

O 31: Surface Chemical Reactions and Heterogeneous Catalysis I

Time: Tuesday 15:45–17:45

Location: H38

O 31.1 Tue 15:45 H38

Theoretical insight into the oxidation of nanoporous carbon materials — ●JOHAN M. CARLSSON and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

Nanoporous carbon(NPC) may be visualized as crumpled graphene sheets with a significant amount of voids. Oxygen can be used to modify its properties and STM indicates that O₂ etches edges and vacancies in graphitic materials[1]. TPD shows desorption of CO and CO₂ indicating the presence of C-O-groups on the surface[2]. However, the characterization of the actual surface structure of oxidized NPC is unsatisfactory and the individual reaction steps for the oxidation are still not well known. We have therefore carried out an extensive study of NPC using ab-initio thermodynamics. Our density-functional theory (DFT) calculations show that O₂ dissociation is endothermic on defect free graphene surfaces, but exothermic at vacancies. The O-atoms attach to the undercoordinated C-atoms at vacancies forming C-O-groups. C-O-C (Ether) groups dominate and C=O (Carbonyl) groups may also appear. The C=O groups are precursors for CO-desorption, but two C-C bonds need to be broken to desorb the CO-molecule. Our thermodynamic treatment shows that CO therefore only desorbs above 700 K from these sites in agreement with the TPD experiment[2]. Based on these results we propose that the oxidative etching of NPC materials proceeds via a sequence of dissociative O₂ adsorption and CO desorption. [1] J. J. Paredes *et al.*, Carbon **38**, 1183, (2000). [2] M. J. Nowakowski *et al.*, J. Am. Ceram. Soc. **76**, 279 (1993).

O 31.2 Tue 16:00 H38

Initial kinetic-energy and isotope dependence of electronic energy dissipation during chemisorption of H/Al(111) — MICHAEL LINDENBLATT and ●ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität Kiel, 24098 Kiel

The amount of energy dissipated into electron-hole pairs during chemisorption or scattering of H-atoms at the Al(111) surface has been investigated as a function of the mass of the incoming hydrogen atom and its initial kinetic energy. The energy dissipation into electronic degrees of freedom, which occurs parallel to the energy dissipation into substrate vibrations, is evoked by electronic friction effects as well as strongly non-adiabatic effects during transfer of the local electronic spin polarization at the incoming H-atom to the substrate upon adsorption [1]. We report results from *ab initio* molecular dynamic simulations based on time dependent spin-density-functional theory combined with Ehrenfest dynamics for the motion of the nuclei. Essentially, the results for the energy dissipated electronically during one passage of the H-atom through the spin transition break down onto a single curve, if plotted versus the velocity of the H-atom at the spin-transition point. The respective Kohn-Sham electronic excitation spectra exhibit an asymmetry between spin-up and spin-down electrons [2], as to be expected for a delayed non-adiabatic transfer of spin polarization from the H-atom to the reservoir of substrate electrons.

[1] M.S. Mizielinski *et al.*, J. Chem. Phys. **122**, 084710 (2005).

[2] M. Lindenblatt, E. Pehlke, Phys. Rev. Lett. **97**, 216101 (2006).

O 31.3 Tue 16:15 H38

Water formation studies on vanadium oxide thin film covered Pd(111) — ●MARKUS KRATZER, JOHANNA STETTNER, and ADOLF WINKLER — Institute of Solid State Physics, University of Technology Graz, Petersgasse 16, A-8010 Graz

The formation of D₂O on vanadium oxide (VO_x) thin film nano structures on Pd(111) has been investigated. Quadrupole mass spectrometry has been used to determine the flux of the reaction products desorbing from the surface. Low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) were applied to monitor possible changes in the surface composition during reaction. The experiments were carried out at sample temperatures of 523 K and 700 K, respectively. The water reaction was fed with atomic deuterium via bulk permeation and simultaneous dosing of molecular oxygen. It turned out that the VO_x coverage as well as the sample temperature have significant influence on the reaction. The D₂O formation rate drops with increasing VO_x coverage and increases with rising sample tem-

perature. Additionally, we found evidence that the VO_x structures change during water formation, especially at 700 K.

O 31.4 Tue 16:30 H38

Local investigation of femtosecond laser induced processes: CO on Cu(111) — ●MICHAEL MEHLHORN, HEIKO GAWRONSKI, and KARINA MORGENSTERN — Institut für Festkörperphysik, Leibniz Universität Hannover, Appelstr. 2, D-30167 Hannover, Germany

A combination of femtosecond laser excitation with a low temperature scanning tunneling microscope is used to study two key processes, diffusion and close approach of reactants, of a non-adiabatic surface reaction for adsorbed CO molecules on a Cu(111) surface in real space. For the first process we obtain two different electron mediated excitation paths by analyzing the dependence of the hopping rate of individual molecules on laser fluence. The first one involves inelastic scattering of one photo-excited substrate electron on the CO molecule whereas for the second process thermalized substrate electrons play the major role. For the second key process we investigate the generation of CO dimers. Femtosecond laser excitation leads to a transient attraction of usually repelling CO molecules. We model both processes quantitatively and extract a diffusion barrier of 87 meV and a CO-attraction energy of 30 meV.

