

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A212 - Session HC+SS-MoM

Utilization of Theoretical Models, Machine Learning, and Artificial Intelligence for Heterogeneously-Catalyzed Reactions

Moderators: Liney Arnadottir, Oregon State University, Sharani Roy, University of Tennessee Knoxville

8:40am HC+SS-MoM-2 Theoretical Study of Acetic Acid Decomposition on Pd (111) using Density Functional Theory, *Kingsley Chukwu, L Arnadottir, Oregon State University*

Acetic acid decomposition on Pd (111) and the effects of water on the decomposition are good model systems for the study of solvent effects on small oxygenates. Numerous studies have found that solvents influence the selectivity and rate of heterogeneous catalytic reactions, so fundamental understanding of how water affects OC-O, C-OH, CO-H, C-H and C-C bond cleavages will give us valuable insight into how water influences selectivity of oxygenates decomposition, further enabling bottom up design of effective catalyst and catalyst system. Here we present density functional theory calculations of the decomposition of acetic acid on Pd (111) and the effects of water on the reaction mechanism. Our results suggest that the most favorable decarboxylation (DCX) and decarbonylation (DCN) mechanisms in vacuum proceed through dehydrogenation of acetic acid (CH_3COOH) to acetate (CH_3COO), followed by dehydrogenation of CH_3COO to CH_2COO . The competition between the most favorable DCN and DCX pathway depends on two endothermic elementary steps, the deoxygenation of CH_2COO to ketene (CH_2CO) and dehydrogenation of the carboxylmethylidene (CH_2COO) to carboxylmethylidyne (CHCOO). Water can affect the different elementary steps by changing the stability of the initial, transition and/or final state or by providing new reaction paths such as through hydrogen shuttling, which can lead to changes in the selectivity of a complex reaction network as presented herein. Here we will discuss how water influences different critical reaction steps and how that effects the overall reaction network.

9:00am HC+SS-MoM-3 Towards a Chemically Accurate Description of Reactions of Molecules with Transition Metal Surfaces, *Geert-Jan Kroes, Leiden University, Netherlands*

INVITED

Heterogeneously catalyzed processes consist of several elementary reactions. Accurately calculating their rates requires the availability of accurate barriers for the rate controlling steps. Unfortunately, currently no first principles methods can be relied upon to deliver the required accuracy. To solve this problem, in 2009 we came up with a novel implementation of the specific reaction parameter approach to density functional theory (SRP-DFT). This allowed us to reproduce experiments for H_2 reacting on copper surfaces, and to determine barrier heights for H_2 -Cu systems, with chemical accuracy. The original procedure used was not extendable to reactions of molecules heavier than H_2 with surfaces, because the metal surface was treated as static. This problem has been solved by combining SRP-DFT with Ab Initio Molecular Dynamics (AIMD). This method was applied to the dissociative chemisorption of methane on a Ni surface, a rate-limiting step in the steam reforming reaction. We were able to reproduce experiments on $\text{CHD}_3 + \text{Ni}(111)$ with chemical accuracy, and have predicted a value of the reaction barrier height that we claim to be chemically accurate. We have new results for $\text{CHD}_3 + \text{Pt}(111)$ that are even better, and which show that the SRP density functional for methane interacting with Ni(111) is transferable to methane interacting with another group X metal surface, i.e., Pt(111). Even more interestingly for applications to catalysis, the SRP functional derived for methane reacting with Ni(111) also gives a very accurate description of molecular beam sticking experiments on $\text{CHD}_3 + \text{Pt}(211)$. Finally, thanks to a collaboration with Jörg Behler (University of Göttingen) we are now able to develop potential energy surfaces also depending on the degrees of freedom associated with the surface phonons, for polyatomic molecules interacting with metals. This has enabled us to compute statistically accurate reaction probabilities for highly activated reactions not open to investigation with AIMD, for which reaction probabilities are less than 0.01.

