O 9: Surface Reactions

Time: Monday 10:30–12:30 Location: H25

O 9.1 Mon 10:30 H25

Co_2 reduction by solvated electrons at the NH_3/Cu(111) interface. — •Maya Heine, Lukas Gierster, and Julia Stähler — Humboldt-Universität zu Berlin, Institut für Chemie

Understanding CO_2 reactivity is crucial; the amount of CO_2 in the atmosphere continues to rise with no imminent peak in fossil emissions in sight [1]. Previously, solvated electrons (e_s) have been suggested to activate CO_2 , e.g. by forming surface bound CO_2^- radicals [2]. With time-resolved two-photon photoemission and the amorphous NH_3/Cu(111) interface, we can study the energetics and dynamics of e_s on femtosecond timescales [3]. Here, the electrons are localised at the surface and their lifetime depends exponentially on NH_3 coverage. On an ultrafast timescale, we can now use e_s to decipher the fundamental rate and steps of CO_2 activation. We observe a systematic decrease in the e_s lifetime as CO_2 is added and conclude that CO_2 opens a new decay channel for e_s. Further, increases in the work function serve as indicators of possible reactions: electron attachment to CO_2 or activated CO_2^- which has a dipole moment. For thick NH_3 films we see a much larger work function increase and bleaching of e_s. This suggests that the film thickness controls the lifetime of charged reaction intermediates and thus the reaction pathway. Moreover, we show that e_s attachment to CO_2 occurs on a 10s of ps timescale.

[1] Friedlingstein et al. **ESDD** (2024)

[2] Hu et al. **Nat. Commun, 14**, 4767 (2023)

[3] Stähler et al. **Chem. Sci. 2, 5**, 907 (2011)

O 9.2 Mon 10:45 H25

Exploring on hydrogen evolution reaction performance of borophene monolayer — •Jing Liu and Axel Gross — Institute of Theoretical Chemistry, Ulm University, Oberberghof 7, 89081 Ulm, Germany

Borophene, a unique graphene-like 2D material composed of boron atoms, has gained significant attention due to its exceptional properties [1]. This study investigates its performance in catalyzing the hydrogen evolution reaction (HER). We focus on four distinct borophene configurations: α, β12, γ3, and trigonal structures [2]. Using density functional theory (DFT), we assess the HER performance of pristine monolayers as well as their interaction with an Ag(111) substrate.

The results show that α, β12, and γ3 monolayers possess exceptional HER activity, evidenced by their optimal Gibbs free energy for H-adsorption. However, their performance is markedly suppressed upon interaction with a Ag(111) support, where borophene-support interaction alters the hydrogen binding properties. By contrast, trigonal structure exhibits limited HER activity in both conditions, reflecting structural characteristics unfavorable for HER.

This work highlights the intrinsic catalytic potential of borophene monolayers while emphasizing the critical influence of substrate interactions.

[1] B. Feng, J. Zhang, Q. Zhong, et al. Experimental realization of two-dimensional boron sheets. *Nature Chem.* 8, 563 (2016).

[2] X. Wu, J. Dai, Y. Zhao, et al. Two-Dimensional Boron Monolayer Sheets. *ACS Nano* 6, 7443 (2012).

O 9.3 Mon 11:00 H25

Realistic Representations of IrO2 Catalyst Surfaces through Extensive Sampling — •Hao Wan, Hendrik H. Heenen, Christoph Scheurer, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Iridium oxides catalyze the oxygen evolution reaction with unparalleled activity and stability, even under harsh acidic conditions. However, this performance is sensitively correlated to strong structural, compositional and morphological changes of the working catalyst. At the atomic level little is presently known about the true active state, aside from the unlikelihood of it being ideal rutile IrO2.

This situation spans a vast configurational space, the extensive sampling of which (e.g. via parallel tempering) would be intractable with predictive-quality first-principles calculations. Training a machine-learning interatomic potential (MLIP) as an efficient surrogate is challenged by an unprecedented diversity of training structures, as even the bulk structure and composition is unknown. To this end, we create a comprehensive training set by first assembling prototype bulk structures for various IrOx stoichiometries from existing databases. In an active learning loop, this set is then augmented through extensive sampling of diverse surface structures created from the prototypes. The resulting trained MLIP identifies hexagonal ring structures on the rutile (110), (100), (111) facets as most stable configurations under operating potential, aligning with experimental indications. Activity evaluations on these structures using established descriptors effectively capture trends consistent with experimental observations.

O 9.4 Mon 11:15 H25

Hydrogen Atom Scattering from Graphene on Nickel — •Sophia Tödter, Yvonne Dorenkamp, and Oliver Bünermann — Institute of Physical Chemistry, Georg-August University, Göttingen, Germany

Previously, H atom scattering from graphene grown on a Pt(111) substrate was investigated in detail by our group [1]. Depending on the experimental conditions, two energy loss channels were observed, one quasi-elastic and one strongly inelastic. For a C-H bond to form, the delocalized electronic structure of graphene has to be locally destroyed. This gives rise to an adsorption barrier. If the hydrogen atom cannot cross the barrier, it is elastically reflected. However, if the atom can cross the barrier, it loses a large amount of energy, which can lead to it sticking to the surface [1]. Pt(111) was chosen because it is a weakly interacting substrate. This allows comparison of the experimental data with simulations of H atom scattering from free-standing graphene. Although good qualitative agreement is achieved between experiment and theory, quantitative agreement cannot be achieved because of the non-negligible substrate effect.

To experimentally study the substrate effect we chose Ni(111) as an additional substrate and performed the same experiments. Ni(111) is a strongly interacting substrate and a much larger substrate effect is expected.

[1] H. Jiang et al., Imaging covalent bond formation by H atom scattering from graphene, Science 264, (2019).

