

**Discussion Meeting on
Catalysis from First Principles
Lyon, France
July 5 - 8, 2000**

Organizers:

- Jürgen Hafner (Institut für Materialphysik, Universität Wien, Wien, Austria)
- Jens Nørskov (Technical University of Denmark, Lyngby, Denmark)
- Matthias Scheffler (Fritz-Haber-Institut der MPG, Berlin, Germany)

Local Organizers:

- Matthias Scheffler (FHI-Berlin)
- Veronica Ganduglia-Pirovano (FHI-Berlin)
- Sönke Lorenz (FHI-Berlin)
- Karsten Reuter (FHI-Berlin)
- Emmanuelle Crespeau (CECAM, Lyon)

Workshop Objective:

The objective of the meeting is to review the status of total-energy calculations as a basis for modeling and understanding of chemical reactions on solid surfaces. A strong focus will be placed on the prospects of calculational methods becoming a tool in the design of new catalysts. An additional objective is to bring together researchers from the electronic structure, the molecular-dynamics, the statistical physics community as well experimental surface-science and catalysis researchers from academia and industry.

Sponsors:

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Center for Atomic-Scale Materials Physics (CAMP)
Center for Computational Materials Science

Program

Where is ?

lectures: salle des theses of Ecole Normale Superieure (see ENS map)

coffee: in front of the lecture hall

lunch: at restaurant of ENS (see ENS map) (all participants will get lunch ticket from Karsten Reuter)

poster session: in front of the lecture hall

conference dinner: to be announced

Wednesday afternoon

14:00	Registration (please see Karsten Reuter)
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Wednesday afternoon

chairpersons: Matthias Scheffler & Michael Payne

15:00	Welcome and more Michel Marechal (director of CECAM) and Matthias Scheffler	
15:10 (35+)	Schlögl, Robert	On the origin of the gaps between fundamental and applied heterogeneous catalysis
15:55 (18+)	Chaka, Anne	Metal oxides in contact with a realistic atmosphere containing oxygen and water
16:20	coffee/tea	
16:40 (18+)	Reuter, Karsten	Destabilization of the Ru(0001) surface upon oxygen adsorption
17:05 (35+)	Goodman, Wayne	Metal Clusters On Planar Oxide Supports
17:50	break	
18:30	poster session and light dinner (organized by Sönke Lorenz et al.)	

Thursday morning

chairpersons: Veronica Ganduglia-Pirovano & Malgorzata Witko

9:00 (35+)	Clausen, Bjerne	Catalysis on nano-particles. Characterization and influence of structural properties.
9:45 (35+)	Landmann, Uzi	Reactivity of nano-particles
10:30	coffee/tea	
10:50 (18+)	Mavrikakis, Manos	Reactivity of small molecules on transition metal surfaces
11:15 (35+)	Hammer, Bjørk	Structure sensitivity of chemical reactions at metal surfaces
12:00 (35+)	Schueth, Ferdi	High throughput approaches in catalysis research
12:45	lunch at restaurant of ENS (see map)	

Thursday afternoon

chairpersons: Robert Schlögl & Wayne Goodman

14:05 (18+)	Morikawa, Yoshitada	Ab initio study of methanol synthesis on Cu surfaces
14:30 (35+)	Payne, Mike	The reaction of methanol in zeolite acid catalysts
15:15 (35+)	Hafner, Jürgen	Ab initio simulations of molecular reactions in zeolites
16:00	coffee/tea	
16:20 (35+)	Toulhoat, Herve	Evaluation of solid/water interfacial energies from first principles molecular dynamics simulations: application to the prediction of precipitated pseudo-boehmite morphologiesite
17:05 (18+)	Bengaard, Hanne	Steam reforming catalysis: the role of promoters and poisons
17:30 (18+)	Evans Jim	Ordering, Percolation, and Diffusion in Atomistic Models for Surface Reactions
17:55	break	
18:30	poster session and light dinner (organized by Sönke Lorenz et al.)	

Friday morning

chairpersons: Jürgen Hafner & Klaus-Peter Bohnen

9:00 (35+)	Sautet, Philippe	Breaking NO on a transition metal surface : a DFT comparison of Rh, Pd and Pd-Mn alloy
9:45 (35+)	Wolf, Martin	Femto-second chemistry of surface reactions
10:30	coffee/tea	
10:50 (35+)	Neurock, Matthew	From First-Principles to Catalytic Turnovers.
11:35 (18+)	Eichler, Andreas	The CO+NO redox reaction on Pt(100)
12:00 (45+)	Ramprasad, Ramamurthy	First principles study of the interplay between surface chemistry and field emission from metal surfaces
12:45	lunch at restaurant of ENS (see map)	

Friday afternoon

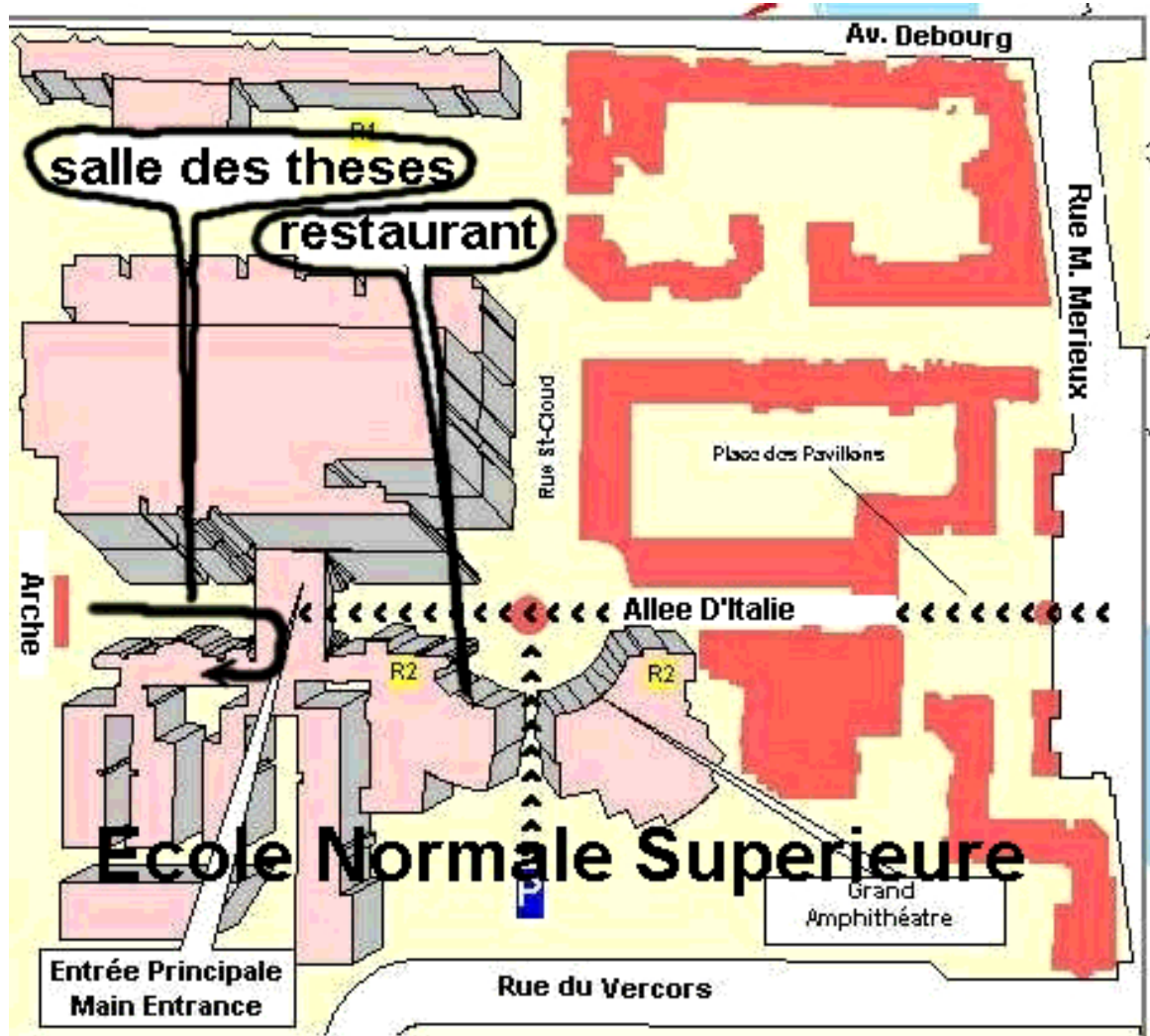
chairpersons: Jens Nørskov & Ferdi Schüth

14:00 (35+)	Bogicevic, Alexander	Understanding and tailoring metal-oxide interfaces from first principles
14:45 (18+)	Pacchioni, Gianfranco	Role of surface defects in the catalytic activation of Pd atoms and clusters on MgO
15:10 (18+)	Kresse, Georg	First-principles calculations for V_xO_y grown on Pd(111)
15:35 (18+)	Hermann, Klaus	Structure and Reactivity of Oxygen Vacancies at Vanadium Pentoxide Surfaces: ab initio DFT cluster studies
16:00	coffee/tea	
16:20 (35+)	Sauer, Joachim	QM-Pot and plane wave studies on the reactivity of solid acid catalysts
17:05 (35+)	Besenbacher, Flemming	STM studies on metal surfaces relevant for model catalysts
18:00	break	
19:00	conference dinner at ?????	

Saturday morning

chairperson: Flemming Besenbacher

9:00 (18+)	Groß, Axel	New insights into the molecular adsorption mechanism by ab initio based tight-binding molecular dynamics simulations
9:25 (35+)	Röthlisberger, Ursula	First-Principles Design of biocatalysts
10:10 (35+)	Nørskov, Jens	Biocatalysis
10:55	THE END	



Talks

On the Origin of the Gaps between Fundamental and Applied Heterogeneous Catalysis

Robert Schlögl, G. Mestl, T. Ressler, and F. Jentoft

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

Fundamental heterogeneous catalysis is a section of chemical kinetics within physical chemistry. From there strong links to surface science and theory are now established. This alliance of sciences has brought about a great insight into principles and details of several catalytic reactions. We are, however, far apart from the possibility which the detailed understanding offers, to predict the course of a catalytic reaction, its best catalyst and its kinetic behaviour. Despite several promises from fundamental science to replace the empirical optimisation strategy of technical catalysts by a design approach, not a single industrial reaction process has been worked out until now in this way.

The following obstacles/problems preventing a more widespread application of fundamental catalysis with higher impact in technical disciplines will be discussed in detail: (1) the non-equilibrium nature of a catalytic system both at the surface and in the bulk of the material, (2) the difficulty to choose the relevant model systems for technical catalysts without in-depth in-situ characterisation of its structures and functions, (3) the relevance of long range order in model systems for their reactivity, (4) the impact of transport limitations on the assessment of catalytic performance, and (5) the lack of synthetic strategies for converting fundamental knowledge into working materials. Each point will be documented with a practical example and general conclusions will be drawn. The developing partnership between theory and practical catalysis requires from the experimentalists investigations with rigorously defined conditions of catalyst and reaction conditions and the application of a manifold of characterisation techniques to give a reasonable complete description of an applied catalytic reaction.

Contact author: Prof. Robert Schlögl
Inorganic Chemistry
Fritz-Haber-Institut der Max-Planck-Gesellschaft
Faradayweg 4-6, 14195 Berlin, Germany
Fax: +49 30 84 13-44 01
E-mail: andrea@fhi-berlin.mpg.de (secretary)

The Effect of the Environment on α -Al₂O₃ (0001) Surface Structures and Stability.

Anne M. Chaka¹, Xiao-Gang Wang², and M. Scheffler³

¹The Lubrizol Corporation, Wickliffe, Ohio USA

²Delphi Corporation, Detroit, Michigan USA

³Fritz-Haber-Institut der Max-Planck-Gesellschaft D-14195 Berlin

The nature of the corundum surface (α -Al₂O₃) has long been of considerable importance in a wide variety of technological applications. Yet, despite considerable experimental and theoretical efforts, the surface structure, and even the surface stoichiometry, is a matter of strong controversy. Recent experimental results^[1-3] indicate that there are several different surface terminations and structures possible, depending on the thermal history and oxygen partial pressure employed. Experiments from various groups also report surface relaxations which are not consistent with each other in either magnitude or direction. Yet theoretical methods ranging from the empirical to the *abinitio* have so far identified only one stable termination stoichiometry for the α -Al₂O₃ (0001) surface, a (1 x 1) aluminum terminated structure. The relaxation predicted for this surface with the *abinitio* methods, however, is 35-70% greater than what is reported experimentally. These discrepancies between experiments, and between theory and experiment are significant and need to be resolved.