9:40am HC+SS-MoM-5 The Apparent Activation Energy for Complex Mechanisms: A Simple Relationship via Degrees of Rate Control, *Zhongtian Mao^{1,2}, C Campbell, University of Washington*

Reactions on surface usually consists of several elementary steps. It is known that the observed reaction kinetics often represents a composite of the contribution from each of these elementary steps. The “rate-determining step” (RDS) assumption is a common approach for dealing with multistep mechanisms, where a single step is assumed to dominate the reaction kinetic behaviors and the kinetic parameters of this RDS (e.g., net rate, activation energy) are good estimation for those of the overall reaction. However, RDS is not a rigorous concept in mathematics and there is no universal definition for RDS. Efforts have been made to clarify the actual physical meaning behind RDS, and the “Degree of Rate Control” (DRC) was raised as a rigorous mathematical approach to quantify to what extent the change of the Gibbs free energy of a species in the reaction scheme can affect the rate of the overall reaction. DRC analysis to reaction kinetics elucidates that there are only rate-determining species with non-negligible DRCs instead of rate-determining steps.

The apparent activation energy E_{app} is determined by fitting the temperature dependence of the reaction rate to the Arrhenius law. It is believed that E_{app} is a direct measurement of energy information in the RDS, which has been challenged by DRC analysis. A general and accurate elaboration of the microscopic origin of E_{app} has not been reported except in cases where there is an analytical rate expression. Here a simple but general mathematical expression of E_{app} in terms of the enthalpies of species in the reaction and their DRCs is derived. To verify the accuracy of this equation, microkinetic modelling of methanol synthesis through CO_2 hydrogenation on Cu-based model catalysts under three different conditions was carried out based on previously-published DFT energetics. On pure Cu(211) at 450 K, there are only one transition state and only one intermediate with non-negligible DRCs, and E_{app} estimated using our equation is within 1 kJ/mol of the true value. When the temperature is raised to 570 K, the surface sites are mostly unoccupied; and, when the model catalyst is promoted by Zn, there are four transition states with non-negligible DRCs, which means the single RDS assumption is not true. In both these complicated cases, the error of the estimated value for E_{app} is still <1 kJ/mol.

10:00am HC+SS-MoM-6 First-Principles Kinetic Monte Carlo Simulation of CO Oxidation on PdO(101): Role of Oxygen Vacancies, *Minkyu Kim, A Asthagiri, The Ohio State University*

CO oxidation on transition metal (TM) oxide surfaces has been widely studied both experimentally and theoretically; however, a healthy debate continues on the coupling between changes in oxide phase and surface reactivity. In this study, we investigated CO oxidation over PdO(101) surface, which has been proposed to be important in Pd oxidation catalysis. In contrast to earlier studies of CO oxidation on TM oxide surfaces, we incorporate neighbor effects of oxygen vacancies on all the elementary surface processes. We employ density functional theory (DFT) to map out the kinetics of 50 elementary surface processes. We find that barriers for elementary steps such as O vacancy, O_2 dissociation, and CO_2 formation can be decreased by 20-40% in the presence of O vacancies, while O_2 desorption is increased by 70%. Using the DFT-derived rate constants, we have developed a lattice-based kinetic Monte Carlo (kMC) framework that can simulate CO oxidation under both ultra-high vacuum (UHV) and reaction conditions.

Initially, the kMC simulations were performed under UHV conditions (low CO partial pressure, no O_2 pressure) as a function of increasing surface temperature. As the CO oxidation proceeds and the surface lattice O atom coverage is depleted, the CO oxidation rate decreases rapidly at 400 K; however, the rate sharply increases at temperatures above 450 K. At 450 K, we find a new complex pathway to CO_2 formation that is activated in the presence of O vacancies and is the source of the increased CO oxidation rate despite the depletion of surface oxygen atoms. These kMC results match UHV isothermal experiments under similar conditions. kMC simulations at steady state conditions of low CO and O_2 pressures ($P_{\text{CO}}: 5 \times 10^{-9}$ Torr / $P_{\text{O}_2}: 1.5 \times 10^{-8}$ Torr), show that the rate-limiting step is O_2 dissociation and this elementary step requires the presence of adjacent oxygen vacancies to be activated at temperatures below 500 K. Without the addition of O vacancy neighbor effects to the kMC model, the PdO(101) surface would be inactive to CO oxidation because surface oxygens cannot

¹ Heterogeneous Catalysis Graduate Student Presentation Award Finalist

² Morton S. Traum Award Finalist

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be healed by gaseous O₂. In addition, we will discuss kMC simulations under reaction conditions at varying CO/O₂ partial pressures.

