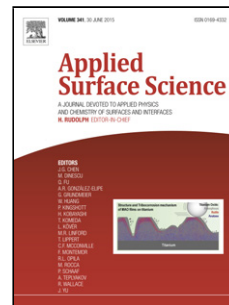


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**Density functional studies of small Au clusters adsorbed on α -FeOOH:
structural and electronic properties**

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Graphical Abstract

Highlight

- On the hydroxylated surface, the adsorption of Au clusters is relatively weak.
- Au-oxide interaction induces a polarization of the Au particles on the bare surface.
- A predominance of planar (111) arrangements was obtained on both surfaces.
- Comparing both surfaces, atom-by-atom nucleation energies show opposite behaviors.

Abstract

We report a density functional theory (DFT) investigation on the interaction of tiny Au_n (n = 1-5) clusters with the bare and hydroxylated (110) surfaces of goethite (α -FeOOH). Both adsorption and atom-by-atom nucleation processes were modeled. The adsorption is shown to be strong on the bare surface and takes place preferentially through the interaction of Au atoms with unsaturated surface oxygen anions, accompanied with an electronic charge transfer from the metal to the support. Au₃, Au₄ and Au₅ planar structures resulted to be particularly stable due to polarization effects; indeed, Coulombic repulsion between basal Au atoms and surface oxygen anions promotes the displacement of the electronic density toward terminal Au atoms producing a Au^{+ δ} (basal)/Au^{- δ} (terminal) polarization. On the hydroxylated surface, Au clusters adsorb more weakly with respect to the bare surface, mainly through monocoordinated surface hydroxyl groups and tricoordinated oxygen ions. Concerning the nucleation mechanism, while on the hydroxylated surface the nucleation energy is governed by the spin of the interacting systems, on the bare surface polarization effects seems to play a predominant role.

Keywords: Goethite, Adsorption, Density functional calculations, Polarization.

1. Introduction

Catalysts formed by gold supported on metal oxides in an extremely dispersed state exhibit a high activity for a wide range of chemical reactions [1,2]. It is known that their activity is very sensitive to the preparation conditions, although there is still no consensus about the actual active sites. Among the possible effects that can affect the catalytic activity, we can mention the size of the Au particles, the nature of the support material, the Au-support interface, metal-support charge transfer and the particle shape [3]. In an attempt to systematize the observations, it has been suggested some years ago [4] that metallic Au⁰ could be the main active species on “inert” supports such as Al₂O₃ and SiO₂; in this case, the catalytic activity is expected to have a direct dependence on the size of gold particles. Conversely, on “active” supports such as Fe₂O₃, NiO and CeO₂, both Au^{δ+} and Au⁰ could contribute to the catalytic performance. However, one type of dispersed Au-based catalysts can catalyze more efficiently a particular reaction than others. For instance, Deng *et al.* [5] reported that reduced gold clusters on ceria or iron oxide supports provide the active sites for the low temperature CO oxidation reaction, while fully dispersed oxidized gold species, strongly bound on these oxide supports, catalyze efficiently the water-gas shift (WGS) reaction.

A traditional way to study a metal-supported catalyst at a fundamental level is by designing model catalysts prepared in ultrahigh vacuum using vapor deposition and characterized by Surface Science techniques. Studies performed using these well-defined systems have demonstrated that the charge transfer between the support and the metal particles can determine their morphology and charge state. For example, in model systems formed by Au deposited on MgO supported on a metal transition (typically, Ag and Mo) one can control the charge transfer between the metal support and Au particles by varying the number of monolayers of MgO [6]. In this way, it is possible to design new catalytically active materials.

From the above-mentioned considerations, it is clear that acquiring a deep knowledge at a molecular level about the shape and charge states of small metal particles is of the major importance. Because of that, a large number of quantum-chemical studies have been performed demonstrating that they can be excellent complementary tools to the experimental information. In particular, for Au-based model catalysts, the growth process of small Au

particles supported on different oxides, their morphology and catalytic activity have been studied using the density functional theory (DFT) [7,8,9].

