

O 95: Metal Substrates: Adsorption of Atoms and Inorganic Molecules

Time: Thursday 15:00–18:15

Location: WIL A317

Invited Talk

O 95.1 Thu 15:00 WIL A317

Visualizing surface X-ray diffraction: the active phase of CO oxidation model catalysts — ●JOHAN GUSTAFSON — Synchrotron Radiation Research, Lund University, Lund, Sweden

Surface X-Ray Diffraction (SXR) is a very powerful surface characterization tool, especially for in-situ investigations. As a diffraction tool, it is closely related to Low-Energy Electron Diffraction (LEED), but is much less used due to the need for intense synchrotrons and the complexity to record and interpret the diffraction data.

The use of large 2D detectors provide the means to facilitate both the collection and the interpretation of the data. As a larger part of reciprocal space is probed simultaneously, larger datasets can be acquired in realistic time frames, which enables a more comprehensible visualization of the data, similar to a LEED-pattern. In addition, significantly more information can be obtained from time-resolved measurements.

We have used SXR with 2D detectors to establish the most active phase of Pd(100) and Rh(111) during catalytic CO oxidation, a subject that has been under debate for about 15 years. In contrast to what is often assumed, these model catalysts behave quite differently, and while the most active phase of rhodium is metallic, for Pd it is a thin oxide film. Some of the conclusions we draw would not have been possible without 2D detectors.

O 95.2 Thu 15:30 WIL A317

Site-specific adsorption of heavy-metal atoms on corrugated graphene: A challenge for first-principles theory — ●GEORG S. MICHELITSCH and KARSTEN REUTER — Technische Universität München

Single, heavy-metal atoms are an appealing ultimate unit in the quest for an ever more miniaturized information storage. Adsorption on corrugated single-layer graphene could thereby protect the magnetic encoding and act as a template for self-assembly. Quantitative first-principles calculations would be a much desired source for independent insight into the geometric, electronic and magnetic properties of such systems. Unfortunately, they are challenged by the prerequisite to accurately describe the localized spin structure on the heavy-metal adsorbate simultaneously with the Moiré superstructure of the extended support. To this end we present systematic density-functional theory (DFT) calculations addressing the adsorption of Dy atoms on corrugated graphene. We compare treatments on the screened hybrid functional with the Hubbard-corrected (DFT+U) level, and discuss approaches to reach electronic self-consistency in this delicate system. The calculations reveal intricate consequences of minor changes in electronic level alignment and state occupation on the preferred adsorption site. This calls for judicious choice and scrutiny of the employed U value in the numerically more efficient DFT+U approach.

O 95.3 Thu 15:45 WIL A317

Adsorption on PtRu surface alloys and stepped surface: A computational study — ●DAVID MAHLBERG¹, JULIA M. FISCHER², SUNG SAKONG¹, TANGLAW ROMAN¹, JÜRGEN BEHM¹, and AXEL GROSS¹ — ¹Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany — ²Australian Institute for Bioengineering and Nanotechnology, TheUniversity of Queensland, St Lucia, QLD 4072, Australia

Bimetallic surface alloys offer the possibility to tailor their reactivity through modifying their composition and/or structure. We have performed a computational study based on density functional theory addressing the adsorption of water on PtRu/Pt(111) surface alloys [1] and the hydrogen adsorption on Pt monolayer islands on Ru(0001) and on stepped Ru(10 $\bar{1}$ 9) surfaces decorated with atomic Pt rows.

We discuss the reactivity of bimetallic alloys using the concept of the ligand and geometric strain effects. It turns out that the Ru atoms interact more strongly than Pt with the adsorbed water molecules thus influences the adsorption geometries of both water monomers and ice-like water layers. The results with respect to hydrogen adsorption indicate that the influence of the surface imperfections on the adsorption properties extends up to two atomic rows away from the edges and steps, in good agreement with recent temperature programmed desorption and spectroscopy experiments [2].

