Report on Cat1P: The Psi-k/CECAM research conference – Catalysis from 1st Principles

Place:

Magleås Conference Center, Denmark

Date:

May 22-26, 2011

Sponsors:

Psi-k, CECAM, CAMD – Technical University of Denmark

Scientific Organizers:

Thomas Bligaard, Technical University of Denmark
Karsten Reuter, Technical University Munich
Jürgen Hafner, University of Vienna
Matthias Scheffler, Fritz-Haber-Institute, Berlin
Jens K. Nørskov, Stanford University

Administrative Organizer:

Marianne Ærsøe, Head of Administration
Center for Atomic-scale Materials Design, Department of Physics, Technical University of Denmark

Web-page:

http://www.cecam.org/workshop-0-569.html

In brief:

The Psi-k and CECAM joint research conference: “Catalysis from 1st Principles” was held May 22-26, 2011 at the Magleås Conference Center in Northern Sjælland in Denmark. Thanks to the 53 participants the conference there was a lively discussion at the conference, which primarily focused on the topics relating to challenges for the design of catalytic materials by first principles simulations. The conference was the 7th in the “Cat1P - Catalysis from first Principles” series that have been arranged by Matthias Scheffler, Jürgen Hafner, Jens Nørskov and colleagues. The meeting thus followed workshops in Magleås, Denmark (1999 and 2004), CECAM Lyon (2000 and 2006), and Vienna (2002 and 2009). It was also inspired by the series of 1998, 2007, and 2009 Psi-k workshops entitled “Theory meets industry” which were organized by Jürgen Hafner and colleagues. This conference was held as a European Gordon-type conference in an isolated site with natural surroundings with exclusively posters and invited talks, afternoons off, and a relatively long time scheduled for discussions around each talk.

Motivation:

Quantum theoretical calculations of extended atomic- scale systems have reached a level of speed and accuracy that allows determining many interesting materials properties directly from simulations. This gives unprecedented possibilities for addressing materials design problems from a bottom-up approach, where theoretical simulations and concepts derived from such simulations are used directly to propose new materials for subsequent experimental synthesis and testing. Solid surfaces are used extensively as catalysts in the chemical and energy industry and the development of new approaches to discovering catalysts with high efficiency, activity, stability, and selectivity are essential.

Objectives and scientific report:

The aim of the meeting was be to bring together researchers who characterize and design technical catalysts in industry, with experimental catalysis researchers, researchers who carry out computer simulations on catalytic materials and reactions, theoreticians who develop methodology enabling larger and more accurate electronic structure calculations on more complex materials and molecules, method developers who are working on the development of methods for more accurate thermodynamic and kinetics sampling, and researchers working on more general aspects of atomic-scale materials design. In this forum the challenges for the design of novel catalytic materials were to be discussed.

The main objectives of the 2011 meeting were: (i) to review and discuss the current status of and future prospects for applying *ab initio* and statistical mechanics approaches to the study of chemical processes at solid surfaces; (ii) to discuss how calculational methods are now being used as a tool for the design of new materials in general and of heterogeneous and electrochemical catalysts in particular; (iii) to discuss recent applications and future prospects of using such approaches to understand interfaces of electrochemical and environmental importance; (iv) to discuss the possibilities for improving the present state of the art towards better describing complex compounds such as oxides and van der Waals-bonded systems; (v) to identify and analyze main obstacles for the atomic-scale simulations to be utilized more broadly as a platform for developing new catalytic materials; (vi) to inspire leading experimental researchers towards identifying which types of future experiments that could be central for synergy with the computational community in order to extend the limited existing methods for computational catalyst screening into the regime of more complex materials and compounds. All these issues were carefully addressed. Especially the roles of the atomic-scale structure at interfacial boundaries and the realistic simulation treatment of reaction conditions and their influence of structure were discussed in detail.

Programme

Sunday 22nd
Check-in possible from 16:00
18:00-19:30 Dinner
Evening session, Chair: T. Bligaard
19:30-20:20 J.K. Nørskov
20:20-21:10 A. Michaelides

Monday 23rd
7:40-8:40 Breakfast
Morning session, Chair: A. Michaelides
8:40-9:30 A. Schäfer
9:30-10:20 P. Sautet
10:20-10:50 Coffee
10:50-11:40 M. Amft
11:40-12:30 T. Ziegler
12:30-13:30 Lunch
13:30-16:00 Free time
16:00-18:00 Poster Session
18:00-19:30 Dinner
Evening session, Chair: P. Sautet
19:30-20:20 S. Piccinin
20:20-21:10 J. Rossmeisl

Tuesday 24th
7:40-8:40 Breakfast
Morning session, Chair: J. Rossmeisl
8:40-9:30 P. Raybaud
9:30-10:20 F. Mittendorfer
10:20-10:50 Coffee
10:50-11:40 N. Lopez
11:40-12:30 K.W. Jacobsen
12:30-13:30 Lunch
13:30-16:20 Free time
Afternoon session, Chair: A. Schäfer
16:20-17:10 R. Schomäcker
17:10-18:00 V. Ganduglia-Pirovano
18:00-19:30 Dinner
Evening session, Chair: P. Sautet
19:30-20:20 G. Pacchioni
20:20-21:10 M. Salmeron

Wednesday 25th

7:40-8:40	Breakfast

Morning session, Chair: F. Mittendorfer

8:40-9:30	K. Reuter
9:30-10:20	S. Dahl
10:20-10:50	Coffee
10:50-11:40	T. Bucko
11:40-12:30	M. Maestri
12:30-13:30	Lunch
13:30-16:20	Free time

Afternoon session, Chair: V. Ganduglia-Pirovano

16:20-17:10	S. Levchenko
17:10-18:00	B. Temel
18:00-19:30	Dinner

Evening session, Chair: N. Lopez

19:30-20:20	R. Horn
20:20-21:10	C. Dellago

Thursday 26th

Before 9:00	Check-out of rooms before 9:00
7:40-8:40	Breakfast

Early morning session, Chair: K. Reuter

8:40-9:30	E. Beret
9:30-10:20	B. Hammer
10:20-10:50	Coffee

Late morning session, Chair: T. Bucko

10:50-11:40	G. Jones
11:40-12:30	F. Abild-Pedersen
12:30-13:30	Lunch

Abstracts

Invited Talks

Some recent progress on understanding water solid interfaces

Angelos Michaelides

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Water covers almost all solid surfaces under ambient conditions. As such, interfacial water is of crucial importance to an endless list of problems in the physical and chemical sciences. We have been working to understand the molecular level details that control the structure and dynamics of water at interfaces. In this talk I will discuss our recent (first principles) computer simulation results that provide insight in to the structure of supported ice nanoparticles, including the so-called “smallest piece of ice” (Nature Mater. 6, 597 (2007)), a novel one-dimensional ice structure built from pentagons (Nature Mater. 8, 427 (2009)), and an ice-like wetting layer *stabilized* by Bjerrum defects (Phys. Rev. Lett 106, 046103 (2010)). I will also show how surprisingly strong quantum nuclear effects can lead to hydrogen bond symmetrisation in certain ice overlayers on metal surfaces (Phys. Rev. Lett. 104, 066102 (2010)) and discuss the role of van der Waals dispersion forces in stabilizing such systems (Phys. Rev. Lett. 106, 026102 (2011)). Time permitting the role of quantum nuclear effects on altering hydrogen bond lengths and strengths will also be discussed (PNAS 106, 6369 (2011)).

This work has been carried out in collaboration mainly with Javier Carrasco, Xin-Zheng Li, Jiri Klimes, Brent Walker, Karina Morgenstern, and Andrew Hodgson and is supported by the European Research Council (ERC), the EPSRC, and the EURYI scheme.

Modeling of homogeneously catalysed reactions with quantum chemical methods

Dr. Ansgar Schäfer
Principal Scientist, Scientific Computing / Quantum Chemistry

Quantum chemical methods are meanwhile an established tool to support the industrial development of homogeneous transition metal catalyst. Using the example of the Rh-catalyzed hydroformylation of olefins, the presentation will show the methods and procedures used to investigate the catalytic mechanisms in detail. Special attention is given to the accuracy of the DFT methods for the reliable determination of rate determining steps and the estimation of the overall selectivity. The need for accurate ab initio methods as a reference is emphasized

Catalytic surfaces and particles under pressure: a view from DFT

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A fundamental approach of catalytic elementary steps at the atomic scale requires understanding both the nature of the catalyst's active site and the reaction pathways for the molecular reactants. The nature of the surface of a solid catalyst is not unique but can be modified by the reactants: molecular decomposition can produce new phases in the near surface region, hence changing the catalytic properties in situ. First-principle calculations, in combination with in situ XPS measurements, show important insights on these surface transformations. The first example will be a Pd surface where a new Pd-C surface phase is formed under a pressure of acetylene, with strong implications on the reactivity of the catalyst [1]. Calculations provide trends among transition metal catalysts for the formation of a surface carbide from a range of reaction conditions involving hydrocarbon molecules or carbon monoxide [2]. Pd, Ni and Fe are found to be most prone to carbon penetration in the subsurface and unsaturated reactants such as acetylene and carbon monoxide are the best sources of carbon. This formation of a surface carbide phase has important implications for a large range of catalytic reactions, including selective hydrogenation and Fischer-Tropsch synthesis. This will be presented on the case of a Fe catalyst, studied in combination with XAFS and XRD [3,4].
The second considered reactant will be hydrogen. We will show how a small Pt_{13} particle deposited on γ-alumina is covered by hydrogen and how its structure is affected under a given gas pressure. High coverage is found, even at low pressure, and the particle is restructured from a bilayer in vacuum to a cuboctahedron shape under H_2 with the formation of a surface hydride species [5]

References:

