

O 69: Surface Reactions and Heterogeneous Catalysis 2

Time: Thursday 15:00–17:45

Location: H4

Topical Talk

O 69.1 Thu 15:00 H4
Theoretical Investigations of Size and Support Effects in Heterogeneous Catalysis — ●FELIX STUDD — Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology

Supported transition metal nanoparticles play an important role as catalysts in heterogeneous catalysis. The extend to which size, shape and metal support interaction influence a catalysts reactivity is still at the forefront of scientific research. Here we use density functional theory calculations on nanoparticles ranging from 0.5 to about 3.5 nm in size in order to gain insight into the particle size effect on a catalysts reactivity. We furthermore investigate how the interaction of nanoparticles with the support alters their reactivity with respect to the binding strength of adsorbates. Using computational models of particle-support interfaces we show how insight into changes in reactivity can be described.

O 69.2 Thu 15:30 H4
Why interlayer exchange is crucial for temperature programmed desorption — ●TOBIAS DICKBREDER, RALF BECHSTEIN, and ANGELIKA KÜHNLE — Physical Chemistry I, Bielefeld University, Universitätsstraße 25, 33615 Bielefeld

Understanding the desorption of molecules from surfaces is fundamental for both natural and application-oriented processes such as dewetting, weathering and catalysis. A powerful method to investigate desorption processes is temperature programmed desorption (TPD) as it offers the possibility to gain mechanistic insights into the desorption kinetics. In the past, several analysis methods have been developed for TPD data. These methods have in common that they rely on the Polanyi-Wigner equation, which requires proposing a desorption mechanism with a single (dominating) desorption path. For real systems, however, several coupled desorption paths can be easily envisioned. Here, we analyze the influence of exchange between the first and the second adsorbate layer on the desorption process. We show that considering this additional desorption pathway alters the desorption spectrum considerably. Thus, our study demonstrates that interlayer exchange can be crucial for the analysis of TPD data.

O 69.3 Thu 15:45 H4
CO oxidation on small size-selected Pt clusters supported on Fe₃O₄(001) — ●JOHANNA PLANSKY¹, SEBASTIAN KAISER¹, FARAHNAZ MALEKI², KE ZHANG³, WOLFGANG HARBICH⁴, UELI HEIZ¹, SERGIO TOSONI², BARBARA A.J. LECHNER¹, GIANFRANCO PACCHIONI², and FRIEDRICH ESCH¹ — ¹Technical University of Munich, Garching, Germany — ²University of Milano-Bicocca, Milano, Italy — ³Technical University of Denmark, Kgs. Lyngby, Denmark — ⁴École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland

Oxide-supported metal nanoparticles and clusters are common catalysts for heterogeneous reactions such as exhaust gas treatment. By studying supported size-selected clusters, we disentangle the influence of cluster size and support on reaction mechanisms. In the Pt_n/Fe₃O₄(001) model system, we observe a complicated interplay between lattice oxygen reverse spillover, cluster encapsulation and gas phase pressure dependence. Sophisticated pulsed-valve reactor experiments (Sniffer-MS) combined with variable temperature scanning tunneling microscopy (STM) reveal the reaction of CO with lattice oxygen occurs on the cluster and not at the interface, but it is rapidly quenched by the strong metal-support interaction (SMSI). We will further demonstrate how UHV-based experiments can be quantified to provide turnover frequencies (TOFs) for comparison with real catalysts.

O 69.4 Thu 16:00 H4
A Model-Free Sparse Approximation Approach to Robust Formal Reaction Kinetics — ●FREDERIC FELSEN, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der MPG, Berlin, Germany

Accurate and transferable models of reaction kinetics are of key importance for chemical reactors on both laboratory and industrial scale. Usually, setting up such models requires a detailed mechanistic understanding of the reaction process and its interplay with the reactor setup. We present a data-driven approach which analyzes the influence of process parameters on the reaction rate to identify effective

rate laws without prior knowledge and assumptions. The algorithm we propose determines relevant model terms from a polynomial ansatz employing well established statistical methods. For the optimization of the model parameters special emphasis is put on the robustness of the results by taking not only the quality of the fit but also the distribution of errors [1] into account in a multi-objective optimization [2]. We demonstrate the flexibility of this approach based on synthetic kinetic data sets from microkinetic models. This way, we show that the kinetics of both the classical HBr reaction and a prototypical catalytic cycle are automatically reproduced. Further, combining our approach with experimental screening designs we illustrate how to efficiently explore kinetic regimes by using the example of the catalytic oxidation of CO.

