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Adsorption of atomic and molecular oxygen on Cu(1 0 0)

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Abstract

We have studied the initial stages of the oxidation of the Cu(1 0 0) surface using ab initio calculations. Both atomic and molecular oxygen are addressed. We show that subsurface oxygen is not energetically favourable, but gets stabilized by on-surface O. We discuss the adsorption of molecular oxygen using elbow plots, which can be used in order to qualitatively understand the measured sticking coefficient at different oxygen coverages.

Keywords: Copper; Density functional calculations; Oxygen; Oxidation

1. Introduction

The adsorption of oxygen and the subsequent oxidation of metal surfaces are important for the understanding of catalysis and other surface processes. For example, it has been shown that on some transition metal surfaces the catalytic reactions actually occur due to the oxidation [1]. Detailed information on the properties of the surfaces with adsorbed oxygen at different coverages is therefore essential in designing new catalysts. The oxidation problem is also interesting from the fundamental point of view: according to the classical theory of oxidation [2], the oxidation layer grows in a layer by layer fashion until a certain critical thickness has been reached. However, recent experiments indicate the formation of different patterns such as triangles, pyramids and elongated rods; which pattern is preferred depends on the temperature [3,4].

In this work, we have addressed the initial stages of the oxidation process in the case of the Cu(1 0 0) surface, namely the adsorption of O_2 molecules on pure and oxygen precovered Cu(1 0 0). We have calculated the elbow plots which are two-dimensional cuts of the true six-dimensional potential energy surface (PES) experienced by the incoming O_2 molecule, in order to understand the adsorption characteristics of the molecule on Cu(1 0 0). As discussed below, the elbow plots can be used in a qualitative interpretation of the experimental results, yet for quantitative understanding more time-consuming ab initio molecular dynamics calculations have to be performed. Moreover, we have performed first principles studies for atomic oxygen at on-surface and subsurface positions. The adsorption energies thus obtained show that the hollow site is preferred for on-surface adsorption whereas, the subsurface hollow site is energetically unfavourable without the presence of on-surface oxygen.

2. Computational details

In our calculations we used Vienna ab initio simulation program (VASP) package [5–7], which uses plane waves as basis functions and the ultrasoft Vanderbilt type pseudopotentials [8] as supplied by Kresse and Haffner [9], and Spanish initiative for electronic structure with thousands of atoms (SIESTA) [10,11], which uses linear combination of atomic orbitals (LCAO) type basis functions and norm conserving pseudopotentials [12–14]. In our calculations the generalized gradient approximation (GGA) scheme was

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used for the exchange and correlation functional. In the plane wave calculations we used a cut-off radius of 330 eV for the plane waves, which was chosen by total energy convergence calculation for bulk copper. To speed up the self-consistent iterations in both methods we used smearing of 0.1 eV in the Fermi–Dirac occupation function. In SIESTA calculations we used optimized basis sets for copper and double zeta basis with polarization for oxygen. In all the calculations for the elbow plots spin polarized formalism was used; the calculations for the on-surface and subsurface atomic oxygen were spin averaged. To model the surface, we have used slabs with six layers, eight atoms per layer. The bottom layer was kept fixed to the bulk coordinates; full atomic relaxations were allowed for the other layers. However, in the PES calculations the surface atoms were fixed to their relaxed positions at the surface without the O_2 molecule. The PES for the O_2 molecule on Cu(1 0 0) were calculated by moving the molecule in the direction normal to the surface stepwise with an interval of 0.25 Å. At each height, the total energy was calculated for different bond lengths, using a step of 0.2 Å.

