

# Monday Afternoon, October 19, 2015

## Surface Science

Room: 113 - Session SS-MoA

### Organics and Ionic Liquids: Surfaces, Layers, Interfaces and Chirality

**Moderator:** Janice Reutt-Robey, University of Maryland, College Park, John Russell, Jr., Naval Research Laboratory

2:20pm **SS-MoA1 ZnTPP, PTCDA, TCNQ, and TTF on TiO<sub>2</sub>(110): Molecule-Oxide Interaction and Electronic Energy Level Alignment.** *Charles Ruggieri, S. Rangan, R.A. Bartynski*, Rutgers, the State University of New Jersey, *J.I. Martinez*, Institute of Materials Science of Madrid, Spain, *F. Flores, J. Ortega*, Autonomous University of Madrid, Spain

The injection of charge between transition metal oxides and organic materials depends crucially on the interface barrier that is determined by the organic electronegativity, the possible space charge layer formed in the oxide, and the chemical interaction between the oxide and the organic. We investigate the interfaces of TiO<sub>2</sub>(110) and four organic molecules, ZnTPP, PTCDA, TCNQ, and TTF, representing a broad range of electronegativities, and the electronic energy level alignment for each interface, using a combination of direct and inverse photoemission spectroscopies and theoretical modelling. In particular, we analyze contributions to the electronic energy level alignment from oxide-molecule chemical hybridization, induced electrostatic dipoles due to molecular distortion, and charge transfer, and the relative importance of these phenomena to each case. In this way, we provide a detailed description of the wide range of interactions influencing the final electronic energy level alignment for weakly and strongly interacting organic on TiO<sub>2</sub> (110).

2:40pm **SS-MoA2 Characterizing the Influence of Water on Charging and Layering at Electrified Ionic-Liquid/Solid Interfaces.** *Hsiu-Wei Cheng*, Max-Planck-Institut für Eisenforschung GmbH, Germany, *P. Stock*, Max-Planck Institut für Eisenforschung GmbH, Germany, *B. Moeremans*, Universiteit Hasselt, Belgium, *T. Bamipos*, Max Planck Institut für Eisenforschung GmbH, Germany, *X. Banquy*, University of Montreal, Canada, *F.U. Renner*, Universiteit Hasselt, Belgium, *M. Valtiner*, Max-Planck Institut für Eisenforschung GmbH, Germany

The importance of water on molecular ion structuring and charging mechanism of solid interfaces in room temperature ionic liquid (RTIL) is unclear and has been largely ignored. Water may alter structures, charging characteristics and hence performance at electrified solid/RTIL interfaces utilized in various fields including energy storage and conversion or catalysis. Here, we utilize Atomic Force Microscopy to directly measure how water alters the interfacial structuring and charging characteristics of [C<sub>2</sub>mim][Tf<sub>2</sub>N] on mica and electrified gold surfaces. On hydrophilic and ionophobic mica surfaces, water-saturated RTILs induce strong ion layering by dissolution of surface-bound cations and a resulting high surface charging. In contrast, layering of dry RTIL at uncharged mica surfaces is weakly structured. At electrified, hydrophobic and ionophilic gold electrodes, significant water effects were found only at positive applied electrochemical potentials. Here, the influence of water is limited to interactions within the RTIL layers, and is not related to a direct electroadsorption of water on the polarized electrode. More generally, our results suggest that effects of water on interfacial structuring of RTIL strongly depend on both (1) surface charging mechanism, and (2) interfacial wetting properties. This may greatly impact utilization and design of RTILs and surfaces for interface dominated processes.

3:00pm **SS-MoA3 Interfaces of Ionic Liquids.** *Hans-Peter Steinrück*, Universität Erlangen-Nürnberg, Germany **INVITED**

Ionic liquids (ILs), salts with melting points below 100 °C, represent a fascinating class of liquid materials, typically characterized by an extremely low vapour pressure. Besides their application as new solvents or as electrolytes for electrochemical purposes, ILs are also used in catalysis. Two important concepts in this context are Supported Ionic Liquid Phase (SILP) and Solid Catalyst with Ionic Liquid Layer (SCILL). In both, a high surface area solid substrate is covered with a thin IL film, which contains either a homogeneously dissolved transition metal complex for SILP, or which modifies catalytically active surface sites at the support for SCILL. Thereby, the interfaces of the IL with the gas phase and with catalytic nanoparticles and/or support materials are of critical importance. It has recently been demonstrated that these interfaces and also the bulk of ILs can be investigated in great detail using surface science studies in an ultrahigh vacuum environment. From angle-resolved X-ray photoelectron spectroscopy, detailed information on the surface and bulk composition of

non-functionalized and functionalized ILs, on segregation and enrichment effects, on the dissolution and reactivity of catalytically active metal complexes in ILs, on the growth of ultrathin IL-layers, and even on liquid phase reactions studied in situ in the IL, can be derived. Various examples will be discussed.

