

Thiolates on copper surfaces: equilibrium, dynamical, and stress induced properties

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Using DFT techniques in both static and dynamics modes we study short-chain thiolates adsorbed on Cu surfaces. For Cu(111) surface at low temperature and higher coverage we find the unsymmetrical bridge site to be energetically favorable. Our results resolve the ambiguity of interpretation of experimental results concerning the Cu–S bond length [1] (hollow v.s. bridge site). The S–C bond energy of 3.28 eV of the free CH₃–S is significantly weakened to 1.26 eV after adsorption [1], again consistent with experiments showing thermal desorption of the CH₃ group already at room temperature. Thiolate adsorption on the Cu(100) was also studied [2]. This phase resembles locally the reconstructed high-temperature phase of thiolated Cu(111). Finally we analyze the adsorbed molecule under stress which emulates conditions arising when the molecule is manipulated by a static AFM tip. Experimental results indicate that, at variance with other coinage metals surfaces, the C–S bond is ruptured [1,3]. Preliminary simulations with both cluster and slab models of the surface are used to simulate the bond rupture. Combination of stress and electric field are envisaged for future studies.

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