Adsorption of small Au clusters on MgO and MgO/Mo: the role of oxygen vacancies and the Mo-support

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Abstract. We report a systematic density functional theory investigation of adsorption of small Au\textsubscript{n} (n = 1–6) clusters on ideal and defected MgO(100) single crystal surfaces and Mo(100) supported thin MgO(100) films. As a model defect, we consider a neutral surface oxygen vacancy (F\textsubscript{s}). Optimal adsorption geometries and energies, cluster formation energies and cluster charges are discussed and compared in detail over four different substrates. For a given cluster size, the adsorption energy among these substrates increases in the order MgO, F\textsubscript{s}/MgO, MgO/Mo and F\textsubscript{s}/MgO/Mo. While cluster growth by association of atoms from gas phase is exothermic on all the substrates, cluster growth by diffusion and aggregation of pre-adsorbed Au atoms is an endothermic process for Au\textsubscript{1} \rightarrow Au\textsubscript{2}, Au\textsubscript{3} \rightarrow Au\textsubscript{4} and Au\textsubscript{5} \rightarrow Au\textsubscript{6} on MgO/Mo and Au\textsubscript{2} \rightarrow Au\textsubscript{3} and Au\textsubscript{5} \rightarrow Au\textsubscript{6} on F\textsubscript{s}/MgO/Mo. The adsorbed clusters are close to neutral on MgO, but adopt a significant anionic charge on other supports with the increasing order: MgO/Mo, F\textsubscript{s}/MgO and F\textsubscript{s}/MgO/Mo. The adsorption strength thus correlates with the amount of negative charge transferred from the substrate to gold.
1. Introduction

For a number of years metal-oxide interfaces have received intensive, both experimental and theoretical, attention due to their role in applications for catalysis, protective coatings and thermal and electric insulators [1, 2]. In particular, size-controlled, oxide-supported metal clusters and nanoparticles have a wide unexplored range of physical and chemical properties and a high potential for chemical, photo-chemical and catalytic applications. Understanding the rich interplay between diverse chemical properties of different-sized particles, variations in the particle-support interactions, ensemble effects and the possible direct activity of the support is a challenging task but in principle it allows tuning of the various factors in order to optimize a ‘nanocatalytic’ process regarding selectivity, sensitivity and turn-over for the desired product channel.

In contrast to bulk-Au [3], nanosized gold particles on various oxide materials have been observed to exhibit an enhanced catalytic activity for several reactions [4]–[7], such as propylene epoxidation [8, 9], hydrogenation of unsaturated hydrocarbons ([10] and references therin), water–gas shift reaction [11] and CO oxidation [12]–[15]. Recently it was found that supported ultra-thin Au films have high activity towards CO oxidation, comparable to the activity of supported Au clusters [16]. The most reactive Au nanoparticles have a diameter of a couple of nanometres [17] but also tiny Au clusters containing only a few Au atoms show catalytic activity towards CO oxidation [18]. Catalytic properties of Au clusters over oxide surfaces are believed to depend on several different factors like charge transfer [19, 20], structural effects [16] and support effects [21], just to mention a few.

Nanosize [22] and tiny [18]–[20] Au clusters on MgO show activity towards CO oxidation and thin (1–5 ML) MgO films, grown on Mo(100) [23] and Ag (100) [24] surfaces, are commonly used to make templates to study the properties of the smallest Au clusters. Recently, small Au clusters on single crystal MgO surfaces have been studied extensively using density functional theory (DFT) calculations [25]–[28]. With increasing computer power it has become possible to construct a model system for a Au atom or cluster on a thin MgO film supported by transition metal, which mimics the situation in experiments where thin films are used [29]–[33].
By means of DFT calculations, it has been shown that Au binding on regular ultra-thin Mo and Ag supported MgO films is stronger than on single crystal MgO [29, 31]. The increased binding is suggested to be due to enhanced charging of gold by direct tunnelling of electrons from Mo/Ag to Au through the ultra-thin oxide film [29]. Honkala and Häkkinen [34] also show an increased Au binding on a Mo supported MgO film compared to single crystal MgO. A Au atom binding and charge state have been recently explored experimentally and theoretically also on Cu-supported insulating ultra-thin NaCl films [35]. Extensive DFT calculations have been performed on Au\textsubscript{8}, Au\textsubscript{16} and Au\textsubscript{20} over a Mo supported regular ultra-thin MgO film [32]. The results show that Mo enhances Au bonding to MgO and induces accumulation of excess electrons to the Au–MgO interfaces, which causes the Au clusters to favour planar geometries instead of the three-dimensional (3D) ones. A very recent experimental work seems to confirm this prediction [36]. The first theoretical results concerning CO oxidation on MgO/Mo supported Au clusters are given in [37]. The reaction barrier was found to be low via both Langmuir–Hinshelwood and Eley–Rideal mechanisms on the edges of a flat Au\textsubscript{20} cluster due to the excess charge on a Au/MgO interface.

Oxide films and surfaces are seldom perfect. Depending on preparation conditions various defects may appear: steps, kinks, adatoms and vacancies [38]. Recent experimental and theoretical studies show that Au atoms and clusters bind strongly to an oxygen vacancy [18]–[20], [23, 28, 34, 39], which acts as a nucleation site for cluster growth. An oxygen vacancy can be present at terraces, steps and corners and it can exist in three different charge states: 0, +1, +2 [23, 40]. Scanning tunneling microscopy (STM) images show that oxygen vacancies are mainly located at the edges and corners of MgO [23]. To our knowledge no theoretical work exists, where the adsorption of a Au cluster on an oxygen vacancy over a Mo supported MgO terrace has been studied.

