

O 11: Surface Reactions

Time: Monday 15:00–17:15

Location: CHE 91

O 11.1 Mon 15:00 CHE 91

Machine-Learning Driven Global Optimization of Surface Adsorbate Geometries — ●HYUNWOOK JUNG, LENA SAUERLAND, SINA STOCKER, KARSTEN REUTER, and JOHANNES T. MARGRAF — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The adsorption energies of molecular adsorbates on catalyst surfaces are key descriptors in computational catalysis research. For the relatively large reaction intermediates frequently encountered, e.g., in syngas conversion, a multitude of possible binding motifs leads to complex potential energy surfaces (PES), however. This implies that finding the optimal structure is a difficult global optimization problem, which leads to significant uncertainty about the stability of many intermediates. To tackle this issue, we present a global optimization protocol for surface adsorbate geometries which trains a surrogate machine learning potential on-the-fly. The approach is applicable to arbitrary surface models and adsorbates and minimizes both human intervention and the number of required DFT calculations by iteratively updating the training set with configurations explored by the algorithm. We demonstrate the efficiency of this approach for a diverse set of adsorbates on the Rh(111) and (211) surfaces.

O 11.2 Mon 15:15 CHE 91

The effect of ultrathin ionic liquid films on the adsorption dynamics of 1,3-butadiene and 1-butene on Pt(111) studied by molecular beam techniques — ●LEONHARD WINTER, CYNTHIA CAROLINA FERNÁNDEZ, AFRA GEZMIS, TIMO TALWAR, STEPHEN MASSICOT, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Ionic Liquids (ILs) are low temperature melting salts. In “Solid Catalysis with Ionic Liquid Layer (SCILL)” systems, IL thin films are used to coat the catalytically active metal and thereby enhance the selectivity of the catalyst; this approach is beneficial, e.g., in the industrially important hydrogenation of 1,3-butadiene to butenes, since further hydrogenation to *n*-butane must be suppressed. We used a supersonic molecular beam to investigate the adsorption dynamics of this reaction in a UHV SCILL model system. Along the method of King and Wells we measured sticking coefficients of 1,3-butadiene and 1-butene on Pt(111) coated with ultrathin layers of the IL 1,3-dimethylimidazolium bis(trifluoromethyl)sulfonate ([C₁C₁Im][Tf₂N]). At 180 K, the sticking coefficients decrease non-linearly with increasing IL coverage. We explain the deviation from a simple site-blocking model with trapping into a mobile precursor state of the hydrocarbon molecules that arrive on top of IL islands. This deviation is less pronounced for films prepared at 250 K, which we attribute to larger IL island sizes.

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O 11.3 Mon 15:30 CHE 91

On-surface synthesis of porphyrinoid monomers and dimers — ●HONGXIANG XU¹, RITAM CHAKRABORTY², BIAO YANG¹, JOACHIM REICHERT¹, ABHISHEK K. ADAK², SHOBHANA NARASIMHAN², JOHANNES V. BARTH¹, and ANTHOULA C. PAPAGEORGIOU^{1,3} — ¹Technical University of Munich, Germany — ²Jawaharlal Nehru Centre for Advanced Scientific Research, India — ³National and Kapodistrian University of Athens, Greece

Porphyrinoid molecules can incorporate a wide array of the elements of the periodic table in a chemical pocket. By engineering their coordination pocket one can tune the functional properties for catalysis, spintronics, electronics and sensors. Here we use a common natural pigment, indigo, with Fe atoms on Au(111). By a series of thermally activated reaction steps including selective C-H activation, we obtain a novel metallated porphyrinoid species with high yield. By McMurry-type coupling on the same surface, this porphyrinoid species fuses into dimers. The reaction products are identified by a combination of scanning tunnelling microscopy, bond resolving atomic force microscopy and density functional theory investigations. Our studies expand the available chemistry for on-surface synthesis of macrocyclic tetrapyrroles [1] and contribute to versatile metal-organic nanostructures with smaller coordination pockets, which are challenging to obtain via solution chemistry.

[1] E. Nardi, et al. *J. Phys. Chem. C* 2014, **118**, 27549; Q. Fan, et al. *Nat. Commun.* 2019 **10**, 5049.

