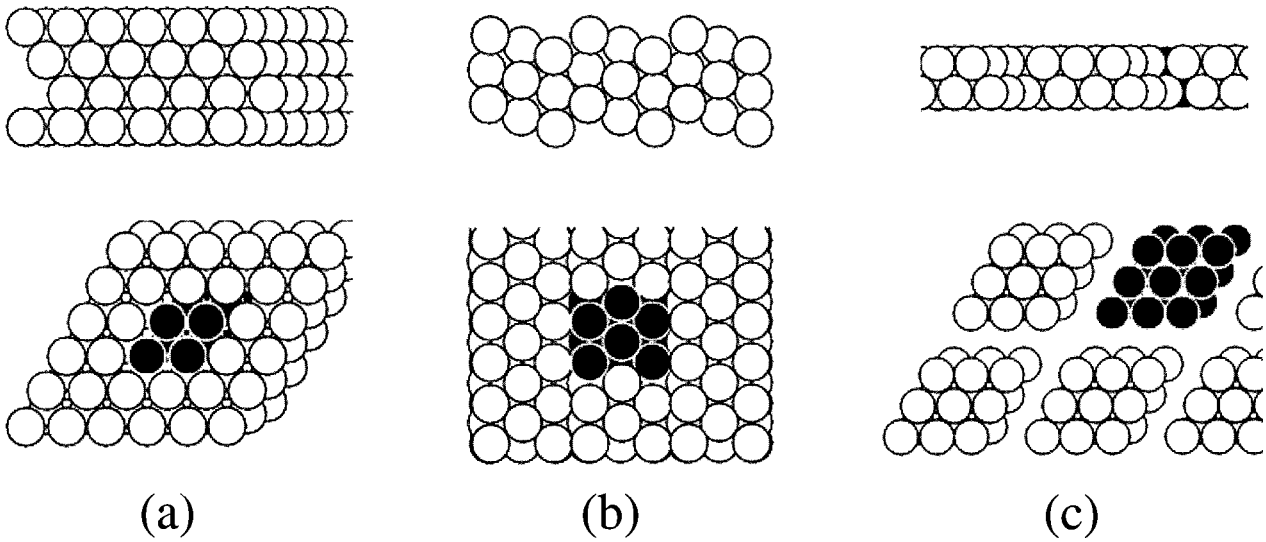

Figure 1. The three types of models used to study the ability of Au surfaces to interact with adsorbates: (a) a four-layer Au(111) slab, as a model for a flat Au surface, (b) a nine-layer Au(211) slab, as a model for a stepped Au surface, and (c) a two-layer Au cluster with a total of 18 Au atoms, as a model of a small Au particle.

is likely that the availability of the reactants on the surface (i.e., adsorbates) is a major rate-limiting factor for surface-catalyzed processes on Au.

Adsorption was allowed on only one of the two surfaces of the (2×2) until cell used for the (111) surface and the (3×2) until cell used for the (211) surface, and the electrostatic potential was adjusted accordingly in both cases. Relaxation of up to the top two (four) metal layers of the (111) ((211)) slabs was allowed, respectively. Full relaxation of all the adsorbates' degrees of freedom was allowed in each case. Ionic cores are described by ultrasoft pseudopotentials [12] and the Kohn–Sham one-electron valence states are expanded in a basis of plane waves with kinetic energies below 30 Ry. The surface Brillouin zone is sampled at 54 special **k** points for the (111) slabs and 64 **k** points for the (211) slab. The convergence of the binding energy for O on the one-layer thick Au(111) slab with respect to **k** point-set was verified with a 162 **k** point calculation. The exchange–correlation energy and potential are described by the generalized gradient approximation (GGA-PW91) [13,14]. The calculated PW91 lattice constant for bulk Au was found to be 4.18 Å, in reasonable agreement with the experimental value of 4.08 Å [15]. In the calculations for strained surfaces, the lattice constant parallel to the surface is varied around this value (4.18 Å). The self-consistent PW91 density is determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi-population of the Kohn–Sham states ($k_{\mathrm{B}}T = 0.1$ eV), and Pulay mixing of the resulting electronic density [16]. All total energies have been extrapolated to $k_{\mathrm{B}}T = 0$ eV.

