O 73: Surface Dynamics: Reactions and Elementary Processes

Time: Wednesday 18:15–20:30

O 73.1 Wed 18:15 Poster A

Near-ambient pressure XPS study of Pt-Ga alloys and their oxidation — •MATHIAS GRABAU¹, SANDRA KRICK CALDERON¹, FLORIAN RIETZLER¹, NICOLA TACCARDI², PETER WASSERSCHEID², FLORIAN MAIER¹, HANS-PETER STEINRÜCK¹, and CHRISTIAN PAPP¹ — ¹Physikalische Chemie 2, FAU Erlangen — ²Chemische Reaktionstechnik, FAU Erlangen

Alloys of 0.7 and 1.8 at.% Pt in Ga and their oxidation were probed by XPS. The Pt surface concentration of metallic alloys was determined as a function of temperature: A constant Pt concentration was observed at high temperature. Phase separation, that is, the formation of a solid Ga₆Pt phase submerged in a Pt-depleted liquid phase, is indicated by a systematic decrease in Pt content at temperatures below 700 and 800 K, respectively. Exposure of the liquid-gas interface of such two-phase systems to oxygen at pressures between $3 * 10^{-7}$ and 1 mbar and at temperatures between 300 and 550 K led to the formation of Pt-enriched Ga_2O_3 films on the surface. Growth and composition of the formed films were examined in- and ex situ as a function of temperature and pressure. Within the examined parameter space, Pt concentration in the formed films is found to be independent of the bulk Pt concentration, growth and thickness of the films. This indicates defined solubility of Pt in Ga_2O_3 or the formation of discrete structural motives during oxidation.

We acknowledge the support of the Cluster of Excellence 'Engineering of Advanced Materials'.

O 73.2 Wed 18:15 Poster A

CO oxidation on TiO₂ nanotube-supported Pt particles at near ambient pressures — •SANDRA KRICK CALDERON¹, MATH-IAS GRABAU¹, JEONG EUN YOO², PATRIK SCHMUKI², HANS-PETER STEINRÜCK¹, and CHRISTIAN PAPP¹ — ¹Physikalische Chemie II, University of Erlangen-Nürnberg, Egerlandstr. 3 — ²Lehrstuhl für Korrosion und Oberflächentechnik, University of Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany

We investigated the oxidation of CO on different platinum model catalysts, i.e., differently sized Pt particles on vertical TiO_2 nanotubes (d=80, l=100 nm); the results are compared to the behaviour on a $TiO_2(110)$ rutile crystal with a similar Pt content and a Pt(111) single crystal. Temperature-programmed reaction experiments at total pressures of 1.0 and 0.1 mbar, and a CO:O₂ ratio of 1:4 and 2:1, were examined by near-ambient pressure XPS in the temperature range from 300 to 800 K. Additionally, we performed online gas analysis. The onset temperature of the reaction on the Pt/TiO_2 nanotube samples was found to be lower than on Pt(111) and $Pt/TiO_2(110)$ and to decrease with decreasing particle size. After reaction onset no adsorbed CO was found on the particles and metallic platinum was the active catalyst. Strong ageing of the TiO₂-supported samples with reaction time was observed resulting in changes of the reaction onset and CO conversion. Further measurements to elucidate the role of UV light for the enhancement of the reactivity will be discussed. The work was supported by Cluster of Excellence "EAM" of the Friedrich-Alexander-Universität.

O 73.3 Wed 18:15 Poster A

In-situ UPS and high-resolution XPS investigations on the norbornadiene/quadricyclane energy storage system on different metal substrates — •UDO BAUER, PHILIPP BACHMANN, CHRISTIAN PAPP, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Germany

