O 52: Heterogeneous Catalysis and Surface Dynamics I

Time: Wednesday 10:30–12:45 Location: TRE Phy

O 52.1 Wed 10:30 TRE Phy

In-situ spectro-microscopy of single PtRh nanoparticles during oxidation — •Jagrati Dwivedi[1], Lydia Bachmann[1,2], Arno Jeromin[1], Liviu C. Tănase[3], Aarti Tiwari[3], Lucas Caldas[3], Thomas Schmidt[3], Thomas F. Keller[1,2], Beatriz Roldán Cuenya[3], and Andreas Stierle[1,2] — [1]CXNS, Deutsches Elektronen-Synchrotron DESY, D-22607 Hamburg, Germany — [2]Physics Department, University of Hamburg, D-20355 Hamburg, Germany — [3]Department of Interface Science, Fritz-Haber-Institut der Max-Planck Gesellschaft, D-14195 Berlin, Germany

Heterogeneous catalysts are an integral part of industrial scale energy production, conversion and storage. However, a detailed understanding of how their shape, size, structural arrangement and chemical composition affect catalytic activity, selectivity and lifetime remains far from understood. The characterization under catalytic conditions remains challenging, therefore, a spectroscopic analysis of individual PtRh nanoparticles can provide direct evidence of the adsorbed species and their oxidation state. Here, we examined core-shell arranged PtRh nanoparticles on niobium-doped STO single crystals that were achieved by dewetting a homogeneous Pt film and subsequent overgrowth with Rh. Ex situ Scanning Auger Microscopy before and after the oxidation showed that the overgrown Rh is sintering. Spatially resolved in situ X-ray photoemission at BESSY II indicates the formation of Rh_2O_3 at partial oxygen pressure. While the nanoparticles surface composition reflects the oxidation and H_2 reduction, the shape of the nanoparticles remains rather unchanged under the applied conditions.

O 52.2 Wed 10:45 TRE Phy

Probing Au(111) Surface Reconstruction by Electrocatalytic Reactions — •Johannes M. Hermann[1], Areeg Abdelrahman[1], Ludwig A. Kibler[1], and Timo Jacob[1,2,3] — [1]Institute of Electrochemistry, Ulm University, Ulm, Germany. — [2]Helmholtz-Institute-Ulm (HIU), Ulm, Germany. — [3]Karlsruhe Institute of Technology, Karlsruhe, Germany.

Au(111) is an extensively studied single crystal and its thermodynamically most stable surface is reconstructed under UHV conditions. Besides the thermally reconstructed and the unreconstructed Au(111) surfaces, in addition, there is also a potential-induced reconstruction in electrochemical environments. The phase transition between the reconstructed and unreconstructed Au(111) electrode surfaces has mostly been investigated by means of *in situ* scanning tunneling microscopy. Kinetic studies are sparse and in the case of potential-induced reconstruction limited to *in situ* surface X-ray scattering. Since the electrocatalytic hydrogen evolution reaction (HER) on gold electrodes is strongly structure-sensitive, here we show how it can be used to monitor structural changes of the Au(111) surface [1]. The electrocatalytic activity is highest directly after the surface reconstruction had been lifted, and decreases while the potential-induced reconstruction proceeds, following a simple first-order rate law. In contrast to expectations from conventional electrode kinetics, the rate of the reconstruction process decreases with more negative potential, as the reconstructed surface is stabilized by increasing negative excess charge.
[1] J.M. Hermann, *et al.* Electrochim. Acta. **2020**, *347* 136287.

O 52.3 Wed 11:00 TRE Phy

Transition metal carbides vs platinum as catalysts for H2 dissociation and hydrogenation of ethylene and acetylene — •Carlos Jimenez-Orozco[1], Elizabeth Florez[1], and Jose Rodriguez[2] — [1]Faculty of Basic Sciences, University of Medellin, Medellin, Colombia — [2]Chemistry Division, Brookhaven National Laboratory, USA