In experiments, clusters can be deposited on a surface essentially in two different ways. In the soft landing method [41] clusters are size selected by means of ion optics in the gas phase and then landed on the surface with low kinetic energies of 1 eV atom\textsuperscript{−1} at maximum. Thus, the clusters do not fragment in the collision to the surface. With the appropriate density of surface defects as trapping sites, where the clusters migrate on the surface, it is possible to deposit isolated size selected clusters on the surface. The second method is the growing of the clusters on the surface via diffusion processes [41]. In this method, the atoms are deposited from gas phase and the first step in the formation of a cluster is the trapping of a single atom to a favourable nucleation site on the surface. Then the clusters grow as more diffusing atoms associate to them. The first steps of these surface growth processes have been studied theoretically in many nucleation sites of MgO for Au in [42, 43]. As far as we know, no predictions for cluster growth on ultra thin MgO/Mo is available in the literature.

In this work, we have applied DFT calculations to study the adsorption of small Au\textsubscript{n} (n =1–6) clusters on defected MgO(100) single crystal and Mo(100) supported thin MgO(100) film terraces and compared the results to our previous study concerning adsorption on regular MgO and MgO/Mo surfaces [44]. Although there are several theoretical works on the adsorption of Au clusters on MgO single crystals [25]–[28], the first systematic comparison between all the cluster sizes up to 10 atoms on both regular and defected MgO was presented only very recently [45]. For MgO/Mo, our study is the very first study where the Au clusters ranging from 2 to 6 atoms have been addressed, both for regular and defected surfaces. First, we present some results concerning gas-phase clusters for reference to the supported clusters and continue by summarizing our previous results for the adsorbed clusters on regular MgO and
MgO/Mo. Then, we discuss the results of adsorption on vacancy sites over MgO and MgO/Mo surfaces, and finally compare the results between all the studied supports and gas phase to reveal the role of Mo below the oxide in Au cluster adsorption energies, geometries and charge transfer. We find that the Mo support plays a role defining the adsorption characteristics of Au clusters. The results show that the optimal geometry, adsorption energy, charge state and cluster growth processes are different at an O vacancy on MgO and MgO/Mo.

The paper is organized as follows. In the next section, we describe the computational details and after that discuss briefly the calculations on gas-phase clusters. Then, we focus on the energetic and geometrical properties of Au$_n$ ($n = 2$–$6$) clusters at an oxygen vacancy ($F_s$) on MgO(100) and MgO(100)/Mo(100) supports. At the end, the results of the Bader charges and density difference analyses are given to address how charges redistribute on supported clusters.

2. Computational method and systems

The DFT calculations were carried out with the Dacapo code (http://dcwww.fysik.dtu.dk/software/) using the RPBE (revised Perdew–Burke–Erzerhof) GGA (generalized gradient approximation) functional [46]. In addition, some non-self-consistent PW91 (Perdew–Wang 91) GGA [47] values are given for literature comparison. The MgO(100) film supported by Mo(100) was modelled with a 3 atomic-layer-thick slab and a (3 $\times$ 3) surface unit cell, see figure 1. For selected larger Au clusters, a p(4 $\times$ 3) unit cell was employed. The vacuum region between adjacent slabs was at least 14 Å. The Mo atoms were aligned with the O anions of the MgO as this is shown to be the optimal interface structure in [48]. The calculational lattice parameters for Mo and MgO are $a_{\text{Mo}} = 3.19$ Å and $a_{\text{MgO}} = 4.30$ Å, respectively. For single crystal MgO, the calculational lattice parameter was used, for MgO/Mo the interface was adjusted to the lattice parameter of Mo, causing 4.9 % tensile strain to MgO, increasing the lattice parameter to 4.51 Å as indicated in figure 1. It was checked that the strain is not behind the stronger adsorption on MgO/Mo. A more detailed description of the computational set-up can be found from [34, 44]. We mostly used a spin unpolarized approach as it was found that on the MgO (MgO/Mo) support the adsorption energies of Au$_1$ and Au$_3$ change only by 0.02 eV (0.01 eV) and 0.01 eV (0.05 eV) when spin polarization was included. The formation energy of Au$_3$ on MgO increases by 0.08 eV atom$^{-1}$ when calculated spin polarized. This is in agreement with the recent findings in [45] which show that on MgO and $F_s$/MgO the total energies of the
Au adsorption systems depend on spin polarization only by 0.05–0.10 eV. Some calculations were done spin-polarized for comparison, and we always mention when a spin-polarized result is given in the text.

The adsorption energies ($E_{\text{ads}}$) of the clusters were calculated according to

$$E_{\text{ads}}(n) = E(\text{Au}_n/\text{sup}) - E(\text{Au}_n) - E(\text{sup}),$$

(1)

where $\text{sup} = \text{support}$, $E(\text{Au}_n/\text{sup})$ is the total energy of the adsorption system, $E(\text{Au}_n)$ is the energy of the most stable gas-phase cluster and $E(\text{sup})$ is the energy of the bare, relaxed support.

To estimate the cluster growth on the surface, we calculated cluster association energies to form an $n$-atom cluster from a single atom at the optimal site and an ($n-1$)-atom cluster according to

$$E_{\text{as}}(n) = E(\text{Au}_n/\text{sup}) + E(\text{sup}) - E(\text{Au}_1/\text{sup}) - E(\text{Au}_{n-1}/\text{sup}).$$

(2)

To analyse atomic charges, we employed the Bader approach [49] to partition electrons to atoms. It is a very natural way to share the electrons between the nuclei as the method includes the possible atom polarization. The recently developed fast implementation of the approach has made the Bader analysis a suitable tool for large systems calculated with DFT and plane waves [50]. We tested the reliability of the method with bulk MgO. An average charge on Mg (O) was obtained to be $+1.7e$ ($-1.7e$) in good agreement with previous results [51] and the fact that MgO bulk forms an ion lattice with nominal charges of $+2.0e$ (Mg) and $-2.0e$ (O).

