

O 101: Heterogeneous Catalysis: Theory I

Time: Thursday 17:00–18:30

Location: TRE Phy

Invited Talk

O 101.1 Thu 17:00 TRE Phy
Density Functional Theory in Surface Science and Catalysis - Successes and Limitations — ●FELIX STUDDT — Karlsruher Institut für Technologie, Institut für Katalyseforschung und -technologie

Theoretical calculation employing density functional theory (DFT) are being widely used to investigate reactions of atoms and molecules on solid surfaces as they occur e.g. in heterogeneously catalyzed reactions. When coupled with a kinetic analysis of the reaction mechanism, reaction rates can be calculated from this data giving insight into the catalytic performance of materials. The success of theoretical calculations will depend on the errors associated with the level of DFT and the approximations used in the models employed for the surface reaction. Herein I will show some examples of how DFT can be used to understand heterogeneously catalyzed reactions and how close one can mimic experimental observations. The complexity associated with surface models for heterogeneously catalyzed reactions can be a challenge requiring sophisticated models and current limitations of theory will be exemplified for the hydrogenation of CO to various products. Finally, the errors of DFT will be addressed and I will show how one can use tools to learn about errors as well as error propagation and what this means for trends that are predicted with DFT.

O 101.2 Thu 17:30 TRE Phy
Computational Screening of MXenes as potential Two-dimensional Materials for Hydrogen Evolution Reaction — ●MOHNISH PANDEY and KRISTIAN S. THYGESEN — Center for Atomic-scale Materials Design, Technical University of Denmark, 2830 Kgs. Lyngby, Denmark

We explore a new class of 2D materials commonly known as MXenes which are primarily carbides and nitrides of transition metals.[1] The stability of bare and functionalized MXenes is assessed via heat of formation. The possibilities of hydrogen evolution from these compounds are explored using the free energy of hydrogen adsorption at equilibrium coverages as activity descriptor.[2] Using a set of criteria, we propose a list of MXenes which can potentially be used as hydrogen evolving catalysts.

[1] M. Naguib, V.N. Mochalin, M.W. Barsoum, and Y. Gogotsi. *Adv. Mater.*, **26**, 92–1005 (2014) [2] M. Pandey, A. Vojvodic, K. S. Thygesen, K. W. Jacobsen, *J. Phys. Chem. Lett.*, **6**, 1577–1585 (2015)

O 101.3 Thu 17:45 TRE Phy
Oxygen Activation and Methanol Oxidation on Nanoporous Gold — ●WILKE DONONELLI¹, LYUDMILA MOSKALEVA², and THORSTEN KLÜNER¹ — ¹Institut für Chemie, Carl von Ossietzky Universität Oldenburg, 26111 Oldenburg, Germany — ²Institut für Angewandte und Physikalische Chemie, Universität Bremen, 28359 Bremen, Germany

Au-based catalysts can be used for fuel cells, the synthesis of esters or the selective oxidation of alcohols. There is a high interest in this gold based catalysts because the selectivity of gold to partial oxidation products is higher than the selectivity of other metal catalysts. Especially Nanoporous gold (np-Au) has recently attracted considerable interest due to its potential use in catalysis. This Au-based catalyst can be used for the selective oxidation of methanol. The bottleneck of this oxidation reaction is the activation of oxygen on the surface. For this study, a kinked au(321) surface introduced by Moskaleva represents one of the reactive surfaces of the nanoporous gold. It consists of (111) terraces and zigzag-shaped steps, which may be favourable as possible adsorption positions for methanol in partial oxidation reactions. The

aim of our work is the elucidation of the detailed mechanisms for total and partial oxidation of methanol on this model surface. So far we analysed the process of the oxygen activation and were able to present a theoretical mechanism that explains the first steps of this oxidation process, where first a methoxy species and in a next step formaldehyde is formed. These catalytic surface reactions are analysed using the PBE functional implemented in VASP.

O 101.4 Thu 18:00 TRE Phy
Ligands Effects on the Structure of Gold Clusters at Finite Temperature — ●DIEGO GUEDES-SOBRINHO¹, JUAREZ L. F. DA SILVA¹, WEIQI WANG², and LUCA M. GHIRINGHELLI² — ¹University of São Paulo, São Carlos, Brazil — ²Fritz-Haber-Institut der MPG, Berlin, Germany

Due to their catalytic properties and consequent importance for *green energy* transformation, gold clusters have been the focus of a large number of experimental and theoretical studies. However, an atomistic understanding of temperature and ligands effects on their structure is far from satisfactory. In this work, we investigate the structural stability and electronic aspects of Au₁₃ – an example of flexible clusters at finite *T* [Beret *et al.* *Faraday Discuss.* **152**, 153 (2011)] – passivated by (CO)_{*n*} (*n* = 1, 6, 10). We use replica-exchange *ab initio* molecular-dynamics, for an unbiased statistical sampling of the phase space. The energy and forces are described via the PBE exchange-correlation functional, including many-body dispersion interactions [A. Tkatchenko *et al.*, *JCP* **138**, 074106 (2013)], as implemented in the all-electron FHI-aims package. For (CO)_{*n*}/Au₁₃, we find an electron-density displacement from Au and C atoms to O, which is more pronounced for *n* = 10. At this high CO coverage and in the temperature range 300 – 700 K, cationic Au clusters with compact (high average coordination) structures are preferred. In comparison, pristine Au₁₃ clusters show a preference for more open (low average coordination) configurations in the same temperature range.

O 101.5 Thu 18:15 TRE Phy
Complex Reaction Networks of Oxygen Activation on Ag Clusters with Multi-Spin States at Finite Temperature — ●WEIQI WANG, MATTHIAS SCHEFFLER, and LUCA M. GHIRINGHELLI — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

To understand the process of the oxygen activation on (noble) metal clusters such as Ag₄, Ag₈, it is critical to take finite temperature effects into account. Transient structures, having their spin ground states different from those of stable structures, could be crucial in promoting the activation of oxygen. The appearance of those transient structures, however, introduces extra complexity into the reaction network. In this work, the reaction network of oxygen adsorption on silver clusters are studied at finite-temperature and different spin states. By estimating the transition matrices, the Markov state models (MSM) are established, based on the trajectories at parallel temperatures obtained from replica-exchange (first-principles) molecular dynamics (REMD). Reaction pathways are then analyzed by transition-path theory (TPT) based on the converged sampling on MSM. The MSMs and the reaction pathways are embedded in 2-dimensions by using the non-linear dimensionality reduction method Sketch-Map. In addition, 2-dimensional free energy plots are also calculated by the Boltzmann-reweighting method multi-state Bennet acceptance ratio (MBAR). We show that the adsorption and activation of oxygen benefits from the transient geometries, with spin states different from the ground state, that are available at finite temperature. This work was supported by the UNICAT cluster of excellence (DFG).