

Water and hydroxyl adsorption on hematite $\alpha\text{-Fe}_2\text{O}_3$ (0001) surface

Tomasz Pabisiak, Adam Kiejna

Institute of Experimental Physics, University of Wrocław, plac M. Borna 9, 50-204 Wrocław, Poland
pabi@ifd.uni.wroc.pl

The interaction of water and hydroxyl with iron oxide surfaces is an important issue, related to the incipient stages of catalytic processes occurring on the oxide surface. We report results of our studies of adsorption of single water and hydroxyl molecules on the two most stable [1] terminations of $\alpha\text{-Fe}_2\text{O}_3$ (0001) surface using density functional theory (DFT+ U) and including correction for the van der Waals interaction. The influence of adsorbed H_2O and OH molecules on the structural, energetic, and electronic properties of both iron- and oxygen-rich terminations of hematite surface is examined. It is found that tilted orientations of molecules are energetically favored, because additional hydrogen bond stabilizes molecules on the surface. Bonding of water is more than 1 eV weaker than OH, and adsorption on the iron termination is ~ 0.3 eV stronger than on the oxygen-terminated surface. Inclusion of the van der Waals interactions yields the same geometries of the molecules on the surface, but increases the adsorption energy by about 10%. In general, with increasing adsorbate coverage the adsorption energy decreases, regardless the type of considered molecule or the substrate termination. On the O-terminated surface increasing amount of either H_2O or OH decreases the work function of the system by 0.2-0.8 eV, relative to the adsorbate-free surface. On the Fe-termination the work function upon adsorption of water decreases more than 0.5 eV with coverage, while significantly increases about 2.7 eV when surface is decorated with adsorbed hydroxyls. The work function is a sensitive property of the surface and provides also information about charge rearrangement in the system. On the Fe-terminated surface adsorbed water and hydroxyl molecules lose some charge, respectively about 0.02 and 0.30 e. This trend is reversed in case of adsorption on oxygen termination, and gives 0.38 e for H_2O and 0.20 e for OH. The majority of charge is transferred to substrate atoms and may also vary with the coverage. Changes in the magnetic and electronic structure for particular surface terminations with respect to the adsorbed H_2O and OH will be also discussed.

References:

[1] A. Kiejna, T. Pabisiak, J. Phys.: Condens. Matter **24**, 095003 (2012).