When the size of a metal particle decreases in one or more dimensions the quasi-continuum of metal states will eventually degenerate into a set of discrete states due to quantum–size effects. Such effects have been observed to give rise to sizable variations in the ability of very small metal clusters to adsorb molecules from the gas phase [17,18], and it is natural to look for similar effects as the origin of the unusual surface properties of small gold particles. The STM images of Au on a TiO_2 surface show the Au particles to be rather flat with a ratio of height to diameter of approximately 0.3 [9]. The quantum–size effects should be primarily linked to the smallest dimension, which is the height in this case. In our DFT calculations we model this by considering a semi-infinite Au(111) slab and vary the number of layers. It turns out that this gives only marginal variations in the binding energy of both atomically adsorbed oxygen and CO, see figure 2. Only the one-layer slab has properties that are significantly different from the rest. For the one-layer slab the adsorption of oxygen is weaker, whereas CO does *not* adsorb at all.

We also considered O and CO adsorption on an array of small, isolated, two-layer thick Au clusters, see figure 1. We consider here only adsorption on the central Au atoms on the cluster; step sites are considered separately below. Adsorption on the small particles is even less favourable than on the slabs, see table 1. We have not made an extensive study of the dependence of the adsorption energies on particle size, so we cannot rule out that some "magic" cluster size gives a stronger adsorption, but it is clear that there is not a simple monotonic increase in reactivity with the opening of gaps in the one-electron spectrum at small particle sizes.

In our search for a structure of gold with enhanced reactivity (stronger binding), we also considered Au steps on a nine-layer Au(211) slab. Here we calculated considerably stronger binding for both CO and oxygen (table 1). On the Au(111) slabs, a shallow minimum was found for CO (the weak van der Waals attraction is not described in the DFT calculations). At the step, on the other hand, the binding is almost as strong as on a flat Cu(111) surface [19]. This is in excellent agreement with the experiments by Ruff et al. [20], where it is found that Au steps give rise to CO