1) D. Teschner, Z. Révay, J Borsodi, M. Hävecker, A. Knop-Gericke, R. Schlögl, D. Milroy, S. David Jackson, D. Torres, P. Sautet, Angew. Chem. Int. Ed. 47, 9274 (2008)
2) P. Sautet, F. Cinquini, Chem. Cat. Chem. 2, 636 (2010)
3) E. de Smit, F. Cinquini, A. M. Beale, O. V. Safonova, W. van Beek, P. Sautet and B. M. Weckhuysen, J. Am. Chem. Soc. 132, 14928 (2010)
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5) C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet and P. Raybaud, ChemCatChem 3, 200-207 (2011)

Small supported gold clusters: adsorption, clustering, and catalytic characteristics

Martin Amft

We studied the adsorption and initial clustering of Au1-4 on graphene by means of ab-initio density functional theory and compare these findings to Au1-4/MgO(100) [1].
In order to explain the experimentally found catalytic characteristics of Au1-4/MgO(100) we performed a comprehensive DFT study of these systems and their ability to (co-)adsorb CO and O2 molecules [2]. We specifically address the influence of spin-orbit coupling on the adsorption behaviors.
Experimentally Au1,2/MgO were found to be inactive under a mixed atmosphere [3]. We show that O2 strongly binds to Au1/MgO and prevents coadsorption. Although a catalytic reaction cycle towards CO oxidation, analogous to the gas phase reaction involving the anionic gold dimer, is energetically possible for Au2/MgO, the cluster will get blocked by a strongly bound CO.
On the other hand, the small catalytic activity of Au3,4/MgO could be explained by their ability to coadsorb CO and O2, hence indicating the occurrence of a Langmuir-Hinshelwood-type reaction mechanism for these clusters.
Finally, we also discuss the synergetic effect of co-adsorbed water molecules on the CO/O2 adsorption and an alternative, H2O mediated, CO oxidation pathway [4], as first suggested for Au8/MgO [5].

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DFT study of electrochemical reactions on the anode-electrolyte interface of solid oxide fuel cells (SOFCs).

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Introduction

Solid oxide fuel cells (SOFCs) are viewed as potential replacements to conventional power sources due to the efficiency of energy production, flexibility of the type of fuel used and low degree of pollutant emission. At heart of SOFC operation is the electrochemical oxidation of fuel molecules (H_2, CH_4, CO) in the anode compartment of a cell, which leads to a transfer of electronic charge from the electrolyte (usually yttria-stabilized zirconia, YSZ) to the metallic part of the anode (Ni). It is well established that electrochemical oxidation of fuel occurs in close vicinity to the interface area, where metal (Ni) and oxide (YSZ) meet (the so called triple phase boundary (TPB)). Although interaction of fuel molecules with both Ni and YSZ surfaces have been investigated in the past, the knowledge on fuel oxidation in the TPB is still lacking. In this work we present our recent results of the study of H_2, CH_4 and CO oxidation on the Ni/YSZ interface based on DFT.

Materials and Methods

All calculations have been performed using the VASP package, which makes it possible to carry out periodic DFT calculations using the plane-wave basis set [1,2]. The spin-polarized approximation has been applied throughout. To describe nuclear-electron interaction, the projector-augmented wave (PAW) method has been employed[3]. To monitor the charges on atoms we relied on the Bader's Atoms in Molecules approach, recently interfaced with the VASP code [4].

Results and Discussion

The model of Ni/YSZ cermet has been constructed and optimized using DFT calculations (Figure 1). We demonstrated that the YSZ surface of the cermet is inert for direct fuel adsorption even in the case of oxygen enriched YSZ, which is known to be more active for fuel oxidation than stoichiometric oxide [5-7]. By contrast oxidation of fuel molecules on the Ni surface of the cermet is possible with thermodynamic pathways of the respective reactions very similar to those on pure Ni surface. The transfer of oxygen atoms to the Ni surface from YSZ (spillover reaction) is only possible from the oxygen enriched YSZ, whereas the high thermodynamic barriers for oxygen spillover from the stoichiometric YSZ rules out the possibility of such a reaction. Similarly hydrogen spillover to oxygen enriched YSZ is possible (with subsequent formation and desorption of water molecule), whereas formation of water on stoichiometric YSZ via hydrogen spillover is much less energetically favorable. Our study also revealed that fuel oxidation, which always results in oxygen removal from YSZ leads to a charge transfer from YSZ to Ni, which accounts for generation of electric current in a SOFC. We shall also discuss the use of other electrolytes than YSZ such as CeO2 [8-9] and CeZrO2.

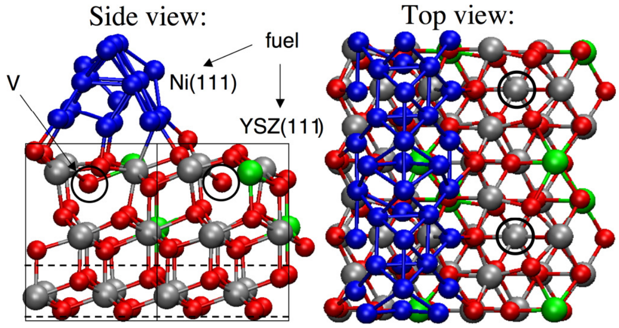

Figure 1. The proposed model of Ni/YSZ cermet (side- and top-view).

Significance

This work has demonstrated that fuel oxidation in the anode TPB results in a charge transfer from YSZ to Ni. We have shown that fuel molecules can adsorb on the Ni surface of the cermet, whereas direct oxidation on YSZ surface is energetically prohibitive. It is also demonstrated that there exists an alternative path for fuel oxidation via the spillover of hydrogen atoms from Ni to YSZ surface with subsequent water formation. Finally our work provides the database of kinetic barriers of elementary reaction steps, which can be used in kinetic modeling of fuel cell operation (Tafel plots, polarization resistance as function of partial pressure, etc.) for optimization of SOFC performance

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Ab-initio modelling of Ru-based homogeneous catalysts for water oxidation

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Splitting water to produce molecular oxygen and hydrogen is a promising way to convert and store solar energy in the form of chemical fuels [1]. Efficient catalysts are needed to promote this electrochemical reaction, which, especially on the oxidation side, is extremely challenging, requiring the loss of four electrons and four protons and the creation of the O-O bond. For this semi-reaction several catalysts have been proposed in the past three decades, both heterogeneous (metals and metal oxide surfaces) and homogeneous (transition metals with organic ligands). Here we present the results of our first-principles Density Functional Theory calculations on the reaction mechanism promoted by an all-inorganic tetraruthenium-polyoxometalate homogeneous catalyst, able to efficiently oxidize water at a low overpotential (~ 0.35 V) [2,3]. We show how state-of-the-art theoretical methods help to shed light on the complex mechanism of this reaction. In particular, we combine hybrid functional calculations for the energetics of the intermediates and metadynamics to explore the free energy surface in the space of a few collective variables. We find that the mechanism proposed in the literature for this system needs to be critically re-examined and we propose an alternative reaction pathway.

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Electro-catalysis for energy conversion

Jan Rosmeisl, DTU

For energy conversion the oxygen reduction and oxygen evolution reactions are of extreme interest. For both reactions a huge over potential is needed to obtain a reasonable current, and in both cases this is mainly due to sluggish catalysis. I study the reasons for the over potential on the basis of density functional simulations

First-principles insights on bulk and surface properties of catalytic materials for renewable energies

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The environmental context prompts the chemical community to develop innovative approaches for improving the control of catalytic reactions in order to produce cleaner and renewable fuels. For that purpose, rational and quantified concepts on bulk and surface properties of catalytic materials are needed for the continuous improvement of existing catalysts and the discovery of new ones.

This lecture will address two challenging questions for catalysis in the field of renewable energies and investigated by first principles calculations.

In the first part, we focus on recent theoretical studies elucidating the origin of the enhanced visible light absorption in N-doped bulk anatase TiO_2 used as photocatalytic materials [1]. We show how DFT calculations including HSE functional and perturbation theory formalism, as implemented in VASP 5.2 [2], help for the accurate determination of the optical properties of N-doped TiO_2 as a function of the nitrogen chemical source. A direct interpretation of the available experimental optical spectra is proposed in order to identify the doping species in the bulk.

In the second part, we address one key question for bio-oils production: the deoxygenation pathways of oxygen containing molecules found in biomass. We investigate hydrodeoxygenation mechanisms catalyzed by the edge sites of the MoS_2 based catalysts, industrially used for hydrodesulfurization. We show how the elementary steps such as C=O hydrogenation and C-O bond cleavage are activated on MoS_2 in presence of H_2 [3]. The promoting effect of Ni is also addressed and compared with experimental data.

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Accurate adsorption energies from many-body perturbation theory

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In the recent years, ab-initio modeling has been established as a complementary approach to the experimental catalysis research. Density functional theory (DFT) based methods usually offer reliable structural models and energetics, and allow to treat systems containing several hundreds of atoms. Yet the accuracy of commonly used semi-local functionals for adsorption studies is severely limited: Depending on the functional, they either yield too high surface energies or too low adsorption energies, but fail to predict both quantities correctly. In addition, non-local (van der Waals) contributions are completely neglected.

In a recent publication [1], we could demonstrate that the evaluation of the correlation energy in a many-electron approach based on the adiabatic-connection fluctuation-dissipation theorem (ACFDT) in the random phase approximation (RPA) leads to a significant improvement. I will present three case studies where traditional DFT calculations fail to predict the correct adsorption behavior: (i) the covalent adsorption of CO on Pt(111), (ii) the adsorption of aromatics on a transition metal surface and (iii) the interaction of graphene with a ferromagnetic Ni(111) surface. In all cases, the RPA calculations yield improved adsorption energies and predict the correct adsorption geometries.

