O 16: Heterogeneous Catalysis: Theory

Time: Monday 15:00–18:15   Location: MA 141

O 16.1   Mon 15:00   MA 141
The devil is in the defects: first-principles modeling of oxide formation at Pd(100) — ●Albert Bruix and Karsten Reuter — Technical University Munich

The surfaces of many late transition metals are oxidized under ambient conditions or at increased oxygen pressures, which has strong implications for corrosion and catalysis. Stable O-enriched states resulting from oxidation may consist of the metal surface with high concentration of adsorbed O atoms, the corresponding metal-oxide, or something in between (e.g. surface oxides). A quantitative atomistic modeling of oxidation reactions catalyzed on transition metals therefore requires an understanding of the properties and formation mechanisms of the oxidized surfaces. In this work, the oxidation of Pd(100) to the corresponding surface oxide phase PdO(101)/Pd(100) formed on it is addressed by means of Density Functional Theory calculations. We focus on the oxidation mechanisms involving the pristine metal surface and different surface defects. The under-coordinated sites at surface steps, kinks, and small clusters or islands are found to play an important role in the oxidation process, affecting both the initial adsorption of oxygen and the transformation to the surface oxide phase.

O 16.2   Mon 15:15   MA 141
Insights into the Relative Importance of Ripening and Particle Migration for Sintering of Pt Nanoparticles — ●Elisabeth Dietze[1], Frank Abild-Pedersen[2], and Philipp N. Plessow[1] — [1]Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany — [2]SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, Stanford, USA

A rational approach to improve the stability of heterogeneous transition metal catalysts requires to understand deactivation mechanisms on an atomic scale. For Pt nanoparticles, simulations have shown that ripening through the gas phase via volatile PtO_2 is relevant for sintering [1], but surface migration could not be excluded as an alternative mechanism. Recently, the migration of Pt particles was modeled from first principles [2] and diffusion constants were extracted. Using these diffusion constants, the importance of particle migration for sintering can now be estimated. To model the position and migration of particles, we use a kinetic Monte Carlo rather than a mean field model. This also allows us to explicitly study the effect of defects. The developed approach is able to simulate both ripening and particle migration and one can therefore compare the relative importance of these two mechanisms. We furthermore investigate how temperature, partial pressure of oxygen, binding strength of defects and the shape of the PSD influence the sintering kinetics.

References: [1] Plessow, P. N.; Abild-Pedersen, F., ACS Catal. 2016, 6 (10). [2] Li, L., et al. J. Phys. Chem. C 2017, 121(8).

O 16.3   Mon 15:30   MA 141
Steps and catalytic reactions: First-principles Kinetic Monte Carlo study on CO oxidation with preadsorbed O on Rh (553) — ●Baochang Wang[1], Chu Zhang[2], Johan Gustafson[2], and Anders Hellman[1] — [1]Department of Physics and the Competence Centre for Catalysis, Chalmers University of Technology, 41296, Sweden — [2]Synchrotron Radiation Research, Lund University, Box 118, 221 00 Lund, Sweden

Many catalytic reactions display strong structure sensitivity, and particular steps and defects are often identified as active sites for the reactions at hand. A controlled way to address this is to use vicinal surfaces where the step density is known. Here we studied the CO oxidation reaction on oxidized Rh(111) and Rh(553) by first-principles methods coupled with Kinetic Monte Carlo (KMC) to provide insight to the structure sensitivity on Rh. Our recent experiment shows that the reaction between CO and preadsorbed O proceeds at lower temperature on a stepped Rh(553) surface than on a flat Rh(111), indicating that stepped surfaces are more catalytically active. After removing half of the oxygen, however, the reaction slows down significantly and the O coverage seem to remain as 25% of the initial coverage. First-principles calculations were performed to investigate the different possible reaction pathways on the surfaces. A lattice KMC model was built based on the calculated barriers. We do, however, find that this is not thanks to reactions on the steps, but rather on the terraces close

to the steps. Our theory results are compared to experimental data, both concerning the CO activity but also core-level spectroscopy.

