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Density functional theory characterization of the formation of copper clusters on F_s and F_s^+ centers on a MgO surface

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Abstract

Electronic structure and chemical reactivity of Cu_n clusters ($n = 1$–4) supported on a regular site (O_{5c}) and on an oxygen vacancy (F_s and F_s^+) of the MgO (100) surface were investigated using density functional theory. It was found that neutral oxygen vacancies, F_s centers, are good trapping sites for Cu atoms and nucleation centers while F_s^+ centers are not.

Both, first ionization potential and the chemical reactivity present odd–even oscillations in the free and supported clusters, these oscillations are related to the electronic nature of the layer open/closed for clusters with odd and even n, respectively, this behavior is similar for supported clusters on an F_s center compared with free clusters. It is also found that the ionization potential and the chemical reactivity are modified when the clusters are supported on the MgO vacancies.

Keywords: Density functional calculations; Electron structure; Surface defects; Oxygen vacancies; Chemisorption; Catalysis; Magnesium oxide

1. Introduction

Fundamental understanding of electronic structure and activity of transition metal atoms and clusters supported on oxide surfaces is of great interest due to their technological importance. The metal-support interface interaction plays a key role in the physical and chemical characteristics of these systems [1,2]. For example, to maximize the catalytic efficiency active transition metal particles are dispersed on inert oxide substrates in order to increase the active centers exposed to the reactants. A molecular-scale understanding of the energetics and mechanisms for formation of such metal clusters on inert oxide surfaces can open new avenues to the design of catalysts with specific functions [3].

In supported catalysts the properties of the deposited nanoclusters are known to depend on the cluster size. When the metal cluster consisting of only few atoms, the size-related catalytic activity for free [4,5] and supported [6,7] clusters is directly related to their intrinsic electronic and geometric properties. For example, the observed size dependence on the catalytic oxidation of carbon monoxide on size selected supported platinum [6] and gold clusters [8,9] can be explained by the distinct electronic and geometric structure of each cluster. Also, the properties of the deposited nanoclusters depend on the oxide substrate and in particular on the presence of point and extended defects where the cluster can be stabilized.

It is well known that defects not only can act as catalytic centers for chemisorption of small species but also as nucleation centers for growing metal clusters and can modify the catalytic activity of these adsorbed metal particles via the metal-support interaction at the interface [10–14]. A number of theoretical studies have been performed to provide fundamental knowledge for elucidating nucleation mechanisms and catalytic activity of supported clusters [15–18]. Mechanisms of growth of nanoclusters on oxide surfaces

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have become a subject of great interest in recent years [10,15–17,19–25]. It has been found that under typical conditions, formation of dimers constitutes the first step in the process of the growth of metal clusters on the oxide surface [26]. It has been found that oxygen vacancies on the MgO surface, which are characterized by the presence of one or two electrons trapped in the cavity, often denoted as F_s^+ and F_s sites, respectively, are good nucleation centers [10,15,25]. For example, Pacchioni and coworkers [15,16], found that formation of palladium dimer on the defective surface is exothermic suggesting that they can be involved in nucleation and growth processes of metal clusters on the MgO surface. Similarly, Pacchioni and coworkers [17] also found that the F_s defect is an excellent candidate for the nucleation of Au clusters. In general, there has been a consensus that the vacancies at the surface of MgO can act as a nucleation site. However, recently, this conclusion has been questioned by Bogicevic and Jennison [27,28], for the case of Pt and, in general, for transition metals located at the right of the periodic table. It was shown that oxygen vacancies do not promote but rather inhibit nucleation of Pt dimers, leaving an open question on the nature of the nucleation sites for transition metal clusters that deserves further investigations.