References:

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Hydrogenation catalysts: a challenge for theoretical simulations

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Different aspects of catalytic hydrogenation have been addressed by theoretical simulations from industrial catalyst employed in the refineries to the complex heterogeneous counterparts used in pharmaceutical industry. The role of different compounds present in the catalyst and the complex interplay between different phases and the catalytic activity is investigated showing the importance of simulations in this particular class of catalysts.

Spatial Reactor Profiles for Validation of Microkinetic Gas and Surface Chemistry Models

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Microkinetic modeling is a powerful tool to gain insight into complex reaction networks encountered for example in heterogeneous catalysis or high temperature gas phase chemistry. Ideally the network of surface and gas phase reactions is formulated as sequence of elementary steps following mass action kinetics. Kinetic parameters in these models such as pre-exponential factors, temperature exponents, activation energies or equilibrium constants can in principle be obtained from theory or from experimental studies. Following this approach detailed microkinetic models have been published for heterogeneously catalyzed reactions involving dozens of surface reaction steps. Gas phase microkinetic models such as for combustion of hydrocarbons are typically even larger involving several hundred reaction steps. Taking into account that each reaction step requires more than one kinetic parameter the number of parameters in such a microkinetic model becomes quickly very large calling for transient experimental data for model validation.

In a flow reactor transient processes are translated into spatial gradients which can be conveniently measured at steady state and basically at any condition of temperature and pressure. It will be outlined in this contribution how reactor variables such as concentrations or molar flow rates of fluid species, fluid and solid temperature and even spectroscopic information about the state of the catalyst can be measured as function of position leading to spatial reactor profiles. After description of the experimental technique it will be illustrated how spatial reactor profiles can be analyzed qualitatively in terms of whether parallel or consecutive reactions occur and whether mass and heat transport influences the investigated reaction. Quantitative analysis will be demonstrated in terms of comparing experimental reactor profiles to microkinetic numerical simulations. Catalytic partial oxidation of methane on rhodium and platinum coated foam catalysts, gas phase methane oxidative coupling and ethane oxidative dehydrogenation on molybdenum oxide catalysts will serve as examples.

The impact of support materials on the activity of vanadium oxide catalysts in oxidative dehydrogenation reactions

Reinhard Schomäcker[1], Benjamin Beck[1], Carlos Carrero[1], Manuel Harth[2], Helmut Schubert[2], Annette Trunschke[3], Neil Hamilton[3], Robert Schlögl[3]

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Vanadium oxide is an important catalyst for many partial and total oxidation reactions. In many industrial catalysts it is applied in complex mixtures several oxides, where the role of the individual component is difficult to identify. In order to elucidate the function of the different material during the catalytic process, model catalysts with less complex composition and structure can be studied. The preparation of supported vanadium oxide catalyst with different metal oxides as support materials results in catalyst with very different performance in the oxidative dehydrogenation of alcohols and hydrocarbons. For the oxidative dehydrogenation of methanol to formaldehyde the activity varies within a series of catalyst with the same loading of vanadium oxide on different support materials by more than two orders of magnitude. I. Wachs and other authors explained this phenomenon mainly with the electronic properties of the support materials, summarized in the Sanderson electronegativity of the metal contained in the support[1]. Although several oxidation reactions have been studied at vanadium oxide catalyst, these conclusion have been drawn mainly from methanol oxidation experiments. In order to identify a parameter that governs the activity of these catalysts, also the oxidative dehydrogenation of ethanol and propane were studied at a series of vanadium oxide catalysts supported on silica, alumina, zirconia, titania and ceria. In all cases a nearly monolayer coverage of the support with vanadium oxide was adjusted by a thermal spreading technique. Although the reactions need to be performed at very different temperatures, the same sequence in the activity of the catalysts is observed, with one exception, VO_x/TiO_2 oxidizes ethanol much faster than all other catalyst. For methanol, ethanol and propane the activity of the catalyst increases in the order of $VO_x/SiO_2 < VO_x/Al_2O_3 < <V_2O_5<VO_x/ZrO_2< VO_x/CeO_2$. Experimental kinetic studies[2] and theoretical calculations[3] show a similar mechanism for all three reactions with the rate determining reduction of the catalyst by the substrate and a much faster reoxidation of the catalyst by molecular oxygen[4]. This results in an empirical scaling of the activities with the H_2-TPR peak temperatures. A derivation of a scaling relation between activity and thermodynamic properties of the different catalysts, like reduction enthalpies, would be more significant and more helpful for the optimization of the catalysts. Unfortunately little data of this type are directly available from experiments. Theoretical support would be greatly appreciated in this field.

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Catalytic oxides at the nanoscale

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The properties of materials change when the dimensions are reduced at the nanometer level. This is true also for oxide materials in the form of ultrathin films on metals or of nanoparticles. Here we discuss three cases, all related to the capability to activate oxygen molecules and facilitate oxidation processes by nano-oxides. In doing this we combine DFT calculations with sophisticated experiments. The first two cases deal with oxide ultrathin films. We report recent results which show the spontaneous formation of superoxo radical anions, O_2^-, by simple adsorption of molecular oxygen on 2-3 layers of MgO grown on Mo(100) [1]. The process involved is the spontaneous tunnelling of electrons trough the MgO thin film and the process is of general importance in the field of oxidative catalysis.

The second example is related to monolayer FeO(111) films grown on Pt(111) which efficiently promote low temperature CO oxidation [2]. The proposed mechanism includes adsorption of O_2, formation of O_2^-, and oxidation of the bilayer FeO film to a trilayer O-Fe-O film. Under CO and O_2 pressures, this system catalyses CO oxidation to CO_2 via a Mars – van Krevelen type mechanism. The reaction is possible only thanks to the high flexibility of the FeO thin layer, a typical property of ultrahin oxide films not present in bulk surfaces.

The last example is related to oxygen activation on stoichiometric and reduced CeO_2 nanoparticles. The interaction of O_2 with the regular CeO_2(111) surface is very weak, while a strong bond occurs with O vacancies (reduced ceria). On O vacancies (two-electron centers), however, only peroxo, O_2^{2-}, and not superoxo species form. We show that superoxo ions can form on reduced ceria nanoparticles where single excess electrons are localized on low-coordinated Ce^{3+} ions. The interaction of O_2 with these one-electron centers leads to the formation of paramagnetic O_2^- ions [3]. These three examples show the importance of dimensionality on the catalytic properties of oxide materials.

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Following Chemical reactions and catalysts structure with in situ microscopy and spectroscopy

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One of the most important goals for Surface Science and Catalysis in the new century is to understand at the atomic and molecular level how chemical reactions proceed with the help of catalysts. This understanding includes the atomic structure of the catalyst and its chemical state, and that of the adsorbed species. It involves also being able to follow how this structure changes with time, with pico, femto and attosecond resolution. In terms of materials, it is of import to develop catalysts, likely in the form of nanoparticles and enzymes that can be structurally designed, with shape and size control, so that new chemical properties, reactivity and selectivity emerge.

To achieve even partially this goal will require great advances in instrumentation to obtain images and spectroscopic information of the catalysts and adsorbed species in situ, i.e., *during the reaction.* In Berkeley we have developed some of these instrumentation, including Scanning Probes (STM and AFM), X-ray spectroscopies (photoemission, absorption), Optical probes and others. Other tools, particularly for high temporal resolution, are planned or under development, both in our laboratory and around the world.

I will discuss recent results where our techniques have been used to explore the structure and chemistry of single crystal model catalysts and metal nanoparticles. Examples will include the Fischer-Tropsch reactions of methanation on Co and Co-Cu alloy nanoparticles, gold nanoparticles for CO oxidation, etc. I will also present other results where electron injection from the STM tip is used to excite quantum states of the molecules that then initiate chemical reactions. These are fundamental processes that can provide understanding of how the excitation energy of specific vibrational and electronic states of adsorbed molecules is transferred to the reaction coordinate.

Beat the heat!
First-principles based modelling of micro- and macroscopic heat dissipation in heterogeneous catalysis

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Energy conversion at interfaces is at the centre of the rapidly growing field of basic energy science. This concerns desired conversions like solar to chemical energy, but also unavoidable by-products like the dissipation of chemical energy into heat. Particularly for highly exothermic catalytic reactions the latter is a crucial factor that needs to be well controlled in order to achieve optimum performance, durability and safety. While effective engineering approaches to account for the released heat at the continuum level are well established, quantitative first-principles based multiscale modelling that treats such effects is only just emerging.

The indispensable basis for such a predictive quality-modelling is first-principles electronic structure theory. For a comprehensive understanding of the surface catalytic function this basis needs to be linked to more coarse-grained approaches that allow following the interplay of the on-going reactions over sufficiently long time spans. First-principles kinetic Monte Carlo (1p-kMC) simulations represent at present the only such approach that can evolve the full system dynamics from picoseconds up to seconds, while fully accounting for the correlations, fluctuations and spatial distributions of the chemicals at the catalyst surface.

In this talk I will present our recent efforts to augment such first-principles multiscale descriptions with an appropriate account of energy dissipation. To one end this concerns the integration of 1p-kMC simulations into a fluid dynamical treatment of the macroscale flow structures in the reactor [1]. To also capture potential atomistic consequences of the reaction heat on the elementary process dynamics we develop a novel QM/Me embedding approach for metal substrates, which enables proper dissipation into a classically described heat bath while simultaneously achieving an accurate description of the metal band structure.

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Monomolecular cracking of short alkanes over acidic zeolites:

Importance of finite temperature effects.

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The monomolecular Haag-Dessau mechanism for propane cracking over acidic chabazite has been studied using dispersion-corrected periodic DFT calculations in combination with ab-initio molecular dynamics (AIMD) simulations, transition path sampling (TPS) and free-energy gradient integrations. Our simulations provide evidence that finite-temperature effects play important role at various stages of the cracking process. The AIMD simulations show that due to the weak specific interaction of the saturated molecule with Brønsted acid sites, the adsorption energy is considerably reduced at elevated temperature and that only a fraction of the molecules adsorbed within the zeolite are sufficiently close to the acid site to form a reactant complex for protonation. TPS shows that the preferred reaction mechanism is the protonation of a terminal methyl group. The direct proton attack on the C-C bond between the methyl and methylene groups is not excluded, but occurs with lower probability. The intrinsic reaction parameters: free-energy and entropy of activation are determined using thermodynamic integration based on constrained molecular dynamics simulations.

