

Report on the Workshop
CATALYSIS FROM FIRST PRINCIPLES
Wien, May 25-28, 2009

The Working Group "Catalysis and Surface Science" of the Ψ_k -Network organizes a biannual series devoted to the discussion of recent progress and methodological advances in first-principles methods applied to catalysis, co-organized by Jürgen Hafner (Universität Wien), Jens Norskov (Technical University of Denmark) and Matthias Scheffler (Fritz-Haber Institute of the Max-Planck Gesellschaft). The sixth workshop in this series was held from May 25 to May 28, 2009 at the Erwin Schrödinger Institute (ESI) for Mathematical Physics in Wien. The workshop was sponsored by the Ψ_k -Network, the ESI, the Center for Computational Materials Science and the institutions of the organizers.

Topical sessions were devoted to the discussion of

- (A) Recent progress in density functional theory of solids - and beyond (invited speakers J.P. Perdew, B. Lundqvist, S. Grimme, G. Kresse, M. Fuchs)
- (B) Ab-initio calculations of free-energy barriers and reaction rates (C. Dellago, M. Parrinello, H. Metiu, T. Bucko, T. Bligaard)
- (C) Materials design (D. Morgan, F. Studt)
- (D) Catalysis by metals and metal-support interactions (G. Pacchioni, S. Piccinin, R. Grybos, P. Raybaud, A. Michaelides, A. Gross)
- (E) Electrocatalysis (M. Koper, J. Rossmeisl, S. Sugino)
- (F) Acid-based catalysis in zeolites and related materials (J. Sauer, L. Benco, R. Catlow, S. Bordiga)
- (G) Catalysis by oxides (R. Schlögl, F. Mittendorfer, C. Noguera, J. van Bokhoven, K. Reuter)

Abstracts of all invited presentations and of all contributed poster presentations are appended below.

Sessions A and B described recent progress in the methodology. Session A concentrated on the development of improved exchange-correlation functionals and on attempts to push the level of theory beyond density-functional methods, with the aim to achieve an improved description of weak "non-bonding" interactions (van-der-Waals forces, hydrogen bonds) by accounting for dynamical many-electron correlations. The presentations in Session B described current attempts to push the theoretical description of chemical reactions beyond the level of harmonic transition-state theory, using concepts such as Monte-Carlo based transition-path sampling and free-energy integrations using molecular dynamics simulations based on collective reaction-path variables. The contributions to Sessions C to G described the state of the art in key areas of catalysis research, from catalysis on metals and oxides over electrocatalysis to nanoporous systems (zeolites and metal-organic frameworks) and included a discussion of multi-scale simulation methods designed to bridge the gaps in the time-, pressure- and temperature-gaps between atomistic simulations and real-world experiments.

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Catalysis From First Principles

Wien, May 25-28, 2009, Austria

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A SEMILOCAL “WORKHORSE” DENSITY FUNCTIONAL FOR ATOMS, MOLECULES, AND SOLIDS

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The TPSS meta-generalized gradient approximation [1] was designed to be computationally efficient (semilocal) and applicable to a broad array of electronic systems. It gave accurate total energies, vibrational frequencies of molecules, atomization energies of molecules and surface energies for solids. However, it only slightly improved the too-long lattice constants of solids predicted by the standard PBE GGA [2]. Recently we proposed a PBEsol GGA [3] that restored the gradient expansion for exchange over a wide range of densities, and so improved lattice constants of solids while worsening atomization energies. Here we construct a revised TPSS [4] (revTPSS) meta-GGA that combines all the TPSS exact constraints with the new insight from PBEsol, and so gives good lattice constants, atomization energies, and surface energies.

[1] J. Tao, J.P. Perdew, V.N. Staroverov, and G.E. Scuseria, *Phys. Rev. Lett.* **91**, 146401 (2003).

[2] J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).

[3] J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, X. Zhou, O.A. Vydrov, G.E. Scuseria, and K. Burke, *Phys. Rev. Lett.* **100**, 136406 (2008).

[4] J.P. Perdew, A. Ruzsinszky, L.A. Constantin, and J. Sun, in preparation.

vdW-DF – A DENSITY FUNCTIONAL APPLIED TO STRONG AND WEAK BONDS

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Sparse matter is abundant and has both strong local bonds and weak nonbonding forces, in particular nonlocal van der Waals (vdW) forces between atoms separated by empty space. It encompasses a broad spectrum of systems, like soft matter, adsorption systems, and biostructures. Density-functional theory (DFT), since long proven successful for dense matter, seems now to have come to a point, where useful extensions to sparse matter are available. In particular, a functional form, vdW-DF [*Phys. Rev. Lett.* **92** (2004) 246401; *Phys. Rev. B*, **76** (2007) 125112], has been proposed for the nonlocal correlations between electrons. It has been applied to various relevant molecules and materials, including layered systems, like graphite and molybdenum sulfide, dimers of benzene, polycyclic aromatic hydrocarbons (PAH's), doped benzene, and DNA base pairs, nonbonding forces in molecules, like hydrogen bonds in water hexamers and DNA base-pair duplexes, to adsorbed molecules, like benzene, naphthalene, phenol, and adenine on graphite, alumina, and metals, polymer and carbon nanotube (CNT) crystals, and hydrogen storage in graphite and metal-organic frameworks (MOFs), and structure of DNA and of DNA with intercalators. Comparison with results from wave function calculations for the smaller systems and with

experimental data for the extended ones shows the vdW-DF path to be promising. This could have important ramifications.

STATUS AND PERSPECTIVES OF DOUBLE-HYBRID DENSITY FUNCTIONALS IN ELECTRONIC STRUCTURE THEORY

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In the double-hybrid density functionals (DHDF) [1] a virtual-orbital-dependent, second-order perturbative correlation energy replaces part of the semi-local GGA correlation contribution in a conventional hybrid density functional. In the most widely used B2PLYP method only two empirical mixing parameters for exact exchange ($a_x=0.53$) and this new non-local correlation part ($a_c=0.27$) are required. The talk addresses first the basic question about the accuracy of this approach for a wide variety of thermochemical benchmark sets and the computation of molecular structures[2] using analytical gradients. Extensions to describe the problematic van der Waals-type complexes (non-covalent interaction energies[3]) and to compute excited state properties (e.g. CD spectra[4]) in a time-dependent framework[5] are described. Various applications of B2PLYP and related functionals[6] also in electronically complicated situations are discussed. The most recent work on DHDF concerns the full optimization of all GGA parameters in the presence of non-local correlation[7] which marks some kind of accuracy limit of the present DHDF approach.

[1] Grimme, S.; J. Chem. Phys. 2006, **124**, 034108.

[2] Neese, F.; Grimme, S. J. Chem. Phys. 2007, **126**, 124115.

[3] Schwabe, T.; Grimme, S.; Phys. Chem. Chem. Phys. 2007, **9**, 3397-3406.

[4] Goerik, L.; Grimme, S.; J. Phys. Chem. A. 2009, **113**, 767-776.

[5] Grimme, S.; Neese, F.; J. Chem. Phys., 2007, **127**, 154116.

[6] Tarnopolsky, A; Karton, A.; Sertchook, R; Vuzman, D; Martin, J. M. L.; J. Phys. Chem. A, 2008, **112**, 3.

[7] Grimme, S.; to be published.

THE CO ADSORPTION PUZZLE: IS THERE A FINAL SOLUTION?

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The CO adsorption puzzle is representative of the fact that present gradient corrected functionals overestimate adsorption energies and predict wrong adsorption sites for many gas-surface reactions. Here, a study of the adsorption of CO on late *4d* and *5d* transition metal (111) surfaces (Ru, Rh, Pd, Ag, Os, Ir, and Pt) considering atop and hollow site adsorption is presented. The applied functionals include the gradient corrected PBE and BLYP functional, and the corresponding hybrid Hartree-Fock density functionals HSE and B3LYP. We find that PBE based hybrid functionals (specifically HSE) yield, with the exception of Pt, the correct site order on all considered metals, but they overestimate the adsorption energies compared to experiment even more than PBE. On the other hand, the

semi-local BLYP functional and the corresponding hybrid functional B3LYP yield very satisfactory adsorption energies and the correct adsorption site for all surfaces. We are thus faced with a Procrustean problem: the functionals that describe the solids best (PBE, HSE), yield inaccurate adsorption energies, whereas those that yield accurate adsorption energies (BLYP, B3LYP) fail to describe the solids [1].

Setting out from these observations, general conclusions are drawn on the relative merits and drawbacks of various semi-local and hybrid functionals. We conclude that no semi-local functional is capable to describe all aspects properly, and including a fixed fraction of non-local exchange also only improves some, but worsens other properties.

As a solution to this problem, we apply Green's function based techniques and evaluate the total energy using exact exchange complemented by the random phase approximation to the correlation energy [2]. We obtain excellent lattice constants for the solids, good adsorption energies across the series, and the correct adsorption site for all considered systems. Although the RPA is expensive, it seems to constitute a major step forward in obtaining accurate materials properties.

[1] A. Stroppa and G. Kresse, *New Journal of Physics* **10**, 063020 (2008).

[2] J. Harl and G. Kresse, *Phys. Rev. B* **77**, 045136-1–8 (2008).

TOWARDS A FIRST PRINCIPLES UNDERSTANDING OF WATER-SOLID INTERFACES

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There are few molecules, if any, more important than water. Yet remarkably little is known about how it interacts with solid surfaces, particularly at the molecular level. This is true despite widespread general interest and compelling environmental and economic incentives. For example, water-solid interactions play a crucial role in the activity of fuel cells, the chemistry of the troposphere, corrosion, catalysis, and so on. Here, some of our recent efforts to address this knowledge-gap and in so-doing obtain fundamental new insight in to the properties of water-solid interfaces will be discussed. Specific examples will include first principles molecular dynamics simulations of liquid-water salt interfaces, ice nucleation on metals, and the surface of ice. This will include a critical assessment of the ability of standard density functional exchange-correlation functionals to treat these and related processes.

