Carboxylic acid on Fe_3O_4 surfaces - new insights from theory and experiment

Kai Sellschopp[1], Björn Arndt[2,3], Marcus Creutzburg[2,3], Heshmat Noei[2], Andreas Stierle[2,3], Stefan Müller[1], Gregor Feldbauer[1]

[1]*Institute of Advanced Ceramics, Hamburg University of Technology, Denickestraße 15, 21073 Hamburg, Germany*
[2]*DESY NanoLab, Deutsches Elektronen-Synchrotron,* Notkestraße 85, 22607 Hamburg, Germany
[3]Physics Department, University of Hamburg, Jungiusstraße 9-11, 20335 Hamburg, Germany
gregor.feldbauer@tuhh.de

The adsorption of organic molecules on magnetite (Fe_3O_4) surfaces is of high interest in diverse fields, ranging from environmental science to catalysis and from biomedicine to material science [1]. As a specific example, magnetite nanoparticles linked via organic acids are able to form hybrid materials exhibiting exceptional mechanical properties [2]. For such applications a detailed understanding of atomistic surface processes is crucial. The structure of the major surfaces of magnetite, namely the (001) and (111) surfaces, has been a matter of debate for a long time. For the clean (001) surface the debate seems to be settled since the subsurface cation vacancy (SCV) reconstruction was found [3]. The termination of the (111) surface has also been a matter of substantial controversy, here new insights have been reported recently [4]. For (001), the associated sqrt(2) x sqrt(2) diffraction pattern changes, however, to a 1x1 pattern upon adsorption of carboxylic acids [5]. In oder to understand this structural change, we investigated the energetics of formic acid adsorption for this system and the implications for surface stability using density functional theory (DFT) calculations. The computational results are compared to surface X-ray diffraction (SXRD) measurements. Furthermore, the analysis of different adsorption sites and the electronic structure gives insight into the mechanisms of this structural change. In addition to the already mentioned computational and experimental methods, also the vibrational behaviour was investigated for the adsorption on the (111) surface to complement infrared spectroscopy experiments. According to our findings, adsorption of carboxylic acids may also affect the termination of the magnetite (111) surface.

References:

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