3. O_2 adsorption on Cu(1 0 0)

Fig. 1(a) and (b) represent the elbow plots for the O_2 molecule approaching horizontally the clean Cu(1 0 0) and the unreconstructed surface with O coverage corresponding to 1/8 ML, respectively. Moreover, in Fig. 1(c) the elbow plot for O_2 on the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ reconstructed surface with a higher O coverage is shown (this reconstruction takes place at O coverage 0.34 ML or higher [15]). In each case, the O_2 is approaching the Cu top site; on the low coverage surface there is one oxygen atom on the surface at the hollow site next to the top site at which the molecule is about to adsorb, and on the reconstructed surface the plot is shown for a top site in the middle of the 'added row'. It is seen in Fig. 1 that the presence of an oxygen atom at the hollow site changes the adsorption characteristics of the O_2 molecule from dissociation to molecular adsorption. On the reconstructed surface, all the potential energy surfaces calculated so far resemble that in Fig. 1(c), i.e. there is a strong barrier in the entrance channel for the incoming O_2 molecule. One should notice that in all these cases the elbow plots represent the same situation, i.e. O_2 approaching the top site horizontally. Moreover, these configurations are the ones with the lowest barrier in each case. It is therefore, obvious that for the reconstructed surface, with a barrier of several eV even in this case, there is a strong hindrance for the O_2 adsorption.

Qualitatively, the above result can be discussed in the light of recent molecular beam experiments [16] as follows: the observed reduction of the measured sticking coefficient at all values of the kinetic energy of the incoming molecule is consistent with our result (c.f. Fig. 1(b)) that there is a molecularly chemisorbed state close to the O atom. Therefore, the O_2 molecules approaching these, randomly distributed sites, get trapped to the deep minima at the PES without the possibility to dissociate. At low O coverage there are few such sites which agrees with the experimental observation that at 0.1 ML coverage there is a small yet clearly visible reduction in the sticking coefficient compared with that at clean Cu(1 0 0). At the reconstructed surface, all the trajectories explored in our calculations show strong minima at the entrance channel, thus yielding molecular adsorption without dissociation. The same thing is reflected in the experimental result [16] showing a strong reduction in the sticking coefficient at 0.5 ML oxygen coverage. To calculate the sticking coefficient would require a large set of dynamical calculations at different energies of the incoming molecule and is thus beyond the scope of the present paper.

