O 107: Heterogeneous Catalysis: Theory II

Time: Friday 10:30–13:00   Location: TRE Phy

O 107.1   Fri 10:30   TRE Phy
Catalytic activity of high index platinum surfaces — •GABRIELE TOMASCHUN and THORSTEN KLÜNER — IfC, CvO Universität Oldenburg, 26111 Oldenburg

The key challenges of the catalysis are to investigate and improve efficient and environmentally friendly processes. This can be realized by changing the composition of the chemical process or by tuning the shape of the catalyst itself. [1] The Pt nanoparticles as catalysts for instance show different catalytic reactivity by varying the surface shape and structure. [2] It has been established, that the higher density of atomic steps and kinks leads to more active sites on the surface. This might lead to an increasing reactivity for these stepped platinum surfaces. The main focus of our research is to analyze the dependence of the catalytic reactivity and selectivity of the industrially relevant reactions, such as condensation of light alcohols and hydrogenation of furfural, on the surface structure of Pt nanoparticles. The different stepped and kinked Pt surfaces provide thereby a lot of active sites for these reactions, thus detailed insight in the reaction mechanisms can be obtained. The theoretical calculations will be performed using the exchange-correlation functional PBE implemented in the Vienna ab initio simulation package (VASP). [3] The analysis of the adsorption and coadsorption sites, adsorption energies, transition states and the favorable reaction pathways of the investigated reactions will be the main objective of this research. [1] K. An, G. A. Somorjai, ChemCatChem 2012, 4, 1512. [2] S. Motoo, N. Furuya, Electroanal Chem 1984, 172, 339. [3] G. Kresse, J. Hafner, Phys. Rev. B 1994, 49, 14251.

O 107.2   Fri 10:45   TRE Phy
CH_2 Stabilization at Steps on Ru(0001) by Co-Adsorbates — XUNHUA ZHAO[1], HARALD KIRSCH[1], ZEFENG REN[2], •SERGEY V. LEVCHENKO[1], and R. KRAMER CAMPEN[1] — [1]Fritz-Haber-Institut der MPG, Berlin, DE — [2]Peking University, Beijing, CN

Despite numerous studies, the stability of various one-carbon (1C) species, which determines the hydrocarbon-chain growth mechanism in industrially important processes such as the Fischer-Tropsch (FT) synthesis, is still debated. In particular, it was shown recently that H co-adsorption at Ru(0001) terraces stabilizes adsorbed CH_2, which makes it a much more likely candidate for the chain building block [1]. In this work, we use DFT with the PBE functional plus a van der Waals interaction correction vdW^{surf} [2] to study the effect of CH co-adsorption on the stability of CH_2 at stepped Ru(0001) surface. We show that both the barrier for CH_2 dissociation and that for the diffusion of CH away from the steps increase 2- to 3-fold compared to isolated 1C species. The theoretical study explains the vibrational sum-frequency generation spectroscopy measurements of this system [3]. The results of the combined theoretical/experimental study highlight the large influence of co-adsorbates on step-bound 1C moieties and provide means of reconciling previous apparently contradictory results on the FT synthesis.—[1] H. Kirsch *et al.*, J. Catal. **320**, 89 (2014); [2] V. Ruiz *et al.*, PRL **108**, 146103 (2012); [3] H. Kirsch *et al.*, JPC C **120**, 24724 (2016).—X. Zhao's current address: Chemistry Department, Princeton University, Princeton, NJ 08544, USA.—This work received funding from the UNICAT Cluster of Excellence.

O 107.3   Fri 11:00   TRE Phy
DFT modeling of formic acid decomposition over late transition metals: on the road to lower activation barriers — •JAN KUČERA and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Low temperature decomposition of formic acid (FA) to regain pure H_2 is among the processes suggested as one of the potential H_2-storage alternatives to designs employing compressed hydrogen. Heterogeneous catalysts based on late transition metals, in particular Pd or Au particles dispersed on oxide supports, selectively decompose formic acid already at low temperatures, however, so far the achieved efficiencies are below those required for commercial polymer electrolyte membrane fuel cells.

The general goal of our computational study - based mainly on periodical density functional theory (DFT) calculations - relates to the identification of the key effects operating in FA decomposition at Pd and Au-based surfaces and at complex metal/oxide interfaces. Despite the fact that in principle only two dehydrogenation steps are involved,

FA decomposition represents a complex catalytic system. We will focus on the elucidation of three phenomena that might be critical for the reaction energetics: (i) modification of catalytic properties by the formation of bimetallic surfaces, (ii) the role of intermolecular forces in the formate decomposition step due to dimer configurations or the interaction with the solvent, and (iii) the effect of Au-hydride formation at the interface with CeO_2.

