O 34: Catalysis and surface reactions I

Time: Tuesday 10:30–12:30 Location: HSZ/0204

O 34.1 Tue 10:30 HSZ/0204

From Global Optimization to Transition State Search: Automatic Workflow for Surface Reaction Kinetics — •Hyunwook Jung[1], Emanuel Colombi Manzi[1], Johannes T. Margraf[1,2], Hendrik H. Heenen[1], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Universität Bayreuth

Reaction-barrier calculations present the major bottleneck in the systematic exploration of surface reaction networks via atomistic simulations. Each involved transition-state search introduces a high-dimensional configuration space, comprised of many initial and final state combinations, that must be explored to identify the minimum-energy pathway with the lowest activation barrier. Typically, this task is delegated to human chemical intuition as user-input to e.g. a nudged elastic band (NEB) calculation, since its automation remains a significant challenge. Here, we introduce a fully automated workflow for transition-state optimization that does not require any human intervention. Initial and final geometries are generated through global optimization and subsequent alignment, followed by an atom-mapping and index permutation to arrive at the nonequivalent transition pathways. This process still leads to a large combinatorial number of possible interpolations from which we select a tractable subset using heuristic reaction-distance metrics. We demonstrate the workflow across a range of reactions and surface combinations from the OC20NEB database and discuss its overall performance.

O 34.2 Tue 10:45 HSZ/0204

Machine-learning Driven Approach of Surface Adsorption Energy Prediction — •Karlo Sovic and Johannes Margraf — University Bayreuth, Bayreuth, Germany

Heterogeneous catalysis is a cornerstone technology across industrial chemistry, materials science, and environmental engineering, effectively promoting and redirecting key chemical reactions in various applications. In these processes, control of surface adsorption energies is paramount for designing efficient catalysts. However, in the case of large adsorbates, the high computational cost of accurate DFT calculations limits comprehensive exploration of the corresponding potential energy surface. Machine-learning interatomic potentials offer a promising solution to this challenge. Leveraging recently reported pre-trained models, the complex interactions crucial for accurate surface chemistry can be captured with effectively via fine-tuning.

Here, a data-efficient workflow for describing the glycerol hydrodeoxygenation mechanisms leading to propanediols on M(111) and M(211) surfaces (M=Pt, Cu, Ni) is reported. With our approach, the fine-tuned model yields high-fidelity adsorption energies with near-DFT accuracy at low computational cost. Furthermore, analysis of thermodynamic properties was carried out to accurately determine the overall Gibbs free energetics of investigated reaction pathways. Based on these comprehensive insights, we propose a versatile workflow for the accelerated screening of catalytic systems, enabling the rapid construction of adsorption energy databases and exploring relevant reaction mechanisms.

O 34.3 Tue 11:00 HSZ/0204

Modeling Solvothermal Reactions at Surfaces with Machine Learning Interatomic Potentials — •Maciej Baradyn[1], Nils Gönnheimer[1,2], and Johannes T. Margraf[1] — [1]University of Bayreuth, Bayreuth, Germany — [2]Fritz-Haber Institute, Berlin, Germany

Dynamical processes such as adsorption, desorption and diffusion are vital elementary reactions involved in heterogeneous catalytic reactions. In solvothermal reactions, the presence of solvent molecules has significant effects on the dynamics of the adsorbates, which must displace hydration layers to diffuse or adsorb on the surface and undergo resolvation during desorption. The presence of solvent molecules also affects the interactions between surfaces and adsorbates, and can contribute to the (de-)stabilization of the adsorbed species.

In this contribution, we explore the robustness of machine learning potentials based on the MACE-MP-0 foundation model for describing dynamical processes under these conditions. This is demonstrated on a representative system of a glycerol molecule interacting with the Cu(111) surface in explicit water. Enhanced sampling methods are used to compute free energy profiles of the studied processes, and to reflect the experimental reaction conditions under which they occur in industrial applications.