PRESSURE INDUCED PHASE TRANSFORMATIONS OF NANOCRYSTALS STUDIED WITH TRANSITION PATH SAMPLING SIMULATIONS

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In a series of recent experiments, Alivisatos and coworkers demonstrated that the pressure-induced transition from the four-coordinate wurtzite structure to the six-coordinate rocksalt structure in CdSe nanocrystals is strongly influenced by crystal size. On a molecular time scale, the transition is a rare event and the resulting long time scales present a challenge for

computer simulations. I will discuss how the transition path sampling methodology provides a framework to address this time scale problem and to study the mechanism and the kinetics of this phase transformation at experimental conditions. From our simulation we obtain the preferred transformation pathway and determine activation enthalpies and volumes, which permit to make contact to experimental results.

FREE ENERGY CALCULATIONS WITH PATH COLLECTIVE VARIABLES

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The continuous increase in computational power and the improvement in the algorithms have allowed ever larger systems to be simulated for longer times. Still the reachable time scales fall short of the physical time scale of many relevant phenomena. Particularly challenging are those cases, often encountered in biology, in which entropy plays a major role. In this context it is more appropriate to consider the free energy rather than the potential energy surface. This poses two problems, one to define a set of descriptors able to describe the ensemble of microstates that characterize the system, the second is the need of finding methods that can quantitatively reconstruct the free energy as a function of these variables. Once computed this surface gives information on the metastable states of the system and can be used to reconstruct a posteriori the system dynamics. It is therefore not surprising that a number of methods have been proposed to estimate the free energy surface. Since a standard evaluation of the free energy surface would be too costly these methods are based on some form of enhanced sampling that allows overcoming the large free energy barriers of the system in a limited computational time^[1;2;3;4].

Unfortunately such descriptors are not a priori known and are hard to find since they should be flexible enough to simulate complex events that might take place in several different ways^[5;6]. Let us first consider the situation in which we want to study the transition between an assigned initial and final state. To this effect we introduce two variables one which describes the progression along a guessed path and the other the distance from the path. Paralleling what is done in the nudged elastic band^[5] or in the finite temperature string method^[6] we introduce ways of improving systematically the quality of the guessed path. However the introduction of the second variable^[7] offers the unique possibility of finding paths very different from the initial guess. The performance of the method will be gauged on the standard test case of an alanine dipeptide in vacuum as well as on much more realistic and challenging cases. In addition we shall discuss a recent extension which is inspired by the dimer method^[8]. Not only this new method is capable of exploring the often complex network of reactive pathways but it also lends itself to a suitable dimensional reduction procedure leading to a concise and illuminating characterization of the system.

References:

[1] B. Roux, „The calculation of the potential of mean force using computer simulations”, *Computer Physics Communications*, v. **91**, p. 275-282, 1995.

[2] F. Wang, D.P. Landau, „Efficient, multiple-range random walk algorithm to calculate the density of state”, *Physical Review Letters*, v. **86**(10), 2050-2053, 2001.

[3] E. Darve, A. Pohorille, “Calculating free energies using average force”, *the Journal of Chemical Physics*, v. **115**(20), p. 9169-9183, 2001.

[4] A. Laio, M. Parrinello, „Escaping free-energy minima”, *Proceedings of the National Academy of the United States of America*, v. **99**(20), p. 12562-12566, 2002.

[5] G. Henkelman, H. Jónnson, „Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points”, *the Journal of Chemical Physics*, v. **113**(22), p. 9978-9985, 2000.

[6] W. E, W. Ren, E. Vanden-Eijnden „Finite temperature string method for the study of rare events”, *the Journal of Physical Chemistry B*, v. **109**, p. 6688-6693, 2005.

[7] D. Branduardi, F.L. Gervasio, M. Parrinello, „From A to B in free energy space”, *the Journal of Chemical Physics*, v. **126**(5), p. 054103, 2007.

[8] G. Henkelman, H. Jónnson, „A dimer method for finding saddle points on high dimensional potential surfaces using only first derivatives”, *the Journal of Chemical Physics*, v. **111**, p. 7010, 1999.

CATALYST ACTIVATION BY MOLECULA SIZED CENTERS

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We examine to what extent we can increase the activity and the selectivity of oxide catalysts by creating on their surface moleculesized centers chosen to disrupt the chemical bonding at the surface. One such disruption is caused by substitutional doping of a fraction of the cations on the oxide surface with other cations. The dopant can induce the following modificationa:

1. It activates the surface oxygen atoms nearby to make the oxide a better oxidant. 2. It adsorbs an O₂ molecule from the gas-phase and activates it; 3. The dopant and a surface oxygen atom nearby are both activated, helping the dissociative adsorption of molecules; 4. The dopant takes an oxygen atoms from the oxide surface to form an active oxidation center. Another “disruption” is achieved by depositing oxide clusters on an oxide support. We examined how supported molybdenum, vanadium, or chromium oxide clusters break the C-H bond during the oxidation of methanol to formaldehyde.

ROLE OF THE THERMAL AND ENTROPY EFFECT IN ALKANE CONVERSION REACTIONS CATALYZED BY ACIDIC ZEOLITES.

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Proton exchanged zeolites are important catalysts in hydrocarbon conversion reactions such as isomerization, cracking, and alkylation. In order to understand elementary steps in these complicated processes, simple prototype reactions are frequently investigated both experimentally and theoretically. In our DFT simulations, we studied proton exchange, protolytic cracking, and dehydrogenation of short alkanes over acidic chabazite. In the first step of each reaction, weakly bound adsorption complexes between alkane and active site are created. As the reaction proceeds, the mobility of reaction intermediates changes along with the interaction strength giving rise to substantial entropy/thermal contribution to the free-energy reaction barrier. We will show that accurate treatment of entropy is crucial for correct description of mechanisms of alkane conversion reactions.

FREE ENERGY TRENDS FROM LINEAR ADSORTION ENERGY RELATIONS

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The development of computational design methodologies for new materials with tailored properties has been a long-standing goal in the electronic structure community.

Computational design case stories have started to appear, and a perhaps surprisingly large fraction of these are from the heterogeneous catalysis field. This could stem from the fact that the synthesis methods of heterogeneous catalysts are quite advanced, there are many materials parameters that can be varied, and the link from the electronic structure/atomic-scale description of the materials to the qualities that a good catalyst must possess is relatively clear. Often, high activity is an important property of a catalyst, and the activity can be estimated from knowledge of the free energy diagram of the reaction pathway. Based on the modern understanding of linear energy relations of adsorbed intermediates and transition state structures it is shown how reliable free energy diagrams can be established using a very limited amount of computational data as input. This allows the determination of activity trends through either microkinetic modelling or conceptual kinetic trend modeling such as the Sabatier Analysis or the Sabatier-Gibbs Analysis, which will be discussed. The linear energy relation-based free energy diagrams can also be used to derive a Le Chatelier-like principle and coverage conservation laws governing the adsorption properties of the optimal catalyst under varying conditions for reactions with a single rate-determining step.

AB-INITIO MODELING OF SOLID OXIDE FUEL CELL CATHODES

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Perovskites are the major class of materials used for modern solid oxide fuel cell (SOFC) cathodes and have the ability to catalyze the oxygen reduction reaction (ORR) on their surfaces. However, difficulties in performing in-situ characterization of well-controlled samples means that the rate limiting steps and structure-property relationships underlying ORR on these materials are not understood. In this talk we will discuss some of the challenges and opportunities associated with using ab-initio techniques to study ORR on SOFC materials. We have used ab-initio based thermokinetic modeling to study (La,Sr)MnO₃ (LSM), which is the primary cathode catalyst used in commercial SOFCs. We have developed a combined bulk and surface defect model in order to better understand surface defect structure and transport. We have also studied lanthanum transition metal oxides LaBO₃ (B=3D Mn, Fe, Co, and Ni) to identify trends in surface oxygen binding, hopping, vacancy formation, and dissociation vs. transition metal types. We use these trends to discuss a possible descriptor for the ORR on SOFC catalysts.

CORE-SHELL NANOPARTICLES FOR PREFERENTIAL OXIDATION OF CO IN H₂

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Most of the world's hydrogen supply is currently obtained by reforming hydrocarbons. 'Reformate' hydrogen contains significant quantities of CO that poison current hydrogen fuel-cell devices. Catalysts are needed to remove CO from hydrogen through selective oxidation. Here, we report a first-principles-based screening, identification, and synthesis of a nanoparticle catalyst comprising a Ru core covered with an approximately 12-monolayer-thick shell of Pt atoms. The distinct catalytic properties of these well-characterized coreshell

nanoparticles were demonstrated for preferential CO oxidation in hydrogen feeds and subsequent hydrogen light-off. For H₂ streams containing 1,000 p.p.m. CO, H₂ light-off is complete by 30 C, which is significantly better than for traditional PtRu nano-alloys (85 C), monometallic mixtures of nanoparticles (93 C) and pure Pt particles (170 C). Density functional theory studies suggest that the enhanced catalytic activity for the core-shell nanoparticle originates from a combination of an increased availability of CO-free Pt surface sites on the Ru@Pt nanoparticles and a hydrogen-mediated low-temperature CO oxidation process that is clearly distinct from the traditional bifunctional CO oxidation mechanism¹.

References:

1. S. Alayoglu, A. U. Nilekar, M. Mavrikakis, B. Eichhorn, Ru@Pt Core-Shell Nanocatalysts For Enhanced CO-Tolerant Catalytic Hydrogen Activation, *Nature Mater.* 2008, **7**, 333.

