O 55: Focus Session: Structure and Chemistry of Metal-Oxide Surfaces II

Time: Wednesday 10:30–13:00 Location: MA 005

O 55.1 Wed 10:30 MA 005

Coverage-Dependent Water Agglomerates on Fe$_3$O$_4$(001): insights from theory — •Matthias Meier[1,2], Jan Hulva[1], Zdeněk Jakub[1], Jiří Pavelec[1], Martin Setvin[1], Michael Schmid[1], Ulrike Diebold[1], Cesare Franchini[2], and Gareth S. Parkinson[1] — [1]Institute of Applied Physics, Technische Universität Wien, Vienna, Austria — [2]University of Vienna, Faculty of Physics and Center for Computational Materials Science, Vienna, Austria

Iron oxides are used in a wide range of applications in which their surfaces interact with water. Recent studies have found significant complexity with mixed-mode adsorption and coverage dependent hydrogen bonding. This study focuses on Fe$_3$O$_4$(001) and its interaction with water. Temperature programmed desorption (TPD) and noncontact atomic force microscopy (ncAFM) are combined with density functional theory (DFT) based calculations.

Quantitative TPD spectra reveals 4 distinct peaks for the desorption of the first monolayer of water, suggesting that stable configurations of water exist. Surfaces with the in the TPD relevant water coverages were prepared and studied in a CO functionalised tip ncAFM experiment. These results will be presented in a previous talk.

DFT predicts partially dissociated dimers and trimers located on Fe cations to be found to be the most stable configurations, in-line with the known concept of cooperativity. The ring-like networks observed in ncAFM, correspond to merged trimers which are connected via additional hydrogen bonded water molecules. The formation of these features is motivated by optimizing available hydrogen bonds.

O 55.2 Wed 10:45 MA 005

cooperative formation of long-range ordering in water ad-layers on fe3o4(111) — •francesca mirabella[1], eman zaki[1], francisco ivars-barcelo[1], jan seifert[1], xiaoke li[2], joachim paier[2], joachim sauer[2], shamil shaikhutdinov[1], and hans-joachim freund[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany — [2]Humboldt Universität zu Berlin, Berlin, Germany

Adsorption of water on magnetite surfaces has intensively been investigated on both single crystals and well-ordered epitaxial films. The initial stage of water adsorption on Fe3O4(111) surfaces remains poorly understood. In this work, we re-examined the water adsorption models on well-characterized Fe3O4(111) films, employing TPD, IRAS, and single crystal microcalorimetry. TPD data revealed sharp desorption peaks in the region 200-300 K. Each desorption peak, showing a first order kinetics, is associated with individual desorption of molecularly adsorbed water molecules having discrete adsorption energies. Both TPD and microcalorimetry results show that the desorption energy considerably decreases at increasing water coverage, from ~100 to ~50 kJ/mol. Also, combined IRAS and TPD measurements suggest that, before the formation of ASW sets in, water readily dissociates on the surface to form two hydroxyl species, involving oxygen atoms from the water itself and from the oxide surface, respectively. These species act as anchors for molecular water which self assemble into a (2x2) ordered structure. The results are rationalized by DFT in the framework of cooperative formation of the hydrogen bonding network.

O 55.3 Wed 11:00 MA 005

Water adsorption on magnetite — Francesca Mirabella[1], Eman Zaki[1], Francisco Ivars-Barcelo[1], Xiaoke Li[2], •Joachim Paier[2], Shamil Shaikhutdinov[1], Joachim Sauer[2], and Hans-Joachim Freund[1] — [1]Fritz-Haber-Institut-der-Max-Planck-Gesellschaft, Berlin, Deutschland — [2]Humboldt-Universität zu Berlin, Deutschland

Fe3O4(001), well known as one of the natural growth facets of the magnetite iron oxide phase, has been recently resolved by Diebold and Parkinson. With respect to the molecular structure of water on that surface, much transferable knowledge has been generated by the pioneering work of Diebold on TiO2 as well as ZnO.

Regarding the Fe3O4(111) surface, its termination was resolved by Freund and coworkers using LEED-I/V resulting in a model with a very small R factor of 0.14. It involves a single Fe cation in its outermost atomic layer. The termination has been confirmed by a combined IRAS and DFT study using CO as a probe molecule. Recently a unique (2x2) long-range ordered structure in water adlayers on Fe3O4(111) has been studied by LEED and TPD. Upon determining relevant water ad-structures starting from 1/4 ML up to one ML coverage using DFT, the TPD can be understood. In the initial stages of H2O adsorption, individual molecules dissociate creating terminal water-related Ow-H and surface Os-H groups, serving as anchors for additional water molecules ordering via H-bonding and thus forming a (2x2) 2D structure. Adsorption energies of the modelled structures cluster in three characteristic regimes corresponding well to observed peak temperatures.