O 9.5 Mon 11:30 H25

On-Surface Photoreactivity via Reactive Intermediates on a Metal Versus an Insulator — •Iheb Baklouti[1], Julien F. Rowen[2], Dave Austin[3], Lilian N. Alsayed[1], Talat S. Rahman[3], Wolfram Sander[2], and Karina Morgenstern[1] — [1]Ruhr-Universität Bochum, Chair of Physical Chemistry I, Bochum, Germany — [2]Ruhr-Universität Bochum, Chair of Organic Chemistry II, Bochum, Germany — [3]University of Central Florida, Department of Physics, Orlando, FL, USA

Organic azides play a pivotal role in click chemistry, serving as versatile precursors in synthesizing complex molecules across synthetic chemistry, pharmacology, materials science, and catalysis. Despite their importance, investigations into the surface reactivity of azides remain sparse. This study elucidates the behavior of 2-azidofluorene (2AF) on two distinct surfaces: metallic Ag(100) and ionic NaBr(100), under cryogenic conditions (7 K). Utilizing Infrared Reflection Absorption Spectroscopy (IRRAS) and Scanning Tunneling Microscopy (STM), reactions initiated by ultraviolet illumination are analyzed. Nitrene formation from 2AF is hindered by charge transfer interactions with Ag(100), emphasizing the need for low-interaction surfaces like NaBr(100). Illumination at 254 nm induces 2AF dissociation, forming 2-fluorenylnitrene. Subsequent exposure to 450 nm light leads to didehydroazepines, a process reversible under 405 nm. This study sheds light on azide surface-mediated dynamics and introduces a framework for investigating reactive intermediates in surface chemistry.

O 9.6 Mon 11:45 H25

Sustainable argon irradiated MWNT-based filters for efficient remediation of methylene blue dye from wastewater: characterization and mechanism — •Emad Elsehly — Physics Department, Faculty of Science, Damanhour University, 22516, Damanhour, Egypt

This study handles the irradiation of the multi-walled carbon nanotubes by argon ion beam and their potential application for dye removal from wastewater. The obtained data revealed that Argon ion irradiation can induce various structural changes and defects in MWNTs as confirmed by Raman spectroscopy. Moreover, the structural integrity of R-MWNTs is preserved during irradiation as shown by SEM. R-MWNTs yielded smaller crystallites, reaching a size of 4.4 nm. The adsorption efficiency of R-MWNTs was examined by remediation of methylene blue (MB) from wastewater. The results demonstrated that the remediation percentage of R-MWNTs enhanced and could reach 98%. The adsorption mechanism of methylene blue onto R-MWNTs is spontaneous, and almost chemical adsorption process. R-MWNTs have greater surface area and more active sites for adsorption. The irradiation tool offers an alternative approach to enhance the structure of MWNTs-based filters and present a highly effective solution for the removal of dyes from wastewater.

O 9.7 Mon 12:00 H25

On-surface Synthesis of Non-Benzenoid Nanographenes Embedding Azulene and Stone-Wales Topologies — •Qifan Chen[1], Kalyan Biswas[2], Sebastian Obermann[3], Ji Ma[3], Diego Soler-Polo[1], Jason Melidonie[3], Ana Barragán[2], Ana Sánchez-Grande[1], Koen Lauwaet[2], Rodolfo Miranda[2], David Écija[2], Pavel Jelínek[1], Xinliang Feng[3], and José Urgel[2] — [1]Institute of Physics of the Czech Academy of Science, CZ-16253 Praha, Czech Republic — [2]IMDEA Nanoscience, C/Faraday 9, Campus de Cantoblanco, 28049 Madrid, Spain — [3]Center for Advancing Electronics Dresden & Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, D-01069 Dresden, Germany

The incorporation of non-benzenoid motifs in graphene nanostructures significantly impacts their properties. Understanding of the specific reaction mechanism of forming non-benzenoid nanographene structures with tailored electronic/magnetic properties remains limited. In this work, we report a theoretical study addressing an on-surface synthetic strategy toward fabricating non-benzenoid nanographenes containing different combinations of pentagonal and heptagonal rings. We employ the Quantum Mechanics/Molecular Mechanics (QM/MM) approach to analyze the optimal reaction pathways on Au(111) surface and explore the roles of an adatom on the activation energy barrier of the reaction. Our work provides atomistic insight into the reaction mechanism of single gold atom-assisted synthesis of novel NGs containing nonbenzenoid motifs.

O 9.8 Mon 12:15 H25

Enhanced Sampling of Chiral Molecules on Chiral PdGa Surfaces Using Machine Learning — •Raymond Christopher Amador[1,2], Umberto Raucci[3], Peilin Kang[3], Enrico Trizio[3], Hannah Bertschi[4], Jacob Wright[2], and Daniele Passerone[1,2] — [1]nanotech@surfaces laboratory, Empa, Zürich, Switzerland — [2]ETH Zürich, Zürich, Switzerland — [3]Italian Institute of Technology, Genova, Italy — [4]Max Planck Institute, Hamburg, Germany

The interaction of chiral molecules with chiral surfaces plays a fundamental role in enantioselective catalysis and molecular recognition processes. In this work, we present a novel machine learning-assisted framework for enhanced sampling of chiral molecule dynamics on chiral PdGa surfaces. Using high-dimensional descriptors of molecular-surface interactions and leveraging state-of-the-art neural network potentials, our approach significantly accelerates the exploration of configurational space while maintaining chemical accuracy. Detailed analysis reveals how chiral PdGa surfaces influence molecular adsorption, orientation, and reaction pathways, providing new insights into the enantioselective mechanisms. These findings demonstrate the potential of integrating machine learning techniques with surface science to address challenges in heterogeneous catalysis.