O 11.4 Mon 15:45 CHE 91

Fischer-Tropsch synthesis on magnetite (111) surface — ●HESHMAT NOEI¹, ROBERT GLEISSNER¹, MICHAEL WAGSTAFFE¹, CHRISTOPHER GOODWIN², MARKUS SOLDEMO², MIKHAIL SHIPILIN², PATRICK LÖMKER², CHRISTOPH SCHLUETER³, PETER AMANN², and ANDREAS STIERLE¹ — ¹Centre for X-ray and Nano Science CXNS, Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany — ²Stockholm Universitet, Department of Physics, Roslagstullsbacken 21, 10691 Stockholm, Sweden — ³Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany

Magnetite (Fe₃O₄) is an important and diverse transition metal oxide with applications in catalysis, data storage and biomedical imaging. In this contribution, we demonstrate an operando Fischer-Tropsch synthesis with a focus on product detection on the magnetite (111) surface and clarify the reaction mechanism and intermediates applying state of the art ambient pressure XPS with ability to measure photoemission spectra 76 at above 1 bar using hard X-ray at PETRA III beamline at DESY in Hamburg and clarify the mechanism of FT synthesis by monitoring reaction products operando on single crystal Fe₃O₄. We show then the dominant product from FT synthesis is a methoxy species and short chain alkanes under our reaction conditions (500 mbar, 400°C) and that no aldehydes and ketones are formed during reaction.

O 11.5 Mon 16:00 CHE 91

On-Surface CO₂ Capturing by Electron-Rich Phosphines: Comparison of the Assembly on Ag(100) and on the NaBr(100) Double Layer — ●VLADIMIR LYKOV¹, FLORENZ BUSS², FABIAN DIELMANN³, and KARINA MORGENSTERN¹ — ¹Ruhr-Universität Bochum, Germany — ²Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Germany — ³Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Center for Chemistry and Biomedicine, Innsbruck, Austria

Electron-rich phosphines exhibit exceptional electron donor properties and form zwitterionic Lewis base adducts with small inert molecules, for instance, carbon dioxide (CO₂) and sulfur dioxide (SO₂) [1]. The main focus of this project is understanding the influence of geometrical confinement on the capturing of CO₂ by electron-rich phosphines. The effect of geometrical confinement is studied with a surface science approach. For this purpose, we use a low-temperature (7 K) scanning tunneling microscope (STM). To understand the influence of the metal surface on carbon dioxide capture, we compare the molecules adsorbed on Ag(100) to those on NaBr(100) double layer, supported by Ag(100). The subsequent deposition of carbon dioxide and electron-rich phosphines confirmed the affinity of CO₂ to these phosphines. The influence of the two surfaces on the product assembly will be discussed in this presentation.

[1] F. Buß, et al. *Chem. Eur. J.* 2022, **28**, e2021040.

O 11.6 Mon 16:15 CHE 91

On-surface synthesis of enetriynes — NAN CAO^{1,2}, ●BIAO YANG¹, ALEXANDER RISS¹, JOHANNA ROSEN², JONAS BJÖRK², and JOHANNES V. BARTH¹ — ¹Physics Department E20, Technical University of Munich, Garching, Germany — ²Department of Physics, Chemistry and Biology, IFM, Linköping University, Linköping, Sweden

Belonging to the enyne family, enetriynes comprise a distinct electron-rich all-carbon bonding scheme. However, the lack of convenient synthesis protocols limits the associated application potential within, e.g., biochemistry and materials science. Herein we introduce a pathway for highly selective enetriyne formation via tetramerization of terminal alkynes on a Ag(100) surface. Taking advantage of a directing hydroxyl group, we steer molecular assembly and reaction processes. Induced by O₂ exposure the terminal alkyne moieties deprotonate and organometallic bis-acetylide dimer arrays evolve. Upon subsequent thermal annealing tetrameric enetriyne-bridged compounds are generated in high yield, readily self-assembling into regular networks. We combine high-resolution scanning probe microscopy, X-ray photoelectron spectroscopy and density functional theory calculations to examine the structural features, bonding characteristics and the underlying reaction mechanism. Our study provides an integrated strategy to

precisely fabricated functional enediyne species, providing access to a distinct class of highly conjugated π -system compounds.