O 55.4 Wed 11:15 MA 005

Benchmarking DFT calculations for metal oxides: geometric adsorption site of copper and silver adatoms on magnetite — Matthias Meier[1,2], Zdenek Jakub[2], Jan Balajka[2], Jan Hulva[2], Roland Bliem[2], Pardeep K Thakur[3], Tien-Lin Lee[3], Cesare Franchini[1], Michael Schmid[2], Ulrike Diebold[2], Francesco Allegretti[4], •David A Duncan[3], and Gareth S Parkinson[2] — [1]University of Vienna, Vienna, Austria — [2]Technical University of Vienna, Vienna, Austria — [3]Diamond Light Source, Didcot, UK — [4]Technical University of Munich, Munich, Germany

Single-site catalysis is a promising field for studying model catalytic reactions. However, to gain true insight into the inner workings of any system, it is necessary to be able to reliably model it with theoretical calculations, and to benchmark these calculations with stringent quantitative experimental constraints. In this work we utilised X-ray standing waves (XSW) to benchmark density functional theory (DFT) calculations of one such system: single adatoms on the Fe3O4(001).

Although the clean surface structure is known [1], the geometry of the adatoms has only been probed by non-quantitative techniques, which do not provide suitable benchmarks for theoretical calculations. The surface structure of Ag and Cu adatoms was directly determined by XSW to occupy the same lateral site at a height of 0.43 Å and 0.96 Å, respectively. The commonly used DFT+U formalisations overpredicted lattice constant, but underpredicted the adatom adsorption height, raising significant questions on its applicability to this system.

[1] R. Bliem, et al., Science 346, 1215 (2014);

O 55.5 Wed 11:30 MA 005

Direct detection of Ni adatoms being driven subsurface on Fe3O4(001) — •Paul T. P. Ryan[1,2], Zdeněk Jakub[3], Jan Balajka[3], Jan Hulva[3], Roland Bliem[3], Pardeep K. Thakur[2], Tien-Lin Lee[2], Francesco Allegretti[4], David J. Payne[1], David A. Duncan[2], and Gareth S. Parkinson[3] — [1]Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ — [2]Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0QX UK — [3]Institute of Applied Physics, TU Wien, 1040 Vienna, Austria — [4]Physics Department E20, Technical University of Munich, 85748 Garching, Germany

Iron oxides are the archetypal cation defect material. For magnetite (Fe$_3$O$_4$) these cation vacancies can play an important role in its surface chemistries. Specifically, Fe$_3$O$_4$ has been observed to pattern the adsorption of a wide range of metal adatoms onto its (001) surface, where two sub-surface octahedral vacancies and one surface tetrahedral interstitial kinetically hinder the sintering of metal adatoms into nanoparticles. Despite this, STM observations of several first row transition metals, e.g. Ni and Co, suggest that these adatoms can be thermally driven into the subsurface octahedral vacancies [1]. Here we present an X-ray standing wave (XSW) study directly demonstrating the co-existence of Ni in a surface tetrahedral site, a subsurface octahedral site and a bulk octahedral site confirming the interpretation of previous STM measurements and quantitatively probing the vertical displacement of the Ni atoms at each location.

[1] R. Bliem, et al. Phys. Rev. B, 92 (2015) 075440

O 55.6 Wed 11:45 MA 005

Adsorption of formic acid on the (001) surface of Fe3O4 studied by surface x-ray diffraction — •Björn Arndt[1,2], Marcus Creutzburg[1,2], Vedran Vonk[1], Elin Graanaes[1], Konstantin Krausert[1,2], Kai Sellschopp[3], Gregor Feldbauer[3], and Andreas Stierle[1,2] — [1]Deutsches Elektron-Synchrotron (DESY) — [2]University of Hamburg — [3]Institute of Advanced Ceramics, Hamburg University of Technology

The clean (001) surface of magnetite shows a $(\sqrt{2}x\sqrt{2})R45°$ surface reconstruction which gets lifted by certain adsorbates, one of them being formic acid. Although the structure of the reconstructed surface is solved with all evidence supporting the SCV model [1,2], the structure of the unreconstructed surface and the lifting mechanisms are still unknown. Formic acid allows the preparation of a nicely defined surface since it only adsorbs up to a coverage of two molecules per unit cell [3]. It also raises interest as a intermediate in the water-gas shift reaction which magnetite catalyzes, and as a model for the surface interaction of longer organic acids with magnetite. In order to get information on the structure of the surface after formic acid adsorption, we investigated it by surface x-ray diffraction measured at the ID03 beamline of the ESRF before and after dosing of formic acid. We present our results on the structure of the unreconstructed surface, compare them to DFT calculations and give insights into the lifting mechanism.