[1] J. J. Filliben, *Technometrics*, 17, 111, 1975.

[2] K. Deb et al., *IEEE Trans. Evol. Comput.*, 6, 182, 2002.

O 69.5 Thu 16:15 H4
Combining Planar Laser-Induced Fluorescence with Stagnation Point Flows for Small Single-Crystal Model Catalysts: CO Oxidation on a Pd(100) — JIANFENG ZHOU¹, ●SEBASTIAN MATERA^{2,4}, SEBASTIAN PFAFF¹, SARA BLOMBERG^{1,3}, EDVIN LUNDGREN¹, and JOHAN ZETTERBERG¹ — ¹Lund University, SE-22100 Lund, Sweden — ²Freie Universität Berlin, D-14195 Berlin, Germany — ³Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8229, USA — ⁴Fritz-Haber-Institut der MPG, D-14195 Berlin, Germany

Mass transfer limitations can have a tremendous impact on catalysts characterization and must be accounted for by an appropriate modelling and, if possible, reactor design. We present a stagnation flow reactor for reaction product imaging by planar laser-induced fluorescence (PLIF), which is amenable to efficient low order modeling. Using CO oxidation over a Pd(100) single crystal as a showcase, we discuss the peculiarities for the case of small single-crystal model catalysts. While the ideal stagnation flow equations are not valid in this limit, a slightly modified theory can be derived, which exploits the information encoded in the PLIF signal. This combination of PLIF and half-theory/half-data driven modelling allows to efficiently analyze the experimental data and to estimate the turnover frequency and the CO₂, CO and O₂ concentrations at the surface from solely the CO₂ profile at some distance of the surface.

O 69.6 Thu 16:30 H4
On-surface collision reactions — ●MATTHEW J. TIMM, KELVIN ANGGARA, LYDIE LEUNG, ZHIXIN HU, and JOHN C. POLANYI — Lash Miller Chemical Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 3H6, Canada

Collisions between atoms and molecules are required for forming chemical bonds, thus they are central to any chemical reaction. The outcome of these collisions depends on the collision energy, geometry, and miss-distance between centers of the colliding reagents (called the impact parameter). As the incoming species - in general - randomly misses the target's center of mass, measurement of the impact parameter is a long-standing problem. Recently, a 'surface-molecular-beam' approach has been demonstrated that can allow for selection of impact parameter in a surface-reaction [1-3]. Energetic, oppositely-recoiling CF₂ or F-atom "projectiles" are formed on a Cu(110) surface by dissociation of chemisorbed CF₃ molecules with the tip of a Scanning Tunneling Microscope (STM). The inherent corrugation of Cu(110) leads to collimated trajectories of these projectiles, allowing them be aimed to collide with nearby molecular "targets" at chosen impact parameters. The pattern of reactive and non-reactive scattering was then determined by STM with the dynamics of the collision elucidated by density functional theory calculations.

[1] Anggara, K.; Leung, L.; Timm, M. J.; Hu, Z.; Polanyi, J. C.; *Sci Adv.*, 2018, 4, eaau2821. [2] Anggara, K.; Leung, L.; Timm, M. J.; Hu, Z.; Polanyi, J. C.; *Faraday Discuss.*, 2019, 214, 89-103. [3] Leung, L.; Timm, M. J.; Polanyi, J. C.; *Chem. Commun.*, 2021, 57, 12647-12650.

O 69.7 Thu 16:45 H4
Faster oxygen adatom diffusion in a more densely packed CO adlayer on Ru(0001): A high-speed STM and DFT study — ●HANNAH ILLNER¹, SUNG SAKONG², AXEL GROSS², and JOOST WINTTERLIN¹ — ¹Ludwig-Maximilians-Universität München,