What has not been previously considered in the theoretical treatment of the α -Al₂O₃ (0001) surface is the effect of the environment on the surface structure and stoichiometry. Under realistic conditions, a surface will exchange atoms with its surroundings. Hence in this work we present an analysis of the Gibbs free energy of the system with respect to its dependence on the chemical potentials of the components present in the material and the environment. For a metal oxide such as α -Al₂O₃, the O₂ partial pressure is obviously the most important factor in the analysis. In addition, the presence of stable hydrogen on the surface also needs to be addressed, as it can be incorporated into the bulk structure during growth, or may result from exposure of the surface to water vapor prior to placement in the UHV chamber.

In this paper we report that the surface stoichiometries, structures, and properties change significantly depending upon the chemical potential of O₂, H₂, and H₂O gasses in equilibrium with the surface. We use the all-electron FP-LAPW method to solve the Kohn-Sham equations and calculate the total energies, forces, and chemical potentials for all reasonable (1 x 1) corundum (0001) surfaces. We find that the metal terminated surface is surprisingly stable across the range of a physically realistic O₂ chemical potential. An oxygen terminated surface becomes stable only if hydrogen is present on the surface, even at partial O₂ pressures which are too high for standard UHV equipment. In addition, including hydrogen on the surface of both the aluminum and oxygen terminated surfaces results in calculated relaxations which agree with the latest experimental results, in both magnitude and direction.

[1] Renaud, G., Surface Science Reports 1998, 32, 1.

[2] Toofan, J.; Watson, P.R., Surface Science 1998, 401, 162.

[3] Ahn, J.; Rabalais, J.W., Surface Science 1997, 388, 121.

Contact author: Anne M. Chaka

The Lubrizol Corporation, 9400 Lakeland Blvd., Wickliffe, Ohio 44092-2298 USA

Fax: 001-440-347-4482

E-mail: chaka@lubrizol.com

Destabilization of the Ru(0001) Surface upon Oxidation

Karsten Reuter, M. Veronica Ganduglia-Pirovano,
and Matthias Scheffler

Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin

Catherine Stampfl

Northwestern University, 2145 Sheridan Road, Evanston IL60208

Recent theoretical work showed that the coverage of O on Ru(0001) is not limited to $\Theta = 0.5\text{ML}$, which was for a long time believed to be the saturation coverage under UHV conditions [1]. Subsequent experiments indicated an exceptionally high catalytic activity of the Ru(0001) surface (compared to other Pd group transition metals), when high loads of O are stored not only *on*, but also *inside* the sample. In these experiments it was also observed that such surfaces are severely destabilized, leading to RuO₂ oxide formation and to RuO_x ($x \leq 4$) fragmentation at elevated temperatures [2,3].

We performed density functional theory calculations using the full potential LAPW implementation to gain an understanding of the nature of the O-Ru bonds and of the ensuing destabilization, when Ru is loaded with oxygen coverages between $0 \leq \Theta \leq 2\text{ML}$. After a full O monolayer is completed on the surface, O starts to penetrate into Ru(0001), yet preferring to stay directly below the first substrate layer and not deeper. We observe a tendency to form sub-surface islands with (1x1) periodicity, where the thus formed O-Ru-O surface film is only loosely connected to the underlying substrate and may be considered as a precursor to oxide formation. The implications of this destabilization on the catalytic activity will be discussed.

[1] C. Stampfl and M. Scheffler, Phys. Rev. B **54**, 2868 (1996).

[2] A. Böttcher, H. Conrad and H. Niehus, J. Chem. Phys. **112**, 4779 (2000).

[3] H. Over et al., Science **287**, 1474 (2000).

Contact author:

Karsten Reuter
Fritz-Haber Institut der MPG
Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

Fax: 0049-30-8413 4701

E-mail: reuter@fhi-berlin.mpg.de

Metal Clusters On Planar Oxide Supports

D. W. Goodman

Department of Chemistry, Texas A&M University, College Station, TX 77842-3012

Model catalysts consisting of metal clusters of varying size have been prepared on single crystal TiO₂, and ultra-thin films of TiO₂, Al₂O₃, and SiO₂ films. The morphology, electronic structure, and catalytic properties of these clusters have been investigated using ISS, TPD, HREELS, IRAS, XPS, STM, and STS with emphasis on the unique properties of those clusters ≤ 5.0 nm in size. Motivating this work is the recent literature reports that gold supported on titanium oxide is active for various reactions including low temperature CO oxidation and the selective oxidation of propylene. These studies illustrate the unique physical and chemical properties of nanosized supported metal clusters.

Contact author: D. W. Goodman

Texas A&M University,
Department of Chemistry

Fax: 779-845-0214

E-mail: goodman@mail.chem.tamu.edu

Catalysis on nano-particles. Characterization and influence of structural properties

Bjerne S. Clausen

Haldor Topsøe Research Laboratories DK-2800 Lyngby, Denmark

Jens K. Nørskov

CAMP, Department of Physics, Technical University of Denmark DK-2800 Lyngby, Denmark

Structural characterization of catalytic nano-particles is a major challenge. The high dispersion, the presence of a support, promoters, etc. as well as the requirement of in situ studies makes most techniques inadequate for the measurements. Extended x-ray absorption fine structure (EXAFS) is one of the few techniques which can provide the desired structural information of catalysts under working conditions. However, the fact that atoms in the surface regions of the nano-particles move in very anharmonic potentials, gives rise to asymmetric pair distribution functions for the atoms, especially at elevated temperatures which are typical at catalytic reaction conditions. The standard EXAFS analysis is not able to take such behaviour into account and erroneous results may be obtained for structural parameters, such as coordination numbers and bond distances. We have developed a model [1] based on molecular dynamics simulations which gives results in nice agreement with structural data obtained by other techniques. The usefulness of the model is demonstrated in the case of supported nano-particles of Cu used in the methanol synthesis reaction and of Au used for preferential oxidation of CO at low temperatures in e.g. fuel cells.

[1] B. S. Clausen and J.K. Nørskov, Topics in Catalysis 10, 221 (2000).

Contact author: Bjerne S. Clausen
Haldor Topsøe Research Laboratory
Nymllevej 55
DK-2800 Lyngby, Denmark
Fax: +45 45 27 29 99
E-mail: bsc@topsoe.dk

Reactivity of nano-particles

Uzi Landman

Physics, Georgia Tech, Atlanta, Ga 30332-0430

Contact author: Uzi Landman

Physics, Georgia Tech,
Atlanta, Ga 30332-0430

Fax: (404) 894 3368

E-mail: uzi.landman@physics.gatech.edu

Reactivity of Small Molecules on Transition Metal Surfaces

Manos Mavrikakis

Department of Chemical Engineering, University of Wisconsin-Madison, Madison, WI
53706, USA

Oxidation reactions are involved in a large number of industrially important catalytic processes. The dissociation of the oxygen molecule often represents the first elementary reaction step towards the oxidation of a variety of molecules. Periodic DFT-GGA calculations are used to investigate the binding modes and binding energy of oxygen molecules and atoms on noble metal surfaces. More specifically, in the first part of the presentation, the details of a dissociation path for O₂ on Cu(111) will be discussed. In the second part of the presentation, the binding of oxygen and CO to flat and stepped Au surfaces is examined. We propose that the unusually high catalytic activity for low temperature CO oxidation of Au nanoparticles could be partly related to a combination of the enhanced binding of the reactants at step sites and a strain effect induced by the support on the active metal particles.

Contact author: Manos Mavrikakis
Department of Chemical Engineering
University of Wisconsin-Madison, Madison, WI 53706, USA
Fax: (608) 262-5434
E-mail: manos@engr.wisc.edu

Structure Sensitivity of Chemical Reactions at Metal Surfaces

Bjørk Hammer

Institute of Physics and Astronomy, University of Aarhus

The role of the surface structure for the catalytic activity of a metal surface is studied using density functional theory. Monatomic steps at close packed Ru and Pd surfaces are identified to be highly reactive for the dissociation of diatomic molecules (NO, CO, N₂). The high reactivity is caused by the existence of a favorable reaction ensemble at which the reaction complex (e.g. stretched NO) coordinates to five surface metal atoms[1,2]. At the less reactive close packed surfaces, the reaction ensemble only involves three to four metal atoms. The reactivity of edges of intersecting Pd(100) and Pd(111) planes is also investigated. The Pd edges are found to be less reactive than the monatomic Pd steps.

The complete $2\text{NO} + 2\text{CO} \rightarrow 2\text{CO}_2 + \text{N}_2$ reaction diagram is presented for Pd(111), Pd(100), stepped Pd, and edged Pd, showing that the step and edge defects are likely to dominate the reactivity of any Pd surface, including the surfaces of nano size Pd clusters[3].

[1]S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist, and J. K. Nørskov, Phys. Rev. Lett. **83**, 1814 (1999).

[2]B. Hammer, Phys. Rev. Lett. **83**, 3681 (1999); Surf. Sci., *in press*.

[3]B. Hammer, *to be published*, see: <http://www.ifa.au.dk/~hammer>.

Contact author: Bjørk Hammer

Institute of Physics and Astronomy, University of Aarhus

Fax: +45 86 12 07 40

<http://www.ifa.au.dk/~hammer>

High Throughput Approaches in Catalysis Research

F. Schüth

Max Planck Institut für Kohlenforschung, P.O. Box 10 13 53, 45466 Mülheim,
Germany

High Throughput approaches are well established in the pharmaceutical industry, but only few publications have appeared in the field of materials and especially catalysis. This is to some extent related to the higher obstacles in these fields, especially in heterogeneous catalysis: The conditions of conventional testing, not even speaking of those for industrial scale processes, are not easy to emulate in high throughput reactors. In addition, the performance of a catalyst in an industrial process results from a delicate interplay between catalyst, reaction conditions and catalytic reactor. It is quite difficult to optimize all factors simultaneously in a high throughput approach. Another very serious challenge in heterogeneous catalysis are changes of the catalysts with time which can be crucial for the success of a new process.

With respect to computational problems, library design for solids is quite difficult. For drug molecules, well developed descriptors exist for different modes of analysis. These descriptor based techniques can probably be extended towards the description of molecular catalysts. However, similar approaches do not exist for solids, so that computer aided methods for library design are still in their infancy. These problems, amongst others, have slowed down the development compared to the pharmaceutical industry. Also data handling problems are more severe, since more methods, and thus more data, are necessary for characterizing the identity of a solid catalyst. Nevertheless, the fact that many very attractive processes exist for which no suitable catalyst has been developed so far, makes the use of high throughput techniques in catalysis highly desirable. The first screening techniques developed were primarily focused on the discovery mode, i.e. procedures, where high sample throughput is accompanied with low information depth. Methods used include infrared thermography, resonance enhanced multiphoton ionization (REMPI), Scanning Mass Spectrometry, or luminescence probing. Common to these publication is the fact, that testing of the catalyst is carried out under conditions very different from a conventional catalytic experiment. Although this is probably justified in a very early stage of the discovery process, high throughput testing closer to conventional catalytic tests is desirable in a subsequent stage of the development of a catalyst. At least as useful are techniques for the automated preparation and testing of heterogeneous catalysts on a scale of 10 to 100 mg in a parallelized fashion, an approach which is pursued in Mülheim. The synthesis system is based on a Gilson automated dispenser equipped with automated precipitation and filtering devices built in house. This system allows preparation of catalysts by impregnation, precipitation or coprecipitation. This system is now in routine use for the preparation of a wide variety of different catalysts. However, here as in most cases the bottleneck in the catalyst development process is not the preparation of the catalysts, but the catalytic test itself, because the catalyst has to be mounted, often activated by exposure to certain atmospheres, heated up to reaction temperature, equilibrated under reaction conditions, and eventually analyzed. Several different reactors for this task are under operation in the group. For gas phase reactions, a 16 tube and a 49 tube parallel reactor are being used. Good temperature and flow homogeneity has been demonstrated for these systems, and the data measured with the parallel reactors are of almost similar quality as for a single tube reactor. The analysis is carried out sequentially by a sampling valve, the system is very flexible with respect to the type of analytical instrument, be it IR, GC, mass spectrometry or any other technique. Due to the high flexibility, a large number of different reactions can be analyzed in such systems. They have been used so far for CO oxidation, methane oxidation, and propene

oxidation. Speeding up of catalyst testing by a factor of about 50 is possible with such systems. For liquid phase reactions or three phase reactions, such as hydrogenations, a 25 well stirred autoclave has been constructed. The reliability also of this system has been thoroughly checked. For very rapid hydrogenation reactions, such as the hydrogenation of crotonaldehyde over Pd/C mass transfer limitations occur. However, for slower reactions reliable kinetic data can be generated. Analysis in this case is off line with an autosampler over night.

The discussion shows, that most components for an integrated high through put approach in catalysis research are at least partly developed. If they are used in an intelligent manner, part of the conventional catalyst research can be replaced by high throughput techniques, and first real discoveries are expected for the next years.

