

## O 49: Surface Chemical Reactions and Heterogeneous Catalysis III

Time: Wednesday 10:30–13:00

Location: PHY C 213

O 49.1 Wed 10:30 PHY C 213

**Hydrogen adsorption on bimetallic PdAg/Pd(111) surface alloys** — ●LUIS MANCERA and AXEL GROSS — Institute of Theoretical Chemistry, University of Ulm, D-89069 Ulm, Germany

Hydrogen adsorption on metallic surfaces has been a very active field of research due to the wide range of technical applications, in areas such as heterogeneous catalysis, energy storage and energy conversion. Bimetallic surface alloy catalysts have in various cases been found to show superior catalytic properties compared to those of the individual species, with the additional advantage of being tunable by doing changes in their compositions. In this contribution, we investigate hydrogen adsorption on PdAg/Pd(111) bimetallic surface alloys, a system that has been found to be thermodynamically stable and to exhibit a catalytic performance that is related to the size of the palladium ensembles [1]. We use periodic density functional theory (DFT) in order to elucidate mechanisms for molecular hydrogen dissociation and to identify active sites for adsorption as a function of palladium ensemble size and hydrogen coverage. In most of cases, similarly to adsorption on pure Pd(111), hydrogen atoms adsorb preferentially at threefold-coordinated hollow sites of palladium ensembles, while adsorption of molecular hydrogen is observed only at top position of isolated Pd atoms in the surface alloy.

[1] L. Mancera *et al.*, Phys. Chem. Chem. Phys. **15**, 1497 (2013).

O 49.2 Wed 10:45 PHY C 213

**Degree of hydrogenation of the reconstructed Si(001)-surface under MOVPE-conditions - A DFT study** — ●PHIL ROSENOW and RALF TONNER — Philipps-Universität Marburg, Fachbereich Chemie, Hans-Meerwein-Str. 4, 35032 Marburg

In order to model the metal organic vapor phase epitaxy of III/V-semiconductors on the silicon surface for the integration of laser devices in electronic circuits, the properties of the surface under the relevant conditions must be known beforehand. Especially the extent of hydrogenation is important for the reactivity of the surface. A DFT-based thermodynamics study has been performed on the reconstructed Si(001) surface in order to assess the validity of the theoretical approach compared to experimental observations and prepare for further adsorption studies.

The frequently used *ab initio*-thermodynamics approach which usually neglects surface contributions to thermodynamic quantities is compared to full phonon calculations. It can be shown that *ab initio*-thermodynamics overestimates the stability of the hydrogenated surface compared to full phonon calculations. The difference between the two can be used as a fitting parameter to obtain an expression for the extent of hydrogenation dependent on any MOVPE-conditions, in accord with experimental observations and allowing for a consistent computational treatment of the adsorption process on an atomistic scale.

O 49.3 Wed 11:00 PHY C 213

**Interaction and reactivity between H<sub>2</sub>O and CO on Au(310)** — ●MATTHIJS VAN SPRONSEN<sup>1</sup>, ANGELA DEN DUNNEN<sup>2</sup>, MAARTEN VAN REIJZEN<sup>2</sup>, CHRISTINE HAHN<sup>2</sup>, KEES-JAN WESTSTRATE<sup>3</sup>, and LUDO JUURLINK<sup>2</sup> — <sup>1</sup>Kamerlingh Onnes Laboratory, Leiden University, PO Box 9504, 2300 RA, Leiden, The Netherlands — <sup>2</sup>Leiden Institute of Chemistry, Leiden University, PO Box 9502, 2300 RA, Leiden, the Netherlands — <sup>3</sup>Technische Universiteit Eindhoven, Postbus 513, 5600 MB, Eindhoven, the Netherlands

Important discoveries show significant activity of supported Au nanoparticles in the oxidation of CO [1]. Furthermore, it also has been showed recently that water promotes the reactivity [2]. Both the remarkable activity of the Au nanoparticles and the promoting effect of water have not been completely understood. To study the effect of low coordinated Au atoms, the interaction between H<sub>2</sub>O and CO has been studied on the stepped Au(310) by Temperature Desorption Spectroscopy and high resolution X-ray Photoelectron Spectroscopy under Ultra High Vacuum conditions. In contrary to the Au(111) surface, desorption of H<sub>2</sub>O occurs in two peaks indicating stronger interaction of H<sub>2</sub>O with the low coordinate sites in the Au(310) surface. However, no fragmentation or reaction with CO has been detected. Electron irradiation of the adsorbed H<sub>2</sub>O layers creates a mixture of H<sub>2</sub>O, OH and O. In this mixture both OH and O show high reactivity to CO

oxidation even at temperatures as low as 123 K.

