Final Report for the workshop

Catalysis from first principles (Cat1P): Heterogeneous catalysis meets electrocatalysis

Castle Reisensburg near Ulm/Germany
May 25-28, 2014
Organizers:

Axel Groß, Ulm University, Ulm/Germany
Karsten Reuter, Technical University of Munich, Garching/Germany

Summary

Catalytic processes are of tremendous technological importance, but they are also of fundamental interest for the understanding of chemical reactions. First-principles calculations have reached a status that they can contribute significantly to a better understanding of the principles underlying catalytic reactions, but also to the development of tailored catalysts for specific purposes. In comparison to heterogeneous catalysis, the theoretical treatment of processes in electrocatalysis is additionally hampered by the complex electrochemical electrolyte/electrode interfaces. Still, on the atomistic level the same underlying principles are relevant for the bond-making and bond-breaking processes.

Therefore, the primary goal of this workshop was to bring together experts from the fields of first-principles modeling of heterogeneous catalysis and electrocatalysis. In addition, the close contact to the experiment and industry is rather important, hence also experts from these areas were invivted contribute to the success of the workshop.

The conference was the eighth in the "Cat1P - Catalysis from First Principles" series that were initially arranged by Matthias Scheffler, Jürgen Hafner, Jens Nørskov and their colleagues. The meeting thus followed successful workshops in Magleas, Denmark (1999, 2004 and 2011), CECAM Lyon (2000 and 2006), and Vienna (2002 and 2009). This workshop was supported by the German Science Foundation (DFG), by CECAM and the Psik-Network through the ESF. Additional funding was provided by the DFG Research Unit FOR 1376 "Elementary Reaction Steps in Electrocatalysis: Theory meets Experiment",

The workshop with 57 participants was characterized by excellent talks and poster contributions and by lively discussion between theoreticians and experimentalists, between experts in heterogeneous and electro-catalysis. The stimulating atmosphere of Castle Reisensburg where all the participants stayed during the whole course of the workshop, contributed significantly to the success of the workshop.

Description of the scientific content of and discussion at the event

Catalytic processes are of tremendous technological importance, but they are also of fundamental interest for the understanding of chemical reactions. First-principles calculations have reached a status that they can contribute significantly to a better understanding of the principles underlying catalytic reactions, but also to the development of tailored catalysts for specific purposes. Although on the atomistic level the same underlying principles are relevant for the bond-making and bond-breaking processes in heterogeneous catalysis and electro-catalysis, the theoretical treatment of processes in electrocatalysis faces additional challenges:

- In electrochemistry, structures and properties of the electrode-electrolyte interfaces are governed by the electrode potential which adds considerable complexity to the theoretical treatment since charged surfaces have to be considered.
- The theoretical treatment of processes at solid-liquid interfaces includes a proper description of the liquid which requires to determine free energies instead of just total energies. This means that computationally expensive statistical averages have to be performed.
- Electronic structure methods based on density functional theory (DFT) combine numerical efficiency with a satisfactory accuracy. However, there are severe shortcomings of the DFT description of liquids, in particular water, using current functionals.

The talks by Jan Rossmeisl, Marc Koper, Suljo Linic, Timo Jacob and Zhi-Pan Liu illustrated the sophisticated level that first-principles calculations addressing electrocatalytic reactions have reached. Reaction pathways including complex reaction networks can be identified, and trends in electrocatalysis can be analysed and explained or even predicted. Still, often the electrochemical environment is only taken into account via a thermodynamic treatment on the basis of the computational hydrogen electrode. The validity of this elegant and efficient approach can still not be assessed reliably because high-level simulations including a realistic modeling of the electrochemical environment are still missing. Possible routes to take this environment into account were presented by Marzari who proposed a multi-scale electrostatic framework. The use of implicit solvent models was discussed by Sakong.

Superficially, semiconductor defect chemistry and electrochemistry seem to be distinct research fields. Still, in the talks by Richter and Neugebauer it became apparent that there can be unifying concepts as both fields are based on the same fundamental building blocks, charged defects/ions.

Theoretical studies addressing reactions in heterogeneous catalysis do not face the problem of including any electrolyte, and the talks by Lopez, Vojvodic, Hafner and Honkala demonstrated the deep insights with respect to heterogeneous catalyis first-principles calculations can provide. Still, the theoretical treatment is still confronted with the structure and pressure gap which means that heterogeneous catalysis usually does not occur at idealized model substrates. To take these issues into account, multiscale approaches are promising which were discussed by Vlachos, Heyden and Oberhofer. Uncertainties associated with such an approach, in particular with respect to the choice of the DFT functional were discussed by Bilgaard.

The contact to the experiment in heterogeneous and electro-catalysis was provided in the talks by Behm and Petterson. The talks by Moses, Sarwar and Kuipers even went further towards the real word by making contact to industrial aspects of catalysis.

The talks stimulated lively discussions. It was agreed that theory can nowadays substantially contribute to the progress in heterogeneous and electro-catalysis. Still, significant efforts towards a more realistic modeling shall be undertaken in order to address issues that are also relevant for industrial catalysis.

All of the topics discussed above were also covered in the posters which were mainly presented by young scientists. All poster presenters introduced their posters in a short presentation. The poster session were well-attended, and lively discussion evolved in front of the posters. These discussions continued during the tasty meals and at night in the “Klause”. They were fostered by the stimulating atmosphere of Castle Reisensburg where all the participants stayed during the whole course of the workshop. Thus the participants had the chance to get to know each other better and discuss in depth scientific issues, but also possible collaborations.

Assessment of the results and impact of the event on the future direction of the field

Theoretical studies of catalytic processes and materials can serve two purposes. As they allow a perfect control of the parameters entering the addressed system, they can provide - if properly analysed - a deep understanding of the principles underlying catalytic reactions. Thus reaction concepts can be established that allow to predict the outcome of catalytic reactions on a qualitative basis. Scaling relations in heterogeneous catalysis represent such a concept. As discussed in the workshop, they provide for example an understanding why the extremely important oxygen reduction reaction (ORR) in electro-catalysis in hampered by a large overpotential which restricts its efficiency. Thus it has become clear that these scaling relations have to be broken in order to improve the ORR. As long as a catalytic reaction with multiple steps is governed by one single descriptor such as the oxygen binding energies, the scaling relations remain valid. Hence one has to design improved catalyst that provide more than one descriptor for catalytic processes so that the efficiency and selectivity of the catalytic processes can be tuned. Thus we expect more studies addressing such scaling relations.

On the other hand, there is also a need for a more realistic modeling of catalytic systems in order to bridge the structure gap. In heterogeneous catalysis, this involves the development of proper multi-scale approaches and tools, and some of them were presented at the workshop. Research will continue to go on along these lines. The same is true for electro-catalysis. However, here the proper description of the eletrolyte and the electrode potential is mandatory for a more realistic modeling. Thermodynamic modeling in which the electrochemical environment is only taken into account as a reservoir will continuie to be popular, but they only allow predictions on a qualitative level. Hence further efforts are required to develop a methodology to take the environment reliably into account. This might include implicit models for the electrolyte but their validity still has to be assessed by comparing to studies with explicit solvent models.

Thus this workshop confirmed the high quality of electronic structure studies addressing catalytic systems, but also the issues that require further research efforts were clearly identified.

The final programme of the meeting including the list of participants is provided in the following.

Catalysis from first principles

Heterogeneous catalysis meets electrocatalysis

Cat1P

Workshop
Mai 25-28, 2014
Castle Reisensburg

DFG Research Unit FOR1376

Elementary reaction steps in electrocatalysis:
Theory meets Experiment

cecam
Centre Européen de Calcul Atomique et Moléculaire

European Science Foundation

DFG Deutsche Forschungsgemeinschaft

Program for the workshop

Catalysis from first principles (Cat1P):

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Program

Schedule Sunday, May 25, 2014

14:00 - 18:30	*Arrival and registration*	
18:30 - 20:00	*Dinner*	
20:00 - 20:05	Axel Groß	*Opening remarks*
20:05 - 20:50	Jan Rossmeisl	*Electrocatalysis at the atomic scale*
20:50 - 21:35	R. Jürgen Behm	*Bimetallic electrodes with well-defined nanostructure - preparation and characterization on an atomic scale*

Monday, May 26, 2014

08:00 - 09:00	Breakfast	
09:00 - 12:30	*Heterogeneous catalysis*	
09:00 - 09:45	Thomas Bligaard	*Error estimation in catalytic trend studies*
09:45 - 10:30	Poul Georg Moses	*Industrial aspects of heterogeneous catalysis*
10:30 - 11:00	Coffee break	
11:00 - 11:45	Norina Richter	*Charge-carrier doping effects on concentrations of defects at metal-oxide surfaces*
11:45 - 12:30	Nuria Lopez	*Theoretical modeling of the Deacon and related reactions*
12:30 - 14:30	Lunch	
14:30 - 16:00	*Electrocatalysis*	
14:30 - 15:15	Marc Koper	*Multiple proton-coupled electron transfer in electrocatalysis: theory vs experiment*
15:15 - 16:00	Suljo Linic	*Analysis of the mechanism of electrochemical oxygen reduction and development of Ag- and Pt-alloy catalysts for low temperature fuel cells*
16:00 - 16:30	Coffee break	
16:30 - 17:00	Sung Sakong	*Modeling of electrochemical reactions with cooperating first-principles and implicit solvent method*
17:00 - 18:00		*Short presentation of posters*
18:00 - 20:00	Dinner	
20:00 - 22:00	*Poster Session*	

Tuesday, May 27, 2014

08:00 - 09:00	Breakfast	
09:00 - 11:45	*Heterogeneous catalysis*	
09:00 - 09:45	Dionisios G. Vlachos	*Multiscale ab initio modeling of catalysts*
09:45 - 10:30	Andreas Heyden	*Theoretical investigation of biomass catalysis at the metal-liquid interface*
10:30 - 11:00	Coffee break	
11:00 - 11:45	Aleksandra Vojvodic	*Scaling relations and beyond in catalysis*
11:45 - 18:00	*Electrocatalysis*	
11:45 - 12:30	Jörg Neugebauer	*Pourbaix diagrams and stability in electrochemical environment*
12:30 - 14:30	Lunch	
14:30 - 15:15	Nicola Marzari	*First-principles simulations in realistic electrochemical environments*
15:15 - 16:00	Timo Jacob	*Bimetallic alloys in action: dynamic atomistic motifs for electrochemistry and catalysis*
16:00 - 16:30	Coffee break	
16:30 - 17:15	Zhi-Pan Liu	*First principles electrocatalytic reactions: from Tafel kinetics to automated reaction prediction*
17:15 - 17:45	Harald Oberhofer	*Quantitative computational water splitting: going beyond proton-coupled electron transfer*
17:45 - 18:15	Misbah Sarwar	*Atomistic Modelling – An Industrial Perspective*
18:30 - 21:00	Conference Dinner	
21:00 -	Social Event	