Contact author: Ferdi Schüth

MPI für Kohlenforschung

Kaiser Wilhelm Platz 1

45470 Mülheim

Fax: +49-208-306 2995

E-mail: schueth@mpi-muelheim.mpg.de

Ab initio study of methanol synthesis over Zn-deposited Cu surfaces

Yoshitada Morikawa^{1,2} and Kiyoyuki Terakura¹

¹JRCAT, National Institute for Advanced Interdisciplinary Research,
1-1-4 Higashi, Tsukuba, Ibaraki 305-8562, Japan

²School of Materials Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

Identifying active sites for catalytic reactions is of crucial importance in heterogeneous catalysis. Although recent development of surface science techniques has enabled us to analyse solid surfaces microscopically, it is still difficult to clarify the active sites only by experiments. The methanol synthesis from CO₂ and H₂ gas mixtures over Cu/ZnO catalysts has been intensively studied by using powder catalysts as well as single crystal Cu surfaces. In this study, we adopt the slab model with a periodic boundary condition and focus on the interaction between the Zn and two important intermediate species, the formate and the dioxomethylene on the Cu(111) surface. Our calculations show that the substitutionally adsorbed Zn is more stable than the Zn adsorbed on the Cu(111) surface and Cu-Zn surface alloys are formed which is in agreement with experimental results. The structural model based on the formate adsorbed on the substitutionally adsorbed Zn/Cu(111) surface, however, cannot reproduce several experimental results such as infrared reflection absorption spectra, core level shifts and thermal decomposition experiments. We have found that the formate molecule stabilizes the Zn atom adsorbed on the Cu surface and forms a tilted bidentate formate bound to the Zn and Cu atoms, which can reasonably well reproduce the experimental results¹⁾. We have also studied the effect of Zn on the hydrogenation of formate to dioxomethylene on the Cu(111) surface. It is found that the substitutionally adsorbed Zn changes the stability of intermediate states and the activation barrier of the hydrogenation process only slightly. On the other hand, the Zn adsorbed on the Cu surface stabilizes all formate, transition state, and dioxomethylene relative to the gas-phase molecules²⁾. Our results suggest that the existence of the intermediate species induces dramatic changes in the adsorption state of Zn and propose a reaction scheme in which the surface structure changes during the methanol synthesis reaction.

1) Y. Morikawa, K. Iwata, J. Nakamura, T. Fujitani and K. Terakura, *Chem. Phys. Lett.*, **304**, 91 (1999).

2) Y. Morikawa, K. Iwata and K. Terakura, *Appl. Surf. Sci.*, in press.

Contact author: Yoshitada Morikawa

JRCAT, National Institute for Advanced Interdisciplinary Research,
1-1-4 Higashi, Tsukuba, Ibaraki 305-8562, Japan.

Fax: +81-298-54-2788

E-mail: morikawa@jrcat.or.jp

The Reaction of Methanol in Zeolite Acid Catalysts

M.C. Payne¹, R. Shah¹, E. Sandré¹, M. Hytha², I. Štich³, J. Gale⁴,
and K. Terakura⁵

¹TCM Group, Cavendish Laboratory, University of Cambridge, Madingley Road,
Cambridge, CB3 0HE, UK

²National Center for High Performance Computing (NCHC), P. O. Box 19-136,
Hsinchu, Taiwan

³Department of Physics, FEI, Slovak Technical University (STU), Ilkovičova 3,
SK-812 19, Bratislava, Slovakia

⁴Department of Chemistry, Imperial College of Science, Technology and Medicine,
South Kensington, London SW7 2AY, UK

⁵CREST, Japan Science and Technology Corporation (JST), Kawaguchi, Saitama
332, Japan.

It is clear that first principles total energy pseudopotential calculations based on density functional theory can be used to accurately determine structural properties, energies and dynamical information. In principle, therefore, these calculations can be an invaluable tool in understanding and enhancing catalytic action. However, the configuration space associated with most catalytic reactions is extremely complex and the biggest challenge in catalysis is usually to identify the reaction paths and the rate limiting steps in the reaction. In this talk, I shall describe the application of total energy pseudopotential calculations to study the first stage of the methanol to gasoline reaction in zeolite acid catalysts. I shall explain how we have used a range of techniques to obtain a detailed understanding of the first stage of the reaction to form dimethyl ether.

[1] *Understanding the catalytic behaviour of zeolites - a first principles study of the adsorption of methanol*, R. Shah, M.C. Payne, M.-H. Lee and J.D. Gale, *Science* 271, 1395 (1996).

[2] *Dynamical observation of the catalytic activation of methanol in zeolites*, I. Štich, J.D. Gale, K. Terakura and M.C. Payne, *Chem.Phys.Lett.* 283, 402 (1998).

[3] *First principles location of the transition state for formation of dimethyl ether in a zeolite*, E. Sandré, M.C. Payne and J.D. Gale, *Chem.Commun.* 2445 (1998).

Contact author: M.C. Payne
Cavendish Laboratory, University of Cambridge
Madingley Road, Cambridge, CB3 0HE, UK,
Fax: +44-1223-337356
E-mail: mcp1@phy.cam.ac.uk

First-principles studies of molecular reactions in zeolites

Jürgen Hafner, Lubomir Benco and Thomas DemuthInstitut für Materialphysik and Center for Computational Materials Science,
Universität Wien
A-1090 Wien, Austria

Recently many attempts have been made to use ab-initio density-functional techniques to investigate the Brønsted acidity of zeolites and to model molecular reactions inside their large cavities. In this paper we review a series of first-principles investigations (performed both in the local-density approximation and using generalized gradient corrections) concentrating on mordenite (which is a frequently used industrial catalyst) and gmelinite. Gmelinite is a natural mineral which is itself not used in catalysis. The interest in gmelinite stems from the fact that the largest cavity in this material (the gmelinite cage) is identical to that in industrially used zeolites such as faujasite which are themselves too complex to be treated by ab-initio techniques.

The crystal structures of both materials have been optimized and the stability and vibrational properties of different acid sites have been calculated by both force-constant calculations assuming a rigid framework and full ab-initio molecular dynamics simulations. Correlations between the OH-stretching frequencies and the geometry of the acid sites could be established. Proton-transfer between different acid sites via the formation of a short-lived hydronium ion has been studied in low-acid zeolite and in the presence of Na counter-ions.

Ab-initio molecular dynamics has been used to investigate hydration and ion-exchange processes based on the substitution of the alkali counter-ions by ammonium ions. A full energetic profile for the ion-exchange-process could be established.

Adsorption of various forms of hydrocarbon molecules (alkanes, alkenes, aromatics) in both purely siliceous and acidic zeolites has been studied. It has been shown that gradient-corrected functionals seriously underestimate the polarization-induced interactions between the adsorbate and the acid-site as well as with the oxygens of the zeolitic framework. In the LDA, on the other hand, excellent agreement with experiment is obtained for the calculated adsorption energies as a function of the concentration of acid sites. The character of the adsorbate-substrate bonds has been studied via a calculation of the difference-electron densities.

Finally, first results of investigations of the activation of alkanes and alkenes and of aromatic substitution reactions will be presented.

Contact author:

Jürgen Hafner

Institut für Materialphysik and

Center for Computational Materials Science

Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria

Fax: 0043-1-4277-9514**E-mail:** Juergen.Hafner@univie.ac.at

Evaluation of Solid/Water Interfacial Energies
from First Principles Molecular Dynamics Simulations:
Application to the Prediction of
Precipitated Boehmite Morphologies.

Herv Toulhoat, Pascal Raybaud, Wendy Wellens,
Radu Iftime and Mathieu Digne.

Molecular Modeling and Computational Chemistry,
Division of Computer Science and Applied Mathematics,
Institut Français du Pétrole,
1-4 Avenue de Bois-Préau,
92852 Rueil-Malmaison Cedex, FRANCE.

Boehmite, or aluminum oxihydroxide AlOOH , is the precursor of the most important of industrial catalysts supports: γ -alumina. Upon controlled calcination under air flow, boehmite undergoes a topotactic transformation into γ -alumina so that the conserved morphology and size of boehmite nanosized particles are reflected in that of the final transition alumina. Therefore all important textural properties of the industrial catalysts (surface area, pore size distribution, pore shapes...) are essentially determined at the boehmite production step. Many factors such as pH, temperature, and aqueous mother solution composition, influence the solid/liquid interfacial energies, which in turn determine the size and morphologies of boehmite crystallites. It is well known however that solid/liquid interfacial energies are not directly accessible experimentally, but at best their ratios can be deduced from the observation of experimental morphologies.

In an effort to develop a well founded prediction of these effects of obvious industrial outcomes, we have developed a strategy for evaluating interfacial energies ab initio: for a given orientation $\langle hkl \rangle$ of the solid-liquid interface we build a slab model of adequate size. The axis perpendicular to the interface is colinear to the $\langle hkl \rangle$ direction. Allowing relaxation of the as cleaved surface against a vacuum, we derive the solid's surface energy $\Gamma_v(hkl)$ for that orientation. Filling the inter-slab space with a molecular liquid (l) like water (w), at the adequate density, and starting again from the as cleaved surface, we further allow the interface to react chemically with the liquid at a specified temperature until quasi-equilibration, by performing first-principle MD in the NVT ensemble. We check for the saturation of adsorption at the interface by eventually "re-filling" the inter-slab liquid space to compensate for the consumption by reactions at the interface. We take the decrease in average total energy per unit area referred to the sum of average total energies of the separate bulk phases (solid and liquid) as a measure of the interfacial energy $\Gamma_{sl}(hkl)$, neglecting in a first approximation the entropic contributions. For these calculations we have used the VASP package^[1], at the DFT/GGA/USPP level. Because such calculations are restricted to neutral unit-cells, we have assimilated the resulting values of $\Gamma_{sl}(hkl)$ to the interfacial energies at the Zero Point Charge (ZPC) of the corresponding surfaces. These values have provided the necessary input for a simple analytical model of the pH and ionic force dependency of the interfacial energies^[2] and finally, the equilibrium morphologies of boehmite have been predicted as a function of pH according to the Gibbs-Curie-Wulff construction. The predictions are in very good agreement with experiments: the initially hydroxyl terminated and therefore chemically inert $\langle 010 \rangle$ basal surface dominates the rhomboedral platelets morphologies in all cases with negligible effect of water adsorption through hydrogen binding ($\Gamma_v(010) = 0.45 \text{ J.m}^{-2}$, $\Gamma_{sw}(010) = 0.47 \text{ J.m}^{-2}$). However the edges have the orientation $\langle 100 \rangle$ at acidic pH ($\Gamma_v(100) = 1.86 \text{ J.m}^{-2}$,

$\Gamma_{sw}(100) = 0.69 \text{ J.m}^{-2}$) and $\langle 101 \rangle$ at pH above overall ZPC ($\Gamma_v(101) = 3.04 \text{ J.m}^{-2}$, $\Gamma_{sw}(101) = 1.28 \text{ J.m}^{-2}$). At pH close to neutrality, the less reactive $\langle 001 \rangle$ surface shows up ($\Gamma_v(001) = 1.20 \text{ J.m}^{-2}$, $\Gamma_{sw}(001) = 1.18 \text{ J.m}^{-2}$), in coexistence with the $\langle 100 \rangle$ and $\langle 101 \rangle$ surfaces. The effect of temperature on morphology is equally well predicted. The configurations of equilibrated surfaces show a variety of reaction products between water and initially coordinatively unsaturated Al or O surface atoms. To our knowledge, this is the first example of successful application of first principle simulations to the derivation of liquid/solid interfacial energies, demonstrating the paramount significance of chemical reactions and/or chemisorption that can occur at the interfaces.

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Contact author:

Dr Herve TOULHOAT

Group Leader, Molecular Modeling and Computational Chemistry
Div. Computer Science and Applied Mathematics, IFP
Director, Groupement de Recherches CNRS G1209:
Dynamique Moleculaire Quantique Appliquee a la Catalyse
Research Group CNRS G1209
Ab Initio Molecular Dynamics Applied to Catalysis
(Scientific Partners: CNRS, IFP, Total, University of vienna, TU Eindhoven.)

Tel: +33-1-47-52-73-50

Fax: +33-1-47-52-70-22

E-mail: herve.toulhoat@ifp.fr

Steam Reforming Catalysis on Ni: the Role of Structure and Promoters

Hanne S. Bengaard^{‡*}, and Jens K. Nørskov^{*}

[‡]Interdisciplinary Research Center for Catalysis (ICAT)

^{*}Center for Atomic-scale Materials Physics (CAMP), Physics Department, Building 307, Technical University of Denmark, DK-2800 Lyngby, Denmark.

