

## O 83: Surface Chemistry and Growth

Time: Thursday 10:30–13:30

Location: MA 144

O 83.1 Thu 10:30 MA 144

**Temperature-dependent Reactions of Phthalic Acid on Ag(100)** — ●MATTHIAS FRANKE<sup>1</sup>, FLORENCIA MARCHINI<sup>2</sup>, QURATULAIN TARIQ<sup>1</sup>, MICHAEL RÖCKERT<sup>1</sup>, FEDERICO JOSÉ WILLIAMS<sup>2</sup>, and HANS-PETER STEINRÜCK<sup>1</sup> — <sup>1</sup>Universität Erlangen-Nürnberg — <sup>2</sup>Universidad de Buenos Aires

Small aromatic molecules on single crystal surfaces are particularly interesting, since they may be used not only as model systems, but also as precursors for the formation of larger organic molecules, e.g. polymers.

We applied high resolution X-ray photoelectron spectroscopy (XPS) using synchrotron radiation and temperature programmed desorption (TPD) to study the temperature-dependent reactions of phthalic acid on Ag(100). After deposition at 110 K, the species adsorbed on the surface can be identified as phthalic acid. Upon heating, both monomeric and polymeric anhydride species are formed. This is accompanied by a change in molecular orientation, as observed by near edge X-ray absorption fine structure (NEXAFS) measurements. The monomer, phthalic anhydride, desorbs at 300 K, whereas the polymeric species remains on the surface until it decomposes above 400 K into phthalic anhydride, water, CO<sub>2</sub> and benzene.

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O 83.2 Thu 10:45 MA 144

**Effect of hydrogen bonds on the adsorption and reactivity of alcohols on noble metal surfaces** — ●RODRIGO GARCÍA-MUELAS and NÚRIA LÓPEZ — Institute of Chemical Research of Catalonia, Tarragona, Spain.

The adsorption and decomposition of alcohols on noble metals has been subject of theoretical studies as a potential renewable source of chemicals. These studies usually omitted the lateral interactions between vicinal alcohol molecules or functional groups, and the effect of the ubiquitous hydrogen bonds on the reactivity in the liquid-metal interface is still a matter of debate. We show that lateral interactions between OH groups can selectively stabilize the OH over CH dehydrogenation, thus altering the preferred reaction path for methanol decomposition on Pt(111). The presence of these lateral interactions can explain the apparent divergence between previous theoretical and experimental studies.

O 83.3 Thu 11:00 MA 144

**Metalation of deuterated tetraphenylporphyrin on Cu(111): Insights into the reaction pathway** — ●OLE LYTKEN, MICHAEL RÖCKERT, MATTHIAS FRANKE, QURATULAIN TARIQ, STEFANIE DITZE, MICHAEL STARK, ANDRE KAFTAN, DOMINIK LUNGERICH, NORBERT JUX, MATHIAS LAURIN, JÖRG LIBUDA, HUBERTUS MARBACH, and HANS-PETER STEINRÜCK — Universität Erlangen-Nürnberg

Temperature-Programmed Desorption (TPD) of the metalation of deuterated 5,10,15,20-tetraphenyl-21,23D-porphyrin on Cu(111) reveals that the metalation reaction proceeds through the transfer of the central aminic deuterium atoms to the Cu(111) surface and not, as might be expected from gas phase calculations, through the combination of the hydrogen atoms to molecular hydrogen above the partial inserted metal center. Experimentally, desorption of mostly hydrogen and very little deuterium is observed as the deuterated porphyrin molecule metalates. Despite the absence of deuterium in the periphery of the molecule before metalation, desorption of deuterium is not observed until the periphery dehydrogenates at higher temperatures. This is caused by hydrogenation and dehydrogenation of the periphery of the molecule exchanging deuterium produced during metalation with hydrogen from the periphery. The reactions have been modeled with a simple micro kinetic model able to describe the main features of the TPD spectra.

O 83.4 Thu 11:15 MA 144

**Effect of metal substrates on immobilised catalyst performance** — ●DAVID A. DUNCAN<sup>1</sup>, PETER S. DEIMEL<sup>1</sup>, ANTHOULA WEINGARTEN<sup>1</sup>, RUNYUAN HAN<sup>1</sup>, KEVIN C. PRINCE<sup>2</sup>, ROBERT G. ACRES<sup>2</sup>, ALBANO COSSARO<sup>2</sup>, ALBERTO VERDINI<sup>2</sup>, LUCA FLOREANO<sup>2</sup>, WILHELM AUWÄRTER<sup>1</sup>, PETER FEULNER<sup>1</sup>, ANTHOULA C. PAPAGEORGIOU<sup>1</sup>, FRANCESCO ALLEGRETI<sup>1</sup>, and JOHANNES V. BARTH<sup>1</sup> — <sup>1</sup>TU München, Germany — <sup>2</sup>Elettra, Trieste, Italy