O 34.4 Tue 11:15 HSZ/0204

Converting MoS_2 to MoO_2 by Thermal Treatment Under Dilute O_2 — •Armin Sahinovic[1], Jixi Zhang[2], Osamah Kharsah[1], Marika Schleberger[1], Rossitza Pentcheva[1], and Rodney Smith[2] — [1]Department of Physics and Center for Nanointegration, University of Duisburg-Essen, 47057 Duisburg, Germany — [2]Department of Chemistry, University of Waterloo, ON N2L 3G1 Waterloo, Canada

The reaction of MoS_2 with O_2 at elevated temperatures introduces the risk of structural and functional degradation that decrease the lifespan of MoS_2-based devices [1]. In experiment, variable-temperature Raman measurements indicate that depending on the O_2 concentration in the environment the MoS_2 is converted into either MoO_3 or MoO_2. To elucidate the specific mechanism of this reaction, density functional theory (DFT) calculations were performed including the van der Walls dispersion correction. We show that the S-vacancy formation energy as well as O substitution energy are lowered with increasing O content. DFT calculations show that at high O contents in $MoS_{2-x}O_x$ the $P2_1/c$ phase is energetically preferred over the 2H-MoS_2 structure. A P-T phase diagram of the Gibbs free energy obtained from DFT shows that the partial O pressure tunes whether MoO_3 or MoO_2 is the dominant product of the reaction. We explored the band structure of multiple vacancies in MoS_2 and find additional in-gap states compared to the monovacancy. Our results offer insight into the conditions that control the degradation of MoS_2-based devices.

[1] J. Gao, et al., ACS Nano, 10 (2), 2628 (2016)

O 34.5 Tue 11:30 HSZ/0204

2D TiS2 Nanoparticles in reductive and oxidative Atmospheres as Model (Photo-)Catalysts — •Niko Kruse[1], Justin Klimek[1], Aaron von Seggern[1], Martin Hedevang[2], Sergi Camposs Jara[2], Jeppe Vang Lauritsen[2], and Lars Morhusen[1] — [1]Carl von Ossietzky Universität Oldenburg, Oldenburg, Germany — [2]iNano Center, Aarhus University, Aarhus, Denmark

Sustainable materials for the thermal and photochemical utilization of (waste) carbon dioxide (CCU) become more and more demanded.[1] Titanium-based 2D materials such as TiS2 can directly harvest sunlight and have demonstrated high CO2 conversion activity.[2] To illuminate atomistic structure-property relationships of such catalytic systems, we present a model system consisting of 2D TiS2 nanoparticles on Au(111) and TiO2 (110) surfaces, rendering it suitable for atomic-level microscopy and spectroscopy. A direct synthesis route was developed by Ti metal evaporation in the presence of benign organic S precursors.[3] The resulting materials were characterized by combined STM, XPS, and NEXAFS experiments, along with DFT calculations.[4] We demonstrate the substrate-dependent structure and compositional detail of the nanoparticles and highlight the chemical potential of S as the relevant shape descriptor. In addition, the surface chemistry of 2D TiS2 nanoparticles in reactive atmospheres will be presented, highlighting the strong stability even in oxidative & reductive conditions. [1] R. Guil-López, N. M. et al., Materials 2019, 12. 3902. [2] A. Aljabour, et al, ACS Catal. 2020, 10, 66. [3] F. Besenbacher et al., J. Catal. 2021, 403, 4. [4] N. Kruse et al., Small 2025, 21, e06023.

O 34.6 Tue 11:45 HSZ/0204

In situ X-ray Imaging of PtPd Core-Shell Nanoparticles under Methane Oxidation Conditions — •Lydia J. Bachmann[1,2], Thomas F. Keller[1,2], Ivan A. Vartanyants[1], and Andreas Stierle[1,2] — [1]Deutsches Elektronen-Synchrotron DESY — [2]University of Hamburg

