O 4: Metal & Semiconductor substrates: Adsorption and reaction of small molecules I

Time: Monday 10:30–12:15 Location: HSZ/0401

O 4.1 Mon 10:30 HSZ/0401

Increasingly incoherent: Effects of adatoms on the structure and characterisation of physisorbed aromatic molecules on Cu(111) — •Henry Thake[1], Matthew Stoodley[1,2], Mariia Radova[1], David A. Duncan[2,3], Lukas Hörmann[4], and Reinhard J. Maurer[1,4] — [1]University of Warwick, UK — [2]Diamond Light Source, UK — [3]University of Nottingham, UK — [4]University of Vienna, AT

X-ray standing wave (XSW) is a quantitative structural characterisation technique for hybrid metal-organic interfaces, providing species-dependent adsorption heights at picometer accuracy. Alongside adsorption heights, XSW measurements provide information on the coherence of the signal, directly related to the structural disorder of the overlayer. A series of recent XSW experiments on physisorbed poly-aromatic hydrocarbons (PAHs) revealed surprisingly low coherent fractions that are inconsistent with structural models produced by Density Functional Theory (DFT) calculations. In this talk, we investigate a hypothesis that this apparent increase in disorder may be related to molecular interactions with surface adatoms that are omnipresent at ambient conditions. Using a frozen transfer learned interatomic potential trained on DFT data of PAHs on Cu(111), we probe the influence of adatoms on dynamic adsorption at the interface. Spectroscopic measurements of these systems reveal perturbations in the electronic structure that are consistent with the co-adsorption of PAHs with adatoms. The inclusion of Cu adatoms to Cu(111) consistently increases the disorder for the PAHs, in line with XSW measurements.

O 4.2 Mon 10:45 HSZ/0401

Interfacial Processes in Ionic Liquid-Modified Catalysts — •Laura Ulm, Cynthia C. Fernández, Hans-Peter Steinrück, and Florian Maier — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg

Solid catalysts with ionic liquid layers (SCILL) provide a powerful route to tailor the selectivity of catalytic reactions. In this context, we study the elementary reaction steps involved in the hydrogenation of 1,3-butadiene to 1-butene, a reaction in which high selectivity is crucial for hydrocarbon processing. We recently demonstrated that ionic liquids (ILs) selectively modify the adsorption of 1,3-butadiene over 1-butene, that is, the initial step of the hydrogenation of 1,3-butadiene on Pt(111). Herein, we now address the next reaction step, namely, how ultrathin layers of the IL $[C_8C_1Im][PF_6]$ influence olefin displacement from Pt(111). Ultrathin films of IL with thicknesses < 1 nm are prepared in situ by physical vapor deposition. Using temperature-programmed X-ray photoelectron spectroscopy (TPXPS), we track structural and compositional film changes and olefin desorption with increasing temperature. We find that i) IL deposition onto a saturated 1-butene layer enhances the displacement and desorption of 1-butene by a factor of 2.8; ii) 1,3-butadiene remains unaffected by the IL; and iii) IL decomposition on Pt(111) is shifted to higher temperatures by 80 ± 10 K.

O 4.3 Mon 11:00 HSZ/0401

Investigating CO Oxidation on Rh(111)/(332) with High-Repetition-Rate Velocity Resolved Kinetics — •Johannes Diedrich, Arved Dorst, and Tim Schäfer — Georg-August-Universität Göttingen, Institut für Physikalische Chemie, Tammannstr. 6, 37077 Göttingen

Velocity resolved kinetics (VRK) allows measuring the temporal evolution of reaction products from surfaces. A recent development is high repetition rate (HRR)-VRK [1]. By using more ionization pulses per molecular beam pulse, the signal-to-noise ratio is significantly improved and data acquisition accelerated.

An ultra-high-vacuum apparatus used for conventional VRK was modified to HRR-VRK by using a 100 kHz femtosecond laser for multiphoton nonresonant ionization and a TimePix3 event camera. This setup enables measururement of the full time of flight spectrum for every laser pulse.

Preliminary results are presented for the oxidation of CO on Rh(111) and (332) facets. This system allows comparison of conventional and HRR-VRK for a previously investigated reaction [2]. Thermal and hyperthermal CO2 channels are distinguished and deviations from the single-exponential decay are discussed. In future work, the decomposition of hydrazine on Ir will be investigated to gain a deeper understanding of Ir-based monopropellant thruster catalysts.

[1] F. Nitz et al., Rev. Sci. Instrum. 96, 055106 (2025).

[2] A. C. Dorst, PhD diss. (Georg-August-University Goettingen 2025).

