



Theoretical study of the structures of MgO(100)-supported Au clusters

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ABSTRACT

A theoretical method, which combines the first-principle calculations and a canonical Monte Carlo (CMC) simulation, was used to study the structures of Au clusters with sizes of 25–54 atoms supported on the MgO(100) surface. Based on a potential energy surface (PES) fitted to the first-principle calculations, an effective approach was derived to model the Au–MgO(100) interaction. The second moment approximation to the tight-binding potential (TB-SMA) was used to model the Au–Au interactions in the CMC simulation. It is found that the Au clusters with sizes of 25–54 atoms supported on the MgO(100) surface possess an ordered layered fcc epitaxial structure.

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1. Introduction

Small Au clusters supported on various oxides have attracted a lot of interest in recent years, due to their excellent catalytic properties in a number of interesting low-temperature oxidation reactions [1,2]. For example, oxide-supported Au clusters are highly active catalysts for CO and H₂ oxidation, NO reduction, water–gas shift reaction, CO₂ hydrogenation, catalytic combustion of methanol, and so on [3]. It is well-known that the cluster size is a key factor to influence the catalytic behavior of supported Au clusters. Goodman and co-workers [4] found that Au clusters with diameter of about 3.5 nm supported on a TiO₂ substrate exhibit the maximum reactivity for catalyzing the oxidation of carbon monoxide. However, the catalytic behavior of supported Au clusters can be influenced not only by the sizes of the clusters but also by the interactions between the clusters and the substrates [5,6]. Schubert and co-workers [5] found that the catalytic activities are different for gold catalysts of similar size supported on different substrates.

A lot of theoretical [7,8] and experimental works [1,9] considered MgO with a regular surface as a substrate for Au clusters. First, Au clusters supported on a MgO surface show high activity in some oxidation reactions [1]. Second, the simple rock salt oxide structure of MgO makes it very suitable for theoretical treatments. Most of the previous theoretical works were focused on the research of adsorption and reaction of Au atoms and dimers supported on MgO(100) by density functional theory (DFT)

calculations [7,10–12]. Landman and co-workers [7] studied the structures of small Au clusters supported on MgO by DFT calculations, and also investigated the low-temperature oxidation reaction of CO to CO₂. However, the DFT-based methods were proved to be inefficient to deal with large-size systems, due to their computational expense. This fact makes it impossible to compare the results of DFT calculations directly with experiments. Therefore, it is necessary to develop effective energetic models between metal and MgO, and then to use atomistic simulation methods to treat complex systems. Mottet and co-workers [13–18] fitted many-body potential energy surfaces (PES) for the Pd–MgO, Ag–MgO, and Ni–MgO interactions by *ab initio* calculations, and then studied Pd clusters, Ag thin films, and Ni clusters deposited on a MgO(100) surface by molecular dynamics simulations. However, data is still scarce for the energetic model of the Au and MgO interaction.

In the present work, we study the structures of small Au clusters supported on MgO(100) surface by using a theoretical method, which combines the first-principle calculations of Au–MgO interaction energy landscapes and the canonical Monte Carlo (CMC) simulation to evaluate the structures of MgO(100)-supported Au clusters. Based on a potential energy surface (PES) fitted to the first-principle calculations, we propose an effective approach to model the Au–MgO(100) interaction.

2. Computational details

2.1. First-principle calculations

The first-principle calculations used for fitting the interaction potentials of Au–MgO(100) were performed in the framework of

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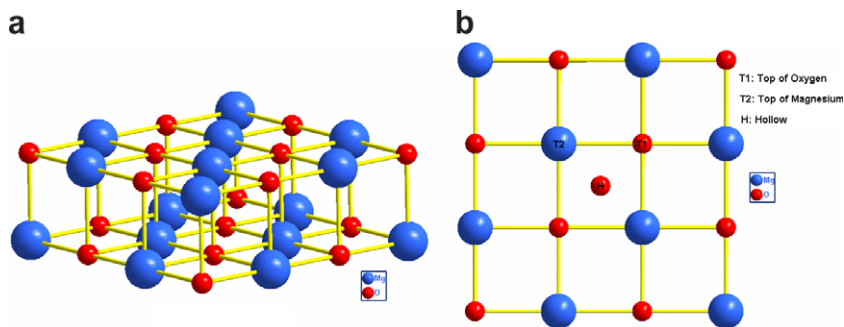


Fig. 1. Schematic representations of (a) the MgO model used in the first-principle calculation, and (b) the three different adsorption sites of the MgO(100) surface.

density functional theory (DFT) with the Gaussian 03 program package [19]. A two-layer-thick MgO slab with a $p(3 \times 3)$ unit cell was adopted. It is worth pointing out that a similar model for MgO(100) was also employed by Molina and Hammer [11], who found only tiny changes (smaller than 0.01 eV) in the adhesion energies when the oxide slab thickness increases up to four layers. Fig. 1a shows a schematic diagram of the MgO model used in the first-principle calculations. It is worth pointing out that Wu et al. [20] and Tran et al. [21] have shown that the first-principles calculation results of GGA (generalized gradient approximation) depend strongly on the exchange-correlation functional used. They suggest that the functionals obeyed the Lieb-Oxford bound, such as PBE developed by Perdew et al. [22] and PW91 by Perdew and Wang [23], are the best ones to model the weak interactions, among the current DFT methods. Thus all the calculations in this paper were carried out by the PW91 exchange-correlation function.