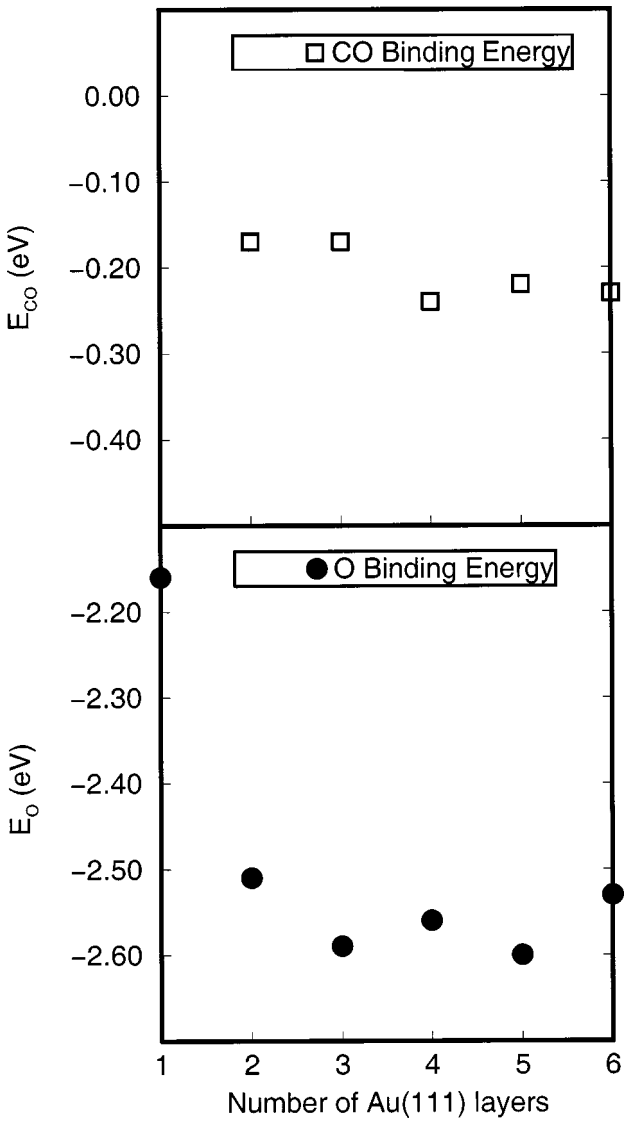

Figure 2. Binding energy of O and CO on Au(111) slabs as a function of the thickness of the slab. The lack of a data point at $x = 1$ in the top panel indicates that CO does *not* adsorb on a monolayer of Au(111). Data correspond to calculations where the positions of the metal atoms are fixed at their bulk-terminated values. All degrees of freedom for he adsorbates were allowed to relax.

adsorption with a thermal desorption temperature close to that of CO on Cu surfaces [21]. Moreover, a combined IR and TPD study of CO chemisorption on a stepped Au(332) surface suggests an initial isosteric enthalpy of adsorption of ca. 55 kJ/mol [22], which is reasonably close to the calculated binding energy of CO on Au(211). Experiments on small Au particles have indicated only minor CO adsorption, but in these experiments the adsorption temperature was 150 K where the desorption rate is already appreciable [4,5].

Similarly, dissociative O_2 adsorption is endothermic on the (111) facets, whereas it is found to be almost thermoneutral at the steps (table 1). Atomic oxygen adsorption has been observed on Au(111) [1,2], and in agreement with our calculations this could only be accomplished by the decomposition of a molecule (O_3 or NO_2) which is considerably less stable than O_2 [1]. The lack of immediate desorption of O_2 in these experiments must mean that adsorption and thereby desorption is activated. We have also considered molecular O_2 adsorption on the (111) and (211) surfaces, and find again that there is no stable molecular state on the (111) facet, whereas O_2 molecules are weakly bound to the step-edge atoms of the Au(211) surface. Since both the molecular and the dissociated states are stabilized at the step, one could expect that the barrier for O_2 dissociation could also be lower at the step, but irrespective of whether the dissociation takes place at the steps or on the support [5], it is clear that the concentration of atomic oxygen on the Au surface can be considerably higher at the steps than on the terraces, and that the oxidation rate could be correspondingly higher in the vicinity of the steps.

Table 1
Calculated binding energies (eV/CO, eV/O_2) for CO, O, and O_2 on Au(111) and Au(211) surfaces and a small Au cluster. All values are referenced to the clean surface and the corresponding gas-phase molecule (CO, O_2) at infinite separation between each other. Negative values correspond to stable configurations. Values for the Au(111) surface are taken from a four-layer, 2×2 unit-cell, slab calculation (with 54 special **k**-points sampling of the first Brillouin zone), where the top two layers were allowed to relax. Values for the Au(211) surface are taken from a nine-layer, 3×2 unit cell, slab calculation (with 64 **k**-points sampling of the first Brillouin zone), where the top four layers were allowed to relax. The lowest energy site is indicated in each case; (t), (f), and (b) denote the atop, fcc, and bridge sites, respectively. The favorite site for CO/Au(211) – at 50% coverage of the step edge – is the bridge site at the step edge. The favorite site for O/Au(211) – at $1/6$ ML total coverage – is also at the vicinity of the step edge, where differences in the site preferences are very small (ca. 0.01 eV). The diffusion barrier for O across the step edge is estimated to be ca. 0.01 eV. Molecular O_2 adsorbs on the step edge of Au(211) with its axis parallel to the direction of the step edge, and its center of mass above the bridge step-edge site. The adsorbed molecular O_2 state preserves a magnetic moment of 1.33 μ_B. Values for the Au cluster are taken from calculations on a two-layer thick cluster containing a total of 18 Au atoms within a 4×4 unit cell (1 **k** point). No surface relaxation was allowed in the cluster calculations. Adsorption was considered only away from step edges and corner atoms of the cluster.