H.-P. Steinrück and P. Wasserscheid, *Ionic Liquids in Catalysis*, Catal. Lett. **2015**, 145, 380.

H.-P. Steinrück, *Recent developments in the study of ionic liquid interfaces using X-ray photoelectron spectroscopy and potential future directions*, Phys. Chem. Chem. Phys. **2012**, 14, 2510.

H.-P. Steinrück, *Surface Science goes liquid !*, Surf. Sci. **2010**, 604, 481.

F. Maier, J. M. Gottfried, J. Rossa, D. Gerhard, P. S. Schulz, W. Schwieger, P. Wasserscheid, H.-P. Steinrück, *Surface enrichment and depletion effects of ions dissolved in an ionic liquid. An X-ray photoelectron spectroscopy study*, Angew. Chem. Int. Ed. **2006**, 45, 7778.

3:40pm **SS-MoA5 Free-Standing Gold Nanoparticles on Ultrathin Ionic Liquid Films Studied by Low Energy Ion Scattering (LEIS) Analysis.** *Thomas Grehl, P. Bruener*, ION-TOF GmbH, Germany, *L. Calabria, P. Migrowski, D.L. Baptista, F. Bernardi*, Laboratory of Molecular Catalysis, UFRGS, Brazil, *H. Brongersma*, ION-TOF GmbH, Germany, *J. Dupont*, Laboratory of Molecular Catalysis, UFRGS, Brazil

Metal nanoparticles (NPs) in ultrathin films have a variety of applications nano-optical and nano-electronic devices. Several methods have been developed in order to synthesize such films. However, those methods result in "capped" NPs, instead of free-standing NPs which would be a more versatile alternative precursor for ultrathin film growth.

Ionic liquids are known to facilitate well-defined formation of Au NPs from sputter deposition and self-organization of the particles close to the surface [1]. The size and potential shape of the NPs can be tailored by the properties of the ionic liquids. Applying this principle of NP formation to ultrathin films of ionic liquids is a promising route by which to easily form free-standing NPs in a well controlled manner.

In this study we analyze silicon wafer supported ultrathin films of both hydrophilic and hydrophobic imidazolium based ionic liquids forming an "ionic carpet like" structure. This structure is decorated with gold NPs having a size of 5 - 10 nm from the application of sputter deposition of gold onto the ionic liquid. A range of analytical techniques is applied to the samples, including XPS, XRD, AFM and electron microscopy. Here we present primarily the results from high resolution and high sensitivity Low Energy Ion Scattering (LEIS).

LEIS is the most surface sensitive technique for the elemental characterization of the outermost atomic layer. Noble gas ions having a kinetic energy of a few keV are scattered from the individual surface atoms. By measuring the energy loss in the scattering event, the mass of the respective surface atom can be determined, while the intensity of the scattering signal is proportional to the surface coverage. LEIS has been successfully applied to ionic liquids by several groups to elucidate the termination of the liquid. In addition the LEIS data contain information on the composition of the first few nm of the sample. The latter is used to determine the thickness of the self-organized layer of NPs and allows the thickness measurement of any film covering the gold.

The gold nanoparticles are deposited by sputtering into the hydrophobic (AMI.NTf2) and hydrophilic (AMI.BF4) ionic liquids on Si(111) for 5 and 10 s. The LEIS spectra show gold signal for the hydrophobic ionic liquid. Apparently the gold NPs are out of the probed range of the LEIS technique (10 nm). In contrast to that, the LEIS spectra of the hydrophilic ionic liquid after gold deposition show the presence of gold below the surface. The mean thickness of the organic layers covering the NPs is 6 nm (5 s deposition) and 4.3 nm (10 s deposition).