[1] J.M. Fischer, D. Mahlberg, T. Roman, and Axel Groß, Proc. R. Soc. A **472**, 20160618 (2016). [2] H. Hartmann, T. Diemant, J. Bansk

mann, and R. J. Behm, PCCP **14**, 10919 (2012)

O 95.4 Thu 16:00 WIL A317

DFT study of water at the stoichiometric and defected Fe(110) surfaces — ●TOMASZ OSSOWSKI¹, JUAREZ L.F. DA SILVA^{1,2}, and ADAM KIEJNA¹ — ¹Institute of Experimental Physics, University of Wrocław, Poland — ²Instituto de Química de São Carlos, Universidade de São Paulo, Brazil

Water adsorption on iron surfaces is important in understanding of corrosion and reduction of iron oxides by hydrogen. Density functional theory (DFT) with van der Waals correction is applied to study molecular water adsorption on stoichiometric and defected Fe(110) surfaces. Structural and electronic properties of the H₂O/Fe(110) system, and a role of the vacancies are analysed. Results show that vacancy prefers sites at the topmost atomic layer, without energy barrier for its diffusion from the interior. The vacancies cause decreasing of the work function and local change the geometry with larger effects for higher vacancy density. At stoichiometric surface water adsorbs flat on top the Fe atoms with the H-O-H plane parallel to the surface, with binding energy of about 0.3 eV/molecule. Moreover, the adsorption energy of flat lying water is degenerated for few different orientation. It suggests possibility of H₂O rotation around direction perpendicular to the surface. At the defected surface, H₂O prefers sites near the vacancy. The binding of water to defected surface is by more than 0.2 eV stronger than to the stoichiometric one. Moreover, the adsorption of H₂O at stoichiometric region of the defected surface is by about 0.2 eV less preferable. It means that water is stronger bound to defected Fe(110) surface and vacancy can be considered as an adsorption centre for H₂O.

O 95.5 Thu 16:15 WIL A317

Transition Metal Complexes as Functional Units on Metal Surfaces - Structure, Properties and Reactivity from Density Functional Theory — ●WOLFGANG HIERINGER — Theoretical Chemistry, University of Erlangen-Nürnberg

Transition metal coordination compounds adsorbed on metal surfaces have received increasing attention in recent years. Not only do they appear as intermediates in on-surface synthesis schemes, e.g. in Ullman coupling reactions, but they may also serve as linking units in the formation of nanostructured networks and coordination polymers, as catalytic centers, or as functional units that tune the electronic properties of the surface. Transition metal complexes also play a central role as precursors in coating processes such as atomic layer deposition. I will present results from density functional theory calculations which aim at a better understanding of the basic properties and reactivity of transition metal complexes adsorbed on metal surfaces. We had shown before that the direct, coordinative interaction of the metal substrate with an adsorbed coordination compound can strongly alter the electronic properties of the central metal. In this contribution, I will discuss how the chemical bond between an adsorbed transition metal center and coordinating ligands can be influenced by the presence of a metal surface. I will analyze the electronic structure of the adsorbed complexes in terms of molecule-substrate charge transfer effects and hybridization of the molecular states with the surface.

O 95.6 Thu 16:30 WIL A317

LT-STM study of the structural and electronic properties of triazatruxene molecules on Ag(111) — ●ANJA BAUER¹, FLORIAN SINGER¹, PHILIPP ERLER¹, MARKUS MAIER², RAINER WINTER², YURIY DEDKOV¹, and MIKHAIL FONIN¹ — ¹Fachbereich Physik, Universität Konstanz, 78457 Konstanz, Germany — ²Fachbereich Chemie, Universität Konstanz, 78457 Konstanz, Germany

The opportunity of tuning the electrical and spin dependent properties of molecules is of great interest since this could enable the fabrication of molecule-based functional devices. Besides the stabilization and controlled manipulation of the charge and spin states, it is important to learn about the structural properties like the adsorption geometry and the orientation of the molecules on different substrates.

We investigated triazatruxene (TAT) molecules on Ag(111) by low temperature scanning tunneling microscopy (STM) and spectroscopy (STS). Coverages up to one monolayer (ML) were deposited by means of electrospray ionization (ESI) in ultra high vacuum. Sub-monolayer

coverages feature the molecules lying flat on the Ag(111) surface with characteristic distances in between them and exhibiting three different types of appearances, possibly due to the interaction with the substrate. By further increasing the coverage they grow in highly ordered structures depending on the density of TAT molecules. STS and time resolved current measurements at individual molecules reveal characteristic excitations beyond a certain threshold energy showing a telegraph noise behaviour with the period depending both on the voltage and the current.

O 95.7 Thu 16:45 WIL A317

Zn on Au(111) - Surface alloy formation and interaction with Oxygen — ●KONSTANTIN M. SCHÜTTLER and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Methanol is a promising molecule for chemical energy storage, e.g., when using H₂ from renewable sources for its synthesis. Au/ZnO was found to be a highly active catalyst for the synthesis of "Green Methanol" from CO₂/H₂ as a "Solar Fuel", suitable also for the specific operation conditions resulting from that application[1]. Previously, CuZn alloys have been used as model systems for the industrially used Cu/ZnO catalysts[2]. For Au/ZnO this approach is similarly plausible.