To get more detailed insight into the charge redistributions, density difference analysis was carried out. The density difference was calculated as

$$n(r)_{\text{dif}} = n(r)_{\text{Au}_n/\text{sup}} - n(r)_{\text{Au}_n} - n(r)_{\text{sup}},$$

(3)

where $n(r)_{\text{Au}_n/\text{sup}}$ is the electron density of the total system, $n(r)_{\text{Au}_n}$ and $n(r)_{\text{sup}}$ are electron densities of the frozen cluster without the support and of the bare support, respectively.

3. Neutral and anionic gas-phase Au clusters

The optimal gas-phase cluster configurations were adopted directly from [52] and re-relaxed with our calculational set-up. No further search to find possible new optimal geometries was done. In agreement with [52], we found that anionic clusters have on average 2.4% longer bond lengths than the neutral ones, if the geometries are similar. Figure 2(a) gives the best geometries of neutral and anionic clusters together with their gas-phase formation energies per atom. The energies of the anionic clusters are lower than those of neutral ones since the gold clusters have high electron affinity. Although our calculational set-up differs from that in [52], the trends of the neutral cluster formation energies are similar.

4. Supported Au clusters

The adsorption of Au$_n$, $n = 1–6$, was studied on two supports: single crystal MgO(100) and an ultra-thin MgO(100) film on Mo(100). We investigated the adsorption on a neutral oxygen vacancy ($F_s$) and compared the results to our previous study on regular MgO(100) and MgO(100)/Mo(100) surfaces [44]. The initial supported cluster geometries were mainly adopted from [19, 27, 45] and from 3 to 6 isomers per cluster size were optimized to find the energetically most favourable configurations. We are aware of a possibility that we have not found the energetically best isomers for some of the 24 adsorbate/support systems.
Figure 2. Energetically the best gas-phase and supported clusters together with the selected higher energy isomers. For each supported cluster top (left) and side (right) views are shown. In panel (a), we give the formation energies per atom in electron volts and in panels (b)–(e) adsorption energies in electron volts are shown. Red: O, blue: Mg and yellow: Au. In (d) and (e) the Au atoms in contact with $F_s$ are green.
Table 1. Selected bond lengths (in Å) of the energetically best cluster geometries averaged over the cluster sizes in the studied systems. The Au–Au bonds are intracluster bonds and Au–MgO is defined as the shortest distance between the cluster atom and the averaged z-coordinate of the top most MgO layer atoms.

| Bond    | Regular surface | Surface with O vacancy |
|---------|-----------------|------------------------|
|         | MgO  | MgO/Mo | MgO     | MgO/Mo |
| Au–Au   | 2.69 | 2.72   | 2.80    | 2.79   |
| Au–Mg   | 3.12 | 2.97   | 2.76    | 2.73   |
| Au–O    | 2.24 | 2.95   | 3.46    | 3.49   |
| Au–MgO  | 2.32 | 2.65   | 1.64    | 1.24   |

However, we believe that this does not prevent us from capturing the general trends in adsorption properties.

The results are presented as follows. We start with a brief discussion of the average bond lengths on each support. Then we summarize the general trends concerning adsorption on regular MgO and MgO/Mo surfaces and after that the results on cluster adsorption at an oxygen vacancy are presented.

The average distances between the oxide and a Au atom in a cluster closest to the support and intracluster Au bond lengths are summarized in table 1. At \( F_5 / \text{MgO} \) the averaged Au–Au bond lengths are longer than on the regular surface and a Mo support changes only slightly the Au–Au distance compared to the single crystal case. Mo below the oxide decreases the cluster-support distance on average by 0.4 Å meaning that the cluster lands deeper into the vacancy. The MgO–Mo distance was found to be 2.2 Å independent of the cluster size or the presence of the vacancy.

Adsorption energies of the most stable clusters as a function of the cluster size both on MgO(100) and MgO(100)/Mo(100) supports are shown in figure 3. The plot shows two main features. The increase, i.e. the more negative value, in \( E_{ads} \) adsorption energy due to (i) the oxygen vacancy and (ii) the Mo support. The latter is seen both on regular and defected surfaces. Additionally, we note that the Au clusters with the odd number of atoms bind more strongly on regular MgO/Mo than even clusters. The odd–even oscillations in adsorption energies are not seen on unsupported MgO or on defected surfaces.

4.1. Au clusters on MgO(100) and MgO(100)/Mo(100)

The optimal cluster geometries on regular MgO and MgO/Mo have already been discussed in detail in [44], and thus we give here only a brief summary. However, in this study we found a new geometry for Au\(_5\)/MgO, which is 0.14 eV lower in energy than the best isomer given in [44], and for Au\(_2\)/MgO/Mo, a new quasi-degenerate isomer, which is not given in [44]. These findings do not significantly change the trends in the energetics found in our previous work.