O 11.7 Mon 16:30 CHE 91

Cold plasma deoxidation of copper and iron surfaces — ●VIKTOR UDACHIN¹, SEBASTIAN DAHLE², and WOLFGANG MAUS-FRIEDRICHS¹ — ¹Clausthal University of Technology, Clausthal-Zellerfeld, Germany — ²University of Ljubljana, Ljubljana, Slovenia

The removal of native oxides, which are present on metals in ambient atmosphere, is an important step in many industrial applications. Cold plasma methods, like dielectric barrier discharge (DBD) plasmas, have gained attention due to the high deoxidation efficiencies and relative simplicity of the setups. Several groups have indicated a reduction of copper oxygen layers using DBD hydrogen-containing plasmas, but no detailed information about reduction kinetics and limitations on different metal systems is available. In this study, we investigated the deoxidation effect of a DBD plasma in Ar/H₂ and Ar/SiH₄ atmospheres on natively oxidized Cu and Fe surfaces at 1000 hPa. We observed deoxidation effect on Cu already at 25 °C in both atmospheres. In contrast, reduction of iron oxide was obtained only at the surface temperature of 200 °C, showing an increase in the efficiency of the plasma-induced thermal treatment in comparison to thermal one. The chemical state of the samples and the kinetics of the reduction of oxides were studied via X-ray photoelectron spectroscopy (XPS). The morphology was characterized with the atomic force microscopy (AFM). By using optical emission spectroscopy (OES), the reactive species within the implemented DBD plasmas were described. Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - Project-ID 394563137 - SFB 1368

O 11.8 Mon 16:45 CHE 91

Multiscale modeling and simulation of texture effects on the corrosion of stainless steel in aqueous media — ●VAHID JAMEBOZORGI^{1,2}, KARSTEN RASIM³, and CHRISTIAN SCHRÖDER^{1,2} — ¹Bielefeld Institute for Applied Materials Research, Bielefeld University of Applied Sciences, 33619 Bielefeld, Germany — ²Faculty of Physics, Bielefeld University, 33615 Bielefeld, Germany — ³Miele & Cie. KG, Center for Materials (CFM), Carl-Miele-Straße 29, 33332 Gütersloh

Texture plays a crucial role in physical processes and properties of condensed matter as it is broadly highlighted in the literature. In

this work we describe a robust methodology to investigate texture effects which does not suffer from common limitations of quantum based computational approaches in time and space but also can provide the same accuracy as atomistic calculations with orders of magnitude less computational costs. Our methodology is based on the finite element method (FEM) and utilizes 3D digital representations of multi grain microstructures. We demonstrate the efficiency of our approach by studying pitting corrosion in stainless steel. As reflected in literature the irregular geometry of pit expansion through pitting corrosion is mostly caused by texture. We found that the texture significantly affects the pitting corrosion rate and consequently causes various irregular pit growth patterns in granular microstructures. These results are consistent with our DFT and reactive force field molecular dynamics simulations which validates our suggested approach.

O 11.9 Mon 17:00 CHE 91

The role of aromaticity in the cyclization and polymerization of alkyne-substituted porphyrins on Au(111) — ●NAN CAO¹, JONAS BJÖRK², EDUARDO CORRAL-RASCON¹, ZHI CHEN^{3,4}, MARIO RUBEN³, MATHIAS O. SENGE⁵, JOHANNES V. BARTH¹, and ALEXANDER RISS¹ — ¹Technical University of Munich, Germany — ²Linköping University, Sweden — ³Karlsruhe Institute of Technology, Germany — ⁴Shenzhen University, China — ⁵Institute for Advanced Study, TUM, Germany

Aromaticity is one of the most practical and versatile concepts for the assessment of the reactivity of organic molecules. However, in on-surface chemistry - where the interaction with the substrate can significantly alter the electronic and geometric structure of the adsorbates - the role of aromaticity is not understood. Here we investigate how aromaticity affects the reactivity of alkyne-substituted porphyrin molecules in cyclization and coupling reactions on a Au(111) surface.[1] We examine and quantify the regioselectivity of the reactions by scanning tunneling microscopy and bond-resolved atomic force microscopy at the single-molecule level. Our experiments show a substantially lower reactivity of carbon atoms that are stabilized by the aromatic diaza[18]annulene pathway of free-base porphyrins. The results are corroborated by density functional theory calculations, revealing a direct correlation between aromaticity and thermodynamic stability of the reaction products. These insights will help to design and understand reactions in on-surface chemistry and heterogeneous catalysis.

1. <https://doi.org/10.21203/rs.3.rs-1271465/v1>