O 107.4   Fri 11:15   TRE Phy
Trends in catalytic activity of Ni-based electrodes for the hydrogen evolution reaction — •HANNAH SCHLOTT[1], MARC LEDENDECKER[2], MARKUS ANTONIETTI[3], MENNY SHALOM[4], and BERND MEYER[1] — [1]Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg — [2]Max-Planck-Institut für Eisenforschung, Düsseldorf — [3]Max-Planck-Institute of Colloids and Interfaces, Potsdam — [4]Chemistry Department, Ben Gurion University of the Negev, Israel

Metallic binary compounds have emerged in resent years as highly active and stable electrocatalysts toward the hydrogen evolution reaction. The origin of their high activity from a theoretical and experimental point of view is elucidated. Different metallic ceramics (Ni_3S_2, Ni_3N, and Ni_5P_4) are grown directly on Ni support in order to avoid any contaminations. DFT calculations were performed to obtain a deeper understanding of possible active adsorption sites and the observed catalytic stability. It is found that the heteroatoms P, S, and N actively take part in the reaction. Due to the anisotropic nature of the materials, a variety of adsorption sites with highly coverage-dependent properties exist, leading to a general shift in hydrogen adsorption free energies ΔG_H close to zero. Extending the knowledge gained about the here described materials, a new catalyst is prepared by modifying a high surface Ni foam, for which current densities up to $100\,\mathrm{mA\,cm^{-2}}$ at around $0.15\,\mathrm{V}$ are obtained.

[1] M. Ledendecker, H. Schlott, M. Antonietti, B. Meyer, M. Shalom, *Adv. Energy Mater.* **2016**, 1601735.

O 107.5   Fri 11:30   TRE Phy
What is the Most Promising Dopant for the Deacon Process at RuO_2 ? — •ZHEN YAO and KARSTEN REUTER — Technische Universität München, Germany

The Deacon process is a sustainable way to recover high purity Cl_2 from waste HCl in chemical industry. RuO_2 is a most promising catalyst for this process, i.e. the catalytic oxidation of HCl to chlorine and water. A currently pursued route to further improve on its activity is a deliberate doping of the bulk oxide. To guide corresponding experimental endeavors we perform a density-functional theory based computational screening study for a wide range of metal dopant atoms at the $RuO_2(110)$ facet. We use a three-dimensional descriptor matrix, evaluating the rate-controlling Cl desorption energy, the dopant surface segregation energy, as well as the dopant stability against precipitation into bulk oxide grains. Our results suggest Cu doping to represent an optimum compromise between stability and catalytic activity enhancement.

O 107.6   Fri 11:45   TRE Phy
Thermal lattice Boltzmann method for catalytic flows — •DANIEL BERGER[1], ANA SMITH[2,3], DAVID SMITH[3], and JENS HARTING[1,4] — [1]Forschungszentrum Jülich GmbH, Helmholtz-Institut Erlangen-Nürnberg for Renewable Energy — [2]Institute for Theoretical Physics I, University of Erlangen-Nürnberg — [3]Ruđer Bošković Institute, Zagreb, Croatia — [4]Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands

Many catalyst devices employ porous or foam-like structures to optimize the surface to volume ratio in order to maximize the catalytic efficiency. The porous structure leads to a complex macroscopic mass and heat transport. Local heat accumulation changes the local reaction conditions, which in turn affects the catalytic turn over rate and eventually compromises the stability of the catalytic device.

We present a thermal multicomponent model based on the entropic lattice Boltzmann method (J. Kang *et al.*, Phys. Rev. B **89**, 063310 (2014)) to simulate catalytic reactions through porous media. This method reproduces the Navier-Stokes equations and allows the tracking of temperature dynamics. The viscosity, diffusivity, and heat ca-

pacities are calculated from the Lennard-Jones parameters of the gases, while the chemical surface reactions are incorporated in a very flexible fashion through the flux boundary conditions at the walls.

To show the strength and flexibility of this model and our implementation, we will report the catalytic turn-over for a wide range of porosities and reaction conditions.

O 107.7   Fri 12:00   TRE Phy

Is DFT accurate enough for modeling chemical kinetics? —
•Sandra Döpking[1], Daniel Strobusch[2], Christoph Scheurer[2], Craig Plaisance[2], Karsten Reuter[2], and Sebastian Matera[1] — [1]FU Berlin, Germany — [2]TU München, Germany

Targeting at an understanding of interplay between bond making and bond breaking and observed reactivity, first-principles based kinetic methodologies for heterogenous catalysis employ energetic information derived from electronic structure calculations. These energies, usually obtained on the density functional theory (DFT) level, have typically a potential error of 0.2 eV-0.3 eV.