On MgO(100), the cluster geometries resemble the neutral planar gas-phase geometries (see figure 2(b)). The clusters are oriented perpendicularly to the surface having one to three atoms of the cluster rim in contact with the surface oxygen anions, similarly to single Au atom. The adsorption is relatively weak and adsorption energies range from −0.7 to −1.4 eV.
In general, the Au\textsubscript{n}–MgO interaction is considered as weak, and to be polarization type [53, 54]. Our results qualitatively agree with the earlier studies [26, 29, 42, 45, 55, 56] although, in some cases, geometries obtained in this work slightly differ from those reported in the literature, and the energies depend on the chosen GGA, but still the trends are similar.

On MgO/Mo, the situation is different: the clusters tend to wet the surface and their geometries (figure 2(c)) are similar to those of anionic gas-phase clusters. This is reasonable as the clusters are negatively charged on average by one electron on MgO/Mo [44]. The interaction with the support is strong and stretches Au–Au distances as a Au atom prefers to adsorb on the four-fold hollow site [34]. The adsorption energy shows odd-even oscillations in the range of −1.2 to −2.8 eV with local maxima at \( n = 1, 3 \) and 5. The oscillations fully correlate to the electron affinity of the gas-phase gold clusters due to the charging effects, but are insensitive to the cluster geometries. An O-top adsorbed upright dimer makes an exception to the above described general trend (see, figure 2(c)) being energetically degenerate with the flat isomer. We will discuss the behaviour of the dimer later in the paper in the light of the Bader analysis.

### 4.2. The adsorption of clusters on an oxygen vacancy

In the coming sections, we will discuss the best geometry candidates, given in figures 2(d) and (e), for various cluster sizes at an oxygen vacancy both on MgO(100) and MgO(100)/Mo(100) surfaces.

#### 4.2.1. The dimer

Three different initial configurations of a dimer were optimized on single crystal \( F_s/MgO \). The energetically most stable configuration, given in figure 2(d), has adsorption energy −3.17 eV, tilting angle of 56 degrees (towards Mg) and the bond length 2.75 Å, which is 0.1 Å longer than found for the dimer on a regular surface. The same geometry was also found to be the best in [42] with the tilting angle and bond length close to ours. However, the adsorption energy (PW91) differs by 1.0 eV from our value. On the other hand,

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**Figure 3.** The adsorption energies of the most stable clusters as a function of cluster size.
in [45] a PW91 adsorption energy of \(-3.76\) eV is given for a similar geometry, which is in full agreement with our non-self-consistent PW91 value \(-3.75\) eV. Rather different geometrical properties are reported in [55] but there the computational set-up is somewhat different to ours with, for example, an embedded cluster approach to model a MgO(100) surface. Also on \(F_s/MgO/Mo\), the tilted dimer is the most stable configuration (figure 2(e)) but adsorption is 0.30 eV stronger than on \(F_s/MgO\) and the tilting is now toward the O atom.

4.2.2. The trimer. Also for a trimer three different initial configurations were studied on \(F_s/MgO\). The configuration similar to the gas-phase geometry (figure 2(a)) has the strongest adsorption, \(E_{\text{ads}} = -3.62\) eV, but the only difference to the second best structure is the different orientation of the cluster on the surface, see figure 2(d). The adsorption energies of the similar trimer structures found from literature [28, 42, 45, 57] are 0.3 – 0.9 eV lower in energy compared to the numbers given here, which is again mainly due to the different flavour of the applied GGA. For example, in [45] a PW91 adsorption energy of \(-4.09\) eV is given, which is very near to our non-self-consistent PW91 value \(-4.18\) eV.

On \(F_s/MgO/Mo\), the triangular geometry (figure 2(e)) is the most stable one, while a linear upright structure is 0.7 eV higher in energy. The presence of Mo strengthens the adsorption by 0.53 eV compared to the adsorption on \(F_s/MgO\).

4.2.3. The tetramer. Three geometries: a tilted planar flake in two different orientations and a 3D tetrahedral \(Au_4\) were optimized on \(F_s/MgO\). Clearly, the planar structure (figure 2(d)) with the adsorption energy of \(-3.58\) eV, is energetically the most favourable one with binding of 1.17 eV stronger than the tetrahedral one (figure 2(d)). The planar cluster has a similar structure to the gas-phase rhombus (figure 2(a)), although the bond lengths differ from those of the neutral gas-phase geometry. The identical cluster geometries are given in [19, 28, 45] but with somewhat stronger binding to the surface than found in this work. For a similar isomer [45] gives a PW91 adsorption energy \(-4.32\) eV, while our non-self-consistent PW91 value is \(-4.18\) eV.

The same three initial geometries were also tested on \(F_s/MgO/Mo\) and additionally the ‘Y’-form structure, which was found to be the most stable on the regular MgO/Mo. The flake form (figure 2(e)) binds again most strongly on the substrate, while the tetrahedral one has 0.52 eV weaker adsorption. For the studied structures, the presence of Mo decreases the difference in adsorption energies compared to the single crystal case and strengthens adsorption, but the average Au–Au bond length remains constant. The ‘Y’ structure is 0.43 eV higher in energy than the flake geometry and the structure opens considerably compared to the regular surface.

4.2.4. The pentamer. We relaxed four different pentamer cluster configurations on \(F_s/MgO\). Figure 2(d) shows the best structure, which has adsorption energy \(-3.13\) eV and a planar structure, somewhat disturbed by the vacancy, but still similar to the optimal gas-phase cluster, given in figure 2(a). The bond lengths in the adsorbed cluster are on average slightly longer than in the neutral gas-phase cluster but shorter than found for the anionic gas-phase cluster. A similar geometry is given in [45] with PW91 adsorption energy \(-3.90\) eV close to our non-self-consistent PW91 value \(-3.95\) eV.