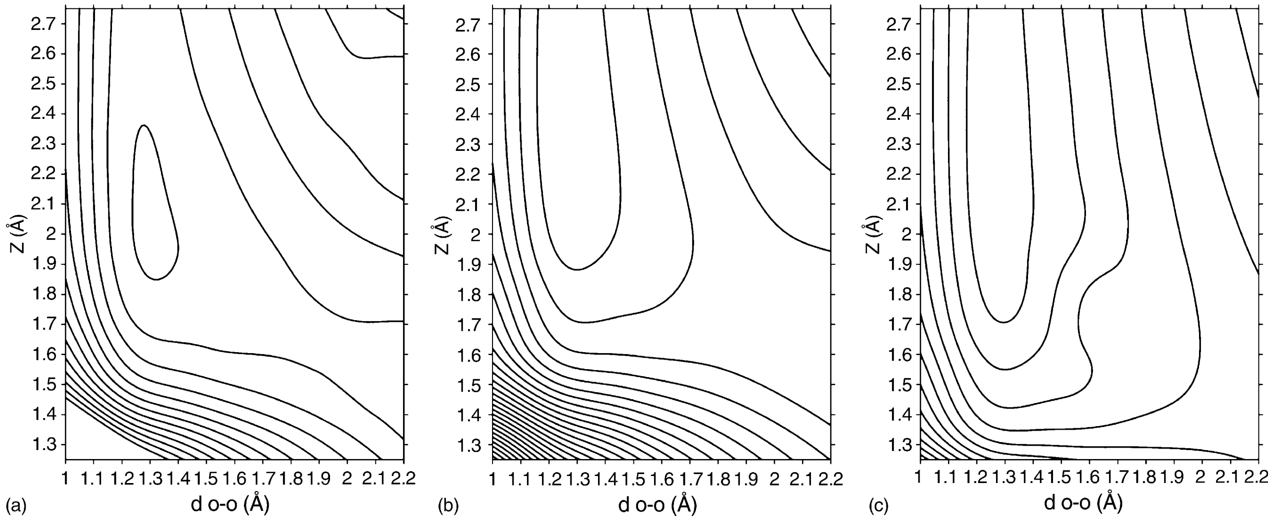

Fig. 1. Potential energy surface for the O_2 molecule approaching the Cu(1 0 0) surface; (a) clean surface, top site; (b) 1/8 mL O coverage, O_2 approaching the top site close to the on-surface O; (c) O precovered, $(2\sqrt{2} \times \sqrt{2})R45^\circ$ reconstructed surface and O_2 approaching horizontally a Cu top site on top of the added row. The spacing between the contours is 1 eV.

The work is in progress to model the dynamics of O_2 on Cu(1 0 0) from first principles.

4. Adsorption of atomic O on Cu(1 0 0)

We have also performed calculations for atomic oxygen in and on the Cu(1 0 0) surface. First, we concentrate on the subsurface oxygen which, to our knowledge, has not been addressed earlier in the case of Cu(1 0 0). Our calculated adsorption energy for the subsurface O atom is 0.08 eV, the positive sign indicating that the subsurface site is not energetically preferable for the O adsorption. Here, the adsorption energy is defined as $E_{\mathrm{ads}} = (E_{\mathrm{tot}} - E_{\mathrm{clean}} - NE_{\mathrm{O}_2}/2)/N$, where E_{tot} is the total energy of the slab containing the O atom(s), E_{clean} is the total energy of the clean Cu slab, E_{O2} is the total energy of an isolated O_2 molecule and N is the number of atoms in the computational supercell. Bringing another O atom to the on-surface site next to the subsurface O lowers the adsorption energy to −1.40 eV per O atom. The presence of the on-surface O therefore stabilizes the subsurface O. For comparison, we also performed a calculation for a subsurface O at the subsurface fcc hollow site at Cu(1 1 1). There the same trend is even clearer; the subsurface location is unstable (with a positive adsorption energy, if the O atom is kept at the subsurface site) for the O atom which, when allowed to relax, moves out of the subsurface position to the hollow site on the surface. Again, bringing in an on-surface O atom stabilizes the situation, the adsorption energy per O atom being −0.97 eV in this case.

Fig. 2 represents the local density of states (LDOS) for the subsurface O and the nearest neighbour Cu atom. It is interesting to notice that the presence of the on-surface O does not change the LDOS at the subsurface site, neither is the surface Cu LDOS appreciably changed. This suggests that the stabilization is not an electronic structure effect. On the other hand, the atomic relaxations do change considerably which is even more surprising in the light of the fact that the changes in the LDOS are small.

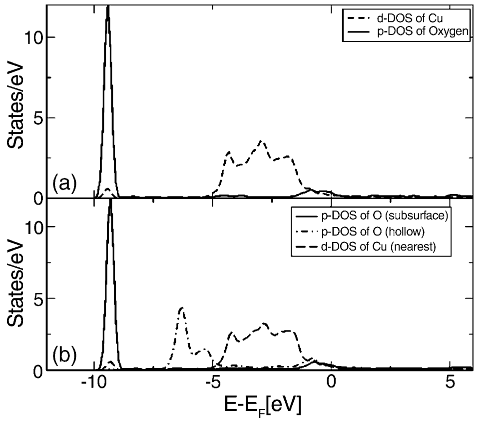

Fig. 2. Local density of states for the O and Cu sites for the subsurface O at Cu(1 0 0); (a) without the on-surface O and (b) with the on-surface O.

Table 1
Adsorption energies for an O atom at different adsorption sites on Cu(1 0 0)

Site	E_{ads}/atom (eV)
Substitutional	−1.41
Hollow	−2.42
Bridge	−1.72
Top	−0.57
Hollow, vacancy	−2.44
Bridge, vacancy	−1.83
Top, vacancy	−0.72

The adsorption energies for the atomistic adsorption of oxygen to different sites on the surface are shown in Table 1. When a vacancy was introduced to the surface the four fold hollow site remained as the most favourable site. Introducing the vacancy increased the adsorption energies for all the sites, but judging by the adsorption energies, the oxygen atom would not go into the vacancy. In fact, the vacancy site was only the third most favourable site.