Wednesday, May 28, 2014

08:00 - 09:00	Breakfast	
09:00 - 12:30	*Heterogeneous catalysis*	
09:00 - 09:45	Herman Kuipers	*CSI (Catalytic surface investigation): Why pathology is not always good enough (or: from the morgue to life patients)*
09:45 - 10:30	Jürgen Hafner	*Intermetallic compounds as heterogeneous catalysts - what distinguishes them from disordered alloys ?*
10:30 - 11:00	Coffee break	
11:00 - 11:45	Karoliina Honkala	*Selectivity in organic transformations on Pt and Pd surfaces*
11:45 - 12:30	Andrew Peterson	*Active-site engineering of electrocatalysts: Theory and experiment*
12:30 - 14:00	Lunch	
14:00	Departure	

Abstracts

Sunday, May 25, 20:05

Electrocatalysis at the atomic scale

Jan Rossmeisl

Department of Physics, Technical University of Denmark, Lyngby/Denmark

So far most electrocatalyst has been designed only based on reactivity of the surface. This single parameter is not sufficient to optimize the activity and selectivity. This means that activities and selectivity can only be optimized to a certain point. The activity as function of the surface reactivity is often represented in volcano curves. Electrocatalytic activity and selectivity is ultimately determined by the atomic and electronic structure of the catalyst surface. By controlling the atomic structure of the catalyst surface it is possible provide more parameters besides the reactivity to tune activity and selectivity beyond the normally limits. I will show some examples on atomic scale design of special electrocatalytic sites for oxygen evolution and oxygen reduction for better selectivity and activity.

Sunday, May 25, 20:50

Bimetallic Electrodes with Well-defined Nanostructure - Preparation and Characterization on an Atomic Scale

R. Jürgen Behm

Institute of Surface Chemistry and Catalysis, Ulm University, D-89081 Ulm/Germany

Bimetallic electrodes with well defined nanoscale surface structure have attracted considerable interest in recent years as model systems for a variety of different applications, including, e.g., electrocatalytic reactions in the area of energy conversion.

The considerable progress in this area is mainly due to two different features. First, high resolution scanning tunnelling microscopy (STM) imaging with chemical contrast has been demonstrated to resolve the different metal species in a surface and thus give direct access to the quantity [1,2] and, after appropriate statistical evaluation, to the lateral distribution of the respective surface species [3,4]. Second, modifying the deposition conditions allows us to vary the structural properties of the resulting bimetallic surfaces, specifically the nature and abundance of specific (bi-)metallic nanostructures, in a controlled way and over a wide range. In addition to electrodeposition, this also includes the use of Surface Science techniques for the controlled preparation and characterization of bimetallic electrode surfaces.

The potential of this approach for the controlled preparation of bimetallic electrodes with well defined nanoscale structure and their application in electrocatalytic studies will be demonstrated using recent results obtained in a coupled ultrahigh vacuum electrochemistry system [5,6].

1. M. Schmid, H. Stadler, and P. Varga, Phys. Rev. Lett. 70 (1993) 1441.
2. F. Maroun, F. Ozanam, O.M. Magnussen, and R.J. Behm, Science 293 (2001) 1811.
3. P.T. Wouda, B.E. Nieuwenhuys, M. Schmid, and P. Varga, Surf. Sci. 359 (1996) 17.
4. H. E. Hoster, A. Bergbreiter, P. Erne, T. Hager, H. Rauscher, and R.J. Behm, Phys. Chem. Chem. Phys. 10 (2008) 3812.
5. S. Brimaud, A.K. Engstfeld, O.B. Alves, H.E. Hoster, and R.J. Behm, Topics Catal. 57 (2014) 222.
6. S. Brimaud, A.K. Engstfeld, O.B. Alves, and R.J. Behm, Electroanal. Chem. 716 (2014) 71.

Monday, May 26, 09:00

Error estimation in catalytic trend studies

Thomas Bligaard
SUNCAT Center for Interface Science & Catalysis, SLAC National Accelerator Laboratory,
Menlo Park, CA 94025, USA

A fitting methodology for empirical exchange-correlation functionals is presented. The method reproduces catalysis-relevant benchmark materials and chemical properties reasonably, while allowing for a quantitative error estimation ensemble to be constructed. The uncertainties on different but related materials properties are typically correlated, and the error estimation ensemble reproduces to some extent such correlations, while being flexible enough to calculate uncertainties on any property calculate by density functional theory. Often, density functional theory results are used as input to subsequent layers of modeling. The use of density functional theory calculations to parameterize microkinetic models in catalysis is one such use of compounded models. If the uncertainty ensemble reproduces the correlated errors well, it means that uncertainties on conclusions based on a compounded model can be accurately evaluated by establishing a compounded model for every functional instance in the error ensemble and evaluating the statistical properties of these compounded models. We utilize this general approach for analyzing the electronic structure uncertainty on catalytic rates over a range of transition metal catalysts. In general the estimated error is significantly reduced due to correlations in the error between various intermediates and surfaces, which highlights the need for systematic methods of error estimation. Uncertainties are shown to be a complex function of reaction condition and catalyst material, and we demonstrate that relative rates between different catalysts are better described than the absolute rates.

Monday, May 26, 09:45

Industrial aspects of heterogeneous catalysis

Paul Georg Moses

Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Kgs. Lyngby/Denmark

The topic for this presentation is the production and utilization of methanol and the fundamental challenges in these catalytic reactions.

Methanol is an important bulk chemical that is most efficiently formed over the industrial Cu/ZnO/Alumina catalyst. The identity of the active site and, in particular, the role of ZnO as a promoter for this type of catalyst is still under intense debate. We will present the thermochemistry of methanol synthesis intermediates over ZnO using density functional theory (DFT) and analyze the methanol synthesis reaction network using a steady-state micro-kinetic model. The kinetic model is used to investigate the methanol synthesis rate as a function of temperature and pressure. The results show qualitative agreement with experiment and yield information on the optimal working conditions of ZnO catalysts. We will also present how structural changes of the catalysts system are strongly dependent on the pretreatment method. These results support the idea that the presence of Zn atoms in the surface of Cu particles is important for increasing the activity of the Cu surface of a Cu/ZnO-based methanol synthesis catalyst.

Methanol is a starting compound for the production of hydrocarbons or DME. To effectively design catalysts for these applications an increased understanding of the role of acid strength and the framework structure is needed. We will present investigations of the role of the zeolite structure in methylation reactions and the consequence of acid strength on the methanol to DME conversion.

Monday, May 26, 11:00

Charge-Carrier Doping Effects on Concentrations of Defects at Metal-Oxide Surfaces

Norina A. Richter[1], S. Sicolo[2], S. V. Levchenko[1], J. Sauer[2], and M. Scheffler[1]
[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft
[2] Humboldt Universität zu Berlin

Point defects can greatly influence the properties and functionality of a material. Therefore, understanding mechanisms that govern defect formation is crucial for functional materials design. However, experiments measuring defect charge states and concentrations in thermodynamic equilibrium as a function of temperature, pressure, and doping concentration are very challenging and therefore scarce. On the other hand, previous theoretical approaches have aimed at a description of isolated defects. In particular, large-scale geometry-dependent electrostatic effects of defect-charge compensation have not been considered. Charge state and concentration of point defects are affected by intentional or unintentional doping. Local effects of doping occur due to a local change in electronic and atomic structure around the dopant, while global effects of doping are due to free charge carriers that are introduced with the dopants. Charge-carrier doping determines the Fermi level, and can lead to formation of a space-charge region and band bending at the surface.

In this talk, I address the challenges for *ab initio* modeling of point defects in different charge states at metal-oxide surfaces. As an example, oxygen vacancies (F centers) in MgO are discussed. We achieve realistic modeling of charge-carrier doping in metal oxides using a variant of the virtual-crystal approximation [1]. Defect stabilities are calculated using *ab initio* atomistic thermodynamics in combination with hybrid density-functional theory (DFT). We optimize the parameters of the hybrid exchange-correlation functional according to a condition on DFT ionization energies using the G_0W_0 method, and we validate formation energies for neutral defects by coupled-cluster CCSD(T) calculations for embedded clusters to obtain accurate defect formation energies with reliable error bars.

For a realistic model of interacting defects including the effects of charge-carrier doping, we extend the standard methodology for calculating defect formation energies and concentrations to include the electrostatic free energy due to space-charge transfer between defects and dopants. We find that due to space-charge effects the concentration of oxygen vacancies at the MgO (100) surface is limited to approximately 1% of F^{2+} centers at realistic conditions [2]. Our results show that space-charge transfer could be utilized to control metal-oxide interface properties, including surface-defect concentrations, adsorption energies or work function changes [2, 3].

[1] L. Vegard, Z. Phys., **5**, 17 (1921) ; M. Scheffler, Physica B+C, **146**, 176–186 (1987)
[2] N. A. Richter *et al.*, Phys. Rev. Lett. **111**, 045502 (2013)
[3] Y. Xu *et al.*, Phys. Rev. Lett. **111**, 226802 (2013)

Monday, May 26, 11:45

Theoretical modeling of the Deacon and related reactions

Nuria Lopez

Institute of Chemical Research of Catalonia, ICIQ Av. Paisos Catalans 16, 43007 Tarragona/Spain

Cl_2 use is at the core of many organic chemical transformation where Cl atoms are needed to functionalize intermediates but removed from final products in the form of HCl. The Deacon reaction corresponds to the oxidation of HCl to generate Cl_2 so that it is possible to reuse the HCl generated in the same industrial facility. In the present talk I will show different aspects of the reaction linked to activity and stability but also how theoretical simulations can provide with hints on how to improve the main design factors in the process.