[1] M. Haruta, *et al*, Chemistry Letters, no. 2, pp. 405-408, 1987.

[2] M. Daté, *et al*, Angewandte, vol. 43, pp. 2129-2132, Apr. 2004.

O 49.4 Wed 11:15 PHY C 213

**Functional Azobenzene based Self-Assembled Monolayers: molecular composition effects and photo switchable properties** — ●SWEN SCHUSTER<sup>1</sup>, ANDREAS TERFORT<sup>2</sup>, and MICHAEL ZHARNIKOV<sup>1</sup> — <sup>1</sup>Applied Physical Chemistry, Heidelberg University, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany — <sup>2</sup>Institute for Inorganic und Analytical Chemistry, Frankfurt University, Max-von-Laue-Straße 7, 60438 Frankfurt, Germany

Control adjustment of work function of surfaces and interfaces by external stimuli is a challenging task. In this context, we designed novel photoresponsive, azobenzene-based self-assembled monolayers (SAMs) on gold and characterized them by synchrotron based high resolution x-ray photoelectron spectroscopy (HRXPS) and near-edge x-ray absorption fine structure spectroscopy (NEXAFS). The SAM precursors consisted of the thiol headgroup, a short aliphatic linker, azobenzene unit, and a functional tail group carrying a certain dipole moment. The length of the linker was varied to control the packing density in the monolayers, based on so called odd-even effect in monomolecular assembly. It was expected that the change in the orientation of the tail group upon the photoisomerization will result in a change of the work function of the entire system. The respective effects were monitored in situ by an ultra-high vacuum (UHV) Kelvin Probe. A clear signature of the photoisomerization behavior accompanied by the pronounced changes in the work function was found. The extent of the observed changes was related to the molecular structure (character of the tail group) and packing density in the SAM.

O 49.5 Wed 11:30 PHY C 213

**On-Surface Azide-Alkyne Cycloaddition on Au(111)** — ●OSCAR DÍAZ ARADO<sup>1</sup>, HARRY MÖNIG<sup>1</sup>, HENDRIK WAGNER<sup>2</sup>, JÖRN-HOLGER FRANKE<sup>1</sup>, GERNOT LANGEWISCH<sup>1</sup>, PHILIPP HELD<sup>2</sup>, ARMIDO STUDER<sup>2</sup>, and HARALD FUCHS<sup>1</sup> — <sup>1</sup>Physikalisches Institut and Center for Nanotechnology, WWU, Münster, Germany — <sup>2</sup>Organisch-Chemisches Institut, WWU, Münster, Germany

Two dimensional chemical reactions have been an uprising field of research in the recent years to obtain new polymeric networks directly at surfaces under ultrahigh vacuum (UHV) conditions [1,2]. Here we present the successful cycloaddition reaction between azides and alkynes on a Au(111) surface at room temperature and under UHV conditions [3]. High-resolution scanning tunneling microscopy images reveal that these on-surface cycloadditions occur highly regioselectively to form the corresponding 1,4-triazoles. Density functional theory simulations confirm that the reactions can occur at room temperature, where the Au(111) surface does not participate as a catalytic agent in alkyne C-H activation but acts solely as a two-dimensional constraint for the positioning of the two reacting moieties. Our results provide new insights about the necessity of copper catalysts for on-surface azide-alkyne "click" chemistry. The on-surface azide-alkyne cycloaddition has great potential for the development and fabrication of functional organic nanomaterials on surfaces.

