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Classical molecular dynamics simulations of gold clusters deposited on rutile TiO_2(1 1 0) surface

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Abstract

Classical molecular dynamic simulations of Au clusters supported on the non-defective rutile TiO_2(1 1 0) surface are reported. The oxide surface is represented by a slab obtained by imposing periodic boundary conditions to a $12 \times 12 \times 1$ supercell. The dynamics of the system is accounted for thorough classical pair potentials describing both the metal–metal and the metal–surface interactions, determined from periodic density functional theory model calculations. Deposited particles show a well defined structure and can be described as hexagonal truncated pyramids mainly exhibiting (1 1 1) facets in agreement with scanning tunnel microscopy experiments conducted under atomic resolution.

Keywords: Density functional theory; Molecular dynamics simulations; Rutile; Gold; Au/TiO_2

1. Introduction

Supported gold particles have raised an enormous interest in the catalytic community since the discovery in 1987 by Haruta and co-workers [1,2] of the high activity as catalysts. In spite of the well-known noble character of gold, when dispersed as nanoclusters on a support, it exhibits an unexpected activity for a number of reactions, in particular in the CO oxidation at and below room temperature. With the aim of understanding and rationalize this behavior, the scientific community has been concerned with the analysis of the structure–activity relationships, particularly at the microscopic level (nm), a size domain often encountered in applied catalytic technologies. In this context, understanding the growth of gold on oxide surfaces has become crucial. A number of supports have been considered, mainly metal oxides, however the (1 1 0) surface of rutile TiO_2 has deserved much attention because both its availability and well-known properties [3]. The morphology and electronic structure of gold nanoclusters supported on TiO_2(1 1 0) have been reported by Goodman et al. from scanning tunneling microscopy (STM) studies ([4] and references in). They concluded that Au (and others like Pd and Ag) clusters grow according to three-dimensional (3D) or Volmer–Weber mechanism on the TiO_2(1 1 0) surface, but that at low coverage, quasi-two-dimensional islands composed by one to two atomic layers of Au have been observed. Moreover, it has been shown that after annealing over 800 K, the rectangular Au crystallites exhibited a dramatic elongation along the [0 0 1] direction parallel to the row structure of the substrate and covered much of the surface. Apparently, Au atoms are more mobile along the close-packed [0 0 1] direction. The large micro-crystals are characterized by a well-defined hexagonal shape and are aligned with two of the six edges along the [0 0 1] direction. This result suggests that the micro-crystals consist of closed-packed (1 1 1) oriented planes. More recently, Madey's group has found the coexistence of Au(1 1 1) and Au(1 1 2) faces at the interface in unstrained Au islands, the latter one, presumably, driven by the intrinsic corrugation of the rutile TiO_2(1 1 0) surface [5].

The Au/TiO_2(1 1 0) interface has also been investigated from a theoretical point of view using modern quantum mechanical methods. Thus, density functional-based calculations carried out on deposited single gold atoms [6,7] show that Au prefers binding the surface at the protruded oxygen rows. The interaction with the surface is relatively weak (0.6–0.9 eV) with only minor charge transfer. The bonding is better described as covalent polar and metal polarization is towards the surface O atoms. Theoretical calculations on small clusters

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have also been reported [8–10] revealing more details about the structure of the interface. However, a theoretical study at the atomistic level of the morphology of large three-dimensional metal particles on this surface has never been accounted.

In the present paper, we present molecular dynamics (MD) classical simulations of the atomistic structure of a gold particle supported on the rutile $TiO_2(1\,1\,0)$ surface. Our main goal is to analyze the structure of the supported clusters with the purpose of obtaining details of potentially active sites. It should be stressed that although the catalytically relevant support is the anatase phase, we preferred the (1 1 0) face of rutile for which detailed structural data (STM) have been reported. The simulations are based on the computational procedure that we recently developed to determine interaction pair potentials and that we successfully employed to simulate the Pd/α-$Al_2O_3(0\,0\,0\,1)$ and Au/TiN(0 0 1) interfaces [11–13]. The preliminary results we bring in here are more concerned with the shape and suitability of the potentials to describe the interface in a reliable way. The article has been organized as follows: in Section 2 we describe the steps which allow us to determine the interaction pair potentials on a first principles basis; in Section 3 we report on the MD simulations of Au clusters deposited on $TiO_2(1\,1\,0)$; and the conclusions are outlined in Section 4.

