Charging of Metal Atoms on Ultrathin MgO/Mo(100) Films

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The chemical activity of supported metal nanoclusters is enhanced by electronic charging induced by the interaction with surface defects. We use density functional theory plane wave calculations to show that charging of metal atoms with high electron affinity like Au is possible also in the absence of defects by atom deposition on ultrathin MgO films (1 to 3 layers) grown on Mo(100). The Au $6s$ level falls below the Fermi level of Mo, leading to electron transfer from Mo to Au by direct tunneling through the insulating MgO film. The effect is not observed for Pd, whose $5s$ empty level falls just above the Fermi level of Mo, or for thicker MgO films.

The catalytic properties of metal atoms and clusters on oxide surfaces depend critically on charging mechanisms at the metal-oxide interface [1]. In the gas phase, Au_2^- efficiently promotes the catalytic conversion of CO to CO_2 [2]. The same reaction has been observed for Au_8 deposited on defect-rich MgO [1,3] where the Au nanoclusters are active in the $CO + 1/2O_2 \rightarrow CO_2$ conversion if stabilized at F centers (oxygen vacancies with two trapped electrons) which efficiently delocalize charge on the supported cluster; on defect-poor MgO the activity of gold clusters is significantly reduced [1,3]. The same effect has been observed also in the cyclization of acetylene to give benzene, $3C_2H_2 \rightarrow C_6H_6$, promoted by Pd atoms on MgO [4]. While a gas phase Pd atom is inert, Pd atoms bound at the F centers of MgO convert acetylene to benzene [4]. These experiments, done on ≈ 20 Å thick MgO films epitaxially grown on Mo(100) single crystals [1,3,4], show the important role of charging in catalysis by supported metal nanoclusters. In these examples, charging is connected to the presence of surface defects (in particular anion vacancies) which act both as anchoring sites (strong bonding with the surface [1,3–5]) and promoting sites (electron transfer at the metal-oxide interface [6]). A typical estimate of the concentration of these defects is about 1% of a monolayer, i.e., 10^{13} defects/cm^2 [3,4]. To modify the chemical activity of supported metal atoms or clusters it is desirable to find methods where charging occurs independently of the presence of defects. A recent example has been reported for Au atoms deposited on a two-layer NaCl film grown on Cu(111) [7]. Using an STM tip it has been possible to control the charge state of deposited Au atoms and to form a stable Au^- anion. However, this single electron manipulation, fascinating from a conceptual point of view, does not provide a viable way to generate an assembly of negatively charged supported atoms or clusters.

We propose that charging can occur by depositing metal atoms with high electron affinity (EA) on ultrathin films of MgO grown on Mo(100). The mechanism, studied by periodic density functional theory (DFT) calculations, can apply to other oxides and metal substrates. We show that electrons can flow from the Fermi level of the Mo substrate to the $6s$ level of Au by direct tunneling through the thin oxide layer. The effect is not observed for atoms with low EA like Pd, whose $5s$ empty level falls just above the Fermi level of Mo, or for thicker MgO films. This Letter describes a new physical mechanism directly related to the nanodimensionality of oxide films grown on metals. The MgO/Mo(100) interface is considered because Mo, a refractory metal that can sustain high annealing temperatures, allows one to grow oxide films of good quality [8].

The calculations are based on DFT using the generalized gradient approximation (PW-91 functional [9]) as implemented in the VASP program [10,11] (plane wave basis set, kinetic energy cutoff at 396 eV, ultrasoft pseudopotentials [12]). The Mo(100) substrate has been modeled by four Mo layers which reproduce well the band structure of bulk Mo. The O atoms of MgO are on top of the Mo atoms while Mg falls in hollow positions. All atoms in the MgO film and in the two surface nearest layers of Mo were relaxed until the atomic forces are less than 0.01 eV/Å. The remaining two Mo layers were frozen at bulk positions. The computed Mo lattice constant [$a_0 = 3.151$ Å; a_0(expt) = 3.147 Å] is 5% larger than the surface MgO one ($a_0 = 2.998$ Å). Therefore, the epitaxial MgO layers are expanded with respect to bulk. We also considered unsupported MgO(100) films computed with two lattice parameters, bulk MgO and Mo. Since the general features are the same, we discuss results only for the expanded films. Pd and Au atoms have been adsorbed on O and Mg sites of MgO(100) and MgO/Mo(100). For the calculations we used $3 \times 3 \times 1$ supercells containing 9 Mg, 9 O, and 9 Mo atoms per layer (L). In the largest system considered, MgO(5L)/Mo(100), we have 45 Mg, 45 O, and 36 Mo atoms in the supercell. The vacuum thickness was varied in the interval 8 to 26 Å. Dipole corrections, introduced in selected cases, do not result in different adsorption properties and do not change the general conclusions of the

