

## O 51: Surface chemical reactions I

Time: Thursday 16:15–19:15

Location: SCH A01

O 51.1 Thu 16:15 SCH A01

**Ab initio molecular dynamics simulation of electronic energy dissipation: A comparison of H/Si(001), H/Al(111), and HCl/Al(111)** — GEORG KRUGEL, MICHAEL GROTEMEYER, JAN VAN HEYS, MICHAEL LINDENBLATT, and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Universität Kiel, Germany

The energy transfer to solid surfaces during chemisorption and surface scattering is of considerable relevance. Energy dissipation via electron-hole pair excitation has attracted much recent interest, see e.g. [1]. To identify the electronic dissipation mechanisms, we carry through ab initio molecular dynamics simulations. The time-dependent Kohn-Sham equations of the electrons are integrated numerically, while the positions of the ions follow from Ehrenfest dynamics. The time-dependent electronic state of the system is compared to the electronic ground state at the respective frozen-in ionic positions. This yields detailed information on the electronic excitations along the trajectory. This method has been applied to chemisorption of H-atoms on Al(111), with results consistent with the time-dependent Newns-Anderson model by Mizielinski and Bird [2]. In case of H/Si(001) we find an energy transfer into electron-hole pairs after one round-trip of the atom in front of the surface comparable to H/Al(111). We explain this unexpected result on the basis of the electronic structure. In case of HCl/Al(111) we find a significant coupling of the HCl molecular vibration to electron-hole pair excitations in the Al-substrate.

[1] A.M. Wodtke *et al.*, *Prog. Surf. Sci.* **83**, 167 (2008).

[2] D.M. Bird *et al.*, *Surf. Sci.* **602**, 1212 (2008).

O 51.2 Thu 16:30 SCH A01

**Real-space investigation of high-barrier diffusion of hydrogen on Si(001)** — M. DÜRR<sup>1,2</sup>, C. H. SCHWALB<sup>1</sup>, and U. HÖFER<sup>1</sup> — <sup>1</sup>Fachbereich Physik und Zentrum für Materialwissenschaften, Philipps-Universität Marburg, D-35032 Marburg — <sup>2</sup>Fakultät Angewandte Naturwissenschaften, Hochschule Esslingen, D-73728 Esslingen

Due to the strong corrugation of Si(001) with its dimer row reconstruction, various diffusion channels exist already on the flat, clean surface. Among the possible processes, diffusion between two dimer rows is associated with the highest diffusion barrier; as a consequence, it has not been observed by means of standard STM experiments up to now.

To probe this high-barrier pathway in real space, we used a combination of STM and nanosecond laser heating [1,2]. STM images taken after different numbers of heating pulses represent snapshots of the surface configurations frozen at various stages of the diffusion process. In this way hydrogen diffusion associated with rates as high as  $10^8 \text{ s}^{-1}$  could be monitored with atomic resolution at 1400 K. We observe that diffusion across the dimer rows is almost as effective as diffusion along the dimer rows. The experiment thus demonstrates the importance of this high-barrier process at elevated temperatures. Considering the large Si-Si distance between the dimer rows, the observed diffusion rate is surprisingly high. It is interpreted in terms of a strong concerted movement of hydrogen and the Si lattice.

[1] M. Dürr *et al.*, *Science* **296**, 1838 (2002).

[2] C. H. Schwab *et al.*, *Phys. Rev. B* **75**, 085439 (2007).

O 51.3 Thu 16:45 SCH A01

**STM investigations of an electron induced switching process in azobenzene-based structures** — JÖRG HENZL and KARINA MORGENSTERN — Universität Hannover, Institut für Festkörperphysik, Abt. Oberflächen, Appelstr. 2, 30167 Hannover

The cis-trans isomerization of azobenzene molecules in gas phase and in solution is a well studied phenomenon. But only in the recent years first studies of azobenzene molecules adsorbed on single crystal surfaces have been emerged. This system is of particular interest not only from a fundamental point of view but also because of its possible applications in nanotechnology as a molecular switch.

Here we present low temperature scanning tunnelling microscopy measurements of 4-anilino-4'-nitroazobenzene on the Au(111)-surface. Upon adsorption at 250 K the molecules form both meandering lines of single molecules which are guided by the Au(111)-herringbone reconstruction, and a chiral star-shaped structures consisting of six molecules each.

A switching process within a single molecule inside the star-shaped structures is induced by placing the tip of the scanning tunnelling mi-

croscope above one molecule and applying a bias voltage of 2.5 V. The other molecules of the star-shaped structure remain unaffected during this manipulation. This reversible and bistable switching process will be discussed in greater detail in this talk.

