

O 78: Poster: Surface Dynamics - Reactions, Elementary Processes and Phase Transitions

Time: Wednesday 18:15–20:30

Location: Poster A

O 78.1 Wed 18:15 Poster A

X-ray photoemission studies of the liquid metal catalyst Pd/Rh-Ga — ●HAIKO WITTKÄMPER¹, MATHIAS GRABAU¹, JANNIS ERHARD³, NICOLA TACCARDI², PETER WASSERSCHIED², CHRISTIAN NEISS³, ANDREAS GÖRLING³, HANS-PETER STEINRÜCK¹, and CHRISTIAN PAPP¹ — ¹Physikalische Chemie 2 — ²Chemische Reaktionstechnik — ³Theoretische Chemie, FAU Erlangen

Mixtures of Pd and Ga on porous silica were shown to be stable and selective alkane dehydrogenation catalysts. The beneficial effects of Ga addition to the active transition metal are due to the fact that the catalyst is in the liquid phase during reaction, which is indicated by SEM and XRD measurements, and termed supported catalytically active liquid metal solution (SCALMS).[1] We herein present XPS studies of Pd-Ga and Rh-Ga alloys as model systems for catalytically-active, supported liquid catalysts. In an effort to understand the underlying principles of the catalyst, the temperature-dependent Pd/Rh concentrations at the surface of the liquid phase were evaluated by quantitative XPS. The observed temperature-dependence is explained by the formation of transition metal-rich intermetallic phases, leading to the depletion of the liquid phase and the surface from the transition metal. For the Pd-Ga alloy, additionally, an inhomogeneous Pd distribution with depletion at the interface is suggested by ARXPS and DFT-based MD simulation. [2] Data on the Rh-Ga system will be presented and compared to the results obtained for the Pd-Ga alloy. [1] Taccardi, N., Grabau, M., et al. *NatChem* 9, 862-867 (2017). [2] Grabau, M., Erhard J., et al. *ChemEurJ* 23, 1-8 (2017).

O 78.2 Wed 18:15 Poster A

enhanced photocatalytic activities of net-like hematite nanoparticle modified with graphene oxide and mechanism insight — ●HUANMING ZHANG¹, MIN ZHOU¹, YANG XU¹, SHIPU XU¹, FANNA MENG², LIHONG QI², YUJIN CHEN², and YONG LEI¹ — ¹Institute für Physics & IMN MacroNano (ZIK), Technische Universität Ilmenau, 98693 Ilmenau, Germany — ²Key Laboratory of In-Fiber Integrated Optics, Ministry of Education, College of Science, Harbin Engineering University, 150001 Harbin, China

In photocatalytic water oxidation, hematite possesses many attractive features, for instance favorable optical band gap (approximately 2.1 eV), chemical stability, natural abundance, nontoxicity and low cost. However, its sluggish surface reaction kinetics, short carrier lifetime and considerably shorter diffusion length of holes compared with the absorption depth hold back its practical application. Thus, A co-catalyst may be an effective way to remedy these drawbacks. Herein, a facile strategy was developed to fabricate net-like hematite nanoparticle (NHN) modified with graphene oxide (GO), in which the degree of oxidization of GO could be controlled by simply changing annealing time, and GO replaces part of hematite as the reaction interface to speed up the oxygen evolution rate. NHG with GO of appropriate oxidization degree and content exhibited much higher photocatalytic activities than hematite nanorods and commercial hematite. The strategy presented here could be expanded as a general method to synthesize other types of photocatalysts modified with GO for applications in photocatalysis.

O 78.3 Wed 18:15 Poster A

Utilization of coke oven gas for the catalytic production of methane and methanol — ●FABIAN RACHOW, KLAUS MÜLLER, and DIETER SCHMEISSER — Brandenburgische Technische Universität Cottbus - Senftenberg, Angewandte Physik-Sensorik, Konrad-Wachsmann-Allee 17, 03046 Cottbus, Germany

Coke oven gas (COG) is a byproduct in the production of carbon rich coke from coal for the steel industry. Apart from a high amount of hydrogen (~60vol%) and methane (~25vol%), COG contains CO (5-8vol%) and CO₂ (1-3vol%), thus making it an attractive feedstock for the production of synthetic energy carriers like methane and methanol via catalytic conversion. The conventional route requires steam reforming of the methane to syngas for further reaction. We however investigate a different approach to directly convert the CO and CO₂ from COG to methane and/or methanol. The process is evaluated by the conversion of CO and CO₂, yield of CH₄ and CH₃OH and selectivity towards higher hydrocarbons for varying temperature and pressure. A surplus of hydrogen in the COG might be compensated

by additional CO₂ from air, flue gas or coal gasification to achieve a higher yield.