A key motivation for surface science is to merge the selectivity of homogenous catalysts with the ease of recovery in heterogenous catalysis. Recent studies<sup>1</sup> in this field have focussed on immobilising metal-organic species at solid surfaces for improved control of catalytic conversions. However, with metal supports the reactivity of surface-anchored species has been lacklustre, frequently requiring either low temperatures or large exposures for axial ligation at complexed metal centres<sup>2</sup> suggesting that the interaction with the substrate has a notable effect. We have studied, in UHV, the reactivity of ruthenium tetraphenyl porphyrin (Ru-TPP) and its Ti analogue towards molecular oxygen when confined to the Ag(111) surface. For surface-confined Ru-TPP, after a dosage of 20,000 L, no oxo-ruthenium species evolved, whereas exposing Ti-TPP to ~100 L induces nearly complete oxidation. This might suggest a shift in the so called “Volcano plot” of the Sabatier Principle towards metal complexes that are traditionally thought of as being too reactive for certain catalytic reactions.

1) B. Hulsken et al Nat Nano, 2007, 2 285; 2) BE Murphy et al. ACS Nano, 2014, 8, 5190; K Seufert et al., Nat Chem, 2011, 3, 114

O 83.5 Thu 11:30 MA 144

**A chrysene derivative as a promising candidate for an on-surface chemical reaction studied by LT-STM/STS** — ●FRANK EISENHUT<sup>1,2</sup>, JUSTUS KRÜGER<sup>1,2</sup>, JÖRG MEYER<sup>1,2</sup>, ROBIN OHMANN<sup>1,2</sup>, GIANAURELIO CUNIBERTI<sup>1,2</sup>, and FRANCESCA MORESCO<sup>1,2</sup> — <sup>1</sup>Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, 01062 Dresden, Germany — <sup>2</sup>Center for Advancing Electronics Dresden, TU Dresden, 01062 Dresden, Germany

On-surface chemistry of  $\pi$ -conjugated carbon-systems become more and more relevant as these systems are interesting for the use in molecular electronic devices. In this study the promising molecule tetramethyldibenzochrysene has been investigated. The desired reaction for this molecule is a dehydrogenation of the methyl groups and subsequently a closing of carbon rings, to form dimethylphenanthroperylene. This study deals with the characterization of the initial molecule via scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) at low temperatures on Ag(100). After the adsorption of the chrysene to the surface, the molecule forms supramolecular assemblies consisting 3 or 4 molecules. Detailed topographic and spectroscopic analysis of the assemblies have been fulfilled. Further the influence of applying voltage pulses to the assemblies and the heating of the system at different temperatures has been investigated.

O 83.6 Thu 11:45 MA 144

**The hydrated electron at the ice surface: insight into the dissociative electron attachment to adsorbates** — ●PHILIPP AUBURGER<sup>1</sup> and MICHEL BOCKSTEDTE<sup>1,2</sup> — <sup>1</sup>Lst. Theor. Festkörperphysik, Friedrich-Alexander Universität Erlangen-Nürnberg, 91058 Erlangen, Germany — <sup>2</sup>FB Materialwissenschaften & Physik, Universität Salzburg, 5020 Salzburg, Austria

On ice, the solvated electron facilitates electron-induced reactions of adsorbates via dissociative electron attachment (DEA) that for instance take place in atmospheric chemistry. The simultaneous interaction of the electron with the molecule and the ice surface enhances the cross section as compared with the gas phase. The current understanding of the physical mechanisms at work is rather incomplete, in particular a picture on the molecular scale is missing. In this work we address this problem within the framework of density functional theory, hybrid DFT, and many body perturbation theory. Prototypical surface electron traps, such as orientational disorder, surface vacancies and vacancy clusters are used as a model system. Halogenated hydrocarbons favor adsorption sites that are strong electron traps. Their antibonding molecular orbitals are scattering states with negative electron affinity. By the interaction with the trap states the binding energy is considerably increased. Our results show clear trends across the series F, Cl, and Br.

O 83.7 Thu 12:00 MA 144

**Extension of energy-resolved XPS towards a quantitative depth-profiling method and its application to ion-surface interactions** — ●MARTIN KÖPPEN<sup>1</sup>, MARTIN OBERKOFER<sup>2</sup>, JOHANN RIESCH<sup>2</sup>, KLAUS SCHMID<sup>2</sup>, ANTJE VOLLMER<sup>3</sup>, and CHRISTIAN LINSMEIER<sup>1</sup> — <sup>1</sup>Forschungszentrum Jülich, Institut für Energie- und

Klimaforschung - Plasmaphysik, Jülich — <sup>2</sup>Max-Planck-Institut für Plasmaphysik, Boltzmannstr. 2, Garching — <sup>3</sup>Helmholtz-Zentrum Berlin für Materialien und Energie, BESSY II, Albert-Einstein-Str. 15, Berlin

XPS as a work horses of surface science is capable of chemical analysis, but quantitative depth-profiles have always been an issue. Since solid state reactions are usually governed by diffusion, the latter is crucial to understand processes at surfaces.