Hydrogenation reactions are key in the chemical industry, many of them use the scarce Pt-group metals as catalysts, limiting their usage in the long term. Transition metal carbides (TMC) emerge as an alternative material. Among TMC, tungsten carbide (WC) stands out as the active phase or as support of metals. There is still a lack in the understanding of the WC performance, limiting their modulation and applications. Here, density functional theory was used to study the performance of WC in hydrogenation of acetylene (C2H2) and ethylene (C2H4) as probe molecules, together with the H2 dissociation capability of WC. Hence, Pt, Pt/WC (Pt monolayer) and WC were compared. Hydrogen surface coverage and atomistic thermodynamics were used to achieve more realistic models. The H2 dissociation on Pt/WC has a Pt-like behavior at high coverage. The pristine WC surface becomes as a machine for H2 dissociation in a wide rage of T and P, achieving high surface coverages. The Pt/WC has the capability to hydrogenate selectively C2H2 into C2H4, avoiding surface poisoning. The results put WC and Pt/WC under the spotlight as a promising systems alternative to Pt for hydrogenation reactions at several T and P conditions and for the selective transformation of C2H2 into C2H4.

Topical Talk O 52.4 Wed 11:15 TRE Phy

Modeling and Design of Single-Atom Alloy Catalysts — Raffaele Cheula and •Mie Andersen — Department of Physics and Astronomy, Aarhus University, Denmark

In this contribution we apply molecular simulations and machine learning (ML) to study CO_2 hydrogenation (reverse water-gas shift) on single-atom alloy (SAA) catalysts, i.e., diluted bimetallic materials. SAAs have been shown to be able to break the scaling relationships that limit conventional catalysts [1]. We target a wide combinatorial space of elements of the periodic table, which makes a direct study with density-functional theory (DFT) computationally prohibitive. Therefore, we produce a database of DFT-calculated energies on a limited number of SAAs and apply physics-inspired ML techniques for the extrapolation to a wide range of materials. We use a graph-based Gaussian Process Regression ML model (WWL-GPR [2]) to calculate adsorption energies, and simpler models (e.g., multivariate regressions) to estimate the activation energies of the new materials. We employ microkinetic modeling to simulate the reaction kinetics; then, we apply sensitivity analysis and uncertainty quantification to identify the parameters that can improve the model predictions, and we refine them with additional DFT calculations. The application of the framework to CO_2 hydrogenation allows us to rationalize how reaction mechanisms and catalytic activity change with the catalyst composition, paving the way toward the design and nano-engineering of SAA catalysts.

[1] RT. Hannagan *et al.*, Chem. Rev. **120**, 12044 (2020)
[2] W. Xu *et al.*, Nat. Comp. Sci. **2**, 443 (2022)

O 52.5 Wed 11:45 TRE Phy

Data-centric approach for uncovering rules to describe the CO_2 activation at metal catalysts — •Herzain I. Rivera-Arrieta, Lucas Foppa, and Matthias Scheffler — The NOMAD Laboratory at the Fritz-Haber-Institut der Max-Planck-Gesellschaft and IRIS-Adlershof of the Humboldt-Universität zu Berlin, Germany

Using CO_2 as a building block in the production of chemicals and fuels requires, in a first step, the activation of this molecule [1]. The materials space is practically infinite, but only a handful of them may enable an effective CO_2 activation. Therefore, this work focuses on the use of artificial intelligence to speed up finding new catalysts for this process. Single-atom alloys (SAA) of transition metals not only provide good model systems, but also show potential as heterogeneous catalysts [2]. Using the mBEEF functional to perform the DFT modeling of the interaction between CO_2 and different surface terminations in Cu-, Zn-, and Pd-based SAA, we generated a dataset including 50 physicochemical parameters characterizing the geometry, and electronic properties of the adsorption sites where the molecule is activated in each material. Then, we applied the subgroup-discovery (SGD) approach [3] to uncover rules correlating key parameters in the SAA with indicators of the CO_2 activation, e.g., a large C−O bond elongation. Having access to these SGD-rules, which only depend on the material, allows a fast screening and prediction of potentially effective catalysts.
[1] H. J. Freund and M. W. Roberts, *Surf. Sci. Rep.*, **25**, 225 (1996).
[2] J. Schumann, *et al.*, *J. Phys. Chem. Lett.*, **12**, 10060 (2021).
[3] B. R. Goldsmith, *et al.*, *New J. Phys.*, **19**, 013031 (2017).