[1] Bliem, R. et al. Science. 346, 1215-1218 (2014)
[2] Arndt, B. et al. Surf. Sci. 653, 76-81 (2016)
[3] Gamba, O. et al. J. Phys. Chem. C 119, 20459-20465 (2015)

O 55.7 Wed 12:00 MA 005

Structural changes in Fe_3O_4 surfaces upon adsorption of organic acids - a DFT study — •Kai Sellschopp[1], Björn Arndt[2,3], Marcus Creutzburg[2,3], Andreas Stierle[2,3], Stefan Müller[1], and Gregor Feldbauer[1] — [1]Institute of Advanced Ceramics, Hamburg University of Technology — [2]DESY NanoLab, Deutsches Elektronensynchrotron, Hamburg — [3]Physics Department, Hamburg University

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 [1]. The associated $\sqrt{2} \times \sqrt{2}$ diffraction pattern changes, however, to a 1×1 pattern upon adsorption of carboxylic acids [2]. In oder to understand this structural change, we investigated the energetics of adsorption for this system and the implications for surface stability using density functional theory (DFT) calculations. Furthermore, the analysis of different adsorption sites and the electronic structure gives insight into the mechanisms of this structural change. Finally, DFT results are compared to surface X-ray diffraction (SXRD) measurements. According to our findings, adsorption of carboxylic acids may also affect the termination of the magnetite (111) surface.

[1] R. Bliem et al., *Science* **346** (6214), 1215-1218, 2014
[2] O. Gamba et al., *J. Phys. Chem. C* **119** (35), 20459-20465, 2015

Invited Talk O 55.8 Wed 12:15 MA 005

Growth and surface chemistry of rutile IrO2(110) — •Jason Weaver — University of Florida, Gainesville, FL, USA

Interest in the surface chemistry of late transition-metal oxides has been stimulated by observations that the formation of metal oxide layers tends to dramatically alter the catalytic performance of transition metals in applications of oxidation catalysis. In this talk, I will discuss our recent investigations of the growth and chemical properties of rutile IrO2 surfaces. I will discuss our studies of the oxidation of metallic Ir surfaces by O-atom beams as well as O2 at pressures above 1 Torr. We find that stoichiometrically-terminated IrO2(110) layers could only be formed by oxidizing Ir(111) and Ir(100) at sufficiently high temperature and O2 pressure. I will also discuss our recent discovery of highly facile methane and ethane activation on the IrO2(110) surface at temperatures as low as 150 K and the subsequent oxidation chemistry.

O 55.9 Wed 12:45 MA 005

Determining the structure of nitrogen doped rutile TiO2(110) — •Francesco Allegretti[1], Michael Wagstaffe[2], David A. Duncan[1,3], Tien-Lin Lee[3], Johannes V. Barth[1], Andrew G. Thomas[2], and Rob Lindsay[2] — [1]Physik-Department E20, Technische Universität München, Germany — [2]School of Materials, University of Manchester, United Kingdom — [3]Diamond Light Source, Didcot, United Kingdom

Titanium dioxide is the prototypical photocatalyst for water cracking, however its wide band gap (>3 eV) means that it only utilises a small percentage of natural sunlight. One approach to narrowing this band gap, to allow more efficient solar water cracking, is the deliberate doping of TiO2 with impurities [1]. Notably, using nitrogen as the dopant leads to a significant enhancement of the photocatalytic functionality under visible light irradiation [2]. Previous angular scanned photoelectron diffraction measurements [3] have suggested that these N3+ ions occupy O2- sites in the bulk unit cell, however the level of agreement, both between O 1s and N 1s core-level data and between theory and experiment was only qualitative. Here we present an X-ray standing wave study of N-doped rutile TiO2(110) that directly demonstrates that the majority of N3+ ions do indeed occupy O2- sites, however a minority bulk-like component with strongly different site was also observed.

[1] Z. Wang, et al., Phys. Chem. Chem. Phys. 16, 2758 (2014) [2] J. Tao, et al., J. Phys. Chem. C 118, 994 (2014) [3] M. Batzill, et al., Chem. Phys. 339, 36 (2007)