This work extends energy-resolved XPS using variable photon energies towards a chemically resolved, quantitative depth-profile analysis. A model is derived which calculates the depth-resolved composition and the composition-dependent electron inelastic mean free path in a self-consistent way. Input is the normalised XPS data.

In fusion research, reactions of first wall materials like Be and W as well as reactions with ions leaving the plasma must be understood for a dynamic description of the surface composition. Formation of compounds is induced by temperature and implantation of particles. The model is applied to describe the interaction of O-ions with Be<sub>2</sub>W. Using this approach it was possible to elucidate the interaction of ions with this surface quantitatively on a nanometre scale.

O 83.8 Thu 12:15 MA 144

**In silico prediction of dissolution rates of molecular crystals** — ●BERNA DOGAN<sup>1</sup>, JULIAN SCHNEIDER<sup>1,2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>QuantumWise A/S, Copenhagen, Denmark

Dissolution testing is not only helpful for quality control of drug formulations, but also provides important information for drug development e.g. to optimize the dissolution kinetics by admixture of pharmaceutically inactive excipients. At present, a rational optimization process is hereby limited by a lack of understanding of the underlying molecular processes during crystal dissolution. We contribute to this context with detailed kinetic modeling based on atomistic molecular dynamics (MD) simulations. Within a spiral dissolution model valid for low undersaturation the velocity of a retracting screw dislocation can be determined from the free energy of kink sites and the rate constant for the molecular detachment process of kink site molecules. We present molecular simulation protocols for both quantities [1,2] and use them to determine a macroscopic dissolution rate of the wide-spread excipient alpha lactose-monohydrate that is fully consistent with experimental rates obtained from single crystals. [1] J. Schneider, C. Zheng, and K. Reuter, *J. Chem. Phys.* **141**, 124702 (2014); [2] J. Schneider and K. Reuter, *J. Phys. Chem. Lett.* **5**, 3859 (2014).

O 83.9 Thu 12:30 MA 144

**Is a surface reconstruction really necessary for an epitaxial Fe growth on a GaAs(001) surface?** — ●DOMINIQUE HANDSCHAK, FRANK SCHÖNBOHM, TOBIAS LÜHR, CHRISTOPH KEUTNER, ULF BERGES, and CARSTEN WETSPHAL — TU Dortmund, Exp. Physik 1, Otto-Hahn-Str.4, 44221 Dortmund, Germany

Multilayer consisting of the ferromagnet Iron (Fe) and the semiconductor Gallium-Arsenide (GaAs) are in the focus of the research in spintronics. The GMR effect arises at the interface, where the electrons are scattered differently depending on their spin and mutual orientation of the magnetization within the Fe-film. Therefore, the knowledge of the chemical composition and structure of the interface are important in order to improve the efficiency of the effect. We report on the interface structure of two similar system, Fe/GaAs(clean) and Fe/GaAs(4x2) using x-ray photoelectron diffraction (XPD) patterns in order to examine the necessity of a reconstruction for an epitaxial Fe growth. It can be shown that the inter-diffusion between the substrate and the adsorbate is prevented if Fe is prepared on a GaAs(4x2)-sample. Furthermore, the predicted stronger out-diffusion of the Arsenic can be confirmed by the XPD patterns of the Fe/GaAs(clean) system.

O 83.10 Thu 12:45 MA 144

**Theoretical evidence for unexpected O-rich phases at corners of MgO surfaces** — SASWATA BHATTACHARYA<sup>1</sup>, DANIEL BERGER<sup>2</sup>, KARSTEN REUTER<sup>2</sup>, ●SERGEY V. LEVCHENKO<sup>1</sup>, LUCA M. GHIRINGHELLI<sup>1</sup>, and MATTHIAS SCHEFFLER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, DE — <sup>2</sup>Technische Universität München, Garching, DE

Introducing charge carriers into MgO via *p* doping greatly reduces

formation energy of an O-vacancy in the bulk and at the (100) surface [1]. In this work, we use hybrid density functional theory to explore O-vacancy and O/O<sub>2</sub>-ad-species defects at corners of MgO surfaces. The defects are modelled using MgO clusters embedded into a field of norm-conserving pseudopotentials and point charges. The long-range response of the oxide to the charge carriers trapped at the defects is taken into account using a polarizable force field. The low-energy defect atomic structures are found using an *ab initio* genetic algorithm [2]. Concentrations of O-vacancies and O-ad-species at realistic temperatures and pressures are obtained with *ab initio* atomistic thermodynamics. Unexpectedly, we find that O-ad-species rather than O-vacancies are dominating defects at realistic conditions. The stability of the O-ad-species over O-vacancies and pristine corners is explained by an interplay between bond-breaking, bond-making, and charge-carrier trapping. — [1] N. Richter *et al.*, *Phys. Rev. Lett.* **111**, 045502 (2013); [2] S. Bhattacharya *et al.*, *New J. Phys.*, in press (2014).