O 4.4 Mon 11:15 HSZ/0401

First-principles structure search study of multi-component alloys for electrocatalysis — Lei Jia, •Guo-Xu Zhang, and Zhenbo Wang — MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, P. R. China

Multi-component alloys (MCA) have gained increasing attention as electrocatalysts due to their tunability of catalytic properties, while vast composites and diverse active sites make them highly challenging to identify configurations of molecules on surfaces. Here, we combined first-principles calculations with an active machine learning approach, Bayesian Optimization Structure Searching (BOSS), which enables efficient and accurate identification of molecular adsorbate structures on the MCA surfaces. This strategy utilizes smart sampling of adsorption energy surface (AES), constructs a surrogate model to predict the AES landscapes, and continuously refines the models to search global and local minima of adsorption configurations. The performance of first-principles calculations with BOSS was illustrated by benchmark data against single-atom, binary and ternary alloy catalysts. The good predictive power of our method suggests an effective way towards large-scale molecular adsorption for MCA electrocatalysts.

O 4.5 Mon 11:30 HSZ/0401

Surface effects during plasma-activated nitrogen splitting for catalytic ammonia formation — •Sabine Auras and Roland Bliem — ARCNL, Amsterdam, The Netherlands

Plasma-assisted catalysis (PAC) enables the activation of stable molecules, e.g. N_2 or CO_2, by generating reactive species that interact with a catalyst, thereby lowering dissociation barriers and creating new reaction pathways. For ammonia synthesis, PAC is particularly attractive as it can operate under milder conditions than the conventional Haber-Bosch process, potentially improving efficiency while reducing energy input. However, plasma fundamentally alters the reaction environment, which limits the applicability of concepts from thermal catalysis. Therefore, in-situ studies of surface properties and adsorbate evolution are needed to understand the surface chemistry under plasma conditions. Here, we present the first in situ XPS data of Ru and Rh surfaces during N_2 plasma exposure, as well as mixed N_2/H_2 plasmas. To correlate surface processes and plasma properties, we further characterize the plasma composition by optical emission spectroscopy and monitor gas-phase products using mass spectrometry. The results reveal distinct differences in how activated N_2 species interact with the catalytic surface. This allows us to identify surface intermediates, assess reaction kinetics, and propose a mechanism for NH_3 formation, taking into account the role of different plasma species. Our findings highlight the need for a combined approach to identify the role that plasma and catalytic surfaces play - and thus to understand the interactions driving plasma-assisted catalysis.

O 4.6 Mon 11:45 HSZ/0401

Bonding properties of a CO molecule with metallic adatoms — •Fabian Stilp, Marco Weiss, Mia Fuerst, Maximilian Krueger, Luis Vendolsky, Nicolas Wirth, Hendrik Weinert, and Franz J. Giessibl — Department of Physics, University of Regensburg, Germany

CO terminated AFM tips are often used to investigate molecules on surfaces as they are a powerful tool to make the internal structure of such molecules visible. Their chemical inertness results in high resolution of the single atoms and bonds in such molecule via Pauli repulsion. However, it was shown by Huber et al. [1] that CO terminated tips can form weak bonds to some species of adatoms on a Cu (111) sample such as Fe and Cu. In contrast, Si adatoms only interact via van der Waals attraction and Pauli repulsion.

Can one predict the strength of the bond between the CO molecule and an arbitrary atom just from its electron configuration? To set the rules for this prediction we expand our collection of AFM measurements with various atomic species.

In total the interaction between the CO molecule and the adatom shows up to five different regimes, two attractive and three repulsive. The forces are distinctly pronounced, which allows to group the atoms in four different types.

We analyze the different atomic species for their different barrier before forming the bond, directionality of the bond and electrostatic interactions.

[1] Huber et al., Science 366, 235-238 (2019).

O 4.7 Mon 12:00 HSZ/0401

Online monitoring of the oxygen adsorption on Cu(110) with PEEM and DRS — •Robert Heller, Thorsten Wagner, and Peter Zeppenfeld — Johannes Kepler University, Institute of Experimental Physics, Surface Science Division, 4040 Linz, Austria

We studied the dissociative adsorption of oxygen on the Cu(110) surface using Photoelectron Emission Microscopy (PEEM) and Differential Reflection Spectroscopy (DRS) simultaneously. Unlike many experiments carried out already in the 1970s and 1980s, our approach focusses on real-time monitoring. For oxygen exposures up to ∼100L, at temperatures between 350K and 420K, the process saturates at an oxygen coverage of 0.5 with a well-ordered (2×1)O superstructure. At intermediate coverages, a regular pattern of alternating Cu and CuO stripes is formed [1].

We used a PEEM with a xenon lamp (Xe) to study changes in the electron yield (EY) during the exposure. Oxygen adsorption causes a decrease in EY and, hence, an increase in the work function. Since our DRS setup uses the same light source as the PEEM, we can synchronously record the change of the reflectance and reliably compare the two signals. Interestingly, the normalised adsorption curves are not identical, indicating that the PEEM and/or the DRS signals are not directly proportional to the oxygen coverage. This could be related to the effect of the formation of the nanostructured Cu-CuO stripe pattern upon oxygen adsorption [1].

[1] K. Kern et al., Phys. Rev. Lett. 67, 855 (1991).