Monday, May 26, 14:30

Multiple proton-coupled electron transfer in electrocatalysis: theory vs experiment

Marc T.M. Koper

Leiden Institute of Chemistry, Leiden University PO Box 9502, 2300 RA Leiden/The Netherlands

This talk will outline a simple but general theoretical analysis for multiple proton-electron transfer reactions, based on the microscopic theory of proton-coupled electron transfer reactions, recent developments in the thermodynamic theory of multi-step electron transfer reactions, and the experimental realization that many multiple proton-coupled electron transfer reactions feature decoupled proton-electron steps in their mechanism. The theory will be discussed in relation to the experimental results for a number of redox reactions that are of importance for sustainable energy conversion, including oxygen reduction and evolution, and the electrocatalytic reduction of CO_2, focusing on their pH dependence and structure sensitivity.

Monday, May 26, 15:15

Analysis of the Mechanism of Electrochemical Oxygen Reduction and Development of Ag- and Pt-alloy Catalysts for Low Temperature Fuel Cells

Suljo Linic

University of Michigan, Dept. Chemical Engineering, Ann Arbor, MI 48109/USA

The oxygen reduction reaction (ORR) is the major source of overpotential loss in low-temperature fuel cells. Expensive, Pt-based materials have been found to be the most effective catalysts, but exploration of alternatives has been hampered by stability constraints at the typical operating conditions of low pH and high potential.

I will discuss how we studied elementary mechanism of ORR on various metal electrodes using kinetic and micro-kinetic analysis of reaction pathways and quantum chemical calculations. These studies allowed us to identify the elementary steps and molecular descriptors that govern the rate of ORR. Using these performance descriptors we have been able to identify families of Pt and Ag-based alloys that exhibit superior ORR performance is acid and base respectively.

We have synthesized these alloys to demonstrate the superior ORR activity with rotating disk electrode experiments. We have also performed thorough structural characterization of the bulk and surface properties with a combination of cyclic voltammetry, x-ray diffraction, and electron microscopy with spatially resolved energy-dispersive x-ray spectroscopy and electron energy loss spectroscopy.

1. A. Holewinski and S. Linic, J. Electrochem. Soc. 159, H864 (2012).

Monday, May 26, 16:30

Modeling of electrochemical reactions with co-operating first-principles and implicit solvent method

Sung Sakong and Axel Groß

Institute of Theoretical Chemistry, Ulm University, 89069 Ulm/Germany

The atomistic description of electro-catalytic reactions requires reacting molecules at the interface between metallic electrode and liquid water under a working electrode potential [1]. However, the electro-chemical systems are practically difficult to be described from first principles, because of the highly computational demand to statistically sample the properties of liquid water. In order to circumvent the difficulty, the water solvent can be implicitly treated, i.e., the water molecules are replaced by a continuous dielectric medium. Then, the system consists of explicit solute described from first principles and implicit solvent described by modified Poisson-Boltzmann equation. As developed by Arias and Hennig [2], when the solvation energy of explicit solute part is defined in terms of solute charge density and electrostatic potential of solvent, the explicit and implicit parts are simultaneously optimized with minimizing the sum of the total energy of the explicit solute and solvation energy of the solute into the implicit solvent.

In order to probe the approach, we discuss the adsorption of simple adsorbates such as H, O and OH at the interface between water and Pt electrode. The liquid water at the interface is simulated by (i) implicit water, (ii) a bilayer of explicit water molecules in vacuum or (iii) a bilayer of explicit water molecules in implicit water. We assume that a bilayer of explicit water molecules in implicit water is the closest description of the interface to liquid water. Practically, in the calculations, we have included an empirical pairwise dispersion correction as suggested by Tkatchenko and Scheffler [3] to improve the adsorption properties of molecules which make non-covalent bondings to the metal substrate. When comparing the adsorption of the simple adsorbates at the three model interfaces, we find that inserting a water bilayer at the interface is less significant as long as implicit water is employed. Furthermore, the influence of implicit water to the electrochemical reactions is tested using the hydroxyl bond breaking of methanol on Pt surface. The calculations in vacuum and in implicit water show that the hydroxyl bond breaking barrier is higher in water by 0.2 eV, that is in excellent agreement with the experimental findings of more probable hydroxyl bond breaking in vacuum [4]. Therefore, we notice that the implicit solvation method is feasible to describe electrochemical systems and reactions.

Finally, we discuss the reaction scenarios based on the energetics of carbon species during the electro-oxidation of methanol on Pt electrode. When the formation enthalpies of reaction intermediates are evaluated in a function of chemical potentials and electrode potential [5], then the relative energies of reaction intermediates are determined according to the reaction conditions. From the formation enthalpies of reaction intermediates, we will discuss possible reaction scenarios according the reaction conditions.

[1] A. Groß et. al., J. Electrochem. Soc. **161**, E3015 (2014).

[2] K. Mathew et. al., J. Chem. Phys. **140**, 084106 (2014).

[3] A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. **102**, 073005 (2009).

[4] K. Franaszczuk et. al., J. Phys. Chem. **96**, 8509 (1992).

[5] J.K. Nørskov et. al., J Phys. Chem. B **108**, 17886 (2004).

Tuesday, May 27, 09:00

Multiscale ab initio modeling of catalysts

Dion Vlachos

Department of Chemical and Biomolecular Engineering, Center for Catalytic Science and Technology, and
Catalysis Center for Energy Innovation, University of Delaware, Newark, DE 19716-3110/USA

In this talk, multiscale simulation will briefly be introduced as an enabling technology that bridges the gap between scales. Understanding the emergent properties of heteroepitaxial catalysts and the in silico prediction of suitable bimetallic catalysts will be elucidated as an application domain. We will demonstrate this methodology for the specific example of ammonia decomposition on single metals and bimetallics. It will be shown that incomplete monolayer bimetallics form an important class of catalytic materials.

Tuesday, May 27, 09:45

Theoretical Investigation of Biomass Catalysis at the Metal-Liquid Interface

Andreas Heyden

Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208/USA

Computational investigations of structural and energetic changes in chemical reactions at metal/-water interfaces pose a unique challenge of properly accounting for the effect of a liquid-phase environment on free energies of reactants, products and transition states while keeping the computational model simple enough to be computationally affordable. Two practical solutions to this challenge are implicit solvation models and a hybrid QM/MM approach. In this talk, I present a novel implicit solvation scheme for metal surfaces and a novel explicit solvation scheme based on QM/MM calculations, classical molecular dynamics simulations, and free-energy perturbation to enable an accurate determination of free-energies of reaction and activation free-energy barriers at periodic metal/water interfaces. Finally, we apply our methodologies to the hydrodeoxygenation of propionic acid over Pd catalysts and reforming of ethylene glycol over Pt surfaces in various solvents

Tuesday, May 27, 11:00

Scaling relations and beyond in catalysis

Aleksandra Vojvodic
SUNCAT Center for Interface Science & Catalysis, SLAC National Accelerator Laboratory,
Menlo Park, CA 94025, USA

One major challenge in theoretical and computational heterogeneous catalysis, electrocatalysis and surface science is to develop models and concepts that are useful in understanding which surface properties that determine the activity and selectivity of a catalyst. More precisely one needs to single out and identify the important and optimal surface parameters that are required for a specific reaction. The first part of the talk will focus on a computational approach based on DFT calculations that can be used for screening of materials. The concept of adsorption scaling and Brønsted-Evans-Polanyi relations that are the cornerstones of this approach will be introduced. Their implications will be discussed using the electrochemical water splitting reaction as an example. The emphasis of the second part of this talk will be on the surface chemistry of transition metal oxides and the need to go beyond scaling relations.

Tuesday, May 27, 11:45

Pourbaix diagrams and stability in electrochemical environment

Mira Todorova and Jörg Neugebauer
Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Str. 1, 40237 Düsseldorf/Germany

Theoretical and modeling concepts in semiconductor defect chemistry and electrochemistry have hugely evolved over the last years and are crucial for their respective fields such as optoelectronics and semiconductor devices or corrosion and battery materials. Despite being based on the same fundamental building blocks - charged defects/ions - the underlying theoretical concepts and communities have little overlap. To bridge the gap we have recently developed a unified approach that is based on a fully grand-canonical description of both ions and electrons and that connects and "translates" the respective concepts [1].

Our method links ab initio calculations quite naturally to experimental observables, such as the pH-scale and the electrode potential, which determine and characterise the state of an electrochemical system. In the first part of the talk it will be shown how employing this approach provides surprising new insight into apparently "old" problems such as water stability, opens new routes to construct electrochemical phase (Pourbaix) diagrams, and gives a handle to an absolute alignment of electrochemical potentials. In the second part the approach will be applied to oxides and we will discuss the impact an electrochemical environment has on the defect chemistry and thermodynamic stability of native bulk point defects.

[1] M. Todorova and J. Neugebauer, Phys. Rev. Applied. 1, 014001 (2014).

Tuesday, May 27, 14:30

First-principles simulations in realistic electrochemical environments

Nicola Marzari

Theory and Simulations of Materials, EPFL, Lausanne/Switzerland

I will present some of our recent methodological developments aimed at performing first-principles simulations in realistic electrochemical environments, starting from a proper description of the solvation medium, an electrolyte, and an applied electrochemical potential in a multi-scale electrostatic framework, and discuss applications ranging from vibrational Stark tuning to the equilibrium shape of platinum nanoparticles under hydrogen under-potential deposition.

Work done in collaboration with O. Andreussi I. Dabo, N. Bonnet, and C. Dupont.

Tuesday, May 27, 15:15

Bimetallic Alloys in Action: Dynamic Atomistic Motifs for Electrochemistry and Catalysis

Jonathan E. Mueller[1], Ludwig A. Kibler[1], Timo Jacob[1,2]
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Much research is being carried out today with the aim of finding better materials and surface structures for a vast array of energy related applications. Multi-component metal surfaces have shown particular promise in this context, and are thus the subject of numerous application-oriented research efforts. In this talk we will highlight unique structural features of bimetallic metal surfaces, which set them apart–as multi-component metal surfaces–from single metal surfaces, and their influence on the surfaces' electrochemical and catalytic properties. Three examples of bimetallic model electrodes/catalysts have been chosen as typical instances of phenomena pertinent to understanding the functionality of bimetallic surfaces under electrochemical conditions: RuPt, NiPt and AuPd. In considering these three model systems, we begin by looking at the role played by average, delocalized electronic properties in RuPt alloys before turning to the role of local structures in NiPt and AuPd alloys. The influence of the catalytic environment on the catalyst's surface structure and composition, leading to a dynamic rather than static catalyst surface, is given special attention, as a vital, but often overlooked, aspect of multi-component transition metal catalysts. We conclude by reflecting on the implications of these phenomena for the rational design for bimetallic and other multi-component metal catalysts and electrodes.