RATIONAL CATALYST DESIGN APPLIED TO THE SELECTIVE HYDROGENATION OF ACETYLENE

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It has long been the ambition of research in heterogeneous catalysis and in surface science to develop methods that would allow the design of catalysts on the basis of insight. In particular, it would be desirable if one could use quantum chemical methods to perform a first screening of possible catalysts for a given reaction. We introduced a new catalyst screening strategy which allows us to use a single descriptor to obtain an overview of reactivity trends. We illustrate the approach by applying it to the identification of new interesting catalysts for the selective hydrogenation of acetylene. Density functional theory calculations were performed that identified relations of heats of adsorption of hydrocarbon molecules and fragments on metal surfaces. This analysis not only verified the facility of known catalysts but identified Ni-Zn alloys as alternatives.¹

1. F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, J. K. Nørskov, *Science* 2008, **320**, 1320.

MODIFYING THE ADSORPTION PROPERTIES OF OXIDE ULTRATHIN FILMS VIA WORK FUNCTION CONTROL

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Ultrathin oxide films supported on a metal single crystal can exhibit unusual and unprecedented properties which have no counterparts in the corresponding bulk surfaces [1-10]. In this talk we will analyze the physical reasons which can lead to charge exchange between adsorbed species and the supporting metal through the thin dielectric layer. In particular, we will focus on the changes in work function of the system which occur when an oxide film is deposited on a metal support and we will consider possible ways to tune the work function so as to induce charge transfers also in those cases where this does not occur

spontaneously. We will present in fact cases where adsorbed species become negatively charged (e.g. Au on MgO/Ag), positively charged (e.g. Au on FeO/Pt) or remain neutral (e.g. Au on SiO₂/Mo(112)) because of the different position of the Fermi level in the oxide/metal support, and we will discuss methods to modify these interfaces. In particular, we will show that this can be obtained by co-deposition of alkali atoms, and examples of this effect will be reported for Li-doped SiO₂/Mo(112) films. Finally, we will show that the occurrence of a charge transfer across the interface can also be used to enhance the magnetic moments of supported Fe clusters.

- 1) G. Pacchioni, L. Giordano, M. Baistrocchi, "Charging of metal atoms on ultra-thin MgO/Mo(100) films", *Physical Review Letters*, **94**, 226104-4 (2005).
- 2) D. Ricci, A. Bongiorno, G. Pacchioni, U. Landman, "Bonding trends and dimensionality crossover of gold nanoclusters on metal-supported MgO thin films", *Physical Review Letters*, **97**, 036106-4 (2006).
- 3) M. Sterrer, T. Risse, U. Martinez Pozzoni, L. Giordano, M. Heyde, H.-P. Rust, G. Pacchioni, H.-J. Freund, "Control of the charge state of metal atoms on thin MgO films", *Physical Review Letters*, **98**, 096107-4 (2007).
- 4) V. Simic-Milosevic, M. Heyde, N. Nilius, T. König, H.-P. Rust, M. Sterrer, T. Risse, H.-J. Freund, L. Giordano, G. Pacchioni, "Au dimers on thin MgO(001) films: flat and charged or upright and neutral?", *J. American Chemical Society*, **130**, 7814-7815 (2008).
- 5) L. Giordano, G. Pacchioni, J. Goniakowski, N. Nilius, E. D. L. Rienks, H. J. Freund, "Charging of metal adatoms on ultrathin oxide films: Au and Pd on FeO/Pt(111)", *Physical Review Letters*, **101**, 026102-1/4 (2008).
- 6) S. Ulrich, N. Nilius, H.-J. Freund, U. Martinez, L. Giordano, G. Pacchioni, "Evidence for a size-selective adsorption mechanism on oxide surfaces: Pd and Au atoms on SiO₂/Mo(112)", *ChemPhysChem*, **9**, 1367-1370 (2008).
- 7) H. J. Freund, G. Pacchioni, "Oxide ultra-thin films on metals: new materials for the design of supported metal catalysts", *Chemical Society Reviews*, **37**, 2224-2242 (2008).
- 8) S. Prada, U. Martinez, G. Pacchioni, "Work function changes induced by deposition of ultrathin dielectric films on metals: a theoretical analysis", *Physical Review B*, **78**, 235423-1/8 (2008).
- 9) V. Simic-Milosevic, M. Heyde, X. Lin, T. König, H.-P. Rust, M. Sterrer, T. Risse, N. Nilius, H.-J. Freund, L. Giordano, G. Pacchioni, "Charge-induced formation of linear Au clusters on thin MgO films", *Physical Review B*, **78**, 235429 (2008).
- 10) S. Ulrich, N. Nilius, H. J. Freund, U. Martinez, L. Giordano, G. Pacchioni, "Modifying the adsorption characteristics of inert silica films by inserting anchoring sites", *Physical Review Letters*, **102**, 016102/1-4 (2009).

THE SYSTEM CHEMISTRY OF AN ALLOY CATALYST INSIGHT FROM DFT CALCULATIONS

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Ag-Cu alloys have been proposed as catalysts for ethylene epoxidation due to their superior selectivity compared to pure silver, the predominant catalyst for this reaction. By means of density-functional theory, together with concepts from atomistic thermodynamics, we study the surface structure of Ag-Cu particles in thermodynamic equilibrium with an oxygen atmosphere. We find that at temperature and pressure of interest for practical applications the particles can display a variety of surface structures, including thin oxide-like structures. We model the ethylene epoxidation reaction on the most relevant surface structures, identifying the minimum energy path, the transition state and the activation energy. We find that the reaction mechanism is structure-dependent and often the reaction does not proceed through the formation of an oxametallacycle intermediate, at variance with the case of pure silver.

Based on the proposed mechanism, we discuss show how Ag-Cu alloys can improve selectivity of the process compared to pure Ag.

SELECTIVE CATALYTIC REDUCTION OF NO BY CH₄ ON Pd-EXCHANGED MORDENITE PERIODIC DFT SIMULATIONS

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Removal of nitrogen oxides from exhaust gases of internal combustion engines is becoming a pressing matter since more and more stringent regulations are being employed in EU and US. Currently, technologies which use ammonia or urea as a reducing agent are being implemented (e.g. BlueTec by Mercedes), but are highly impractical and cumbersome for regular vehicle users. Therefore an effort is made to find catalysts which could use hydrocarbons for NO_x reduction. Noble metals embedded in zeolites are very promising for this task, although the zeolite framework tends to collapse when too much water vapor is present in the exhaust stream. One of the most stable and active systems found is palladium in mordenite (Pd-MOR). Shimizo et al. [1] proposed a mechanism of NO reduction by methane on Pd-MOR. It is, however, rather unclear. At one point it requires two Pd²⁺ sites in close vicinity, for the reaction between adsorbed NO and CH_x. It is rather unlikely, given low Pd concentration in the working catalyst (ca. 1.5 wt%), unless Pd²⁺-NO or Pd²⁺-CH_x species are able to effectively move in the zeolite channels. Indeed, calculations have shown that adsorption of NO considerably weakens the Pd-zeolite bonding. There is also a possibility that palladium species are not in fact Pd²⁺ but adsorption sites on a palladium cluster. This, however, would go against the widely accepted notion that it is the dispersed Pd²⁺ cations that constitute the reaction sites.

In this work we will show a systematic approach to solving the catalyst structure and elementary reaction mechanisms by first principles methods - the periodic DFT. The Al/Si ratio of 11 was assumed, what coincides with two substitutions per monoclinic primitive supercell used in the study. Calculations showed no clear preference of Al for any particular tetrahedral site - from the thermodynamic point of view the Al distribution should be uniform. The stability of ion-exchanged Pd²⁺ cations is closely related to the number of bonds between palladium and "activated" oxygen atoms - the ones directly connected to Al sites. The number of Al sites in the vicinity plays a secondary role. There is also a reverse relationship between the stability of the Pd²⁺ cation itself and its NO adsorption capacity - more stable cations exhibit smaller adsorption energies. Therefore a wide range of different Pd sites in mordenite should be expected: a large number of thermodynamically stable sites which adsorb and thus activate NO rather weakly, and a few less stable sites, which compensate for their number with increased activity. Calculated N-O bond vibrations correlate well with the experimental spectra and support the existence of many different Pd²⁺ sites.

In the course of the reaction, palladium cations undergo sintering and create palladium clusters of varying size. Their stability and reactivity is governed by a rather complicated interaction of several aspects: the geometry of the cluster and the zeolite wall, electron transfer between cluster, zeolite and the adsorbate, and orbital rehybridization upon adsorption of NO or CH_x. All interactions are extensively studied for clusters in mordenite and in the gas phase.

[1] K. Shimizu, F. Okada, Y. Nakamura, A. Satsuma and T. Hattori, J. Catal. 195 (2000) 151

EFFECT OF γ -ALUMINA ACIDITY ON THE STABILITY OF METALLIC NANOPARTICLES

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The determination and control of oxide supported metallic nano-aggregates morphologies represent challenging questions for numerous applications in heterogeneous catalysis and photocatalysis.

Using density functional theory calculations, we firstly present a comprehensive investigation of the structural trends of low dimensional late 4d (from Tc to Ag) and 5d (from Re to Au) transition metal systems including 13-atom clusters. Energetically favorable clusters not being reported previously are discovered by molecular dynamics simulation based on the simulated annealing method [1]. They allow a better agreement between experiments and theory for their magnetic properties. The structural periodic trend exhibits a non monotonic variation of the ratio of square to triangular facets for the two rows, with a maximum for Rh₁₃ and Ir₁₃. In contrast, for Pd₁₃ and Pt₁₃ clusters, the stable structures tend to maximize the triangular facets.

In a second step, we show how the interaction with the γ -alumina surfaces influences the stability Pd₁₃ and Pt₁₃ clusters morphologies. In particular, the hydroxylation state of the γ -alumina (110) surface modifies the adhesion energy of the metallic particles and changes their wetting properties [2]. In the same spirit as highlighted in previous theoretical works [3], the presence of hydroxyl groups decrease significantly the metal-support interaction. As a result, the metallic particles deposited on hydroxylated surfaces behave similarly as isolated particles regarding their stable morphologies and adsorption properties, whereas in absence of hydroxyls the stronger metal-support interaction modify these properties.