The above results were calculated using a slab with eight atoms per layer, which is equivalent to 0.125 ML coverage. Our preliminary results for different coverages [17] indicate that the adsorption energies for subsurface O increase with increasing O coverage. On the other hand, the adsorption energy at the on-surface hollow site decreases when increasing the coverage from 0.25 to 0.75 ML [17]. A similar behaviour was observed by Gajdoš et al. in the case of O adsorption on Ag(1 0 0) [18]. These results are consistent with each other in the sense that in order to the oxidation or even reconstruction to take place the O atoms eventually have to go below the surface. Based on the present calculations, however, it is hard to draw conclusions on the exact nature of the onset of the oxidation process.

We now consider the adsorption energies for on-surface O from the electronic effects point of view. Fig. 3 represents the LDOS plots for the oxygen in the hollow, bridge, and top sites. In Fig. 3, it can be seen that in all the sites there is some hybridization between the DOS of the nearest Cu and the DOS of O. The hybridization can be observed more clearly in the cases where the oxygen is in the top and bridge sites. What makes the hollow site more favourable than the other sites is the fact that in the DOS for the hollow site there is more occupation in the lower, bonding state, which also seems to be lower in energy.

5. Discussion

The information obtained using the elbow plots is in qualitative agreement with the experimentally measured sticking coefficients, especially when considering the qualitative behaviour at different coverages. However, some discrepancies do exist. The fact that the measured sticking coefficient for the clean surface goes to zero at low kinetic

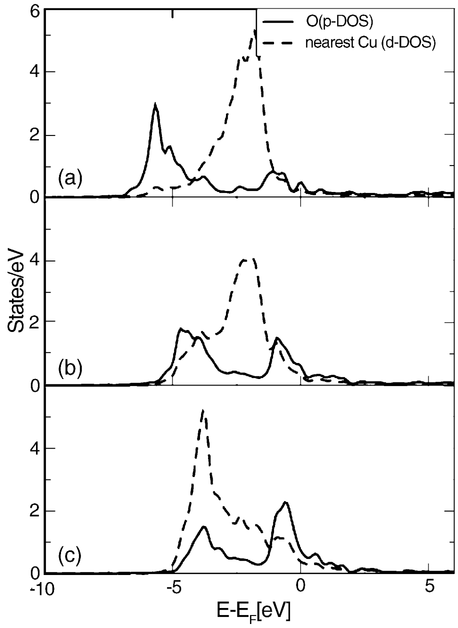

Fig. 3. Local densities of states for an O atom at different adsorption sites on Cu(1 0 0) and that of the Cu atom next to the O atom in each case; (a) O at the hollow site, (b) O at the bridge site and (c) O at the top site.

energies is an indication of the existence of an adsorption barrier in the entrance channel. Such barriers have, however, not been found in our earlier [19] and present calculations. This indicates the existence of a steering effect, guiding the molecules away from the sites with the largest possibility to dissociate, to the sites with, e.g., molecular chemisorption. Such steering has earlier been observed in calculations for O_2 on Cu(1 1 0) [20] and our preliminary results indicate that similar effects could play a role in O_2 adsorption on Cu(1 0 0), too.

6. Conclusions

We have performed first principles calculations for the atomic and molecular adsorption of oxygen on the Cu(1 0 0) surface. Our results for the O_2 molecule on Cu(1 0 0) with different oxygen coverages are in qualitative agreement with the molecular beam experiments, yet there is an indication of the existence of a steering effect, the study of which requires extensive dynamical calculations. Such work is in progress and preliminary results seem to corroborate the above conclusion. For atomic oxygen we predict that subsurface oxygen is not energetically favourable at 0.125 ML coverage, but gets stabilized by the presence of an on-surface oxygen.

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