We present a systematic approach to address the propagtion of these errors to the kinetic model's result based on adaptive sparse grids for the sampling of the error space. We demonstrate the approach on a model for the oxygen evolution on Co_3O_4[1]. Our results indicate that the simulated reactivities carry an uncertainty of more than five orders of magnitude, questioning the trustability of the model. However, a decomposition of this uncertainty into contributions of different input errors reveals that only a small number of DFT energies have an impact. So, it is still possible to draw conclusions about the potential driving forces behind catalytic activity, although the activity itself can not be estimated accurately. Besides a qualified discussion of the effect of the modeling error, the approach can be employed for the reduction of the number of expensive first-principles simulations or for computational materials screening. [1] C. Plaisance and R. A. van Santen, J. Am. Chem. Soc. 137, 14660-14672 (2015)

O 107.8   Fri 12:15   TRE Phy

Solving the master equation without kinetic Monte Carlo: Tensor train approximations for a CO oxidation model —
•Patrick Gelss[1], Sebastian Matera[1], and Christof Schütte[1,2] — [1]Freie Universität Berlin, Germany — [2]Zuse Institut Berlin, Germany

Kinetic Monte Carlo (kMC) simulations have become an important tool for modeling chemical kinetics on catalytic surfaces. Their appealing feature is the unbiased solution of the Markovian master equation, which results from a given microkinetic mechanism, while not being affected by the *curse of dimensionality*. However, the need to perform one reaction step after the other makes kMC ineffective for stiff problems, which are characterized by a large disparity in the values of the employed rate constants. We have developed an alternative approach with tunable accuracy, which directly solves the master equation by exploiting the Tensor Train Format[1]. Using a reduced model for the CO oxidation on $RuO_2(110)$, we benchmark the approach against highly accurate kMC simulations. We demonstrate that numerical accuracy and linear scaling in the system size can be achieved for a large range of input parameters. The advantage over the kMC approach is illustrated for a problem with increasing stiffness, where our approach is hardly affected but the computational costs for kMC explode.

[1] P. Gelß, S. Matera, C. Schütte, J. Comput. Phys., 314, pp. 489–502 (2016)

O 107.9   Fri 12:30   TRE Phy

On the effect of electromagnetic field heterogeneities on the chemical kinetics on nano-structured photocatalysts —
•Sebastian Matera[1], Martin Hammersachmidt[2], Sandra Döpking[1], Sven Burger[2], and Frank Schmidt[2] — [1]FU Berlin, Germany — [2]Zuse Institute Berlin, Germany

When going from single crystal surfaces to structured catalysts, such as powders or nano-particles, the complexity of the problem dramatically increases. Besides the obvious higher structural complexity, the electromagnetic field, driving photocatalysis, might become heterogeneous on a nanoscale level. We present a simple model for the CO_2 reduction on titania anatase, which addresses the impact of these heterogeneities on the photocatalytic kinetics by coupling kinetic Monte Carlo with electromagnetic wave simulations. Our results indicate that catalytic activity might vary significantly on a single facet of a nanocrystal. Moreover, the coverage situation might change laterally on this facet and we have a concomitant change of the rate-determining steps. This heterogeneity on all levels of photocatalytic activity makes it extremely difficult to draw mechanistic conclusions from experimental studies on such structured catalysts, where only the spatially averaged activity can be addressed.

O 107.10   Fri 12:45   TRE Phy

Water-Gas Shift Reaction Catalysis in Supported Ionic Liquid Phase —
•Robert Stepić[1], Nataša Vučemilović-Alagić[1,2], Daniel Berger[1,4], Christian Wick[1,2], Jens Harting[4,5], Ana-Sunčana Smith[1,2], and David M. Smith[2,3] — [1]PULS Group and Exellence Cluster: EAM, FAU, Erlangen, Germany — [2]CLS Group, RBI, Zagreb, Croatia — [3]CCC, FAU, Erlangen, Germany — [4]Forschungszentrum Jülich, Helmholtz Institute Erlangen-Nürnberg for Renewable Energy, Nürnberg, Germany — [5]Department of Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands

The water-gas shift reaction is one of the most important reactions in industry, as it is a key step in the production of hydrogen. Novel systems have been developed with highly active transition metal catalysts immobilized in a thin layer of ionic liquid on a porous support. Here we present a joint study of such a system using methods of quantum chemistry and molecular dynamics. The mechanism and energetics of the water-gas shift reaction catalysis via a ruthenium-based transition metal complex is determined with density functional theory calculations using a series of constrained optimizations and transition state searches. The ionic liquid on alumina support is studied by fully atomistic molecular dynamics simulations, where a proper force field is characterized by reproducing the experimentally observed x-ray reflectivity and diffusion coefficients. The ultimate goal of this study is to bridge the gap between multiple scales and provide a theoretical prediction of output, and optimization, of these important catalytic systems (see also modeling of gas flows by Daniel Berger et al.).