Alkali metals are important as catalyst promoters in steam reforming. The mechanism of promotion and poisoning of the dissociative chemisorption of methane on Ni(111) and Ni(100) surfaces has been studied in a series of DFT calculations. It was found that the barrier for dissociation of methane is increased by about 0.2 eV when potassium ($\Theta(\text{K})=1/8$) is pre-adsorbed on the Ni(111) and Ni(100) surfaces. The calculations predict that potassium is an inhibitor and this is in agreement with sticking experiments. Also the calculated magnitude of the barrier is in reasonable agreement with what is found experimentally[1]. The reason for adding potassium to nickel steam reforming catalysts is its ability to suppress the reactions leading to graphite formation and blocking of the reactor.

A simple electrostatic interaction can account for the effect of K on the barrier: methane in the transition state has an induced dipole moment where electrons are pushed towards the surface. This moment interacts with the electrostatic field induced by the potassium atoms on the surfaces. The increase in barrier height due to potassium is found to correlate with this electrostatic interaction.

We also investigated the structural effects on methane dissociation using different Ni surfaces. Results for the flat Ni(100) and Ni(111) surfaces and a stepped surface (Ni(211)) are presented together with results for dissociation on the Ni(111) surface with a Ni ad-atom. The variations in barrier height for the different surfaces are analysed using the center of the metal d bands as a simple parameter.

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Contact author: Hanne S. Bengaard

Fax: +45932399

E-mail: bengaard@fysik.dtu.dk

Ordering, Percolation, and Diffusion in Atomistic Models for Surface Reactions

Jim Evans, Da-Jiang Liu

Ames Laboratory - USDOE, Iowa State University

Mike Tammaro

Department of Physics, University of Rhode Island.

Our research program focuses on the analysis of atomistic lattice-gas models for surface reactions with the goal of obtaining exact (non-mean-field) reaction-diffusion equations which describe mesoscopic spatiotemporal behavior (i.e., chemical waves and pattern formation) [1]. Two fundamental aspects of these models which have received little attention to date are: (i) the nature of adlayer ordering in the non-equilibrium reactive steady states; and (ii) the chemical diffusion of mobile adspecies through the disordered environment provided by coadsorbed species. This diffusion is important as it controls spatial pattern formation. In general, it is influenced by the adlayer ordering, and both diffusion and ordering reflect the details of adspecies interactions.

To explore these issues, we consider a simple model for CO-oxidation with highly mobile adsorbed CO, and superlattice ordering of adsorbed oxygen [2]. A non-equilibrium order-disorder transition is found in this model. This transition strongly influences the percolation behavior of superlattice domains of oxygen, which in turn is shown to control the chemical diffusion of coadsorbed CO. The latter constitutes a new type of problem involving transport in disordered media.

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Contact author: Jim Evans

Iowa State University,

Ames, Iowa, 50011 USA

Fax: 515-294-0266

E-mail: evans@ameslab.gov

Breaking NO on a transition metal surface :
A DFT comparison of Rh, Pd and Pd-Mn alloy

David Loffreda, Daniel Simon and Philippe Sautet

Institut de Recherches sur la catalyse, 2 Av A. Einstein, 69626 Villeurbanne, France
Ecole Normale Supérieure de Lyon, 46 Allée d'Italie, 69364 Lyon, France

The reduction of NO in nitrogen is a key reaction performed by car exhaust catalysts. The dissociation of NO is in many cases the rate limiting step of this reaction. Rh metal is known to be especially efficient for the reduction of NO but is very rare and expensive. The activation of NO is much more difficult on the other metals taking part to the catalyst, Pd and Pt. In contrast, recent reports suggest that the dissociation of NO is much faster on a PdMn alloy than on Pd, reaching an efficiency close to that of Rh.

In order to get insights in the compared activity of various transition metal surfaces for the dissociation of NO, we have performed DFT periodic calculations using the VASP code. We have considered Rh, Pd and PdMn alloy metal surfaces and the influence of the surface structure has been addressed by the comparison of (100), (111) and stepped surfaces. Adsorption geometries and dissociation pathways will be presented, together with a complete vibrational analysis of the chemisorption and transition states. Dissociation rates have been obtained from the Transition State Theory. Compared to Pd, the dissociation barrier is strongly reduced on the Pd-Mn alloy, reaching a value close to that on Rh. The influence of the molecular coverage on the dissociation reaction barrier will also be discussed.

Contact author: Philippe Sautet

Institut de Recherches sur la Catalyse, Villeurbanne, France

Fax: 00 33 72 44 53 99

E-mail: sautet@catalyse.univ-lyon1.fr

Femtosecond Chemistry and Time-resolved Vibrational Dynamics at Surfaces

Martin Wolf

Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

We discuss recent experiments using femtosecond laser spectroscopy to elucidate the microscopic mechanisms and time scales of energy flow in photoinduced surface reactions. Femtosecond excitation of hot substrate electrons allows to open new reaction pathways, which are not accessible with conventional thermal heating, i.e. under conditions where the electrons and phonons are in equilibrium. This is demonstrated for the reaction between coadsorbed atomic oxygen and CO on Ru(001) [1]. In this process fast coupling of transiently excited hot electrons to an antibonding state of the O-Ru bond leads to vibrational excitation of atomic oxygen, as evidenced by the observed sub-picosecond reaction dynamics, pronounced isotope effects and from density functional calculations. The activated oxygen subsequently reacts with CO to form CO₂. In contrast, the desorption of CO molecules is caused by coupling of the adsorbate to the phonon bath of the Ru substrate on a picosecond timescale.

We use time-resolved vibrational sum-frequency generation to record spectroscopic snapshots of the excited adsorbate layer during femtosecond laser-induced desorption of CO from Ru(001). Analysis of the transient frequency shift of the CO stretching mode provides insights in the contribution of lower frequency vibrational modes, which are anharmonically coupled to the CO stretch [2]. The use of spectrally broad infrared pulses allows also to excite and probe vibrational overtones. By varying the coverage and thus the dipole coupling between the CO molecules, we can study the transition between localized excitations on single oscillators and the delocalization of vibrational energy within the adsorbate layer.

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Contact author: Martin Wolf

Fritz-Haber-Institut der MPG,

Faradayweg 4-6, 14195 Berlin, Germany,

Fax: +49 30 8413 5106

E-mail: wolf_m@fhi-berlin.mpg.de

From First-Principles to Catalytic Turnovers

Matthew Neurock

Department of Chemical Engineering, University of Virginia, Charlottesville, VA
22903

Considerable progress has been made over the past few years in advancing both theory and simulation to understanding surface reactivity. First-principle quantum chemical methods, for example, can begin to predict structural conformations, energies, and even activation barriers. First-principle quantum chemical calculations can also be used to elucidate and in some cases quantify the nature of the adsorbate-surface bond strength. The application of these methods to actual catalytic processing, however, is limited due to the nature of extrinsic factors such as coverage effects, defect sites, metal support interactions, solvent effect, and surface composition. Extrinsic factors can considerably alter the metal-adsorbate surface interaction and thus affect the surface kinetics. We will describe an approach in which we integrate first-principle DFT calculated activation barriers, reaction energies, adsorption energies and lateral interactions into a site-explicit dynamic Monte Carlo algorithm in order to simulate surface catalytic kinetics. We will discuss the application of this technique to the first-principle based modeling of selective oxidation and hydrogenation chemistries on transition metal surfaces.

Contact author: Matthew Neurock
Department of Chemical Engineering
University of Virginia
Charlottesville, VA 22903-2442
Fax: (804) 982-2658
E-mail: mn4n@virginia.edu

The CO+NO redox reaction on Pt(100)
studied from first principles.

Andreas Eichler and Jürgen Hafner

Institute for Materials Science and Center for Computational Materials Science,
University of Vienna,
A-1090 Wien, Austria

The importance of heterogeneous catalysis in modern industry has motivated the great interest in theoretical and experimental studies of gas–solid surface interactions. Especially the catalytic reduction of NO by CO is one of the central reactions in car exhaust catalysts. On the other hand this reaction is quite interesting from a more technical point of view. It takes place in an explosive manner and exhibits also an oscillatory behaviour in time.

All steps of this reaction over the Pt(100) surface have been modelled via ab-initio local-density functional calculations using the Vienna ab-initio simulation package (VASP):

- the adsorption of NO and CO on the Pt(100) surface including co-adsorption effects,
- the catalytic dissociation of NO,
- the recombinative desorption of N₂ via a molecular intermediate
- and finally the oxidation of carbon monoxide followed by
- the desorption of CO₂.

All relevant energy barriers along the reaction pathway have been determined using the nudged-elastic-band (NEB) method. For each reaction step activation energy and attempt frequency were calculated.

Contact author: Andreas Eichler
Institut für Materialphysik
Sensengasse 8/12, 1090 Wien,
Austria.
Fax: +43-1-4277-9514
E-mail: andreas.eichler@univie.ac.at

First Principles Study of the Interplay between Surface Chemistry and Field Emission from Metal Surfaces

R. Ramprasad

DigitalDNA Laboratories (Motorola, Inc.) 2100 E. Elliot Rd., EL 740, Tempe, AZ
85284

The field-assisted emission of electrons from materials is a phenomenon that is currently being harnessed in various applications, including flat panel displays. Electron sources currently being explored in these field emission displays (FED) are Mo tips and carbon based materials (e.g., diamond like carbon, nanotubes, etc.). The variation of the work function of the emitting surface with environment is one of the factors that determines the efficiency of the device. The main focus of the first part of this talk will be the work function of an array of graphene ribbons and Mo surfaces, in the presence of various types of adsorbates typically found in FEDs. All calculations are based on density-functional theory within the local density approximation using nonlocal pseudopotentials. The second part of the talk will address the dependence of the surface coverage and the metal surface work function on the partial pressure of the gas phase adsorbate. A lattice Monte Carlo method, which uses pair wise and three body adsorbate interactions obtained from density functional calculations, was used to aid in this study. Finally, a formalism based on the Bardeen transfer Hamiltonian (BTH) method for calculating the field emission current from a surface will be presented, and applied for the test case of a jellium surface. The applicability of this method is quite general, is considerably more sophisticated than the conventional semi-classical Fowler-Nordheim description of field emission, and is much less expensive than intensive scattering-theoretic techniques.

Contact author: Dr. R. Ramprasad
DigitalDNA Lab (Motorola, Inc.)
2100 E. Elliot Rd., EL 740, Tempe, AZ 85284
Fax: 480 413 7918
E-mail: R.Ramprasad@motorola.com

Understanding and tailoring metal-oxide interfaces from first principles

Alexander Bogicevic

Ford Research Laboratory

Systematic studies of metal-oxide interactions provide insight into ways to control the interface chemistry between two important classes of materials. First-principles density-functional calculations offer a means to filter out observables that govern key materials properties, and provide in-depth understanding needed to further the field. This approach has been employed to study the adhesion and wetting, as well as diffusion kinetics and nucleation, of various metal particles on thin films and crystals of Al₂O₃, MgO, and TiO₂. To better connect to experimental conditions, these studies also address the roles of common surface defects and water by-products. In this talk, I will discuss how the nature of the metal-oxide bond changes with coverage, what physical observables govern bond strengths, and how point defects and contaminants affect the wetting, adhesion, and dispersion of metal particles on oxides [1-6]. I will also demonstrate how certain electronegative co-adsorbates can induce wetting of nominally non-wetting metal-oxide systems, drastically increase the adhesion of the metal to the oxide, and smoothen out the morphology of the growing film (patent pending).

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Contact author: Alexander Bogicevic

Ford Research Laboratory

Fax: +1 313 845-8625

E-mail: abogicev@ford.com

Role of Surface Defects in the Catalytic Activation of Pd Atoms and Clusters on MgO

Gianfranco Pacchioni, Anna Ferrari, Livia Giordano

Dipartimento di Scienza dei Materiali, INFN, Università di Milano-Bicocca, via Cozzi
53, 20125 Milano, Italy

Notker Rösch

Fachgebiet für Theoretische Chemie, Technische Universität München, D-85747
Garching, Germany

Ulrich Heiz, Wolf-Dieter Schneider

Institut de Physique de la Matière Condensée, Université de Lausanne, CH-1015
Lausanne, Switzerland

Quantum-chemical methods have been used to understand the cyclization reaction of acetylene to benzene on Pd. This reaction occurs at very low temperature and pressure as well as in real catalytic conditions. It has been extensively studied experimentally using a variety of surface science techniques. Theory has provided an important complement to experiment for the identification of the reaction intermediates and the interpretation of spectroscopic measurements. Recently, the same process has been studied on size-selected Pd clusters supported on MgO thin films (1). The activity of these supported particles opens new questions about the minimum number of metal atoms needed to catalyze the reaction, the effect of the MgO substrate, the role of surface defects, like low-coordinated sites and oxygen vacancies.