O 31.5 Tue 16:45 H38

Interaction of O₂, CO, and Methanol with Bimetallic Model Catalysts — T. NOWITZKI¹, B. JÜRGENS¹, H. BORCHERT¹, ●V. ZIELASEK¹, T. RISSE², H.-J. FREUND², S. GIORGIO³, C.R. HENRY³, and M. BÄUMER¹ — ¹Institut für Angewandte und Physikalische Chemie, Universität Bremen — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ³CRM-CNRS, Campus de Luminy, Marseille

Bimetallic particles may exhibit catalytic activities which reach far beyond those of the monometallic components. For the Co/Pd combination which is, e.g., of technological relevance for the hydrogenation of CO on the route from natural gas to liquid fuel, we have studied the interaction of model catalysts with CO, O₂, and methanol on the molecular scale. Experiments were performed in UHV by TPD, FTIR, and ferromagnetic resonance, as well as in ambient conditions by DRIFTS and gas phase analysis. In UHV, mono- and bimetallic nanoparticles were prepared by physical vapour deposition on thin epitaxial alumina films on NiAl(110). Upon exposure to O₂ and annealing, a complex oxidation-reduction scheme of the particles is observed which involves the substrate and depends on the particle composition. After exposure to methanol, we find a CO-desorption-limited route of decomposition via C-H bond scission which is universal for monometallic and bimetallic particles. We will show close correlations between the results obtained in UHV and turn-over experiments for CO oxidation and methanol decomposition at Pd and CoPd nanoparticles on MgO in ambient conditions.

O 31.6 Tue 17:00 H38

Electronic energy dissipation of deuterium and hydrogen atoms on gold and platinum surfaces — BEATE MILDNER, ECKHART HASSELBRINK, and ●DETLEF DIESING — Fachbereich Chemie and Centre for Nanointegration (CeNIDE), Universität Duisburg-Essen, D-45117 Essen, Germany

Chemical surface reaction as adsorption and Langmuir Hinshelwood (LH) reaction may dissipate their excess energy to substrate and adsorbate vibrations or to electronic degrees of freedom. The latter ones can only be detected externally by light emission or when the dissipated energy exceeds the electronic work function Φ of the metal. Electronic surface excitations $E < \Phi$ can be monitored on the surface of thin film tunnel devices. We use tantalum-tantalum oxide-top metal tunnel junctions. As top metal 5 nm thick Pt films or 12 nm thick Au films were used. Both enable a ballistic transport of excited electrons (holes) with excess energies up to 1 eV from the surface to the oxide interface. The excited carriers are then detected in the tantalum backelectrode as a tunnel current. Bunches of H and D atoms ($5 \cdot 10^{15}$ atoms in 20 seconds) were emitted to the top metal. On Au surfaces the tunnel current trace can be assigned predominantly to LH reactions. H atoms cause a 4.5 times higher tunnel signal than D atoms. On Pt surfaces the tunnel current trace is dominated by the adsorption process which is reasonable due to the higher binding energy. On Pt surfaces the tun-

nel current signals of hydrogen and deuterium are comparable. The results are compared to recent DFT calculations.

O 31.7 Tue 17:15 H38

(4x4)O structure on Ag(111): LEED-I/V analysis and high-pressure STM — ●ROBERT REICHELT, SEBASTIAN GÜNTHER, JOOST WINTTERLIN, and WOLFGANG MORITZ — Ludwig-Maximilians-Universität, München, Germany

The (4x4)O structure on Ag(111) plays a central role in the Ag/O system, and it is assumed that structurally similar oxygen species contribute to the ethylene epoxidation on Ag surfaces. Several models of the (4x4)O structure on Ag(111) have been discussed in the past. We have performed a LEED-I/V (low-energy electron-diffraction) analysis using two different experimental setups. One was a conventional LEED system mounted into a laboratory UHV system, the second was a LEEM (low-energy electron microscope). The (4x4)O structure was prepared by exposure to NO₂. The two data sets agree very well with each other, demonstrating that I/V structure analyses can be performed either with LEED or with LEEM. The structure obtained in the analysis confirms a recently proposed model that involves a reconstruction of the Ag(111) surface. Previous models based on a thin layer of Ag₂O are disproved. The (4x4)O structure was also investigated by high-pressure STM in an attempt to study its role in the partial oxidation of ethylene. The formation of the (4x4)O structure could be monitored in situ, under oxygen pressures in the mbar regime and at elevated temperatures. When ethylene was added massive structure changes occurred, indicating that the (4x4)O structure is most likely not the active phase under reaction conditions.

O 31.8 Tue 17:30 H38

Photothermal patterning of H-terminated Si(100) substrates: Experiments in an ultrahigh vacuum environment — ●MAREIKE MATHIEU, RAFAEL BAUTISTA, NILS HARTMANN, and ECKART HASSELBRINK — Fachbereich Chemie, Universität Duisburg-Essen, Universitätstr. 5, 45117 Essen

Silicon substrates are widely used as platforms in many micro- and nanofabrication schemes, e.g. in order to build up organic templates [1,2]. For this purpose suitable patterning techniques are needed. In a previous study, we reported a simple laser-assisted technique for patterning of H-terminated Si(100) substrates under ambient conditions [1]. A focused beam of an argon ion laser at a wavelength of 514 nm is used to create well-confined, ultra-thin oxide structures. Despite a laser spot diameter of about 2.5 microns line widths down to 300 nm are reached. In order to investigate the underlying mechanism, recent experiments were carried out at well-defined conditions in an ultrahigh vacuum environment. HF etched Si(100) substrates, Si(100)-(1x1)-dihydride and Si(100)-(2x1)-monohydride adsorbate phases were prepared for patterning. On the basis of the results, the nonlinear dependence of the patterning process on the laser intensity is traced back to the interplay between the laser-induced temperature rise and the thermally activated hydrogen desorption.

[1] T. Balgar, S. Franzka, N. Hartmann, E. Hasselbrink, Langmuir 20 (2004) 3525

[2] D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, Nano Letters 6 (2006) 2358