Tuesday, May 27, 16:30

First Principles Electrocatalytic Reactions: From Tafel Kinetics to Automated Reaction Prediction

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Recent years have seen rapid progress in the development of first principles method for simulating electrochemical processes. To investigate the solid-liquid interface structure and the reactions occurring at the interface, we developed periodic continuum solvation model based on modified Poisson-Boltzmann equation [1-5]. The method is integrated with periodic first principles calculations and can be applied in general for reactions at the charged surface in solution, as those occurred under electrochemical [1,5] and photochemical conditions[2,3]. We have utilized this method for calculating both the static properties of the interface, e.g. the potential of zero charge, differential capacitance[5], and the dynamics properties of the reactions at the interface. By combining this method with our recently-developed general-purpose potential energy surface (PES) searching method namely, stochastic surface walking method (SSW) [6-8], we are now able to investigate the dynamic structure reconstruction and explore reactions automatically under electrochemical conditions. Our recent progress to generalize the Tafel kinetics of surface reactions at the metal-water interface will also be presented.

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Tuesday, May 27, 17:15

Quantitative computational water splitting: going beyond proton-coupled electron transfer

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In recent years, quantitative theoretical understanding of the important (photo-)electro-catalytic water oxidation reaction has become possible through thermodynamic approaches, such as the highly successful computational hydrogen electrode method by Nørskov and Rossmeisl [1]. At the heart of this scheme lies – due to physical as well technical considerations – the assumption that every oxidation step proceeds via proton-coupled electron transfer (PCET). Using a version of this approach modified for co-catalyst/catalyst screening [2] we show that this is not necessarily the case. Indeed, regarding only PCET can lead to an underestimation of the viability of certain catalyst/co-catalyst combinations.

In going beyond PCET calculations one needs to be able to compare relative energies of charged surface intermediates, which typically suffer from a vast finite size effect in periodic supercell calculations. To avoid this we im- plemented a number of embedding techniques, both on the side of the surface via solid-state QM/MM [3] and with regards to the solvent effect via implicit solvation techniques, into the all-electron DFT and beyond code FHI-AIMS [4]. To demonstrate our embedding approach we also show first results for defect formation energies on TiO_2 surfaces.

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Wednesday, May 28, 09:00

CSI (Catalytic Surface Investigation): Why pathology is not always good enough (or: from the morgue to life patients)

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Catalysis is not a science, but a technology. However, the productivity of catalysis research in industry can hugely benefit from the predictive value generated by scientific support to catalysis. Particularly in heterogeneous catalysts virtually all parameters related to their performance are averages of some sort, which makes correlations vague and dependent on conditions. Moreover, clean scientific studies frequently make use of moderate conditions, whereas in practical catalysis the reactants have to fight for their adsorption and reaction sites against a multitude of competitors. Mass transport through porous media leads to changes in reactant ratios from the rim to the core of the pellets, which can drastically alter the catalysis. In plug flow reactors reaction products accumulate towards the outlet, whereas reactants are depleted. By the same token the incremental conversion is changing from inlet to outlet, which can have a strong impact on the temperatures through the catalyst bed and even pellet. Last but not least: most catalysis studies are executed during typically hours, seldom days. In practice however the first use of a catalyst may be regarded as the final stage of its preparation. Typical break-in periods range from days to weeks. Still, catalysis research is essential for staying competitive in catalytic processing. A few partial solutions will be summarized.

Wednesday, May 28, 09:45

Intermetallic compounds as selective hydrogenation catalysts: Insights from DFT

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Selectivity is an ubiquitous challenge in the development of improved catalysts. During recent years the product selectivity in the hydrogenation of alkynes to alkenes has received particular attention. The reasons are the industrial importance of the process (for example the semi-hydrogenation of acetylene to ethylene as a step in the production of polyethylene) and the model character of this seemingly rather simple reaction. Pd is known to be a very active catalyst for various hydrogenation and reforming reactions, but its properties must be modified such that the selective hydrogenation of triple bonds is promoted, while the reaction stops at the stage of double bonds. A high selectivity can be achieved if the adsorption energy of ethylene is low enough such that desorption is favored over further hydrogenation. A reduced adsorption strength can be achieved if Pd is mixed with a less reactive simple or noble metal. It turned out, however, that this is not enough. Reaction between co-adsorbed unsaturated hydrocarbons can lead to the formation of undesired side-products by oligomerization. Suppression of oligomerization can be achieved by the isolation of active sites, which also hinders the formation of carbonaceous deposits leading to a de-activation of the catalysts. At high hydrogen to hydrocarbon ratios the reactivity of the catalyst can lead to high concentrations of hydrogen in surface and sub-surface sites and to undesired further hydrogenation, while high partial pressures of hydrocarbons can lead to the formation of sub-surface carbides and an improved selectivity . For bi-metallic catalysts the surface composition can change under different reaction conditions.

Hence the problem with bi-metallic catalysts is that the composition and/or structure of their active surface can change under reaction conditions, affecting both reactivity and selectivity. Hence the challenge is to find a material whose intrinsic catalytic properties match those of Pd-C subsurface alloys, but which can be prepared in a controlled manner and exhibit better stability. Intermetallic compounds formed by transition-metals (TM) such as Pd, Co or Fe with simple metals (SM) such as Ga or Al meet these requirements. They are single-phase materials with an often rather complex crystal structure stabilized by at least partially covalent interactions and hence an electronic structure and chemical reactivity very different from those of the elements forming the compound. Intermetallic compounds of Pd with Ga (GaPd, $GaPd_2$, Ga_3Pd_5,...), but also compounds free of precious metals such as Co_4Al_{13} and Fe_4Al_{13} have been identified as highly stable and selective catalysts for the semi-hydrogenation of acetylene to ethylene.[1]

The main difficulty in developing an atomistic scenario for the reactions catalyzed by intermetallic compounds is the insufficient knowledge of their surface properties which are still largely unexplored. In this contribution we shall review density-functional investigations of the structural and electronic properties of the low-index surfaces of AlPd[2], GaPd[3, 4, 5], $GaPd_2$ and Ga_3Pd_5 (Ref. [6]) and of Co_4Al_13 (Ref. [7]) serving as the basis for the development of a detailed reaction scenario for the hydrogenation of acetylene. The important result of these studies is that the active centers are not the TM atoms (Pd, Co) alone, but consist of small, in most cases triangular clusters of two SM (Al, Ga) and one TM atoms. Acetylene and vinyl (the product of the first reaction step) are strongly di-σ-bonded in a bridging configuration involving at least one SM atom, while ethylene is only weakly π-bonded on top of a TM atom. Selectivity results from a desorption energy of ethylene which is lower than the activation energy for further hydrogenation. The distance between the active centers is large enough to suppress side-reactions such as oligomerization. A sufficiently high surface-concentration of the SM atoms is essential for achieving a high selectivity. The theoretical results are discussed in relation of experimental investigations of the surface properties and of the catalytic reactions. We conclude with an outlook on current studies of intermetallic compounds as catalysts for steam-forming reactions.

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Wednesday, May 28, 11:00

Selectivity in organic transformations on Pt and Pd surfaces

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Propene can be produced via dehydrogenation of propane on Pt-based catalysts; however, the catalysts are plagued by low selectivity toward propene and high coke formation. The selectivity can be improved and the coke formation reduced by alloying Pt with Sn. The alloying is known to weaken the binding of propene, which in part explains the improved performance. We conducted density functional theory calculations to study the dehydrogenation of propene on flat and stepped Pt and Pt_3Sn surfaces. The steps on Pt dehydrogenate propene readily, whereas, on Pt_3Sn, the steps are inert because they are decorated with Sn. Our results indicate that the high selectivity and low coking on the Pt-Sn catalyst can result from a lack of active Pt step sites.

The second example deals with chemoselective hydrogenation of α, β unsaturated aldehydes to corresponding saturated aldehydes and unsaturated alcohols on Pt and Pd surfaces. The chemoselective hydrogenatin to desired unsaturated alcohols is difficult to achieve as the hydrogenation of the C=C bond is thermodynamically preferred over the C=O bond. Previous DFT calculations suggested that the reaction favors the hydrogenation of the C=O bond on Pt but the chemoselectivity is determined by desorption energy difference between the two products finally leading to desorption of unsaturated aldehyde.

Herein, we present the new DFT calculations which directly favor the hydrogenation of the experimentally observed C=C bond selectivity. The results also correlate well with other experimental results and DFT-studies on a silver surface. We suggest a different explanation to chemoselectivity compared to previously published computational results, where activation energy to the formation of unsaturated alcohol is lower and the process if therefore favored. This is based on two findings. First, our calculations show that the lowest transition state to hydrogenate a C=C bond is through the -bonded intermediate and not the di-sigma-bonded one. Second, we found that surface coverage has a major role on the relative heights of activation barriers. Finally, the obtained results present excellent BEP correlations.

Wednesday, May 28, 11:45

Active-site engineering of electrocatalysts: Theory and experiment

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Electronic structure methods have made great strides in understanding and rationalizing catalytic activity in electrochemical applications, such as CO_2 reduction, H_2 evolution, and oxygen evolution/reduction reactions. However, interactions at the level of the active site can have tremendous impacts on the selectivity and efficiency. In this talk, I will give three examples of how we are using an interaction of theoretical calculations and experimental measurements in order to describe how we can use an active-site level description to engineer reactivity. First, I will show how surface reactivities change under the high-coverage conditions encountered in carbon dioxide reduction catalysis, and how this changes the catalyst activity for the hydrogen evolution reaction. We will introduce a new design principle for effective CO_2 reduction catalysts. Second, I will describe how nanostructuring can isolate different types of active sites on gold nanoparticle catalysts, and how we can change particle morphology to enhance certain types of these sites and achieve excellent selectivity. Finally, I will describe collaborations with experts in solid mechanics in which we use mechanically applied strain in order to change the catalytic activity of active sites for the oxygen evolution reaction.