Letter. Sampling of the Brillouin zone using a $(4 \times 4 \times 1)$ k points mesh resulted in a converged total energy. Spin polarized calculations have been performed for Au adsorption.

The MgO films, either supported on Mo(100) or unsupported, exhibit interlayer distances of 2.04–2.05 Å (2.12 Å in bulk MgO), and a small surface corrugation. In MgO(3L)/Mo(100) the MgO-Mo interface distance, 2.15 Å, remains constant with the number of layers. Only for MgO(1L)/Mo(100) the interface distance is reduced, 2.10 Å, reflecting a stronger adhesion energy, $E_{adh} = 0.161$ eV/Å^2. E_{adh} decreases drastically (25%) for MgO(2L)/Mo(100) and converges to 0.145 eV/Å^2 for thicker films. The density of states (DOS) curves for MgO/Mo(100) (not reported here) show a small mixing of the O $2p$ states with the Mo $4d$ band at the Fermi level (E_F), which is not restricted to the 1L film but is present also for the 2L and the 3L films. This reflects the stronger adhesion of MgO to Mo than to other metals like Ag [13,14]. However, for MgO(3L)/Mo(100) the general structure of the DOS of the top layer is similar to that of a MgO(100) slab, in analogy with theoretical results obtained on the Ag(100) support [13,14]. Thus, one could expect a similar behavior of metal atoms adsorbed on the MgO(100) surface or on MgO/Mo(100) films.

The properties of Pd and Au atoms on MgO(100) do not differ from what was reported in previous studies [15]. Metal atoms prefer to adsorb on O anions; on a 3L or 4L slab Pd binds with $E_a = 1.53$ eV and a vertical distance $z = 2.05$ Å; on Mg the bonding is almost 3 times smaller, 0.58 eV, and the surface distance is 0.5 Å longer (2.54 Å; see Table I). Slightly different adsorption properties are found on a 1L MgO slab, but the preference for O anions is confirmed and actually enhanced. A 2L MgO slab exhibits essentially the same adsorption properties as thicker films, showing a rapid convergence with the number of layers.

TABLE I. Properties of Pd and Au atoms adsorbed on top of O or Mg ions of unsupported and supported MgO (nL) films.[a]

site	Pd				Au			
	O		Mg		O		Mg	
nL	E_a, eV	z, Å	E_a, eV	z, Å	E_a, eV	z, Å	E_a, eV	z, Å
MgO(100) 1	1.87	2.03	0.68	2.49	1.35	2.24	0.63	2.63
2	1.50	2.05	0.58	2.54	0.98	2.24	0.48	2.69
3	1.53	2.05	0.58	2.54	1.01	2.24	0.49	2.70
4	1.52	2.05	0.58	2.54	1.01	2.24	0.49	2.70
MgO/Mo(100) 1	1.52	2.15	1.06	2.49	2.0	2.68	2.27	2.55
2	1.69	2.11	0.99	2.55	2.06	2.76	2.21	2.58
3	1.55	2.07	0.80	2.57	1.64	2.76	1.87	2.57
4	1.54	2.07	0.73	2.57	1.42	2.70	1.61	2.61
5	···	···	···	···	1.29	2.63	1.44	2.64

[a]nL = number of layers; E_a = adsorption energy; z = vertical distance.