O 78.4 Wed 18:15 Poster A

Segregation Study of Size-Selected Bimetallic Nickel-Cobalt Nanoparticles for Partial Oxidation of Methane — ●PETER FRANZ ZAJAC¹, IOANNIS ZEGKINOGLU¹, LUKAS PIELSTICKER¹, and BEATRIZ ROLDAN CUENYA^{1,2} — ¹Department of Physics, Ruhr University Bochum, 44780 Bochum, Germany — ²Department of Interface Science, Fritz-Haber Institute of the Max Planck Society, Berlin 14195, Germany

Alloying and segregation phenomena in bimetallic nanoparticle catalysts crucially affect their elemental surface composition and are often responsible for synergistic effects which enhance their catalytic performance in comparison to their monometallic counterparts. We used *in situ* X-ray photoelectron spectroscopy, both in ultra-high vacuum and under near-ambient pressure conditions (NAP-XPS), in combination with atomic force microscopy (AFM), to investigate the morphological stability, chemical state and surface composition of size-selected bimetallic nickel-cobalt nanoparticles supported on silicon dioxide substrates as a function of temperature and gas environment for the catalytic partial oxidation of methane (CPOM). The studies demonstrated the remarkable stability of surface cobalt oxide species under reducing conditions and indicate that pretreatment of the nanocatalysts by plasma etching or annealing can help tune their catalytic properties.

O 78.5 Wed 18:15 Poster A

Modeling Nonadiabatic Effects in Gas-Surface Dynamics by Means of Electronic Friction — ●SIMON P. RITTMAYER and KARSTEN REUTER — Technische Universität München

Energy transfer at and across the interface fundamentally governs the dynamics of surface chemical reactions, e.g., in heterogeneous catalysis. On frequently employed metal catalysts, likely dissipation channels are the adsorbate interaction with substrate phonons and the nonadiabatic excitation of electron-hole (*eh*)-pairs in the surface. Despite considerable effort spent in the past decades, however, a general assessment of the relative importance of these competing energy dissipation channels has still not been achieved. In parts, this is attributable to the uncertainty that comes with effective models for the nonadiabatic energy dissipation—such as the electronic friction approach—inevitable for large scale simulations.

In order to improve upon this situation, we demonstrate the validation of the popular local density friction approximation (LDFA) for electronic friction by comparing to experimentally measured vibrational lifetimes [1], scrutinize underlying assumptions using explicitly evaluated *eh*-pair excitation spectra [2], and ultimately invoke this effective model to disentangle the role of the competing energy dissipation mechanisms in the context of thermal adatom diffusion [3].

[1] S.P. Rittmeyer *et al.*, *Phys. Rev. Lett.* **115**, 046102 (2015).

[2] S.P. Rittmeyer *et al.*, *Phys. Rev. Lett.* **119**, 176808 (2017).

[3] S.P. Rittmeyer *et al.*, *Phys. Rev. Lett.* **117**, 196001 (2016).

O 78.6 Wed 18:15 Poster A

Dynamics and reactivity of long-lived excess electrons in DMSO films on Cu(111) — ●ANGELIKA DEMLING, SARAH B. KING, KATHARINA BROCH, and JULIA STÄHLER — Department of Physical Chemistry, Fritz Haber Institute of the MPG, Faradayweg 4-6, 14195 Berlin, Germany

DMSO is a widely used non-aqueous solvent with the potential to be used in lithium-oxygen batteries due to its ability to catalyze the superoxide formation and to stabilize the products. In this work we investigate the electron dynamics in DMSO films on Cu(111) using time-resolved two-photon photoemission. We show that films of a thickness > 2 monolayers exhibit two surface-bound electronic states at 2.41 ± 0.05 eV and 2.30 ± 0.05 eV above the Fermi level with lifetimes on the order of several seconds. Both are formed from the same precursor state, a small polaron in the second monolayer. Due to their long lifetime and binding location on the DMSO surface, we assign these states to electrons residing in deep traps at the DMSO/vacuum interface. Moreover, the photoemission signal from the trapped electrons decreases and the work function increases over time under illumina-

tion. Both effects are discussed as possible results of light-induced reorganization of molecules at the surface. Further experiments in an oxygen atmosphere suggest the surface-bound electrons react with oxygen, making these findings of high relevance for the understanding of the formation of superoxide in lithium-oxygen batteries.

O 78.7 Wed 18:15 Poster A

New molecular beam set-up to study dynamics at ionic liquids surfaces — ●RADHA GOBINDA BHUIN, HANS-PETER STEINRÜCK, and FLORIAN MAIER — Lehrstuhl für Physikalische Chemie II, FAU, Erlangen, Germany

More than a decade surfaces and interfaces of ionic liquids (ILs) have been studied extensively. These studies mostly concern 'static' properties of ILs such as interface composition, molecular orientation and surface termination, enrichment and layering effects, surface tension, and adsorption of small molecules.^{1,2,3} However, the dynamics of the transfer of the gases through the interface and its dependence on the interface properties have not been studied so far, despite their importance in catalysis and separation technologies.⁴ Therefore, to investigate the dynamical interaction processes at the ionic liquid surfaces we have designed and built a new molecular beam setup which combines a supersonic molecular beam with a rotatable mass spectrometer and an X-ray photoelectron spectrometer for in situ XPS-investigations. Using this set-up we will address in particular the question how gases pass through the gas/liquid interface depending on the gas / IL physico-chemical properties. RGB and HPS thank the ERC for financial support through an Advanced Investigator Grant to HPS. References [1] H.-P. Steinrück, *Phys. Chem. Chem. Phys.* 14, 5010 (2012). [2] H.-P. Steinrück, *Surf. Sci.* 604, 481 (2010). [3] K. R. J. Lovelock et al., *Chem. Rev.* 110, 5158 (2010). [4] N. V. Plechkovaa and K. R. Seddon, *Chem. Soc. Rev.* 37, 123 (2008).

