

O 102: Heterogeneous Catalysis on Metals

Time: Thursday 10:30–13:30

Location: TRE Phy

Invited Talk

O 102.1 Thu 10:30 TRE Phy
Video STM of particle diffusion on crowded surfaces — ●JOOST WINTTERLIN — Dept. of Chemistry, University of Munich, Germany

Fast surface diffusion of adsorbed particles is important for catalytic reactions as it randomizes the adsorption layer and determines transport to active sites. However, under reaction conditions a catalyst can be highly covered by particles. One expects that surface diffusion is then no longer a simple hopping of separate particles but that interactions and correlations in the "crowded layer" play a role. Such effects have been investigated by means of variable-temperature high-speed STM. Movies consisting of several 1000 frames were recorded over extended temperature ranges, providing the amount of data necessary for a statistical analysis. The experiments were performed with coadsorbed oxygen atoms and CO molecules on a Ru(0001) surface, which can be seen as a catalytic model system. Individual O atoms surprisingly moved through an ordered layer of CO molecules almost as fast as on the bare surface. It was shown that this high mobility can be understood by a new surface diffusion mechanism in which fast density fluctuations in the CO layer drive the diffusion of the oxygen atoms. Because combinations of similar types of adsorbates are present in many catalytic reactions the mechanism may play a general role.

O 102.2 Thu 11:00 TRE Phy
Diffusion of oxygen atoms on a highly CO-covered Ru(0001) surface — ●HANNAH ILLNER, ANN-KATHRIN HENSS, and JOOST WINTTERLIN — Chemie Department, Ludwig-Maximilians-Universität München, Deutschland

It was recently shown that oxygen atoms on a Ru(0001) surface covered with 0.33 monolayers (ML) of coadsorbed CO could travel through the CO layer by means of a new diffusion mechanism (Henß et al., Science 2019). The term "door-opening mechanism" indicated that the diffusion of the O atoms was facilitated by fluctuations in the CO layer that frequently opened low-energy paths for the oxygen. Here we report about investigations at higher CO coverages (0.50 ML). The experiments were performed between 239 and 280 K by means of a variable-temperature, high-speed STM that achieves imaging rates of up to 60 frames per second. In the investigated temperature range an ordered ($2\sqrt{3} \times 2\sqrt{3}$)R30° CO structure, which was observed at 70 K, had undergone an order-disorder transition. The trajectories of the O atoms through the disordered CO layer were analyzed, and hopping frequencies and an activation energy were extracted. It turned out that the surface diffusion of the O atoms was even faster than at the lower CO coverage and also faster than on the bare surface. We explain this finding by the weakened binding strength of the O atoms to the surface caused by CO.

O 102.3 Thu 11:15 TRE Phy
Active site representation in first-principles microkinetic models: Data-enhanced computational screening for improved methanation catalysts — ●MARTIN DEIMEL, MIE ANDERSEN, and KARSTEN REUTER — Chair for Theoretical Chemistry and Catalysis Research Center, Technical University of Munich, Germany

Reductionist first-principles microkinetic models have largely contributed to our trend understanding and computational screening of transition metal (TM) and TM alloy catalysts. As a key enabling step, these models draw much of their computational efficiency from scaling relations that reduce the required first-principles input to only a few adsorption energies of key reaction intermediates. Notwithstanding, as these relations need to be established separately for every surface site considered, the predictive power of existing such models might be jeopardized by an overly simplistic representation of the active catalyst surface. Here we employ a recently established compressed-sensing approach [1] that (once trained) provides the required adsorption energies of ALL involved reaction intermediates at ALL high-symmetry sites from a single density-functional theory calculation of the clean TM or binary TM alloy surface. This enables refined microkinetic models considering multiple active sites. We revisit existing work investigating methanation catalysts on the basis of a less detailed microkinetic model [2] and show that the explicit consideration of hitherto neglected step and terrace sites indeed yields new mechanistic insights and highly active materials. [1] M. Andersen *et al.*, ACS Catal. **9**, 2752 (2019); [2] A. C. Lausche *et al.*, J. Catal. **307**, 275 (2013).

O 102.4 Thu 11:30 TRE Phy
Fluctuating nature of adsorbate layers on metal surfaces — ●SUNG SAKONG and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

The dynamics of adlayers on surfaces is a fundamental feature influencing heterogeneous catalysis and electrocatalysis, because they determine whether adsorbed reaction partners can meet on a catalyst surface. Recently, video scanning tunneling microscopy (V-STM) experiments have addressed the O adatom dynamics in CO adlayers on a Ru(0001) surface [1] and of CO molecules on a Pt(111) electrode [2]. In spite of advances in the scan rate, the experiments are not capable of imaging all microscopic details of the adlayer dynamics due to the limited time resolution. Here, quantum chemistry can play a decisive role in elucidating the adlayer dynamics on the atomic level. We will discuss the fluctuating nature of CO adlayers on Ru(0001) and Pt(111) based on first-principles calculations and kinetic Monte Carlo simulations and demonstrate how fluctuations through a so-called door-opening mechanism can facilitate adatom diffusion on a crowded surface.