From the wide variety of Au-based catalysts, those supported on iron oxides are among the more catalytically active [1]. However, in catalysts operating in real conditions, iron oxide-based supports present a high degree of structural complexity and the corresponding structure depends on the preparation method. For instance, coprecipitation method leads to the formation of ferrihydrite, a structurally disordered material, and goethite, which after calcination transforms to hematite [10,11]. Using other methods and starting from iron hydroxide, firstly a mixture of magnetite (Fe_3O_4) and hematite is obtained after calcination, and at a higher temperature the magnetite transformed to $\gamma\text{-Fe}_2\text{O}_3$ [12]. However, in all the cases very active catalysts are obtained. Evidently, in order to study a model catalyst composed by dispersed Au aggregates on an iron oxide from a theoretical point of view, it is necessary to select one of the many varieties of this oxide. Goethite ($\alpha\text{-FeOOH}$) appears as an interesting option. It is the most common and most stable iron oxyhydroxides. Their surfaces present heterogeneity in terms of surface sites, with different types of hydroxyl groups and oxygen anions, which can be considered as possible sites for gold anchoring. Furthermore, the possible influence of surface hydroxyl groups appears as an interesting topic because it has been suggested that they can participate in the stabilization of supported metal particles [13]. It is interesting to mention that Au dispersed on different phases of FeOOH have been used as catalysts and molecular sensors [14,15,16,17]. Systems formed by Au supported on goethite have not been explored using quantum-chemical approaches up to now. The DFT approximation has proved to be a reliable technique to describe the interaction between Au particles and the surface of iron oxides. For example, it was found that adsorbed Au atoms acquire a negative charge on the iron-terminated surfaces of $\text{Fe}_3\text{O}_4(111)$, and a positive charge on the oxygen-terminated surfaces [18], the latter in agreement with experimental observations [19]. The chemical reactivity at the Au-iron oxide interface was also analyzed in the framework of DFT. For instance, a recent experimental study has shown that Au particles containing around ten atoms supported on iron oxide supports are very efficient to catalyze the CO oxidation [20]. Later DFT calculations have demonstrated that the dissociation of O_2 is energetically favorable at the interface between a model of Au_{10} particle and the $\alpha\text{-Fe}_2\text{O}_3(0001)$ surface, with two surface Fe cations and Au atoms taking part in the adsorption site [21]. The resulting O adatoms can react with CO to form CO_2 thus suggesting a plausible explanation of the high activity of these small Au particles.

In this work, we have investigated the adsorption and growth processes of tiny Au aggregates on two different (110) surfaces of goethite: a bare surface constructed by a direct truncation of the bulk structure, and a fully hydroxylated surface obtained by hydration of the first one. The main objectives is to identify preferred adsorption sites and geometries of deposited Au clusters, to explore the nature of the metal-support bonding, and to quantify adsorption and nucleation energies. Polarization effects present on the bare surface are analyzed with particular interest.

2. Computational details

The calculations were performed using the density functional theory (DFT) as implemented in the Vienna Ab-initio Simulation Package (VASP) [22,23,24]. In this code, the Kohn–Sham equations are solved using plane wave basis sets. Electron exchange and correlation effects are described by the generalized gradient approximation (GGA) using the functional developed by Perdew and Wang (PW91). A number of eight valence electrons for Fe atoms ($3d^74s^1$), six valence electrons for O atoms ($2s^22p^4$) and eleven valence electrons for Au atom ($5d^{10}6s^1$) were taken into account. The remaining (core) electrons together with the nuclei were described by pseudo-potentials in the framework of the projected augmented wave (PAW) method [25,26]. For H, the ultrasoft PAW potential was used.