In order to gain more insight into the formation and nature of active sites, the formation, structure, electronic and chemical properties of bimetallic Zn/Au(111) surfaces serving as structurally well-defined 2D model catalysts were studied. The reactivity of Zn surface atoms, which may be crucial for the catalytic performance of ZnO supported MeOH synthesis catalysts, was studied by exposing Zn/Au(111) to oxygen. Also, the influence of temperature on Zn growth behavior was studied both by varying the Zn deposition temperature and by subsequent annealing. Resulting consequences of these findings on the structure of realistic Au/ZnO catalysts are discussed.

- [1] Y. Hartadi et al., *ChemSusChem* 8 (2015), 456
 [2] J. Nakamura et al., *Catal. Lett.* 31 (1995), 325

O 95.8 Thu 17:00 WIL A317

Oxidation of the Zr(0001) Surface — PETER LACKNER¹, WEN MA², BILGE YILDIZ², ULRIKE DIEBOLD¹, and ●MICHAEL SCHMID¹ — ¹Institute of Applied Physics, TU Wien, Vienna, Austria — ²Dept. of Nuclear Science & Engineering, Massachusetts Institute of Technology, USA

The first stages of oxidation of Zr(0001) were studied by scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). Dosing oxygen at room-temperature does not lead to ordered structures. Upon annealing to $\approx 550^\circ\text{C}$, we observe two types of ordered phases. The first one shows a hexagonal lattice with an in-plane lattice parameter of 331 pm, significantly smaller than bulklike ZrO₂(111) (≈ 361 pm) and the ultrathin ZrO₂(111) films obtained by oxidation of Zr alloys (≈ 350 pm, Refs. [1,2]). The second phase exhibits a moiré structure perfectly fitting a ZrO₂(100) lattice on the Zr substrate. Previous studies of ultrathin ZrO₂ films created by reactive deposition of Zr [3] and oxidation of Zr alloys [1,2] have always resulted in the non-polar ZrO₂(111) orientation, which has the lowest surface energy [4]. To our knowledge, this is the first atomic-scale observation of a ZrO₂(100) surface, opening new possibilities for studying this technologically important material.

- [1] Antlanger et al., *Phys. Rev. B* 86, 035451 (2012).
 [2] Choi et al., *J. Phys.: Condens. Matter* 26, 225003 (2014).
 [3] Meinel et al., *Phys. Rev. B* 74, 235444 (2006) and Refs. therein.
 [4] Christensen & Carter, *Phys. Rev. B* 58, 8050 (1998).

O 95.9 Thu 17:15 WIL A317

The chemical properties of PtCu/Ru(0001) monolayer surface alloys — ●THOMAS DIEMANT and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm

Bimetallic catalysts are well known for their unusual catalytic properties, which often excel those of the respective individual components with respect to activity, selectivity or long term stability. Studies of the adsorption / reaction properties of bimetallic model surfaces with defined structure and composition can contribute significantly to an improved understanding of the microscopic origin of this effect.

We studied the chemical properties of structurally well-defined CuPt monolayer surface alloys by temperature programmed desorption (TPD) and IR measurements using CO as probe molecule. These surface alloys were created by sequential deposition of Cu and Pt on

a Ru(0001) surface; their structural properties were clarified already before by our group using scanning tunnelling microscopy (STM) with chemical contrast [1]. We studied the change of the chemical properties (CO adsorption) of the alloy layers as a function of the alloy composition. We will correlate our findings to the results of structural characterization and compare to a previous study of similar type on the CO adsorption on PdCu/Ru(0001) monolayer surface alloys [2].

- [1] A. Engstfeld et al., *Surf. Sci.* 643 (2016) 65. [2] T. Hager et al., *Surf. Sci.* 558 (2004) 181.

O 95.10 Thu 17:30 WIL A317

Crystallographic Structure of the Oxidized Rh(100) Surface — ●TILMAN KISSLINGER, PASCAL FERSTL, M. ALEXANDER SCHNEIDER, and LUTZ HAMMER — Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany

In this study we combine quantitative LEED-IV, STM and DFT calculations to reinvestigate the adsorption behavior of oxygen on the Rh(100) surface in the coverage regime up to 0.67 ML.