Due to the high global warming potential of methane, the release of any methane into the atmosphere needs to be avoided. Therefore, catalysts are used for the emission control. Common catalyst nanoparticles (NPs) for methane oxidation consist of Pd or Pt. Combining them allows to build more stable NPs. Since the surface chemical composition is crucial for the activity, segregation and mixing processes need to be taken into account. In this study we successfully tuned the initial chemical composition of one core-shell and one partially alloyed NP. We confirmed these elemental distribution by Bragg coherent diffraction imaging (BCDI). During in situ BCDI measurements under methane oxidation at temperatures between 320°C and 560°C, Pt segregated to the {111} oriented facets of the initial core-shell NP. Conversely, the initially partially alloyed NP did not exhibit such facet-dependent segregation, but rather observed the formation of a Pd core, Pt shell structure at 680°C. Since the initial Pt core, Pd shell NP showed Pd-Pt mixing at 620°C, we hypothesize that this NP would form such an inverted core-shell structure under higher temperatures as well. These results demonstrate opportunities for systematically investigating promising core-shell NPs and their catalytic activity, offering valuable insights for the design of advanced catalysts.

O 34.7 Tue 12:00 HSZ/0204

The mechanism and Rate-Determining Step of Catalytic Ammonia Oxidation on Pd(332) at High Temperatures — •Jan Fingerhut[1], Jessalyn DeVine[2], Rongrong Yin[3], Mark Bernard[2], Alice Bremer[4], Dmitriy Borodin[2], Kai Golibrzuch[2], Theofanis Kitsopoulos[5], Daniel Auerbach[2], Hua Guo[3], and Alec Wodtke[2] — [1]Leiden Institute of Chemistry, Leiden, the Netherlands — [2]Max-Planck-Institute for Multidisciplinary Science, Göttingen, Germany — [3]University of New Mexico, Albuquerque, USA — [4]Georg-August-Universität, Göttingen, Germany — [5]University of Southern Mississippi

Despite its immense practical importance in industrial production of nitric acid, the mechanisms of catalytic ammonia oxidation on platinum group metals remain controversial. In this work, we employ velocity-resolved kinetics to study ammonia oxidation on a model Pd(332) catalyst between 600 and 700 K. We obtain the temporal evolution of gas-phase reactants (NH_3), products (NO, H_2O) and - with the help of femtosecond laser-induced desorption - of a reaction intermediate, N*. The reaction exhibits the prompt appearance of H_2O and the delayed formation of NO; the rate-determining step is the reaction $N^* + O^* \rightarrow N^*O$ occurring at step sites. This means that N* is the longest-lived reaction intermediate, an insight that helps explain formation of byproducts like N_2 and N_2O. We present a mechanism that explains all experimental observations, based on transition-state theory calculations and using input from density functional theory. We also show that N*O desorption is accelerated by coadsorbed oxygen.

O 34.8 Tue 12:15 HSZ/0204

Promoting Role of Isolated Surface Hydroxyls on Selective Dehydrogenation of 2-Propanol over Co3O4 Catalyst — •Jan Smyczek[1], Patrick Hubert[1], Hauke Scheele[2], Carsten Schröder[1], Sharif Najafishirtari[2], Paul Kohlmorgen[1], Malte Behrens[2], and Swetlana Schauermann[1] — [1]Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Str. 1, 24118 Kiel, Germany — [2]Institute of Inorganic Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Str. 2, 24118 Kiel, Germany

This study investigates the catalytic decomposition of 2-propanol to acetone over Co_3O_4 catalysts, examining both powdered materials under ambient pressure and model $Co_3O_4(111)$ surfaces in ultrahigh vacuum. Water pretreatment at elevated temperatures substantially enhanced acetone formation rates. Scanning tunneling microscopy and infrared spectroscopy revealed that high-temperature water pretreatment creates isolated hydroxyl groups (O_sH) involving lattice oxygen atoms, whereas low-temperature deposition forms an extended, partly dissociated OH/H_2O network layer. The role of isolated O_sH groups can most likely be attributed to their function as hydrogen acceptors for H atoms leaving from either 2-propanol or the propoxy intermediate. Critically, dissociation occurs only with isolated O_sH species, not within the extended OH/H_2O network, which nearly completely suppresses both abstraction steps. The isolated O_sH groups function as efficient hydrogen acceptors, proving substantially more effective than adsorbate-free lattice oxygen.