2. Determinations of the interactions pair potentials

The starting point in a classical MD simulation concerns the choice of the force field governing the behavior of the system. It is generally accepted that a simple and suitable description of a set of interacting particles can be achieved by means of additive pair potentials V_{ij}. Following the strategy previously described [11], two qualitatively different types of pair potentials were used in this work. The first accounts for the interaction between surface species, i.e., between titanium and oxygen ions, and the second accounts for the interaction between Au atoms and surface ions, as well as between Au atoms themselves.

To describe the Ti–O interaction, a pair potential built up as a sum of Coulombic and short-range terms is used:

$$V_{ij} = \frac{q_i q_j}{r_{ij}} + V_{ij}(s-r)$$

where q_i, and q_j are the effective charges and r_{ij} the interparticle distance. The short-range potential $V_{ij}(s-r)$ is accounted for through a Buckingham type expression:

$$V_{ij}(s-r) = -\frac{C_i C_j}{r_{ij}^6} + f(B_i B_j)\exp\left(\frac{A_i + A_j - r_{ij}}{B_i + B_j}\right)$$

where the parameters A, B, C and f, as well as the effective charges q_i, and q_j were those given by Matsui and Akaogi [14]. Although this potential does not explicitly account for the large polarizability of the O^{2-} ions, we have found it a reasonably approximation in previous simulations [15–17].

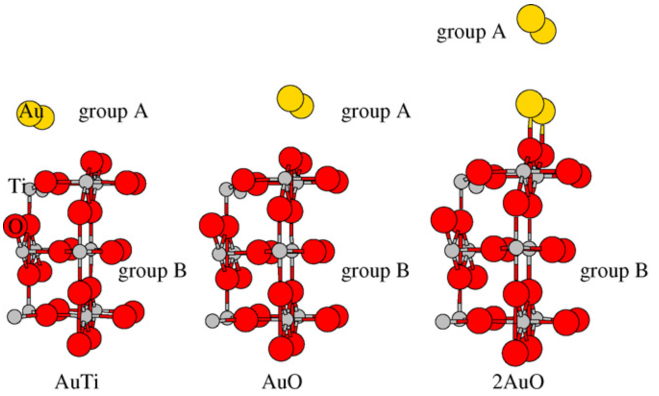

Fig. 1. The three initial configurations used to determine the pair potentials describing the interaction of Au with the surface.

The pair potentials representing the interaction Au–O, Au–Ti and Au–Au have been determined on a first-principles basis from density functional calculations (DFT) according to the procedure detailed in previous works [12,13]. As stated above, Au atoms prefer to bind the $TiO_2(1\,1\,0)$ surface on the protruded oxygen atoms, with small charge transfer towards the surface [6]. Preliminary DFT calculations carried in this work showed that when Au_2 dimers are supported on this surface the charge transfer is negligible. A similar behavior was also observed in the Au_2/TiN(0 0 1) interface where adsorption of the metal dimer involved only a small polarization [18]. Moreover, it is expected that when the number of metal cluster atoms is increased, the charge transfer/by atom ratio will be even lesser. As in previous works, this feature enables us to limit the interaction potential of Au to the short-range contribution. According to the method described in Refs.