Atomic-scale understanding of complex chemical processes through hierarchical multiscale approach.

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The identification of the prevalent reaction mechanism is the center piece in the quest towards an atomic-scale understanding of a catalytic process[1]. In essence, the prevalent reaction mechanism is the result of the interplay of phenomena that occur at different time and space scales. It consists of the chemical pathways and intermediate species through which the reactants convert to the products at specific operating conditions. In this view, the development of fundamental mathematical models that link insights across all relevant time and space scales is required, spanning from the microscale (making and breaking of chemical bonds, electronic structure) to the macroscale (reactor and reaction engineering). In this respect, methodological approaches that efficiently integrate the various levels of theories into one multiscale analysis are of particular relevance and still represent a great challenge especially for complex processes of real technological interest[2, 3].

In this talk, I will present recent results on the hierarchical multiscale analysis of chemical catalytic processes. Challenges and proposed solutions at the different scales will be shown. In particular, I will discuss how to efficiently employ first-principles calculations in complex reaction networks, where an exhaustive first-principles treatment is prohibitive[4].

As show-case, I will present selected results from the multiscale analysis of the CH_4 partial oxidation on Rh catalysts for short-contact-time hydrogen production. This study has substantially contributed to the comprehension of the molecular level mechanisms underlying the complex experimental evidence[5-8]. On one hand, these findings have been of primary interest for the interpretation of the complex experimental evidence. On the other hand, they have been of direct use for the design and scale-up of short-contact-time reformers for small scale hydrogen production in the sustainable energy field[9].

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Surfaces of doped MgO at realistic temperatures and pressures: defect concentration, distribution, and charge states

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Native defects can dramatically modify the chemical properties of oxide surfaces. Even for a clean flat surface of a binary oxide, there is a variety of different types of intrinsic defects, for example oxygen and metal vacancies, interstitials, self-interstitials, and others. Moreover, the defects can be present in different charge states. However, experimental determination of the defect concentration at realistic temperatures and pressures is a challenging task.

In this work, we calculate electronic structure and formation energies of neutral and charged oxygen vacancies in the bulk and at the MgO (100) and (111) surfaces [1], and estimate their concentration and distribution at realistic temperatures and pressures using density functional theory (DFT) and the *ab initio* atomistic thermodynamics approach [2]. We determine the stability of different charge states of the oxygen vacancy as a function of the Fermi level position within the band gap (simulating the global effect of doping). We also analyze how the proximity of a dopant providing localized acceptor states changes the vacancy formation energies (local effect of doping). We use the Li substitutional defect as a prototype of such a dopant.

Li-doped MgO had been proposed to be a promising catalyst for oxidative coupling of methane [3]. An improved catalytic performance was attributed to the presence of Li substitutional defects at the surface of the material. However, recent theoretical and experimental studies [4,5] have raised serious doubts in that the role of the Li substitutional defects can be reduced to producing isolated active sites on MgO surfaces at catalytic conditions. Using the *ab initio* atomistic thermodynamics approach including effects of configurational entropy, we show that Li doping destabilizes the (100) surface of MgO, promoting a change in the surface morphology at elevated temperatures, in agreement with experimental results [4].

The effects of electron exchange and correlation on our results, in particular the self-interaction error and the band-gap problem, are discussed in detail. In case of a low-valence substitution such as Li in MgO, DFT with standard exchange-correlation functionals based on local- and generalized gardient approximations (LDA and GGA) fail to describe correctly the localization of the associated unpaired hole, and even the calculated equilibrium geometry of the defects is incorrect. These problems are addressed by employing hybrid range-separated exchange-correlation functionals HSE06 and PBE0.

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Inhibitors in hydrodesulfurization: The story of pyridine

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Abstract

In the presence of nitrogen or sulfur containing organic compounds the hydrodesulfurization (HDS) activity of MoS_2-based catalysts is severely inhibited. This effect is particularly pronounced with basic nitrogenous compounds, which are known to impede the hydrogenation pathway.

Pyridine adsorption on MoS_2 is considered as a representative model for basic nitrogenous inhibitors in HDS. In this talk, I will present a series of pyridine adsorption studies by DFT, IR and STM on MoS_2 catalysts under several relevant HDS conditions at the Mo-edge, including the presence of surface SH groups and the sulfur vacancies. The results show that while pyridine alone adsorbs weakly, it can readily form pyridinium ions by proton transfer from adsorbed hydrogen. Pyridinium is likely to be responsible for the inhibition effects and we present evidence for its presence on the catalyst.

Oxygen defect formation in ceria and its *non-innocent* role as support for oxidation catalysts

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In the many applications of ceria-based materials in heterogeneous catalysis, the reducibility of ceria is essential to the catalytic function. Moreover, the strong influence of the support on the reactivity of ceria supported vanadium oxides (VO_x) in oxidation reactions is not yet understood. To this end, we apply density-functional theory (DFT) with the HSE hybrid functional as well as the DFT+U approach to study the $CeO_2(111)$ surface [1] and $VO_n/CeO_2(111)$ model catalysts [2]. To compare their catalytic activity in oxidation reactions, we calculate the energy of oxygen vacancy formation (which relates to the reaction energy), and the energy of hydrogenation (which relates to the energy barrier of the rate determining step). We show that subsurface vacancies at the $CeO_2(111)$ surface are energetically more favourable than surface ones. Furthermore, we combine DFT with statistical thermodynamics and discuss the stability of VO_n species as function of the oxygen partial pressure and temperature. We argue that the high catalytic activity of vanadia supported on ceria has its origin in the ability of ceria to stabilize reduced states by accommodating electrons in localized *f*-states, which is promoted by the supported vanadia species [3]. We further show that the preference for subsurface vacancies and the stabilization of the +5 oxidation state of vanadium upon reduction, are the result of defect-induced lattice relaxation. In addition, we find that vacancies at the $CeO_2(111)$ surface are likely to be bound to Ce^{4+} ions rather than to Ce^{3+} as priorly suggested [4]. This prediction has been recently confirmed by means of STM imaging and spectroscopy [5].

*This work has been performed in collaboration with J. L. F. Da Silva, C. Popa, and J. Sauer at the Humboldt University in Berlin and with the Department of Chemical Physics at the Fritz Haber Institute in Berlin.

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Challenges in the simulation of nucleation processes: from transition pathways to reaction coordinates

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Computer simulations of first order phase transitions occurring via nucleation and growth are demanding for several distinct but related reasons. Particularly close to coexistence, the free energy barrier separating the metastable from the stable phase can be high, leading to nucleation times that vastly exceed the time scales accessible to molecular dynamics simulations. Other difficulties arising in the simulation of nucleation processes consist in detecting local structures characteristic for the stable and metastable phases and in identifying the degrees of freedom that capture the essential physics of the transition mechanism. In this talk, I will discuss how these problems can be addressed using transitions path sampling, neural networks, and likelihood optimization, respectively. The freezing of a soft sphere fluid and the pressure induced structural transformation of nanocrystals will be used as illustrative examples.

Free Gold Clusters: Fluxionality and Ligand Adsorption

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The thermodynamical stability of free, pristine gold clusters at finite temperature and of cluster+ligands complexes at finite temperature and in the presence of an atmosphere composed of O_2 and CO is studied employing parallel tempering [1] and *ab initio* atomistic thermodynamics [2]. We focus on Au_{13}, which displays a significant fluxional behavior: Even at low temperature (100 K) this cluster exhibits a multitude of structures that dynamically transform into each other. At finite temperature, the preference of this cluster for three-dimensional versus planar structures is found to result from entropic effects. For gold clusters containing from one to four gold atoms in an O_2 + CO atmosphere, we apply *ab initio* atomistic thermodynamics. On the basis of these considerations, we single out a likely reaction path for CO oxidation catalyzed by gold clusters.

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Special reaction sites on Ru, Pt, and Au model catalysts

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The physical state of Ru, Pt, and Au catalyst surfaces under reaction conditions is discussed. The transition metal, Ru, is found to be fully oxygen covered at reasonable reaction conditions and shows no sign of activity towards CO oxidation at the Ru basal planes. However, at steps special reactive sites exist even in the presence of an oxygen adsorption layer of saturation coverage[1]. The late-transition/platinum-group metal, Pt, is found to be only moderately covered with oxygen at close-packed terraces while a one-dimensional oxide forms at the monatomic steps[2]. Despite of the oxygen atoms in the step-bound oxide being differentially stronger bound than the oxygen atoms at the terraces, it is found both experimentally and theoretically that it is the oxygen atoms within the one-dimensional step-oxide that are involved in CO oxidation [2]. The noble metal, Au, shows very little affinity toward oxygen adsorption on basal planes, but for nano-scale clusters supported on metal oxides special sites are found at the perimeter of the Au/oxide interface [3,4].

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Using first principles catalysis in industry: The state of our art and future challenges and perspectives.

Glenn Jones

Computational catalysis is a maturing field that is now successful, not only in providing fundamental insight into the chemistry involved in catalytic process, but also in predicting and influencing the catalyst design process. As such there is increased interest from industry to move into the field. However, despite the rapid evolution of the field over the past couple of decades there still remain numerous gaps to be bridged. The challenges to overcome are manifold and include, those of a technical nature (length scales, complexity), interdisciplinary (physics, chemistry and engineering), economic and cultural (academic vs. industrial).