Fossil fuel-based energy technologies lack a long-term perspective. The further development of existing renewable energy concepts is needed regarding energy distribution and storage. One possible scenario is the storage of energy by chemical means in the form of strained organic molecules, e.g. the multi-cyclic hydrocarbon quadricyclane (QC) and its strain-released counterpart norbornadiene (NBD). By absorption of light, NBD is transformed to the energy rich QC, followed by a catalytic energy release to reform NBD. We investigated the adsorption as well as the conversion of QC to NBD and their decomposition over different catalytically active metal surfaces. Ultraviolet photoelectron spectroscopy (UPS) provides characteristic spectra of NBD/QC on Ni(111) and Au/Ni(111) but not on Pt(111). By applying heating ramps, we observe the conversion of QC to NBD at certain temperatures except for the Pt(111) surface, where the reaction takes Location: Poster A

place below 120 K. HR-XPS (high-resolution X-ray photoelectron spectroscopy) spectra of the adsorption (120 K) and during the heating ramps reflect the different interaction strength between molecules and surface and reveal a fundamentally changed decomposition behavior of NBD at higher temperatures for each surface. The work was supported by the Cluster of Excellence Engineering of Advanced Materials (EAM).

O 73.4 Wed 18:15 Poster A XPS Characterization of Sulphur Transformations during Operation of Li-S Batteries with Ultramicroporous Carbon-Sulphur Cathodes — •THOMAS DIEMANT¹, M. HELEN², M. ANJI REDDY², MAXIMILIAN FICHTNER^{2,3}, and R. JÜRGEN BEHM^{1,2} — ¹Institute of Surface Chemistry and Catalysis, Albert-Einstein-Allee 47, Ulm University, D-89081 Ulm — ²Helmholtz Institute Ulm, Helmholtzstr. 11, D-89081 Ulm — ³Institute of Nanotechnology, Karlsruhe Institute of Technology, P.O. Box 3640, D-76021 Karlsruhe

Lithium-sulphur (Li-S) batteries are discussed as potential successors of Li-ion cells. However, mainly due to the 'poly-sulphide shuttle', Li-S batteries suffer at present from poor cycle life. One promising approach to overcome this problem is the use of microporous carbon confined sulphur, which eliminates the formation of higher order poly-sulphides. In this study, electrodes based on an ultramicroporous carbon-sulphur (UC-S) composite (46% S) were investigated. We studied the chemical state of sulphur in the UC-S cathodes at different stages of the lithiation/delithiation cycle by XPS analysis of the surface and subsurface region of the electrodes. Reasons for the capacity fading over cycling of the UC-S electrodes were elucidated. The structural properties were revealed using transmission electron microscopy (TEM). The results of XPS analysis together with the electrochemical performance measurements demonstrate the single step transformation of sulphur to Li₂S₂/Li₂S and vice versa during the discharge/charge process. The UC-S electrodes used in this study exhibited a reversible capacity of $700~{\rm mAh/g}$ at C/5 even after 100 cycles.

O 73.5 Wed 18:15 Poster A

Controlling Alkyne Catalysis on an Atom-By-Atom Basis — MARIAN D. RÖTZER, ANDREW S. CRAMPTON, •MAXIMILIAN KRAUSE, FLORIAN F. SCHWEINBERGER, and UELI HEIZ — Technische Universität München, Dept. of Chem. and Catalysis Research Center, Chair of Physical Chemistry, Lichtenbergstr. 4, 85748 Garching, Germany

Alkanes, alkenes and alkynes are major feedstocks for the chemical industry and their reactions on supported metal nanoparticles are applied in a variety of processes for the synthesis of important chemicals. To be able to develop new and efficient catalysts for those reactions a deep fundamental understanding with respect to adsorption, mechanistic details, poisoning, etc. has to be gained. Size-selected clusters supported on thin films under UHV conditions meet the requirements of a defined model system for unraveling underlying catalytic principles. To this end, we investigated the surface chemistry of 3-hexyne on size-selected Pt_n clusters on MgO(100)/Mo(100). This model system is characterized by TPR and IRRAS and compared to the Pt(111) surface. Depending on the cluster size, different reaction pathways are favored or even completely blocked. The selectivities towards such pathways are size-dependent, though not linearly. IRRAS experiments showed re-emerging free surface sites when the reaction products are desorbed, though a characteristic red-shift of the CO-stretch signal points to the remainder of carbonaceous species, as supported by AES.