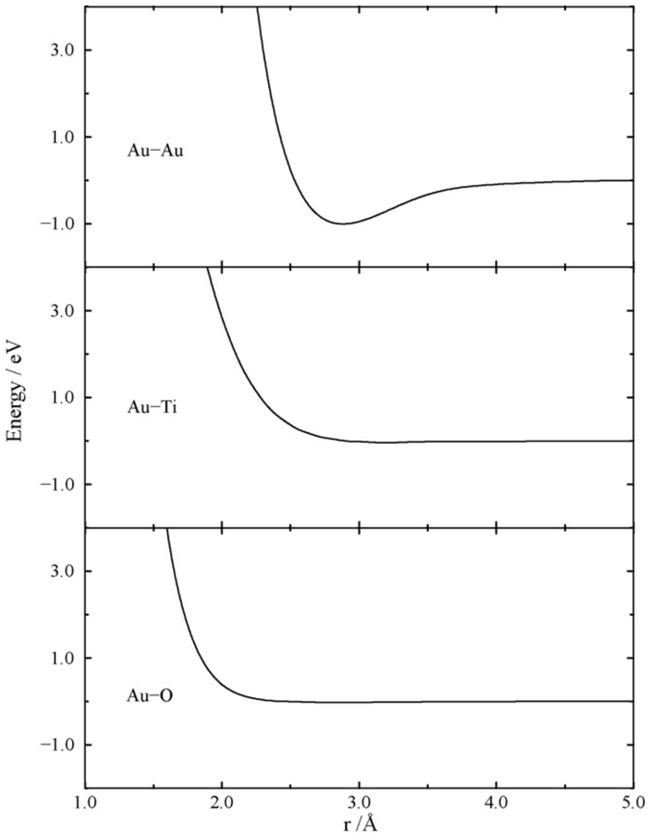

Fig. 2. Interaction potentials for Au–Au, Au–Ti, and Au–O.

Table 1
Binding energies (eV/atom) of selected model clusters obtained in this work, with the Sutton–Chen potentials and from DFT calculations [23]

	Model cluster						
	L2	P8_1	P8_2		T13_1	T13_6	T13_7
This work	1.01 (14)	1.90 (−5)	2.04 (3)	2.21 (3)	2.63 (25)	2.27 (13)	2.46 (28)
SC	2.23 (91)	2.81 (40)	2.86 (45)	2.95 (38)	3.06 (45)	3.10 (55)	3.12 (62)
DFT	1.17	2.01	1.97	2.14	2.11	2.00	1.92

Errors (%) with respect to the values obtained from DFT calculations are given in parentheses.

[12,13], to determine the pair interaction potentials Au–Ti, Au–O, and Au–Au we start by choosing three initial configurations (Fig. 1): group A always consisted of a gold dimer while group B was either a slab of 2 × 2 TiO_2(1 1 0) six-layer thick or two gold atoms deposited on such slab. Gold atoms were placed on top of Ti and on top of O [Fig. 1(left and center)]. In Fig. 1(right) two gold atoms of group A interact with two gold atoms of group B, allowing us to estimate the interaction potential for the adsorbed gold/gold pair. The complete set of values of interaction energies $(E'_{\mathrm{MD}}\mathrm{short}(A, B, d_i))$ was then obtained by variation of the distance d so that $1.0\ \text{Å} < d < 5.0\ \text{Å}$. To this aim, DFT calculations with periodic boundary conditions were performed using the VASP 4.4.5 [19,20] code under the generalized gradient approach (GGA) proposed by Perdew et al. [21]. Ultrasoft pseudopotentials [22] were employed to remove the core electrons from the calculations and plane wave basis set was used.

The values of interaction energy were then written as a linear combination of interaction potentials on discrete form $P^t_{j,k}$ for the pairs Au–Au, Au–Ti and Au–O defined in the 1.0–5.0 Å interval:

$$E'_{\mathrm{MD}}\mathrm{short}(A, B, d_i) = \sum_{\substack{j \in A \\ k \in B}} \sum_{t=1}^{t=N_{jk}} \alpha_{i,jkt} P^t_{jk}$$

After solving this system of equations, the short-range contribution to the pair wise interaction potential was obtained. The total pair interaction potentials are shown in Fig. 2.

