

O 55: Metal Oxide Surfaces III: Adsorption and Reactivity

Time: Wednesday 15:00–17:45

Location: H5

O 55.1 Wed 15:00 H5

Determination of the co-adsorption site of formate and hydroxyls on Fe₃O₄(001) — ●PAUL T. P. RYAN^{1,2}, TIEN-LIN LEE¹, DAVID J. PAYNE², and DAVID A. DUNCAN¹ — ¹Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0QX UK — ²Department of Materials, Imperial College London, Exhibition Road, London SW7 2AZ

Magnetite nanoparticles are a popular substrate for biofunctionalization, due to their low toxicity and their magnetic moment. These bio-functional materials are typically linked to magnetite via a carboxylate anchoring group. Thus, understanding the adsorption of formic acid on Fe₃O₄(001) finds continued interest.

A previously published STM and LEED study[1] and unpublished SXRD results[2] show that formic acid dissociatively adsorbs onto the Fe₃O₄(001) surface at room temperature, resulting in adsorbed formate and hydroxyl species. The prior SXRD measurements clearly indicate bidentate coordination of the formate species, but is insensitive to the surface hydroxyl, whose presence may play a fundamental role in the surface chemistry of Fe₃O₄(001).

We have exploited the chemical sensitivity of the photoelectron diffraction and X-ray standing wave techniques to directly probe the adsorption of the hydroxyl species, and how it relates to the reconstruction of the magnetite surface. [1] O. Gamba, et al., *J. Phys. Chem. C* 2015, 119, 35, 20459-20465 [2] B. Arndt, et al., O 55.6 DPG 2018 Berlin

O 55.2 Wed 15:15 H5

Carboxylic acids on magnetite surfaces: insights from DFT — ●KAI SELLSCHOPP¹, BJÖRN ARNDT^{2,3}, MARCUS CREUTZBURG^{2,3}, HESHMAT NOEI², ANDREAS STIERLE^{2,3}, STEFAN MÜLLER¹, and GREGOR VONBUN-FELDBAUER¹ — ¹Institute of Advanced Ceramics, Hamburg University of Technology — ²DESY NanoLab, Deutsches Elektronensynchrotron, Hamburg — ³Physics Department, Hamburg University

Magnetite (Fe₃O₄) is a versatile material with applications ranging from catalysis over decontamination of water to hybrid materials made from magnetite nanoparticles with organic linker molecules.^{1,2} The structure of and interaction with the major surfaces of magnetite plays a crucial role in most of these applications. In this presentation recent work on the adsorption of organic acids at the magnetite (001) and (111) surfaces studied with density functional theory (DFT) is shown. The mechanism behind the structural change of the magnetite (001) surface upon exposure to formic acid is elucidated from a thermodynamics point of view and by comparison to experimental data from surface X-ray diffraction (SXRD). Calculating the vibrational modes, we find that this structural change in turn also affects the vibrational spectrum of the molecule adsorbed at the surface, which also fits to infrared spectroscopy data. Finally, first results on the adsorption of formic acid at the magnetite (111) surface are shown.

[1] G. Parkinson, *Surf. Sci. Rep.* **71**, 272-365 (2016)

[2] A. Dreyer et al., *Nature Materials* **15**, 522-528 (2016)

O 55.3 Wed 15:30 H5

Adsorption of Carboxylic Acids on Magnetite Single Crystal Surfaces — ●MARCUS CREUTZBURG^{1,2}, HESHMAT NOEI¹, BJÖRN ARNDT^{1,2}, VEDRAN VONK¹, ELIN GRÄNÄS¹, KAI SELLSCHOPP³, GREGOR VONBUN-FELDBAUER³, and ANDREAS STIERLE^{1,2} — ¹DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — ²Fachbereich Physik, Universität Hamburg — ³Institute of Advanced Ceramics, Hamburg University of Technology

Magnetite (Fe₃O₄) is an 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]. To give further insight on how these nanoparticles interact with organic molecules, it is crucial to study the flat single crystal surfaces. In this contribution, we present surface X-ray diffraction results in combination with infrared reflection absorption spectroscopy, X-ray photoelectron spectroscopy and scanning tunneling microscopy to investigate the clean magnetite (111) surface and study the adsorption of formic acid and oleic acid on the magnetite (111) and (001) surfaces under UHV conditions.