Poster Abstracts

Monday, May 26, 20:00

N_2 formation by pick-up of N-adsorbates off Ag(111): an efficient Eley-Rideal process

Maria Blanco-Rey[1,2], Estibaliz Diaz[2], Gisela Bocan[3], Ricardo Diez Muino[2,4], Maite Alducin[2,4] and J. Inaki Juaristi[1,2,4]

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The performance of a catalyst is largely dictated by its hability to replenish its surface active sites. This fact has motivated a number of studies on gas-surface reactions that result in molecule recombination and desorption. In particular, the fast Eley-Rideal (ER) recombination mechanism has received considerable attention. This reaction takes place when an incoming gas-phase species picks up a surface adsorbate to conform a molecular compound that desorbs afterwards. ER processes on metals were hitherto thought to be a marginal phenomenon restricted to not too energetic light projectiles, such as H and D, where most recombination events proceed through the slower hot-atom (HA) process. Since it is not experimentally possible to distinguish ER from HA, theoretical input is needed in order to understand these recombination process.

Using molecular dynamics and potential energy surfaces (PES) built from ab-initio data, we show that hyperthermal gas-phase N atoms, with kinetic energies in the order of several eV, can pick up N adsorbates off densely covered Ag(111). The angular energy distribution of the resulting desorbed N_2 molecules is in agreement with that of related molecular beam experiments [1], which shows convincingly that such experiments contain the first ever observed fingerprint of N_2 formed by ER recombination [2,3]. More importantly, we find that at least 35% of the incident N will recombine following this mechanism even for incident energies as large as $E_i = 7\,\mathrm{eV}$. This remarkably high efficiency poses a new scenario for the study of gas-surface interactions, where now fast direct pick-up should be seen as a relevant product desorption channel. The high N_2 yield found here is a consequence of the relatively long-ranged attractive and barrierless nature of the N-N interaction PES on the Ag(111) surface.

We have also analysed how the energy released during bond formation is partitioned among the degrees of freedom of the system. We find that most of the available energy, about 7 eV, is stored in the N_2 rovibrational degrees of freedom independently of the Ei value. Only $< 20\%$ of the total available energy is transferred to the surface. The latter term is correlated with the N_2 translational degrees of freedom, but not with the rovibrational ones [4].

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The Electroreduction of Nitric Oxide on Platinum Surfaces from First Principles

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Nitric Oxide reduction is a key intermediate step in a series of environmental and fuel cell reactions. Even though the reduction of nitric oxide (NO) is prevalent in many electrocatalytic processes, the precise mechanistic details are not well understood. Here, we study the electroreduction of NO on single crystal platinum surfaces using density functional theory. At low potentials and coverages, we find NO will reduce to ammonia on both Pt(100) and Pt(111) surfaces. Based on the analysis, we illustrate the 100 surface is the most catalytically active for the breaking of the N-O bond. The results provided shed light on the illusive detailed mechanism of NO reduction on platinum surfaces[1].

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Constant-charge reaction theory for potential-dependent reaction kinetics at solid-liquid interface

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To understand the potential-dependent kinetics of reactions at solid-liquid interface, we derive a constant-charge reaction theory for understanding the coupled charge transfer during the chemical bond making/breaking [1-5].Using the constant-charge theory, the charge transfer coefficient (CTC)can be explicitly calculated based on the first principles calculations without the need to assume the redox behavior of the elementary reactions and thus provide a unique possibility to evaluate and compare the magnitude of CTC for different reactions across different surfaces. By examining a series of interface reactions and comparing the calculated CTC values, we propose simple rules to understand and predict the charge transfer coefficient of three classes of the interface elementary reactions. The role of surface dipole, solvation and molecular adsorption strength on the CTC can now be clarified from first principles calculations.

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Multi-particle interactions and effective dielectric constant in colloidal system

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The spatial distribution of particles in colloidal media in contact with a metallic electrode affects the average dielectric properties of this system and can alter response of the electrode at the interface with the metal. We present a simulation method for the numerical estimate of these distributions as a function of the electrode configuration and loading. In our Monte-Carlo-Poisson simulator, the colloidal system is described with single particle resolution. This characteristic allows for taking into account volume forces and particle-particle interactions usually neglected in the continuum effective medium approximation. In turn, a large number of particles and large systems can be simulated to meet the electrochemical device design needs. In an experimentally verifiable case study, we discuss the role of the multi-particle interactions in high and moderate density regimes. A key point is the features of the electric field at the solid/liquid interface as well as its propagation inside the wet device where the particles in the colloidal solution are free to move. The simulation code coupled with well-designed experiments allows us to validate our models, gaining insight into the microscopic processes occurring at a solid/liquid interface as well as in the electrolyte environment.

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Ab initio prediction of the equilibrium shape of supported Ag nanoparticles on α-Al_2O_3 (0001)

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The epoxidation of ethylene to form ethylene oxide (EO) is one the most important heterogeneous catalytic reactions representing a multibillion dollar worldwide process [1]. Industrially, the traditional catalyst employed for ethylene epoxidation reaction contains silver particles dispersed on alumina. By means of a DFT-based Wulff-Kaichew construction, we provide a fundamental understanding of the Ag nanoparticle shape and composition under applied conditions for the EO production. We predict the growth of three-dimensional nanoparticles on stable α-Al_2O_3 (0001) terminations.ii This result is in agreement with the common description of Ag microcrystals in the form of hemispheres attached to the surface of the -alumina.

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Modelling the delithiation pathway of Li_2FeSiO_4

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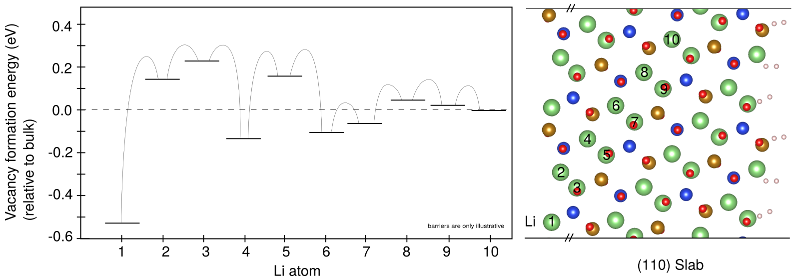
Orthosilicates are promising new cathode materials for Li-ion batteries. We combine ab initio quantum chemical computations with an elastic continuum model to understand the delithiation pathway in the phase separating material Li_2FeSiO_4.

We model the delithiation mechanim as a nucleation and growth process of lattice matched $LiFeSiO_4$ inside a Li_2FeSiO_4 matrix. The approach allows us to determine the effects of strain on nucleation and delithiation which is typically ignored in ab initio modelling of Li ion batteries. We find that in fact strain accommodation is the major driving force for size, shape and energetics of critical nuclei. We derive homogeneous nucleation barriers for different applied voltages and show that heterogeneous nucleation is favorable at {010} and {001} surfaces, unfavorable however at {110}. By comparison with the dominant diffusion direction we can draw conclusions on how the delithiation will proceed after nucleation.

Furthermore we analyse the vacancy diffusion landscape close to the {110} surface by calculating vacancy formation energies. We find that the surface adds an additional barrier of 0.2 eV due to larger vacancy formation energies which reduce to bulk values 8 below the surface (see figure).



From qualitative to atomistic: First-principles kinetic modeling of Pd surface oxide reduction by CO

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Obtaining detailed atomistic insight into oxide formation and reduction at metal surfaces is a key step to understand and ultimately engineer the function of these surfaces in a multitude of applications, not least in oxidation catalysis. On the modeling side, the analysis of kinetic measurements in terms of reaction rate laws is traditionally employed to extract qualitative information. First-principles calculations, on the other hand, describe the microscopic processes underlying the actual phase transition. Firstprinciples microkinetic models offer the prospect to join these two strands and subject atomistic models to scrutiny against measured kinetic data. We illustrate this approach with first-principles kinetic Monte Carlo (1p-kMC) simulations of the reduction of a $(\sqrt{5} \times \sqrt{5})R27^\circ$ surface oxide on Pd(100) in a CO atmosphere, and reference against kinetic data derived from X-ray photoelectron spectroscopy [1]. In full agreement with the experimental rate law analysis our atomistic simulations demonstrate that the reduction process can not occur via a homogeneous decomposition of the oxide phase. We overcome prevalent limitations to lattice-based 1p-kMC through a novel multilattice approach and present a mechanistic model that includes the full transformation from oxide to metal. This model fully rationalizes the measured data and proves that under the investigated gas-phase conditions the reduction is a phase-boundary controlled process.

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Ti in DSA electrodes is an active and selective site for electrochemical production of chlorine

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Dimensionally stable anodes (DSA) are the dominant anode type used for industrial electrolytic production of chlorine and sodium chlorate. DSA electrodes consist of an oxide coating with an overall formula $Ru_{0.3}Ti_{0.7}O_2$ on a Ti substrate. The main advantage of DSA electrodes is their high stability. However, DSA electrodes also have the advantage of increased selectivity for production of chlorine over oxygen, versus that of pure RuO_2 [1, 2]. It has been suggested that the increase in selectivity is due to separation of active Ru sites by inactive Ti-sites [2]. However, the fundamental reason for this improvement in selectivity is still unknown.

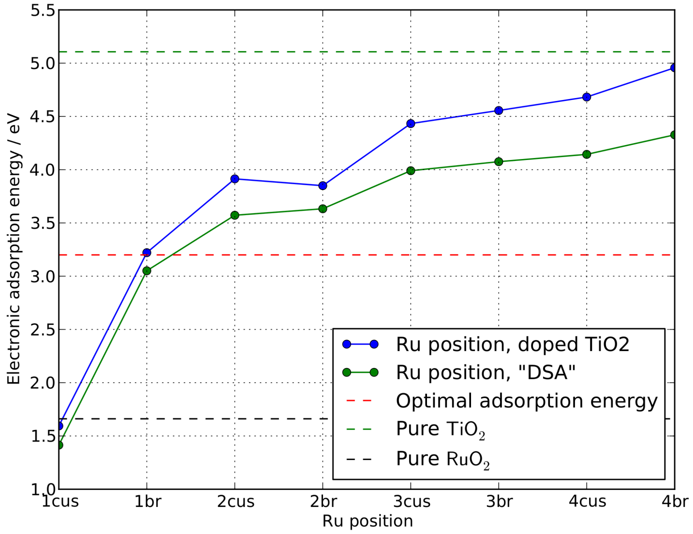

Fig 1: Adsorption energy of O as a function of the Ru position in doped TiO_2 and in DSA.