On \(F_s/MgO/Mo\), six initial pentamer configurations were optimized. A structure similar to the gas-phase one (figure 2(a)) was initially placed in three different upright orientations and in two different lying-down positions. In addition, a pyramidal 3D cluster was investigated.
It was found that the lying-down, flat configurations adsorb about 0.23 eV stronger than the best upright geometry. The two flat configurations differ from each other by their rotational orientation with respect to the surface atoms, and they are energetically degenerate. However, surprisingly the 3D geometry (figure 2(e)) binds 0.6 eV stronger than the best planar geometry (figure 2(e)). In general, all the other best geometries in this study are planar regardless of an adsorption site and a substrate, but the 3D pentamer on \( F_s/\text{MgO/Mo} \) is an exception.

4.2.5. The hexamer. Three initial geometries, a \( \text{Au}_6 \) triangle similar to the gas-phase cluster (figure 2(a)) in two different orientations, and the octahedral geometry were optimized both at \( F_s/\text{MgO} \) and \( F_s/\text{MgO/Mo} \). On single crystal MgO, the triangular structure with one atom in contact with the surface (figure 2(d)) binds 0.56 eV stronger than the 3D octahedron (figure 2(d)). Note that the adsorption of the octahedral geometry is now exothermic, whereas on the regular surface it is endothermic. The average bond length in the vacancy-adsorbed triangle increases slightly compared to the \( \text{Au}_6 \) on the regular surface or in the gas-phase.

Surprisingly, despite the fact that in [45] a triangle with three atoms in contact with the surface is found to be the best structure on \( F_s/\text{MgO} \) with PW91 GGA, we found that it is unstable with RPBE GGA. The same feature was also found on regular MgO, where we checked that the choice of GGA really changes the optimal geometry. However, the choice of GGA does not change the geometries of smaller clusters as dramatically, which can be seen by comparing our RPBE geometries to the structures given in [28, 42, 45, 57].

On \( F_s/\text{MgO/Mo} \), the octahedron geometry (figure 2(e)) is 0.39 eV lower in energy than the triangular geometry with one atom in contact with the surface, namely with the vacancy. On the other hand, a deformed triangle with three atoms on the surface is 0.32 eV lower in energy than the octahedron. In addition, we found that a flat, lying-down triangle with one apex in the vacancy (figure 2(e)) is 0.07 eV lower in energy than the other three isomers. The triangular geometry has the longest average bond length, 2.82 Å, which is longer than found for \( \text{Au}_6 \) on other substrates or in the gas-phase.

4.3. Formation of the clusters

In experiments, clusters are often formed on a surface via a single atom diffusion, where a surface is first exposed to a beam of gas-phase atoms, which adsorb to a surface, and then diffuse to appropriate nucleation sites, like \( F_s \). The clusters grow as more and more atoms diffuse and associate to an atom at the nucleation site. Thus, two important quantities governing the formation of clusters can be distinguished: (i) adsorption energy to a nucleation site and (ii) single atom association energy from a support to an adsorbed cluster. We have calculated the association energies of gold atoms from the surface (surface association energy) to MgO and MgO/Mo adsorbed clusters both on the colour centre and the regular site.

Table 2 together with figures 4 and 5 summarize the surface association energies determined according to equation (2). We see that the presence of Mo induces changes in association energies both on regular and defected surfaces compared with the values calculated on a single crystal surface. The results show how much energy changes if a single gold atom from a surface is added to an adsorbed cluster and show whether the growth atom by atom is an exothermic (negative value) or endothermic (positive value) process.

On a regular MgO surface, the association to a dimer is preferred by 2.0 eV to the adsorption of two Au atoms at the O-top sites, which agrees with earlier findings [42, 56].

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Table 2. The association energy (in eV) of a single gold atom from a terrace to a cluster \( \text{Au}_{n} \) on terrace and vacancy sites.

| Format of \( \text{Au}_{n} \) | Terrace site | O vacancy |
|-----------------------------|--------------|-----------|
|                             | \( \text{MgO} \) | \( \text{MgO/Mo} \) | \( \text{MgO} \) | \( \text{MgO/Mo} \) |
| 2                           | \(-2.01\)     | 0.52      | \(-2.22\)     | \(-0.79\)      |
| 3                           | \(-0.39\)     | \(-0.55\) | \(-0.80\)     | 0.30           |
| 4                           | \(-1.74\)     | 0.68      | \(-1.63\)     | \(-0.38\)      |
| 5                           | \(-0.78\)     | \(-0.35\) | \(-0.85\)     | \(-0.37\)      |
| 6                           | \(-1.91\)     | 0.15      | \(-1.44\)     | 0.39           |

Figure 4. The association energy of one Au atom from the surface to a cluster on the regular surface.

On \( \text{MgO/Mo} \), a dimer formation is not favoured, but is endothermic by 0.52 eV. On \( \text{Fs/MgO} \), the dimer formation from one atom in a vacancy and the other one at the O-top site is highly favourable and the process is exothermic by \(-2.22\) eV in agreement with the value reported in [56]. The authors of [42] give 0.2 eV lower and [28] 0.35 eV higher association energy than ours. The differences are most probably due to the different choices for GGA functional and other simulation parameters. Despite the small differences in numerical values, all the results unambiguously show that the vacancy increases the exothermic nature of dimerization on single crystal \( \text{MgO} \). For \( \text{Fs/MgO/Mo} \) substrate, the dimerization energy is only \(-0.79\) eV but still the reaction is exothermic in contrast to regular \( \text{MgO/Mo} \).

