O 85: Heterogeneous Catalysis I

Time: Thursday 10:30–12:45 Location: TC 006

O 85.1 Thu 10:30 TC 006

Gazing into Reactors: Adaptive Experimental Design with Concentration Profiles — •Maryke Kouyate, Frederic Felsen, Christian Kunkel, Christoph Scheurer, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Effective kinetic models of heterogeneous catalytic processes are an indispensable tool for reactor design, optimization and control. Employing simple functional forms like power laws, the adjustable parameters of such models are traditionally fitted to kinetic data measured along local line scans, i.e. by systematically changing individual reaction parameters like a reactant concentration or temperature. Besides the uncertainty of which line scans will optimally determine the model's parameters, this is generally a laborious endeavor involving numerous separate kinetic measurements.

Here we explore the use of profile reactors for an efficient parametrization of effective kinetic models. Developed originally to provide *operando* information along the axis of tubular reactors, a measured concentration profile is effectively nothing but a more complex line scan that provides the kinetic information for all reaction conditions probed along the tube. We propose an adaptive design algorithm that harnesses this wealth of data and provides guidance as to which initial reaction conditions for the next measurement will yield a line scan with maximally complementary information. As demonstrated with simulated data from a plug-flow reactor model, this surpasses conventional adaptive design approaches with "black box" reactors in terms of parameter convergence and required experiments.

O 85.2 Thu 10:45 TC 006

Machine-Learning Assisted Realistic Description of Catalytic Active Centers on the Ternary M1 (Mo,V)O$_x$(100) Surface — •Kyeonghyeon Nam, Yonghyuk Lee, Liudmyla Masliuk, Thomas Lunkenbein, Annette Trunschke, Christoph Scheurer, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

The surface structure and composition of complex heterogeneous catalysts can differ noticeably from assumed, idealistic cuts derived from the bulk material's structure. As a crucial first step toward realistic models of the active surface, we explore the evolution of local atomic-scale structural motifs presented by the catalyst under conditioning and operating conditions. Our focus is on the industrial M1 catalysts used for the selective oxidation of light alkanes. The large primitive cell of the M1 catalyst poses a challenge for a detailed study of all surface terminations using predictive-quality first-principles calculations. To address this challenge, we deconstruct the primitive cell into 'pillar structures' of surface motifs with varying oxygen content. Machine-learned Gaussian approximation potentials, trained against this structural library [1], are used to identify *operando* stable (100) surfaces of ternary M1 catalysts via *ab initio* thermodynamics and comparison to experimental data from electron microscopy. Subsequent electronic structure calculations provide a detailed picture for various (*hk*0) surfaces, shedding light on the impact of surface stabilization on catalytic centers.

[1] L. Masliuk *et al.*, J. Phys. Chem. C **121**, 24093 (2017).

O 85.3 Thu 11:00 TC 006

Infra-red spectra prediction of functionalized copper nanoparticles using machine learning force fields — •Nitik Bhatia, Ondrej Krejci, and Patrick Rinke — Department of Applied Physics, Aalto University, FI-00076 AALTO, Finland

Vibrational spectroscopy serves as a powerful tool for in vivo chemical reaction analysis, allowing the identification of distinctive peaks as markers for specific chemical groups. Despite yielding valuable insight, the qualitative and quantitative analysis of IR spectra is aggravated by the presence of other, neighboring species. In this work we investigate the vibrational spectra of several small molecules adsorbed on copper nanoparticles, commonly used in heterogeneous catalysis. We compute the infrared spectra using ab initio molecular dynamics (AIMD) [1]. We achieve excellent agreement with experimental results, but at a high computational cost. We therefore train neural network force fields like FieldSchNet [2] on our AIMD data to capture pertinent spectral properties more efficiently ($\sim$2500 times faster). FieldSchNet achieves remarkable accuracy for simple molecules ($<$20 cm^{-1} shift in peak positions). However, functionalized copper nanoparticles introduce a more complex chemical environment and the predicted peak positions are only accurate to $\sim$100 cm^{-1}. To improve the predictive accuracy, we are enhancing our dataset quality and exploring alternative machine learning strategies for fine-tuning the models.

[1] M.-P. Gaigeot, M. Sprik, J. Phys. Chem. B **107**, 10344-10358 (2003). [2] M. Gastegger, K. T. Schütt, K.-R. Müller, Chem. Sci. **12**, 11473-11483 (2021).