[1] A. Dreyer et al., *Nature Materials* **15**, 522-528 (2016)

O 55.4 Wed 15:45 H5

Adsorption of molecules on KTaO₃ (001) and their coupling to the 2D electron gas — ●ZHICHANG WANG, IGOR SOKOLOVIC, MICHAEL SCHMID, MARTIN SETVIN, and ULRIKE DIEBOLD — Institute of Applied Physics, TU Wien, Vienna, Austria

The intrinsic polarity of the KTaO₃ (001) surface can be compensated in various ways - by defects, surface reconstructions, or a hydroxylated overlayer¹. The influence of the polarity on molecule adsorption is a fundamental question with further impact on practical applications. Here, we employ a combined scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) system to study CO adsorption on the bulk-terminated KTaO₃ (001) surface. CO preferentially adsorbs on TaO₂-terminated terraces and we discuss its possible coupling with 2DEG-like electronic states of the substrate. Two distinctly different adsorption configurations were found, where the corresponding CO molecules show significantly different chemical interaction with the AFM tip, and are arranged in a pattern similar to the electronic standing waves induced by the 2DEG.

Reference: 1. M. Setvin et al., *Science* 359, 572 * 575 (2018)

O 55.5 Wed 16:00 H5

Acetone on Rutile TiO₂: Studying Adsorption via DFT and FTIRS — TIM WÜRGER^{1,2}, KAI SELLSCHOPP¹, WOLFGANG HECKEL¹, YUEMIN WANG³, HESHMAT NOEI⁴, ANDREAS STIERLE^{4,5}, STEFAN MÜLLER¹, and ●GREGOR FELDBAUER¹ — ¹Institute of Advanced Ceramics, Hamburg University of Technology — ²MagIC-Magnesium Innovation Centre, Helmholtz-Zentrum Geesthacht — ³Institute of Functional Interfaces, Karlsruhe Institute of Technology — ⁴DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — ⁵Physics Department, Universität Hamburg

The adsorption and potential subsequent chemical reactions of acetone on TiO₂ surfaces are highly relevant to various applications ranging from photocatalysis to the formation of hybrid interfaces. In the latter case, acetone may act as a competitor to coupling agents like carboxylic acids. Here, the adsorption geometry, energetics, and vibrational modes of acetone molecules on the rutile TiO₂ (110) surface are studied using density functional theory (DFT). Especially, the importance of sampling the adsorption configuration space and of including non high-symmetry geometries is shown. The computational results are complemented with temperature-dependent ultrahigh-vacuum Fourier transform infrared spectroscopy measurements. At low temperatures the calculated and measured IR spectra agree very well, while upon increasing the temperatures emerging IR bands are seen in the experiments. The modifications of the spectra indicate thermal-induced reactions and their nature is further examined using DFT.[1]

[1] T. Würger et al., *J. Phys. Chem. C* **122**, 19481-19490, 2018

O 55.6 Wed 16:15 H5

Water and methanol adsorption on vicinal ZnO — ●ELIN GRÄNÄS¹, BJÖRN ARNDT^{1,2}, MICHAEL BUSCH³, FREDRIK JOHANSSON⁴, CHRISTOPH SEITZ¹, KONSTANTIN SIMONOV⁴, MICHAEL WAGSTAFFE¹, ANDERS SANDELL⁴, HENRIK GRÖNBECK³, and ANDREAS STIERLE^{1,2} — ¹Deutsches-Elektron Synchrotron (DESY), Germany — ²University of Hamburg, Germany — ³Chalmers University of Technology, Sweden — ⁴Uppsala University, Sweden

Zinc oxide (ZnO) plays an important role in catalysis, where it is often used together with metal nanoparticles in important chemical reactions such as methanol synthesis and low temperature water-gas shift. The detailed reaction mechanisms and role of the ZnO are topics under discussion. Previously we have determined the structure of the bare vicinal ZnO(10-14) surface [1], here we continue with studies of how the under-coordinated Zn- and O-atoms on the surface interact with water and methanol under UHV conditions. Using x-ray photoelectron spectroscopy we have followed the evolution of species present on the surface as a function of coverage and temperature. The distribution of products reveal insights into the influence of the surface steps. Further, based on scanning probe microscopy and surface x-ray diffraction studies we will discuss structural changes occurring upon water exposure.