3. MD Simulations of Au clusters deposited on TiO_2(1 1 0)

As a first test of the Au–Au pair potential, we carried out a series of simulations on selected clusters and the results were compared with those recently reported by Xiao et al. [23] obtained from DFT calculations. Beyond a dimer Au_2 (L2), both planar (P) and three-dimensional Au (T) arrangements were considered. Binding energies estimated for Au_8 and Au_{13} clusters are reported in Table 1, in which we strictly follow the notation given in Ref. [23]. For the sake of comparison we also include the results obtained using the widely used set of parameters introduced by Sutton and Chen [24]. As can be seen our values are reasonably close to those obtained from DFT even taking into account that our potentials have been fitted to reproduce a quite singular situation intended to describe the interaction between two Au atoms, one of which is actually polarized by the transition metal oxide surface. On the other hand we can see that our potential performs better than the Sutton–Chen one, which is not surprising because these parameters were obtained by fitting the properties of bulk Au.

MD simulations of the Au/TiO_2(1 1 0) system were undertaken in the microcanonical ensemble using the DL_POLY code [25]. The computational box was a (12 × 12) supercell of size 55.032 Å × 35.448 Å side accommodating a TiO_2 slab six-layer thick (532 TiO_2 units) and a vacuum gap between slabs. In the simulations, the two lowest layers were kept frozen. The initial configurations in our MD simulations were Au clusters of different sizes deposited on TiO_2(1 1 0) surface previously relaxed. The simulations started by assigning initial velocities

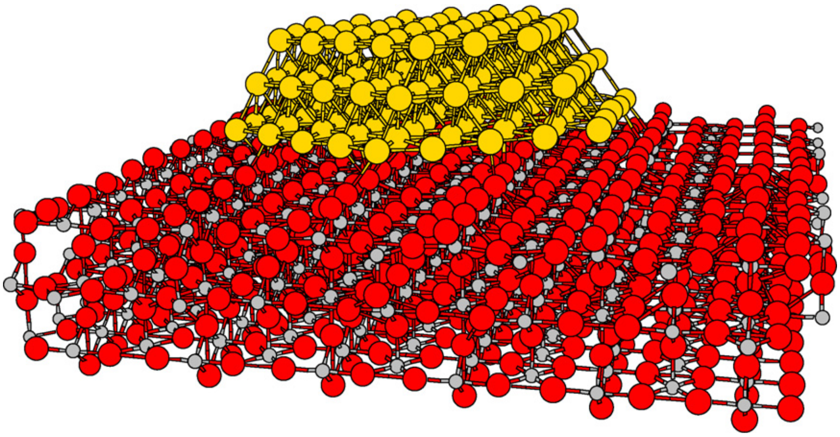

Fig. 3. Snapshot of the Au_{145} cluster deposited on the rutile TiO_2(1 1 0) surface.