We have used density functional theory calculations on the GGA and GGA+U levels to study the impact of doping TiO_2 with Ru. Our calculations show that Ti surface atoms in TiO_2 are activated by the presence of nearby Ru dopant atoms (Fig. 1). Similar trends are observed in a DSA model system. A previous model has suggested high Cl_2 selectivity and activity at oxygen binding energies in the intermediate range between TiO_2 and RuO_2 [3]. Ru-doped TiO_2 and the DSA model system show oxygen binding energies near this highly selective and active range, providing a reason for the high selectivity of DSA. Our results suggest that the increase in selectivity is not due to separation of Ti sites, but rather due to an electronic effect resulting in activation of Ti by Ru. We also present calculations for two model electrode coatings which could be prepared to experimentally verify our predictions.

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The mechanism of trichloroethene hydrodehalogenation: a first principles kinetic Monte Carlo study

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Hydrodehalogenation (HDC) reaction of trichloroethene (TCE) has gained a lot of interest due to its possible application in water purification. TCE is a dangerous compound that can cause cancer and liver damage, so its removal from exposure areas such as groundwater is essential [1]. Heterogeneous, especially palladium-based, surface catalysts have proven very effective in this respect[2, 3] but the reaction mechanisms involved have been subject to much controversy. In this work [4], HDC of TCE on Pd(111) was examined by carrying out kinetic Monte Carlo simulations based on DFT-calculated input parameters.[5] Obtained kMC results propose this reaction to follow the so-called direct pathway: after adsorption on the catalyst surface, TCE quickly dechlorinates producing CH-C and then, more slowly, hydrogenates to form hydrocarbon products. An indication towards this mechanism has previously been obtained using DFT methods. The effect of chlorinechlorine repulsions in the surface intermediate compositions and the reaction mechanism was also assessed: surface chlorine atoms that are formed in the course of reaction make further dechlorination steps moderately slower, which results in less effective HDC. This is in line with experimental investigations. References

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An atomistic picture of the PtElectrolyte interfaces: A QM/MM Simulation of the Electrical Double Layer

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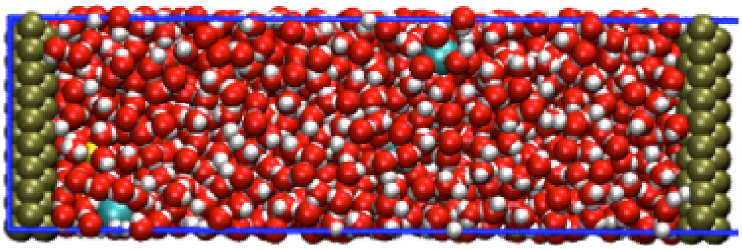
In recent years, there has been increasing interest in electrochemistry. Here, fuel cells have played an important role, triggered, for example, by the desire for ecologically sound and economically efficient use of energy resources. However, electrochemical reactions occur in a multicomponent environment (including, e.g., oxygen, water, and impurities) and under conditions of finite temperature, pressure, and electrode potential, leading to extremely complex systems. In particular, the presence of an electrode potential, which results in the formation of an electric double layer, influences the structure of the electrode/electrolyte interface. All of these factors make experimental and computational studies most challenging.



In this work, we highlight progress toward fundamental understanding of EDL with its historically difficult aspects. It has been already reported that the electrostatic potential is strongly affected by many second order type phenomena such as: surface heterogeneity, (sub)surface transformations, charge transfer reactions, and additional potential jumps at crystal face edges and/or Schottky barriers.

Here, we have analyzed and interpreted the electrostatic potential at crystal/electrolyte interfaces using Hybrid Quantum Mechanical/Molecular Mechanics (QM/MM) simulation technique. The simulations are motivated by the need to reduce ambiguities in EDL model parameterization.

Substrate-induced modifications of the electrocatalytic properties of noble metal monolayer films

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We aim at the investigation of the relationship between the catalytic properties and the modified electronic characteristics of metal monolayers (ML) induced by the metal substrate (i.e. strain and vertical ligand effects).

Experimental observations show that the electrooxidation of a saturating CO adlayer on Pt-ML on Au substrate is initiated at remarkably higher potentials than on shape-selected Pt nanocubes ca. 10 nm size, while this reaction on Pd-ML and 20 nm shape-selected Pd nanocubes occurs at the same potential This result is relatively surprising regarding the similar lattice mismatch (ca. 4%) between Pt and Au and Pd and Au. To elucidate the structure–function relationship, we propose first to determine the electronic properties of adsorbed CO employing a combination of in situ IR spectroscopy and periodic DFT calculations

Bimetallic Alloys in Action: Adsorbate-Induced Surface Segregation and Ensemble Formation in NiPt and AuPd Nanoparticles

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Bimetallic alloys show great promise for applications in a wide range of technologies related to electrochemistry and heterogeneous catalysis. The alloyed nature of these materials supports the existence of surface phenomena and structural motifs not present in single-component materials, which can have a profound influence on their electrochemical and catalytic behaviors. The presence of adsorbates under operational conditions is capable of transforming the surface morphology of alloyed materials at the atomistic level, thereby altering the surfaces electrochemical and catalytic properties. The surface composition and structure of NiPt and AuPd nanoparticles in the presence of adsorbed hydrogen were studied in-situ using X-ray absorption spectroscopic (XAS), and modeled using density functional theory (calculations). A unified interpretation of the extended X-ray absorption fine structure (EXAFS) data and DFT results reveals adsorbate-induced surface segregation in the case of NiPt and adsorbate-induced ensemble formation in the case of AuPd.

Adsorption Process of Water on Pt(111): Ab initio Molecular Dynamic studies

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The interaction of water with surfaces plays a very important role in many different areas, in particular in the field of electrochemistry, but also in corrosion or atmospheric chemistry. Ab initio molecular dynamics (AIMD) simulations of surface adsorption processes have been performed to address the adsorption of water molecules on Pt(111). The AIMD simulations are based on periodic density functional theory calculations within the supercell approach. The RPBE functional [1] within the generalized gradient approximation (GGA) is used in connection with dispersion corrections [2]. As RPBE-D approach reproduces the correct wetting behavior of water on close-packed metal surfaces [3]. Water is relatively weakly interacting with metal substrates, hence the sticking probability is rather low. Special attention is paid to the role of the internal degrees of freedom of the water molecules upon impinging on the Pt substrate, as temporarily kinetic energy from the center-of-mass motion might be transferred into vibrations and rotations thus leading to a more efficient energy dissipation necessary for molecular adsorption [4].

Furthermore, preliminary results of simulations of water molecules impinging on Pt(111) precovered by some water molecules will be presented in order to assess the sticking probability as a function of coverage. On the other hand, water is a prototypical molecule forming networks on surfaces. Thus, also the initial processes of the formation of a water network on metal surfaces shall be identified in the analysis of the AIMD trajectories.

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Ab initio study of Cu(111) chlorination

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In heterogeneous catalysis, 3d metals are often used as catalysts and halocarbons as promoters. After dissociation of adsorbed halocarbonmolecules, all steps of surface transformations for molecule radicals and halogens are needed to understand. In particular, halogens desorption process is rather interesting. For copper as catalyst and for chlorine as promoter, we have contradictory information about desorption process. Conclusion that chlorine desorbs as atoms is made on the base of thermal desorption spectroscopy (TDS) experiments [1] and Density Functional Theory (DFT) calculations [2]. On the other hand, only cooper chloride was detected in thermal desorption spectra for chlorinated Cu(111) and Cu(100) in [3,4]. Taking into account that chlorinated cooper surface is catalyst in 1,2-dichloroethane production as a part of industrial oxychlorination reaction, the resolution of this contradiction is important.

To understand surface processes at the atomic level, we carried out detailed ab initio theoretical study of different steps of Cu(111) chlorination: Cl2 adsorption, Cl and Cu atoms diffusion, surface structure transformations, and thermal desorption of reaction products. All DFT calculations were carried out with Vienna Ab initio Simulation Package (VASP) [5]. Energy barriers are evaluated with Nudged Elastic Band (NEB) method [6]. Range of chlorine coverage on Cu(111) was used from separate atoms to saturated monolayer. In contrast to the previous study [2], we consider Cl atoms not only on perfect Cu(111) surface, but also near defects like Cu adatoms and step edges. All atomic structures were modeled in accordance with experimental STM images obtained in [3]. Several scenarios have been tested. We obtained for all coverage, that CuCl was preferable as desorbing species in which chlorine atom together with cooper atom from the step edge are combined into molecule. The simulation desorption curve demonstrates temperature of 795 K, which is in good agreement with experimental value of 800 K in TDS [3, 4]. As a main result of present work, weve determined both desorption species (CuCl) with temperature of 795 K and initial positions for CuCl desorption at step-edges sites.

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Trends in the adsorption and dissociation of water clusters on flat and stepped metallic surfaces

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The structure and dynamics of water adsorbed at metal surfaces is of central importance in a variety of processes such as catalysis, corrosion and electrochemistry. Whereas water adsorption on flat surfaces was extensively studied in the past, the chemistry of water at stepped surfaces, occuring in realistic situations, is largely unexplored.

By means of density functional theory calculations, we explore the adsorption and dissociation of water clusters on flat and stepped surfaces of several transition metals: Rh, Ir, Pd and Pt. We find that water binds preferentially to the edge of the steps than to terrace sites, so that isolated clusters formed at the step are stabilized by the cooperative effect of chemical bonds with the metal and hydrogen bonding. The enhanced reactivity of metal atoms at the step edge and the cooperative effect of hydrogen bonding enhance the chances of partial dissociation of water clusters on stepped surfaces [1]. For example, water dissociation on Rh and Ir surfaces turns from endothermic at terraces to exothermic at steps. Moreover, the inclusion of zero point energy corrections, which are of the order of 0.1-0.2 eV, can significantly favor the dissociation process, particularly for the stepped Pd and Pt surfaces.

We achieve a detailed interpretation of water dissociation by analyzing changes in the electronic structure of both water and metals, especially focusing on the interaction between the lone-pair electrons of water and the d-band of the metals. The shift in the energetics of water dissociation at steps is expected to play a prominent role in catalysis and fuel cell reactions, as the density of steps at surfaces could be an additional parameter to design more efficient anode materials or catalytic substrates.