The structure of bulk goethite can be described as a distorted hexagonal close packing of O and OH groups with iron ions occupying half of the octahedral interstitial holes. For magnetic materials such as FeOOH, where d electrons are strongly correlated, conventional DFT fails to predict the correct electronic ground state. A systematic study of several physical properties of bulk goethite was previously performed in our group by varying the value of the effective on-site repulsion term (U), through the so-called GGA+ U approximation [27]. A value of $U = 6.0$ eV gives better results for geometrical parameters, magnetic and elastic properties. The unit cell parameters of the optimized bulk were $a= 4.601$, $b=9.994$ and $c=3.035$ Å, with an antiferromagnetic (AFM) arrangement, where each Fe ion is surrounded by other two with opposite magnetic moments along the b -vector axis of the bulk cell.

In natural and synthetic goethite it was established that the dominant face is the (110) surface (referred space group Pbnm) [28]. In our model, it was constructed by a stoichiometric truncation of the bulk using a 1×4 supercell and containing four Fe layers (Figure 1). A vacuum gap in z -direction of approximately 15 Å was employed. After truncation, four Fe-O and four O-H bonds per supercell were broken. As a consequence,

unsaturated fivefold coordinated Fe surface are exposed, together with a row of oxygen ions linked in bridge position with sixfold coordinated Fe. We refer to this surface as the “bare” surface. Besides, a fully “hydroxylated” surface was modeled by saturating all the bonds of the bare one with OH and H (Figure 1). This hydroxylated surface presents singly coordinated (μ_1 -OH), doubly coordinated (μ_2 -OH), and three-fold coordinated (μ_3 -OH) hydroxyl groups.

The eight O ions of the bottom part of the supercell, formerly linked with Fe ions in the bulk structure, were saturated with H atoms in order to simulate the structure continuity. With these added H atoms the hydroxylated surface takes the FeOOH stoichiometry. During the optimization procedure, the O atoms belonging to these eight OH groups, the other eight (structural) OH located at the bottom of the slab, and the eight innermost Fe atoms were fixed at the bulk values. The rest of the atoms of the goethite surface and those of the adsorbed Au cluster were fully optimized without any restriction. The resulting geometries of the clean surfaces are very similar than those reported by Russell *et al.* [29] To model the Au_n supported particles, we have taken the optimized geometry of the Au_{n-1} cluster as a starting structure, then placing an additional Au atom in different positions. Apart from this criterion, other configurations were considered by simply varying the geometry of the adsorbed Au cluster. However, we do not exclude the existence of other minima on the potential energy surface.

Spin-polarized calculations were carried out for all the systems. The two-dimensional Brillouin integrations were performed using a (2×2×1) Monkhorst–Pack *k*-point grid. The self-consistent field was considered converged when the forces on atoms were smaller than 0.01 eV/Å. The fixed convergence of the plane wave expansion was obtained with a cut-off energy of 450 eV.

In the experimental design of model catalysts, metal clusters can be deposited on a surface essentially in two different ways [30]. In the soft landing method, clusters are firstly size selected by means of ion optics in the gas phase and then landed on the surface with a very low kinetic energy to prevent fragmentation. The second method is the growth of the metal particles on the surface via diffusion processes. Here, metal atoms are deposited from the gas phase and trapped on a favorable site on the surface. From these anchored atoms the clusters grow as more diffusing atoms associate to them. Taking into account these experimental procedures, we can define the following energetic parameters. The adsorption energy (E_{ads}) is defined as,

$$E_{\text{ads}} = E(\text{Au}_n/\text{surf}) - E(\text{surf}) - E(\text{Au}_n), \text{ with } n=1-5$$

where the $E(\text{Au}_n/\text{surf})$ is the total energy of the supported system, $E(\text{surf})$ the energy of the goethite surface, and $E(\text{Au}_n)$ is the most stable gas phase metal particle at the same level of calculation (nonlinear for the trimer, rhombic for the tetramer, and trapeze-shaped for the pentamer).

To model the cluster growth on the surface, the nucleation energy is defined as follows:

$$E_{\text{nuc1}} = E(\text{A}_n/\text{surf}) - E(\text{A}_{n-1}/\text{surf}) - E(\text{Au}), \text{ with } n=2-5$$

This energy is thus associated with an ideal atom-by-atom growth by adding sequentially Au atoms from the gas phase. Note that the defined adsorption energy is a parameter in direct relation with the physical process of the soft landing method. Conversely, the nucleation energy may be associated with the diffusion process mechanism, although for simplicity the atom diffusion is not explicitly calculated but the Au atoms are considered to come from the gas phase.