The presence of an unpaired electron in the diffuse $6s$ orbital of Au prevents the atom from getting close to the MgO surface so that the $5d$ orbitals have a smaller overlap with the O $2p$ orbitals of MgO and the bonding is weaker. On a MgO(100) 3L slab Au binds to the O sites with $E_a = 1.01$ eV and $z = 2.24$ Å; see Table I. On a 4L slab the results are identical. Compared to Pd, the bond is about 30% weaker and the distance is 0.2 Å longer; the bonding on Mg is weak, $E_a = 0.49$ eV, and the distance is very long, $z = 2.70$ Å. By reducing the MgO film thickness, there is an increase of the Au-MgO bond for 1L films, as for Pd, but again on a 2L MgO film the adsorption properties are nearly converged; see Table I. We conclude that on the MgO(100) surface both Pd and Au atoms prefer to bind on the O anions through a bonding which has mixed covalent and polarization character [15] and, more important, that the atoms are basically neutral since the charge transfer at the interface, if any, is small.

Let us consider now adsorption on MgO/Mo(100) films, starting from Pd. On MgO(3L)/Mo(100) Pd binds to the O sites with $E_a = 1.55$ eV and $z = 2.07$ Å, Table I, two values very close to those computed for the unsupported MgO 3L slab ($E_a = 1.53$ eV and $z = 2.05$ Å; see Table I). A small difference is found for the less favorable Mg sites of MgO/Mo(100): E_a is 0.80 eV and $z = 2.57$ Å (Table I); on MgO(100) $E_a = 0.58$ eV and $z = 2.54$ Å (Table I). Thus, while the distance from the surface is almost the same, the binding to Mg is slightly enhanced on MgO/Mo(100). These effects are more pronounced for MgO(1L)/Mo(100), due to the reduced dimensionality of the oxide film. By increasing the film thickness the effect tends to disappear, and for MgO(4L)/Mo(100) the Pd adsorption properties are close to those of a MgO(100) surface; see Table I. Actually, a small difference is present in the adsorption energy of Pd on the Mg cations: this is 0.58 eV on MgO(100) and 0.73 eV on MgO(4L)/Mo(100). The origin of this small difference becomes clear from the analysis of the DOS curves of Pd/MgO(100), Fig. 1(a), and Pd/MgO(3L)/Mo(100), Fig. 1(b) (we show the DOS curves for Pd adsorbed on O^{2-}; very similar curves have been obtained for Pd on Mg^{2+}). The Pd $4d$ states are about 1 eV above the top of the O $2p$ valence band and well separated from the empty $5s$ level. There is a moderate mixing of the Pd $4d$ states with the O $2p$ levels of the oxide anion to which Pd is bound. A closer inspection of Fig. 1 reveals that the $4d$ and $5s$ levels of Pd are shifted to higher energies with respect to the top of the O $2p$ valence band in MgO/Mo(100). Another small difference is that while the $5s$ level of Pd is empty on the MgO(100) surface, Fig. 1(a), it falls just above E_F of Mo in the MgO/Mo(100) case, Fig. 1(b). This means that there is a small but nonzero occupation of this level in MgO/Mo(100). This leads to a tiny negative charge on Pd, Pd$^{\delta-}$, which enhances the electrostatic interaction with Mg^{2+} sites. However, the
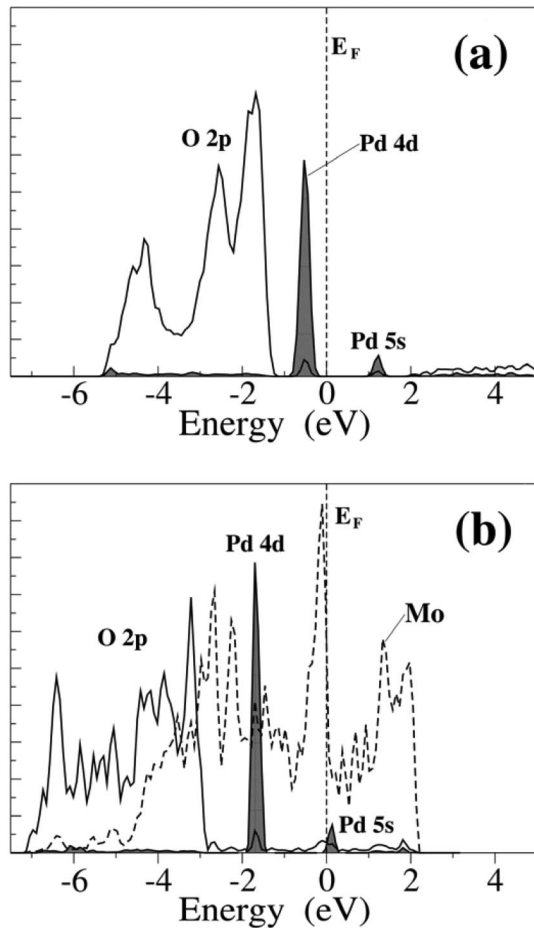
FIG. 1. DOS curves for a Pd atom adsorbed on top of O.
(a) MgO(100) 3L; (b) MgO(3L)/Mo(100). DOS of Pd $\times$ 2.