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Contact author: Gianfranco Pacchioni
Dipartimento di Scienza dei Materiali, INFN,
Università di Milano-Bicocca, via Cozzi 53, 20125 Milano
Fax: +39-02-6448 5403
E-mail: gianfranco.pacchioni@mater.unimib.it

First principles calculations for V_xO_y grown on Pd(111)G. Kresse

Institut für Materialphysik, Universität Wien and Center for Computational Material
Science, Sesengasse 8, A-1090 Wien, Austria

S. Surnev, M.G. Ramsey, F.P. Netzer

Institut für Experimentalphysik, Karl-Franzens-Universität Graz A-8010 Graz,
Austria

First principles calculations for thin films of V_xO_y on Pd (111) are reported. More than 50 structural models are considered with varying stoichiometry and coverage, and detailed results for the energetic stability are presented. The general principles for the growth of thin vanadium oxide films on Pd(111) are discussed, and the experimental results are interpreted in the light of the first principles calculations. The approaches used in the present work might prove useful for a wide variety of metal-supported oxides.

Contact author:

Georg Kresse

Institut für Materialphysik,
Universität Wien and Center for Computational Material Science

Sesengasse 8, A-1090 Wien, Austria

Fax: +43-1-4277-9514**E-mail:** Georg.Kresse@univie.ac.at

Structure and Reactivity of Oxygen Vacancies at Vanadium Pentoxide Surfaces: ab initio DFT cluster studies

K. Hermann¹, M. Witko², R. Družinić¹, and R. Tokarz²

¹ Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

² Institute of Catalysis and Surface Chemistry, PAS, ul. Niezapominajek, PL-30 239 Cracow, Poland

Vanadium oxide surfaces are widely used in catalytic reactions of technological importance, such as hydrocarbon oxidation where surface oxygen participates in the reaction. As a result, oxygen vacancies are created at the oxide surface which can influence its reactivity. In the present theoretical work we have examined geometric and electronic properties of different oxygen vacancies at the $V_2O_5(010)$ surface using cluster models where the electronic structure is calculated by ab initio density functional theory (DFT) together with gradient corrected exchange-correlation functionals (RPBE). The substrate clusters form sections of the bulk terminated surface where embedding is achieved by saturating peripheral oxygen - metal bonds with hydrogen. Surface oxygen vacancies are studied by removing oxygen atoms from specific sites (1-, 2-, 3-fold coordinated) O(1-3) of the cluster after which the electronic structure of the vacancy cluster is evaluated, both keeping all atom positions fixed (frozen vacancies) and allowing the atoms near the vacancy to relax until local equilibrium is reached (relaxed vacancies).

Computed vacancy formation energies range between 6.5 and 7.2 eV suggesting that surface oxygen is bound very strongly at $V_2O_5(010)$. In contrast, energetic contributions due to vacancy induced surface relaxation are quite moderate (0.5 - 1.0 eV). The geometric effect of surface relaxation is described by both lateral contributions and by those normal to the surface where the latter affect inter layer binding in V_2O_5 and may give rise to major surface/bulk reconstruction. The presence of surface oxygen vacancies leads to chemical reduction of nearby vanadium atoms which manifests itself by increased V 3d occupation as shown in corresponding orbital analyses and partial densities of states. This is confirmed by experimental photoemission data. Further, oxygen vacancy healing by oxygen (O_2) adsorption and by diffusion as well as adsorbate assisted vacancy formation has been examined by the cluster models and will be discussed in detail.

Contact author: Prof. Dr. K. Hermann
Fritz-Haber-Institut der MPG
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: ++49-30-8413 4701
E-mail: hermann@fhi-berlin.mpg.de

QM-Pot and plane wave studies on the reactivity of solid acid catalysts

Joachim Sauer, Marek Sierka, and Frank Haase

Arbeitsgruppe Quantenchemie, Institut für Chemie Humboldt-Universität, D-10117
Berlin/Germany

Substantial progress has been made in recent years in the application of ab initio theory to heterogeneous catalysis. This is largely due to the fact that periodic calculations have become feasible even for problems requiring the definition of a large repeating cell. Two complementary methods are presented: plane wave pseudopotential calculations often combined with the Car-Parrinello molecular dynamics approach, and a combined quantum mechanics - interatomic potential function (QM-Pot) technique [1]. The former is fully ab initio, while the latter is a hybrid method that describes the reaction site quantum mechanically and the periodic structure by an analytical potential function. We highlight this development for different examples of catalysis by solid acids. Employing the Car-Parrinello Molecular Dynamics (CPMD) code ab initio simulations have become feasible even for unit cells as large as those of zeolite ZSM-5 which has a size of 20.2 x 20.0 x 13.5 Å and includes 288 atoms. We examine the adsorption of a single methanol molecule in the acidic zeolites theta-1, ferrierite and ZSM-5 [2]. We always find a physisorbed molecule as a stable structure. Comparison is made with previous calculations on methanol in chabazite which used the same techniques [3]. The adsorption energies (as well as the deprotonation energies) show differences of only 20 kJ/mol and there is no indication of a strong effect of the zeolite framework structure on the reactivity of the active site. However, protonation of methanol is easily achieved for loadings of two molecules per site and possible mechanisms of C-C bond formation can be studied by constraint dynamics [4]. Our combined QM-Pot technique has been successfully employed in studies of the site and framework dependence of reaction energies related to zeolite acidity such as the energy of deprotonation [5] and the heat of ammonia chemisorption [6]. Use is made of this approach to localize transition structures for intra-site proton jumps in Brønsted sites of different protonated zeolites, CHA, FAU and MFI (see refs. [1,4] for preliminary reports). The predicted jump rates show large variations, from 10^{-5} to 10^5 s⁻¹ at room temperature, and vary between different jump paths for a given site and between Brønsted sites in different frameworks.

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Contact author: Prof. Joachim Sauer

Fax: +(49)30-20192 302

E-mail: js@qc.ag-berlin.mpg.de

STM Studies On Model Systems Relevant For Catalysis

Flemming BesenbacherInstitute of Physics and Astronomy and Center for Atomic-scale Materials Physics,
University of Aarhus, Denmark

Scanning tunnelling microscopy (STM) has proven to be a fascinating and powerful technique in the field of surface science. The fact that sets STM apart from most other surface sensitive techniques is its ability to resolve single atoms and molecules on surfaces and furthermore to reveal the dynamics of surface processes by recording many sequential STM images with a fast-scanning, variable-temperature STM [1,2]. In this talk, I will show how STM can be used to give unprecedented new insight into model systems relevant for catalysis. I will show how STM studies have led to new insight in the morphology and edge structures of MoS₂ nano-clusters [3], and how promotor atoms like Co perturb the morphology of the MoS₂ nano-clusters [4]. These systems are of interest as model systems for hydrodesulfurization catalysts. I will also present recent results for the atomic-scale structural response of a Cu (110) surface to ambient H₂ gas at pressures ranging from 10⁻¹³ to 1 bar using a novel high-pressure STM. From atom-resolved images we conclude that the surface responds identically to hydrogen at UHV and at atmospheric pressures, and thus the results provide strong support for the surface science approach to heterogeneous catalysis.

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Contact author: Flemming Besenbacher

Address, Institute of Physics and Astronomy, Building 520 Ny Munkegade, University of Aarhus, DK-8000 Aarhus, Denmark

Fax: +45 86120740**E-mail:** fbe@ifa.au.dk

New insights into the molecular adsorption mechanism by ab initio
based tight-binding molecular dynamics simulations

Axel Groß

Technische Universität München, D-85747 Garching, Germany

Andreas Eichler and Jürgen Hafner

Universität Wien, A-1090 Wien, Austria

Florian Kirchhoff

Ohio State University, Columbus, OH-43210, USA

Michael J. Mehl and Dimitrios A. Papaconstantopoulos

Naval Research Lab, Washington, D.C. 20375-5345, USA

We have performed tight-binding (TB) molecular dynamics simulations of the adsorption of $O_2/Pt(111)$ using the NRL-TB method [1,2]. The tight-binding Hamiltonian was derived from density functional theory calculations [3]. The Pt-Pt interactions were kept to the original values that fit the pure Pt surface energies well [1] while a new fit was performed to determine the Pt-O and the O-O TB parameters.

The experimental results are well-reproduced by our simulations. In particular, due to the microscopic insight into the adsorption mechanism we are able to explain why at low surface temperatures O_2 does not dissociate on Pt(111) even at high kinetic energies which are much larger than the dissociation barrier. The large decrease of the sticking probability with increasing incident kinetic energy of the molecules at low energies is usually explained by trapping into a shallow physisorption well. We demonstrate, however, that the whole dependence of the sticking probability on the incident kinetic energy can be solely understood by trapping into a chemisorption state, i.e., the usual interpretation of the sticking curves invoking a physisorbed precursor leads to an incorrect estimation of the underlying potential energy surface.

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Contact author:

Axel Groß

Physik-Department T30

Technische Universität München

D-85747 Garching, Germany

Fax: +49 89 289 12296

E-mail: agross@ph.tum.de

First-Principles Design of Biocatalysts

Ursula Röthlisberger

Laboratory of Inorganic Chemistry, ETH Zentrum, ETH Zürich,
CH-8092 Zürich, Switzerland

During millions of years of evolution, nature has developed its own mild, efficient and highly selective way of doing chemistry. The idea of making direct use of this reservoir of elegant synthetic routes emerges therefore quite naturally. Of particular interest in this respect, is the design of small synthetic analogs of enzymatic sites capable of mimicking the *in vivo* chemistry. The search for such biomimetic compounds however, is far from trivial and only relatively few systems are known that can reproduce the essential chemistry of natural systems with high fidelity. One reason for the limited progress is the fact that in many cases detailed mechanistic knowledge of the enzymatic processes is not available. Enzymatic reactions take place in a very complex, heterogeneous environment and it is difficult to pinpoint all the crucial factors governing the enzymatic processes with the aim of incorporating them in a small synthetic analog.

We have performed a parallel modelling approach based on mixed QM/MM Car-Parrinello simulations to develop novel (stereo)selective oxidation catalysts mimicking the copper enzyme galactose oxidase. Through a detailed characterization of the catalytic cycle of the natural system and an existing biomimetic compound it was possible to design new highly efficient biomimetic catalysts.

Contact author: Ursula Röthlisberger

ETH Zentrum Zürich

Laboratory of Inorganic Chemistry, Universitaetstrasse 6, 8092 Zürich,
Switzerland.

Fax: 0041-1-632 10 90

E-mail: uro@inorg.ethz.ch

Biocatalysis

Jens K. Nørskov

Center for Atomic-scale Materials Physics (CAMP), Physics Department, Building
307, Technical University of Denmark, DK-2800 Lyngby, Denmark.

Contact author: Jens K. Nørskov

Fax: +45932399

E-mail: norskov@fysik.dtu.dk

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Surface Composition of Bimetallic Alloys - the Influence of Adsorbates

Ebbe Christoffersen^{1,2}, Jens K. Nørskov² and Per Stoltze³

¹ Interdisciplinary Research Center for Catalysis (ICAT), Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

² Center for Atomic-scale Materials Physics (CAMP), Department of Physics, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

³ Department of Chemical Engineering, Ålborg University Esbjerg, DK-6700 Esbjerg, Denmark

Alloys have been shown in a number of cases to have superior catalytic properties compared to elementary metals. Alloy catalyst surfaces will typically have a reactivity which is different from each of the constituents. Examples of alloy catalysts include the platinum-rhodium catalyst used in cars to clean the exhaust gas and the platinum-ruthenium catalyst used in fuel cells in order to increase the CO tolerance. Segregation in an alloy will depend on the presence of adsorbates on the surface since the interaction of the two metals with a given adsorbate will not in general be the same.

We have developed a theoretical method to calculate the surface composition of a bimetallic alloy as a function of bulk composition, partial pressure of molecules in the gas phase and the degree of dispersion of the catalyst particles. From the clean surface segregation energy and knowledge of the adsorption energy of an adsorbate on the individual metal components and possible effects of alloying, we calculate the surface composition using a Monte Carlo technique.

Results for the Pt-Rh alloy system and the Pt-Ru system with and without CO in the gas phase are presented. For the Pt-Ru system it is seen that the presence of CO increases the amount of Ru in the surface. It has been shown experimentally that Pt overlayers on a Ru(0001) surface bonds CO weaker than clean Pt(111) [1]. Our simulations suggest that this effect can explain the increased CO tolerance of the alloy. Even though the surface contains Ru, which is completely covered by CO, the amount of free Pt atoms in the surface is increased.

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Contact author: Ebbe Christoffersen

Department of Physics, Building 307, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

Fax: (+45) 45 93 23 99

E-mail: ebbec@fysik.dtu.dk

DFT Studies of Adsorbate Induced Surface Relaxation: N/Pt(111) and H/Mo(111)

A. Fahmi, M. Arnold, W. Frie, L. Hammer, K. Heinz

Lehrstuhl für Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91
058, Erlangen, Germany.