10:40am **HC+SS-MoM-8 Accelerating *ab initio* Simulations using Surrogate Machine Learning Models**, *Jose A. Garrido Torres, P Jennings, M Hansen*, Stanford University; *T Bligaard*, SLAC National Accelerator Laboratory

Typically, first-principle calculations are computationally expensive. This problem is usually accentuated when modeling materials due to the large number of atoms involved in the models. Therefore, the development and implementation of robust and fast optimizers have always been a hot topic in this field. The desired algorithms must minimize the number of *ab initio* function calls as much as possible without compromising the accuracy of the simulated properties. Our approach is based on a surrogate machine learning model which allows to substantially reduce the number of function calls in the search of the optimal solution. Here, we present the evidence of the aforementioned acceleration for two of the most commonly encountered optimizations problems in computational catalysis: structural relaxations and transition-state search, such as energy minimization and Nudged Elastic Band (NEB) calculations.

11:00am **HC+SS-MoM-9 Integrating Materials Databases and Autonomous Workflows for the Discovery of New Heterogeneous Catalysts**, *Kirsten Winther, T Bligaard*, SLAC National Accelerator Laboratory

With the accelerating amount of electronic structure data being generated in materials research, data-driven approaches have a huge potential to guide the discovery of new materials and catalysts. This paradigm relies on the development of sophisticated tools and software for storing, sharing and generating calculational results.

Several open materials databases, including Materials Project and the Open Quantum Materials Database (OQMD), have been successful in making the results of electronic structure calculations openly available, where vast amount of crystalline materials data has been generated. Recently, we developed the Catalysis-Hub.org database platform[1], which is suited to handle the complexity of computational catalysis.

In my talk I will present the Catalysis-Hub platform, which consists of a database for surface reactions containing 105,000+ reaction energies from more than 50 publications, as well as several in-browser apps, such as atomistic machine learning predictions for adsorption energies [2] and generation of crystal [3] and surface-adsorbate geometries[4]. Next, I will discuss how these efforts can be integrated into computational workflows for generating atomic geometries and calculations. This includes how machine learning predictions in an active learning framework can be used for an autonomous exploration of new catalytic materials.

[1] K.T. Winther, M.J. Hofmann, O. Mamun, J. R. Boes, M. Bajdich, T. Bligaard. *Scientific Data*, Accepted (2019).

[2] M.H. Hansen et al. <https://arxiv.org/abs/1904.00904> (2019).

[3] A. Jain, T. Bligaard *Phys. Rev. B* 98, 214112 (2018).

[4] J.R. Boes, O. Mamun, K. T. Winther and T. Bligaard. *JPCA* 123, 2281–2285 (2019).

11:20am **HC+SS-MoM-10 Knowledge-Based Approaches in Catalysis and Energy Modelling**, *Karsten Reuter*, Technical University of Munich, Germany

INVITED

Reflecting the general data revolution, knowledge-based methods are now also entering theoretical catalysis and energy related research with full might. Automatized workflows and the training of machine learning approaches with first-principles data generate predictive-quality insight into elementary processes and process energetics at undreamed-of pace. Computational screening and data mining allows to explore these data bases for promising materials and extract correlations like structure-property relationships. At present, these efforts are still largely based on highly reductionist models that break down the complex interdependencies of working catalysts and energy conversion systems into a tractable number of so-called descriptors, i.e. microscopic parameters that are believed to govern the macroscopic function. For certain classes of materials like transition metal catalysts, corresponding human-designed models have indeed established trend understanding and spurred a targeted materials design. Future efforts will concentrate on using artificial intelligence also in the actual generation and reinforced improvement of the reductionist models. This is expected to better capture complexities

like incomplete understanding or operando changes of interfacial morphology, to provide access to structured and compound materials classes, or ultimately to even fulfill the dream of an inverse (de novo) design from function to structure. In this talk, I will briefly survey these developments, providing examples from our own research, in particular on adsorption energetics at bimetallic catalysts and data mining for the design of organic semiconductors.

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