O 51.4 Thu 17:00 SCH A01

**Theoretical cluster studies on the catalytic sulfidation of MoO<sub>3</sub>** — XUERONG SHI<sup>1,2</sup>, JIANGUO WANG<sup>2</sup>, and KLAUS HERMANN<sup>1</sup> — <sup>1</sup>Theory Department, Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin and Sfb 546 "Transition Metal Oxide Aggregates", Berlin (Germany). — <sup>2</sup>State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, P. R. China

Sulfidation of molybdenum trioxide, MoO<sub>3</sub>, yielding local surface regions of molybdenum disulfide, MoS<sub>2</sub>, is an essential step to improve the hydrotreating activity of Mo catalysts. Therefore, theoretical studies of sulfided MoO<sub>3</sub> surfaces can contribute to an understanding of detailed reaction mechanisms at corresponding catalyst surfaces. We apply density functional theory together with large cluster models to obtain information about the behavior of oxygen and sulfur adsorbates at local sections of the MoO<sub>3</sub>(010) surface with and without oxygen vacancies. In all cases, adsorbed oxygen is found to bind more strongly with the substrate than sulfur with binding distances that are shorter than those for the sulfur adsorbate. S/O exchange reactions at the substrate surface are always energetically preferred over sulfur adsorption. In addition, the first and second sulfur substitution takes place preferentially at the singly coordinated oxygen site O(1). Finally, the calculations show that pre-adsorbed hydrogen can facilitate the sulfidation process at the MoO<sub>3</sub>(010) surface.

O 51.5 Thu 17:15 SCH A01

**Theoretical investigations on the electrochemical hydrogen evolution on Pt-hydride surfaces** — FEDOR STRIGUNOV, JOHN KEITH, and TIMO JACOB — Institut für Elektrochemie, Universität Ulm, 89081 Ulm

Noble metals are a common component of electrodes that drive electrochemical reactions. Despite their nobility, electrode surfaces may take on many different structures or morphologies under electrochemical environments. Using periodic density functional theory, we calculated the surface free energies for several different surfaces of a variety of bulk Pt-hydride morphologies. In combination with the extended ab initio thermodynamics approach [1,2] we present a first phase diagram showing under which experimental temperature, activity, and electrode potential conditions hydrogen is present on the surface and which Pt-hydride surface orientation and structure is stabilized. On the basis of the most relevant Pt-hydride surfaces we then evaluated the adsorption of atomic hydrogen as well as the barriers for hydrogen evolution. This data will be used as the grounds for further understanding reactions on electrochemical electrodes.

[1] M. Scheffler, J. Dabrowski, *Phil. Mag.*, **A 58**, 107 (1988). [2] T. Jacob, *J. Electroanal. Chem.*, **607**, 158, (2007).

O 51.6 Thu 17:30 SCH A01

**CO oxidation on planar Au/TiO<sub>2</sub> model catalysts: activation energy and influence of reaction atmosphere** — MENHILD EYRICH, STEFAN KIELBASSA, JOACHIM BANSMANN, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The high interest in oxide supported Au catalysts and in particular in the low-temperature CO oxidation reaction on these catalysts, in combination with the still unknown reaction mechanism, has stimulated model studies on planar model catalysts. Analogously to the respective powder catalysts, also the activity of the planar model catalysts strongly depends on the catalyst preparation. Here we report results of reaction measurements on differently reduced Au/TiO<sub>2</sub>(110) model catalysts. The activation energy for CO oxidation on these model systems was determined, and the influence of the reactant gas composition (CO/O<sub>2</sub> ratio) on the catalytic activity was evaluated. The results will be compared to the findings for other Au/TiO<sub>2</sub> (model) catalysts, and possible reasons for the significant reactivity enhancement for reduced model catalysts will be discussed.

O 51.7 Thu 17:45 SCH A01

**Interaction of Thin Nickel Oxide Layers with Carbon Oxides** — ●MICHAEL PETER ANDREAS LORENZ<sup>1</sup>, REGINE STREBER<sup>1</sup>, CHRISTIAN PAPP<sup>1</sup>, MARIE-MADELEINE WALZ<sup>1</sup>, ANDREAS BAYER<sup>1</sup>, SANDRA KÜNZEL<sup>2</sup>, REINHARD DENECKE<sup>2</sup>, and HANS-PETER STEINRÜCK<sup>1</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen — <sup>2</sup>Wilhelm-Ostwald-Institut für Physikalische und Theoretische Chemie, Universität Leipzig, Linnéstr. 2, 04103 Leipzig

NiO is an important material in heterogeneous catalysis. Under ambient conditions, reaction with CO<sub>2</sub> can easily lead to the formation of carbonates, which could block active sites and thereby influence the catalytic reactivity. Behm and Brundle [1] reported carbonate formation on Ni(100) by simultaneously dosing molecular oxygen and CO<sub>2</sub>. We have now studied the interaction of CO<sub>2</sub> and also CO on an oxidised Ni(111) surface in great detail by in situ XPS applying synchrotron radiation at BESSY II. For both, characteristic peaks develop in the O 1s and C 1s spectra, albeit with different intensities, indicating the formation of carbonate layers. Similar results are obtained for thick oxidised Ni layers (~2 ML) grown on Cu(111). In contrast, thin oxidised Ni layers (~0.5 ML) on Cu(111) exhibit a significantly reduced reactivity towards carbonate formation. The decomposition of the carbonate species was determined in situ by XPS during heating. This work was supported by BMBF (05 ES3XBA/5) and the DFG through the Cluster of Excellence "Engineering of Advanced Materials".