O 16.4   Mon 15:45   MA 141
Finite-Temperture Statistical Study of Small Silver Clusters Ag_n (n= 4-13) interacting with O_2 molecules — ●Weiqi Wang and Luca M. Ghiringhelli — Fritz-Haber-Institut der MPG, Berlin

Due to their unique physical and chemical properties, noble-metal clusters have attracted tremendous interest in recent decades. In this work, we systematically study both the static and the dynamical properties at finite temperature of sub-nanometer-sized neutral silver clusters Ag_n (n= 4-13), with and without adsorbed O_2, in order to reveal correlations between the structure, the local charge, and the bond dynamics.

Clusters with different (fixed) spin states are sampled at different temperatures by replica-exchange *ab initio* molecular dynamics, where the forces bewteen atoms are described via density-functional theory.

Regarding dynamical properties, we focus our attention on the bond life-time, studied by means of the bond auto-correlation function.

Interestingly, we find a correlation between the local charge state of bonded atom pairs, estimated via the Hirschfeld charge partitioning, and the bond life-time. In particular, negatively charged Ag binded pairs (with elongated Ag–Ag bond) tend to have shorter bond life times. Since O_2 molecules tend to adsorb onto these negatively charged sites, the O–O bond gets activated upon adsorption. This suggests that the local charge may be a good descriptor for the identification of active sites on the nanoclusters.

O 16.5   Mon 16:00   MA 141
Ethanol dehydrogenation and oxygen dissociation on the Ni- and Rh-doped Au(111) surface — ●Ozan Dernek[1], Hande Üstünel[1], and Daniele Toffoli[2] — [1]Department of Physics, Middle East Technical Univesity, Dumlupinar Boulevard 1, 06800, Ankara, Turkey — [2]Dipartimento di Scienze Chimiche e Farmaceutiche, Universita degli Studi de Trieste Via L. Giorgieri 1 , I-34127, Trieste, Italy

The byproducts of the combustion reaction of alcohols find uses in a wide range of applications in food, pharmaceutical, polymer and plating industries along with many others. As a result, there are considerable economical interests in the design of efficient, low-cost and environmentally low-impact synthetic routes of these products.

The aim of this study is to design Au surfaces by means of doping the surface with Ni and Rh atoms in low concentrations to increase the performance of the surface for selective oxidation of ethanol and dissociation of O_2. We utilize arguably the most successful theoretical method to ever have been used in surface science, namely Density Functional Theory (DFT), to understand the selective oxidation of ethanol and dissociation of O_2 to atomic oxygen. We present the the reaction pathways and activation barriers for both reactions.

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O 16.6   Mon 16:15   MA 141
Promotoreffekt von Alkalimetallen bei Epoxidation von Ethylen über Silberkatalysatoren — ●Matej Huš und Anders Hellman — Fakultät für Physik, Technische Hochschule Chalmers, SE-41296 Göteborg, Schweden

Die Oxidation von Ethylen zu Epoxiden ist eine der wichtigsten Reaktionen in der chemischen Industrie. Im industriellen Maßstab werden üblicherweise Silberkatalysatoren verwendet. Zur Vermeidung der vollständigen Oxidation zu CO_2 muss CsCl als Promotor beigemischt werden. Der Mechanismus, welcher zu einer Erhöhung der Selektivität führt, ist umstritten. Basierend auf Dichtefunktionaltheorie-Rechnungen haben wir den Einfluss der Alkalimetalle auf die Selektivität untersucht. Unsere Rechnungen zeigen, dass alle Alkalimetalle die Selektivität signifikant erhöhen während die Aktivität des Katalysator reduziert wird. Der Effekt ist umso ausgeprägter je elektropositiver das Alkalimetall. Die Ursache für die Erhöhung der Selektivität und Absenkung der Aktivität ist ein durch die Alkalimetalle auf der Katalysatoroberfläche induziertes elektrisches Feld. Durch die Beimischung von Cl kann die Aktvität ohne Verlust von Selektivität wieder hergestellt werden. Unsere Rechnungen zeigen, dass die Kombination von elektronegativem Cl und elektropositivem Cs einen optimalen

Kompromiss aus Aktivität und Selektivität bietet.

