O 8: Surface Reactions

Time: Monday 10:30–13:00 Location: MA 141

O 8.1 Mon 10:30 MA 141

Reactivity of single metal atoms in different coordination environments — •Nan Cao, Longfeng Huang, Johannes V. Barth, and Alexander Riss — Physics Department E20, Technical University of Munich, 85748 Garching, Germany

Metal centers within metalorganic networks hold promise for applications in single-atom catalysis, gas storage and sensing. Their activity is not only determined by the chemical nature of the metal, but is also significantly influenced by the bonding configuration. It is of fundamental scientific and technological relevance to understand how the reactivity of these sites can be controlled via chemical design.

In this work we present direct measurements of the interaction forces of single metal atoms[1] in different metalorganic coordination environments via atomic-scale atomic force microscopy (AFM) experiments. In particular, we examine how the interaction of metal sites with different types of probe atoms (directly attached to the AFM tip) changes as a function of their bonding configuration. Our measurements show that while chemically relatively inert CO-functionalization yields little discrimination between metal centers in different environments, Cl-functionalization gives rise to significant differences: low-coordinated metal atoms exhibit notably stronger interactions with the probe atom.

Such atomic-scale studies provide means to characterize active sites within complex metalorganic architectures, thus aiding in a rational design strategy toward materials with tailored catalytic properties.

[1]*Science* 2019, **366**, 235-238; *J. Phys. Rev. Lett.* 2020, **124**, 096001.

O 8.2 Mon 10:45 MA 141

On-Surface Isomerization of Indigo within 1D Coordination Polymers — •Hongxiang Xu[1], Ritam Chakraborty[2], Abhishek Kumar Adak[2], Arpan Das[2], Biao Yang[1], Dennis Meier[1], Alexander Riss[1], Joachim Reichert[1], Shobhana Narasimhan[2], Johannes V. Barth[1], and Anthoula C. Papageorgiou[1,3] — [1]Technische Universität München, Germany — [2]Jawaharlal Nehru Centre for Advanced Scientific Research, India — [3]National and Kapodistrian University of Athens, Greece

We present surface-confined metallosupramolecular engineering of coordination polymers using natural dyes as molecular building blocks: indigo and the related Tyrian purple. Both building blocks yield identical, well-defined coordination polymers composed of (1 dehydroindigo : 1 Fe) repeat units on two different silver single crystal surfaces. These polymers are characterized atomically by submolecular resolution scanning tunneling microscopy, bond-resolving atomic force microscopy and X-ray photoelectron spectroscopy. On Ag(100) and on Ag(111), the *trans* configuration of dehydroindigo results in N,O-chelation in the polymer chains. On the more inert Ag(111) surface, the molecules undergo thermally induced isomerization from the *trans* to the *cis* configuration and afford N,N- plus O,O-chelation. Density functional theory calculations confirm that the coordination polymers of the *cis*-isomers on Ag(111) and of the *trans*-isomers on Ag(100) are energetically favored. Our results demonstrate post-synthetic linker isomerization in interfacial metal-organic nanosystems.

O 8.3 Mon 11:00 MA 141

Thioetherification of Br-Mercaptobiphenyl Molecules on Au(111) — Ana Barragan[1], Roberto Robles[2], Nicolas Lorente[2,4], and •Lucia Vitali[1,2,3,4] — [1]Advanced Polymers and Materials: Physics, Chemistry and Technology, Chemistry Faculty (UPV/EHU) — [2]Centro de Física de Materiales CFM/MPC(CSIC-UPV/EHU), — [3]Ikerbasque Research Foundation for Science, Bilbao 48009, Spain; — [4]Donostia International Physics Center (DIPC), 20018 San Sebastián,

Thioether polymers are fundamental for a variety of applications. Their synthesis is, however, more challenging than that of other metal-catalyzed reactions due to the reported detachment of the S atom during thermal activation. In this study, it has been demonstrated unambiguously that thermal annealing results in the thioetherification of the 4-bromo-4-mercaptobiphenyl molecule (Br-MBP) adsorbed on the surface of Au(111). Through complementary techniques, such as scanning tunneling microscopy, spectroscopy, and first principle calculations, we have identified four reaction steps, involving sulfhydryl or bromine molecular functional groups and leading to the formation of intermolecular C-S bonds. To form the thioether polymer and to overcome the competitive formation of C-C bonds, two reaction steps, the dehalogenation, and dissociation of the S-Au bond, must occur simultaneously. We detail the electronic properties of the phenyl-sulfur bond and the polymer as a function of the ligand length. This result suggests a wider perspective of this chemical synthesis.