[1] D. F. Perepichka, F. Rosei, Science 2009, 323, 216 [2] L. Grill *et al.*, Nature Chemistry, 2012, 4 (3), pp. 215-220 [3] O. Díaz Arado *et al.*, ACS Nano, 2013, 7 (10), pp. 8509-8515

O 49.6 Wed 11:45 PHY C 213

**Chemical reactions and electronic structure of single molecules at surfaces** — ●ALEXANDER RISS<sup>1,2</sup>, SEBASTIAN WICKENBURG<sup>1</sup>, LIANG Z. TAN<sup>1,3</sup>, HSIN-ZON TSAI<sup>1</sup>, PATRICK GORMAN<sup>1</sup>, DIMAS G. DE OYTEZA<sup>1,4</sup>, YEN-CHIA CHEN<sup>1,3</sup>, STEVEN G. LOUIE<sup>1,3</sup>, FELIX R. FISCHER<sup>1,3</sup>, and MICHAEL F. CROMMIE<sup>1,3</sup> — <sup>1</sup>University of California, Berkeley, USA — <sup>2</sup>Institute of Applied Physics, Vienna University of Technology, Austria — <sup>3</sup>Lawrence Berkeley National Laboratory, Berkeley, USA — <sup>4</sup>Centro de Física de Materiales CSIC/UPV-EHU-Materials Physics Center, San Sebastián, Spain

We investigated intra- and intermolecular reactions by imaging the chemical structure of single molecules by non-contact atomic force microscopy (nc-AFM). Additionally we used scanning tunneling mi-

crosscopy and spectroscopy (STM/STS) to probe how coupling of molecules affects their electronic properties. In our studies we:

- resolved the structural changes and bond rearrangements associated with complex cyclization cascades of enediyne molecules [1],
- revealed multiple steps of cyclization and coupling reaction mechanisms by real-space identification of intermediate species, and
- probed the combined structural and electronic properties of conjugated polymers formed through radical coupling reactions. We observed the formation of a low-energy 1D conducting channel along the backbone of polymer chains, which can be explained by pi-orbital overlap between monomer building blocks [2].

[1] D.G. de Oteyza et al.; *Science* **340**, 1434–1437 (2013)

O 49.7 Wed 12:00 PHY C 213

**Substrate induced dehydrogenation: Transformation of octaethylporphyrin into tetrabenzoporphyrin** — ●MERLIN SCHMUCK<sup>1</sup>, DENNIS VAN VÖRDEN<sup>2</sup>, MANFRED LANGE<sup>2</sup>, JOHANNES SCHAFFERT<sup>2</sup>, MAREN COTTIN<sup>2</sup>, CHRISTIAN BOBISCH<sup>2</sup>, and ROLF MÖLLER<sup>2</sup> — <sup>1</sup>Department of Physical Chemistry I, Ruhr-University Bochum, 44801 Bochum — <sup>2</sup>Faculty of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Lotharstr. 1-21, 47048 Duisburg, Germany

Solids of organic molecules can exhibit semiconducting properties but have many more possibilities to manipulate their electronic properties than compound semiconductors. That makes them interesting for numerous technical applications. One of such organic molecules is the porphyrin molecule, which is already in use for solar cells. Its electronic properties can be manipulated through different metallic core atoms and different ligands like ethyl groups or benzene rings or even more complex side groups. During the characterization of octaethylporphyrin iron (III) chloride via topographical STM imaging, we observed the thermally induced transformation of such a porphyrin derivative on a Cu(111) substrate to tetrabenzoporphyrin (TBP) by annealing the sample at about 450 K. The TBP was identified by comparing the newly formed molecules with iron phthalocyanine in mixed layers. Furthermore, an activation energy of this process was determined by counting the number of events for various temperatures. (D. van Vörden et al., *J. Chem. Phys.* **138**, 211102 (2013))

O 49.8 Wed 12:15 PHY C 213

**Structure and Reactivity of K[VO(O<sub>2</sub>)Hheida]: DFT Studies on the Interpretation of IR and NEXAFS Spectra** — ●LILI SUN and KLAUS HERMANN — Inorganic Chemistry Department, Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin

The identification of structural details of catalyst particles is important for a reliable description of structure-reactivity relationships. Here we consider an oxoperoxovanadium(V) compound chelated with N-(2-hydroxyethyl) iminodiacetic acid, [VO(O<sub>2</sub>)Hheida]. This complex is an efficient functional model for the vanadium haloperoxidase enzyme which acts as a halide oxidant. It includes various oxygen species next to its vanadium atom in very different local coordination. Thus, the [VO(O<sub>2</sub>)Hheida] complex offers an ideal test case for examining differently coordinated oxygen in the same system.