Top layer of clean Pt(111) surface experiences an outward relaxation of +2% (exp. +1%). Upon Nitrogen adsorption this relaxation is increased up to +4%. Metal atoms coordinated to nitrogen are pulled outward whereas the other atoms experience an inward relaxation. Nitrogen shows a slight preference for fcc sites compared with hcp sites, an energy difference of 4 kcal/mol. The behaviour of Mo(111) is different, the two top layers of the clean surface experience a large inward relaxations of -23 and -21% respectively (exp. -19%) [1]. Upon hydrogen saturation with three adatoms per surface unit cell, the drastic contraction of the first layer remains unchanged. However, the second layer de-relaxes completely up to the bulk value. Hydrogen is found to adsorb at sites with twofold coordination, bonding to atoms of first and second layers, shifted off the ideal bridge position.

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Contact author: A. Fahmi
Norsk Hydro ASA,
P. O. Box 2560, 3907 Porsgrunn, Norway,
Fax: +47 35 92 27 22
E-mail: Adil.Fahmi@hydro.com

Understanding the mechanism of water adsorption on metal surfaces: the structure of the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ bilayer of H_2O on $\text{Ru}(0001)$

Giuliana Materzanini and Peter Saalfrank

University College London, Chemistry Department & Centre for Theoretical and Computational Chemistry (CTCC), London WC1H 0AJ, United Kingdom

Philip J. D. Lindan

CLRC Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

Water adsorption at metal surfaces is of fundamental interest in electrochemistry and catalysis. In particular, the $\text{H}_2\text{O}/\text{Ru}(0001)$ system has attracted the attention of the experimentalists since the early '80s, and a structural model based on the arrangement of the molecules in the hexagonal phase of ice (I_h), the so-called bilayer, has been proposed for the adsorption geometry [1].

Recently [2], this structural model was partially contradicted by new experimental evidences coming out from a complete LEED-IV analysis of an ordered water bilayer adsorbed on the $\text{Ru}(0001)$ surface. The most unexpected feature of the new adsorption geometry is the out-of-plane compression of the water bilayer that makes it rather a 'buckled' monolayer.

Despite the amount of experimental work on this subject, theoretical studies on the adsorption of H_2O on transition metals are rare, and they are missing for the specific $\text{H}_2\text{O}/\text{Ru}(0001)$ system. To fill this gap and to address the new experimental evidences, we have performed gradient-corrected Density Functional Theory (DFT) calculations on naked and water covered $\text{Ru}(0001)$ surfaces, using the Cambridge Serial Total Energy Package (CASTEP) that employs plane-wave pseudopotential techniques and the method of the supercell[3]. In the fully relaxed calculations we allowed the Hydrogens in the $p(\sqrt{3} \times \sqrt{3})R30^\circ$ surface cell to assume all the possible arrangements with respect to hcp substrate, i.e. we studied a slab with a (3×3) - $6\text{H}_2\text{O}$ - $\text{Ru}(0001)$ surface cell. Results for the geometry and energetics are reported and analyzed. We notice that the computed adsorption geometry reproduces rather closely the buckled monolayer structure [2]. The interplay between the hydrogen-bonding in the bilayer (described at a high degree of accuracy by the gradient-corrected functional) and the metal-water interactions is discussed as responsible for the bilayer compression. The smaller $p(\sqrt{3} \times \sqrt{3})R30^\circ$ - $2\text{H}_2\text{O}$ - $\text{Ru}(0001)$ system will be analyzed in order to see how the ordering of the Hydrogen atoms can influence the final results.

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Contact author: Giuliana Materzanini
University College London, Department of Chemistry,
20 Gordon Street, WC1H 0AJ, United Kingdom.

Fax: 0044-207-380 74 63

E-mail: giuliana@chem123.chem.ucl.ac.uk

First-principles MD simulations of SiO₂-Water ClusterHai-Ping ChengDepartment of Physics and Quantum Theory Project,
University of Florida, Gainesville FL 32611, USA

Structure, chemical bond breaking, and dissociation of water molecule have been investigated using Barnett-Landman (BL) Born-Oppenheimer local spin molecular dynamics (BO-MD-LSD) method [1] with generalized gradient corrections (GGA). The nature of Si-O bond has been investigated as a function of the number of water molecule in the cluster. Our studies indicate that the size of the cluster plays an important role. Further investigations are under the way to understand the complete picture of bond breaking and formation in this system.

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Contact info (June 1-Dec. 31, 2000): Hai-Ping Cheng

Tel: 0041-1-724 85 69

Fax: 0041-1-724 89 83

E-mail: hch@zurich.ibm.com

Permanent: Tel: 001-352-392-6256

Fax: 001-352-392-8722

E-mail: hch@zurich.ibm.com

Stressed Pt islands on Co(0001) and CO adsorption.

P. LégaréLERCSI, ECPM, Universit Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg,
France.

G.F. Cabeza and N.J. Castellani

Departamento de Fisica, Universidad Nacional del Sur, Avda Alem 1253, 8000 Bahia
Blanca, Argentina.

The growth of Pt on Co(0001) has been followed by photoemission (XPS and UPS), Scanning Tunneling Microscopy (STM) and Low Energy Electron Diffraction (LEED). At submonolayer coverages, Pt grows essentially as one-layer-thick islands on the Co terraces and along the steps. A second Pt layer starts growing around 0.4 ML but remains in minority even for 1 ML Pt equivalent deposit. Although no atomic resolution could be obtained, STM provides data which could be explained by Pt-Pt distance shortening by at least 7 (111) surface. This is reinforced by the electronic structure characterized by a low density of Pt states at the Fermi level and Pt states centered around 4 eV below. CO adsorption at room temperature was used to characterize the chemical properties of the overlayer. XPS signals from the Co and Pt areas could be separated. The O 1s and Pt 4f peaks showed that CO is adsorbed in on-top sites on the Pt islands with a maximum coverage of 1/3 ML and a LEED pattern similar to the pure Pt(111) surface. However the adsorption energy is only about 0.8 eV i.e. about 30 ascribed to the high in-plane compression suffered by the Pt overlayer.

Contact author:

Pierre Légaré

ECPM-LERCSI

25 rue Becquerel

67 087 Strasbourg Cedex 2

Fax: (0)3 88 13 69 68**E-mail:** e-mail legare@chimie.u-strasbg.fr

Site switch of on-surface oxygen adatoms on Rh(111) – a DFT study

M. V. Ganduglia-Pirovano, M. Scheffler

Fritz-Haber-Institute der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

Oxygen adatoms on Rh(111) at low coverage are known to occupy fcc adsorption sites, but recent experiments indicated that at higher coverages, when oxygen also occupies subsurface octahedral sites, the on-surface adatoms switch from the fcc to the hcp adsorption sites [1]. We report density-functional theory calculations to analyze the nature of the surface chemical bond of adsorbed oxygen and how this changes with coverage. This also yields to an understanding of the preferred on- and sub-surface sites. We find that if subsurface O was to occupy octahedral sites, the hcp on-surface sites would indeed be preferred. Yet, the most stable geometry in our calculations is obtained, when the on- surface O sits in fcc sites and the sub-surface O in tetrahedral sites. We thus suggest that the experimentally observed geometry corresponds to a metastable phase, which is only established during the incorporation of sub-surface O.

In this context we argue that the Rh_{3d} and O_{1s} core level shifts (CLSs) and the adsorption induced change of the work function provide most useful information for analyzing such systems. We compute initial- and final-state contributions to the CLSs as a function of oxygen coverage on the surface, and compare when possible our results (geometry as well as CLSs) to recent experimental data [2]. The dominant factor stabilizing the on-surface fcc sites, with or without subsurface O formation, is found to be an increased *ionic* contribution to the binding compared to the less stable hcp hollow sites.

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Contact author: M. Veronica Ganduglia-Pirovano

Theory Department, Fritz-Haber-Institute

Faradayweg 4-6, D-14195 Berlin, Germany

Fax: +49 30 8413 4701

E-mail: pirovano@fhi-berlin.mpg.de

Oxidation of the Basal Graphite Plane by Atomic Oxygen: An ab initio Study

Andrei Incze and Alain Pasturel

Laboratoire de Physique et Modélisation des Milieux Condensés, CNRS
BP 166, Grenoble, France

Christian Chatillon

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques, INPG
F-38402, Saint Martin d'Hères, France

Both study of carbon gasification and stability of active carbons require an accurate description on the bonding at surface. Early studies of Graphon oxidation showed different adsorption sites¹. Each site is defined by its activation energy (while adsorption of molecular oxygen) and by its position at the cristal surface. The basal surface -(0001)- is less active than edge surfaces.

First, we have studied the atomic oxygen adsorption at different coverages on the basal graphite surface (0001) at the sites with high symmetry. Second, oxygen atoms were introduced between two basal planes.

The study was made in the framework of density-functional theory (DFT) and the pseudopotential theory using VASP (Vienna Ab initio Simulation Package). The dissolution was done using LDA (Local Density Approximation) and GGA (Gradient Generalized Approximation) while adsorption was studied only in GGA. Pseudopotentials were carefully checked in bulk phase before using them.

The atomic oxygen adsorption was studied at three imposed coverages: 50%, 25%, 5,5%, and at three sites: "bridge"(middle of the C-C bond), "top" (above a carbon atom) , and "hex" (in the center of the hexagons defining a graphene layer). The binding energy difference between the bridge and top sites is between 0,4 and 0,5 eV, in the case of low coverages. For 50%, this difference is three times larger. This shows that the diffusion at surface is easier to activate at low oxygen concentrations. The oxygen atoms could migrate from site to site to reach the edge surface (very active), where they could produce the carbon gasification. This is in concordance with the idea that basal surface is like a "reservoir" of oxygen in graphite oxydation. The dissolution (at one fixed concentration) shows that the "bridge" configuration is the most stable, the same as for basal planes. The binding energy for one oxygen atom is 2.68 eV in GGA and 3.63 eV in LDA, larger than in the surface. A buckling of the graphite plane is also present.

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Contact author: Andrei Incze

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques , INPG F-38402,
Saint Martin d'Hères, Laboratoire de Physique et Modélisation des Milieux Condensés,
CNRS BP 166, Grenoble

Fax:+33 (0)4 76 82 66 63

E-mail: incze@belledonne.polycnrs-gre.fr

The structural and electronic relaxation
of the
 α -Al₂O₃ (0001) surface

P. Reinhardt

Université Paris VI, France

F. Illas, J.R.B. Gomes, I. de P.R. Moreira

Universitat de Barcelona, Spain

The geometrical structure of the polar, Al-terminated surface of corundum has been investigated by different theoretical methods ranging from empirical pair potentials to periodic Hartree-Fock or Density Functional Theory calculations. Qualitatively, all the methods agree on a large inward relaxation of the outermost Al layer and less pronounced differences from bulk position for the other Al positions. Significant differences occur, however, when regarding the results more closely; empirical potentials seem too crude for employing them in surface structure optimizations, and on the other hand we propose that the largest relaxations, observed from DFT calculations including pseudopotentials, are rather an artefact of the method than a physical effect.

Another question addressed in the present contribution is the generation of a net dipole moment perpendicular to the relaxed surface. A simple ionic model may serve for explaining the presence of the dipole moment, and, of course, the direction of the observed geometrical relaxations. Charge polarization on the surface atoms in all-electron calculations is not enough to compensate the moment arising from the point-charge model.

