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Theoretical study of Sn adsorbed on the MgO(100) surface with defects

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ABSTRACT

In this study, the adsorption of Sn atom at various sites on the MgO(100) surface was characterized using a theoretical approach based on density functional theory calculations. Both regular adsorption centers (O^{2-} and Mg^{2+}) and defects (such as neutral and charged O and Mg vacancies) were considered. Several key parameters for these sites with the adsorbed Sn atom were determined to provide its geometric, energetic, and electronic characterization. The interaction between Sn and the Mg vacancy sites is very strong and is associated with a relatively small distance of the adsorbed Sn atom from the surface and with a large electronic charge transfer from Sn to the surface. A much smaller strength of Sn atom adsorption is observed for the O vacancies and regular sites. Among them, the F_s^0 center binds the Sn atom strongest and, in consequence, this atom acquires a significant amount of electronic charge.

1. Introduction

Magnesium oxide (MgO) plays an important role in heterogeneous catalysis [1,2]. Its single crystal (100) surface has received a great deal of attention because this surface itself is catalytically active toward some reactions [2–4], and in addition, it can serve as a substrate for supported metal catalysts [5–9]. The (100) face is more stable in terms of its surface energy than other faces of MgO [10,11]. It is also easy to prepare [12] and possesses well-defined stoichiometry and a simple rock-salt structure that does not exhibit any significant relaxation [13,14]. Due to these features, MgO(100) constitutes a useful model surface for fundamental studies of supported metal catalysts [15]. On an MgO(100) single crystal there are always surface defects (ca. 10^{12}–10^{13} defects/cm^2) [16] that modify catalytic properties of both the surface and adsorbed metals [17]. For instance, some surface point defects, such as oxygen vacancies, trap electronic charge and thus can promote catalytic reactions through electron transfer [18]. Furthermore, it is known that metals deposited on MgO exhibit diverse catalytic properties, depending on the kind of adsorption site, whether it is a regular site or a defect [19–21].

In the field of heterogeneous catalysis, catalysts containing tin deposited on MgO have found applications in the selective hydrogenation of α,β-unsaturated aldehydes [22] and the selective dehydrogenation of alkanes [23,24]. In these catalysts, platinum is doped with tin to introduce desired promoting effects [25]. Tin in the Pt–Sn/MgO catalysts suppresses side reactions on the support surface and inhibits Pt particle sintering [22]. It is known that the activity of the Pt–Sn catalyst in butadiene hydrogenation is lower than that of the Pt catalyst but the former is more selective toward the formation of butenes, which is industrially important [26]. The presence of Sn in a catalyst may also open a new reaction path, as it happens for benzene production from acetylene on Sn/Pt(111) [27]. A promising application of tin-modified Pt catalysts for the electrooxidation of CO, formaldehyde, formic acid, and methanol was also reported [28].

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A microscopic view of metal adsorption on MgO(100) can be easily obtained from electronic structure methods based on density functional theory (DFT) [17,29]. Such methods are capable of (1) providing an electronic description of adsorption sites and (2) estimating the strength of metal–surface interactions. There are plenty of theoretical studies in which DFT calculations have been carried out to characterize metal adsorption on MgO(100), for example, Refs. [30–47]. Most of these studies are focused on the adsorption of transition metal atoms [30–44]. As compared to the large number of theoretical studies devoted to the adsorption of Pt on MgO(100) [30,32,33,37,39,40,42], little attention has been paid to the theoretical characterization of Sn adsorption on this surface. To our knowledge, one theoretical study dealing with Sn/MgO(100) is available [48]. In this study, molecular dynamics calculations were performed to simulate the wetting behavior of liquid tin on MgO(100). Similarly, there have been merely a few efforts devoted to the theoretical examination of Sn adsorption on other oxides, such as CeO_2(111) [49], Fe_3O_4(100) [50], and γ-Al_2O_3(110) [51].

The aforementioned distinct lack of electronic structure investigations of Sn/MgO(100) has encouraged us to perform DFT calculations for a series of model systems simulating a Sn atom adsorbed at various sites on the MgO(100) surface. Both regular sites (O^{2-} and Mg^{2+} surface adsorption centers) and defective sites (such as neutral and charged O and Mg surface vacancies) are taken into account. Geometric, energetic, and electronic properties of the Sn atom adsorbed at these sites are calculated in this study to characterize Sn adsorption on MgO(100) at the atomic level.