O 85.4 Thu 11:15 TC 006

Design of Palladium-Based Alloys for the Catalytic Hydrogenation of Concentrated Acetylene via Mechanochemical Synthesis and Artificial Intelligence — •Lucas Foppa[1], Jacopo de Bellis[2], Klara S. Kley[2], Jonathan Mauss[2], Rohini Khobragade[2], Ferdi Schüth[2], and Matthias Scheffler[2] — [1]The NOMAD Laboratory at the FHI of the MPG and IRIS-Adlershof of the HU Berlin, Germany — [2]MPI Für Kohlenforschung, Germany

The discovery of new materials for catalysis is challenged by the intricate interplay of underlying processes governing the performance. Here, we combine consistent experimental and theoretical data [1] and apply symbolic regression (SR) in order to identify nonlinear relationships between the measured performance and key physicochemical parameters. These parameters are correlated with the most relevant underlying processes governing the reactivity. We apply this approach to the selective hydrogenation of concentrated acetylene on palladium-based alloys synthesized by ball milling.[2] The SR models highlight the crucial interaction of carbon with the catalyst and describe the evolution of the catalyst selectivity with time on stream. Guided by the SR models, new bimetallic and trimetallic alloys are synthesized and their catalytic performance is tested.

[1] R. Miyazaki *et al.*, DOI:10.26434/chemrxiv-2023-x (2023).

[2] K. S. Kley *et al.*, Catal. Sci. Technol. 13, 119 (2023).

O 85.5 Thu 11:30 TC 006

Fischer-Tropsch Kinetics on Cobalt Single Crystals Monitored by Operando STM — •Sebastian Kläger, Katharina M. Golder, and Joost Wintterlin — Ludwig-Maximilians-Universität München, Munich, Germany

The mechanism of the Fischer-Tropsch (FT) synthesis, the reaction of hydrogen and carbon monoxide to give synthetic fuels, is arguably one of the most complex in heterogeneous catalysis. The reaction is highly sensitive to reaction conditions and catalyst pretreatment, and apparent activation energies show poor reproducibility and considerable variations. We present a study in which this issue has been approached on two paths: Single crystal cobalt surfaces have been used as model catalysts on which the FT kinetics could be measured by gas chromatography, and operando scanning tunneling microscopy has been used to image the surfaces under the same conditions. At pressures of 1 bar and temperatures of $\sim$500 K, FT-active, well-controlled systems have been realized that are not disturbed by the complexities affecting the kinetics on supported catalysts. An apparent activation energy has been determined that agrees with a majority of studies on supported catalysts, and also the hydrocarbon selectivity shows similar characteristics. By means of single crystal cobalt surfaces with varying step densities, the kinetic role of atomic steps has been investigated. Our models reproduce the properties of the idealized systems applied in microkinetic simulations, allowing us to test the predictions of recent simulations.

O 85.6 Thu 11:45 TC 006

The relation between substrate, Sm alloy, and surface sensitivity of ceria (111)- and (100)-oriented nano-islands on Ru(0001) and Cu(111). — •Raquel Sanchez-Barquilla, Rudi Tschammer, Lars Buss, Carlos Morales, and Jan Ingo Flege — Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Germany

Inverse oxide/metal catalysis allows achieving better catalytic performance than its traditional counterpart. For example, in cerium-based inverse catalyst systems, the Ce^{3+} states have been shown to be the active sites for methanol synthesis. This suggests that the activity can be enhanced by promoting those through alloying with trivalent, catalytically active rare-earth metals, as, e.g. Sm. We present low-energy and

X-ray photoemission electron microscopy (LEEM/XPEEM), investigations that show how epitaxially grown (100)- and (111)-oriented CeO_2 islands may be modified and/or alloyed by post-deposited metallic Sm. For the $Ce_{1-x}Sm_xO_{2-\delta}$/Ru(0001) system, the CeO_2 (111)-oriented islands undergo a structural change, concomitant with a partial conversion from Ce^{4+} to Ce^{3+}. Surprisingly, for $Ce_{1-x}Sm_xO_{2-\delta}$/Cu(111) the result is found to be face-dependent since only (100)-oriented CeO_x islands were reduced whereas the (111)-oriented islands remained unaltered. Both systems have been exposed to reducing (H_2) and oxidizing (CO_2) conditions, resulting in higher reduction and in a complete recovery of the Ce^{4+} states, respectively. These unexpected results indicate a complex interaction not only between cerium and the doping element, but also an intricate interplay with the metallic substrate.