From figure (4), we see that the trimer formation is slightly exothermic on \( \text{MgO} \): the energy gain calculated with respect to associating an isolated-terrace Au atom to the adsorbed dimer is \(-0.39\) eV, whereas on \( \text{MgO/Mo} \) it is slightly larger. On \( \text{Fs/MgO} \), the trimer formation from an adsorbed Au atom and a vacancy-adsorbed dimer is favoured by 0.8 eV, which is close to values \( 0.99 \) and \( 0.75 \) eV given in [42] and [28], respectively. Thus, on the single crystal surface also the trimer formation is stabilized by the vacancy whereas on \( \text{Fs/MgO/Mo} \) it is endothermic.
Figure 5. The association energy of one Au atom from the surface to a cluster in the O vacancy.

by 0.3 eV. This implies that not only on a regular but also on a defected surface cluster growth processes may depend on the presence of Mo, and the vacancy is not always able to stabilise the growth on MgO/Mo at UHV (ultra high vacuum) conditions.

In general, on MgO the growth is always exothermic and thus thermodynamically favourable (figure 4). Clearly, there exist even–odd oscillations in the association energy as a function of cluster size. This is due to the even–odd oscillations in the single gold atom adsorption energies to an adsorbed cluster while the reference adsorption energy to a surface stays constant, $E_{\text{ads}} = -0.66$ eV. In agreement with the earlier studies [58], similar oscillations are also seen for neutral gas-phase clusters (figure 6). This implies that the clusters with even number of atoms are more stable on MgO or in gas phase than the odd-atom clusters. This can be rationalized as follows: even-atom Au clusters have a singlet electronic ground state while in odd-atom clusters electrons form a doublet state. Electron pairing via association of a new atom stabilizes the cluster and thus leads to increased association energies.

On MgO/Mo, the situation is clearly somewhat different as shown in figure 4. First, the phase of the oscillations shifts. Second, as the single atom adsorption energy to the support is strengthened by 1.33 eV due to high electron affinity of Au atom and the extra charge originating from the metal [44], the association energies shift to more positive values i.e. to a more endothermic direction. In other words, the Mo makes a single Au very stable species and the surface association more difficult. In addition, as the adsorption energies of the clusters on regular MgO/Mo correlate to the electron affinities of the gas-phase clusters [44], the association energies correlate to the electron affinity, and show oscillations. From these facts, it follows that Au association on a surface to an odd-atom cluster becomes endothermic and thus thermodynamically unfavourable.

The similar phase shift in association energy oscillations is also seen for the formation of neutral and anionic gas-phase clusters (figure 6) [58]. The oscillation phenomena on MgO/Mo is related to the anionicity of the clusters. As the cluster gains an extra electron from the support, the HOMO of a cluster with an odd number of atoms is paired and a singlet state is formed.
The association energies of a neutral gas-phase Au atom to neutral and anionic gas-phase clusters. This was checked by the analysis of spin polarized local density of states for Au$_3$/MgO/Mo. The odd–even oscillations are seen for vacancy-adsorbed clusters on MgO or MgO/Mo but the phase shift effect is absent (figure 5). This indicates that although the cluster is charged both on an oxygen vacancy of MgO and on regular MgO/Mo the resulting ground state is different, which is also supported by the Bader analysis discussed later. Note that the exception seen in oscillations on F$_5$/MgO/Mo is due to the higher stability of Au$_5$, see figure 3, the lowest curve.

Overall this implies that the cluster growth process via single atom surface diffusion may be different on MgO/Mo than on MgO and on regular and defected surfaces. To get a more realistic model of the processes one should also calculate diffusion barriers. Our results show, in agreement with the previous studies [28, 42, 45, 56, 57], that on a single crystal MgO, cluster growth atom by atom is always favourable.

5. Bader charge analysis

Cluster charge and charge accumulation at a cluster–support interface are believed to affect the catalytic properties of the supported gold clusters [18]–[20]. Therefore, we performed the Bader analysis to obtain quantitative information about the adsorption-induced charge transfer to a cluster. Particularly, we focus on the cluster charges on F$_n$/MgO and F$_n$/MgO/Mo systems and the effect of Mo. In addition, we performed a density difference analysis to get more detailed insight into a possible polarization of the oxide. The obtained results are compared to our previous results on Au-cluster adsorption on regular MgO and MgO/Mo surfaces in [44].

Figure 7 presents cluster Bader charges as a function of cluster size in four cases. The curves show that, both on regular and defected substrates, Mo enhances charge transfer to a cluster compared with single crystal MgO. In general, cluster charge is almost independent of the number of atoms in a cluster. Two exceptions were found: first, a Au atom at a vacancy on MgO and MgO/Mo is less charged than dimer and larger clusters. This is due to the filling of
Figure 7. The cluster charge as a function of cluster size.

A 6s state of the atom and can be seen in the local density of states, in [34], where the 6s state of a Au atom adsorbed on $F_s$ lies entirely below the Fermi level. For a regular surface, the shift is shown in [29, 59]. Thus, a Au atom is able to accommodate at most one electron, no matter that there are more available from the vacancy or Mo metal. Second, at $F_s$/MgO/Mo the cluster charge increases and oscillates slightly as a function of cluster size.

As the total charge transfer is independent of the cluster size, the numbers given below are averaged over all cluster sizes, the only exception is $F_s$/MgO/Mo, where clear cluster size dependence exists (see figure 7).

A cluster gains an average 0.39e on regular MgO and is slightly polarized so that Au atoms further away from the oxide are more negative than those close to the substrate. The charge comes from the topmost oxide layer. The weak polarization bonding to the MgO support was previously reported in [53, 54].