This work has been supported by the Clariant Produkte (Deutschland) GmbH in the framework of the Munich Catalysis (MuniCat) program, a strategic alliance between TUM and Clariant.

O 73.6 Wed 18:15 Poster A STM Tip-Induced Manipulation of Tetrahydrofuran and Diethyl Ether on Si(001) — •TAMAM BOHAMUD¹, MARCEL REUTZEL¹, GERSON METTE¹, MICHAEL DÜRR^{1,2}, and ULRICH HÖFER¹ — ¹Philipps-Universität, 35037 Marburg — ²Justus-Liebig Universität, 34392 Gießen

In the last decades, the adsorption of organic molecules on silicon surfaces has been subject of intense research. The resulting hybrid structures provide a promising tool to increase the functionality of semiconductor devices. In most cases, the respective adsorbate reactions are thermally induced; however, electronically induced processes may open additional reaction pathways and/or better control of single reaction channels. In this study, we investigate both lateral movement as well as chemical conversion of ether molecules on Si(001) induced by tunneling electrons from a STM tip.

The adsorption mechanism of ether molecules on Si(001) is well understood: At low temperature, a dative bond between the oxygen atom of the intact ether molecule and the D_{down} state of the buckled silicon dimer is established. At room temperature, ether cleavage leads to covalent Si-O and Si-C bonds [*ChemPhysChem* **15**, 3725 (2014), *JPCC* **119**, 6018 (2015)]. For Diethyl Ether, a tip-induced hopping of a $-C_2H_5$ fragment is observed at positive sample bias. For Tetrahydrofuran, the tunneling electrons can induce the transition from the datively bonded intermediate state to the covalently bonded final state. In both cases, we observe a dependence on tunneling voltage and current which are discussed in terms of the underlying excitation mechanism.

O 73.7 Wed 18:15 Poster A

A transition metal complex transformation in ionic liquids monitored by photoelectron spectroscopy — •BENJAMIN MAY, MICHAEL HÖNLE, HANS-PETER STEINRÜCK, and FLORIAN MAIER — Chair Physical Chemistry II, FAU University Erlangen-Nürnberg, Germany

Ionic liquids (ILs) — salt melts with melting points below 373 K do exhibit an extremely low vapor pressure making them suitable for surface science investigations under ultra-high vacuum conditions, in contrast to conventional molecular liquids. Within the last years, our group performed various types of fundamental reaction studies in ILs in combination with X-ray photoelectron spectroscopy (XPS).[1] Here, we report on a temperature-dependent IL metal complex transformation.

The transition metal IL [EMIM]₂[Co(NCS)₄][2] was mixed with the IL [EMIM][NCS]. Osborne *et. al.* reported thermochromic behavior for a similar system: in the presence of an excess of free thiocyanate anions, the blue tetrahedral $[Co(NCS)_4]^{2-}$ complex anion reversibly forms below 223 K a pink octahedral $[Co(NCS)_6]^{4-}$ complex.[3]

In our study, IL signals were monitored by XPS and UPS between room temperature and 213 K. Below the transition temperature, changes in the Co2p line were observed indicating a shift of the complex equilibrium towards the octahedral complex.

H.-P. Steinrück, Phys. Chem. Chem. Phys. 2012, 14, 5010-5029.
T. Peppel, et. al., Angew. Chem. Int. Ed. 2010, 49, 7116-7119.
S.J. Osborne, et. al., Dalton Trans. 2015, 44, 11286-11289.

O 73.8 Wed 18:15 Poster A Theoretical model for the time evolution of a diffusion grating at a solid-liquid interface — ALEXANDRA C. DÁVILA¹, •ECKHARD PEHLKE¹, DANIEL BEICHT², and OLAF MAGNUSSEN² — ¹Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel — ²Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität zu Kiel

Diffusion at electrochemical interfaces is a fundamental process in electrochemistry. It is the crucial factor determining, e.g., the growth mode during electrolytic deposition and thus, ultimately, the quality of the deposited films. Under UHV conditions, surface diffusion coefficients have been measured by various techniques [see, e.g., J.V. Barth, Surf. Sci. Rep. **40**, 75 (2000)], for instance by analyzing the evolution of adsorbate concentration profiles on the surface. Here we go beyond the situation in UHV and present a mathematical model for the time evolution of the concentration profile of a concentration grid at a solid-liquid interface created by Laser induced thermal desorption. The desorption of particles from the adsorbate layer into the liquid, the diffusion in the liquid, and the adsorption back onto the surface are accounted for. The effect of diffusion of the adsorbate through the liquid will be discussed.