This talk will use a case study to illustrate how first principles calculations, when used in combination with a wide range of experimental methods, can be used to understand what makes a catalytic reaction tick. In turn the insight gained can be used in computational models to predict novel catalyst candidates for synthesis and testing in the lab. It will be shown that often the difficult stage of the process is identifying the crucial steps of a reaction and ensuring the material studied computationally is a relevant model of the real catalyst. This highlights the need for direct communication between experimental catalytic scientists and modelling scientists to ensure like is being compared with like. The catalyst characterisation required to make this comparison is often a non-trivial task and requires significant emphasis on continued development of experimental methods. Following the case study discussion will turn to the barriers which hinder take-up of modelling within industry and conclude with a look to the future at some of the 'grand' and perhaps 'not so grand' challenges we face within industrial computational catalysis and how we are beginning to tackle them. This includes thinking about the multi-scale nature of the catalytic process and placing the fundamental chemical reactions in the context of the engineering and process development.

Extending the scaling relations for design of heterogeneous catalysts

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Understanding the details behind some of the key factors in chemical reactions is of the outmost importance if one wants to expand the applicability of advanced Density Functional Theory (DFT) calculations. DFT provides the perfect tool for rapidly getting insight into changes in reaction energetics on different surfaces and surface structures. The analysis of reaction energies from DFT has over the last two decades or so provided an enormous insight in the field of catalysis. This insight has helped relate adsorption energies and activation energies to energies that can be accessed much more easily and hence it defines an approach suitable for screening studies.[1,2,3] These relations have proven very useful in studying the reactivity trends of various materials based on simple descriptors and in a few cases it has given new ideas to catalysts for certain reactions.[4,5,6,7,8,9] Increasing interest in not only the reactivity but also the selectivity of a material towards a certain reaction product sets certain limitations to this approach. This is because it narrows down the important energy range significantly and hence will depend on smaller variations in activation energies and the specific reactants. In this talk I will address these limitations and discuss how existing models can be modified to incorporate such variations.

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Posters

Blocking of catalytic sites on NiO(111) surfaces by hydroxylation and carbonate formation

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NiO is used as main or co-catalyst in heterogeneous catalysis, for example, for dimerization and oligomerization reactions of ethylene. H_2O, CO and CO_2 are commonly present during catalytic reactions and strongly interact with NiO surfaces. It is observed that they permanently block surface sites or alter the surface structure by hydroxylation and carbonate formation and thereby poison a catalyst.

In our study of the response of NiO to these gas phases we have focused on the polar NiO(111) surfaces since they are particularly susceptible to surface reconstructions and reactions with adsorbates as their bulk-truncated structure is intrinsically unstable. We performed spin-polarized GGA+U calculations for more than 60 possible reconstructions of the NiO(111) surface in contact with water and modified by adsorption of hydroxyl groups and protons. A thermodynamic formalism was applied under the assumption of two separate O and H particle reservoirs to deduce a phase diagram of the energetically most stable surface structures depending on temperature and pressure conditions.

In agreement with experiment we find that the phase diagram is dominated by a fully hydroxylated (1×1)-OH configuration at ambient and low temperature UHV conditions and a (2×2)-O-octopolar structure after high temperature annealing. However, a transformation pathway between those two stable phases has to include the diffusion of Ni and O surface atoms. This gives rise to additional activation barriers which explains the experimentally observe high thermal stability of the surface hydroxylation. More detailed calculations on the kinetics of the phase transformation between (1×1)-OH and (2×2)-O-octopolar are currently in progress.

Considering the interaction of CO and CO_2 with NiO(111), we find that none of the structures of the previous phase diagram remains a lowest-energy structure, but a adsorbate-covered missing-row termination becomes thermodynamically most favorable. Upon CO and CO_2 adsorption tridentate carbonate complexes including surface O atoms are formed.

Trends in the Catalytic Activity of Surfaces of Transition Metals

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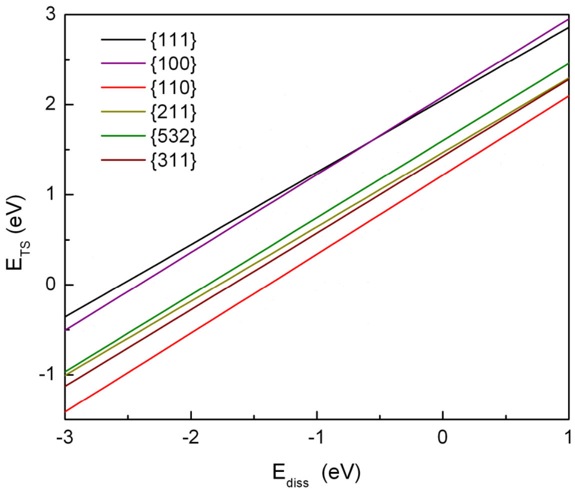
Nanoparticles are used as catalysts in the chemical industry. The surface of the nanoparticles typically exposes a number of different configurations of the metal atoms, among which are surfaces, steps and kinks. An important question is which of these local geometries constitute the active sites where the catalysis actually takes place.



Based on density functional theory calculations on the dissociative chemisorption of NO, N_2, and O_2 on a number of transition metal facets; {111}, {100}, {110}, {211}, {311} and {532}, trends in reaction and transition state energies from one metal to the next and from facet to facet is discussed based on scaling relations between reaction energies and transition state energies.

Adsorptions of Keto/Enol-Acetophenone on Pt(111) surface

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On Pt(111) acetophenone (AP) can undergo keto-enol tautomerization at room temperature. The enol species subsequently form dimer and trimer self-assembled structures.[1] To understand the mechanism of keto-enol transition and self-assembly, it is necessary to study the adsorptions of keto-AP and enol-AP molecules. In this work, we have systematically investigated the adsorption structures of the single and double AP molecules using the finite difference mode in the grid-based projector-augmented wave density functional theory code, GPAW.[2] For the single keto-AP molecules, there are one vertical stable adsorption site with the side group perpendicular to the surface and three flat stable adsorption structures with the side group parallel to the surface. The adsorption energy of the keto-AP molecule mainly results from the interaction between the phenyl group and the Pt(111) surface. The flat adsorption structures have small energy differences, because of the shift up of carbonyl group due to the steric repulsion. For enol-AP molecules, there are also two kinds of adsorption structures, vertical vs. flat, with the vertical adsorption energy about 0.6 eV lower than the flat ones. The adsorption energy of enol-AP molecules is much higher than that of keto-AP molecules; however, the energy difference of the flat adsorption structures is small, less than 0.1 eV.

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Do hybrid functionals improve the description of adsorption sites in Cu- and Co- exchanged zeolites?

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When testing a new theoretical method usually benchmark tests on predefined systems are performed. While calculations in these toy-systems are usually good indicators for the performance of these methods for very specific aspects of the given problem, the overall picture is sometimes overlooked.

With this in mind we started rigorous tests of the performance of screened (HSE) and unscreened (PBE0) hybrid functionals describing the adsorption sites in Cu- and Co-exchanged chabazite comparing it to the performance of the more common Generalized Gradient Approximations (PBE, PW91).

We compare our results to experimental data available for structural quantities as well as for emission and adsorption spectroscopy of the metal exchanged zeolite. Furthermore we describe the adsorption of the tracer-molecules (experimentally used to identify adsorption sites) CO and NO, their adsorption energies, IR-frequencies and the influence of the choice of functional when describing the gas phase carbonyls and nitrosyls.

Electrochemical ammonia synthesis on highly under-coordinated reaction sites.

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Abstract

In today's world, an energy-efficient method is desired for chemical synthesis of ammonia (NH_3) from molecular nitrogen (N_2) in air. Over 100 million metric tons of NH_3 are produced annually, with 80% used as fertilizer. Currently, ammonia synthesis is achieved by the Haber-Bosch process, which is energy-intensive due to the required high temperature and pressure. In the past several years, numerous studies have examined ammonia synthesis and offer excellent insight into the challenges faced with developing new catalytic materials for this reaction. It has been shown in previous studies that ammonia synthesis is very structure sensitive on metals[1,2]. Furthermore, it has been shown that a similar reaction, CO oxidation, can be performed at low temperature on transition state nanoparticles[3,4]. The present work suggests that nanoparticles can be used for N_2 reduction because of the increased activity of these under-coordinated metal nanoparticles. We have investigated the reaction intermediates for the dissociative and associative mechanism on the M12 nanoparticle model system for most transition metals and developed similar scaling relations compared to stepped and close packed metal surfaces. From this ground, an electrochemical analysis can be constructed and overpotentials can be estimated for the electrochemical nitrogen fixation.

Relevant background literature

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Parameterization of an Interaction Model for Adsorbate-Adsorbate Interaction

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Abstract:

The effect of adsorbate-adsorbate interaction on adsorption energy of adsorbates is not negligible. The adsorbate-adsorbate interaction affects the adsorption energy of the adsorbates and also the transition states of reactions. So we need to include these adsorbate-adsorbate interactions in our microkinetic model if we want to tailor a new catalyst by using our theoretical calculations.

We propose a new interaction model where the adsorption energy varies linearly with the coverage.

The average adsorption energy per adsorbate:

$E^{avg}(\theta) = E^{avg}(n, N) = \dfrac{E_{n-ads+slab(N)} - nE_{gas} - E_{slab(N)}}{n}$ can be calculated directly from DFT, where coverage $\theta = n/N$, n is the number of adsorbates and N is the number of surface sites available in the unit cell.