Contact author:

Peter Reinhardt

Laboratoire de Chimie Théorique

Université Paris VI

4, place Jussieu, tour 22-23

F — 75252 Paris CEDEX 05

France

Fax: 0033-1-44 27 41 17

E-mail: Peter.Reinhardt@lct.jussieu.fr

Structural and Electronic Properties of Mo-O oxides: Ab Initio Density Functional Theory Studies

R. Tokarz-Sobieraj, M. Witko

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul.
Niezapominajek 8, 30239 Cracow, Poland

K. Hermann

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin,
Germany

Molybdenum trioxide, MoO₃, is a functional component of catalysts in a large number of chemical process examples being conversion of hydrocarbons to other products. From a commercial point of view, the reaction of selective oxidation is most important. It proceeds according to a nucleophilic mechanism where the hydrocarbon molecule loses one or two hydrogen atoms and as a next step oxygen is incorporated into it. In both steps, surface oxygen ions participate by inducing H abstraction, forming surface OH/H₂O species, and being inserted into the organic molecule. The incorporation of surface oxygen into the organic species as well as the desorption of surface H/H₂O groups creates surface oxygen vacancies, which may undergo re-oxidation by gaseous oxygen or give rise to more extended defects. As a result molybdenum trioxide may become reduced to dioxide, MoO₂. In the present theoretical work we study the local electronic structure of the clean and reduced MoO₃(010) surface as well as of the clean MoO₂(011) surface using DFT method. The clean/reduced MoO₃(010) surface is represented by Mo₁₅O₅₆H₂₂ and Mo₁₅O₅₆H₂₂-O bilayer clusters (where -O in the second cluster denotes the removal of oxygen from one of the different surface sites) while the MoO₂(011) surface is modeled by a Mo₇O₂₄H₂₀ (one-layer) cluster. In order to identify the chemical reactivity of each type of surface oxygen, the adsorption of one or two hydrogen atoms (leading to surface OH or H₂O species) at respective oxygen sites of MoO₃(010) is studied. The ideal (010) surface is characterized by three types of structurally different surface oxygen centers, terminal (molybdenyl) oxygen, O(1), coordinated to one molybdenum atom, bridging oxygen, O(2), coordinated asymmetrically to two Mo centers, and O(3) coordinated symmetrically to three molybdenum atoms. At the MoO₂(011) surface there are only bridging oxygen atoms, two types of O(3), coordinated symmetrically to three molybdenum atoms and two types of O(2) coordinated to two Mo atoms. Formation of oxygen vacancies is a local process and leads to reduction of nearby molybdenum centers at the MoO₃(010) surface. It results in an electronic structure similar to that of the MoO₂(011) surface. The creation of oxygen vacancies is facilitated by the presence of hydrogen forming surface OH or H₂O species that can desorb more easily. Total DOS (Density of States) as well as PDOS (Partial, Atomic Density of States) curves obtained for clean and reduced MoO₃(010) as well as for clean MoO₂(011) give a clear picture of the reduction mechanism. The (P)DOS results for reduced MoO₃ and for clean MoO₂ are found to be similar. Reduction of MoO₃ leads to the occupation of metal d-type orbitals, which induces a semiconductor to metal transition.

Contact author: Malgorzata Witko

Fax: 0048-12-4251923

E-mail: ncwitko@cyf-kr.edu.pl

Reactions on Surfaces with Neural Networks

Sönke Lorenz, Axel Groß*, and Matthias Scheffler

Fritz-Haber-Institute der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

* Physik-Department T30, TU Munich, D-85747 Garching, Germany

Theoretical studies of chemical-reaction dynamics require a knowledge of the potential-energy surface (PES) of the system under investigation. Ideally such a PES should be derived from reliable first-principles calculations. However, total-energy calculations only provide a discrete set of energies for a limited number of configurations while in dynamical simulations a continuous representation of the relevant PES is needed.

In recent years feedforward neural networks (NN) have been applied to model global properties of the PES - mainly of molecules in the gas phase - from information obtained by *ab initio* calculations [1-3]. We present the use of a neural network to interpolate the results of first-principles calculations in order to model reactions of molecules on metal surfaces, i.e. the dissociation of H₂ on a potassium covered Pd(100) surface and the photodesorption process of CO from Cr₂O₃(0001). As a test problem we applied the NN to fit an analytical PES for the clean as well as the sulfur covered Pd(100) surface where all six degrees of freedom of the molecule are included in the fitting procedure [4,5,6]. As an additional check of the accuracy of the obtained NN-model, we performed classical molecular dynamics (MD) calculations and compared the results to MD calculations performed on the analytical PES.

We show, that in order to properly describe the process of bond-breaking within a very localised region of a detailed PES and at the same time modelling a smooth function outside that region, a large number of fermi-like basis functions is needed. For a very detailed PES with the presence of activated as well as non-activated dissociation pathways the number of parameters is higher than 1000, whereas for surfaces with only activated paths it is considerably less. Furthermore, it is necessary to include additional positions of the molecule in the surface unit cell rather than the commonly used high-symmetry sites.

We show, that the NN is not only able to model the PES with errors smaller than 0.1 eV but can also accurately reproduce the sticking probabilities of analytical fits for the same systems as well as experimental data.

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Contact author:

Sönke Lorenz
Theory Department, Fritz-Haber-Institute
Faradayweg 4-6, D-14195 Berlin
Germany
Fax: +49 30 8413 4701
E-mail: slorenz@fhi-berlin.mpg.de

On the Nature of RuS₂ HDS-Active Sites: Insight from *ab-initio* Theory

M.E. Grillo¹, P. Sautet² and B. Bigot²

¹Fritz-Haber Institut der Max-Planck Gesellschaft Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

²Institut de Recherches sur la Catalyse, 2 Av. A. Einstein, 69626 Villeurbanne Cedex, France; and Laboratoire de Chimie Theorique, Ecole Normale Supérieure de Lyon, 69364 Lyon Cedex 07, France

Over the past few years much attention has been given to the study of the activation of sulfur-containing compounds. Besides the academic interest, this tendency is due to the worldwide increasing environmental restrictions set to fossil fuel feedstocks, as well as refined oil-cuts. As a consequence, the challenging task of developing always more efficient hydrotreating catalysts is set to the refining industry. The catalytic process of sulfur removal involves both a carbon-sulfur bond cleavage (hydrodesulfurization, HDS) and hydrogenation (HYD) steps. Despite the extensive research on these processes, the general mechanistic details of the HDS/HYD reactions over transition metal sulfides have not been well understood. Thiophene, on the other hand, comes out to be a good model-molecule in typical oil-cuts, being still accessible for *ab initio* theory. In this contribution, the adsorption of thiophene over different hydrogenated RuS₂(111) defect-surface termination models has been studied based on *ab-initio* density functional theory. Although, the standard industrial catalysts involve nickel-promoted molybdenum sulfides, ruthenium disulfide, RuS₂, has proved to be the most active catalyst for HDS of thiophene among all transition metal-sulfides, and is about 15 times more active than the standard industrial catalyst. Using the Vienna *Ab-initio* Simulation Programm VASP [1], the η_1 and η_5 adsorption configurations were examined, for the molecule with the ring perpendicular or parallel to the surface, respectively. The η_5 -coordination corresponds to both the highest adsorption energy and activation. Thiophene-activation with respect to the α -C-S bond breaking is obtained for the π -ring centered on a sulfur-unsaturated hydridic H-Ru site on an under-stoichiometric surface termination, consistently with previous experimental studies [2]. Participation of hydridic surface species in the activation process is analyzed in terms of the relative position of the density of H-s-states for both protonic (H-S) and hydridic (H-Ru) species at the surface. The mechanisms governing the activation are discussed based on the change of the thiophene electronic structure over interaction with the model active-surfaces.

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¹On leave from PDVSA-INTEVEP, S.A., Res. & Technol. Support Ctr., Petróleos de Venezuela, P.O. Box 76343, Caracas 1070A-Venezuela

Density Functional simulation of the catalytic reaction in the
Protein-Tyrosine Phosphatase, PTP1B

Jan Rossmeisl and Jens K. Nørskov,

Center for Atomic-scale Material Physics, Department of Physics, Technical
University of Denmark

Ole H. Olsen,

Novo Nordisk Park, Novo Nordisk A/S DK-2760 Måløv, Denmark.

The activity of many enzymes depends on whether the enzyme is phosphorylated or not. One branch of the dephosphorylating enzymes is the protein-tyrosine phosphatases which is known to play an essential role in many cell functions such as growth, metabolism, and signaling.

The catalytic mechanism of a specific tyrosine phosphatase proceeds in two steps: The first step is a phosphate transfer from the substrate to the phosphatase giving an intermediate state. The second step is a hydrolysis of the intermediate yielding a free phosphate group and the phosphatase back in its initial state¹.

The first step of the dephosphorylation has been investigated using *ab initio* density functional theory on a model system containing only the reactive parts of the protein and the substrate. A reaction mechanism has been established and the influence of the electrostatic potential from the catalytic site has been studied in some detail. The energy contribution origin from conformational changes near the catalytic site has been estimated and subsequently been added to the energy barrier.

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Contact author: Jan Rossmeisl
Center for Atomic-scale Materials Physics (CAMP)
Department of Physics, Building 307
Technical University of Denmark
DK-2800 Lyngby, Denmark
Fax: +45 4593 2399
E-mail: jross@fysik.dtu.dk

The Mechanism of Enantioselective Palladium Catalyzed
Hydrosilylation of Olefins with Trichlorosilane:
An ab initio Molecular Dynamics Study.

Alessandra Magistrato and Ursula Rothlisberger

Laboratory of Inorganic Chemistry, ETH Zentrum, ETH Zürich,
CH-8092 Zürich, Switzerland

Tom K. Woo

University of Western Ontario, London, Ontario, Canada.

Hydrosilylation with trichlorosilane offers a powerful tool for the "one pot" conversion of olefins into alcohols, via oxidation of the alkyltrichlorosilane intermediate by the method developed by Tamao. In this regard hydrosilylation has been widely investigated and efforts have been made to clarify the reaction mechanism^[1]. The bis(trichlorosilyl) 1-(R)-1-[(S)-2-(diphenylphosphino- κ P)ferrocenyl]ethyl-3-(2,4,6-trimethylphenyl)-1H-pyrazole- κ N palladium catalyst exhibits in fact an high enantioselectivity with a variety of substrates. Among them styrene shows particularly interesting properties: (a) the regioselectivity on the α -carbon is up to 99%; (b) the enantioselectivity is up to 70%, but there is a reversal due to a remote substituent in the substrate.

In order to examine the reaction pathways we performed DFT and combined quantum mechanics and molecular mechanics (QM/MM) calculations. Our calculations show that the rate determining step of the catalytic cycle is the coordination of the styrene to the central metal.

Our calculations of the Chalk-Harrod mechanism^[1] suggest that the insertion of the styrene into the Pd-H bond ($E_a=3.6$ kcal/mol) is the most likely event. This step is accompanied by η^3 -coordination mode of the benzylic intermediate. The formation of the allylic structure stabilizes the insertion product by ~ 10 kcal/mol and explains also the reason for the observed regioselectivity. Moreover, the formation of the final product proceeds through migration of the silane on the α -carbon and the elimination of alkyltrichlorosilane.

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Contact author: Alessandra Magistrato

ETH Zentrum Zürich

Laboratory of Inorganic Chemistry, Universitaetstrasse 6, 8092 Zürich,
Switzerland.

Fax: 0041-1-632 10 90

E-mail: ale@rgac3.ethz.ch

Thermodynamics of Catalytic Formation of Dimethyl Ether from Methanol in Acidic Zeolites

Marek Hytha^{†,‡,Δ}, Ivan Štich[∇], Julian D. Gale[§],
Kiyoyuki Terakura^{¶,◇} and Mike C. Payne[□]

Contribution from: *Department of Crystallography, University of Kiel, Olshausenstrasse 40, D-24 098 Kiel, Germany[†]; National Center for High Performance Computing, P. O. Box 19-136, Hsinchu, Taiwan[‡]; Institute of Physics, Czech Academy of Sciences, Cukrovarnická 10, 162 53 Prague 6, Czech Republic^Δ; Department of Physics, FEI, Slovak Technical University, Ilkovičova 3, SK-812 19, Bratislava, Slovakia[∇]; JRCAT, Angstrom Technology Partnership, 1-1-4 Higashi, Tsukuba, Ibaraki 305-0046, Japan[¶]; Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, U.K.[§]; JRCAT, National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Ibaraki 305-8562, Japan[◇]; CREST, Japan Science and Technology Corporation, Kawaguchi, Saitama 332, Japan; Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, U.K.[□]*

We present a theoretical study of the formation of the first intermediate, dimethyl ether, in the methanol to gasoline conversion within the framework of an **ab initio** molecular dynamics approach. The study is performed under conditions which closely resemble the reaction conditions in the zeolite catalyst including the full topology of the framework. The use of the method of thermodynamic integration allows us to overcome the large energy barrier to dimethyl ether formation and to extract the free energy profile along the reaction coordinate. We find that the entropic contribution to the reaction qualitatively alters the free energy profile compared to the total energy profile. Different transition states are found from the total and free energy profiles. The entropy contribution varies significantly along the reaction coordinate, and is responsible for stabilizing the products and for a slight barrier lowering. The variation of the entropy can be understood in terms of elementary processes which take place during the chemical reaction.

Contact author: Marek Hytha
Department of Crystallography,
University of Kiel, Olshausenstrasse 40,
D-24098 Kiel, Germany.
Tel: +49-431-880 2569
Fax: +49-431-880 4457
E-mail: mh@min.uni-kiel.de

Stability of Zn(II) cations in chabazite studied
by periodical Density Functional theory.

L. A. M. M. Barbosa, R. A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology
P.O.box 513, 5600 MB Eindhoven, The Netherlands.

J. Hafner

Institut für Theoretische Physik, Technische Universität Wien
Wiedner Hauptstrasse 8-10, A-1040, Wien, Austria.