	CO/Au	O/Au	O_2/Au
Au(111)	−0.30 (t)	+0.18 (f)	No adsorption
Au(211)	−0.66 (b)	+0.02 (f)	−0.12 (2-fold, ‖)
Au cluster	−0.07 (t)	+1.54 (f)	No adsorption

We, therefore, suggest that one important parameter determining the reactivity of small Au particles is the step density. In figure 3 we show a model calculation of the step dispersion as a function of the particle size for Au on TiO_2. For each particle size we have calculated the equilibrium shape of the Au particle from a Wulff-like construction[1] involving the *surface energies* of the three low-index Au surfaces and the *interface energy* between Au and the support. The former we take from self-consistent DFT cal-

[1] We use an atomic model in the construction of the crystallites, but otherwise proceed as in the Wulff construction, see [23]. As the Wulff construction gives the optimal shape in the continuum limit and some of the crystallites we consider consist of rather few atoms we use the term *Wulff-like* to describe the procedure.

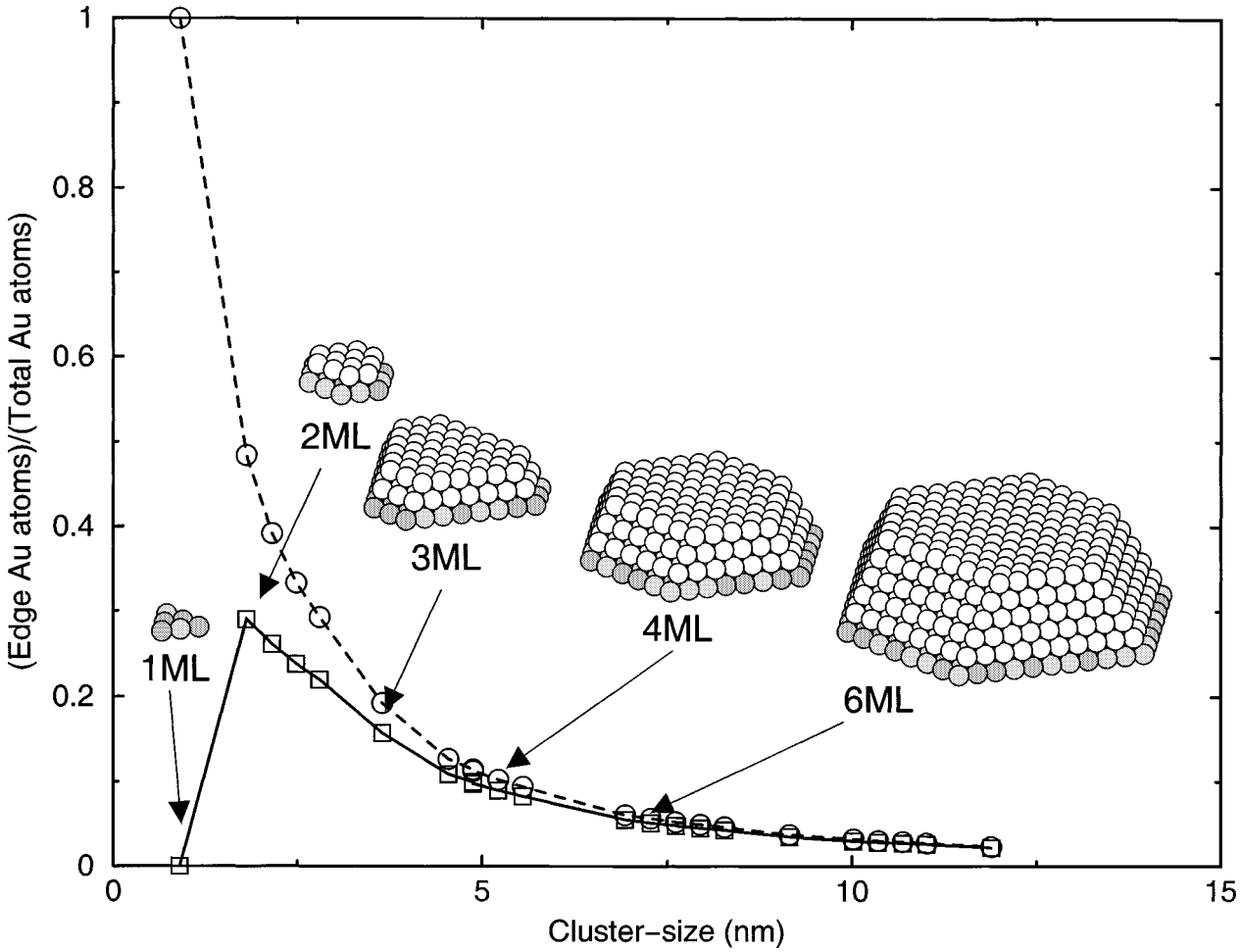

Figure 3. Calculated step density for Au particles on TiO_2 as a function of particle size. (○) and (□) correspond to the total and "free" step sites on the Au particles. "Free" are the step sites *not* in direct contact with the support. Lines through the two sets of points are only drawn as a guide to the eye. Insets illustrate the corresponding Wulff constructions for selected particle sizes.

culations [24]. The latter we estimate from the ratio of height to diameter for Au/TiO_2, as determined in the STM experiments by Valden et al. [9]. Several experimental reports and theoretical studies have concluded that fcc is the most stable structure for small Au clusters (supported or not) regardless of their size [25,26], suggesting that Wulff-like models for Au clusters are realistic choices. It is clear that such a model does not take into account effects such as the dependence of the surface energy on cluster size and edge energies, but the general results below do not depend critically on such details.