O 83.11 Thu 13:00 MA 144

**Monitoring the formation of quasicrystalline barium titanate on Pt(111) using XPS and NEXAFS** — ●ALIREZA BAYAT<sup>1</sup>, STEFAN FÖRSTER<sup>1</sup>, RENE HAMMER<sup>1</sup>, EVA-MARIA ZOLLNER<sup>1</sup>, WOLF WIDDRA<sup>1,4</sup>, REINHARD DENECKE<sup>2</sup>, SILVANO LIZZIT<sup>3</sup>, PAOLO LACOVIG<sup>3</sup>, and KARL-MICHAEL SCHINDLER<sup>1</sup> — <sup>1</sup>Institut für Physik, Martin-Luther-Universität, Halle-Wittenberg, D-06120 Halle, Germany — <sup>2</sup>Wilhelm-Ostwald-Institut, Universität Leipzig, D-04103 Leipzig, Germany — <sup>3</sup>Elettra-Sincrotrone Trieste S.C.p.A. I-34149 Basovizza, Trieste, Italy — <sup>4</sup>Max-Planck-Institut für Mikrostrukturphysik, D-06120 Halle, Germany

The discovery of a 2D quasicrystalline BaTiO<sub>3</sub>-derived (BTO) layer on Pt(111) opened a new field in fundamental physics as well as applications [1]. Using high-resolution XPS and NEXAFS, we have determined chemical states and coordination environments of all elements in the layer. In addition, the reversible transformation between BTO(111) islands and the quasicrystalline layer has been monitored using fast-XPS. The XPS spectra show that the islands contain titanium only as Ti<sup>4+</sup> and are fully oxidized. The quasicrystalline layer contains Ti<sup>3+</sup> and Ti<sup>4+</sup> in approximately equal amounts and their formations from Ti in the islands happen simultaneously. The chemical shifts indicate that the coordinations of both Ti species in the quasicrystalline layer are different from bulk. NEXAFS spectra at Ti L- and O K-edges in normal and grazing incidences confirm an anisotropy in the quasicrystalline layer, presumably arising from a planar or near planar coordination of Ti. [1] S. Förster *et al.*, *Nature*, **502** (2013) 215-218

O 83.12 Thu 13:15 MA 144

**nc-AFM study of C<sub>60</sub> islands on organic compound crystals** — ●SARA FREUND<sup>1</sup>, ANTOINE HINAUT<sup>1</sup>, RÉMY PAWLAK<sup>1</sup>, SHI-XIA LIU<sup>2</sup>, SILVIO DECURTINS<sup>2</sup>, ERNST MEYER<sup>1</sup>, and THILO GLATZEL<sup>1</sup> — <sup>1</sup>Department of Physics, University of Basel, Switzerland — <sup>2</sup>Department of Chemistry and Biochemistry, University of Bern, Switzerland

Organic layered compound crystals have rarely been investigated by the means of room temperature noncontact atomic force microscopy (nc-AFM). This kind of material offers the possibility to design surfaces with different chemical compounds and molecular orientations [1]. The study of adsorbed molecules on such surfaces under ultra-high vacuum (UHV) conditions might be of great interest in the field of optoelectronics. In this study the behaviour of fullerene (C<sub>60</sub>) molecules on the salt bis(benzylammonium)bis(oxalate)cuprate(II) (BNL) was investigated. BNL is a transition-metal oxalate complex which exhibits layer-type crystal structures [2]. The C<sub>60</sub> molecules were deposited on the substrate by thermal deposition and formed small islands. High resolution images of the substrate and the C<sub>60</sub> islands were obtained. Manipulations of the molecular islands have been induced by controlled tip interactions. It was observed that they can be split up and redistributed by these interactions to form larger islands. Tip-induced shape modifications of these C<sub>60</sub> islands was also observed and analysed.

[1] G. Fessler *et al.*, *Appl. Phys. Lett.*, **98**(8), 083119, 2011.

[2] S. Decurtins *et al.*, *Mol. Cryst. Liq. Sci. Technol., Sec A* **305**, 227, 1997.