In this range three distinct phases exist: A (2×2) -O [1], a (2×2) -O [2] and a (3×1) -2O structure [3]. The proposed models of these phases are verified by low R-factors between 0.07 and 0.10. For the (2×2) -O phase we corroborate the hollow site adsorption with additional 13 parameters determined. In case of the (2×2) -2O structure the clockwise-/ anticlockwise reconstruction of the substrate is confirmed. However, contrary to [2] our LEED analysis correctly accounts for all symmetry elements observed in experiment. It turned out that this does not change the structural parameters significantly, but alters the interpretation of the underlying physical processes. Instead of statistically disordered domains a statistical occupation of adjacent threefold coordinated sites by oxygen is the result of our structure determination ($R_P = 0.098$). Regarding the (3×1) -2O phase the proposed model by Gustafson *et al.* is validated with structural parameters similar to those of the Pt₇₅Rh₂₅(100)- (3×1) -2O structure [4].

- [1]: Oed *et al.*, *Surf. Sci.* 207, 55 (1988) [2]: Baraldi *et al.*, *Phys. Rev. Lett.* 82, 4874 (1999) [3]: Gustafson *et al.*, *J. Phys. Cond. Mat.* 24, 225006 (2012) [4]: Sporn *et al.*, *Surf. Sci.* 416, 384 (1998)

O 95.11 Thu 17:45 WIL A317

Solvation in molecularly thin water films and their growth — ●BARBARA A J LECHNER^{1,2}, SABINE MAIER³, YOUNGSOON KIM⁴, HEON KANG⁴, and MIQUEL SALMERON¹ — ¹Materials Sciences Division, Lawrence Berkeley Lab, Berkeley, CA — ²Department of Chemistry, Technical University of Munich — ³Department of Physics, Friedrich-Alexander University of Erlangen-Nürnberg — ⁴Department of Chemistry, Seoul National University, Seoul, Korea

The first water layer on hexagonal single crystal surfaces typically forms rotated hexagons, pentagons and heptagons of molecules in addition to strongly bound hexagonal rings commensurate with the substrate. Furthermore, the water monolayer does not expose any dangling hydrogen bonds in a vacuum environment. The growth of the entropically favorable proton-disordered ice, however, requires flipping some of the molecules in the first layer to expose dangling bonds. Using scanning tunneling microscopy (STM) we studied this transition from the first layer to water multilayers on Pt(111) and Ru(0001). We observed that a second layer initially forms an amorphous structure when grown on the crystalline monolayer. To facilitate the growth of ice in a bulk-like hexagonal arrangement, the first wetting layer needs to rearrange into a purely hexagonal structure commensurate with the surface. Ammonia (NH₃) molecules can adsorb to certain water molecules in the monolayer on Pt(111), specifically those that are slightly elevated from the surface and weakly bound to the metal. Ammonia molecules thus detect locations in the wetting layer where a water molecule can change its orientation relatively easily to flip up a hydrogen atom.

O 95.12 Thu 18:00 WIL A317

Field emission microscopy study of nonlinear dynamics during NO₂ hydrogenation — ●CÉDRIC BARROO¹, YANNICK DE DECKER¹, PIERRE GASPARD¹, NORBERT KRUSE¹, and THIERRY VISART DE BOCARMÉ² — ¹Université libre de Bruxelles, Brussels, Belgium — ²Washington State University, Pullman WA, USA

Field emission microscopy (FEM) is a technique that enables to probe reactions and their dynamics at the scale of a single nanoparticle. This study reports on the observation and analysis of various nonlinear behaviors during the catalytic hydrogenation of NO₂ on Pt. A tip-sample is used to study reactions during the ongoing reactive processes and down to 10nm². By changing a control parameter, it is possible to ob-

serve different behaviors, among which self-sustained periodic oscillations, and to determine the type of bifurcation leading to the emergence of the oscillations. In the case of periodic oscillations, the robustness is quantified via Fourier transform and temporal autocorrelation functions analyses. We also show how the dynamical attractor and the phase space dynamics can be reconstructed from experimental time series, and we prove that the periodic oscillations can be linked to a

limit cycle. Experiments at high temporal resolutions show the presence of propagating processes at the surface of the catalyst, and the propagation of chemical waves on a single facet of the nanocrystal is also observed. These waves take the form of target patterns with a velocity in the order of a few $\mu\text{m/s}$, in good agreement with previous studies of catalytic reactions at the mesoscale. The experiments prove the robustness of nonlinear behaviors down to the nanoscale.