The atomic net charges were calculated according to the atoms in molecules approach of Bader [31]. The electronic structure has been studied through a topological analysis of the electron localization function (ELF) [32].

3. Results and discussion

3.1- Au adsorption on the bare and hydroxylated FeOOH(110) surfaces.

In Figure 2, the optimized structures of Au clusters supported on the bare surface are shown, and some selected results are presented in Table 1. As a starting point to model the different adsorbed Au particles, we have performed a detailed study of the preferential adsorption sites of atomic Au. We have found that Au atoms prefer to adsorb with unsaturated surface O ions. A slight preference for bridge position was predicted with respect to the top orientation (Fig. 2a-b). Concerning the Au dimer, the preferential geometry is that one with both Au atoms interacting simultaneously with O ions, which results to be 0.75 eV more stable than the one oriented perpendicular to the surface (Fig. 2c-d). For Au₃ we have obtained two geometries, one forming a triangle and the other with the three Au atoms aligned over the unsaturated oxygen ions, being the former 1.11 eV more stable than the latter (Fig.

2e-f). For Au₄, we have found four isomers (see Fig. 2g-j). At the lowest energy local minimum, the cluster has the shape of a rhombus (the same shape characterizing the global minimum as isolated species). Two of the other isomers are Y-shaped, one linked with surface O anions and the other one bonded also with an Fe ion. The remaining tetramer has the form of a tetrahedron. The four structures have similar adsorption energies, with an energy difference of only 0.5 eV between the most stable and the less stable. With respect to Au₅, we have also obtained four isomers (Fig. 2k-n). Three of them are trapeze-shaped structures, linked to the surface with a different number of Au atoms. The most stable corresponds to the one with three basal metal atoms interacting with O ions. The remaining structure has the shape of a trigonal bipyramid (Fig. 2m). It is important to note that the most stable isomers for trimers, tetramers and pentamers correspond to planar geometries with the metal atoms arranged according to the Au(111) structure.

In all the studied cases, an electronic charge transfer occurs from Au to the support (Table 1). However, for each size of particle, the ordering of stability (measured by the adsorption energy values) does not correlate with the net charge of Au cluster. Considering only the preferential configurations for each size of cluster, the charge transfer results to be significant, varying in the range from 0.4 to 0.7*e*. With respect to magnetization, Au₅ present the highest value (0.50 μ_B).

As before, an exhaustive study were carried out for the more active sites for atomic Au on the hydroxylated FeOOH(110) surface. The two preferred sites are indicated in Figure 3a-b, in which the metal atom interacts with a monocoordinated hydroxyl (the most stable) and with a tricoordinated O anion. From the most stable configuration, we have modeled the larger particles by adding Au atoms one-by-one, obtaining Au₂, Au₃ and Au₄ (Fig. 3c-e). For the pentamer we have found three isomers (Fig. 3f-h): the most stable is X-shaped linked with the surface through a monocoordinated OH and with a tricoordinated O anion (Fig. 3f); the other two are a trapeze-shaped isomer interacting with one monocoordinated OH (Fig. 3g), and a non-planar structure with a double anchorage with the surface (Fig. 3h). As in the case of the bare surface, for the larger clusters the preferred configurations are planar. The charge of Au clusters are always negative, but lower in magnitude in relation with the adsorption of the bare surface, in the range of -0.10 to -0.18*e* (Table 2). Considering only the most stable cases for each size of particle, we can see that on the hydroxylated surface the magnetization is large on the Au particles with an odd number of atoms, and nearly null with an even number of atoms.