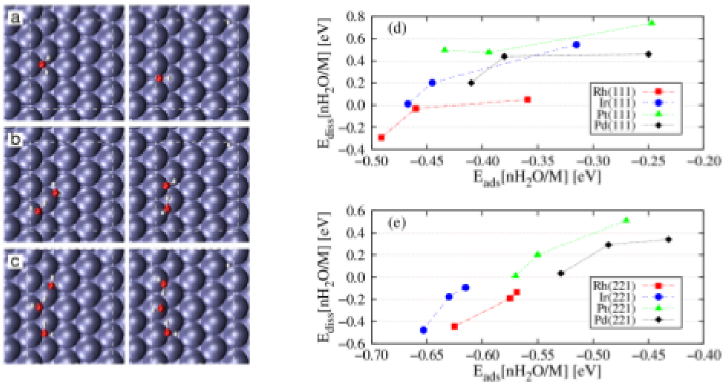

Figure 1: The structure of water clusters at Pt(221) surface: (a) water monomer, (b) dimer and (c) trimer in their intact (left) and dissociated (right) configurations. The adsorption versus dissociation energies of water clusters on (d) (111) and (e) (221) surfaces.

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Towards First-Principles Modeling of Solvent Effects in Photo-Catalytic Water Splitting

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In the context of solar energy conversion the search for new materials for photo-catalytic water splitting has received new impetus. While in general powerful, computational screening approaches are struggling with the complexity of the underlying physical processes at the solid-liquid interface. Recent work points in particular at the necessity to include at least an efficient description of solvent screening effects to compute meaningful descriptors even in simple computational hydrogen electrode approaches. To this end, we present an implementation of the modified Poisson-Boltzmann (MPB) implicit solvation model in the highly parallel and numerically efficient all-electron DFT code FHI-aims. Optimally integrating into this code environment, we solve the MPB equation in a novel approach based on an expansion of the electrostatic potential in the localized basis functions of FHI-aims. In contrast to common numerical multi-grid solvers this approach can directly make use of the optimized integration schemes used to reach self-consistency and removes the need for numerical interpolation between different grids. We demonstrate the approach and its efficiency for a range of molecular test systems, and show first results for catalytic water splitting on gold nano-clusters.

Non-adiabatic vibrational damping of O_2 on Ag(100): Implications for light-enhanced catalysis?

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Motivated by the need for a more efficient and thus responsible use of energy, an age of light-enhanced heterogeneous catalysis is dawning. As for instance Linic *et al.* have convincingly shown on silver nano catalysts, even photons from sunlight can be used to accelerate various oxidation reactions, if their energy is selectively and efficiently transferred into the O–O stretch mode of adsorbed O_2 molecules [1]. However, on metal catalysts resulting athermal mode populations are generally challenged by rapid energy dissipation into the continuum of easily accessible electron-hole pair excitations within the substrate. Assessing corresponding non-adiabatic vibrational lifetimes is hence crucial to answer important key questions as to the feasibility and efficiency of such light-enhanced catalytic reaction steps.

As going beyond the Born-Oppenheimer approximation for the description of metal-adsorbate interactions is still an emerging field of first-principles based modeling, we pursue and further develop two approaches both relying on very different approximations to calculate the non-adiabatically dissipated vibrational energy for O_2 on Ag(100). The first is electronic friction theory within the local density friction approximation (LDFA), which has so far been included in the nuclear dynamics of "real" systems by superimposing its damping effects on independent atoms on immobile surfaces [2]. We introduce a simple and computationally very efficient strategy to take both molecular effects and surface mobility into account. Second, a perturbative approach rooted in time-dependent density functional theory (see Ref [2] and references therein) is extended to obtain electron-hole pair excitation spectra and thus concomitant dissipated energies for the vibrational dynamics of O_2 on Ag(100).

Given the lack of accurate experimental reference data for this system concerning the non-adiabatic vibrational damping, the presented theory-theory comparison allows to estimate the error margin of the theoretical predictions for the vibrational lifetime of O_2 on Ag(100).

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How does a realistic electrode-electrolyte interface behave?

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Understanding solid-liquid interfaces is of great importance in electrocatalysis and electrochemical energy conversion applications. But while the electrode-electrolyte interface has been the subject of countless experimental and theoretical investigations, the details of its structure remains an open subject. In this presentation we outline recent progress made in understanding structures and processes at electrochemical interfaces from first principles calculations using DFT, including ab initio molecular dynamics simulations which describe the interface at more realistic conditions. We have considered the explicit treatment of water at the electrode-electrolyte interface [1,2], looking at water at different contact layer densities, effect of the presence of hydrogen on the electrode, as well as trends in work function changes brought about by charged adatoms on metal surfaces [3-5].

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The Pt(111)/O_2 solid-gas interface: A reactive MD approach

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Introduction

The importance of the Pt(111)/O_2 solid gas interface has been characterized by various surface science studies, which have clarified fundamental aspects related to some of its numerous technological applications, e.g. catalytic converters. The literature is littered with theoretical investigations, which, while ranging over the entire hierarchy of computational modeling methods, are dominated by ab-initio based methods, i.e. mainly DFT, which attempt to address crucial microscopic reaction steps, structural information, etc.

However, the application of ab-initio based methods is still limited to small systems (hundreds of atoms) and short timescales (ps), whereas classical force field methods are able to handle large systems (tens of thousands of atoms) over longer time scales (μs) but are incapable of describing chemical reactions. Reactive force fields (e.g. ReaxFF) are capable of bridging this gap [1].

By applying DFT we obtained electronic and structural information related to elementary reaction steps occurring at the Pt(111)/O_2 interface [2,3]. Based on our DFT studies we developed a ReaxFF parameter set, allowing the calculation of geometries and energies of larger, more realistic systems. Using this force field approach, we investigated elementary phenomena at the Pt(111)/O_2 interface, including the O_2 adsorption, dissociation, the oxygen diffusion and finally the stability of different oxygen overlayers.

Acknowledgement: The research leading to these results has received funding from the European Community's Seventh Framework Programme (FP7/2013-2016) for the Fuel Cell and Hydrogen Joint Technology Initiative under grant agreement CATAPULT n.325268

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Atomistic Modelling – An Industrial Perspective

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The poster will give an overview of how atomistic modelling is being used in industry to understand the structure and activity of catalytic materials and how this understanding can be used to predict new catalysts for a number of applications. Highlights of where DFT has been used to predict new alloys for the cathode of PEM fuel cells based on both activity and stability of the catalyst will be presented along with recent work on understanding metal-support interactions and predicting new candidate support materials. An overview of how QM/MM, monte carlo and molecular dynamics simulations are being used to enhance our understanding of current emissions controls catalysts and to guide the design of new catalysts will be presented. Future direction and challenges for modelling including those associated with different time and length scales will also be discussed.

Minima Hopping Guided Path Search: An Efficient Method for Finding Complex Chemical Reaction Pathways

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The Minima Hopping global optimization method uses physically realizable molecular dynamics moves in combination with an energy feedback that guarantees the escape from any potential energy funnel. For the purpose of finding reactions paths, we argue that Minima Hopping is particularly suitable as a guide through the potential energy landscape and as a generator for pairs of minima that can be used as input structures for methods capable of finding transition states between two minima. For Lennard-Jones benchmark systems we compared this Minima Hopping guided path search method to a known approach for the exploration of potential energy landscapes that is based on deterministic mode-following. Although we used a stabilized mode-following technique that reliably allows to follow distinct directions when escaping from a local minimum, we observed that Minima Hopping guided path search is far superior in finding lowest-barrier reaction paths. We therefore suggest that Minima Hopping guided path search can be used as a simple and efficient way to identify energetically low-lying chemical reaction pathways. Finally we applied the Minima Hopping guided path search approach to 75-atom and 102-atom Lennard Jones systems. For the 75-atom system we found paths whose highest energies are significantly lower than the highest energy along the previously published lowest-barrier path. Furthermore, many of these paths contain a smaller number of intermediate transition states than the previously publish lowest-barrier path. In case of the 102-atom system Minima Hopping guided path search found a previously unknown and energetically low-lying funnel.

Towards an implicit solvent model for photoelectrochemical processes

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Photoelectrochemical systems are widely explored to drive energy-relevant redox reactions like water splitting or CO_2 reduction. The detailed analysis of the involved elementary processes via first-principles calculations is challenged by the necessity to simultaneously account for the extended semiconductor photocatalyst and the liquid electrolyte.

Going beyond the traditionally employed proton-coupled electron transfer mechanism we are furthermore faced with charged intermediate states stabilized by the polar liquid environment. This necessitates a method which captures electrostatic solvent effects whilst being computationally inexpensive in order to allow for an efficient catalyst screening.

To this end, we implemented an implicit solvation scheme based on the Multipole Expansion (MPE) method [1] in the DFT package FHI-aims. Within this approach we de

ne the solvent cavity as an iso-density surface which we represent as a collection of points sampled with an efficient restraint dynamics scheme. Finally, we also show early test results of the implicit solvent model.

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First-Principles Kinetic Monte Carlo Simulation of the Deacon Process on RuO_2(110)

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HCl is a major byproduct in most chemical industries, which can be recycled back to high purity Cl_2 through a sustainable catalytic oxidation reaction called Deacon process [1]. A RuO_2 catalyst has shown a remarkable activity for this process. However, the very limited availability of the precious metal Ruthenium makes the latter very expensive. It is therefore of crucial industrial demand to substitute that Ru-based catalyst by an alternative of comparable activity and stability.

The rather "severe" experimental conditions under which the catalytic oxidation of HCl occurs call for in-depth insights into the reaction mechanism in order to optimize the catalyst performance over a wide range of operational conditions. Available macrokinetic mean-field models [2] are fitted to a small range of experimental data, thus providing only limited predictive quality for the former. In the present work, however, the reaction mechanism is studied microscopically by looking at different elementary steps on RuO_2(110) catalyst surface. First, for each such step, the concomitant energy barriers are obtained from density-functional theory (DFT) calculations. Afterwards, they are incorporated into a kinetic Monte Carlo (kMC) scheme in order to determine turn-over frequencies from first principles. First results of our kMC+DFT model will be critically discussed and compared to the available macro- [2] and microkinetic models [3].