[1] E. Gränäs, M. Busch, B. Arndt, M. Creutzburg, G. Dalla Lana

Semione, A. Schaefer, J. Gustafson, V. Vonk, H. Grönbeck, A. Stierle. "A non-polar, highly reactive vicinal oxide surface". In preparation.

O 55.7 Wed 16:30 H5

Methanol on SrTiO₃: adsorption sites and geometry — ●VLADYSLAV SOLOKHA^{1,2}, DEBI GARAI^{1,3}, AXEL WILSON¹, HADEEL HUSSAIN¹, THERESIA GREUNZ², DAVID A. DUNCAN¹, KURT HINGERL², and JÖRG ZEGENHAGEN¹ — ¹Diamond Light Source Ltd., Didcot, UK — ²Johannes Kepler University, Linz, Austria — ³Amity University, Noida, India

Mechanistic understanding of interaction of small organic molecules with oxide surfaces fosters the development of novel oxide-based catalysts. Using I09 beamline[1] at Diamond Light Source, we investigate the surface chemistry of methanol on SrTiO₃ (001) from cryogenic to room temperature with a combination of hard and soft X-ray photoelectron spectroscopy (XPS) and x-ray standing waves (XSW). SrTiO₃ is a prototypical perovskite and a transition metal oxide possessing (photo)catalytic properties. In our study, we find that methanol dissociates upon adsorption on the surface of strontium titanate forming various species, e.g. methoxy.

In the talk we discuss, adsorption sites and adsorption geometry of methanol and its dissociation products, as evidenced by XPS-XSW.

[1] T.-L. Lee and D. A. Duncan (2018), *Synchr. Rad. News*, 31:4, 16-22, DOI:10.1080/08940886.2018.1483653

O 55.8 Wed 16:45 H5

STM Reveals the Mechanism of Anatase (001) Nanocatalyst Activation — ●WILLIAM DEBENEDETTI and MELISSA HINES — Cornell University, Ithaca NY, USA

Metal oxide nanocrystals such as TiO₂ have garnered a great deal of attention for environmental remediation applications and photocatalysis. Despite years of study, an atomic-scale picture of the surface chemistry and structure of these materials under operating conditions remains elusive, due to the complex nature of ambient reaction environments. Do these nanocatalysts adopt a bulk-terminated structure in solution environments, or do they reconstruct to minimize their reactivity? Using a newly developed solution-based approach, we will show that shape-controlled crystal growth methods produce films of oriented anatase (001) nanocrystals that are amenable to scanning probe techniques such as STM. Despite being grown in solution and handled in air, the surface of these nanocrystals are surprisingly clean and passivated by a monolayer of fluorine, protecting the surface against adventitious contamination. Using a combination of STM, XPS, and *ab initio* simulations, we will then show that carboxylic acid solutions, the most common TiO₂ functionalization chemistry, cause a spontaneous reorganization of the surface sites, giving rise to a *five-fold increase* in the number of reactive sites on the surface, which reveals a mechanism of nanocatalyst site activation. This structural transformation is not observed in analogous reactions in vacuum and demonstrates the importance of studying these materials under operating conditions.

