

Adsorption of Alkanethiols on Coinage Metals. A Density Functional Theory Investigation

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Alkanethiols have been widely investigated on gold surfaces because of the tendency of thiolate species to form self-assembled monolayers (SAMs). On more active metals such as copper, the formation of SAMs has been less investigated either in solution or in ultrahigh vacuum (UHV). The protective nature of the monolayers against the copper oxidation was recognized from the early studies [1]. The structures of 1-octanethiol [2] observed on Cu(111) at room temperature by STM were strikingly similar to those for methanethiolate [3] on this surface. This behavior was attributed to a significant stronger sulfur-metal bond of the thiolates to Cu(111) indicating that the interaction potential is more corrugated by the substrate periodicity than in the case of gold surfaces [2]. The S-C bond was found to be oriented considerably closer to the surface normal on Cu than on Ag which was interpreted in terms of a higher ionicity of the sulfur-copper bond [4].

The above studies show that the sulfur-metal bond plays an important role in the formation of alkanethiol monolayers. However, the nature of this bonding has not been investigated yet systematically on the coinage metals. Ab initio investigations have been mainly restricted to gold [5-7] and there are some reports on Pd(111) [8], Pt(111) [8] and Ni(111) [9].

In the present communication we investigated systematically the adsorption of n-alkanethiols (with n=1, 2 and 3) on the 111 surface of copper, silver and gold using density functional theory (DFT). The Kohn-Sham equations were solved in the so-called DFT-GGA approximation. The Vosko-Will-Nusair [10] form of the local density approximation (LDA) was used, and the generalized gradient approximation (GGA) was employed by including self-consistently the Perdew and Wang functionals [11] which give non-local gradient corrections for the exchange and correlation parts of the total electronic energy.

Two approaches were employed to model the metal surface. For studies in the low coverage limit the surface was modelled using metal clusters of about thirty atoms distributed in three layers. On the other hand, the high coverage situation was modelled under periodic conditions using three-layer metal slabs.

The nature of the chemical bond was investigated using several tools such as the total and projected density of states, electron density difference plots, Mulliken populations, etc. The sulfur metal bond is more ionic on copper than on gold. Under low coverage conditions, the binding energies of the alkanethiol radicals (RS·) are rather insensitive to the chain length. Binding energies

are around 50 kcal/mol on the coinage metals.

Under low coverage conditions, the potential energy surfaces for the alkanethiol-surface interaction were calculated on the fcc hollow, hcp hollow, ontop and bridge sites. For each sulfur-surface distance, the atoms of the alkyl chain as well as the metal atoms in the primary chemisorption site were relaxed. Thus, the different contributions to the binding energy were determined.

The periodic slab calculations were used to investigate the adsorption of methanethiol with a ($\sqrt{3} \times \sqrt{3}$) R30° structure on the 111 surface. The adsorbates were placed on the fcc hollow sites. The density of states around the Fermi energy was investigated and STM images were simulated for different bias voltages and different planes above the surface using the Tersoff and Hamann approximation [12].

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