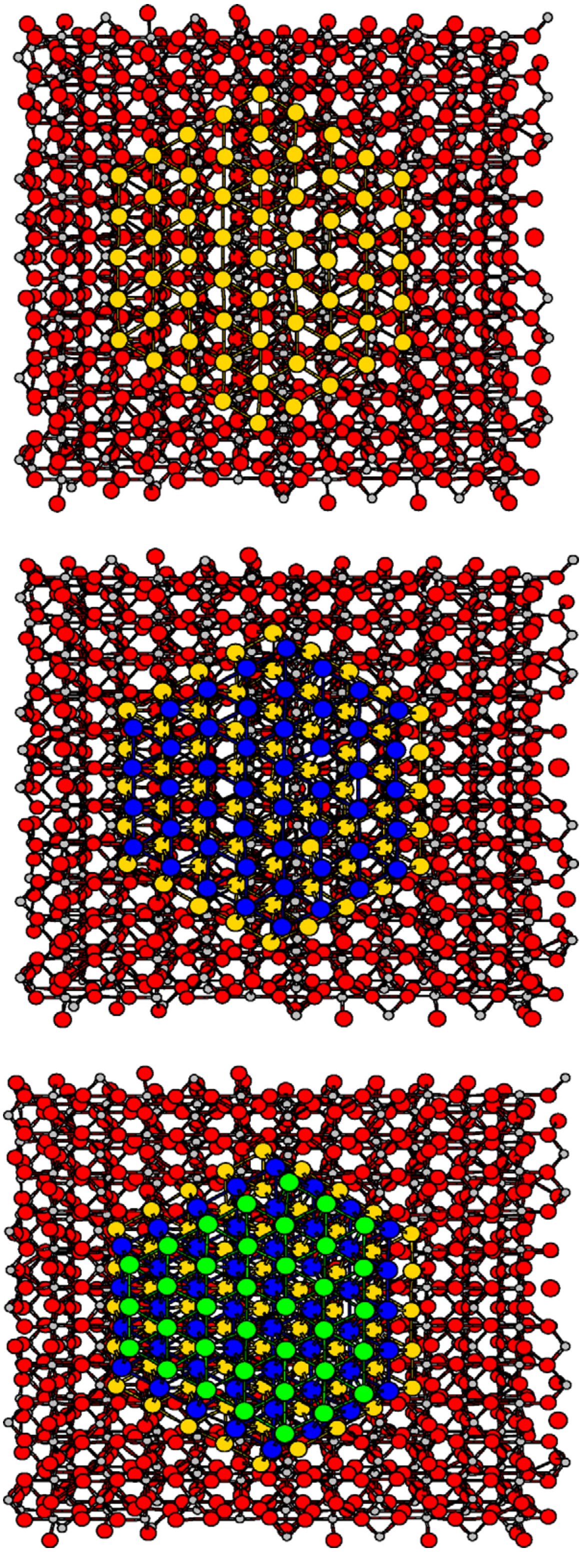

Fig. 4. Layer-by-layer views of the Au_{145} cluster deposited onto the rutile TiO_2(1 1 0) surface.

to all atoms according to a Maxwell–Boltzman distribution, followed by solving the Newton's equations of motion through numeric integration using the leap-frog algorithm with a time step of 0.1 fs [26]. The simulations schedule consisted of a thermalization run of 10 ps at 300 K followed by a simulation of 10 ps without temperature control to ensure that the system reached equilibrium. After this stage, a simulation of 30 ps was carried out to collect data for statistics. The conservation of energy was better than 1 in 10,000.

Several Au clusters were considered to simulate the Au/TiO_2 system interface, with sizes ranging between 16 and 200 atoms, however, for the sake of the analysis only a medium-sized gold particle (145 atoms) will be discussed here. A snapshot of the system after the simulations is reproduced in Fig. 3. At first glance one can be observed that beyond a certain degree of disorder the particle exhibits a relatively well-defined shape, with a truncated pyramid like structure. To obtain a deeper insight into the structure of this particle, an analysis of the Au atoms positions layer by layer was carried out. The results are displayed in Fig. 4, where the projection along the [1 1 0] direction of the surface, after progressive Au layers addition, is displayed. It should be noted that, with the aim of facilitating this analysis, the color of the Au atoms have been arbitrarily modified. The top of Fig. 4 corresponds to the Au layer directly adsorbed onto the rutile surface. It appears that there is a quite regular arrangement of Au atoms forming a well-defined hexagonal shape. Two of the six edges are aligned with the surface oxygen rows, in particular along the [0 0 1] direction, in agreement with experimental results [4]. The atoms of the second adlayer (Fig. 4, middle) occupies the center of the first layer Au triangles, according to both hexagonal and fcc