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CH-Bond Activation via electronically excited SO₂ on TiO₂-Anatase-(101) and -Rutile-(110). *Ab Initio* Electronic Structure Investigation — ●LUCA GERHARDS and THORSTEN KLÜNER — Carl von Ossietzky Universität, Oldenburg, Germany

The photocatalytic heterogeneous sulfoxidation on titanium dioxides, which requires visible light, seems to be a promising new and more energy efficient alternative to the industrially applied reaction via UV-light.[1,2] Experimental investigations on the mechanism revealed that the adsorption of SO₂ and its electronic excitation lead to a formation of a charge-transfer complex on the surface which catalyzes the subsequent chain reaction.[1] These results stand in contrast to the industrial mechanism and need a deeper investigation. In this con-

tribution, we examine the adsorption and electronic excitation of SO₂ and the CH-bond activation of alkanes on ideal TiO₂-anatase-(101) and -rutile-(110) surfaces from a quantum chemical perspective. Both mechanisms (heterogeneous and industrial) will be analysed via high accuracy multireference methods like CASSCF and NEVPT2 to attain a clearer insight into the behavior of this complex radical reaction. An embedded cluster model is designed and compared to calculations with periodic boundary conditions.

[1] F. Parrino, A. Ramakrishnan, H. Kisch, *Angew. Chem. Int. Ed.*, **47**(37), p. 7107-7109, 2008.

[2] R. Graf, *Textilhilfsmittel-Laboratorium der Farbwerke Hoechst*, 50-82, 1952.

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(Photo-)oxidation Studies on Titania Rutile(110) — ●JESSICA KRÄUTER, LARS MOHRHUSEN, TIM THIEDEMANN, and KATHARINA AL-SHAMERY — Carl-von Ossietzky University of Oldenburg, Institute of Chemistry, Oldenburg, Germany

In chemical industry acetone is produced homogeneously catalysed by the cumene process with explosive peroxides as intermediates.^[1] To avoid these, heterogenous catalysed processes are discussed. Earlier work already demonstrated the photo-oxidation of 2-propanol to acetone on MnO, however with low yield.^[2] As titania is a well-known photocatalyst, we started model studies under UHV conditions on the interaction of 2 propanol and acetone adsorbed on a rutile TiO₂(110) surface. Titania was chosen as recently own work demonstrated the reductive coupling of benzaldehyde and the deoxygenation reaction of methanol which were influenced by bulk defects.^[3,4] We have also investigated the effect of oxygen and water coadsorption and tested the photocatalytic performance under UV irradiation. Here, we present Temperature Programmed Reaction Spectroscopy (TPRS) studies to monitor reaction products and polarized Fourier-Transformation Infrared Reflexion Absorption Spectroscopy (FT IRRAS) to identify possible reaction intermediates and their orientation on the surface.

[1] V. M. Zakoshansky, *Petroleum Chemistry*, 2007, 47, 4, 273.

[2] H. Cao, S. L. Suib, *J. Am. Chem. Soc.*, 1994, 116, 5334.

[3] P. M. Clawin, C. M. Friend, K. Al-Shamery, *A European Journal*, 2014, 90, 7665.

[4] M. Osmić, L. Mohrhusen, K. Al-Shamery, DOI: 10.1021/acs.jpcc.8b02953.

O 55.11 Wed 17:30 H5

Probing Photoexcited Charge Dynamics of Single Oxygen Vacancies on TiO₂(110) at Atomic Scale — ●CHAOYU GUO, XIANGZHI MENG, QIN WANG, and YING JIANG — Peking University, Peking, China

A Titanium dioxide (TiO₂) is well known as one of the most widely studied materials in photocatalysis and solar energy conversion. Photoexcited charge dynamics of near-surface defects such as oxygen vacancies plays a critical role in the photocatalytic process of TiO₂, but the atomic-scale mechanism is yet to be elucidated. With laser-combined scanning tunneling microscopy, tracking carrier dynamics with high spatial and temporal resolution simultaneously is possible. Here we succeeded to probe the photoexcitation and transient relaxation process of individual oxygen vacancies on rutile TiO₂(110) surface. Upon visible-laser illumination, the in-gap states derived from surface oxygen vacancies exhibit prominent downward energy shift accompanied with a suppression of valence tail states, which were attributed to photoexcited electronic transition between the defect levels and conduction band. We found that the photogenerated electrons and holes exhibit rather different carrier dynamics due to the atomic-scale environment variation. Those results shed new lights onto the visible photoresponse of reduced-TiO₂ materials and reveal the influence of atomic defects on the electron-hole recombination dynamics in real space.