DFT calculations are performed to obtain the equilibrium geometry of the [VO(O<sub>2</sub>)Hheida]<sup>-</sup> ion and the results agree well with experiments for a K[VO(O<sub>2</sub>)Hheida] single crystal where potassium ions form the positive counterpart. The analysis of vibrational modes al-

lows an identification of differently coordinated oxygen species, such as vanadyl and di-oxo, although corresponding modes are not well localized. The theoretical spectrum fits with experimental data from IR and Raman measurements. Theoretical O 1s NEXAFS spectra are also evaluated. The corresponding partial NEXAFS spectra show substantial differences amongst the different oxygen species which allows an easy discrimination. These results confirm the experimental O K-shell NEXAFS data.

O 49.9 Wed 12:30 PHY C 213

**Surface reaction steps of dicyclohexylmethane/diphenylmethane on Pt(111)** — ●CHRISTOPH GLEICHWEIT<sup>1</sup>, OLIVER HÖFERT<sup>1</sup>, NICOLE BRÜCKNER<sup>2</sup>, PETER WASSERSCHIED<sup>2</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, and CHRISTIAN PAPP<sup>1</sup> — <sup>1</sup>University Erlangen-Nuremberg, Chair of Physical Chemistry II, Egerlandstr. 3, 91058 Erlangen, Germany — <sup>2</sup>University Erlangen-Nuremberg, Institute of Chemical Reaction Engineering, Egerlandstr. 3, 91058 Erlangen, Germany

The liquid organic hydrogen carrier pair dicyclohexylmethane (DHM) and diphenylmethane (DPM) was studied on Pt(111) by high-resolution X-ray photoelectron spectroscopy and temperature programmed desorption (TPD) in order to elucidate the reaction steps. Using physical vapor deposition, the molecule was first adsorbed under ultra high vacuum conditions, and subsequently the surface reaction was monitored during heating. The signals of the individual surface species during the reaction of the loaded carrier (DHM) are compared to the ones of the unloaded carrier (DPM), giving information on the dehydrogenation mechanism. During adsorption, the development of monolayer and multilayer signals is observed clearly in the C 1s region for both DHM and DPM. When heating the sample continuously, the multilayer of DHM desorbs at about 230 K. Subsequently, the dehydrogenation of DHM follows successively in the range of 250 to 320 K. For comparison, we measured TPD of the unloaded carrier DPM showing dehydrogenation at the CH<sub>2</sub> group above 310 K, leading to the first decomposition product. Upon further heating up to 800 K complete decomposition to carbon fragments happens.

O 49.10 Wed 12:45 PHY C 213

**Computational screening study towards redox-active metal-organic frameworks** — ●JELENA JELIC<sup>1</sup>, DMYTRO DENYSSENKO<sup>2</sup>, DIRK VOLKMER<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>Universität Augsburg, Germany

The metal-organic framework (MOF) MFU-4l containing Co(II) centers and Cl<sup>-</sup> ligands [1] has recently shown promising redox activity. Aiming for further improved MOF catalysts for oxidation processes employing molecular oxygen we present a density-functional theory (DFT) based computational screening approach to identify promising metal center and ligand combinations within the MFU-4l structural family [2]. Using the O<sub>2</sub> binding energy as a descriptor for the redox property, we show that relative energetic trends in this descriptor can reliably be obtained at the hybrid functional DFT level and using small cluster (scorpionate-type complex) models. Within this efficient computational protocol we screen a range of metal center / ligand combinations and identify several candidate systems that offer more exothermic O<sub>2</sub> binding than the original Co/Cl-based MFU-4l framework.

[1] S. Biswas *et al.*, *Dalton Trans.* 6487 (2009).

[2] J. Jelic *et al.*, *New Journal of Physics* **15**, 115004 (2013).