In the present work, we carried out a systematic study using density functional theory to characterize the formation of copper clusters up to four atoms in size on F_s and F_s^+ centers on the MgO (100) surface. Cu is a transition metal in the right side of the periodic table and has the same electronic configuration with Au namely $n\text{d}^9(n+1)\text{s}^1$. Our key objective is to help clarify the roles of defects as nucleation centers for formation of clusters. This is done by showing how these defects can induce modifications in the electronic, geometric and chemical properties of the supported clusters compared with gas phase clusters. The paper is organized as follows. In Section 2, we give details of the calculations and of the used model. Section 3 reports results of energetic and geometric data as well as the first Ionization Potentials, (IP) values. Section 4 describes the results found for the chemical reactivity of the supported copper clusters based in the study of the Fukui function.

2. Computational details and models

The defective MgO (100) surface is modeled by an embedded cluster approach. In this approach, a cluster of $Mg_{13}O_{12}$ is selected from the MgO (100) surface to represent an oxygen vacancy where the surface oxygen atom in the center of the cluster is removed. In the embedded cluster approach, the quantum cluster is surrounded by a set of total ion model potentials (TIMP) for all Mg^{2+} ions that are nearest to any oxygen atom, and an array of point charges forming a unit cell of 1.2 nm. These TIMP and point charges ($PC = \pm 2$) are located at the lattice positions, which were taken from the experimentally determined MgO bulk structure. With these TIMP's, the artificial polarization of oxygen anions at the cluster borders can be reduced [29,30]. The Madelung potential of the remaining extended MgO surface is represented by a set of surface charges derived from the Surface Charge Representation of the External Embedded Potential (SCREEP) method [31,32].

The quantum mechanical region is treated at the Density Functional Theory level by using the BLYP exchange-correlation. In a previous work [33], it has been demonstrated that this exchange-correlation functional satisfactorily describes the electronic structure of neutral and anionic copper clusters. The copper atoms were treated by a small electron core potential, Hay-Wadt ECP and double-ξ plus polarization basis set [34], which explicitly includes the $3s^2 3p^6 3d^{10}$-$4s^1$ as active electrons. In order to improve the performance of the pseudopotential the corresponding basis set was augmented with s, p, and diffuse functions. The 6-31G(d, p) basis set was used for selected surface Mg and O atoms close to the adsorption center, namely the four surface Mg atoms and five surface O atoms around the center O atom for the perfect surface; and the four nearest neighbor surface O atoms of the oxygen vacancy. The 3-21G(d, p) basis set was used for the remaining cluster. For the hydrogen atoms the basis set 6-311G(d, p) was used.

The Cu_n ($n = 1$–4) clusters are adsorbed on an oxygen vacancy. In each case we have performed full geometry optimization of the Cu clusters on an F_s or an F_s^+ site. The optimizations were carried out starting from various initial structures.

Electronic structure calculations were carried out using the GAUSSIAN 03 program [35]. The Fukui function was evaluated using a modified version of the Top-Mod program [36,37].

Although the formulation of the condensed Fukui function has been previously described [33,38], for a complete description of our system a brief overview is given here.

Parr and Yang [39], defined the Fukui function as

$$f(\vec{r}) = \left(\frac{\delta\mu}{\delta\upsilon(\vec{r})}\right)_N \tag{1}$$

where μ is the electronic chemical potential and $\upsilon(\vec{r})$ is the external potential. The functional derivative must be at a constant number of electrons, N.

It has been shown that this derivative presents a discontinuity at integer N, and that in a first approximation the Fukui function is equal to the square of the respective frontier orbital, the HOMO, when the limit of the derivative is taken from the left, f^-, and to the LUMO when the limit of the derivative is taken from the right, f^+ [39]. In the Kohn–Sham scheme the Fukui function can be defined as [40].

$$f(\vec{r}) = \left(\frac{\delta\mu}{\delta\upsilon_{KS}(r)}\right)_N \tag{2}$$

where $\upsilon_{KS}(\vec{r})$ is the effective Kohn–Sham potential. This derivative is exactly equal to the square of the respective frontier orbital,

$$f^\alpha(\vec{r}) = |\phi^\alpha(\vec{r})|^2 \tag{3}$$