2. Computational methods

The applied computational methodology makes use of the B3LYP hybrid density functional [52–54], which has been successfully used to study metal adsorption on MgO(100) [34,35,38,39,41,42]. This functional is combined with the DFT-D3(BJ) empirical dispersion correction [55,56] to account for dispersion interactions. In a recent study of N_2O adsorption on MgO(100) [57], it was shown that this correction performed better than other kinds of Grimme's dispersion corrections proposed for B3LYP (the choice of dispersion correction is discussed further in Section S2 of Supporting Information). The regular and defective adsorption sites on MgO(100) are simulated by means of respective embedded cluster models (details can be found in Section S1 of Supporting Information). In short, stoichiometric two-layer clusters $Mg_{13}O_{13}$ are used to represent the surface O^{2-} and Mg^{2+} centers (see Fig. 1). These clusters possess the structure of an ideal MgO crystal lattice. Clusters simulating the defective sites are formed by removing the central atom or ion from the surface layer of the $Mg_{13}O_{13}$ clusters. The removal of O, O^-, O^{2-}, Mg, Mg^+, or Mg^{2+} produces a center labeled as F_s^0, F_s^+, F_s^{2+}, V_s^0, V_s^-, or V_s^{2-}, respectively (see Table 1). These labels are widely used to classify point defects on MgO [17,18]. Their superscripts indicate the formal charge of a defect, whereas their subscripts refer to defect location on the surface. All the clusters are embedded in a large array of ±2 point charges placed at the positions of an ideal MgO lattice. The positive point charges at the boundary with the clusters are replaced by total ion model potentials. A single Sn atom is adsorbed in the center of the clusters and the perpendicular distance from the Sn atom to the surface layer of clusters is optimized. During the Sn adsorption, the Mg and O atoms directly interacting with Sn are allowed to relax, whereas more distant Mg and O atoms are kept frozen. Further in this study, the denotation "Sn/site" refers to a structure with its Sn atom adsorbed at a given site on MgO(100).

For all considered clusters, their Mg and O atoms directly involved in the interaction with the Sn atom are described by the 6-31+G(d) basis set [58–60]. These atoms are surrounded by Mg and O treated with 6-31G(d). The 6-31G basis set is ascribed to the Mg and O atoms that are most distant from each adsorption center. The suitability of such a mixed basis set scheme for modeling MgO(100) by means of cluster models was confirmed in several previous works [61–63]. The total ion model potentials use the LANL2 effective core potential of Mg^{2+} [64]. The LANL08d

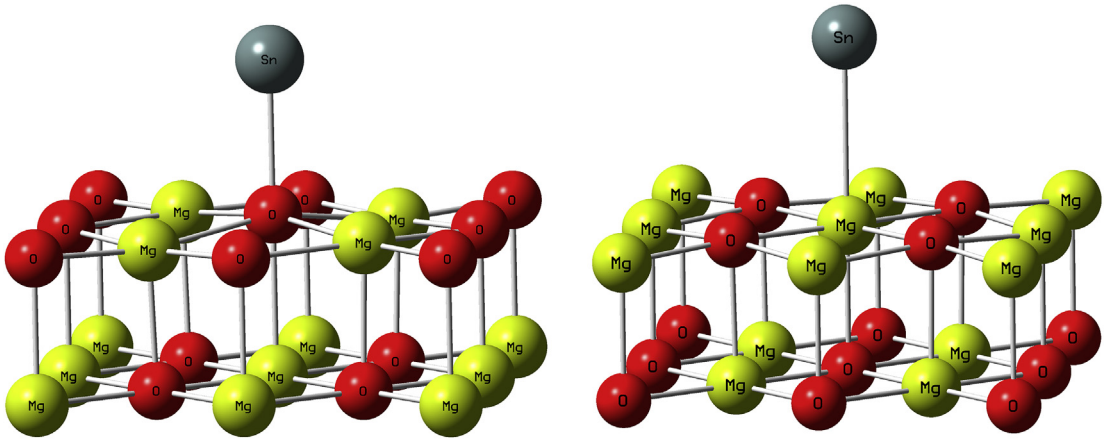

Fig. 1. $Mg_{13}O_{13}$ clusters used in the models representing the O^{2-} (left) and Mg^{2+} (right) centers. Optimized structures of the clusters with the adsorbed Sn atom are shown.