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Modelling Heterogeneous Electrocatalytic CO_2 Valorization

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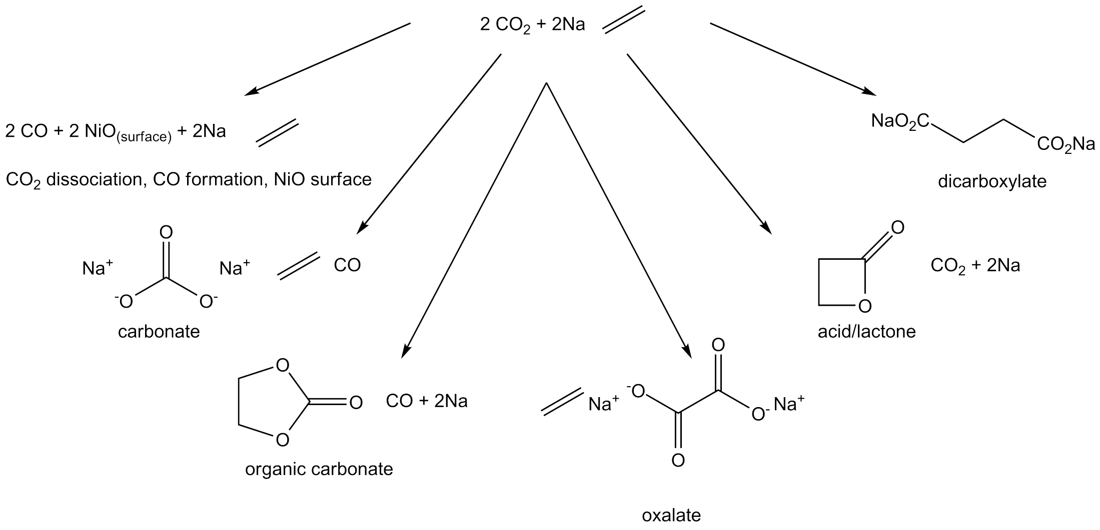
Increasing levels of greenhouse gases and dwindling fossil resources emphasize the need for sustainable chemical synthesis. Conceptually, CO_2 valorization, i.e., the conversion of CO_2 into valuable chemicals, is highly attractive, since it closes the carbon cycle which human activity has put out of balance. Due to its very nature as the energy depleted carbon "sink", CO_2 has a very low reactivity. Electrocatalysis offers the most attractive means to activate CO_2 through reduction: the electron is the "cleanest" reducing agent whose energy can be tuned to the thermodynamic optimum. In practice, a catalyst is required and the overpotentials need to be minimized. Computational investigations of the reaction mechanism of such electrocatalytic reactions are the first step towards rational (in silico) catalyst design. Despite recent progress in modelling electrocatalytic reactions, determining the actual mechanism and selectivities between competing reaction pathways is still not straight forward. In this contribution we will present prototypical results for the coupling of CO_2 to alkenes assessed with three well established models for accounting for the electrochemical conditions: The computational (hydrogen) electrode method of Norskov and coworkers,[1] the Filhol-Neurock approach[2] where a uniform background countercharge is introduced to access formally charged periodic unit-cells and the effective screening model (ESM) of Otani and coworkers[3] where the countercharge is introduced as a surface charge of an implicit counterelectrode. Assumptions and shortcomings leading to contrasting results of these models will be illustrated by their application to a complex reaction network. Furthermore, we will discuss the perspectives to include solvent effects for these complex reactions.



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Exploring PretreatmentMorphology Relationships: Ab Initio Wulff Construction for RuO_2 Nanoparticles under Oxidizing Conditions

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We present a density-functional theory based Wulff construction of the equilibrium shape of RuO_2 particles in an oxygen environment. The obtained intricate variations of the crystal habit with the oxygen chemical potential allow for a detailed discussion of the dependence on the oxidizing pretreatment observed in recent powder catalyst studies. The analysis specifically indicates an incomplete particle shape equilibration in previously employed low temperature calcination. Equilibrated particles could be active CO oxidation catalysts with long-term stability in oxidizing feed and then represent an interesting alternative to the previously suggested core-shell concept.

Global Structure Optimization and New Design of Nanoparticles for Electrocatalytic Oxygen Reduction

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Electrocatalytic oxygen reduction reaction (ORR) on nanoparticles has attracted much attention in recent years for its significance in fuel cell applications [1-2]. It is important to pinpoint the active site at the atomic level and thus guide the design of new catalyst [3]. A major concern is that the structure of the catalyst is not invariant but may change under reaction conditions. Fundamental understandings on the structure versatility and their catalytic consequence are much needed towards unveiling the catalytic mechanism under realistic reaction conditions. Here new strategies to design better Pt nanocatalyst are proposed based on theoretical simulation. We combine the recently-developed stochastic surface walking (SSW) global optimization method [4-5] with first principles method to sample the potential energy surface (PES) of Pt particles supported on carbon nanotube. The periodic continuum solvation model based on modified-Poisson-Boltzmann (CM-MPB) electrostatics [6] is used to analyzed the ORR activity on a set of differently-sized Pt nanoparticles in order to identify the optimum particles for better designed catalyst. We show that the PES of metal particles varies significantly under different environment: not only the strength of the metal-support interaction but also the shape of the interacting field is critical to the PES. We propose a type of new nanocatalyst for electrocatalytic oxygen reduction: the new catalyst has the inert metal Au as the frame for the Pt nanoparticle and the exposed Pt{111} sites are the active site for oxygen reduction. Such an architecture can not only prevent the initial O corrosion at the edge sites but also significantly improve the activity.

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Probing the potential energy surface for the proton equilibrium on gold

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One major challenge for the investigation of the proton transfer from aqueous solution to a metal electrode lies in the correct description of the charged species, since a free proton cannot exist in water. Instead, complexes such as the Hydronium, Eigen or Zundel ions are formed. An adequate description of the structure and interconversion between these species and the subsequent discharge (i. e. proton transfer to the surface) can be reached through reactive force fields such as an empirical valence bond model [1].

In this work we determine the necessary set-up for an adequate description of the potential energy surface of the proton transfer from a Hydronium ion (H3O+) to gold (111) surface where we use a simplified model which excludes any additional solvent. We probe the potential energy surface using the ab initio program VASP [2]. We discuss not only total energies but also structural properties, possible discharge pathways and other features of the potential energy surface.

This work is part of the Cluster of Excellence Ruhr Explores Solvation (RESOLV) (EXC 1069) funded by the Deutsche Forschungsgemeinschaft.

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Carbide core-shells: Platinum-carbide catalysts for fuel cell applications

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Industrial applications in fuel cells still look to Platinum as the optimal catalytic material. However, to achieve the required activity a high Pt loading is employed which often leads to Pt agglomeration resulting in a loss of mass activity and additional and unnecessary expensive Pt use. Core-shell particles, where an atomically thin layer of platinum encases a less expensive material provide a possible solution to this problem. The resultant catalyst would have a significantly lower Pt loading whilst maintaining the high catalytic availability of the Pt [1]. The current work seeks to identify promising carbide core materials (CCM) for further experimental evaluation in collaboration with the Johnson Matthey Technology Centre, Reading, UK.

Having modelled Pt over layer adsorption on a variety of carbides, the geometric lattice mismatch between carbide and Pt were then analysed and the alteration of the electronic structure through the Pt over layer examined. Whilst the presence of the carbides result in expanded Pt lattice parameters, the d-band centres of the first Pt monolayers display the ligand effect of bonding interactions with the core which are dependent on the metal present there [2].

The activity and stability of the Pt over layers are key to the success of the proposed core-shell systems. The effect of the carbides on reagent adsorption to the Pt over layer is under investigation and alteration of oxygen and hydroxide binding energies with regard to pure Pt has been observed. Initial results suggest that the Pt activity towards ORR could be enhanced with the use of carbide cores. Having considered the d-band model [3] as a possible description for the Pt behaviour, we are beginning to investigate the effect of the CCMs in terms of surface resonances [4].

On carbide surfaces which are not wetted by the Pt, metallic tie layers have been inserted with the aim of identifying materials which will subsequently allow for good Pt coverage of all facets of the carbide nanoparticles. Via calculation of segregation energies, some transition metals appear to be able to provide a stable basis for further Pt wetting. However, work on the possibility of alloying these surfaces and their stability in the presence of reagent molecules is ongoing.

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Water@surface: Vibrational signature of water molecules in asymmetric hydrogen bonding environments.

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The O-H stretching vibrational modes of water molecules are sensitive to their local environments. Here, we combine the strength of DFT-based MD, effective normal modes analysis (ENM) and novel energy decomposition analysis (ALMO-EDA) to investigate the hydrogen bonding network in liquid water and aqueous interface. As the first step, we revealed the interwined correlation between the instantaneous hydrogen bonding asymmetry [1] and frequency separation of O-H stretching modes in vibrational spectra [2]. This finding is generally applicable for any reasonably accurate model of water and useful for interpreting experimental Raman, infrared and sum-frequency generation (SFG) spectra of interfacial water molecules.

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The CO recombination reaction in the steam methane reforming by Pt catalysts

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Steam methane reforming (SMR) process is investigated by quantum-chemical DFT calculations for planar and stepped Pt surfaces with three different pathways towards CO formation from adsorbed CH and O. The conventional pathway with CH bond breaking first is in competition with the pathway involving a formyl (CHO) species. Pre-adsorption of oxygen plays an important part in CO formation [1] and H2O dissociation [2]. The O generating from OH bond splitting is very difficult on all planar and stepped Pt surfaces and the low O surface coverage leaves little probability for CH react with O. The main difference between Rh and Pt is the difficulty for water dissociation which can supply oxygen in the system, also which makes Rh a better catalysis in SMR. We also present the results of micro-kinetic simulations based on the previously reported activation energies and reaction energies of the elementary reactions that form the overall catalytic cycle.

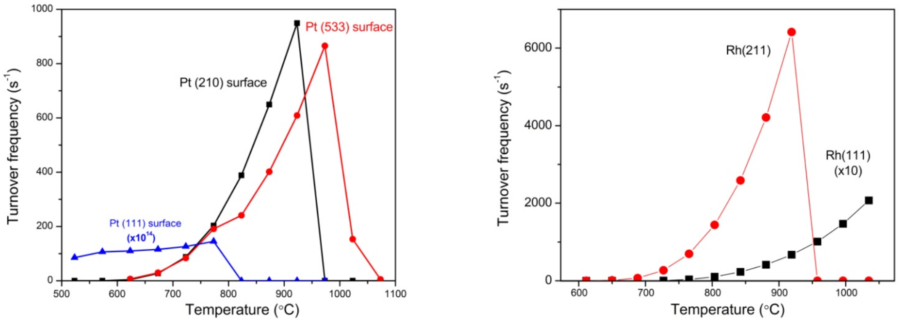

Figure1. Turnover frequency (in s^{-1}) of steam methane reforming on the Pt and Rh surfaces as a function of temperature (in K).

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