

O 78: Surface chemical reactions

Time: Thursday 15:00–16:15

Location: WIL B122

O 78.1 Thu 15:00 WIL B122

Investigations on induced dissociation of Dicobaltoctacarbonyl — ●JOHANNES SCHWENK, EVGENIA BEGUN, FABRIZIO PORRATI, ROLAND SACHSER, and MICHAEL HUTH — Physikalisches Institut, Goethe-Universität, D-60438 Frankfurt am Main, Germany

Dicobaltoctacarbonyl ($\text{Co}_2(\text{CO})_8$) is used as a precursor gas for focused electron beam induced deposition (FEBID) performed in a scanning electron microscope. In order to understand the processes which lead to the dissociation of the precursor we performed in situ electrical conductivity measurements during the FEBID process and right after it. In particular, the influence of the composition of the residual gas in the vacuum chamber on a possible autocatalysis of the $\text{Co}_2(\text{CO})_8 \rightarrow \text{Co}$ reaction was studied. We observed an enhanced spontaneous dissociation of $\text{Co}_2(\text{CO})_8$ on thermal silicon dioxide surfaces after using a plasma downstream asher. For a characterisation of the obtained films we performed an X-ray diffraction analysis and made temperature-dependent conductivity and magnetotransport measurements.

O 78.2 Thu 15:15 WIL B122

Reversible bond formation in an atom-molecule complex as a molecular switch — ●FABIAN MOHN¹, JASCHA REPP^{2,1}, LEO GROSS¹, GERHARD MEYER¹, MATTHEW S. DYER³, and MATS PERSSON^{3,4} — ¹IBM Research – Zurich, 8803 Rüschlikon, Switzerland — ²Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany — ³Surface Science Research Centre, Department of Chemistry, University of Liverpool, Liverpool, L69 3BX, UK — ⁴Department of Applied Physics, Chalmers University of Technology, SE-412 96, Göteborg, Sweden

We report on the formation of a metal-molecule complex that can be used as a molecular switch. Using a cryogenic scanning tunneling microscope, a covalent bond was formed reversibly between a gold atom and a perylene-3,4,9,10-tetracarboxylic dianhydride molecule supported by a thin insulating film. Atomic force microscopy molecular imaging [Gross et al., *Science* **325**, 1110 (2009)] was employed to determine precisely the atomic structure of the complex, and the experimental results were corroborated by density functional theory calculations. The switching between the bonded and the nonbonded state of the complex was found to be accompanied by a considerable change in the tunneling current and could be reliably controlled by locally applying voltage pulses of according polarity. A new mechanism of bond formation, which involves different charge states of the metal-molecule complex, was identified as the reason for the enhanced reliability compared to bond activation by inelastic electron tunneling.

O 78.3 Thu 15:30 WIL B122

Photoinduced generation of defect bound atomic oxygen by N_2O dissociation on thin MgO films — ●PHILIPP GIESE, HARALD KIRSCH, CHRISTIAN FRISCHKORN, and MARTIN WOLF — Fritz-Haber-Institut, Abt. Physikalische Chemie, Faradayweg 4-6, 14195 Berlin

Photoinduced dissociation of N_2O adsorbed on thin MgO films (4 - 30 monolayers) grown on Ag(100) has been studied with temperature programmed desorption spectroscopy (TPD). After irradiation with 248 nm light from a KrF laser four processes can be identified by post-irradiation TPD: Depletion of the initial N_2O coverage, generation of molecular nitrogen desorbing at 55 K, tightly bound atomic oxygen desorbing associatively at 550 K and a shift of the N_2O and N_2 desorption peaks towards higher temperatures. Analysis of the reaction yield

as a function of photon exposure confirms a defect driven reaction. However, since the amount of generated atomic oxygen exceeds the amount of generated nitrogen significantly, a second reaction channel with a high nitrogen desorption cross section needs to be incorporated. Our results are interpreted as a reaction mediated by electron hole pair generation at edges of the MgO film followed by electron trapping at defects leading to the N_2O dissociation. This interpretation is corroborated by a saturation of the oxygen generation with increasing N_2O adsorption on edges.

O 78.4 Thu 15:45 WIL B122

Electronic energy dissipation of vibrationally excited HCl/Al(111): model study and *ab initio* results — ●MICHAEL GROTEMEYER and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Universität Kiel, Germany

Molecular dynamics simulations based on time-dependent density functional theory have revealed an unexpected scaling of the dissipated energy with the mass of the nuclei in case of highly vibrationally excited HCl molecules in front of an Al(111) surface. The energy transfer from the molecular vibrations into electron-hole pair excitations is traced back to a molecular orbital which is unoccupied in the equilibrium geometry and which periodically shifts towards the Fermi level of the metal when the molecule vibrates. We suggest a simple one-dimensional tight binding model, which is capable of explaining our observations from the *ab initio* simulations. Our approach is similar in spirit to a recent (three-dimensional) model studied by Mizielinski and Bird [1]. Both the TDDFT simulations as well as the one-dimensional tight-binding model yield electron-hole pair excitation spectra that differ distinctly from a simple exponential decay. The dissipation mechanism essentially occurs independent of the orientation of the molecule with respect to the metal surface.

[1] M. S. Mizielinski, D.M. Bird, *J. Chem. Phys.*, **132**, 184704 (2010)

O 78.5 Thu 16:00 WIL B122

Theoretical elucidation of the competitive electro-oxidation mechanisms of Formic Acid on Pt(111) — ●WANG GAO, JOHN A. KEITH, JOSEF ANTON, and TIMO JACOB — Institut für Elektrochemie, Universität Ulm, Albert-Einstein-Allee 47, D-89069 Ulm, Germany

The mechanisms of formic acid (HCOOH) oxidation on Pt(111) under electrochemical conditions have been studied using density functional theory, itself an very important reaction in energy conversion. Compared with the analogous gas-phase reaction,[1] HCOOH oxidation at a water-covered surface behaves substantially differently than those in gas phase or using a solvation model involving only a few water molecules. Using these models, we evaluated the detailed reaction process, including energies and geometric structures of intermediates and transition states under the influence of different solvation models and electrode potentials. Our calculations indicate that this potential-dependent electrochemical oxidation proceeds via a multi-path mechanism (involving both the adsorbed HCOOH and HCOO intermediates), a result succinctly rationalizing conflicting experimental observations. Moreover, this study highlights how subtle changes in electrochemical reaction environments can influence (electro-) catalysis.[2] The results provide a conceptual basis to better interpret the complicated reaction kinetics of HCOOH electro-oxidation.

[1] W. Gao, J. A. Keith, J. Anton, T. Jacob, *Dalton Trans.*, **39**, 8450 (2010).

[2] W. Gao, J. A. Keith, J. Anton, T. Jacob, *J. Am. Chem. Soc.*, in press