Since the nature of hydroxyl groups depends directly on the Brønsted acidic properties of the γ -alumina, we finally illustrate how it is possible to tune the Brønsted acidity of the γ -alumina surface either by chlorine doping [4] or by amorphization induced by contacting with silica [5].

- [1] C.H. Hu, C. Chizallet, H. Toulhoat, P. Raybaud, Phys. Rev. B (in press).
- [2] C.H. Hu, M. Corral-Valero, P. Sautet, H. Toulhoat, P. Raybaud (in preparation).
- [3] M. Corral Valero, P. Raybaud and P. Sautet, Phys. Rev. B 75 (2007) 045427.
- [4] M. Digne, P. Raybaud, P. Sautet, D. Guillaume, M. Digne, J. Am. Chem. Soc. 130 (2008) 11030.
- [5] C. Chizallet, P. Raybaud, Angew. Chemie Int. Ed. 48 (2009) 2891.

HALOGEN-INDUCED CORROSION PLATINUM

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Halogens are commonly used to initiate changes on platinum surfaces for the preparation of catalysis and serve as platinum mobilizer in both deposition and corrosion or etching processes. By means of a combined experimental (STM&LEED) and theoretical (DFT)

analysis we have studied halogen-platinum interactions by depositing bromine and chlorine on Pt(110). Although bromine did not attack the surface, platinum atoms could be extracted by chlorine on heating. This led to the self-assembly of PtCl₄ clusters and the formation of a long-range-ordered mixed Cl-PtCl₄ adsorbed layer, almost identical to that formed by depositing PtCl₄ units from an electrolyte solution on gold surface (100). Furthermore, co-adsorption of less reactive species is observed to promote corrosion by converting chlorine in PtCl₄, thus indicating that the highly ordered Cl/PtCl₄/metal system reported here is a universal transition state in both erosion and deposition.

E. Dona, M. Cordin, C. Deisl, E. Bertel, C. Franchini, R. Zucca, J. Redinger; *J. Am. Chem. Soc.* 131 (8), 2827 (2009).

TOWARDS AN EXACT TREATMENT OF EXCHANGE-CORRELATION IN MATERIALS

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Electronic structure and total energy calculations play a central role in the theoretical analysis, understanding, and modeling of materials and their properties. Density-functional theory (DFT) has proven to be a powerful technique for such calculations. The main limitation of this approach is the approximation used to describe many-electron exchange-correlation (XC). State-of-the-art local-density and gradient-corrected XC functionals (LDA and GGA) are often usefully accurate, but they are not as good for certain types of interactions or properties, examples being strong correlation, London dispersion forces, and excited states. Thus, checking and improving the description of XC remains an important theme in the field. Yet this still poses challenges when complex or extended systems are considered, say defects in the bulk and at surfaces. Definite experimental data are often scarce and, unlike for molecular systems, accurate theoretical reference data are not readily, if at all, obtained from advanced DFT-XC functionals (examples being hybrid functionals and the random phase approximation) or correlated quantum chemistry methods. Here, I discuss a cluster correction approach to describe XC of extended systems beyond the LDA and GGA [1]. Applications to different problematic systems (including transition metal surfaces, CO adsorption) demonstrate the nature of some of the limitations of present-day XC functionals and illustrate how they may be systematically corrected.

Work with A. Soon, B. Li, X. Ren, P. Rinke, and M. Scheffler.

[1] Q.-M. Hu, K. Reuter, and M. Scheffler, *Phys. Rev. Lett.* **98**, 176103 (2007); *ibid.* **99**, 169903 (2007).

REACTION STEPS IN C1 CHEMISTRY ON METAL SURFACES STUDIED FROM FIRST PRINCIPLES

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The interaction of methanol with Cu(110) has served as a benchmark system for the study of the catalytic oxidation and synthesis of methanol. Using density functional theory together with transition state theory and kinetic Monte Carlo simulations we addressed the partial and

total oxidation on clean and oxygen-covered Cu(110) [1-3]. These studies demonstrated the important role of different oxygen species in the single reaction steps and provided a rather complete picture of the total oxidation. We have now extended this work and addressed the synthesis of methanol from CO₂ on Cu(110) under hydrogen exposure. We find that a correlated reaction mechanism not only lowers the barriers but also avoids the formation of volatile reaction intermediates.

Methanol oxidation is also of importance in electrocatalysis. Furthermore, a correlated reaction mechanism was identified as well in the methanol oxidation on water-covered Pt(111) [4]. We will therefore present our first steps addressing the solid-liquid interface from first principles.

References

- [1] S. Sakong and A. Groß, *J. Catal.* **231**, 420 (2005).
- [2] C. Sendner, S. Sakong, and A. Groß, *Surf. Sci.* **600**, 3258 (2006).
- [3] S. Sakong and A. Groß, *J. Phys. Chem. A* **111**, 8814 (2007).
- [4] C. Hartnig and E. Spohr, *Chem. Phys.* **319**, 185 (2005).

THEORY AND EXPERIMENT OF THE ELECTROCHEMICAL CO OXIDATION

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The mechanism of the electrochemical oxidation of CO is discussed for both platinum and gold single-crystalline electrodes. Whereas the CO oxidation appears self-poisoning on Pt, by inhibiting the adsorption of the OH oxidant, in agreement with theory and the observed non-linear behavior, on gold the electrochemical oxidation appears self-promoting, by enhancing the adsorption of the OH oxidant, as also confirmed by DFT calculations. Furthermore, it is found that there are important differences between acidic and alkaline media, which we will attempt to relate to the different electrochemical potential in the two different media. The implications of these findings for other electrocatalytic reactions will be discussed.

SEARCHING FOR ELECTRO-CATALYST MATERIALS FOR OXYGEN REDUCTION REACTION.

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Ab-initio simulations on electrocatalytic reactions have developed rapidly within the last five years. However, the number of new electrode materials designed directly from ab initio calculations is still limited, due to the complexity of the reaction. The first task is to obtain an understanding of reaction mechanisms at the atomic level. The aim is to find the descriptors that determine the catalytic properties of the material and that are easily calculated applying density functional theory simulations. The descriptor analysis provides, linked with stability estimations, a basis for searching for new electrocatalysts. I will show an example for oxygen reduction reaction, where a new type of catalyst materials is suggested based on the approach and subsequently tested in experiments.

A COMBINED DYNAMICAL AND STATIC APPROACH TO ELECTROCATALYSIS

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The fuel cell reactions occur catalyzed on the electrode and interfaced by acid or alkaline solution. The bias and solution effects make these electrocatalytic reactions distinct from catalytic reactions that occur under the vacuum condition, and therefore theoretical tools should take them into account. It is important to model both the electrode and the solution sides equally accurately. In this regard, we have developed a first-principles molecular dynamics approach to handle the biased, and therefore electrified, electrode/solution interface. With our novel approach, called effective screening medium (ESM) [1], we have described the electrode dynamics where a hydronium ion H_3O^+ in the liquid water is combined with excess surface electron of Pt(111) and is adsorbed on the surface as a neutral species $H(ad)$, that is the Volmer step of the hydrogen evolution reaction [2]. The ESM approach is effective in characterizing the electric double layer in terms of the structure of the water molecules and the reaction dynamics in terms of the dynamic response of the water at the contact layer [2,3]. We will show in detail the electrocatalysis focusing on solution side of the interface. All the electrochemical reactions do not necessarily occur on the ground state, but there are reactions where the excited states are concerned. Theoretical approach should also take the nonadiabatic dynamics into account, although such has not been established thus far. As a step towards the goal, we have recently developed a density functional scheme to compute the nonadiabatic couplings (NACs) [4], and demonstrated a full quantum and a surface hopping simulation of the photo-isomerization dynamics of a small molecule [5] where no approximations are introduced to the electrons except for the adiabatic and local approximations (ALDA). On those bases we will discuss future prospect of the catalyst research.

[1] M. Otani and O. Sugino: Phys. Rev. B 73 (2006) 115407. [2] M. Otani, I. Hamada, O. Sugino, Y. Morikawa, T. Ikeshoji, and Y. Okamoto: J. Phys. Soc. Jpn. 77 (2008) 024802. [3] M. Otani, I. Hamada, O. Sugino, Y. Morikawa, T. Ikeshoji, and Y. Okamoto: Phys. Chem. Chem. Phys. 10 (2008) 3609. [4] C.P. Hu, H. Hirai, and O. Sugino, J. Chem. Phys. 127 (2007) 064103. [5] H. Hirai and O. Sugino, now available on line in Phys. Chem. Chem. Phys.

ADSORPTION AND REACTION STEPS IN NANO-POROUS SYSTEMS – ACCURATE PREDICTION BY QUANTUM CHEMISTRY AND MOLECULAR STATISTICS

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Accurate quantum chemical predictions of adsorption and reaction steps for nanoporous systems such as metal-organic frameworks (MOF) and zeolites are limited by the inability of currently used density functionals to properly account for dispersion interactions. We employ a hybrid approach which combines MP2 calculations for the

reaction site with DFT calculations for a large system under periodic boundary conditions [1] and apply it to catalytic hydrocarbon reactions in zeolites [2], adsorption of CH₄ on MgO surfaces, and adsorption of H₂ in metal-organic frameworks [3]. For the latter case, adsorption isotherms are predicted by a multi Langmuir model.

1. C. Tuma, J. Sauer, Phys. Chem. Chem. Phys. **8**, 3955 (2006).
2. S. Svelle, C. Tuma, X. Rozanska, T. Kerber, J. Sauer, J. Am. Chem. Soc. **131**, 816 (2009).
3. K. Sillar, A. Hofmann, J. Sauer, J. Am. Chem. Soc. **131**, 4143 (2009).

