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Effects of metal–support interactions on the electronic structures of metal atoms adsorbed on the perfect and defective MgO(1 0 0) surfaces

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Abstract

The electronic structures of Ni, Pd, Pt, Cu, and Zn atoms adsorbed on the perfect MgO(1 0 0) surface and on a surface oxygen vacancy have been studied at the DFT/B3LYP level of theory using both the bare cluster and embedded cluster models. Ni, Pd, Pt, and Cu atoms can form stable adsorption complexes on the regular O site of the perfect MgO(1 0 0) surface with the binding energies of 19.0, 25.2, 46.7, and 17.3 kcal/mol, respectively, despite very little electron transfer between the surface and the metal atoms. On the other hand, adsorptions of Ni, Pd, Pt, and Cu atoms show strong interaction with an oxygen vacancy on the MgO(1 0 0) surface by transferring a significant number of electron charges from the vacancy to the adsorbed metal atoms and thus forming ionic bonds with the vacancy site. These interactions on the vacancy site for Ni, Pd, Pt, and Cu atoms increase the binding energies by 25.8, 59.7, 85.2, and 19.1 kcal/mol, respectively, compared to those on the perfect surface. Zn atom interacts very weakly with the perfect surface as well as the surface oxygen vacancy. We observed that the interaction increases from Ni to Pt in the same group and decreases from Ni to Zn in the same transition metal period in both perfect and vacancy systems. These relationships correlate well with the degrees of electron transfer from the surface to the adsorbed metal atom. The changes in the ionization potentials of the surface also correlate with the adsorption energies or degrees of electron transfers. Madelung potential is found to have significant effects on the electronic properties of metal atom adsorptions on the MgO(1 0 0) surface as well as on an oxygen vacancy, though it is more so for the latter. Furthermore, the Madelung potential facilitates electron transfer from the surface to the adsorbed metal atoms but not in the other direction.

Keywords: Magnesium oxides; DFT/B3LYP method; Oxygen vacancy; Transition metals; Adsorption

1. Introduction

Transition metals supported on oxide surfaces have broad applications in catalysis, coating for thermal applications, corrosion protection, and other technologically important fields [1,2]. Particularly, the recent discovery of enhanced catalytic activity of oxide supported metal particles in the nano range size has significantly increased the interest in understanding the fundamental aspects of metal–support interaction. Efforts have been focused on better characterizing the electronic and geometric properties of the metal–support interface [3,4]. In this respect, the MgO single crystal surface has often been used as a support for dispersed metal particles owing to its relatively well-defined surface structure and stoichiometry [5]. Shinkarenko et al. [6], Xu et al. [2], Nasluzov et al. [7], and Matveev et al. [8] have experimentally and theoretically studied the adsorption properties of different metal atoms and metal clusters deposited on the MgO(1 0 0) surface. For

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example, Cu supported by MgO crystal has been experimentally considered as the active part of catalysts for petroleum reactions [6,9]. Pd supported on MgO has the ability to trap the nitric species formed in automotive engines during the combustion of fuels under oxygen-rich conditions [4]. Sophisticated computational methods have also been shown to be quite useful as tools for providing insights into the properties of these systems [10–20]. For example, it has also been demonstrated from quantum chemistry calculations by Pacchioni and co-workers [10] that highly dispersed Pd atoms on an MgO(100) thin film exhibit high catalytic activity for the acetylene cyclotrimerization reaction.