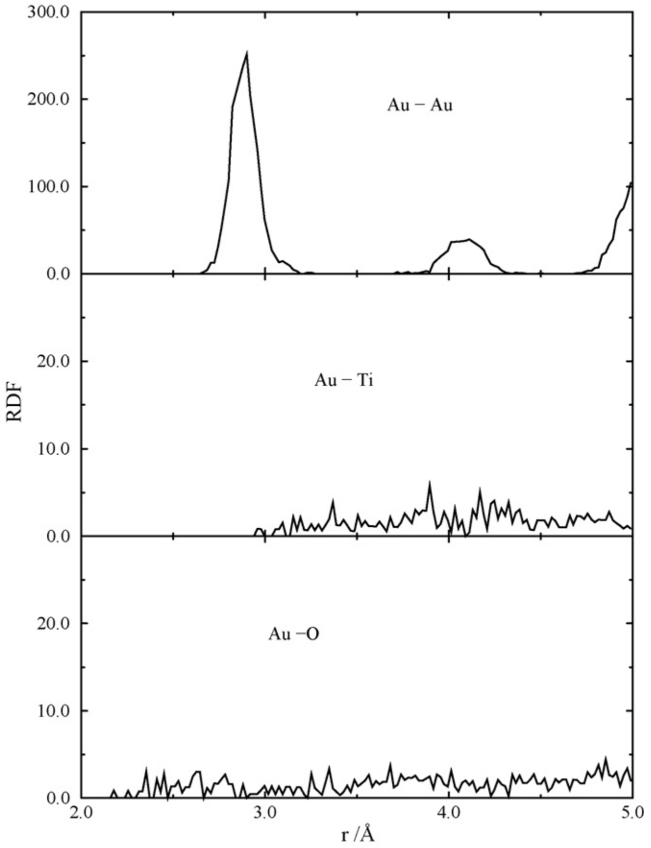

Fig. 5. Radial distribution functions (RDFs) for Au–Au, Au–Ti, and Au–O pairs obtained from the MD simulations of Au clusters deposited on rutile TiO_2(1 1 0) surface.

packing. The third layer (bottom of Fig. 4), confirms an A–B–C pattern according to cubic packing. The final structure could be described as a hexagonal pyramid exposing (1 1 1) and (1 0 0) facets and truncated by the (1 1 1) plane. These findings are in excellent agreement with the STM images obtained under atomic resolution showing the regular structure of deposited Au particle [4].

In Fig. 5, the radial distribution function, $g(r)$, for the Au–O, Au–Ti, and Au–Au pairs are reported. The main peak of the Au–Au curve approximately appears at 2.9 Å, which is close to the experimental distance of 2.88 Å [27]. On the other hand, $g(r)$ functions corresponding Au–O and Au–Ti pairs show an unstructured profile indicating the absence of well-formed pairs along the simulation. When this striking behavior is monitored under a dynamic graphical environment it turns out that the Au particles slowly move on the surface in such a way that they swing between the protruded oxygen atom rows to which they are aligned. Furthermore, we found out that the period of the swinging depends on the size of the particle, the smaller ones moving faster. This result would agree with the experimentally observed trends that indicate that small Au clusters have a higher mobility [4,28]. An essential aspect of the Au mobility on the surface is of course the estimation of diffusion coefficients for a range of cluster sizes and shapes, and computations in this direction are currently undergoing in our lab.

4. Conclusions

Classical MD simulations of Au clusters deposited on the rutile $TiO_2(1\,1\,0)$ surface are reported. The pair potential functions used to describe the metal–metal and metal–surface interaction were derived on a purely a priori basis from supercell periodic DFT calculations using a GGA exchange correlation functional and plane waves as basis set. The simulations show that the adsorbed Au particles are 3D clusters in agreement with the 3D Volmer–Weber growth mechanism suggested for this system. The structural analysis shows the cubic packing of the microcrystals whose shape appears to be hexagonal pyramids truncated by the (1 1 1) plane, and exhibiting (1 1 1) and (1 0 0) facets. These results are in excellent agreement with the STM images reported by Goodman and co-workers [4].

Acknowledgments

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