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A systematic density functional study of ordered sulfur overlayers on Cu(1 1 1) and Ag(1 1 1): Influence of the adsorbate coverage

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Abstract

The interaction of atomic S with the Cu(111) and Ag(111) surfaces has been studied using density functional calculations and periodic slab models. Relevant properties were obtained as a function of the S coverage reaching values as low as $\theta = 1/28$ ML. Some properties such as perpendicular distance from the S atom to the surface, the adsorbate net charge or the vibrational frequency for the normal model corresponding to the perpendicular distance to the surface can be considered as converged a relatively high coverage ($\theta = 1/4$ ML). However, the adsorption energy and properties related to the electronic structure of the metal substrate exhibit small but noticeable variations depending on the coverage. A particularly interesting finding is that presence of a small amount of S on the metal surface provokes significant distortions of the topmost atomic layer and induces a significant variation of the surface work function. The implications of these findings for the reactivity of the S covered Cu(111) and Ag(111) metal surfaces are discussed.
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1. Introduction

Transition metal surfaces are typical constituents of industrial catalysts and therefore have been the subject of a very large number of experimental and theoretical studies [1–3]. The catalyst surfaces are usually complex and difficult to control their composition and structure. However, extraordinary control of the surface structure and reactivity, especially for metallic surfaces, is achieved by using single crystals with well defined faces and ultra-high-vacuum conditions. In spite of the clear differences between real catalysts and single crystal surfaces, the study of the latter has proven to be extremely useful to determine active sites and to understand many important issues [4], the ultimate goal being the design of "a la carte" catalysts [5].

A typical problem encountered in many catalytic systems is deactivation of the active component, usually the metallic one, by some poisoning species. Sulfur poisoning is a paradigmatic example not only in applied catalysis [6] but also in surface science studies using single crystal surfaces and UHV conditions [7]. The presence of sulfur strongly affects many important catalytic processes such as hydrogenation, methanation, Fischer–Tropsch synthesis, steam reforming and fuel cell power production [8]. Sulfur poisoning normally occurs because atomic S, produced for instance arising from the decomposition of H_2S generated in the hydrodesulfurization treatment of crude oil, adsorbs very strongly on the metallic surface thus preventing or modifying further adsorption of reactant molecules [9]. Nevertheless, in a number of industrial processes one may wish to intentionally modify the catalyst to improve its selectivity. We mention for instance the addition of S and P to Ni catalysts to improve isomerization selectivity

in the fats and oils hydrogenation industry [8]. Addition of S to single crystal surfaces has also been used to modify the selectivity of several surface reactions [10]. A particular case where S acts as a promoter instead of as a poison is the chemoselective catalytic hydrogenation of crotonaldehyde either on practical Cu dispersed catalysts [11] or on single crystal Cu(1 1 1) [12]. Lambert et al. found that 100% conversion of adsorbed crotonaldehyde into crotyl alcohol is achieved at very low sulfur coverage; this rather curious effect has been attributed to a direct interaction between the organic molecule and the adsorbed S atom [13]. Interestingly enough, adding S to Cu(1 1 1) also promotes bonding of unsaturated hydrocarbons [14]. Finally, theoretical studies have also shown that addition of S to Cu(1 1 1) makes water dissociation on that surface more difficult whereas addition of S to Au(1 1 1) promotes it [15].