The results shown in figure 3 clearly indicate that the step density, defined as the fraction of atoms in the particle having seven or less neighbors, increases continuously as the particle size decreases. If, however, the number of step-edge atoms of the particles in direct contact with the support is subtracted from the total number of step-edge atoms of the particles, a maximum emerges, characteristic of two-layer thick Au particles. The step-edge atoms of the particles in direct contact with the support are responsible for bonding the metal particles to the support, presumably via the oxygen atoms of the oxide, and they can perhaps be considered as poisoned for futher chemisorption of either O or CO. Even if the interaction with the support is weak, one-layer thick particles are inactive towards chemisorption of CO and O (see figure 2). Therefore, one-layer thick particles provide the lowest activity limit to the left of the maximum. Very large particles have much smaller relative concentration of step-edge sites, providing the other limit of low activity to the right of the maximum. The agreement between our results and the experimental data of Goodman and coworkers [9] is reasonably good (see figure 3), further supporting our arguments for the role of steps as a major factor determining the unusual catalytic activity of small Au particles on TiO_2.[2]

It is known that the reactivity of Au depends to some extent on the oxide support [3]. In addition to the possible

[2] The non-zero activity corresponding to the smallest particle size of the experimental data is probably due to two reasons: (i) the fact that the particle size distribution in these experiments will cause the presence of some bigger particles and thus some measurable activity, and (ii) a stretched monolayer of Au may be formed on top of the oxide support, which – as will be argued in the next few paragraphs of the text – would exhibit some measurable activity for O and CO chemisorption and reaction.

role of the support in, e.g., dissociation of O_2, this can be due to differences in the particle size and/or in the morphology of the Au particles. The *particle size distribution* will depend strongly on the support through parameters such as the Au diffusion rate or the nucleation-site density on the oxide surface. The *morphology*, on the other hand, will depend on the interface energy between the Au metal and the support.