We have performed a more detailed study of the charge transfer between Au and the support. For that, we have taken the case of Au₅ adsorbed on the bare surface, in which the metal particle acquires a large positive charge. We have computed the net charge of the three O ions directly linked with the basal Au atoms of this metal particle, and the charge of the four Fe ions bonded with those O. These values are then compared with the charges of the same ions at the clean surface (i.e., without Au particle). We have observed that approximately a half of the charge transferred from the metal to the oxide is taken by these O ions, and, to a lesser extent, by the Fe ions; the rest is acquired by surrounding ions. By going from the clean surface to the supported Au₅ system, the charges of the O and Fe ions change from -1.03 to -1.12e, and from 1.98 to 1.96e, respectively. Making a similar comparison, the spin values change from 0.07 to 0.12 μ_B /atom for O ions, and from 4.13 to 4.34 μ_B /atom for Fe ions. Thus, the oxidation state of the nearby Fe ions undergoes a negligible modification after Au deposition.

3.2- Adsorption and nucleation energies: polarization effects.

In Figure 4 we have plotted the adsorption energy values for the Au particles on both goethite surfaces. Only the most stable configurations for each size of particle are presented. Interestingly, on the bare surface a strong stabilization is observed by going from Au₁ and Au₂ (E_{ads} of around -2.6 eV) to the planar structures of the larger particles, i.e., Au₃, Au₄ and Au₅ (E_{ads} values of -4.1/-4.5 eV). On the hydroxylated surface, on the contrary, the values show less variation with minimum at Au₃.

We now focus our attention in the behavior of E_{ads} changes on the bare surface. In Table 3, the Au atomic charges for the most stable configurations are reported. In Au₃, Au₄ and Au₅, we can observe that meanwhile the basal Au atoms acquire a positive charge, the terminal ones are negatively charged suggesting a polarization of the metal particle. The resulting O²⁻/Au ^{δ +} attraction at the metal-oxide interface is reminiscent of the concept of “chemical glue” suggested by Bond and Thompson to explain the great stability of gold particles on oxidized oxide surfaces [33].

In Figure 5, ELF maps are depicted for the adsorption on the bare surface. We can see that adsorbed Au₁ shows a rather symmetric distribution of the electronic cloud. In Au₂, due to the internal Coulombic repulsion between surface oxygen anions and gold, the dimer undergoes a polarization with the electronic density away from the oxide surface to minimize repulsion. Concerning the larger clusters, and in line with the atomic charges presented above,

ELF maps show extended clouds surrounding the terminal Au atoms on Au₃, Au₄ and Au₅, and more contracted clouds on the basal Au atoms, showing the already mentioned polarization of the gold aggregates. In these clusters, the electronic charge is distributed over a more extended structure than the cases of Au₁ and Au₂, allowing a more remarkable polarization. However, this effect is somewhat less pronounced on the particle with an even number of atoms, Au₄, than on Au₃ and Au₅; for this reason the tetramer is slightly less stable.

In Au particles, valence s orbitals can extensively hybridize with d orbitals because of the relativistic contraction of the former [34,35]. The resulting s–d mixing allows a strong polarization of the electronic cloud when the metal cluster is subjected to an external electric field. Indeed, remarkable polarizabilities in the lateral directions were predicted by DFT on planar 2D Au clusters at gas phase [36]. We can conclude that the electronic clouds of planar Au₃, Au₄ and Au₅ clusters result to be distorted owing to the interaction with surface oxygen anions (formerly unsaturated at the clean bare surface), producing a polarization of these particles. For this reason, they are strongly stabilized in relation with Au₁ and Au₂, thus explaining the abrupt change of E_{ads} values (Fig. 4). In Figure 5f, the ELF plot of Au₅ deposited on the hydroxylated surface is shown for comparison. Although the values of the net charges are negative at the terminal Au atoms (Table 3), the clouds surrounding the metal atoms are significantly contracted in comparison with the metal clusters on the bare surface, indicating a poor polarization. It is interesting to mention that the enhanced catalytic activity observed in some supported Au-based catalysts has been suggested to be originated by the polarization undergone by the metal particle due to its interaction with the support [37,38].