[1] A.-K. Henß, S. Sakong, P. K. Messer, J. Wiechers, R. Schuster, D. C. Lamb, A. Groß, and J. Wintterlin, Science **363**, 715-718 (2019).

[2] J. Wei, R. Amirbeigi, Y.-X. Chen, S. Sakong, A. Groß, and O. Magnussen, submitted.

O 102.5 Thu 11:45 TRE Phy
Chemical bond formation showing a transition from physisorption to chemisorption — FERDINAND HUBER¹, ●JULIAN BERWANGER¹, SVITLANA POLESYA², SERGIY MANKOVSKY², HUBERT EBERT², and FRANZ J. GIESSL¹ — ¹University of Regensburg, 93040 Regensburg, Germany — ²LMU Munich, 81377 Munich, Germany

Surface molecules can transition from physisorption through weak van der Waals forces to a strongly bound chemisorption state by overcoming an energy barrier [1,2]. We show that a carbon monoxide (CO) molecule adsorbed to the tip of an atomic force microscope (AFM) [3] enables a controlled observation of bond formation, including its potential transition from physisorption to chemisorption. During imaging of copper (Cu) and iron (Fe) adatoms on a Cu(111) surface, the CO was not chemically inert but transitioned through a physisorbed local energy minimum into a chemisorbed global minimum, and an energy barrier was seen for the Fe adatom. Density functional theory reveals that the transition occurs through a hybridization of the electronic states of the CO molecule mainly with s -, p_z -, and d_z^2 -type states of the Fe and Cu adatoms, leading to chemical bonding. The absence of hybridization 200 pm off-center the individual Fe and Cu adatoms results in the appearance as repulsive tori [4] in the AFM's image [5].

[1] A. Zangwill, Physics at Surfaces, Cambridge Univ. Press (1988)

[2] H. Ibach, Physics at Surfaces and Interfaces, Springer (2006)

[3] L. Gross *et al.* Science **325**, 1110 (2009)

[4] M. Emmrich *et al.* Science **348**, 6232 (2015)

[5] F. Huber *et al.* Science **366**, 235 (2019)

O 102.6 Thu 12:00 TRE Phy
Combining Planar Laser-Induced Fluorescence with Stagnation Point Flows for Small Single-Crystal Model Catalysts: CO Oxidation on a Pd(100) — JIANFENG ZHOU¹, ●SEBASTIAN MATERA², 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

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 modelling. 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 analyse the

experimental 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 102.7 Thu 12:15 TRE Phy

Ligand-Induced Heterogeneous Catalysis: Selective Hydrogenation of Acrolein on Ligand-Modified Pd(111) — ●CARSTEN SCHRÖDER, MARVIN C. SCHMIDT, and SWETLANA SCHAUERMANN — Physikalische Chemie, CAU Kiel, Max-Eyth-Str. 2, 24118 Kiel

A major challenge in heterogeneous catalysis is obtaining control over selectivity in multi-pathway transformations of hydrocarbons. Recently, a new approach was introduced, which is based on employing catalytic surfaces functionalized with organic ligands. The intermolecular interactions between the reactants and the co-adsorbed ligand species were shown to be capable of promoting the desired reaction pathway. In our recent studies, on acrolein hydrogenation over Pd, almost 100% selectivity in the formation of the target product unsaturated alcohol propenol was detected, which arises from the presence of the oxopropyl-ligand species formed at the initial stages of reaction. In this contribution, we present a mechanistic study on hydrogenation of acrolein over ligand-modified Pd(111) surface. We employ a combination of infrared reflection adsorption spectroscopy and scanning tunneling microscopy along with the molecular beam techniques to obtain detailed information on the mechanisms and kinetics of acrolein partial hydrogenation to propenol. First experiments show, that the induction period of the formation of propenol, which is typically observed for acrolein hydrogenation, can be significantly reduced by precovering the surface with 2-methyl-2-pentenal as a ligand. Spectroscopic observations suggest fast formation of the desired reaction intermediate - propenoxy-species - on the ligand-modified surface.

O 102.8 Thu 12:30 TRE Phy

Exploring electrochemical CO₂ reduction towards C₂+ products beyond copper — ●GEORG KASTLUNGER, HENDRIK H. HEENEN, and KAREN CHAN — Department of Physics, Technical University of Denmark

Electrochemical reduction of CO₂ and CO into high value chemical fuels would represent an ideal candidate for sustainable energy storage and conversion. Its application is, however, limited by the availability of efficient and selective catalysts for the production of longer chain hydrocarbons. To this day, no viable catalyst other than copper based materials lead to reasonable faradaic efficiencies.