O 52.6 Wed 12:00 TRE Phy

Machine learning interatomic potential for metallic and oxidized copper surfaces — •Felix Riccius, Nicolas Bergmann, Nicolas G. Hörmann, Hendrik H. Heenen, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin, Germany

Copper (Cu) is a promising catalyst for the electrochemical reduction of CO_2 to chemicals and fuels since it yields many possible reduction products. The selectivity between these products is hypothesized to be altered by partial oxidation of the catalysts* surface. The extent of

Cu surface oxidation, as well as accompanying morphological transformations are, however, unclear. Predictive atomistic simulations could potentially uncover this surface chemistry but time and length scales necessary for the required sampling are intractable by first-principles methods. Machine learning interatomic potentials (MLIP) trained to first principle data can overcome this limitation by retaining predictive accuracy at a fraction of the computational cost. In this work, we use Gaussian Approximation Potentials to train a MLIP for metallic Cu and Cu oxides. We design a workflow tailored to the problem at hand. Via iterative parallel tempering simulations, we sample the relevant phase space for Cu oxidation at various oxidation states during training. We demonstrate the viability of our approach, which results in a reliable potential capable of describing the chemically important regions of the configuration space. The potential gives access to (surface)phase diagrams and surface reconstruction phenomena following surface reduction and oxidation. The atomic insight may shine light on the role of (surface)oxidation in Cu electrocatalysts.

O 52.7 Wed 12:15 TRE Phy

Selectivity Trends and Role of Adsorbate–Adsorbate Interactions in CO Hydrogenation on Rhodium Catalysts — •Martin Deimel[1,2], Hector Prats[3], Michael Seibt[2], Karsten Reuter[1], and Mie Andersen[4] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]Chair for Theoretical Chemistry, Technical University of Munich, Germany — [3]Department of Chemical Engineering, University College London, UK — [4]Aarhus Institute of Advanced Studies and Department of Physics and Astronomy, Aarhus University, Denmark

Rh is one of the most promising elemental catalysts for the conversion of syngas (CO and H_2) into hydrocarbons and oxygenates, especially toward valuable higher oxygenates. Experimentally, an inverse relationship between activity and selectivity of the main products methane and acetaldehyde was identified with conflicting explanations for this trend.[1,2] Here, we revisit the question of the role played by step and terrace sites, represented by the Rh(211) and Rh(111) facets, on activity and selectivity trends.[3] We use an accelerated kinetic Monte Carlo (KMC) approach including a cluster expansion to treat lateral interactions. By comparing our results to corresponding mean-field models and experiment,[1,2] we find that only the KMC models can correctly capture the experimental selectivity trends and that quantitatively correct activity predictions require correction for well-known errors in the density functional theory parametrization of our models.

[1] N. Yang *et al.*, J. Am. Chem. Soc. **138**, 3705 (2016)
[2] M. Schumann *et al.*, ACS Catal. **11**, 5189 (2021)
[3] M. Deimel *et al.*, ACS Catal. **12**, 7907 (2022)

O 52.8 Wed 12:30 TRE Phy

Estimating Free Energy Barriers for Heterogeneous Catalytic Reactions with Machine Learning Potentials and Umbrella Sampling — •Sina Stocker[1], Gábor Csányi[2], Karsten Reuter[1], and Johannes T. Margraf[1] — [1]Fritz-Haber-Institut der MPG, Berlin, Germany — [2]University of Cambridge, United Kingdom

Predictive-quality first-principles based microkinetic models are increasingly used to analyze (and subsequently optimize) reaction mechanisms in heterogeneous catalysis. In full rigor, such models require the knowledge of all possible elementary reaction steps and their corresponding reaction barriers. Unfortunately, for complex catalytic processes (such as the generation of ethanol from syngas) the number of possible steps is so large that an exhaustive first-principles calculation of all barriers becomes prohibitively expensive.

To overcome this limitation, we develop machine learned (ML) interatomic potentials to model the early steps of syngas conversion on Rhodium. These ML potentials can be used to determine free energy reaction barriers at a fraction of the computational cost of the underlying first-principles method. Specifically, we use here the Gaussian Approximation Potential (GAP) framework and explore iterative training in combination with umbrella sampling for the CHO decomposition as an example.