[1] R. J. Behm, C. R. Brundle, Surf. Sci. 255 (1991) 327

O 51.8 Thu 18:00 SCH A01

**The Surface Selective Chlorination of RuO<sub>2</sub>(110)** — ●JAN PHILIPP HOFMANN<sup>1</sup>, STEFAN ZWEIDINGER<sup>1</sup>, MARCUS KNAPP<sup>1</sup>, ARI PAAVO SEITSONEN<sup>2</sup>, KARINA SCHULTE<sup>3</sup>, EDVIN LUNDGREN<sup>3</sup>, JESPER ANDERSEN<sup>3</sup> and HERBERT OVER<sup>1</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Justus-Liebig Universität Gießen, Heinrich-Buff-Ring 58, D-35392 Gießen — <sup>2</sup>IMPMC, CNRS & Université Pierre et Marie Curie, 4 place Jussieu, case 115, F-75252 Paris — <sup>3</sup>Dept. of Synchrotron Radiation Research, Lund University, Sölvegatan 14, S-22362 Lund

Chlorinated ruthenium dioxide plays an important role in the heterogeneously catalysed oxidation of hydrogen chloride to chlorine (Deacon process)[1]. High resolution core level shift spectroscopy (HRCLS) and temperature programmed reaction (TPR) experiments together with density functional theory (DFT) calculations were used to elucidate the chlorination mechanism of ruthenium dioxide RuO<sub>2</sub>(110) by hydrogen chloride exposure on the atomic scale. The surface selective chlorination proceeds via the diffusion of chlorine atoms in surface vacancies, which are formed by the desorption of water. H<sub>2</sub>O is produced either by the dissociative adsorption of HCl adjacent to a surface hydroxyl group or by the chlorine assisted recombination of two neighbouring surface hydroxyl groups [2].

[1] Crihan, D. et al.; Angew. Chemie Int. Ed. 2008, 47, 2131-2134.

[2] Hofmann, J. P.; Zweidinger, S.; Knapp, M.; Seitsonen, A. P.; Schulte, K.; Andersen, J. N.; Lundgren, E.; Over, H.; J. Phys. Chem. C, submitted.

O 51.9 Thu 18:15 SCH A01

**HREELS study of Cu clusters deposited on the O-terminated ZnO(000-1) surface** — ●HENSHAN QIU, YUEMIN WANG, and CHRISTOF WÖLL — Physical Chemistry I, Ruhr-University Bochum, 44780 Bochum, Germany

The interaction of metal clusters and films with oxide substrates plays a key role as regards the microscopic mechanisms of many processes in heterogeneous catalysis. In this work, the interaction of Cu clusters with the O-terminated ZnO(000-1) surface was studied by high-resolution energy loss spectroscopy (HREELS), together with thermal desorption spectroscopy (TDS) and low-energy electron diffraction (LEED). It was found that Cu deposition on O-ZnO leads to the formation of well-defined islands with the Cu(111) facets. For the small clusters the partial oxidation of Cu<sup>0</sup> into Cu<sup>+</sup> was clearly identified by the characteristic changes in the C-O stretch frequencies of CO molecules adsorbed on the Cu atoms. Upon heating the Cu atoms undergo, instead of desorption, diffusion into the O-ZnO bulk. The doping of ZnO by Cu leads to the formation of shallow donor states, in which the electrons can be thermally excited into the conduction band and, as a result, give rise to the plasmon-induced broadening of the quasielastic peak in HREELS [1]. From the observed temperature dependence, the donor level ionization energy was determined. This unexpected doping effect of ZnO by Cu has important consequences

for its chemical activity, as confirmed by detailed studies on CO<sub>2</sub> adsorption. [1]H. Qiu, B. Meyer, Y. Wang, Ch. Wöll, Phys. Rev. Lett. in press (2008).