On MgO(100) surface, there are three typical adsorption sites: top of oxygen, top of magnesium, and hollow. Fig. 1b shows the three different adsorption sites of the MgO(100) surface. For the Au–MgO(100) systems studied, a single Au atom is first located at three different adsorption sites, respectively; then a series of potential energies between Au and the surface can be obtained by varying the Au–MgO(100) distance in the first-principle calculations. Fig. 2 shows the potential energy curves of Au interaction with the MgO(100) surface at different adsorption sites, as calculated using a vertically approaching mode. It is found in Fig. 2 that Au atom adsorbing on the oxygen-top sites oriented perpendicularly to the surface is the most favorable adsorption mode. This phenomenon is also found in several previous works [11,24].

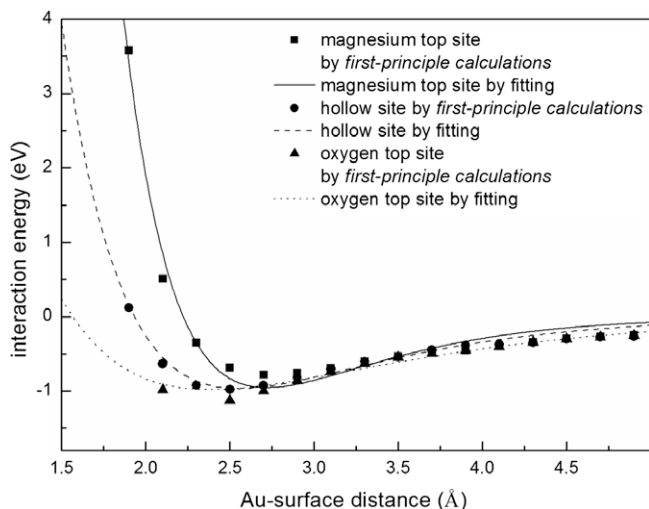


Fig. 2. The fitted Au–MgO(100) potential energy surface, issued from the calculated points at different adsorption sites by the first-principle calculations.

2.2. Fitting the Au–MgO(100) interaction

In order to implement the atomistic simulations of Au–MgO(100) systems, an effective approach to model the metal–MgO(100) interaction is necessary, which should be as close as possible to that determined by the first-principle calculation. In this work, a potential energy surface (PES) was used to model the Au–MgO(100) interaction, which was derived by fitting the results of the first-principle calculations in the previous section. In this PES, for each Au atom, the interaction with the MgO(100) substrate depends on its horizontal position (x, y), and on its elevation z above the MgO surface. The PES is based on a Morse potential. Similar approach has been used successfully to fit the Pd–MgO, Ag–MgO, and Ni–MgO interactions determined by *ab initio* calculations [17,18].

Derived by a Morse potential, the PES analytical form of the Au–MgO(100) interaction can be written as

$$E_{\text{Au–MgO}} = \sum_i a_1 (e^{-2a_2(z_i - a_3)} - 2e^{-a_2(z_i - a_3)}) \quad (1)$$

where z_i is the distance between the i th Au atom and the MgO(100) surface. While, according to the Ref. [18], a_i ($i = 1, 2, 3$) can be written as

$$a_i(x, y) = c_{1,i} + c_{2,i} \left[\cos\left(\frac{2\pi}{l}x\right) + \cos\left(\frac{2\pi}{l}y\right) \right] + c_{3,i} \left[\cos\left(\frac{2\pi}{l}(x+y)\right) + \cos\left(\frac{2\pi}{l}(x-y)\right) \right] \quad (2)$$

where l is the lattice parameter of MgO, which is 4.21 Å in this work. The potential parameters, $c_{i,j}$ ($i, j = 1, 2, 3$), were obtained by fitting to the interaction energies obtained by the first-principle calculations. The parameters, $c_{i,j}$ ($i, j = 1, 2, 3$), of the Au–MgO(100) interaction are shown in Table 1. Fig. 2 shows the fitted dependences, compared with the points calculated by the first-principle calculations. It should be mentioned that the PES analytical form defined in this study is not exactly the same as the one described in Ref. [13–18] because it does not take into account the metal–metal interaction effects in the adsorption of the metal to the MgO(100) surface. However, for very small clusters, this effect is negligible since a majority of metal atoms are less coordinated than 4.

2.3. Monte Carlo simulations

In this work, MgO is considered as a rigid material. There are two potential models adopted in our simulations: one is the interaction between Au atoms, the metal–metal interaction energy, E_{metal} , and the other is the interaction between Au atoms and MgO, the metal–MgO interaction energy, $E_{\text{metal–MgO}}$. Thus, the total energy of the system, E_{Total} , can be defined as $E_{\text{Total}} = E_{\text{metal}} + E_{\text{metal–MgO}}$. The Au–MgO interaction is modeled using the PES in the previous section.

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