effect is small and the properties of Pd adsorbed on MgO/Mo(100) or MgO(100) are practically the same.

Things change dramatically for gold. On MgO(3L)/Mo(100), Au binds to the O sites by 1.64 eV with $z = 2.76$ Å; on Mg, E_a is 1.87 eV and the distance is shorter, 2.57 Å; see Table I. Thus, not only the absolute values of the interaction energy and of the distance have changed with respect to the unsupported MgO slab, but now adsorption on Mg is preferred, at variance with the MgO(100) surface. The difference is not only quantitative, but qualitative. The effect is even more pronounced if we consider thinner MgO layers. Clearly we are in the presence of a modified electronic structure of the adsorbed atom. While the results tend to converge as the thickness of the MgO film is increased, even for a supported 5L film they are quite different from those of the MgO(100) surface; see Table I.

What are the reasons for the different behavior of Au/MgO(100) and Au/MgO/Mo(100)? And why is this not observed for Pd? The answer comes from the analysis of the DOS curves for Au/MgO(100), Fig. 2(a), and Au/MgO/Mo(100), Fig. 2(b) (the curves refer to 3L films

and adsorption on O^{2-} sites). The DOS of Au/MgO(100), Fig. 2(a), show that the spin is localized on the 6s level of Au (half filled); the configuration is atomiclike, $5d^{10}6s^1$. The Au 5d states fall below the top of the O 2p valence band, while the Au 6s level, slightly mixed with the O 2p orbitals, lies ≈ 1 eV above the top of the O 2p band. Things are quite different for Au adsorbed on MgO(3L)/Mo(100); see Fig. 2(b). In fact, the Au 6s level lies *below* E_F of Mo; therefore, both α and β components of the Au 6s level are filled, and Au carries a net negative charge, becoming Au^- (configuration $5d^{10}6s^2$-like). As a result, no spin polarization is left on Au. Because of the negative charge, both the 5d and 6s levels of Au are shifted to higher energies with respect to the O 2p band due to the increased Coulomb repulsion. The formation of Au^- is accompanied by a substantial surface relaxation, not present for Au on MgO(100) and reminiscent but less pronounced than that observed on NaCl films [7]. In particular, on MgO(3L)/Mo(100) the adsorption on Mg is accompanied by an outward displacement of the surface cation by 0.36 Å, while the O neighbors do not move significantly. The adsorption on O^{2-} induces a downward displacement of -0.20 Å and an outward movement of the Mg neighbors by 0.15 Å. This substantial geometric rearrangement stabilizes the Au^- species. By increasing the
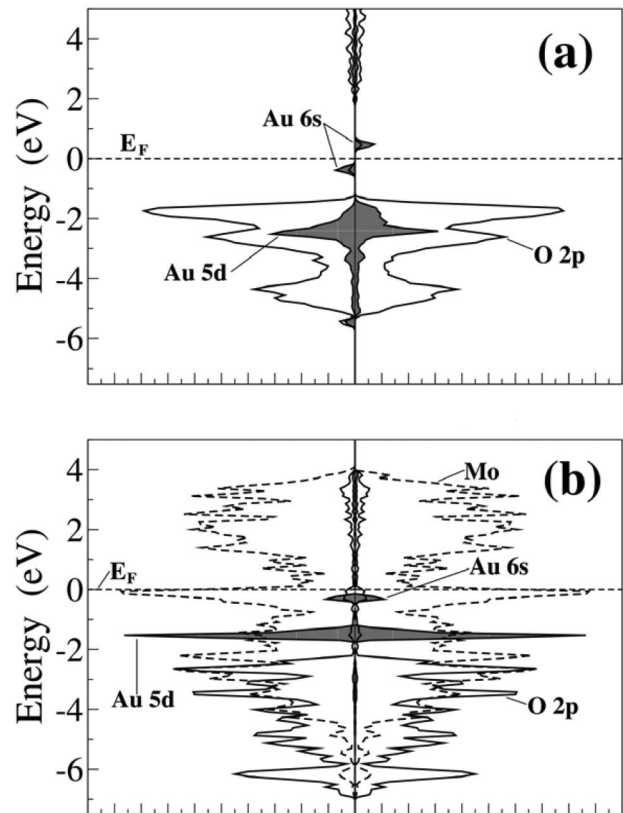