O 73.9 Wed 18:15 Poster A

Electrochemical etching of proton irradiated p-GaAs — •ALRIK STEGMAIER, ULRICH VETTER, and HANS HOFSÄSS — 2. Physikalisches Institut, Georg-August-Universität Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen

Microelectromechanical systems (MEMS) combine electrical and mechanical features on the micrometer scale and are used for an increasing number of applications, including energy harvesters, accelerometers and pressure sensors [1]. Proton beam writing (PBW) is a maskless lithographic method for the production of microstructures for such applications [2]. With PBW it is possible to produce three dimensional structures by varying only the fluence of the proton irradiation on a p-GaAs sample, followed by electrochemical etching [3].

As such, the electrochemical etching of the sample is of large importance for producing high quality final structures. While electrochemical etching of defect poor GaAs is reasonably well understood [4] there is comparatively little published work on highly irradiated material.

Here the electrochemical etching with KOH of p-GaAs irradiated with protons (energies up to several MeV) is investigated experimentally, improving upon previous findings [5].

[1] V. Cimalla et al., J. Phys. D: Appl. Phys., 40(20), 6386, 2007

[2] J.A. van Kan et al., Appl. Phys. Lett., 83(8), 1629, 2003

 $\left[3\right]$ P. Mistry et al., Nucl. Instr. Meth. Phys. Res. B, 237, 188, 2005

[4] P. Allongue et al., J. Electroanal. Chem., 317, 77-99, 1991

[5] M. Schulte-Borchers et al., J. Micromech. Microeng., 22, 025011, 2012

O 73.10 Wed 18:15 Poster A

Investigation of Calcium-Silicate surfaces with UHV-IRRAS to understanding the first step in the corrosion of concretes — •CARSTEN NATZECK, PETER WEIDLER, CHRISTOF WOELL, and PETER THISSEN — Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

The well-oriented Calcium-Silicate substrate Wollastonite as our model sample is a chemically well characterized mineral (CaSiO₃). It has versatile physical properties for use in industry, reaching from medicine with the formation of artificial bones due to its bioactivity to construction chemistry with Calcium-Silicates (CS) as model system e.g. for cement and concrete. The surface chemistry of this CS substrate has been studied using infrared reflection-absorption spectroscopy under ultrahigh-vacuum conditions (UHV-IRRAS) using water and methanol as probe molecules. Exposure of the cooled substrate (100 K) to H_2O leads to the formation of surface OH-species. This proton transfer, which is a crucial step in the corrosion of concrete, is found to be absent when the same surface is exposed to methanol. These results are analyzed on the basis of a detailed, first-principles computational study employing densitiv function theory (DFT) and allow to derive a consistent picture on the chemical properties of this important mineral surface. Implications for corrosion protection of concrete in harsh environments will be discussed.

O 73.11 Wed 18:15 Poster A Molecular Level Understanding of the Sorption of the Phosphorus-Containing Compounds on Mineral Surfaces — •ASHOUR AHMED and OLIVER KÜHN — Institute of Physics, University of Rostock, Rostock, Germany.

The future of universal supply with phosphorus (P) fertilizer has got a critical attention that alarmed the public research platforms and also initiated novel ones. Improvement of our understanding to the soil P cycle needs advances in analytical and theoretical methods of investigation. In the current contribution, we are going to explore the optimal quantum-chemical strategy to describe P-related processes at soil mineral surfaces. Since P exhibits a great diversity of inorganic and organic P species, we investigate the different binding motifs and energies of these species at different mineral surfaces using density functional theory. Particular attention is paid to unravel the competition between P- and organic compounds for mineral surface sites in the presence of water.