The discussion above strongly suggests that electronic properties of sulfur on Cu(1 1 1) and, in particular, the role of S coverage may be crucial and needs to be understood. Several studies have been focused on the study of the S on Cu(1 1 1) using a variety of experimental (LEED, STM, NIXSW, SEXAFS and SXRD) techniques [16–23]. However, a difficulty appearing in the experiments is the tendency of this system to strongly reconstruct and to exhibit disordered overlayers [24]. In fact, at room temperature a well ordered $(\sqrt{7} \times \sqrt{7})R19.1°$-S structure is observed with a S coverage of 0.43 [16–19,23]. The atomic structure of this overlayer has been the subject of some debate although nowadays it seems quite clear that it involves two different layers of sulfur atoms; the inner layer consisting of S atoms at hollow sites of an unreconstructed (1 1 1) surface and the upper layer involving Cu_4S clusters with the S atoms directly on top of a Cu atom of the unreconstructed surface [19,25]. A $(\sqrt{7} \times \sqrt{7})R19.1°$-S ordered overlayer appears to be stable in electrochemical conditions although the corresponding structure is not yet completely resolved [26]. The formation of a $(\sqrt{7} \times \sqrt{7})R19.1°$-S structure with S coverage of 0.43 has been also observed on Ag(1 1 1) but the resulting atomic structure is also complex with a triplet of sulfur atoms in the unit cell [27]. Low coverage structures with a defined periodicity could be studied at sufficiently low temperatures although these experiments may be rather involved. Alternatively, one can make use of theoretical model systems which permits one to study the changes in the electronic structure and in the structural properties of S on these metal surfaces with respect to adsorbate coverage. In the present work, we make use of this strategy and present a systematic periodic density functional study of the interaction of S on Cu(1 1 1) and Ag(1 1 1) surfaces focusing, in particular, in the change of S related properties with coverage. To this end we use different types of unit cells covering a broad number of situations including rather low coverage regimes and analyze in details the properties of adsorbed sulfur. We will show that while some properties such as perpendicular distance from the S atom to the surface, net charge on the S atom or vibrational frequency for the normal mode corresponding to the perpendicular distance to the surface can be considered as converged at a relatively high coverage ($\theta = 1/4$ ML), the electronic properties of the underlying metal substrate exhibit small but noticeable variations depending on coverage. The implications of these findings for the reactivity of the S covered Cu(1 1 1) and Ag(1 1 1) metal surfaces are discussed.

2. Surface models and computational details

The Cu(1 1 1) and Ag(1 1 1) surfaces were modeled using a periodic slab model. The slabs contain four atomic layers with a 12 Å vacuum width between the vertically repeated slabs. Different unit cells were employed to represent different degrees of S coverage on these metal surfaces. The unit cells were always constructed from the optimized lattice parameter, as usual, within the density functional method described below. The optimized lattice parameters for the bulk metals yield 363.2 (361.5) and 415.9 (408.5) pm for Cu and Ag, respectively, with the experimental data [28] given in parentheses. Two different types of unit cells were used having either the same symmetry as the naked surface unit cell (primitive or p) or the one corresponding to the $(\sqrt{7} \times \sqrt{7})R19.1°$-S structure. In all cases a single S was placed at the fcc or on the hcp threefold hollow sites of the corresponding surface model. The following primitive supercells have been considered: p(1 × 1), p(2 × 1), p(2 × 2), p(3 × 3) and p(4 × 4) which represent situations with S coverage of 1, 1/2, 1/4, 1/9 and 1/16 ML, respectively. Following the same strategy, $(\sqrt{7} \times \sqrt{7})R19.1°$, $(\sqrt{7} \times 2\sqrt{7})R19.1°$ and $(2\sqrt{7} \times 2\sqrt{7})R19.1°$ supercells were constructed which correspond to sulfur coverage of 1/7, 1/14 and 1/28 ML, respectively. For the largest $(2\sqrt{7} \times 2\sqrt{7})R19.1°$ supercell modeling a coverage as low as 0.036, the slab model contains 112 metal atoms. Representative examples of these supercell surface models are displayed in Fig. 1. The adsorption energy (E_{ads}) is defined in the standard way as

$$E_{ads} = E_{slab} + E_S - E_{slab+S} \qquad (1)$$

where E_{slab} is total energy of the naked surface supercell, E_S is the total energy of the sulfur atom and E_{slab+S} is the total energy of the slab with one sulfur atom in either fcc or hcp sites. The S atomic energy was computed without imposing symmetry. However, the difference between the energy difference with respect to the symmetric solution obtained by computing S in a cubic box and hence having p orbitals threefold degenerated is of 0.04 eV only. The total energies in Eq. (1) correspond to the optimized geometries using the PW91 exchange correlation functional [29] within the generalized gradient approach (GGA) implementation of density functional theory. In all models, the two outermost metallic layers and the position of S above the surface have been allowed to relax. The electron density has been expanded in a basis of plane waves with cutoff energy below 415 eV and the effect of core electrons in the total density has been taken into account by means of the projector