FIG. 2. DOS curves for a Au atom adsorbed on top of O.
(a) MgO(100) 3L; (b) MgO(3L)/Mo(100). DOS of Au $\times$ 2.

film thickness, the 6s level of Au is pushed towards the Fermi level of Mo by the effect of the flattening of the potential, so that the charge transfer is reduced.

On this basis it is easy to rationalize the different behavior of Pd and Au: the Pd 5s level is above E_F of Mo, and very little charge flow occurs for this atom, resulting in very similar adsorption properties on MgO(100) and MgO/Mo(100), at variance with Au. This is fully consistent with the different EA's of the two atoms, 0.56 eV for Pd and 2.31 eV for Au [16] (the computed values are 0.41 and 2.31 eV, respectively [17]). Stated differently, while Au^- is a stable species on MgO/Mo(100), Pd^- is not. It is also interesting to note that the binding of Au^- to MgO/Mo(100) films is enhanced with respect to the MgO(100) surface independent of the adsorption site, O^{2-} or Mg^{2+}. In part this is due to a larger orbital mixing (covalency), but an important contribution comes from the formation of an image charge in the metal in response to the presence of an ionic adsorbate, an effect more pronounced for thinner films.

The calculations show that in the ground state of Au/MgO/Mo(100) charge flow occurs from Mo to the Au adsorbate. However, in a "real" system charge transfer is prevented by the presence of the insulating oxide. Nevertheless, at least three mechanisms can lead to a direct charge transfer. One, less likely, is related to the presence of islands, grain boundaries, and defects acting as hole or electron traps within the MgO film. If the potential energy difference between the empty states of the adsorbed atom (or cluster) and the Fermi level of the metal substrate results in an electric field $>1.5 \times 10^{-2}$ V/Å (the condition for dielectric breakdown in MgO), charging of the adsorbed atoms can occur. This corresponds roughly to the field generated by 10^{13} cations/cm^2 on the MgO surface. Dielectric breakdown is however unlikely by deposition of neutrals but could be stimulated by the application of an external electric field. The second mechanism can occur only at high temperatures and is related to thermal excitations of electrons through the dielectric barrier (thermionic emission).

Much more effective is the third mechanism, i.e., direct tunneling from the Mo conduction band states to the Au empty states. For a thin insulating barrier (< 10 Å) separating two metals, there is a significant probability that an electron which impinges the barrier will tunnel through it. This is measured by the transmission coefficient,

$$|S|^2 \approx \exp[-4\pi a/h\sqrt{2mW}], \tag{1}$$

where a and W are the width and the height of a square potential barrier, respectively, and m is the mass of the

electron. Taking for W the work function of Mo, 4.5 eV, and $a = 4$ Å (2 layers), S is $\approx 10^{-4}$; for a monolayer, $a = 2$ Å, $S \approx 10^{-2}$. These values increase for a more realistic continuous potential barrier and indicate a significant tunneling probability. STM imaging is possible for supported MgO films containing up to three layers [13,18]. In particular, even for a small negative bias of the substrate, electrons flow from the sample to the tip, a situation similar to that represented by Au atoms at contact with the MgO surface. With a metal like Mo, which shows a high density of states at the Fermi level, the number of electrons potentially involved in the tunneling process is comparatively higher than with other metals.

In conclusion, we suggest that charging of metal atoms is possible on ultrathin oxide films grown on metal substrates by combining adsorbed metal atoms with high EA (like Au) with metals with low work function. In this case, it should be possible to form and stabilize charged species with chemical properties completely different from those of the same atoms or clusters adsorbed on oxide surfaces or thick films.

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