In addition to the effects of morphology, there is a possibility that *strain*-related effects can change the catalytic properties of the Au particles, as it has already been shown to be the case for other metals [27]. We have assumed above that the Au lattice constant parallel to the surface is equal to the bulk Au value. This is not necessarily the case. Both the surface tension at the surface of the Au particles and the tension at the Au–support interface can change the lattice constant of Au and hence its reactivity.

By calculating the adsorption energy associated with dissociative chemisorption of O_2 (E_{O_2}) on a four-layer slab with three different parallel lattice constants a we find $\mathrm{d}E_{O_2}/\mathrm{d}\ln a = 13$ eV. Therefore, a 1% increase in the lattice constant gives an increase in the O_2 binding energy of ca. 0.13 eV. Similarly, we calculate that $\mathrm{d}E_{CO}/\mathrm{d}\ln a = 4.7$ eV, implying a ca. 0.05 eV increase in the binding energy for CO for a 1% increase in Au lattice constant. For comparison we calculate that the surface tension alone will give rise to a contraction of 0.8% for a four-layer Au(111) slab and 1.7% for a two-layer slab compared to the bulk value of the lattice constant. Such contractions have been observed in experiments on various supported transition metal clusters [28–34]. The surface tension alone thus acts to *decrease* the reactivity of the smaller particles. The support may, however, reverse this trend if it induces an expansion of the Au lattice constant, via a strong interaction with the Au particle. The latter has been experimentally reported for small Au particles (less than 4 nm in size) epitaxially grown on MgO(100), where a 2.9% increase of the Au lattice spacing, compared to the bulk value, was measured [35]. A strain of this size would make O_2 adsorption 0.38 eV more exothermic on the (111) facet. Strain induced by mismatch at the interface between the metal particle and the support will extend over the whole particle as long as it is small. For larger particles, misfit dislocations are created and the lattice constant at the surface will approach the bulk metal value. This effect will, therefore, also be stronger for the smallest particle sizes.

There is also the possibility that the support influences the reactivity of the surface Au atoms through direct electronic interactions. Such an effect should be the strongest for the smallest particle sizes. Our calculations cannot rule out such an effect. It is worth noting, however, that the screening is strong enough that the surface of a two-layer Au slab has very similar chemical properties to the surface of a six-layer slab, indicating that adsorbates cannot feel whether you have vacuum or another layer of Au atoms two layers down in the material.

We note that, whereas the effect of steps and the effect of strain can be understood in terms of simple reactivity models for transition metal surfaces [27], the relative inability of the single-layer slab and of the small clusters to make bonds to adsorbates cannot be described simply in terms of shifts in the d-states of the surface atoms. Clearly, the discrete nature of the one-electron spectrum makes these systems quite different from the more extended ones. Nevertheless, the trend we have calculated so far suggests that both small Au clusters and an Au monolayer are less reactive in terms of their ability to bind simple atoms and molecules from the gas phase. We point out, in this connection, that the one-layer Au slab calculations presented here do not include neither of two possible effects: (1) chemical interactions of the adsorbates with the metal oxide support through the slab, and (2) considerably large expansions of the Au lattice constant, which could be sustained in the metal layer by the metal oxide support. Both effects could make a single supported Au layer more reactive than a thicker slab, as suggested by Bondzie et al. [36].

In conclusion, we have investigated in some detail three effects which might make gold surfaces more chemically reactive towards O_2 and CO adsorption: (i) quantum–size effects in one dimension, (ii) the effect of steps, and (iii) the effect of strain. We have shown that for thin, flat Au slabs, there is no dependence of the adsorption properties of O_2 and CO on the number of Au layers. Steps, on the other hand, appear to be more active than the flat Au(111) surfaces are. Since the step density increases as the particle size decreases this provides one explanation of the unusual catalytic activity of nano-sized gold particles. Finally, we have shown that an expansive strain can increase the reactivity of gold surfaces. Such a strain must be induced by the interaction with the support, and again this strain effect must increase rapidly with decreasing particle size.

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