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O 8.4 Mon 11:15 MA 141

Real-Space Imaging of Surface Reactions: Deprotonation and Metalation of Phthalocyanine — •Andreas Christ, Matthias Bode, and Markus Leisegang — Physikalisches Institut, Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

On-surface reactions of phthalocyanines allow to drastically change the molecular properties as well as the interaction with a substrate. Several studies have demonstrated metalation process with both co-deposited atoms and by substrate atoms [1]. However, insights into the process related with metalation by means of direct observation on a single-molecule level have rarely been reported.

In our study, we investigate the temperature-driven self-metalation from H_2Pc to CuPc on a Cu(111) surface by means of STM. We find that the metalation process proceeds at a significantly higher temperature threshold than previous reported [2] and that it competes with a deprotonation process. All three molecule species, H_2Pc, H_0Pc, and CuPc, can unambiguously be identified by their distinct STM-induced rotational behavior. This allows us to determine the species of each individual adsorbed molecule and thus gain a detailed insight into the temperature dependence of both surface-induced reactions [3].

[1] J. M. Gottfried, Surf. Sci. Rep. **70**, 259 (2015)
[2] M. Chen *et al.*, J. Phys. Chem. C **118**, 8501 (2014)
[3] A. Christ *et al.*, Phys. Chem. Chem. Phys. **25**, 7681 (2023)

O 8.5 Mon 11:30 MA 141

Surface Chemistry of Porphyrins: Studying Molecular Transformations with XPS and STM — •Eleanor Frampton[1], Matthew Edmondson[2], Michael Clarke[2], Ailish Gray[2], and Alex Saywell[2] — [1]MAX IV Laboratory, Lund, Sweden — [2]School of Physics, University of Nottingham, UK

Porphyrin molecules may participate in a number of on-surface reactions [1], the dynamics of which may be influenced by several factors, including temperature, chemistry of the porphyrin species, choice of substrate, etc. Porphyrin molecules themselves are extremely versatile and act as building blocks in the self-assembly of 2D molecular arrays [2], which can be tailored to have specific electronic, optical or catalytic properties. By employing a combination of spectroscopy and imaging techniques, these reactions can be studied in detail. [1-3]

The presentation will focus in particular on the on-surface transformations of trans-Br2TPP on Cu(111). This molecule is known to undergo Ullman coupling, an intramolecular ring closing reaction, and self-metalation on this surface. The stepwise progression of the reaction will be discussed, particularly how these processes can be probed using techniques such as scanning tunnelling microscopy (STM) and x-ray photoelectron spectroscopy (XPS). I detail how these techniques can be complementary when applied to on-surface chemistry. [1] Gottfried, J. M. (2015), Surf. Sci. Rep., 70(3), 259-379.[2] L. Grill, S. Hecht, Nat. Chem. 12, 115*130 (2020) [3] Edmondson, M., Frampton, E.S. * & Saywell, A. (2022), Chem. Commun. 58(42), 6247-6250.

O 8.6 Mon 11:45 MA 141

Plasmon-driven/enhanced N-N and C-C coupling reactions — •Radwan M. Sarhan — Helmholtz Zentrum Berlin fur Materialien und Energie, Berlin, Germany

Plasmon-induced catalysis, driven by light and noble metals (e.g., Au, Cu, and Ag), offers a promising, ecofriendly and efficient alternative strategy to conventional thermochemistry, thereby driving chemical reactions via resonant excitation of the plasmonic nanoparticles. After excitation of the surface plasmon of the particles, energetic charge carriers (hot electrons and holes) and a high local temperature are generated, which would initiate and/or enhance chemical transformations of the adsorbed molecules. However, the exact contribution of the hot electrons and heat in the overall reaction performance and mechanism is still a hot topic. In this talk, I will present various plasmonic particles with tunable plasmon resonances (e.g., AuNRs and AuPd NRs), which have been used to achieve efficient solar-to-chemical/thermal energy conversion. In addition, I will show our recent results on different chemical reactions ranging from a reduction of small nitroaromatic molecules to more complex N-N and C-C coupling reactions (e.g., Heck reactions) that have been driven via the hot electrons or enhanced by the high local heat. Moreover, different experimental analysis will be shown to unfold the main driving force of the reaction mechanism.

