Water and Organic Molecules on Magnetite Single Crystal Surfaces

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Magnetite (Fe_3O_4) is a very important and diverse transition metal oxide with applications in catalysis, data storage and biomedical imaging. In a recent study magnetite nanoparticles linked by oleic acid molecules show exceptional isotropic mechanical properties [1]. It was demonstrated by FT-IR spectroscopy that the oleic acid molecules remain stable on the particle surface until 350°C at which crosslinking of the organic phase starts and a formation of well defined (111) and (100) facets sets in. The adsorption mechanism and adsorption-induced near surface structural changes however still remain unknown. The interface between the oleic acid molecules and the distinct facets of the magnetite nanoparticles is essential for an understanding of the advanced mechanical properties. To give further insight on how these nanoparticles interact with organic molecules it is crucial to study the structure and adsorption behavior at magnetite single crystal surfaces. The focus is on the surface orientations (111) and (001) since they are also present on the nanoparticle facets. The (111) surface of magnetite has six possible bulk terminations (fig. 1), which can be divided into two oxygen-terminated (O1 and O2) and four iron-terminated surfaces (tet1, oct1, tet2, oct2). The correct termination of the clean surface structure is still under debate. Previous LEED *I-V* studies favor the Fe_{tet1} termination with 6 Å distance between neighboring iron atoms [2]. Recent studies on the water adsorption on magnetite (111) however support the Fe_{oct2} termination [3].

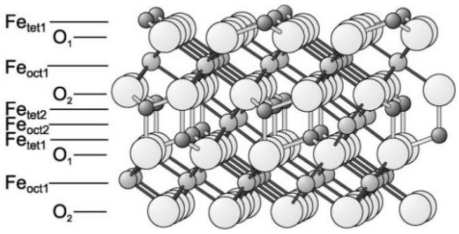

Fig. 1: Bulk terminations of magnetite (111) [2]

We investigated the clean surface structure of magnetite (111) by STM. The surface presents flat terraces with a step height of 4.8 Å. This is exactly the length of repetition of the different terminations and indicates a homogeneous termination. Formic acid adsorption on the magnetite (111) surface was studied by XPS and FT-IR spectroscopy. We find that the molecule dissociates on the surface. Formic acid binds to the surface in bidentate and monodentate configuration which is different to the (001) surface, where only bidentate adsorption was observed [4].

Furthermore we show results on the adsorption of water and organic molecules like formic acid and oleic acid on magnetite (111) under UHV conditions obtained by FT infrared spectroscopy and X-ray photoemission spectroscopy. These findings are complemented by surface X-ray diffraction data obtained at Soleil Synchrotron.

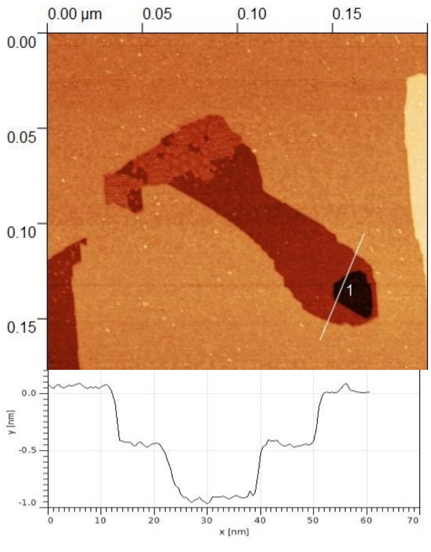

Fig. 2: 200x200 nm^2 STM image of clean magnetite (111), line profil shows 4.8 Å step height

References:
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