In Figure 6 we have plotted the atom-by-atom nucleation process. For comparison, the growth of free Au clusters are also presented. A zigzag behavior of E_{nuc} values is observed in the three cases. At gas phase and on the hydroxylated surface the relative changes are very similar, with minima at Au₂ and Au₄. This behavior can be explained looking at the spin values of the gold particles, showing in Figure 7. Indeed, when two Au atoms at gas phase bond each other, or when a Au atom at gas phase interacts with a Au atom supported on the hydroxylated surface, two open-shell fragments are interacting thus producing a strong bond. The same argument can be used to explain the formation of Au₄ from Au₃ and Au₁ fragments.

However, the zigzag oscillation of E_{nuc} values is opposite on the bare surface, with minima at Au₃ and Au₅. At first sight, this is an unexpected result because the variation of the spin is similar on the bare surface in comparison with the other two cases (except for Au₁, Figure 7); therefore, similar changes of E_{nuc} on the bare surface should be expected. We can

explain the minima at Au₃ and Au₅ using also the concept of polarization. When the third Au atom is incorporated to form Au₃, and the fifth Au atom is added to form Au₅, a strong polarization takes place, thus producing very stable configurations. In this way, while on the hydroxylated surface the nucleation energy is governed by the spin of the interacting systems, on the bare surface polarization effects seems to play a fundamental role achieving an enhancement of the metal-support bonding.

The fact that the two types of surfaces produce Au particles with different charge offers the possibility of controlling the charge transfer between the support and Au according to the degree of calcination of the oxide, and in turn, the possibility of tuning the active surface in the desired direction. For example, the negatively charged Au clusters presented on the hydroxylated surface should facilitate the bonding with electron-acceptor molecules (CO, SO₂, O₂, C₂H₄, etc.).

4. Conclusions

The interaction between tiny Au_n (n=1-5) particles and the bare and fully hydroxylated (110) surfaces of goethite was studied using DFT+U. In relation with the surface active sites, we can conclude that while on the bare surface Au particles prefer to adsorb mainly with the unsaturated surface O anions, on the hydroxylated surface monocoordinated hydroxyls and tricoordinated oxygen anions are the favorite adsorption sites. Concerning the lowest-energy structures, we find a predominance of planar configurations on both surfaces. On the other hand, while on the bare surface the charge of Au clusters are always positive (reaching values of around 0.7*e*), those deposited on the hydroxylated surface acquires a negative charge (around -0.1*e*).

On the bare surface the adsorption energies, i.e., the calculated energies associated with the deposition of the Au metal clusters coming from the gas phase, present a noticeable change by going from atomic Au and Au₂ to larger aggregates, showing a very strong interaction in the latter case. We have observed that the stabilizing contribution of Au₃, Au₄ and Au₅ derives from the polarization of the electronic cloud of the metal cluster in the electric field produced by the oxide surface. A substantial concentration of electrons in the outside region of these Au particles are observed from ELF plots.

Concerning the one-by-one nucleation process, a zigzag behavior of the corresponding nucleation energies is obtained. For the gas phase situation and on the hydroxylated surface, the variations are similar, with minima at Au₂ and Au₄, a behavior that could be associated

with the spin of the interacting systems. However, the zigzag oscillation of the nucleation energies is opposite on the bare surface, with minima at Au₃ and Au₅, attributable to polarization effects which enhance the metal-support bonding.

In view of the results presented in this work, we can conclude that, at least in principle, it should be possible to control the charge transfer between the oxide surface and the Au particles by varying the calcination degree of the oxide. This would offer the possibility of tuning the active surface in the desired direction.

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Figure Captions

Figure 1. Slabs used to represent the (a) bare and (b) hydroxylated FeOOH(110) surfaces. Top figures: top views. Bottom figures: lateral views, along the $[00\bar{1}]$ direction. I: monocoordinated surface OH; II: dicoordinated surface OH; III and IV tricoordinated surface OH. Red, green and light blue balls correspond to oxygen, iron and hydrogen atoms, respectively.

