

Oxygen adsorption on flat and stepped Ag surfaces

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We present the results of a theoretical study aimed to understand the role of steps on the adsorption and dissociation of oxygen on Ag(001). We focus on energetics and structures of molecular oxygen on Ag(001) and of atomic and molecular oxygen on Ag(410). Our calculations are based on density functional theory (DFT) within the generalized gradient approximation. We use a plane-wave basis and ultrasoft pseudopotentials.

Atomic O adsorption on Ag(001) has been recently investigated [1], but no DFT calculation exists for the O₂ molecule on this surface. Our results show that the most stable adsorption site is the four-fold hollow site, with the O–O axis parallel to the surface. This chemisorbed state has a chemisorption energy of about 0.5 eV and is characterized by a substantial increase of the O–O bond length (1.44 Å) compared to the gas phase value (1.24 Å) and no magnetic moment. We show that these features are due to the charge transfer from the substrate to the oxygen π^* anti-bonding orbital.

In order to understand of the role of steps we consider the Ag(410) surface which consists of three-atom-row wide (100) terraces and (110) steps. Our results for the atomic O adsorption on this surface show that at low coverage [(2×1) geometry] the hollow sites on the terraces are the most stable chemisorption sites. At higher coverage [(1×1) geometry] oxygen atoms decorate the upper side of the (110) steps. We discuss a possible explanation of these results.

[1] G. Cipriani, D. Loffreda, A. Dal Corso, S. de Gironcoli and S. Baroni, *Surf. Sci* **501** (2002) 182.