In this contribution we present a density functional theory based study which focusses on understanding the general requirements for a catalyst to be viable for the electrochemical production of C₂+ products. A larger scale theoretical study of this reaction cascade has historically been limited by the correct description of the crucial C-C coupling step and its potential dependence. Explicitly taking into account this key ingredient, we conducted a volcano type analysis exploring which interplay of the potential dependent binding energy of relevant intermediates opens up the path towards the desired products. Based on the discovered design principles, an alloy screening study going beyond copper will be presented, extending the palette of potential materials for the conversion of CO₂ into higher value hydrocarbons.

O 102.9 Thu 12:45 TRE Phy

Atomistic simulation of the surface reactions: O₂, H₂O and CO adsorption and dissociation on Zr- and B-terminated ZrB₂(0001) surfaces — ●YANHUI ZHANG and STEFANO SANVITO — CRANN, Trinity College Dublin, Dublin, Ireland

ZrB₂ as a prototypical ultra-high temperature ceramic (UHTC) in combustion environment of aerospace applications are exposed to chemically aggressive gases like O, CO and H₂O etc.. A detailed picture of the different channels of surface reactions involved are important for the development of ablation-resistant hot sections of the next generation aircraft. In this work, we have systematically studied the adsorption and dissociation of O₂, CO and H₂O on multiple active

sites of ZrB₂ (0001) surfaces by atomistic simulations based on density functional theory. The adsorption strength of O₂ is the highest, followed by CO, and lastly H₂O. Meanwhile, the hollow and bridge sites are largely preferred. The dissociative adsorption of O₂ without activation barriers prevail in case of lateral approaching. Interestingly, the surface reconstruction of B-terminated (0001) surface is also observed to mediate surface reaction processes. Additionally, the surface reaction phase diagrams have been built up by searching the reaction barriers by climbing-image NEB method. Our results indicate the activation energy barriers of CO are the highest, while those of O₂ are the lowest. This work provides insights into the initial processes of surface reactions at atomistic scale, and highlights the importance of surface treatment to the final performance of UHTC materials.

O 102.10 Thu 13:00 TRE Phy

Characterisation of Disordered Porous Solids: Perspectives from the Serially Connected Pore Model — ●HENRY R. N. B. ENNINFUL¹, RICHARD KOHNS^{1,2}, DIRK ENKE¹, and RUSTEM VALIULLIN¹ — ¹Universität Leipzig, Leipzig, Germany — ²Philipps Universität Marburg, Marburg, Germany

Elaborate determination of the pore structure of mesoporous solids offers important guidance towards optimal design of various applications such as catalysis, molecular separations and adsorption, among others. Routinely used characterisation tools, such as gas sorption, typically utilise the general adsorption isotherm (GAI) equation derived for ordered pore systems. The complex morphology of disordered porous solids, with its resulting cooperativity effects in thermodynamic phase transitions, renders characterisation more complex than what the GAI provides.

In this talk, we present a recently developed serially connected pore model (SCPM), which extends the GAI by incorporating cooperativity effects in phase transitions arising from pore complexity. Modelled as statistically disordered linear chain of pores, the SCPM will be validated with data from phase transitions in a synthesized porous silica material of similar pore construct, MCM-41. As an analogue to gas sorption (adsorption/desorption) studies, solid-liquid phase transitions (freezing/melting) of water in porous materials will be employed to correlate with the theoretical model.

References [1] Scientific Reports, 7, 7216, 2017. [2] Journal of Physical Chemistry C, 123, 16239, 2019.

O 102.11 Thu 13:15 TRE Phy

Adsorption Geometry of 2-Iodotriphenylene on Ag(111) and Cu(111) — ●ALEXANDER IHLE¹, SEBASTIAN AHLES², TOBIAS SCHLÖDER³, DOREEN MOLLENHAUER³, HERMANN A. WEGNER², ANDRE SCHIRMEISEN¹, and DANIEL EBELING¹ — ¹Institute of Applied Physics, Justus Liebig University Giessen, Germany — ²Institute of Organic Chemistry, Justus Liebig University Giessen, Germany — ³Institute of Physical Chemistry, Justus Liebig University Giessen, Germany

On-surface chemistry is a powerful tool for building covalent molecular structures. In particular, the catalytic properties of the metal substrate as well as the 2D confinement facilitate the synthesis of new structures that are not accessible via solution chemistry. In order to control the bottom up formation process precise knowledge about the adsorption geometry of the molecular precursors is needed since this will help to understand the reaction mechanisms in detail. Here we studied the adsorption geometry of 2-iodotriphenylene on Ag(111) and Cu(111). By using low temperature atomic force microscopy with CO-functionalized tips we are able to identify the precise adsorption position of the molecules and their orientation with respect to the substrate lattice. On both substrates we find one preferred and one less preferred adsorption configuration, which are directed by metal atoms in the surface and the sub-surface layer. Due to different molecule-substrate interactions these adsorption configurations differ significantly from each other for the two substrate materials. Hence, the adsorption position can be actively controlled by the choice of substrate material.