ACTIVITY AND REACTIVITY OF Fe²⁺ CATIONS IN THE ZEOLITE. AB INITIO FREE-ENERGY MD SIMULATION

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Dynamic conditions of the reaction in a zeolite can lead to a redistribution of extra-framework cations thus changing their adsorption and reaction properties. First-principles periodic calculations are used to investigate the stability and adsorption properties of the bivalent Fe²⁺ cation exchanged into ferrierite. The reactivity of cations is inspected via the temperature-dependent molecular dynamics (MD) simulation of the N₂O dissociation. With the increase of the cell volume an increase of flexibility of the zeolite framework is observed allowing local deformations. Depending on the stability of the configuration a large variation of the adsorption energy is observed ($E_{\text{ads}} = 4 \text{ - } 50 \text{ kJ/mol}$) but only a small variation of the activation energy ($E_{\text{a}} = 40 \text{ - } 50 \text{ kJ/mol}$) and the reaction rate ($\ln A = 0.9 \times 10^{14} \text{ - } 1.8 \times 10^{14}$) of the N₂O dissociation. Dynamic conditions of the reaction in a zeolite leading to a redistribution of extra-framework cations can cause a variation of adsorption properties of active sites. This variation, however, exhibits only small influence on reaction properties of cations.

VIBRATIONAL SPECTROSCOPIES TO DESCRIBE ACID-BASED REACTIVITY IN MICROPOROUS MATERIALS

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Microporous solid acid are deeply investigated by combined use of spectroscopies and molecular modelling by considering their response to both probe molecules and reactants.

As far as probe molecules, for both Lewis and Brønsted sites, CO is one of the most widely used probe. More recently hydrogen attracts much attention because of its numerous advantages as probe. In fact: (i) its small dimension should, in principle, allow penetration in the narrowest pores of solids; (ii) the H₂ $\nu(\text{HH})$ mode is only Raman active and any perturbation associated with the adsorption process leads to IR activity; (iii) small perturbations of the single H-H bond induced by the interaction with surface centers leads to shifts of the $\nu(\text{HH})$ stretching vibration band larger than those observed for the stretching bands of probes containing multiple bonds (N₂, O₂, CO) [1]. A limitation is usually represented by the very low interaction energy with adsorbing centers, a fact which requires very low T to achieve reasonable H₂ coverages [2-6]. As for microporous materials are concerned it is worth noticing that at temperature as low as 20 K, cavities and channels become

filled by condensed H₂, and this offers the opportunity to study the vibrational properties of a condensed phase of H₂ entrapped in restricted spaces.

Infrared spectroscopy has been also widely used to follow the reactivities towards a large variety of hydrocarbon in order to help the understanding of the related reaction mechanisms [7,8]. Also in this case the combined use of controlled temperature and pressure set up were the key points to allow the recognition of different reaction steps that sometimes have been also subjects of molecular modelling calculations [9].

1) E.N. Gribov, D. Cocina, G. Spoto, S. Bordiga, G. Ricchiardi and A. Zecchina, *PCCP*, 2006, **8**, 1186

2) S. Kotrel, J. H. Lunsford and H. Knozinger, *J. Phys. Chem. B*, 2001, **105**, 3917.

3) V. B. Kazansky, *J. Mol. Catal. A: Chemical*, 1999, **141**, 83.

4) S. Bordiga, G. Turnes-Palomino, C. Paze and A. Zecchina, *Microp. Mesop. Mater.*, 2000, **34**, 67.

5) A. Zecchina, S. Bordiga, J.G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjørgen, K.P. Lillerud *J. Am. Chem. Soc.* 2005, **127**, 6361

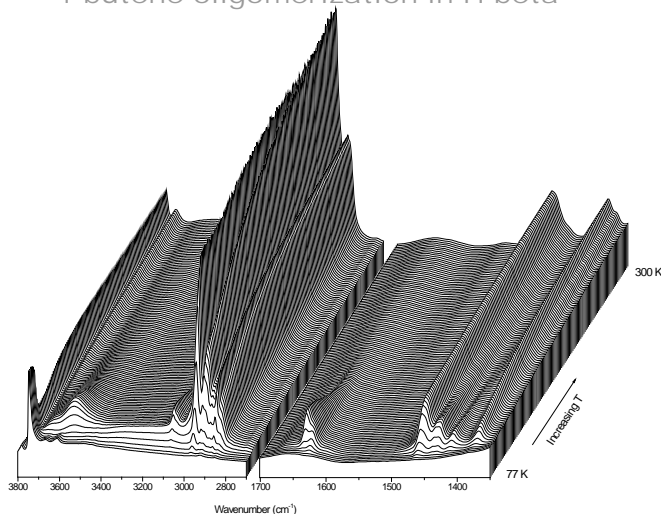
6) Vitillo, J. G.; Regli, L.; Chavan, S.; Ricchiardi, G.; Spoto, G.; Dietzel, P. D. C.; Bordiga, S.; Zecchina, A. *J. Am. Chem. Soc.* 2008, **130**, 8386–8396

7) M. Bjørgen, F. Bonino, S. Kolboe, K.P. Lillerud, A. Zecchina, S. Bordiga *J. Am. Chem. Soc.* 2003, **125**, 15863.

8) M. Bjørgen, K.P. Lillerud, U. Olsbye, S. Bordiga and A. Zecchina, *J. Phys. Chem. B* 2004, **108**, 7862

9) J. Hafner, L. Benco and T. Bučko, *Topic in Catalysis*, 2006, **37**, 41

1-butene oligomerization in H-beta



SIMPLE AND COMPLEX OXIDES IN SELECTIVE OXIDATION REACTIONS

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The oxidation of unfunctionalized alkanes is a critical step to produce all monomers for chemical industry in the near and distant future when oil-refining processes are no longer possible. Today, these reactions are in some cases not possible and in some cases operate with poor yields leading to enormous wastes of chemicals and energy and respective carbon footprints.

The common origin of these shortcomings is our lack of ability to control the reactivity of oxygen in the presence of hard-to-activate substrates. In addition, in all relevant reactions the products are thermodynamically less stable than the educts posing additional constraints on the reactivity of the catalyst.

Besides possible novel designs of catalytic reactors enabling a more even profile of the chemical potential throughout the active mass it is most relevant to understand without critical simplifications the mode of operation of the catalyst. At present we operate with a set

of empirical rules referred to as „pillars of selective oxidation“ that lack, however physical foundation.

In this context it turns out that simple oxides such as vanadia or complex oxides such as MoVWNBTeO_x are not discriminated in their accessibility to the functional part of their surface. All of these catalysts provide enormous challenges in synthesis operation and functional characterisation. The support of surface science models is very useful but mostly limited as they do not provide the necessary functionality when they are well ordered in their structure.

It will be demonstrated that a concept of adaptive sites being part of a cluster-like surface termination of active materials can provide a unified structural concept towards understanding selective oxidation. After all, most of these reactions are combination of C-H activation and oxygen transfer for which similar elementary steps should operate. This concept was derived from a synopsis of model studies and in-situ functional analysis. The role of solid-state chemistry driving the expression of the active sites under reaction conditions will be highlighted.

COMPUTER MODELLING OF ACTIVE SITES IN MICROPOROUS MATERIALS

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The catalytic action of microporous materials (zeolites and ALPOs) is due to the presence of acid or metal sites. This lecture will describe how the structures, properties, reactivities and formation mechanisms of such centres can be investigated in detail using a range of electronic structure techniques. We will show how, in addition to the conventional Bronsted and centre, reaction of water with zeolites can generate a fascinating range of hydrogen containing defect centres. We will also describe modelling of metal centres based on transition metal substitutionals in framework sites, with strong emphasis on microporous titanosilicate catalysts, where we will again show that reaction with water can create a range of sites which play important roles in catalytic processes.

LOW DIMENSIONAL SURFACE OXIDES IN THE OXIDATION OF Rh

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Transition metal particles are commonly used catalysts for a wide range of oxidation reactions. Nevertheless, only the systematic studies performed in the recent years have led to the discovery of ultrathin surface oxide films. We have studied the surface oxides formed on various facets of Rh with the help of density functional theory (DFT) calculations using the Vienna Ab-initio Simulations Package (VASP). We find the formation of 2D surface oxides with a common structure on all low-indexed surfaces, while the presence of step edges leads to the formation of 1D stripes on the higher indexed surfaces. The surface oxides play an important role for two different aspects of the oxidation process: On the one hand the thermodynamic stability of the 2D oxides results in an increased presence of low-indexed

facets of Rh particles at high oxygen partial pressures. On the other hand, the 1D stripes decorating the step edges are a nucleation center for the formation of the 2D oxides. Differences in the structure of the 1D stripes are predicted to lead to a preferred growth direction of the 2D oxides, in agreement with experiment.

ELECTROSTATIC FORCES AND POLARITY: FROM SEMI-INFINITE OXIDE SURFACES TO ULTRA-THIN FILMS

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Polar surfaces of insulating materials result from the piling of charged atomic layers whose electrostatic stabilization involve very specific processes and leads to peculiar atomic or electronic surface configurations. The richness of surface processes related to polarity and their potential applicability in catalysis or electronics have encouraged efforts to synthesize and understand them, during the last ten years. With the reduction of size, as in the case of nano-objects and ultra-thin films, polarity effects gain an additional dimension but the relevant electrostatic forces differ from those on semi-infinite surfaces, and are largely size-dependent. Relying upon first principles simulations, we will show how electrostatic laws manifest themselves at different sizes and which unusual structural and electronic characteristics they induce.