On regular MgO/Mo, on average 1.0e transfers to the cluster and most of the charge is located in the atoms in contact with the surface. A more detailed analysis reveals that the charge distribution of individual Au atoms is not homogeneous but resembles that of anionic gas-phase clusters [44]. Note that, we have found two energetically degenerate configurations for the dimer (figure 2(b)). These configurations correspond to two different charge states. The ‘upright’ dimer is slightly negatively charged (0.4e) whereas the ‘lying-down’ one is strongly anionic (0.9e). A similar correlation between charge and the local adsorbed structure has been previously seen for Au/NaCl/Cu [35].

At the vacancy on MgO, the cluster obtains 1.72e. This is essentially equal to the Mg → O charge transfer calculated for bulk MgO implying that the cluster basically gets all the charge available at the vacancy. More detailed analysis shows that on average 1.10e is localised to a Au atom in contact with the vacancy while the rest is dispersed inhomogeneously to the other cluster atoms. Typically the corner atoms of the cluster are more negative than the central ones, qualitatively in a similar manner to the gas-phase anionic clusters and the clusters on regular MgO/Mo [44].
Figure 8. A top view of a density difference plot of Au\(_2\) adsorption. Red (blue) colour indicates charge accumulation (depletion). The cut plane is chosen according to the average MgO plane.

At \(F_s/\text{MgO}/\text{Mo}\) the cluster charges increase compared to \(F_s/\text{MgO}\) and depends on the cluster size (figure 7). The Au atom obtains least extra charge: only \(-1.09e\) while \(\text{Au}_6\) obtains most: \(-2.48e\). Also at \(F_s/\text{MgO}/\text{Mo}\) the atom at the vacancy has the highest charge among the all cluster atoms while the others are inhomogeneously charged.

6. Density difference analysis

The density difference plots, determined according to equation (3), provide a visual insight into the charge redistribution in the studied systems. Next, we consider only a Au dimer, but in general similar features are also seen for larger clusters.

Figures 8(a) and 9(a) support the picture of the weak polarization interaction between Au and MgO [53, 54] since only minor charge redistribution is seen. From two energetically degenerate configurations on regular MgO/Mo, the lying-down configuration is chosen for the density difference analysis. As seen from figure 8(b), the dimer induces a quite wide and delocalized charge depletion region at the Au/surface interface. The neighbouring O ions are remarkably polarized leading to a polarization effect that ranges through the oxide having influence even to the Mo atoms (figure 9(b)). In the topmost Mo layer, the atoms lose charge from their d-like states. Note that this is not very well seen in figure 9(b) due to the selection of the cut plane. The spatial pattern of the excess anionic charge has a local \(\sigma^*\)-symmetry on gold, see figure 9(b).

In the case of an oxygen vacancy, the situation looks very similar for both MgO (figures 8(c) and 9(c)) and MgO/Mo (figures 8(d) and 9(d)). The main charge depletion seems
Figure 9. A side view of a density difference plot from Au$_2$. Red (blue) regions indicate charge accumulation (depletion) upon dimer adsorption.

to be from the vacancy which supports the fact that the vacancy donates or shares its two electrons to/with the cluster. Again, some polarization pattern is seen in the support. However, the polarization of the oxide is almost absent in the case of $F_s$/MgO/Mo. The density difference plots support the results of the Bader analysis: On $F_s$/MgO, MgO/Mo and $F_s$/MgO a cluster gains charge from the support, while on regular MgO it does not. The extra charge originates from the vacancy and the Mo film.

7. Summary and conclusions

In this work, we have concentrated on the Au cluster adsorption on defected MgO(100) and MgO(100)/Mo(100) surfaces and the comparison of the results with those obtained by us earlier for the regular substrates [44].

For the defected MgO film, the role of the Mo support is less profound than for the regular one. The small clusters are not flat and there is no clear structural similarity to the anionic gas-phase clusters. On both $F_s$/MgO and $F_s$/MgO/Mo, clusters are charged, but like on a regular surface, Mo increases charging. The extra charge originates from $F_s$ and the Mo metal, and both on $F_s$/MgO and $F_s$/MgO/Mo, approximately one electron is located on the atom in contact with the vacancy, while the rest of the charge is dispersed inhomogeneously to the other cluster atoms. Similar to a regular surface, the adsorption is stronger on supported MgO. However, the adsorption energy difference induced by the metal does not oscillate and the polarization effect of the substrate is essentially absent.

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Our present results predict that the cluster growth is probably different on single crystal MgO and Mo-supported MgO films. On a regular surface site, Mo makes the growth of odd-atom clusters endothermic in contrast to single crystal MgO, where the growth is always exothermic. Interestingly, it was also found that despite the fact that, in general, the oxygen vacancy increases the cluster adsorption both on MgO and MgO/Mo some growth steps are endothermic also at $F_s$/MgO/Mo.