The total adsorption energy $E^{\mathrm{T}}(\theta)$ per surface site and the differential adsorption energy $E^{diff}(\theta)$ can be obtained from $E^{avg}(\theta)$ as: $E^{\mathrm{T}}(\theta) = \theta \cdot E^{avg}(\theta)$ and $E^{diff}(\theta) = \mathrm{d}E^{\mathrm{T}}(\theta)/\mathrm{d}\theta$. In other form, $E^{\mathrm{T}}(\theta)$ can be also presented as an line integral, $\int_0^{\theta} E^{diff}(\theta)\,\mathrm{d}\theta$. Until second order, the $E^{\mathrm{T}}(\theta)$ can be expanded as function of coverage as $E^{\mathrm{T}}(\theta) \approx E_{\theta=0}^{Trans} \cdot \boldsymbol{\theta} + \frac{1}{2}\, \boldsymbol{\theta}^{Trans} \cdot \boldsymbol{\varepsilon} \cdot \boldsymbol{\theta}$. Where $\boldsymbol{\varepsilon}$ is the lateral interaction matrix, and $E_{\theta=0}$ is the differential adsorption energy at coverage $\theta = 0$.

We will use this model to get the model parameters and use them in our microkinetic model to get the trends of activity of a catalytic process. Thus we will be able to include the adsorbate-adsorbate interaction in our theoretical model for more rational approach towards the tailoring of new catalyst.

SELECTIVE HYDROGENATION OF VALYLENE

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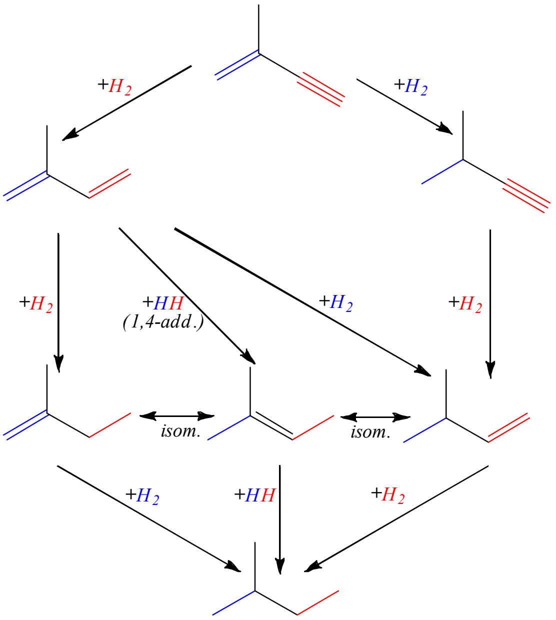
Increasing selectivity is nowadays a principal task when designing sustainable industrial processes. We present an *ab-initio* study on the catalytic hydrogenation of valylene (2-methylbut-1-en-3-yne) towards isoprene (2-methylbuta-1,2-diene). Since the isoprene is a valuable bulk chemical, we were in the search of chemo- and regioselective pathways for its production. Heterogeneous catalytic hydrogenation may do the trick.

The results of the plane-wave DFT calculations using PW91 functional within the VASP code [1] are used to explain the formation of the desired product and all possible by-products of this complex reaction scheme.



The large number of transition states of all elementary steps in this complex reaction scheme (right-hand figure) was only possible to be located using recently implemented algorithm: the improved dimer method [2].

Detailed theoretical study was carried out side-by-side with the hydrogenation experiments, performed in a continuous reactor on supported transition-metal catalysts. Upon understanding all aspects of the peculiar partial hydrogenation of the triple bond by theory, it is possible to estimate the products ratio for other substrates as well.

Therefore, in a chemical analogy to valylene, selectivity in hydrogenation of vinylacetylene (but-1-en-3-yne) to buta-1,3-diene was also investigated by both theory and experiment. This reaction scheme is very similar to that of valylene, yet there are differences in the catalytic behavior.

Both substrates are a step forwards compared to the previous studies on smaller alkynes (ethyne, propyne) hydrogenation [3]. The aim is to tune-up a suitable metal catalyst to increase the selectivity (isoprene yield) and avoid the production of undesired by-products (ovehydrogenation and green-oil formation).

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Active Sites for Methane Activation in MgO and Li doped MgO

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C-H bond activation is a subject of immense practical and fundamental interest. Particularly conversion of methane into more valuable chemicals and fuels represents a challenge for the future [1]. A chemical of particular importance is ethene, which can be obtained by oxidative coupling of methane (OCM).

A prototype catalyst for the OCM reaction is lithium doped magnesium oxide.[2] It is believed that the $O^{\bullet-}$ oxygen radical anion, which is formed after substitution of magnesium ion by an lithium ion, is the oxidizing species responsible for hydrogen abstraction from CH_4 and the formation of methyl radicals. The same type of oxygen radicals can be formed on ionization of $(MgO)_n$ gas phase clusters yielding $(MgO)_n^+$ ions.

Based on the hypothesis that $Li^+O^{\bullet-}/MgO$ is the active site for OCM surface reactions we first studied methane activation by $(MgO)_n^+$ [3] and $LiO(MgO)_{n-1}$ gas phase clusters. However recent studies could not find evidence for $Li^+O^{\bullet-}$ species under OCM relevant conditions. Moreover, it was shown that Li is not necessary for C-H activation, but addition of Li enhances the OCM activity most likely by restructuring the material accompanied by creating more defects such as edges, corners and kinks.[4] Therefore, in addition to models of $Li^+O^{\bullet-}$ sites we considered different types of defect sites on MgO, and study their reactivity towards methane.

Our results show that methane activation proceeds in a similar way (the same reaction steps, similar structures) for $Li^+O^{\bullet-}$ sites and all types of modeled defects and it is in agreement with the mechanism proposed by Schröder and Roithová.[5] The H abstraction energy barriers for Li doped MgO clusters are smaller than 25 kJ/mol, while for the Li doped slab model the barrier increases till 84 kJ/mol. Similar apparent energy barrier was also calculated for solid OCM catalyst by Catlow et al. (74 kJ/mol) [6], whereas the observed one is almost twice higher (147 kJ/mol) [7]. This indicates that the $Li^+O^{\bullet-}$ species is too reactive and it is not responsible for the rate-determining step in OCM.

Our calculations, together with experimental results [4] show that the current hypothesis about $Li^+O^{\bullet-}$ sites being responsible for OCM activity of Li-doped MgO needs to be revised.

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Adsorption energies of H, O and OH on Pt55 nanoparticle by using all-electron scalar relativistic calculation

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Density functional theory calculations have been successfully used for understanding catalytic interactions and designing novel catalysts. Most of the calculations have used the combination of plane-wave pseudo-potential (PWPP) methods and slab configurations because the computational efficiency and accuracy of the combination were superior to other combinations. However, the combination of all-electron (AE) and nano-cluster is necessary to obtain more accurate and realistic results for designing a novel catalyst. AE method can be used for a reference compare to PP method and nano-cluster can be used for understanding the gap between single crystal surfaces and nano-particles used in real industry.

In this study we used FHI-aims code that uses numerical atom-centered basis functions, which shows a good scalability in 0-D systems such as nano-clusters. A cubo-octahdedron shaped Pt55 cluster was constructed. The adsorbed species were H, O and OH, which is important species in PEMFC. In this study we focused on adsorption energies with respect to sites such as on-top, bridge, edge and vertex. For comparison, we also calculated the adsorption energies of molecules both on Pt(001) and Pt(111) surfaces.

Adsorption energies in this calculation showed 0.05~0.2 eV less than those of PP results, which implies that PP result overestimates the adsorption energies. When comparing the adsorption energies between the surface and the nanoparticles, maximum energy differences for the most stable sites of molecules were 0.12 eV, 0.36 eV, 0.64 eV for H, O, and OH, respectively. The details of the comparison will be presented.

Abstract for poster to Magleås conference:

A computational feasible Anharmonical Normal Mode Analysis for surface science

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In this project a method has been developed to correct the entropy contribution, in the harmonic normal mode analysis, from the weak or negative normal modes. This is a problem when focused on e.g. large intermediates or molecules that have low barrier rotational modes or weak vibrational modes. To better estimate the entropy, the full partition function is found for the problematic modes, and combined with the harmonic partition function of the harmonic modes, to better estimate the thermodynamic contribution of the vibrations, rotations and translations. The implementation includes; smooth fitting along the normal modes with few samples, finite difference solving of the 1D Schrödinger equation and a Romberg extrapolation scheme for correcting the calculated eigenenergies.

Metal ammines and hydrates – phases and surface states

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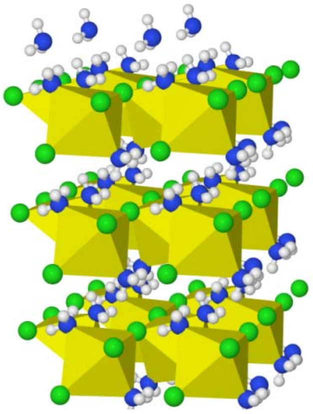
The development of new materials for energy storage is of great importance if the transportation infrastructure is going to be based on sustainable energy in the future. Strontium ammines are interesting for both energy storage [1] and selective catalytic reduction of NO_x gases [2].

Metal ammines generally have a high ammonia density and exhibit fast ab- and desorption kinetics [3]. These qualities can potentially also enhance ammonia production by removing reaction products and hindering water access. We have made theoretical investigations confirming this.

We have performed ammonia pressure measurements during the ab- and desorption cycles of strontium ammines, and DFT calculations to verify the experimental findings. The experiments have revealed that the diammine phase, $Sr(NH_3)_2Cl_2$, often disregarded in the literature, is stable at slightly elevated pressures. Furthermore, two pressure regimes in the absorption cycle indicate the presence of a stable surface state, never before reported.

Since the atomic structure of the strontium ammine phases are not reported, testing of structures for similar materials or found from a simulated annealing algorithm [3] resulted in good agreement with x-ray diffraction patterns especially at low ammonia content. By including van der Waals forces in the exchange correlation functional [4], desorption enthalpies and the surface state enthalpy are well reproduced by DFT and the observation of the diammine at slightly elevated pressures can be explained.



The structure of the diammine – $Sr(NH_3)_2Cl_2$. The NH_3 molecules at the top are situated in the stable surface state.