The location of the Zn^{2+} cation in Zn-exchanged chabazite has been studied by periodical Density Functional method. Chabazite was chosen as a zeolite model, since it contains three different types of rings, commonly found in the zeolite structures: 4, 6 and 8-membered rings. Two aluminium atoms have been employed to substitute the Si atoms in the same D6R unit cell of the zeolite framework. This leads to different arrangements for the Brønsted site pair and the Zn(II) cation.

The two Brønsted sites are found to be more stable when placed in the small ring ("4T" ring) than in the other rings. This suggests that the most reactive Brønsted sites are located in the large rings. Two Brønsted sites prefer to follow the O(H)-Al-O-Si-O(H)-Al sequence in the same ring, instead of being located in two different rings. This resembles the Al distribution in the small 4-membered ring and agrees with the Bond Order Conservation rules.

The cation stability is markedly influenced by the distortions of the framework. Other factors that also contribute to the stabilization are the Al content near the cation and the stability of the original Brønsted sites. The Zn^{2+} cation is more stable in the large rings than in the small ones, the 6-membered one being the most stable configuration. In the small rings the cation is, therefore, more reactive.

Contact author: L. A. M. M. Barbosa
Institut de Recherches sur de la Catalyse (IRC),
Centre National de La Recherche Scientifique (CNRS)
2, Av. Albert Einstein, Villeurbanne Cedex France
Fax: 0031 47 244 53 99
E-mail: lbarbosa@catalyse.univ-lyon1.fr

Stress in heteroepitaxial growth: Ag/Pt (111)

K.-P. Bohnen and R. Heid

Forschungszentrum Karlsruhe, Institut für Festkörperphysik

Recent measurements of interface stress in the system Ag/Pt (111) show very large values [1,2] which seem to be in disagreement with elasticity theory. These results strongly suggest that surface energy and lattice mismatch are not sufficient to determine growth modes. To explain the unexpected experimental results ab initio density functional calculations using a mixed basis pseudopotential formalism have been performed for the system Ag/Pt (111) up to four monolayers of Ag. Calculated stress values are in good agreement with the measured ones. A detailed analysis shows that only in the monolayer range strong deviations from elasticity theory occur. Beyond the monolayer regime the stress increase with Ag-thickness can be accounted for by elasticity theory if the lattice mismatch of 4.2% is properly taken care of.

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Contact author: Klaus-Peter Bohnen
Kernforschungszentrum Karlsruhe
Postfach 3640
Fax: ++49-7247-82-2421
E-mail: bohnen@ifp.fzk.de

List of Participants

List of Participants

Luis Antonio Miguel Marques Barbosa

Centre National de la Recherche Scientifique (CNRS)
Institut de Recherches sur la Catalyse (IRC)
Groupe Theorie et Modelisation, room 212
2 Av. Albert Einstein 69626 VilleUrbanne cedex, France
Fax: 0033 (0) 472 44 53 99
E-mail: lbarbosa@catalyse.univ-lyon1.fr

Hanne S. Bengaard

Interdisciplinary Research Center for Catalysis (ICAT),
Center for Atomic-scale Materials Physics (CAMP),
Physics Department, Building 307, Technical University of Denmark,
DK-2800 Lyngby, Denmark.
Fax: (+45) 45 93 23 99
E-mail: bengaard@fysik.dtu.dk

Flemming Besenbacher

Address, Institute of Physics and Astronomy,
Building 520 Ny Munkegade, University of Aarhus,
DK-8000 Aarhus, Denmark
Fax: +45 86120740
E-mail: fbe@ifa.au.dk

Alexander Bogicevic

Ford Research Laboratory
Fax: +1 313 845-8625
E-mail: abogicev@ford.com

Klaus-Peter Bohnen

Kernforschungszentrum Karlsruhe
Postfach 3640
D-76050 Karlsruhe
Fax: ++49-7247-82-2421
E-mail: bohnen@ifp.fzk.de

Anne M. Chaka

The Lubrizol Corporation
Research Division MS151-B
29400 Lakeland Blvd.
Wickliffe, Ohio 44092-2298 USA
Fax: 001-440-347-4482
E-mail: chaka@lubrizol.com

Hai-Ping Cheng

Fax: 0041-1-724 89 83
E-mail: hch@zurich.ibm.com
Permanent: Fax: 001-352-392-8722
E-mail: hch@zurich.ibm.com

Ebbe Christoffersen

Department of Physics, Building 307, Technical University of Denmark,
DK-2800 Kgs. Lyngby, Denmark
Fax: (+45) 45 93 23 99
E-mail: ebbec@fysik.dtu.dk

Bjerne S. Clausen

Haldor Topsøe Research Laboratory
Nymllevej 55
DK-2800 Lyngby, Denmark
Fax: +45 45 27 29 99
E-mail: bsc@topsoe.dk

Andreas Eichler

Institut für Materialphysik
Sensengasse 8/12, 1090 Wien, Austria.
Fax: +43-1-4277-9514
E-mail: andreas.eichler@univie.ac.at

Jim Evans

Iowa State University,
Ames, Iowa, 50011 USA
Fax: 515-294-0266
E-mail: evans@ameslab.gov

A. Fahmi

Norsk Hydro ASA,
P. O. Box 2560, 3907 Porsgrunn, Norway,
Fax: +47 35 92 27 22
E-mail: Adil.Fahmi@hydro.com

M. Veronica Ganduglia-Pirovano

Fritz-Haber-Institut der MPG
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: ++49-30-8413 4701
E-mail: pirovano@fhi-berlin.mpg.de

D. W. Goodman

Texas A&M University,
Department of Chemistry
Fax: 779-845-0214
E-mail: goodman@mail.chem.tamu.edu

Maria Elena Grillo

Fritz-Haber-Institute der MPG
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: ++49-30-8413 4701
E-mail: grillo@fhi-berlin.mpg.de

Axel Groß

Physik-Department T30
Technische Universität München
D-85747 Garching, Germany
Fax: +49 89 289 12296
E-mail: agross@ph.tum.de

Jürgen Hafner

Institut für Materialphysik and
Center for Computational Materials Science
Universität Wien, Sensengasse 8/12, A-1090 Wien, Austria
Fax: 0043-1-4277-9514
E-mail: Juergen.Hafner@univie.ac.at

Bjørk Hammer

Institute of Physics and Astronomy, University of Aarhus
Fax: +45 86 12 07 40
E-mail: hammer@ifa.au.dk

K. Hermann

Fritz-Haber-Institut der MPG
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: ++49-30-8413 4701
E-mail: hermann@fhi-berlin.mpg.de

Marek Hytha

Department of Crystallography,
University of Kiel, Olshausenstrasse 40,
D-24098 Kiel, Germany.
Fax: +49-431-880 4457
E-mail: mh@min.uni-kiel.de

Andrei Incze

Laboratoire de Thermodynamique et Physico-Chimie Métallurgiques , INPG
F-38402, Saint Martin d'Hères, France,
Laboratoire de Physique et Modélisation des Milieux Condensés, CNRS
BP 166, Grenoble, France
Fax: +33 (0)4 76 82 66 63
E-mail: incze@belledonne.polycnrs-gre.fr

Georg Kresse

Institut für Materialphysik,
Universität Wien and Center for Computational Material Science
Sesengasse 8, A-1090 Wien, Austria
Fax: +43-1-4277-9514
E-mail: Georg.Kresse@univie.ac.at

Uzi Landman

Georgia Tech, Physics
Atlanta, Ga 30332-0430
Fax: (404) 894 3368
E-mail: uzi.landman@physics.gatech.edu

Pierre Légaré

ECPM-LERCSI
25 rue Becquerel
67 087 Strasbourg Cedex 2
Fax: (0)3 88 13 69 68
E-mail: e-mail legare@chimie.u-strasbg.fr

Sönke Lorenz

Theory Department, Fritz-Haber-Institute der MPG
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: +49 30 8413 4701
E-mail: slorenz@fhi-berlin.mpg.de

Giuliana Materzanini

University College London,
Department of Chemistry, 20 Gordon Street, WC1H OAJ,
United Kingdom.
Fax: 0044-207-380 74 63
E-mail: giuliana@chem123.chem.ucl.ac.uk

Alessandra Magistrato

ETH Zentrum Zürich
Laboratory of Inorganic Chemistry, Universitaetstrasse 6, 8092 Zürich,
Switzerland.
Fax: 0041-1-632 10 90
E-mail: ale@rgac3.ethz.ch

Manos Mavrikakis

Department of Chemical Engineering
University of Wisconsin-Madison, Madison, WI 53706, USA
Fax: (608) 262-5434
E-mail: manos@enr.wisc.edu

Yoshitada Morikawa

JRCAT, National Institute for Advanced Interdisciplinary Research,
1-1-4 Higashi, Tsukuba, Ibaraki 305-8562, Japan.
Fax: +81-298-54-2788
E-mail: morikawa@jrcat.or.jp

Matthew Neurock

Department of Chemical Engineering
University of Virginia
Charlottesville, VA 22903-2442
Fax: (804) 982-2658
E-mail: mn4n@virginia.edu

Jens Nørskov

Center for Atomic-scale Materials Physics (CAMP),
Physics Department, Building 307, Technical University of Denmark,
DK-2800 Lyngby, Denmark.
Fax: (+45) 45 93 23 99
E-mail: norskov@fysik.dtu.dk

Gianfranco Pacchioni

Dipartimento di Scienza dei Materiali, INFM,
Universit di Milano-Bicocca, via Cozzi 53, 20125 Milano
Fax: +39-02-6448 5403
E-mail: gianfranco.pacchioni@mater.unimib.it

M.C. Payne

Cavendish Laboratory, University of Cambridge,
Madingley Road, Cambridge, CB3 0HE, UK,
Fax: +44-1223-337356
E-mail: mcp1@phy.cam.ac.uk

R. Ramprasad

DigitalDNA Lab (Motorola, Inc.)
2100 E. Elliot Rd., EL 740, Tempe, AZ 85284
Fax: 480 413 7918
E-mail: R.Ramprasad@motorola.com

Peter Reinhardt

Laboratoire de Chimie Théorique
Université Paris VI
4, place Jussieu, tour 22-23
F — 75252 Paris CEDEX 05
France
Fax: 0033-1-44 27 41 17
E-mail: Peter.Reinhardt@lct.jussieu.fr

Karsten Reuter

Theory Department, Fritz-Haber-Institute der MPG,
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: +49 30 8413 4701
E-mail: kreuter@fhi-berlin.mpg.de

Ursula Röthlisberger

ETH Zentrum Zürich
Laboratory of Inorganic Chemistry, Universitaetstrasse 6, 8092 Zürich,
Switzerland.
Fax: 0041-1-632 10 90
E-mail: uro@inorg.ethz.ch

Jan Rossmeisl

Center for Atomic-scale Materials Physics (CAMP)
Department of Physics, Building 307
Technical University of Denmark
DK-2800 Lyngby, Denmark
Fax: +45 4593 2399
E-mail: jross@fysik.dtu.dk

Joachim Sauer

Humboldt-Universität, Institut für Chemie
Arbeitsgruppe Quantenchemie
Jägerstrasse 10/11
D-10117 Berlin, Germany
Fax: +(49)30-20192 302
E-mail: js@qc.ag-berlin.mpg.de

Philippe Sautet

Institut de Recherches sur la Catalyse, Villeurbanne, France
Fax: 00 33 72 44 53 99
E-mail: sautet@catalyse.univ-lyon1.fr

Matthias Scheffler

Fritz-Haber-Institut der MPG
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: ++49-30-8413 4701
E-mail: scheffler@fhi-berlin.mpg.de

Robert Schlögl

Fritz-Haber-Institut der MPG
Faradayweg 4-6, D-14195 Berlin, Germany
Fax: ++49-30-8413 4401
E-mail: andrea@fhi-berlin.mpg.de

Ferdi Schüth

MPI für Kohlenforschung
Kaiser Wilhelm Platz 1
45470 Mülheim
Fax: +49-208-306 2995
E-mail: schueth@mpi-muelheim.mpg.de

Herve Toulhoat

Group Leader, Molecular Modeling and Computational Chemistry
Div. Computer Science and Applied Mathematics, IFP
Institut Français du Pétrole,
1-4 Avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, FRANCE
Fax: +33-1-47-52-70-22
E-mail: herve.toulhoat@ifp.fr

Malgorzata Witko

Institute of Catalysis and Surface Chemistry,
Polish Academy of Sciences,
ul. Niezapominajek 8, 30239 Cracow, Poland
Fax: 0048-12-4251923
E-mail: ncwitko@cyf-kr.edu.pl

Martin Wolf

Fritz-Haber-Institut der MPG,
Faradayweg 4-6, 14195 Berlin, Germany,
Fax: +49 30 8413 5106
E-mail: Wolf_M@fhi-berlin.mpg.de