Germany — ²Universität Ulm, Germany

Oxygen atoms on a Ru(0001) surface covered with 0.33 monolayers (ML) of coadsorbed CO travel through the CO layer by the so-called door opening mechanism. It is facilitated by structural fluctuations in the CO layer and leads to an enhanced diffusion constant [Henk et al., *Science* 363, 715 (2019)]. Expecting a lower diffusion constant on a more densely CO-covered surface we have investigated how this mechanism changes when the CO coverage is enhanced. The experiments were performed by means of a variable-temperature, high-speed STM. In the analyzed temperature range between 239 and 280 K the CO layer is disordered at a coverage of 0.47 ML. The obtained trajectories of the O atoms show that jumps occur in six equivalent directions with the same probability, in contrast to 0.33 ML, where three directions are preferred. Surprisingly, the Arrhenius plot of the hopping rates suggests a lower activation energy for the diffusion at the higher CO coverage than at 0.33 ML of CO. Density functional theory calculations suggest that at $\theta(\text{CO}) > 0.33$ ML clusters form at which the CO density is locally enhanced, and that the configurations of the O atoms with respect to CO molecules are modified. However, the door opening mechanism is still efficient. A weaker binding of the O atoms in the dense CO layer effectively leads to a lower diffusion barrier.

O 69.8 Thu 17:00 H4

Machine-learning Gaussian Approximation Potentials to solve a longstanding puzzle about RuO₂ surfaces —

•YONGHYUK LEE, JAKOB TIMMERMANN, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany

Machine-learning Gaussian Approximation Potentials (GAPs) have recently evolved as a powerful class of surrogate models to computationally demanding first-principles calculations. Along with structure exploration techniques, they enable us to examine the potential energy surface of interest with a hitherto unforeseen combination of physical accuracy and computational efficiency and to achieve global surface structure determination (SSD) for increasingly complex systems. This can be leveraged e.g. to discover novel surface motifs which are critical in understanding the “living” state of heterogeneous catalysts and their degradation under dynamic operating conditions. In our preceding study, this versatility could be leveraged by a general and data-efficient iterative training protocol that allows for the on-the-fly generation of GAPs via the actual surface exploration process. The iterative refinement of GAPs identifies plenty of unknown low energy terminations of RuO₂ even within the restricted sub-space of (1 × 1) surface unit-cells. Moreover, by extending the protocol to larger surface unit-cells, we discovered new surface structures, which provide solutions to longstanding questions in heterogeneous catalysis.

[1] J. Timmermann *et al.*, *Phys. Rev. Lett.* **125**, 206101 (2020)

[2] J. Timmermann *et al.*, *J. Chem. Phys.*, **155**, 244107 (2021)

O 69.9 Thu 17:15 H4

Hydrogen cleaning induced surface changes of GaAs(110) —

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For the nanoscopic analysis of III/V nanowire (110) surfaces, hydrogen cleaning is a commonly used procedure. While hydrogen cleaning is reported to be destruction free [1] and to achieve clean, atomically flat surfaces—as they are present directly after growth—the actual processes and dynamics during cleaning are rarely examined. However, a detailed understanding of these issues is crucial for the interpretation of electronic surface properties, of the growth of Nanowires, as well as of built-in and distribution of dopands.

Here, we investigate the modifications of GaAs(110) as model system upon atomic hydrogen exposure at room temperature and under commonly used cleaning conditions at the atomic level. For depiction and measurement at the atomic scale, we used scanning tunneling microscopy and spectroscopy under UHV conditions. Using these methods we study the geometric arrangement of the adsorbed atoms as well as adsorption induced additional electronic states, band bending, defect states, and Fermi level pinning.

[1] Webb et al., *Nano Lett.* 15, 8, 4865-4875 (2015)

O 69.10 Thu 17:30 H4

In-situ characterization of cyclic reduction and reoxidation of CeO_x(111) and CeO_x(100) islands on Cu(111) —

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Cerium oxide (CeO_x) is of special interest due to its catalytic activity and various other electronic and optical applications. The inverse model catalyst CeO_x on Cu(111) has a high activity for methanol synthesis from H₂ and CO₂. For the activation of CO₂, Ce³⁺ sites have to be present at the surface, which means that the CeO_x has to be reduced to some extent. This may be achieved by exposure to H₂ at elevated temperatures. We studied the interaction of H₂ and CO₂ with CeO_x islands on Cu(111) with low-energy electron microscopy (LEEM) and X-ray absorption spectroscopy (XAS). From earlier studies, the orientation of the CeO_x is known to be decisive for its catalytic activity. In our experiments (100) and (111) CeO_x islands are grown side by side on the metal substrate, so that identical reaction conditions prevail during the experiment. At a high temperature of 550 °C, exposure to H₂ leads to partial reduction, and exposure to CO₂ leads to reoxidation of the CeO_x. The differences observed for the two island orientations regarding structure and composition will be discussed.