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First-Principles kinetic Monte Carlo Simulations of Ammonia Oxidation at RuO_2(110): Selectivity vs. semi-local DFT

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Reaching a detailed mechanistic understanding of high selectivity in surface catalytic processes is one of the central goals in present-day catalysis research. The Surface Science approach to this problem focuses on the investigation of well-defined model systems that reduce the complexity but still capture the relevant aspects. In this respect, the almost 100% selectivity reported in detailed experiments for the oxidation of NH_3 to NO at RuO_2(110) [1] presents an ideal benchmark for a quantitative theoretical analysis. To this end we perform detailed kinetic Monte Carlo (kMC) simulations based on kinetic parameters derived from density-functional theory (DFT). The obtained turnover frequency for molecular nitrogen is in rather good agreement with the experimental data. However, even with an extended set of elementary processes we are not able to reproduce the experimental findings for the production of NO and therewith the selectivity. The central quantities that decisively determine the latter are the binding energy of NO and the N diffusion barrier. Suspecting the approximate energetics obtained with the employed semi-local DFT functional as reason for the discrepancy, we recalculate the kinetic parameters with different functionals and discuss the resulting effects in the kMC simulations.

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Investigation of the mechanism of Fischer-Tropsch Synthesis from First Principles

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The application of *ab initio* techniques to the study of industrial Fischer-Tropsch catalysis is challenging due to both the complexity of the catalysts employed and the diversity of the products formed. In Fischer-Tropsch synthesis (FTS), fossil resources such as coal and natural gas are converted via synthesis gas (a mixture of CO and H_2) into chemicals and hydrocarbon transportation fuels. Co- and Fe-based catalysts are commonly employed in combination with promoters, and such catalysts may be dispersed on an oxide support, or may be unsupported. Under operating conditions, the catalysts can undergo phase transformations and reconstruction, and may eventually deactivate over time. An atomic-level understanding of the mechanism of FTS, and the underlying catalytic properties that influence catalyst activity and selectivity in FTS, can lead to improvements in catalyst longevity, and provide a predictive understanding of changes in product distribution and catalyst behaviour as a function of operating conditions.

In this work we present an overview of our research in which *ab initio* techniques based on periodic density functional theory calculations are being used to investigate the mechanism of FTS. Examples from our work on Co- and Fe-catalysed FTS, and on the γ-Al_2O_3 support, will be given. In the case of Fe-based FTS, we focus on Hägg iron carbide (χ-Fe_5C_2), which is observed to form during FTS and has been associated with FTS activity [1,2]. In light of our recent detailed study of the structure and stability of χ-Fe_5C_2 surfaces [3], we focus on three surface terminations that enable a comparative study of the reactivity of surface sites as a function of local environment to be made. The role of step sites and surface vacancies in facilitating CO activation is demonstrated [4], and the importance of CO dissociation through a hydrogenated intermediate is shown to be surface dependent. The study is extended to include elementary reactions of methane formation, where the energetic preference of the CH_x intermediate for the surface vacancy site is found to diminish with increasing degree of hydrogenation of the C_1 intermediate. The implications for the structural basis of the mechanism of Fe-FTS are discussed.

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Adsorption and Diffusion of Benzaldehyde on Pt(111)

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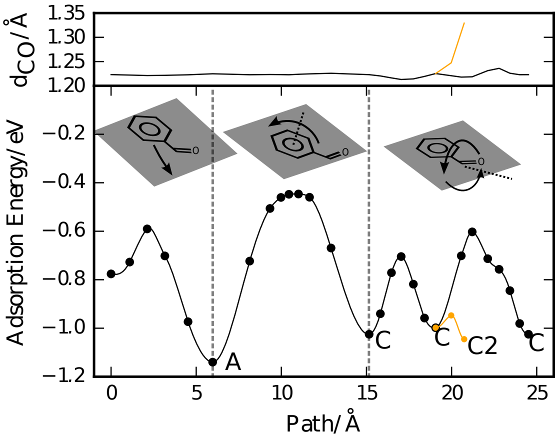

We present a density functional theory investigation of the adsorption, diffusion and internal rearrangement of benzaldehyde on Pt(111). The aromatic ring interacts strongly with the Pt surface causing a clear site preference with the ring centered over the Pt-Pt bridge site and the C-C bonds aligned at a 30-degree angle to the Pt-Pt bonds. The aldehyde group may point in three different directions with respect to the Pt surface atoms, defining three distinct stable conformers that we denote A, B, and C.

In A and B, the carbonyl function of the benzaldehyde points away from the surface and retains the characteristics of a double bond. In the C conformer, a similar conformation appears in conjunction with a state in which the carbonyl bends toward the surface, opens up as a CO single bond, and forms a metallocycle involving two Pt atoms. Similar metallocycles for the A and B conformers would only involve one Pt atom, possibly explaining why they are not found. The four stable states of benzaldehyde are bound to the surface with adsorption energies in the range 1.0-1.1 eV. The energy barriers for the transition between these local minima are calculated with the nudged elastic band method to be 0.8 eV or less. In particular the barrier for the formation of the metallocycle is found to be small, <0.1 eV, suggesting that the metallocycle may easily form as a first step in hydrogenation reactions. The barrier for diffusion of the benzaldehyde from the Pt-Pt bridge site to the less stable hcp site is found to be 0.5 eV indicating that the benzaldehyde molecules are expected to be highly mobile at reasonable temperatures.

The molecules are found to form weakly bound dimers via creation of two aryl-CH…O bonds. Unraveling the mechanisms at play in the bonds within these dimers and the role of the Pt surface in templating the molecular interaction will have implication on understanding molecular self-assembly and more specifically on understanding modifier directed surface reactions. An example of the latter is the Orito reaction in which alpha-ketoesters are hydrogenated to hydroxyester at cinchonidine or related surface modifiers. Preliminary work of relevance to such reactions will be presented.

First Principle Investigation of Zinc-anode Dissolution in Zinc/air Battery

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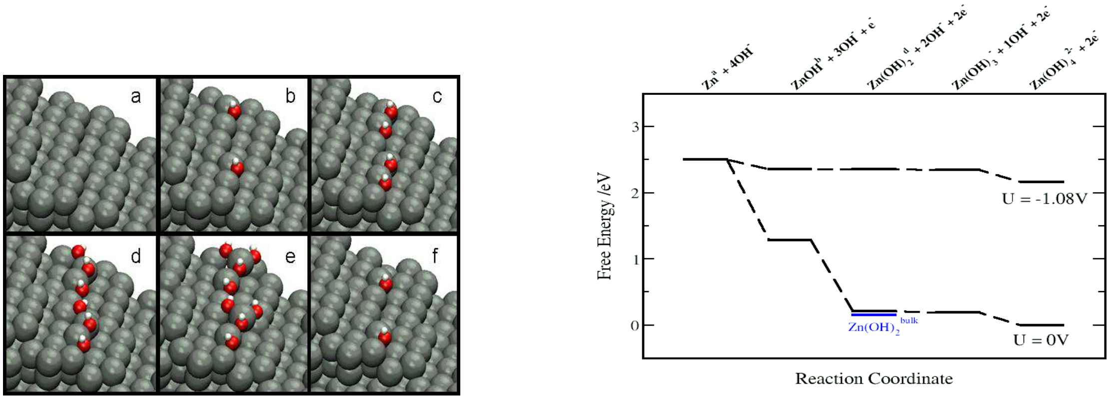
Batteries are energy storage devices with closed thermodynamic systems that store energy chemically. There is a huge interest in the technology of zinc/air batteries due to its very high gravimetric and volumetric energy density. The zinc/air battery is cheap to produce, a safe chemistry battery and environmentally friendly. It only relies on oxygen from the atmosphere to generate current and does not require volatile materials. With the help of density functional theory calculation we have modeled surface reactions in the zinc anode and presented a simple analysis of the anode dissolution in the zinc/air battery using a kinked surface as a model system. Invariance of the surface morphology before and after dissolution of a kink atom enabled us to calculate potential steps in one dissolution cycle (Figure 1a). From the calculated OH adsorption energies and the experimental dissolution potentials we mapped out the free energy diagram (Figure 1b) and showed that there is a very small overpotential of 0.17 V associated with this reaction. This result agrees well with the experiment findings which measured 0.05 - 0.1 V overpotential [1,2]. The work presented here clearly demonstrates the versatility of DFT in modeling dissolution processes on metal surfaces.



a

b

Figure 1. a) *Snapshot a is a bare Zn kink, while snapshots b-f illustrate steps in one dissolution cycle. b) Free energy diagram for Zn dissolution at the anode, shown at two potentials, 0 V and -1.08 V respectively.*

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Volcano Relations for the Oxidation of Hydrogen Halides over Rutile Oxide Surfaces

A. Toftelund, I. Man, F. Studt, H.A. Hansen, F. Abild-Pedersen, J. Rossmeisl and T. Bligaard

Today a huge amount of methane is wasted in gas flaring, because it can not be economically transported or converted to high value liquids.

Traditionally the liquefaction of methane, is either done by steam reforming followed by Fischer-Tropsch synthesis or by directly conversion of methane into methanol. Both of these methods are only economically viable on very large scale, and require huge plants.

A method that in principles can be applied in small scale, is to couple halide-methanes i.e. CH_3Cl, CH_3Br or CH_3I, together to form longer chains of hydrocarbons. The problem is that HCl, HBr, or HI is created in the process.

In this study we are looking at the processes of oxidizing the hydrogen-halides in order to form Cl_2, Br_2 or I_2, which then can be reused together with methane to form CH_3Cl, CH_3Br or CH_3I.

We have established an activity relation for the heterogeneous catalytic oxidation of hydrogen halides over rutile oxide catalysts by combining density functional theory calculations (DFT) with microkinetic modeling. Linear relations for the energies relevant for the elementary reaction steps are obtained from the DFT calculations and used to establish descriptors for the catalytic activity. The descriptors employed are the adsorption energy of oxygen and hydroxide. It is found that in case of chlorine the known RuO_2 catalyst is close to optimal.