[1] Kauling et al., Langmuir 2013, 29 (46) 14301

4:00pm **SS-MoA6 Early-Stage Solid-Electrolyte Interphase (SEI) Formation: Probing Molecular Carbonate Decomposition Pathways and Artificial Lithium Ethylene Dicarboxylate Monolayers.** *Wentao Song, J.E. Reutt-Robey*, University of Maryland, College Park

The Solid Electrolyte Interphase (SEI) formed at the Li-ion battery (LIB) anode plays a major role in battery cycle life and safety. The ethylene carbonate (EC) electrolyte is known to undergo reduction to a mixture of lithium salts at the onset of SEI formation, but the product branching and sensitivity to electrode structure have not been determined. We report the use of temperature programmed desorption (TPD) and reaction spectroscopy (TPRS) to quantify interactions between the molecular carbonates, ethylene carbonate (EC) and dimethyl carbonate (DMC), and

model Li-C(0001) anode surfaces prepared in situ. Both EC and DMC interact weakly with the clean C(0001) surface with adsorption energies of  $0.60 \pm 0.06$  and  $0.64 \pm 0.05$  eV, respectively. Submetallic lithiation of C(0001) significantly increases the binding energies of molecular carbonates, and the range of measured values indicates EC solvation of lithium ions. In the presence of metallic lithium, 1.5 monolayers of EC undergoes complete decomposition, resulting in 70% organolithium products and 30% inorganic lithium product. Further structural analysis of the early stage organolithium salt, lithium ethylene dicarbonate (LEDC), was performed with UHV-STM. A pulsed microaerosol molecular beam source permitted controlled deposition of LEDC (from dimethyl formamide solvent) on Ag(111). Elongated LEDC monolayer islands spontaneously form in three distinct 120 degree rotational domains, all aligned with the close-packed silver direction. Further deposition increases island size and density, with little change in island shape. Molecularly resolved STM images reveal a LEDC monolayer structure with a  $1.1874 \pm 0.0079$  nm x  $0.5793 \pm 0.0055$  nm unit cell containing one LEDC. A structural model is presented that accounts for the anisotropy of the LEDC islands. The O-Li-O linkages in the structural model define the long-axis (fast growth direction) of the islands. The LEDC islands are thermally stable up to at least 80°C, and can be imaged over days under UHV. Preliminary STS measurements (performed in Z-V mode) are consistent with significant differences in the local density of electronic states for LEDC islands relative to the Ag(111) substrate.

4:20pm **SS-MoA7 Racemization and Enantioselectivity on Metal Surfaces**, *Georg Held*, University of Reading, UK **INVITED**

The last decade has seen a dramatic increase in research into chiral surface systems, driven by the growing demand for optically pure chemicals in drug manufacturing and, hence, a desire for enantioselective heterogeneous catalysts. These avoid the problem of phase separation inherent in homogeneous enantioselective processes which are predominantly used today. So far, significant success has been achieved by modifying achiral surfaces with chiral molecules thus creating stereo-selective reaction environments [1,2]. Alternatively, intrinsically chiral metal and mineral surfaces show enantioselective behavior without such modifiers [3,4], although these mechanisms are much less well understood. In our work we use synchrotron-based spectroscopies, such as XPS and NEXAFS, alongside LEED and temperature-programmed desorption to characterize the thermal stability, bond coordination and orientation of chiral probe molecules on achiral and intrinsically chiral model catalyst surfaces. The talk will present examples of adsorption systems on both types of surfaces. Particular emphasis is on small chiral amino acids (e.g. alanine, serine), which show racemization as well as enantioselectivity at several levels depending on the substrate and the length of the side-chain of the molecule [5-8].

- [1] A. Baiker, *J. Mol. Catal. A* 115 (1997) 473.
- [2] C. J. Baddeley, *Top. Catal.* 25 (2003) 17.
- [3] C.F. McFadden, P.S. Cremer, A.J. Gellman, *Langmuir* 12 (1996) 2483.
- [4] G. A. Attard, *J. Phys. Chem. B* 105 (2001)
- [5] G. Held, M. Gladys, *Topics in Catalysis*, 48 (2008) 128;
- [6] T. Eralp, A. Cornish, A. Shavorskiy, G. Held, *Topics in Catalysis* 54 (2011) 1414
- [7] T. Eralp, A. Ievins, A. Shavorskiy, S. J. Jenkins, G. Held, *JACS* 134 (2012) 9615.
- [8] S. Baldanza, A. Cornish, R. E. J. Nicklin, Z. V. Zheleva, G. Held, *Surf. Sci.* 629 (2014) 114.