INSIDE A REACTOR: TIME- AND SPACE-RESOLVED STRUCTURE OF A HETEROGENEOUS CATALYST

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The design and construction of better catalysts requires knowledge of the structure performance relation. However, more often than not, the structure of the catalytically active site is unknown. Because the catalyst structure is dynamic, its structure has to be determined under true reaction conditions. Using X-rays to study catalysts is very attractive, because of the high penetration depth of high energy X-rays. Over the years, we have performed XAS studies on supported metal catalysts and aimed at determining the ensemble of atoms that forms the catalytically active site. We have explored high-energy resolution XAS, X-ray emission spectroscopy, which enables the spin-selective detection of the valence band under in situ conditions. This provides valuable information about the reactivity of transition metal catalysts.

The structure of a heterogeneous catalyst may vary over time and even within its position in a catalytic reactor. We have determined the structure of a functioning heterogeneous catalyst over time as function of its position in a catalytic reactor and identified strong variations. It will be shown that catalyst characterization is essential to occur in situ, time and space resolved and that if these requirements are met, structure performance relations can be determined.

FROM UHV TO IN SITU: MULTISCALE MODELING ACROSS THE PRESSURE GAP

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In-situ studies of model catalysts at near-ambient pressure conditions can reach much higher conversion rates than traditional experiments in ultra-high vacuum. In order to assess concomitant heat dissipation and mass transport limitations we present a first-principles based multiscale modeling approach that integrates a detailed description of the reaction chemistry and the macro-scale flow structures. Using RuO₂(110) as a representative substrate for the frequently studied CO oxidation reaction we illustrate that at flatfaced thin single-crystals factors like a suppressed heat conduction at the sample backside and the build-up of a product boundary layer above the surface may readily mask the true catalytic function.

FIRST-PRINCIPLES INSIGHT INTO THE HYDROGEN EVOLUTION AND OXIDATION REACTIONS

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The hydrogen evolution reaction (HER) and its microscopic reverse, the hydrogen oxidation reaction (HOR), are of great importance for technological applications such as energy storage via H₂ production and hydrogen fuel cells. Despite extensive experimental research efforts it is still unclear which reaction pathway, Volmer-Tafel or Volmer-Heyrovsky, is dominating on different metal surfaces at different potentials. However, the recent success of first-principles modelling techniques in probing electrochemical reactions [1,2,3] offers hope of a solution to this issue. Here we first give a short review of a recently developed density functional theory (DFT) based model of the electrode-electrolyte interface. In particular, it is shown how accurate energetics for charge transfer reactions can be obtained. The model is then used to establish the full energetics of the three elementary HER/HOR steps – Volmer, Heyrovsky and Tafel – on a number of metal electrodes. Combined, these DFT results suggest a preferential pathway and also clearly indicate that the hydrogen adsorption free energy is the most important parameter in describing the HER/HOR activity of an electrode.

[1] R. Jinnouchi and A.B. Anderson, *J. Phys. Chem. C* **112**, 8749 (2008).

[2] J.-S. Filhol and M. Neurock, *Angew. Chem. Int. Ed.* **45**, 402 (2006).

[3] M. Otani and O. Sugino, *Phys. rev. B* **73**, 115407 (2006).

INSIGHT INTO ICE FORMATION ON METAL SURFACES

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Heterogeneous nucleation of water plays a key role in fields as diverse as atmospheric chemistry, catalysis, and biology. Ice nucleation on metal surfaces offers an opportunity to watch this process unfold, providing a detailed molecular-scale description of the initial stages of heterogeneous ice nucleation and growth at a well-defined, planar interface. Here we discuss an extensive range of density-functional theory studies on a variety of metal surfaces specifically designed to understand the fundamental nature of the water-metal interaction^{1,2}. Specifically, the structure and dynamics of ice nanoclusters on Ag(111) and Cu(111) have been examined, along with 1D and 2D ice structures that form on Cu(110). These systems reveal an unanticipated structural adaptability of water-ice films and, in particular, the widespread belief that structures must necessarily be built from hexagons or bilayers is shown not to be true. For example, the ca. nanometer wide water-ice chains that nucleate and grow on a Cu(110) surface³ are built from a face sharing arrangement of water pentagons². We also explore the reactivity of water on clean and O pre-adsorbed Cu(110), trying to understand the mechanism behind water dissociation on this system, where experimentally OH dimers are observed on the surface at low coverages. Overall, our results show that the structure and reactivity of different substrates contribute to yield a rich and novel variety of structures, which forsakes previous assumptions and universally applicable models such

as, for instance, the bilayer wetting model.

¹ H. Gawronski, J. Carrasco, A. Michaelides and K. Morgenstern, Phys. Rev. Lett. **101**, 136102 (2008).

² J. Carrasco, A. Michaelides, M. Forster, S. Haq, R. Raval and A. Hodgson, Nature Mat. (in press).

³ T. Yamada, S. Tamamori, H. Okuyama, Phys. Rev. Lett. **96**, 036105 (2006).

TEMPERATURE DEPENDENT VIBRATIONAL FINGERPRINTS OF GOLD NANO CLUSTERS: AN AB INITIO STUDY

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The study of gold nanoclusters is a flourishing topic, due primarily to its importance for catalysis. Here, we apply the recently developed all-electron ab initio code FHI-aims for the density functional (DFT) study of the relative energies and vibrational properties of known isomers of small Au_n (n<10) clusters. In particular, besides the calculations of the traditional harmonic frequencies, we focus on the less common evaluation of the (temperature dependent) vibrational power spectrum, obtained via Fourier transformation of the velocity dipole and velocity autocorrelation functions, where dipoles and velocities are sampled along a DFT Molecular Dynamics trajectory at the given temperature. We underline differences between harmonic and anharmonic spectra at different temperatures and compare with available experimental data.

FIRST PRINCIPLES SIMULATIONS OF TEMPERATURE PROGRAMMED DESORPTION OF H₂O FROM Au AND Ru WITH PRECOVERED OXYGEN

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We present first principles simulations of temperature programmed desorption of H₂O from Au(111) and Ru(0001) with precovered Oxy-gen. Adsorption energies and angularly resolved pair interactions are calculated using Density Functional Theory. These parameters are used as input to Monte Carlo simulations of the temperature programmed desorption. The desorption step is treated kinetically while the diffusion, rotation of adsorbed species and the reaction $\text{H}_2\text{O} + \text{O} \rightleftharpoons 2\text{OH}$ are treated in equilibrium.

We find that OH forms the island edges at 2:1 H₂O:O precoverage while H₂O forms the island edges for 4:1 H₂O:O precoverage. A $(\sqrt{3} \times \sqrt{3})$ -OH/H₂O structure is formed on the surface due to the fact that OH-H₂O forms more attractive adsorbate interactions than H₂O-H₂O.

TRENDS IN CO OXIDATION RATES FOR METAL NANOPARTICLES AND CLOSE-PACKED, STEPPED, AND KINKED SURFACES

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Using density functional theory calculations, we study trends in the CO oxidation activity for different metals and surfaces. Specifically, we show how the activity of (111) close-packed surfaces, (211) stepped surfaces, (532) kinked surfaces, 55 atom cuboctahedral clusters, and 12 atom cluster models changes with the coordination number of atoms at the active sites. This effect is shown to be electronic in nature, as low coordinated metal atoms, which bind reactants most strongly, have the highest energy metal *d* states.

DFT STUDY OF Au NANOSTRUCTURES ON RUTILE TiO₂(110)

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Since the discovery of enhanced catalytic properties of dispersed gold nanoparticles on oxide supports adsorption of metal atoms and formation of nanostructures on the oxide surfaces attracted a lot of interests. Recently, it has been proposed that one-dimensional Au structures can be formed in a controlled manner, using ordered oxygen vacancies created on a TiO₂(110) surface during irradiation. We examine the adsorption of small Au aggregates (atomic rows and clusters), of a size ranging from a monomer to a dozen of Au atoms per cell, on a partially reduced rutile TiO₂(110). The calculations apply density-functional theory, plane wave basis, and the projector augmented wave method. Our previous results for the infinite monomer, dimer, and triple Au rows are extended to higher Au coverages and finite rows, and supplemented by results for clusters. The discussion is focused on the structure and bonding of one-dimensional Au rows on the missing row defected TiO₂(110)

surface and their comparison with the respective properties of Au clusters and finite rows adsorbed on the partially defected bridging O row. The calculations show the strong bonding to the substrate and the metallic nature of the Au rows. The adhesive bonding of gold clusters to the vacancy defected bridging oxygen row at the $\text{TiO}_2(110)$ is of covalent nature. We examine electron charge transfer and discuss the charging of clusters and its dependence on the cluster size. Results from this study give an insight into the nature of Au-Ti bond, the role of the amount of deposited metal on the observed electronic properties, and the growth behaviour of Au nanostructures on $\text{TiO}_2(110)$.

TRENDS FOR METHANE OXIDATION AT SOLID OXIDE FUEL CELL CONDITIONS

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With overall fuel utilization efficiencies as high as 75% as well as being very flexible with respect to fuel types, solid oxide fuel cells (SOFCs) are promising candidates for future power plants. We investigate the trends in methane oxidation activity on SOFC anodes. The study is based on detailed first-principle calculations of the reaction energetics at Ni {111} and {211} surfaces. To accommodate for the elevated SOFC operational temperature we include thermodynamic corrections. The Ni energetics is further extended through scaling relationships to describe both the reaction energies and barriers over other transition metals in terms of only two descriptors: the carbon and oxygen adsorption energies. A simple free energy analysis as well as more elaborate microkinetic modelling allows us to present anode activity landscape in terms of those two descriptors. This not only simplifies the view of the combustion process, it also gives insight into which reaction pathways are likely to be dominant over the different transition metal anode materials. Most importantly, the method reveals the theoretically optimal carbon and oxygen binding energies for the reaction under consideration, which allows for a systematic search for promising anode alloys in the most interesting catalytic regime.

AB INITIO ATOMISTIC THERMODYNAMICS OF Li-DOPED MgO(100) SURFACES

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Li-doped magnesium oxide efficiently catalyzes conversion of methane to ethylene and ethane in the presence of oxygen (oxidative coupling of methane process, OCM). The activity of this catalyst was attributed to the formation of $[\text{Li}^+\text{O}^-]$ centers at the surface. However, the concentration of these centers at the surface and in the bulk, and the surface composition and structure in general remain unknown at the reaction conditions.