15 min. break

O 16.7 Mon 16:45 MA 141

Cheap and Accurate Descriptors for the Computational Screening of Bimetallic Catalysts Identified Using Compressed-Sensing — ●Mie Andersen[1], Sergey V. Levchenko[2], Matthias Scheffler[2], and Karsten Reuter[1] — [1]Theoretical Chemistry, Technische Universität München, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Computational screening for new and improved catalyst materials requires cheap and accurate descriptors for energy trends in surface adsorption. To this end, simple and intuitive physical models such as the d-band model or scaling relations have proven highly successful for transition metal catalysts [1]. Here we apply SISSO [2], a recently developed compressed-sensing method, to identify more accurate descriptors for surface adsorption using a training data set of adsorption energies of atomic and molecular adsorbates on the fcc(211) facets of elemental transition metals. The descriptors are constructed as nonlinear functions of primary features, which can be obtained at low computational cost from the clean metal surface. Examples of primary features are d- and sp-projected density of states at the Fermi level, d-band filling, d-band center, and the Pauling electronegativity of the metal atom. We illustrate the superior predictive performance of the found descriptors on a test data set of adsorption energies on alloy surfaces and apply the new model to the computational screening of bimetallic catalysts for methanol synthesis.

[1] F. Abild-Pedersen, Catal. Today **272**, 6 (2016)
[2] R. Ouyang *et al.*, arXiv:1710.03319

O 16.8 Mon 17:00 MA 141

Evaluation of the Density Functional based Tight Binding method for the study of graphene nucleation on Cu catalysts — ●Juan Santiago Cingolani, Mattia Peluchetti, Mie Andersen, and Karsten Reuter — Chair of Theoretical Chemistry, Technische Universität München, Germany

Graphene nucleation on a liquid Cu surface has been shown to produce uniform monolayer continuous films [1] and thus has gained attention in recent years. Molecular dynamics (MD) simulations could provide insights into the processes involved, but the system sizes and timescales required lie outside of the scope of Density Functional Theory (DFT) methods. The Density Functional based Tight Binding (DFTB) method, which provides a significant speedup while retaining a reasonable accuracy, could prove to be a viable alternative. We evaluate the performance of a set of DFTB parameters developed by Li et al [2] by making a series of calculations on the interaction of C atoms on a Cu (111) surface and comparing these results with literature DFT data. We then benchmark selected snapshots from DFTB-driven MD simulations against DFT. Remarkably, reaction and activation energies for monomer diffusion and C-C nucleation are reproduced within 0.1 eV. While our results are promising, further benchmarks against experimental data need to be carried out to validate the use of DFTB in the study of graphene nucleation on molten Cu surfaces.

[1] L. Tan, M. Zeng, T. Zhang, L. Fu, Nanoscale 7, 9105 (2015)
[2] H.-B. Li, A. J. Page, C. Hettich, B. Aradi, C. Kohler, T. Frauenheim, S. Irle, K. Morokuma, Chem. Sci. 5, 3493 (2014)

O 16.9 Mon 17:15 MA 141

Water splitting reaction on polar Lithium Niobate surfaces — ●Christof Dues[1], Wolf Gero Schmidt[2], and Simone Sanna[1] — [1]Institut für Theoretische Physik, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 16, D-35392 Gießen — [2]Department Physik, Universität Paderborn, Warburger Str. 100, D-33098 Paderborn

Water splitting is a highly promising environment friendly approach for hydrogen production. It is often discussed in the context of carbon-dioxide-free combustion and storage of excess electrical energy after conversion to chemical energy. Since the oxidation and reduction reactions are related to significant over-potentials, the search for a suitable catalyst is of particular importance. Ferroelectric materials, e.g. Lithium Niobate (LN), attracted considerable interest in this respect. On the one hand, the spontaneous internal polarization results in enhanced life-times of photo-generated charge carriers. At the other hand, the presence of surfaces with different polarization and chemistry leads to spatial separation of oxidation and reduction reactions. Employing DFT and a simplified thermodynamic approach to calculate Gibbs energy differences, we present an efficient method to estimate the over-potentials related to the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) on both polar $LiNbO_3(001)$ surfaces. Our calculations show that the OER and HER over-potentials are lower on the negative (1.27 V) and positive (0.39 V) LN surface, respectively. Calculations within the NEB method reveal the barrier height between the intermediate steps of the OER and HER reactions.