O 51.10 Thu 18:30 SCH A01

**Adsorption and diffusion of H and NH<sub>x</sub> as key steps of the NH<sub>x</sub> dehydrogenation reaction at the V<sub>2</sub>O<sub>5</sub> (010) surface** — ●MATHIS GRUBER and KLAUS HERMANN — Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin and Sfb 546, Berlin (Germany)

Various selective oxidation reactions as the Selective Catalytic Reduction (SCR) of NO<sub>x</sub> or the ammoxidation of propane/propene to acrylonitrile are processed on vanadium based metal-oxide catalysts in the presence of ammonia. In the reactions the intermediates NH<sub>2</sub>, NH<sub>3</sub>, and NH<sub>4</sub> are involved indicating that the adsorption and dehydrogenation of NH<sub>x</sub>,  $x < 4$ , are important steps. We have performed theoretical studies of corresponding reaction steps where the catalyst is simulated by a finite section of the V<sub>2</sub>O<sub>5</sub> (010) surface. The calculations apply density-functional theory combined with clusters modeling the adsorbate system. The substrate lowers corresponding dehydrogenation energies considerably compared with values for the gas phase reaction. However, the lowering is too small to make dehydrogenation of NH<sub>3</sub> likely to happen. Our results on the role of oxygen vacancies for the dehydrogenation indicate that such surface defects become important for the reaction. Besides the energetics also the diffusion at the surface influences the reaction. A Nudged Elastic Band (NEB) routine has been implemented to evaluate diffusion paths and barriers. Hydrogen diffusion on the surface will be discussed and additional examples for NH<sub>x</sub> diffusion will be shown. Based on these results possible reaction scenarios for the dehydrogenation reaction will be presented.

O 51.11 Thu 18:45 SCH A01

**PrO<sub>2-x</sub>/Si(111) – A model system for praseodymium oxide based catalysts** — ●ANDREAS SCHAEFER<sup>1</sup>, SEBASTIAN LAMBERTI<sup>1</sup>, VOLKMAR ZIELASEK<sup>1</sup>, JENS FALTA<sup>2</sup>, THOMAS SCHRÖDER<sup>3</sup>, and MARCUS BÄUMER<sup>1</sup> — <sup>1</sup>Institut für Angewandte und Physikalische Chemie, D-28359 Universität Bremen — <sup>2</sup>Institut für Festkörperphysik, D-28334 Universität Bremen — <sup>3</sup>IHP microelectronics, D-15236 Frankfurt (Oder), Germany

Praseodymium (Pr) oxides are promising candidates for applications in catalysis and microelectronics due to their variable valency along with a high oxygen mobility. Thin films of the oxide prepared on a Si(111) surface in an UHV environment provide a simplified two-dimensional model system of the oxide catalyst. Such a model system allows insight into the atomic details of oxygen transport and transfer when exposed to adsorbed molecules. Additionally, details on the defect structure of such oxide films can be obtained, which is a crucial point for applications in microelectronics. The films were prepared by molecular beam epitaxy of hex-Pr<sub>2</sub>O<sub>3</sub> and subsequent *ex-situ* annealing in oxygen atmosphere to obtain cubic PrO<sub>2</sub>. Here we report on a study on cleaning, reduction and reoxidation of a PrO<sub>2-x</sub> ( $x = 0-0.5$ ) starting film to obtain a surface with defined oxidation state and stoichiometry. Annealing experiments with and without gas dosage during heating will be compared as well as H<sub>2</sub> and O<sub>2</sub> plasma treatment. The surfaces have been studied using x-ray photoelectron spectroscopy and low-energy electron diffraction. First thermal desorption spectra of CO adsorbed on the differently prepared surfaces are presented.

O 51.12 Thu 19:00 SCH A01

**Ferrocene Affinity Label for the Electrochemical Detection of Enzymes down to a Single Molecule Level** — ●CLAUDIA BAIER, ALICE SCHLICHTIGER, JÖRG EPPINGER, and ULRICH STIMMING — TU München, Garching, Deutschland

The research field of biosensors and bioelectronics offers a large potential for the development of functional devices. In this presentation, we show that we are able to electrochemically detect enzymes which are originally not redox-active such as papain and trypsin by using ferrocene affinity labels. These ferrocene-based affinity labels are ideally suited since they combine the electrochemically active ferrocene moiety which is stable under physiological conditions with the selectivity and activity sensing properties of the affinity label concept. The redox-labeled enzymes are immobilized on highly oriented pyrolytic graphite (HOPG) and are electrochemically investigated using cyclic voltammetry and impedance measurements. Furthermore, we established a nano-scale readout i.e. the detection of direct electron transfer processes on a single molecule level by in-situ SPM visualization. Therefore, potential dependent in-situ electrochemical scanning tunneling microscopy (EC-STM) studies and first results of scanning electro-

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chemical potential microscopy (SECPM) will be presented. SECPM, which is the latest invention of the electrochemical SPM techniques, uses the electrochemical potential at the solid/liquid interface as feed-

back signal by measuring the potential difference between a potentiometric tip and the potential controlled working electrode.