O 73.12 Wed 18:15 Poster A Adsorption and diffusion of cobalt phthalocyanine molecules on the Ag(100) surface — GRAZYNA ANTCZAK¹, •WOJCIECH KAMIŃSKI¹, AGATA SABIK¹, CHRISTOPHER ZAUM², and KARINA MORGENSTERN³ — ¹Institute of Experimental Physics, University of Wrocław, Wrocław, Poland — ²Institut für Festkörperphysik, Leibniz Universität Hannover, Hannover, Germany — ³Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, Bochum, Germany Surface diffusion is essential to many technological processes, such as crystal growth, catalysis, sintering, etc. It influences the stability of functional and technologically important materials. The surface diffusion of adatoms on surfaces has been already widely investigated, but it is still the remaining challenge to probe and fully understand the motion of bigger objects, such as organic molecules.

We investigate the geometry, the electronic structure, and the diffusion mechanism of CoPc molecules adsorbed on the Ag(100). The measurements were performed using the LT-STM and supported with the DFT calculations. We demonstrate that the complex surface diffusion mechanism of CoPc molecules involves, in the same temperature range, a combined translational and rotational molecular motion. Both processes are associated with similar activation energies; however, the translation is more frequently observed. Two channels for surface diffusion were identified: the first provides only a channel for translation, while the second couples the translational and the rotational molecular motion on the transition path. The existence of the two channels explains a higher rate for the translation determined in experiment.

O 73.13 Wed 18:15 Poster A

Pt single atoms and nanoclusters stabilized by ultrathin oxide film: performance and oxygen vacancy creation in CO oxidation — •XIONG ZHOU^{1,2}, KAI WU¹, and WEI CHEN² — ¹BNLMS, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China — ²Department of Chemistry, National University of Singapore, Singapore 117543, Singapore

A series of model catalysts consisting of Pt single atoms and nanoclusters supported by monolayered CuO film grown at Cu(110) were successfully prepared, which could be stabilized well above room temperature and exhibited a high performance in CO oxidation at temperatures as low as ~360 K. Combined scanning tunneling microscopy and temperature-programmed desorption measurements directly evidenced that at the initial CO oxidation stage, oxygen vacancy in the CuO lattice was generated at the nearest neighbour of the Pt nanoclusters. The experimental measurements showed that the oxidation activity was inversely proportional to the Pt nanocluster size. In contrast, the Pt single atoms possessed no surface reactivity for the CO oxidation due to the early and complete desorption of CO before its oxidation on the model catalysts commenced.

O 73.14 Wed 18:15 Poster A Photon Induced Processes in CH₄:D₂O Interstellar Ice Mimics Initiated by Femtosecond XUV Pulses — \bullet John Thrower, Tushar Suhasaria, Robert Frigge, Sebastian Roling, and Hel-Mut Zacharias — Physikalisches Insitut, Westfälische Wilhelms-Universität Münster, Münster, Germany

Solid state physical and chemical processes on dust grain surfaces play an important role in the chemical evolution of the interstellar medium. In dense molecular clouds, these grains are coated with layers of H₂O dominated molecular ices doped with carbon containing species including CO, CH_3OH and CH_4 . Star formation can lead to these ices being bathed in a flux of XUV and soft X-ray photons, providing a non-thermal energetic input that can lead to the production of more complex species as well as providing a low temperature desorption route for returning molecules to the gas phase. We have used femto second XUV ($\lambda = 30.4$ nm) pulses generated by the Free-Electron Laser in Hamburg (FLASH) to irradiate interstellar ice mimics consisting of D_2O and CH_4 deposited on an HOPG substrate at 15 K. Time-of-flight mass spectrometry, combined with multiphoton ionisation, reveals a rich variety of neutral and ionic desorption products including ejected ionic clusters. The ion desorption yield is found to be non-linear with respect to the photon flux, permitting the probing of reaction dynamics using two correlated pulses, temporally separated by 0.5-6 ps.