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References

[1] Heinrich V E and Cox P A 1994 The Surface Science of Metal Oxides (Cambridge: Cambridge University Press)
[2] Woodruff D P (ed) 2001 Oxide Surfaces: The Chemical Physics of Solid Surfaces vol 9 (Amsterdam: Elsevier)
[3] Hammer B and Nørskov J K 1995 Nature 376 238
[4] Bond C G and Thompson D T 1999 Catal. Rev. Sci. Eng. 41 319
[5] Meyer R, Lemire C, Shaikhutdinov S K and Freund H J 2004 Gold Bull. 27 72
[6] Hutchings G J and Haruta M 2005 Appl. Catal. A 291 1–261
[7] Thompson D T 2006 Top. Catal. 38 231
[8] Hayashi T, Tanaka K and Haruta M 1998 J. Catal. 178 566
[9] Sinha A K, Seelan S, Tsubota S and Haruta M 2004 Top. Catal. 29 95
[10] Haruta M 2002 Cattech 6 102
[11] Andreeva D 2002 Gold Bull. 35 82
[12] Haruta M 1997 Catal. Today 36 153
[13] Choudhary T V and Goodman D W 2002 Top. Catal. 21 25
[14] Bond G C and Thompson D T 2000 Gold Bull. 33 41
[15] Haruta M 2004 Gold Bull. 37 27
[16] Chen M S and Goodman D W 2004 Science 306 252
[17] Valden M, Lai X and Goodman D W 1998 Science 281 1647
[18] Sanchez A, Abbet S, Heiz U, Schneider W D, Häkkinen H, Barnett R N and Landman U 1999 J. Phys. Chem. A 103 9573
[19] Häkkinen H, Abbet S, Sanchez A, Heiz U and Landman U 2003 Angew. Chem. Int. Edn. 42 1297–1300
[20] Yoon B, Häkkinen H, Landman U, Worz A S, Antonietti J M, Abbet S, Judai K and Heiz U 2005 Science 307 403
[21] Arrii S, Morfin F, Renouprez A J and Rouset J L 2004 J. Am. Chem. Soc. 126 1199
[22] Grisel R J H and Nieuwenhuys B E 2001 J. Catal. 199 48
[23] Sterrer M, Fischbach E, Risse T and Freund H J 2005 Phys. Rev. Lett. 94 186101
[24] Schintke S, Messerli S, Pivetta M, Patthey F, Liboulle L, Stengel M, De Vita A and Schneider W D 2001 Phys. Rev. Lett. 87 276801
[25] Molina L M and Hammer B 2003 Phys. Rev. Lett. 90 206102
[26] Molina L M and Hammer B 2004 Phys. Rev. B 69 155424
[27] Molina L M and Hammer B 2005 J. Chem. Phys. 123 161104
[28] Barcaro G and Fortunelli A 2006 J. Phys. Chem. B 110 21021
[29] Pacchioni G, Giordano L and Baistrocchi M 2005 Phys. Rev. Lett. 94 226103

New Journal of Physics 9 (2007) 339 (http://www.njp.org/)
[30] Giordano L, Baistrocchi M and Pacchioni G 2005 Phys. Rev. B 72 115403
[31] Giordano L and Pacchioni G 2006 Phys. Chem. Chem. Phys. 8 3335
[32] Ricci D, Bongiorno A, Pacchioni G and Landman U 2006 Phys. Rev. Lett. 97 036106
[33] Walter M, Frondelius P, Honkala K and Häkkinen H 2007 Phys. Rev. Lett. 99 096102
[34] Honkala K and Häkkinen H 2007 J. Phys. Chem. C 111 4319–27
[35] Repp J, Meyer G, Olsson F E and Persson M 2004 Science 305 493
[36] Sterrer M, Risse T, Heyde M, Rust H P and Freund H J 2007 Phys. Rev. Lett. 111 6668–77
[37] Zhang C, Yoon B and Landman U 2007 J. Am. Chem. Soc. 129 2228–9
[38] Noguera C 1996 Physics and Chemistry at Oxide Surfaces (Cambridge: Cambridge University Press)
[39] Wahlström E, Lopez N, Schaub R, Thostrup P, Rønnau A, Africh C, Lægsgaard E, Nørskov J K and Besenbacher F 2003 Phys. Rev. Lett. 90 026101
[40] Sterrer M, Fischbach E, Heyde M, Nilius N, Rust H P, Risse T and Freund H J 2006 J. Phys. Chem. B 110 8665
[41] Abbet S, Judai K, Klinger L and Heiz U 2002 Pure Appl. Chem. 74 1527–35
[42] Del Vitto A, Pacchioni G, Delbecq F and Sautet P 2005 J. Phys. Chem. B 109 8040
[43] Giordano L and Pacchioni G 2005 Surf. Sci. 575 197–209
[44] Frondelius P, Häkkinen H and Honkala K 2007 Phys. Rev. B 76 073406
[45] Molina L and Alonso J 2007 J. Phys. Chem. C 111 6668–77
[46] Hammer B, Hansen L B and Nørskov J K 1999 Phys. Rev. B 59 7413
[47] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R and Singh D J 1992 Phys. Rev. B 46 6671
[48] Goniakowski J 1999 Phys. Rev. B 59 11047
[49] Bader R 1998 Atoms in Molecules (Oxford: Oxford University Press)
[50] Henkelman G, Arnaldsson A and Jónsson H 2006 Comput. Mater. Sci. 36 354
[51] Henkelman G, Uberuaga B P, Harris D J, Harding J H and Allan N L 2005 Phys. Rev. B 72 115437
[52] Häkkinen H and Landman U 2000 Phys. Rev. B 62 R2287
[53] Bogicevic A and Jennison D R 1999 Phys. Rev. Lett. 82 4050
[54] Yudanov I, Pacchioni G, Neyman K and Rösch N 1997 J. Phys. Chem. B 101 2786
[55] Walter M and Häkkinen H 2005 Phys. Rev. B 72 205440
[56] Bogicevic A and Jennison D R 2002 Surf. Sci. 515 L481–6
[57] Barcaro G and Fortunelli A 2005 J. Chem. Theor. Comput. 1 972
[58] de Heer W A 1993 Rev. Mod. Phys. 65 611
[59] Giordano L, Cinquini F and Pacchioni G 2005 Phys. Rev. B 73 045414