O 8.7 Mon 12:00 MA 141

Unfolding Chemical Diversity in ORR Catalysts: A DFT Study on Experimentally-Inspired Bimetallic-Organic Monolayers — •Juan Manuel Lombardi[1,2], Doris Grumelli[3], Rico Gutzler[4], Fabio Heriberto Busnengo[1], and Paula Abufager[1] — [1]IFIR, Rosario, Argentina — [2]Fritz-Haber-Institut der MPG, Berlin — [3]INIFTA, La Plata, Argentina — [4]MPI for Solid State Research, Stuttgart

In the quest for more efficient catalysts for the oxygen reduction reaction (ORR), the synergy between metallic and organic components presents a promising avenue for catalytic innovation. We focus on self-assembled monolayers (SAM) of FeTPyP on Au(111) and their bimetallic-organic counterpart, the metal-organic coordination network (MOCN) FeTPyP+Co complex on Au(111), which is experimentally prepared through Co atom sublimation. Using Density Functional Theory (DFT), this study elucidates the intricate electronic behavior of the active metal sites in these systems and their mechanistic roles in ORR. We find that the FeTPyP+Co complex on Au(111) achieves a more balanced adsorption of ORR intermediates, owing to a more diverse electronic environment induced by the bimetallic interaction within the metal-organic framework. This study not only widens the spectrum of chemical landscapes for ORR catalysts but also establishes a theoretical basis that could inspire the proposal and conceptual development of novel catalysts.

O 8.8 Mon 12:15 MA 141

Free Energy Barrier Calculation for Catalytic Hydrogen Assisted CO Dissociation using Machine-Learning Surrogate Models — •Hyunwook Jung, Karsten Reuter, and Johannes T. Margraf — Fritz-Haber-Institut der MPG, Berlin

The calculation of accurate reaction rate constants of elementary processes is a central element of computational surface catalysis research. At present, this proceeds prevalently via transition state theory, with the process free energy barrier as primary input. Ideally, such barriers are obtained through extensive sampling of configurations along the transition path, using techniques such as umbrella sampling. However, the associated biased molecular dynamics simulations are prohibitively expensive at the density functional theory level, making the more efficient but less accurate harmonic approximation a common practice in most studies. In order to overcome this limitation, we develop a machine learning surrogate model using an iterative training workflow. We apply this computationally undemanding surrogate model to hydrogen assisted CO dissociation as the key rate limiting step in synthesis gas conversion on Rh, Cu, and Ru surfaces. Obtaining significant thermal effects not captured in the harmonic approximation, we investigate the consequences on product selectivities.

O 8.9 Mon 12:30 MA 141

Dynamics of enantioselective surface chemistry on chiral intermetallic substrates — •Raymond Christopher Amador[1,2], Hannah Bertschi[1,2], and Daniele Passerone[1,2] — [1]Empa, Dübendorf, Switzerland — [2]ETH Zürich, Zürich, Switzerland

In this work, we explore the enantioselective surface adsorption and reaction of two representative organic molecules (DBBA and 9AP) on intermetallic palladium gallium (PdGa) chiral substrates. By briefly analysing dispersive forces in conjunction with density-functional theory, we elucidate the enantioselective interactions between the (pro)chiral molecules and the PdGa surface, focusing on the dynamic processes that govern adsorption/desorption and surface diffusion. We study kinetics and thermodynamics of the processes by means of tailored molecular dynamics simulation methods (metadynamics) that are able to sample the free energy landscape of the process at realistic temperatures. Adsorption configurations and free energy barriers are obtained and enlighten the dynamics of chirality sensitive reactions. The presented findings contribute to a deeper understanding of the molecular mechanisms governing chiral selectivity in catalytic systems, providing insights that can guide the design and optimization of enantioselective catalysts, with possible applications to the pharmaceutical and chemical industry.

O 8.10 Mon 12:45 MA 141

Propionic Acid at Air/water Interface: An Ab initio Molecular Dynamic Simulation Study — •Ali Ghiami-Shomami[1], Dominika Lesnicki[2], and Marialore Sulpizi[1] — [1]Faculty of Physics and Astronomy, Department of Physics, Ruhr Universität Bochum, NB6, 44780, Bochum, Germany — [2]LPCT UMR 7019 CNRS, Université de Lorraine 54506 Vandoeuvre-lès-Nancy Cedex, France

Organic materials are abundant in Earth's atmosphere and are present in aerosols. Particularly, organic acids can catalyze reactions on aerosols and also contribute to atmospheric acidity and regulate precipitation pH [1-2]. Therefore, understanding the structural, dynamical, and acidic properties of such acids at the air/water interface is important. Extending our previous work [3], we employ here ab initio molecular dynamics (AIMD) simulations to investigate propionic acid's behavior in the bulk and at the air/water interface. In particular we use DFT-based simulations at the BLYP level to investigate cis and trans conformers. We find that in bulk the cis conformer is more stable and this observation is in line with findings for formic acid as parent of propionic acid. Moreover, structural analysis indicate that there is no isomerization during simulation time. Additionally the solvation structure for the acid in bulk and at the interface is discussed and compared to other small organic acids. Finally the relative acidity between bulk and interface molecules is also presented.

References [1] P. G. Blower et al., J. Phys. Chem. A, 2013, 117, 2529. [2] B. Franco et al., Nature, 2021, 593, 233. [3] D. Lesnicki et al., Phys. Chem. Chem. Phys., 2022, 24, 13510.