O 73.15 Wed 18:15 Poster A

XUV photochemistry of CO and $^{13}\mathrm{CD}_3\mathrm{OD}$ ice mixtures on HOPG — •TUSHAR SUHASARIA, JOHN THROWER, ROBERT FRIGGE, SEBASTIAN ROLING, and HELMUT ZACHARIAS — Physikalisches Institut, Universität Münster, Germany

In the interstellar medium (ISM), photochemical reactions occur on

the surface of dust grains. In cold regions the grains are covered by mixed molecular ices. In these ice matrices, high-energy radiation from young stars leads to the formation of new molecules. On a cold (ca. 15 K) highly-oriented pyrolytic graphite (HOPG) surface, a mixture of CO and ¹³CD₃OD was irradiated by 30.4 nm femtosecond XUV pulses from the Free-electron laser in Hamburg (FLASH). The resulting desorption products were identified by time-of-flight mass spectrometry and are dominated by low mass fragment ions from the adsorbed molecules along with some higher mass clusters. In addition, a (2+1) resonance enhanced multi-photon ionization (REMPI) scheme via the B¹ $\Sigma \leftarrow X^{1}\Sigma$ transition of CO molecules at 230 nm was used to probe the internal energy content of desorbing neutral CO. The desorbing ions and neutral products show a non-linear intensity dependence which allows the determination of the reaction dynamics by two-pulse correlation measurements.

O 73.16 Wed 18:15 Poster A

Ultraschnelle Dynamik von Photooxidationsreaktionen auf Titandioxid — •FLORIAN KNALL und THORSTEN BERNHARDT — Universität Ulm

Titandioxid ist ein wichtiger Photokatalysator, dessen Einsatzbereiche von der Entfernung organischer Schadstoffe in der Umgebungsluft über Abwasser-Aufbereitung bis hin zu selbstreinigenden Oberflächenbeschichtungen reichen. Die Photooxidation von organischen Molekülen ist in all diesen Bereichen von Bedeutung. Allerding sind in vielen Fällen sehr wenige molekulare Details der oft hochkomplexen Reaktionen bekannt. Ein molekulares Verständnis der elementaren Reaktionsschritte bildet jedoch die unbedingte Voraussetzung zur gezielten Optimierung moderner photokatalytischer Materialien. Wir verwenden eine neue experimentelle Methode, die Oberflächen-Pump&Probe-Laser-Massenspektrometrie, welche ideal geeignet ist, um derartige Reaktionen zu untersuchen. In diesem Beitrag wird diese neue Technik auf die Photooxidation organischer Adsorbate auf Titandioxid angewendet, um so erstmalig einen Einblick in die elementaren molekularen Reaktionsdetails photokatalytischer Reaktionen an Oxidoberflächen zu erhalten.

O 73.17 Wed 18:15 Poster A **Pump-probe photoemission spectroscopy of O**₂ on Pt(111) at a Free-Electron Laser — •GIUSEPPE MERCURIO¹, LUKAS WENTHAUS¹, FLORIAN HIEKE¹, HENRIKE HÜMPEL¹, GÜNTER BRENNER², HARALD REDLIN², and WILFRIED WURTH^{1,2} — ¹Physics Department and Center for Free-Electron Laser Science, University of Hamburg, Hamburg, Germany — ²DESY Photon Science, Hamburg, Germany

The interaction of oxygen with the platinum surface has been the subject of extensive experimental and theoretical studies in the last decades because of its technological relevance in many catalytic reactions. In order to improve heterogeneous catalysis at surfaces to achieve more efficient catalysts and less undesired by-products it is essential to gain a microscopical understanding of fundamental chemical reactions. To this purpose we investigate chemisorbed oxygen molecules on a Pt(111) surface by means of time-resolved photoemission spectroscopy in a pump-probe experiment. We used as pump fs laser pulses at 800 nm and as probe free-electron laser pulses from FLASH at DESY in Hamburg at 566 eV. In this way the dynamics of the adsorbed molecule and the energy exchange with the surface leading to the excitation of the adsorbates could be investigated with a time resolution better than 500 fs for several ps after the absorption of the pump pulse at the surface.