5:00pm **SS-MoA9 Mapping of Enantioselective Reaction Kinetics across Surface Structure Space: Tartaric and Aspartic Acid on Cu(111) Structure Spread Single Crystals**, *Andrew Gellman, A. Reinicker*, Carnegie Mellon University

On single crystal metal surfaces, enantioselectivity is, perhaps, the most subtle form of structure sensitive surface chemistry. Enantioselectivity can be observed on naturally chiral metal surfaces with structures that are traditionally described as having flat low Miller index terraces separated by kinked step edges, thereby lacking mirror symmetry. This work has mapped the enantiospecific decomposition kinetics of tartaric acid (TA) and aspartic acid (Asp) on 225 different single crystal planes exposed by the surface of a Cu(111) Surface Structure Spread Single Crystal ( $S^4C$ ). The Cu(111)  $S^4C$  is a single crystal polished into a spherical dome shape that exposes a continuous distribution of surface orientations vicinal to the Cu(111) plane. During isothermal decomposition, XPS has been used to map the temporal evolution of the coverages of TA and Asp at points across the Cu(111)  $S^4C$ . On Cu surfaces, both TA and Asp decompose by an explosive, vacancy-mediated decomposition mechanism consisting of an initiation step and a vacancy-mediated explosion step. The rate law for this process is parameterized by an initiation rate constant,  $k_i$ , and an explosion rate constant,  $k_e$ . Under isothermal conditions, the measured extent of reaction

versus time at each point on the  $S^4C$  has been used to fit the decomposition rate law and estimate the values of  $k_i$  and  $k_e$  as functions of local surface structure across the Cu(111)  $S^4C$ . These maps reveal that  $k_i$  is maximum on surfaces with high densities of the close packed (100) steps and minimum on surfaces with high densities of the close packed (110) steps. As the angle between the surface and the (111) plane increases,  $k_i$  increases linearly with step density. Along the direction containing the surfaces with (100) steps, the initiation step dominates and the kinetics look first-order. Along the directions exposing (110) steps the kinetics are dominated by the explosion step. In the case of Asp decomposition on the Cu(111)  $S^4C$ , the decomposition kinetics are also sensitive to the chirality of the local surface orientation. Collectively, these data provide the deepest insight yet obtained in to the structure sensitivity of surface explosion reactions and the structural origins of enantioselectivity on naturally chiral surfaces.

5:20pm **SS-MoA10 Enantioselective Adsorption on Platinum Surfaces**, *S. Karakalos, Francisco Zaera*, University of California

Enantioselectivity in the adsorption of chiral compounds on solid surfaces may lead to preferential crystallization, a possible route to chiral separation of racemic mixtures, and also to a way to design enantioselective catalytic chemical reactions. Tests on the uptake of simple molecules on metal single-crystal surfaces as a function of the enantiocomposition of the adsorbate has revealed several interesting kinetic and thermodynamics. Specifically, we have been exploring possible enantiospecific behavior during the uptake of propylene oxide (PO) on Pt(111) surfaces. Three related observations will be reported here. In the first set of experiments, the amplification of enantioselectivity during adsorption was demonstrated for the case of a surface seeded with a small amount of enantiopure PO and then dosed with propylene, a non-chiral molecule, as the amplifier. Chiral chemical titration and isothermal kinetic adsorption experiments using collimated effusive molecular beams indicated the possibility of reaching enantioselectivity excesses of over 60% this way. Monte Carlo simulations provided a kinetic explanation for this effect in terms of both an adsorbate-assisted adsorption process and a bias in the chiral configuration the propylene molecules are driven to upon adsorption on the surface. The second example refers to the uptake of PO itself, where lower saturation coverages are seen with the racemic mixtures versus enantiopure samples by approximately 20%. This behavior could be explained in terms of adsorbate-assisted adsorption with different probabilities for homo- versus hetero-enantiomeric pairs. Finally, it was determined that the enantiomeric composition of PO monolayers eventually reverses the direction of the enantiospecific enrichment seen in the kinetic uptake.

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