Figure 2. Optimized Au clusters on the bare FeOOH(110) surface. In some cases (a, b, c, e, f, g and h), the structures are shown from a different perspective (as viewed along the $[\bar{1}00]$ direction) in relation to the side view depicted in Figure 1. Distances in Å. Red, green, light blue and yellow balls correspond to oxygen, iron, hydrogen and gold atoms, respectively.

Figure 3. Optimized Au clusters on the hydroxylated FeOOH(110) surface. Distances in Å. Atom colors as in Figure 2.

Figure 4. Adsorption energy values as a function of the number of Au atoms for the bare and hydroxylated goethite surfaces.

Figure 5. Electron localization function (ELF) plots for Au clusters on goethite surfaces. From a) to e): most stable structures of Au₁, Au₂, Au₃, Au₄ and Au₅ on the bare surface, respectively; f) most stable geometry of Au₅ on the hydroxylated surface. The pictures are drawn in the plane that contains the Au particle.

Figure 6. Nucleation energies as a function of the number of Au atoms for the bare and hydroxylated goethite surfaces, and at gas phase.

Figure 7. Magnetization of Au clusters as a function of the number of atoms for the bare and hydroxylated goethite surfaces, and at gas phase.

Tables

Table 1- Adsorption energies, total charge and total magnetization of adsorbed Au clusters on the bare (110) surface of goethite.

Au cluster	Fig. 2	E_{ads} (eV)	q_t (e)	μ_T (μ_B)
Au ₁	a	-2.62	0.41	0.07
Au ₁	b	-2.59	0.33	0.03
Au ₂	c	-2.54	0.68	0.09
Au ₂	d	-1.79	0.21	0.41
Au ₃	e	-4.44	0.55	0.27
Au ₃	f	-3.33	0.58	0.28
Au ₄	g	-4.14	0.69	0.11
Au ₄	h	-4.06	0.67	0.11
Au ₄	i	-3.91	0.83	0.06
Au ₄	j	-3.64	0.16	0.32
Au ₅	k	-4.53	0.70	0.50
Au ₅	l	-3.96	0.44	0.02
Au ₅	m	-3.43	0.59	0.22
Au ₅	n	-3.31	0.41	0.02

Table 2- Adsorption energies, total charge and total magnetization of adsorbed Au clusters on the hydroxylated (110) surface of goethite.

Au cluster	Fig. 3	E_{ads} (eV)	q_t (e)	μ_T (μ_B)
Au ₁	a	-0.74	-0.12	0.40
Au ₁	b	-0.63	-0.10	0.39
Au ₂	c	-1.39	-0.14	0.01
Au ₃	d	-1.57	-0.17	0.45
Au ₄	e	-1.50	-0.14	0.01
Au ₅	f	-1.42	-0.18	0.41
Au ₅	g	-1.18	-0.12	0.48
Au ₅	h	-1.11	-0.17	0.47

Table 3- Atomic net charges for the lowest-energy structures of Au clusters on the bare and hydroxylated surfaces. The numbering of the Au atoms are indicated in Figures 2 and 3.

Bare surface		Hydroxylated surface	
Au ₂ (Fig. 2c)	Au(1): 0.41 Au(2): 0.27	Au ₂ (Fig. 3c)	Au(1): 0.10 Au(2): -0.24
Au ₃ (Fig. 2e)	Au(1): 0.30 Au(2): 0.39 Au(3): -0.14	Au ₃ (Fig. 3d)	Au(1): -0.03 Au(2): -0.07 Au(3): -0.07
Au ₄ (Fig. 2g)	Au(1): 0.62 Au(2): 0.22 Au(3): -0.06 Au(4): -0.09	Au ₄ (Fig. 3e)	Au(1): 0.23 Au(2): 0.02 Au(3): -0.16 Au(4): -0.23
Au ₅ (Fig. 2k)	Au(1): 0.44 Au(2): 0.29 Au(3): -0.21 Au(4): -0.14 Au(5): 0.32	Au ₅ (Fig. 3f)	Au(1): 0.16 Au(2): -0.17 Au(3): 0.06 Au(4): 0.02 Au(5): -0.25