First-Principles Modeling of the Electrified Solid-Liquid Interface

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First-principles methods for studying reactions at the electrochemical interface have just started to appear [1, 2, 3]. Despite differences in formalism and implementation they all face the same fundamental problems: tuning the bias, creating a realistic potential drop at the interface, linking the potential to a known reference scale and keeping the electrode potential fixed during charge transfer reactions.

In the model presented here, the bias is generated by introducing hydrogen atoms in discrete quantities in the first water layer on the metal surface. The structure of water has been inferred from UHV experiments supported by the 0 K and finite temperature density functional theory simulations [4, 5]. After addition of a hydrogen atom, charge separation occurs instantaneously, with the electron escaping to the surface leaving the protonated water layer behind. The potential drop thus created is identical to the Helmholtz picture of the electrical double layer and it produces, as well, the correct electric field [6, 7]. In order to compare results to experiments one needs to relate the potential to some known reference scale. If we chose the chemical potential of hydrogen to equal the free energy of H_2 at standard conditions, the minimum of the free energy stored in the electrical double layer yields, by definition, the absolute standard hydrogen electrode potential (ASHEP). This finding enables us to refer all the potentials to the SHE potential scale [8]. Moreover by analyzing the dependence of the ASHEP with respect to a dozen different water structures, we establish three necessary conditions (no net dipole, no charge transfer and high flexibility) that a water structure should possess in its uncharged (potential of zero charge) state in order to bring the theoretical ASHEP close to the experimentally measured 4.44 V [9, 10].

However, even though the values of ASHEP depend on the interfacial water structure, the differences cancel out if an internal reference scale is used. Henceforth, when studying energetics of charge transfer reactions, we could model the simplest possible water structure (single water bilayer) with no concerns about the accuracy of the results.

Since the charge sets up the potential, a problem appears when protons (charge) are allowed to react. Proton discharge from the water layer changes the potential of the cell along the reaction coordinate, hindering any reliable determination of reaction energies. This problem is, in fact, an artifact of the small unit cell sizes used in the simulations, imposed by the computational limitations. In reality a proton transfer occurs over a large surface area which leaves the cell potential constant. To alleviate this constraint, we have successfully devised a method to extrapolate the energies to the limit where the potential does not change during a charge transfer reaction using a set of relatively small unit cell sizes. To prove the strength of our method we have subsequently applied it to modeling of hydrogen evolution/oxidation reactions [6], where we used the proposed scheme to treat the Volmer and Heyrovsky charge transfer steps.

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A Systematic Study of Gold Octamers on MgO(100) F-centers

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Gold has been studied extensively in a catalytic context since the pioneering work by Haruta et. al in the 1980s. Nanometric gold has been shown to exhibit a high catalytic activity in low temperature catalytic processes involving O-O, C-C and C-H bonds. Notably applications are in CO-oxidation, SO_2 removal and fuel cell technology.

Many explanations have been given for nanometric gold's high chemical activity [1-3]. Some of the key factors are support effects, low coordinated sites, quantum size effects and structural fluctionality. One system showing these four effects is Au-8 supported on an oxygen vacancy in MgO(100). In this system the support donates two electrons to the gold cluster thus making it able to weaken the bond of an adsorbed oxygen molecule and the cluster is so small that low coordinated edge/substrate sites dominates it. The supported cluster has furthermore been shown to exhibit a high structural fluctionality making it capable of accommodating many different types of species. Supported Au-8 has been shown to exhibit a high chemical activity but the theoretical predicted binding energies of O_2 have previously seemed too weak to explain the high activity.

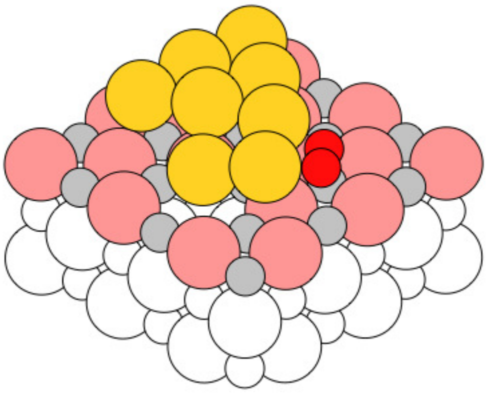

Figure 1 O_2 adsorption site at a very stable structure of Au8 adsorbed onto MgO(100) with an F-site.

In this work we present an automated genetic algorithm which searches for the most stable isomer of adsorbed clusters. We show how this algorithm makes it possible to find previously unreported structures of gold octamers supported on an oxygen vacancy in MgO(100). We further show how the use of a meta GGA can help elucidate the issue of 2D- or 3D-like structures on the surface and we present a correlation between the difference in binding energies as calculated with the PBE and M06-L functional and the structure of the adsorbed clusters.

[1] H. Häkkinen, S. Abbet, A. Sanchez, U. Heiz, and U. Landman, Angewandte Chemie (International ed. In English) 42, 1297 (2003).
[2] B. Yoon, H. Hakkinen, U. Landman, A. S. Worz, J.-M. Antonietti, S. Abbet, K. Judai, and U. Heiz, Science 307, 403 (2005).
[3] L. M. Molina and B. Hammer, Physical Review B 69, 155424+ (2004).

Optimizing xc-approximations for DFT surface chemistry studies: A Bayesian error estimation approach

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Abstract

Density functional theory (DFT) is today a main tool within theoretical catalysis and surface science. DFT using exchange-correlation (xc) functionals within the generalized gradient approximation (GGA) has proven to work well for describing strong interactions within molecules as well as between adsorbates and reactive surfaces. However, it is also widely agreed that GGAs fail to correctly account for the weeker but ubiquitous van der Waals (vdW) interactions. The vdW-DF [1] family of xc-functionals was designed to improve on this. Furthermore, recent work shows that it may be difficult to obtain high computational accuracy for different sorts of strongly interacting matter simultaneously, within a GGA framework. While certain popular GGA functionals appear accurate for solid-state properties such as lattice constants and surface energies (e.g. PBEsol, AM05) they provide severely overestimated chemisorption energies for simple molecules on surfaces, while the picture is turned around for other GGA xc-functionals (e.g. RPBE, BLYP) [1].

Using concepts from Bayesian statistics and databases of condensed matter quantities derived from high-level theory or experiments, we here apply a fitting procedure to the GGA and vdW-DF level of theory for design of exchange-correlation functionals which apply equally well for description of solid-state properties as for simulation of chemistry.

References

[1] D.C. Langreth *et al.*, J. Phys.: Condens. Matter **21**, 084203 (2009)
[2] G. Kresse *et al.*, Nature Materials **9**, (2010), p. 741

Trends and Origin of Stability in Perovskite Oxides

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In [Angew. Chem. Int. Ed. 2010, 49, 7699], the authors studied the trends in stability of perovskite oxides (ABO_3), with groups metals at A site, and 3d transition metals (Ti to Cu) at B site. In present paper, we extended B site cations to 5d transition metals. Besides the phenomena in [Angew. Chem. Int. Ed. 2010, 49, 7699], new phenomena were revealed from the comparison between 3d and 5d perovskites. Namely,
[1] Perovskites with a group of A site cations, and particular B site cation, have approximately constant stability;
[2] The linear relation between the stability and atomic number of B site cations;
[3] The higher (lower) oxidation states on A (B) site cations, the less slope and more stable perovskite oxides.
[4] For rare-earth and alkaline-earth metal at A site, 3d transition metals perovskite oxides are more stable than 5d transition metals perovskite oxides, while it is opposite for alkaline metal at A site and A site vacancy.

For the origin of above trends, we gave a full explanation basing on A-O and B-O interaction. We found that trend [1] and [3] in stability are related with the A-O interaction in ionic crystal, trend [2], [4] and [3] in slope are related with B-O interaction and the intrinsic nature in transition metals.

The above finding opens a way to estimate the stability of perovskites reasonably from calculation or available stability of relevant materials.

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PSI-K WORKSHOP FINANCE REPORT

Title of the Workshop	Catalysis from 1st Principles
Workshop Organisers	Thomas Bligaard, Karsten Reuter, Jürgen Hafner, Matthias Scheffler, Jens K. Nørskov
Location of the Workshop	Magleås Kursuscenter, Høsterkøbvej 6, 3460 Birkerød, Denmark
Dates of the Workshop	May 22-26, 2011
Total Grant from Psi-k	15.000 euros

EXPENDITURE

(Please complete the tables using numbers ONLY in the amounts fields - the spreadsheet will calculate the totals for you)

WORKSHOP DELEGATES / SPEAKERS			
Name and Country of Claimant	**Travel**	**Accommodation**	**Total (€'s)**
Karsten Reuter, Germany	€ 222.94	€ -	€ 222.94
Thomas Bligaard, USA	€ 819.73	€ -	€ 819.73
Bjørk Hammer, Denmark	€ 128.05	€ -	€ 128.05
			€ -
			€ -
			€ -
			€ -
			€ -
			€ -
			€ -
		Total Travel & Accommodation	**€ 1,170.72**

WORKSHOP REFRESHMENTS / CONFERENCE DINNERS			
Date	**Tea / Coffee**	**Lunch / Dinner**	**Total (€'s)**
Accommodation 22-26/5			€ 11,763.36
Meals 22-26/5			€ 20,557.06
			€ -
			€ -
			€ -
		Total Refreshments	**€ 32,320.42**

MISCELLANEOUS EXPENDITURE	
Details	**Total (€'s)**
Rent of posterboards	€ 453.02
Total Miscellaneous	**€ 453.02**

Total Travel & Accommodation	**€ 1,170.72**
Total Refreshments	**€ 32,320.42**
Total Miscellaneous	**€ 453.02**

TOTAL EXPENDITURE	**€ 33,944.16**