O 16.10 Mon 17:30 MA 141

Tensor-train approximations for catalytic reaction systems — ●Patrick Gelss[1], Sebastian Matera[1], and Christof Schütte[1,2] — [1]Freie Universität Berlin, Germany — [2]Zuse Institute Berlin, Germany

For modeling heterogeneous catalytic processes, kinetic Monte Carlo (kMC) simulations have become an important tool since direct molecular dynamics simulations of rare-event systems are prohibitive. However, the drawback of kMC is the large number of simulations needed to capture the relevant dynamics. We present an alternative approach, which mitigates the curse of dimensionality and directly solves a Markovian master equation corresponding to a given microkinetic mechanism by exploiting the tensor-train (TT) format [1]. Different numerical integration methods and step-size adaptation techniques enable a tunable accuracy and linear scaling in the system size for a large range of input parameters. We benchmark the TT approach against highly accurate kMC simulations for catalytic processes based on nearest-neighbor interactions [2], e.g. a model for the CO_2 fixation into methanol at a Cu/ZrO_2 interface [3].

[1] P. Gelß, S. Matera, C. Schütte, J. Comput. Phys., 314, pp. 489-502 (2016)
[2] P. Gelß, S. Klus, S. Matera, C. Schütte, J. Comput. Phys., 341, pp. 140-162 (2017)
[3] Q.-L. Tang, Q.-J. Hong, Z.-P. Liu, J. Catal., 263, pp. 114-122 (2009)

O 16.11 Mon 17:45 MA 141

Enthalpy consistent finite difference lattice Boltzmann method for catalytic flow simulations — ●Daniel Berger[1], Ana-Sunčana 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 coupled finite differences thermal lattice Boltzmann model (FD-LBM) to simulate catalytic reactions through porous media. The thermal LBM is used to solve the heat and mass transport in the gas domain, while the chemical surface reactions are incorporated in a very flexible fashion through the flux boundary conditions at the walls. This scheme is further augmented by a finite difference solver to solve the heat equation in the solid and across the gas-solid interface for a consistent treatment of the reaction enthalpy.

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 16.12 Mon 18:00 MA 141

Atomic and Electronic Structure of Alkali-Doped Zeolites from First Principles — ●Debalaya Sarker, Sergey V. Levchenko, and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin 14195, Germany

Zeolites posses a crystalline nanoporous aluminosilicate framework with tunable composition, making them ideal candidates for catalytic applications. The substitution of $[SiO_4]$ tetrahedra by negatively charged $[AlO_4]^-$ requires inclusion of counterions. In addition, zeolites readily accommodate dopants, in particular alkali metals [1]. The distribution and concentration of dopants and counterions determine solvated electron density distribution and the electrostatic field inside the zeolitic pores, which have a strong influence on sorbed molecules. We study pristine and M-doped MX and MY zeolites (M = Na, K, Cs), using density-functional theory with a semi-local (PBE) and a hybrid (HSE06) functional with an *ab initio* van der Waals correction [2]. For

different species of the alkali metals, the positions of the counterions in undoped zeolites are found to vary, contrary to the commonly assumed particular cation sites in FAU-type zeolites [3]. Also, the position of counterions with respect to the six-membered ring is found to correlate with electronegativity of the M atom. We found that the distribution of solvated electrons inside the pores is strongly affected by the dopant type and location.

[1] L. R. M. Martens *et al.*, Nature **315**, 568 (1985)
[2] A. Tkatchenko and M. Scheffler, PRL **102**, 73005 (2009)
[3] D. H. Olson, Zeolites **15**, 439 (1995)