In this study, we use the first-principles *ab initio* atomistic thermodynamics approach to assess relative stability of Li-doped MgO (100) surfaces of different stoichiometry, and calculate concentrations of surface defects at realistic temperatures and pressures. The electronic structure of surfaces and defects is described using periodic DFT with GGA PBE

exchange-correlation (XC) functional. We also analyze the effect of exact exchange and electron correlation on localization of the electronic hole accompanying the $[\text{Li}^+\text{O}^-]$ centers, and on defect formation energies, by using hybrid XC functionals and MP2 in an embedded cluster framework.

MICROKINETIC ANALYSIS OF THE CATALYTIC PARTIAL OXIDATION OF CH_4 ON Rh

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In this work, we have combined our previously derived microkinetic model (based on UBI-QEP theory) for CH_4 partial oxidation (CPO) on Rh with a detailed modeling of the reactor to elucidate the pathways leading to syngas. The analysis points out the importance of transport phenomena in dictating the dominant pathways to syngas, revealing the occurrence of up to three reaction zones: a deep combustion of methane at high O^* coverage, followed by a zone where direct formation of syngas in parallel with catalytic combustion occurs, and finally a steam reforming and WGS zone, when oxygen is no longer available. These findings may reconcile the long debated mechanistic differences regarding direct vs. indirect pathways in CPO, and underscore the importance of the long postulated interplay of mass transfer and surface chemistry, pointing out that an accurate description both of transport effects and chemical kinetics is required for a proper account of chemical events and of data.

FROM ELECTRONS TO REACTIVE FLOW: COUPLING FIRST-PRINCIPLES KINETIC MONTE CARLO WITH CONTINUUM LEVEL SIMULATIONS

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First-principles kinetic Monte Carlo (kMC) simulations have evolved into an important tool in the modelling of heterogeneous catalytic processes. The success of the approach relies on the accurate treatment of two central aspects for the reactive surface chemistry: A first-principles description of the involved elementary processes and an evaluation of their statistical interplay that fully accounts for the correlations, fluctuations and spatial distributions of the chemicals at the catalyst surface. Particularly for technologically more relevant environments, i.e. ambient pressures and elevated temperatures with concomitant higher product formation rates, a third aspect in form of the heat and mass flow in the system becomes increasingly important. We investigate these effects by coupling first-principles kMC simulations self-consistently with continuum level simulations for the gas and solid phase transport, considering a stagnation point flow geometry as a model for recent *in situ* measurements over single-crystal model catalysts. Applying our method to the CO oxidation over $\text{RuO}_2(110)$ [1], we demonstrate how the build-up of temperature and pressure gradients over the active surface influence the observed catalytic activity and surface composition.

[1] K. Reuter and M. Scheffler, Phys. Rev. B **73**, 045433 (2006).

EXPLORING THE RANDOM PHASE APPROXIMATION: APPLICATION TO THE CO ADSORPTION PUZZLE, BULK METALS, AND WEAKLY BONDED MOLECULES

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Density-functional theory within the generalized gradient approximation has been immensely successful in describing the ground state properties of a diverse range of materials. However, inherent strong self-interaction effects and the absence of van der Waals interactions are two prominent examples of GGA's failures. The random phase approximation (RPA) as formulated within the adiabatic connection fluctuation dissipation theorem presents a promising way to overcome these deficiencies. However, despite the considerable interest the RPA has generated, a comprehensive assessment of its performance is not available. Using CO@Cu(111), a selection of bulk metals, and the benzene dimer--a prototypical π -conjugated system as examples, we demonstrate the performance of the RPA for different types of systems. We show that the potential-energy surface of CO adsorbed on Cu(111) can be correctly described within RPA at a quantitative level. The binding energy of the benzene dimer, on the other hand, is considerably underestimated.

FIRST-PRINCIPLES INVESTIGATIONS OF GRAPHENE GROWTH

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Catalytic carbon deposition on Ni nanoparticles and surfaces is the first step towards coking of steam reforming Ni catalysts and metal dusting (carbon-induced corrosion) on Ni-alloys [1,2]. The fundamental processes at the atomic scale are essentially the same, therefore an atomistic understanding of how the gas-phase components influence carbon deposition and nucleation is necessary. The growth of graphene on the Ni surface is a necessary step in both processes. Recent DFT [3] studies have shown that steps on the metal surface act as growth centers for graphene. On the basis of first principles calculations done with the Dacapo code, we present a general model for the growth of graphene on metal surfaces, including a discussion of the growth centers, the influence of the metal properties and the reaction conditions, the example of the Ni₃Sn alloy is presented.

[1] H.J. Grabke, *Materials and Corrosion* **54** 736 (2003)

[2] J.R. Rostrup-Nielsen, *Catalytic Steam Reforming*, In: “ ‘Catalysis Science and Technology’ “ vol. 5, Springer-Verlag, Berlin 1984.

[3] F. Abild-Pedersen et. al. *Phys. Rev. B* **73** 115419 (2006)

UNDERSTANDING SURFACE ENERGIES OF TRANSITION METALS IN DENSITY-FUNCTIONAL THEORY AND BEYOND

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Determining index-specific surface energies of metals is, to date, still a challenge, both theoretically and (even more so) experimentally. Density-functional theory (DFT) calculations within the local-density approximation (LDA) for exchange-correlation (XC) have provided understanding of qualitative trends. Yet, absolute surface energies, in particular of d-metals, still exhibit significant uncertainties related to the description of XC. Here we analyze the surface energies of 4d-metals with (semi-)local functionals, using the all-electron FHI-aims code¹. Relating the bulk cohesive energy and surface energy via an improved bond-cutting model we find that recent gradient corrected functionals like PBEsol and AM05 can indeed correct the poorer results of the usual PBE. In addition, we consider methods beyond (semi-)local DFT such as hybrid XC functionals (B3LYP, PBE0, HSE03) as well as DFT+RPA using a cluster correction scheme,² and discuss their effects on the calculated surface energies.

[1] V. Blum *et al.* *Comp. Phys. Comm.* accepted (2009);

[2] Q.-M. Hu *et al.*, *Phys. Rev. Lett.* **98**, 176103 (2007); **99**, 169903(E).

DESCRIPTOR FOR THE ACIDITY OF ZEOLITES

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In this study the effect of local changes in both geometry and chemical compositions on the acid strength of the bridging OH group in zeolites has been investigated through density functional theory calculations. The chemical composition locally around the OH group of all Al-substituted zeolites are the same. Consequently, the variations in acid strength of the OH groups must originate in the geometry of the zeolite. In this study, it has been investigated how variations in acid strength of different OH groups correlates with small changes in the local geometry, i.e. variations in Si-OH-Al angle. An increase in acidity with increasing angle is observed. Furthermore, an investigation of the variations of acid strength of OH groups in zeolites with a range of transition metals substituted for Al has been carried out. Both investigations show a strong correlation between the acid strength of the OH group and the level of the LDOS p-band center of the active oxygen. The acidity is increasing with decreasing energy level of the oxygen p-band. Also shown is a clear correlation between the d-band center of the substituted metal in its bulk state and the p-band center of the active oxygen in the zeolite.

AB INITIO INVESTIGATION OF THE ADSORPTION PROPERTIES OF METAL-ORGANIC FRAMEWORKS: THE INTERACTION OF CO AND CO₂ WITH CPO-27-M (M=Mg, Ni, Zn)

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The adsorption of CO and CO₂ molecules with metal-organic frameworks CPO-27-M (M=Mg, Ni, Zn) were simulated with the periodic ab initio CRYSTAL program by adopting an all-electron basis set and the B3LYP level of theory; the binding energies of the molecules were computed by including the dispersion energy by means of the empirical

Grimme's scheme. The effect of partially occupied *d*-orbitals in Ni is reflected in the adsorption process of CO, where the Ni—CO bond is remarkably shorter (2.18 Å-exp 2.11 Å-) than for Mg and Zn (more than 2.50 Å). The adsorption of CO shows an increasing interaction in the sense Zn<Mg<Ni. For CPO-27-Ni the computed binding energy (46 kJ/mol) is in good agreement with experimental calorimetric data (55±5 kJ/mol). Results for CO₂ (Zn<Ni<Mg) show similar agreement with experiments. Vibrational frequency calculations (IR and Raman) were also performed to estimate CO and CO₂ frequency shifts (~35 cm⁻¹ for CO).

STABILITY AND REACTIVITY OF GRAFTED Cr(CO)₃ SPECIES ON MOFs

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The possibility to design MOFs (Metal-Organic Frameworks) with the aim to modulate the properties of grafted Cr(CO)₃ species has been investigated by DFT methods, characterized by a different HF exchange proportion. The effect of the benzene substituents nature on the stability of the (η⁶-arene)Cr(CO)₃ adduct and on the shift of ν_{CO} has been considered. Different electron-donor (e.g. -CH₃) and electron-acceptor (e.g. -COOH) substituents have been used and compared with benzene. C₆H₄(COOZnOH)₂ and C₆H₄(Zn₄O₁₃C₆H₅)₂ clusters have been also adopted as models of the MOF-5 linker. This study indicates that e-acceptor substituted MOF linkers facilitate the substitution of CO by incoming molecules, whereas the use of e-donors ones would improve the stability of the Cr(CO)₃ adduct and the ring acidity. A linear dependence of the Cr(CO)₃ binding enthalpies on the calculated Δν_{CO}, d(Cr-CO) and d(Cr-arene) was found suggesting that the stability of the Cr(CO)₃ adduct can be inferred experimentally from vibrational and XRD data.