New experimental methods developed in the last few years for the deposition and/or growth of small metal particles and nanoclusters on the well-defined face of thin films under ultrahigh vacuum (UHV) conditions make it possible to study the nature of these supported metals and metal particles as functions of the support interface and cluster size [21,22]. It is well known that point defects on a substrate have a direct influence on the properties of adsorbed species [23]. Defects not only act as catalytic centers for chemisorption of small species but also as nucleation centers for growing metal islands or clusters and can modify the catalytic activity of these adsorbed metal particles via the metal–support interaction at the interface [23–25]. For example, Ferrari et al. [10] have shown that Pd atoms deposited at the regular 5-fold coordinated sites of the MgO surface are inert for the acetylene-to-benzene cyclization and only when bound to defect sites, either low-coordinated O anions or O vacancies (Fs center) characterized by two electrons localized in this cavity, do they become catalytically active for this reaction [24,26,27]. They suggested that the large enhancement in the activity of supported Pd atoms is due mainly to the electron transfer from the cavity to the supported metal. It was found experimentally that the catalytic reactivity of metal–supported MgO crystal depends greatly on the metal cluster size [28,29], although the lateral interactions among metal atoms are critical for the growth of metals on an MgO surface [30–33]. This strongly size-dependent behavior of metal particles is related to the distinct electronic and geometric properties of the metal clusters, making this new class of materials extremely interesting for the understanding of the structure–property relationship. Therefore, studies on the activity of a single supported metal atom on the MgO surface can provide a fundamental clue for elucidating the nature of metal–support interaction and how it affects the properties of adsorbed metal particles.

Although a number of theoretical studies [8,15,18–20,34–36] using cluster and periodic models to study a number of transition metals adsorbed on the perfect and reduced MgO(100) surfaces have been reported, systematic investigations, especially, on the trends in the adsorption properties of metals in the same transition-metal period as well as in the same group, and the effects of metal–support interaction on the electronic structures of the adsorbed metal have been limited. In the present work, we carried out DFT/B3LYP calculations on Ni, Pd, Pt, Cu, and Zn atoms adsorbed on the perfect and reduced MgO(100) surfaces using both an embedded cluster and bare cluster models. Our aims are (1) to find relationships in the adsorption properties for transition metals in a same period or group, more importantly (2) to understand how metal–support interactions, in particular, an oxygen vacancy on the MgO(100) surface, affect the electronic structures of the adsorbed metal atoms; and (3) to determine the effects of the Madelung potential on the adsorption properties.

2. Computational details and models

The perfect and defective MgO(100) surfaces are modeled by both bare cluster and embedded cluster approaches. In these approaches, the clusters of an embedded $Mg_{21}O_{13}$ and a bare $Mg_{13}O_{13}$ are selected from the MgO(100) surface to represent the oxygen adsorption site since metal atoms have been known to adsorb on the five-coordinated oxygen atom on the MgO(100) surface. This cluster is treated quantum mechanically along with the adsorbate. To represent an oxygen vacancy, the surface oxygen atom in the center of the above cluster is removed. Both cluster models for the regular site (O_{5c}) and vacancy of the MgO(100) surface are shown in Fig. 1. In the embedded cluster approach, these quantum clusters are surrounded by a set of total ion model potentials (TIMP)

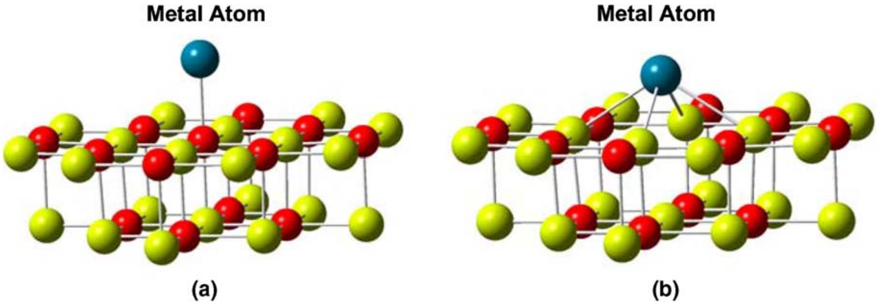

Fig. 1. Cluster models $Mg_{21}O_{13}/Mg_{21}O_{12}$ with the metals adsorbed at the adsorption center: (a) model of the perfect MgO(100) surface; (b) model of the oxygen vacancy on the MgO(100) surface.