O 85.7 Thu 12:00 TC 006

MoS2-based model catalysts for hydrotreatment of biooils: Combined insights from STM & XPS from UHV to operando conditions — •Lars Mohrhusen, Martin Hedevang, and Jeppe V. Lauritsen — Aarhus University, interdisciplinary Nanoscience Center (iNano), Aarhus, Denmark

Hydrotreatments of (fossil) oils using MoS2-based catalysts are well-established processes for heteroatom removal. The process is becoming relevant in the energy transition, e.g. for upgrading of biooils from sustainable feedstocks, f.ex. from biomass pyrolysis, which however appear as complex feedstocks rich in impurities and heteroelements (O, N) and thus remain challenging due to catalyst deactivation.

In contrast to the established use in (oxygen free) hydrodesulphurization (HDS), where in-situ formed S vacancies act as active sites, the sulphide catalyst will be exposed to nitrogenates and oxygenates in the desired hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN) processes. Thus, S atoms may be partially exchanged by N or O, triggering a strong catalyst degradation on the long term.

Herein, we present combined insights from scanning tunnelling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) from UHV to near-ambient pressure (NAP) conditions to mimic hydrotreatments on 2D MoS2 nanoparticles on Au (111) as our model system. Our results show that the MoS2 nanoparticles are surprisingly robust but respond to elevated H2O levels by a small uptake of oxygen leading to an ongoing restructuring of the catalyst. The rate of the oxidation can be steered by the presence of hydrogen in the feed.

O 85.8 Thu 12:15 TC 006

Labile Oxygen-rich Mullite for Ozone Activation to Produce Highly Oxidizing Surface Peroxide — •Linfeng Su[1], Xu Chen[2], Huaping Zhao[1], Zhiyi Lu[2], and Yong Lei[1] — [1]Fachgebiet Angewandte Nanophysik, Institut für Physik & IMN MacroNano, Technische Universität Ilmenau, 98693 Ilmenau, Germany — [2]Key Laboratory of Advanced Fuel Cells and Electrolyzers Technology of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, CAS, Ningbo, Zhejiang, 315201, PR China

Materials with labile oxygen (Olab) have represented great potential in catalysis owing to their unique electronic structure over conventional adsorbed oxygen and lattice oxygen. In this work, we demonstrate that the Olab can be generated in Mullite-Olab by introducing Al-O4 tetrahedral. The bridging oxygens between Al-O4 and M-O4 (M=Al or Si) are identified as Olab. Mullite-Olab exhibits excellent performance in catalytic ozone activation with a high quasi-first order rate constant (k=0.112 min-1) for degradation of atrazine, while the degradation constant closes to 0 for mullite without Olab. Operando Raman and DFT simulations further reveal that Olab is the catalytic active center, which activates ozone via an unusual surface peroxide pathway to generate surface high-oxidative Olab-O* species. Additionally, the catalytic ozonation based on Mullite-Olab also plays a crucial role in treating actual acrylic fiber wastewater. This work provides an advanced Mullite-Olab catalyst with an unconventional ozonation mechanism, promising for future non-biodegradable wastewater treatment.

O 85.9 Thu 12:30 TC 006

Method development for gas adsorption measurements on proton exchange membrane fuel cell catalyst layers. — •Maria Kolla[1,2], Kläre Christmann[1], Sophia Gierse[1], Ulf Groos[1], and Andreas Bett[1,2] — [1]Fraunhofer ISE, Freiburg, Germany — [2]Albert-Ludwigs-Universität, Freiburg, Germany

This work focuses on developing a method to analyze the porosity and surface area characteristics of materials employed in Proton Exchange Membrane (PEM) fuel cells using gas adsorption technology. A comprehensive understanding of porosity's impact on cell efficiency is essential for designing materials that boost fuel cell performance. Enhanced fuel cell durability, especially in electric vehicles, contributes to transportation advancements. The core of the PEM fuel cell is the catalyst coated membrane (CCM), which consists of a membrane with electrode on each side, called catalyst layers (CL). CL requires substantial porosity to enable gas flow for the occurring reactions. Porosity arises through porous carbon-based powder, but by inserting platinum (Pt) particles as catalyst material and ionomer as binder, porosity is reduced. Hence, the variation in carbon support, Pt particle sizes and amount, amount of ionomer, and finally operation of the CCM, the porosity can vary. To study the impact of the material, and operation variations on the porosity, gas adsorption studies are concluded on a small amount of sample material. Reduction of the material needed for a reliable analysis, is the ultimate objective of this work. The proof of concept will be performed by analyzing different materials and finally comparing the porosity of a fresh and an aged CCM.