CATALYSTS DESIGN FOR STEAM REFORMING OF METHANE

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Steam reforming of methane ($CH_4 + H_2O = CO + 3 H_2$) is one of the most important methods of producing hydrogen. It was commercialized in the 1960s; however, there are still limitations in this process. An industrially used catalyst demands not only high reactivity, but also high stability and low price. Sometimes, there is compromise between these properties. The efforts to find a reactive, stable and cheap catalyst for this reaction were never stopped. This poster presents an example of designing alloy catalysts by combination of first principle calculation, scaling relations, BEP relations and micro kinetic simulation, as well as the database of calculated properties of materials.

DIRECT NO DECOMPOSITION OVER STEPPED SURFACES OF TRANSITIONMETAL ALLOYS

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The increasingly stringent emission requirements for diesel engines require NO_x abatement technology, which is effective under lean-burn conditions. To remove NO, the selective catalytic reduction (SCR) process using other reductant gases has been applied for decades. However, the direct catalytic decomposition of NO has been considered the best technique for NO removing since direct NO decomposition into N₂ and O₂ is thermodynamically favorable. The question is we need to find a heterogeneous catalytic surface which is both active and oxidation-resistant. Here we study the screening for ideal stepped transition-metal surfaces among alloys. Then catalytic activity trend can be understood based on two descriptors, the dissociative chemisorption energy of N₂ and O₂. Also the stability property of those alloy surfaces are investigated. We show that stepped alloy surfaces appear in a narrow band when plotting the dissociation energy of N₂ as function of dissociation energy of O₂. There are still spaces to improve compared with pure transition-metals in both catalytic activity and costs.

OXIDATION OF PALLADIUM AND PLATINUM SURFACES

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Platinum group metals play a fundamental role in oxidation catalysis, and clarification of the interaction of their surfaces with oxygen is crucial to understand the catalytic process at atomistic level. We have investigated formation of adsorption structures and surface oxides on selected Pd and Pt surfaces by first-principles techniques as complement to experimental investigations. In particular we have calculated phase diagrams for surface phases by first-principles thermodynamics. On Pd(111), a large variety of metastable structures has been observed to coexist with the thermodynamically stable Pd₅O₄ surface oxide. On palladium surfaces, surface oxide monolayers PdO_x form with x between 0.8 and 1, whereas on Pt surfaces α-PtO₂-like structures are most stable. Consistently, as in the bulk case, platinum in surface oxides reaches higher oxidation states than Pd under the same conditions of temperature and pressure. Although atomic structure of surface oxides may be not directly related to the bulk oxide structure, local coordination of individual atoms show regular patterns in all structures considered.

PALLADIUM IN SELECTIVE HYDROGENATION CATALYSIS

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Carbon deposited on a palladium catalyst heavily influences activity and selectivity of the catalyst for reactions of partial hydrogenation of hydrocarbons. The exact nature of these carbon phases and their role are still unclear. We have employed density functional theory

together with molecular dynamics and genetic algorithms to investigate the Pd-C configuration space and stability of possible phases. Taking into account calculated formation energies and core level shifts, formation of Pd carbides can be excluded. Presence of dissolved carbon and intercalated graphite better explains the experimental findings.

RPA-ACFDT LATTICE CONSTANTS AND ATOMIZATION ENERGIES

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Density functional theory (DFT) applying the LDA or GGA for the description of the exchange-correlation energy provides an efficient method for a wide range of applications. Nevertheless, errors in the bond length are of the order of 1% and atomization energies are not reproduced with chemical accuracy (1 kcal/mol). Furthermore, the (semi-)local LDA and GGA do not properly account for long-range van der Waals interactions.

Therefore, the adiabatic connection fluctuation dissipation theorem (ACFDT), which links the electron correlation to the response function and provides, in principle, an exact expression for the correlation energy, has received increased interest in the recent years (e.g., [1]-[4]). We have evaluated lattice constants and atomization energies of extended systems within the ACFDT framework applying the random phase approximation (RPA). The RPA routines have been implemented in the Vienna Ab-initio Simulation Package (VASP).

The RPA energy includes exact exchange and a compatible correlation energy that also accounts for long-range van der Waals interactions. We found that atomization energies and lattice constants of the rare-gas solids Ne, Ar, and Kr are improved compared to LDA and GGA and the correct long-range $1/V^2$ volume dependence could be reproduced [4]. For insulators and metals, covalent and ionic bonded systems, RPA lattice constants are found to deviate on average by only 0.25 % from experiment. Atomization energies, however, are throughout too small (≈ 0.2 eV/atom). But although the mean error in the atomization energies remains close to the DFT-PBE one, RPA yields improved heats of formation.

[1] F. Furche, Phys. Rev. B **64**, 195120 (2001). [2] M. Fuchs and X. Gonze, Phys.Rev. B **65**, 235109 (2002). [3] A. Marini, P. García-González, A. Rubio, Phys. Rev. Lett. **96**, 136404 (2006). [4] J. Harl, G. Kresse, Phys. Rev. B **77**, 045136 (2008).

CO-ADSORPTION IN Cu-EXCHANGED CHABAZITE-A COMPARATIVE DFT- AND HYBRID FUNCTIONAL STUDY

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For Cu-exchanged zeolites experiments show that CO bonds preferably to Cu⁺-sites, whereas only very unstable bonds are reported for Cu²⁺-sites. In order to understand the reason for this site-preference on a theoretical level, we performed ab initio simulations based on Density Functional Theory, applying the Vienna ab-initio simulation package (VASP) in its latest release 5.2. We investigated the adsorption of CO in Cu-exchanged chabazite in a comparative study using standard GGA-functionals like PW91 and PBE and the hybrid functionals PBE0 and HSE03. Our results indicate that the experimental behaviour can not be reproduced at a standard GGA-level. Only by including exact exchange using hybrid

functionals like PBE0 and HSE03 the experimentally observed site preference is reproduced. Another important issue in our investigations was to compare experimental and calculated IR-spectra. Experimentally measured frequencies range between 2166cm^{-1} and 2153cm^{-1} . In our calculations yield too low frequencies at the GGA-, and too high frequencies at the hybrid functional level, respectively.

KINETIC MONTE CARLO SIMULATIONS OF TEMPERATURE PROGRAMMED DESORPTION

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We have simulated Temperature Programmed Desorption experiments of the system O/Rh(111) applying Kinetic Monte Carlo techniques. A comparison between a single-site and a multi-site Lattice Gas model which takes fcc- and hcp-hollow sites into account has demonstrated that using a multi-site model is necessary at high coverages but differences in the calculated spectra can also be found at low coverages. The Lattice Gas Hamiltonian (LGH) was constructed by fitting to the energies of about 80 system configurations, which were calculated with the Vienna Ab Initio Simulation Package (VASP) using Density Functional Theory. The accuracy of the LGH was optimized by applying the procedure of cross validation. We compared the calculated desorption spectra with experimental results.

AB-INITIO MODELING OF SOLID OXIDE FUEL CELL CATHODES

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Perovskites are the major class of materials used for modern solid oxide fuel cell (SOFC) cathodes and have the ability to catalyze the oxygen reduction reaction (ORR) on their surfaces. However, difficulties in performing in-situ characterization of well-controlled samples means that the rate limiting steps and structure-property relationships underlying ORR on these materials are not understood. In this talk we will discuss some of the challenges and opportunities associated with using ab-initio techniques to study ORR on SOFC materials. We have used ab-initio based thermokinetic modeling to study (La,Sr)MnO₃ (LSM), which is the primary cathode catalyst used in commercial SOFCs. We have developed a combined bulk and surface defect model in order to better understand surface defect structure and transport. We have also studied lanthanum transition metal oxides LaBO₃ (B=3D Mn, Fe, Co, and Ni) to identify trends in surface oxygen binding, hopping, vacancy formation, and dissociation vs. transition metal types. We use these trends to discuss a possible descriptor for the ORR on SOFC catalysts.

CATALYSIS FROM FIRST PRINCIPLES
Wien, May 25-28, 2009

Datum	Text	Aus	Ein
25.05.09	Reisekostenzuschüsse für eingeladene Sprecher	5.100,00	
29.05.09	Druckkosten + Bindung (inkl.Deckblätter zuschießen)	1.224,00	
05.06.09	Arbeitsessen Organizing Committee	137,30	
05.06.09	CAT1P, Edith Wolfsgruber Werkvertrag Sekretariatsarbeiten	1.050,00	
05.06.09	Hotel Bleckmann, Übernachtungen für 5 Teilnehmer	1.440,00	
05.06.09	Arcotel Boltzmann, Übernachtungen für 24 Teilnehmer	6.232,00	
05.06.09	AUSTRIA TREND-Hotel Albatros, Übernachtungen für 16 Teilnehmer	3.420,00	
16.06.09	CAT1P, Catering Fuchs: Kaffeepausen, Poster-Session	3.193,71	
		21.797,01	
	Vorfinanzierung		
	Center for Computational Materials Science		
25.05.09	Reisekostenzuschüsse für eingeladene Sprecher	5.100,00	
05.06.09	Arbeitsessen Organizing Committee	137,30	
05.06.09	CAT1P, Edith Wolfsgruber Werkvertrag Sekretariatsarbeiten	1.050,00	
05.06.09	Hotel Bleckmann, Übernachtungen für 5 Teilnehmer	1.440,00	
16.06.09	CAT1P, Catering Fuchs: Kaffeepausen, Poster-Session	3.193,71	
		10.921,01	
	AG Computergestützte Materialphysik, Universität Wien (Drittmittel)		
05.06.09	Arcotel Boltzmann, Übernachtungen für 24 Teilnehmer	6.232,00	
05.06.09	AUSTRIA TREND-Hotel Albatros, Übernachtungen für 16 Teilnehmer	3.420,00	
		9.652,00	
	Globalbudget Computergestützte Materialphysik		
29.05.09	Druckkosten + Bindung (inkl.Deckblätter zuschießen)	1.224,00	
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