O 78.8 Wed 18:15 Poster A

Molecular motors on a surface studied by scanning tunneling microscopy — ●MONIKA SCHIED¹, JAMES M. TOUR², and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, University of Graz, Austria — ²Department of Chemistry, Rice University, USA

Artificial molecular motors can translate an external stimulus into controlled motion. They have seen great developments in the last decades [1]. While many studies exist in solution, only very little is known how such functional molecules behave on a surface, although such a setup holds the advantage of a fixed point of reference. This is of importance for a key property of molecular machines, the directionality of their motion in a static environment.

In this study, artificial motor molecules have been investigated, all based on a combination of double bond isomerization and helix inversion, which are the key processes responsible for rotation of the so-called Feringa motor. This type of motor has already been used to successfully drive lateral translation of molecules at surfaces [2, 3]. Experiments were done by low temperature scanning tunneling microscopy (STM) to enable imaging of one and the same molecule before applying an external stimulus. The focus of our study is on the adsorption of such molecules at metallic surfaces and what type of motion can be induced by either STM manipulation or illumination by light.

[1] W. R. Browne and B. L. Feringa, *Nat. Nanotech.* 1, 25 (2006)

[2] T. Kudernac et al., *Nature* 479, 208 (2011)

[3] A. Saywell et al., *ACS Nano* 10, 10945 (2016)

O 78.9 Wed 18:15 Poster A

Model catalytic studies of liquid organic hydrogen carriers: Pyridine / piperidine on Ni(111) — ●MARIE FREIBERGER, JOHANN STEINHÄUER, PHILIPP BACHMANN, FLORIAN SPÄTH, UDO BAUER, FABIAN DÜLL, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Lehrstuhl für Physikalische Chemie II, FAU Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

A strong effort for the implementation of renewable energy sources was made by constructing large-scale wind farms and solar plants, which replace power plants with non-renewable fuels. The availability of these energy sources is unsteady and unpredictable due to environmental influences. Therefore, energy storage becomes more important in the near future. One concept is the use of liquid organic hydrogen carriers (LOHC), which enable hydrogen storage under ambient conditions. In an LOHC system, when excess energy is available, organic molecules are catalytically loaded with hydrogen to form an energy- and hydrogen-rich compound. Afterwards, when energy is needed, hydrogen is catalytically unloaded and the hydrogen lean form is re-

stored. Herein, we present detailed studies on the LOHC system pyridine and its hydrogenated form piperidine. This LOHC system is investigated in a model catalytic approach on a Ni(111) surface under ultra-high vacuum conditions. Using synchrotron radiation-based high-resolution X-ray photoelectron spectroscopy we are able to observe the adsorption, desorption and reaction behaviour of the LOHC system. Furthermore, insights on the structure-reactivity relationship in dehydrogenation catalysis of heterocyclic compounds are provided.

O 78.10 Wed 18:15 Poster A

Motorized molecules studied by scanning tunneling microscopy — ●PETER JACOBSON¹, JAMES M TOUR², and LEONHARD GRILL¹ — ¹Department of Physical Chemistry, University of Graz, 8010 Graz, Austria — ²Department of Chemistry, Rice University, Houston, Texas 77005, USA

Motorized molecules are envisioned as cargo carriers at the nanoscale. Critical to their success is the controlled activation of motion using external stimuli. In Feringa type motors, UV light triggers a sequence of isomerization and helical inversion steps leading to the unidirectional rotation of the motor. When incorporated into larger molecules, these motors are a potential source of unidirectional translation at surfaces. Scanning probe microscopy is an ideal tool to investigate the single molecule dynamics of these molecular machines, but commonly used metal substrates have drawbacks, such as the quenching of excited states by conduction electrons. An alternate approach is to deposit them on semiconducting substrates, thereby reducing the adsorption strength of the molecule on the surface and removing a potential path for quenching. Here, I will present initial results on motorized molecules containing a Feringa motor on semiconducting surfaces.

O 78.11 Wed 18:15 Poster A

On the kinetics of the self-metalation reaction of 2H-tetraphenylporphyrin derivatives on Cu(111) with different peripheral CN functionalization — ●MANUEL MEUSEL, MICHAEL LEPPER, JULIA KÖBL, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany.

In this contribution, we present a detailed scanning tunneling microscopy (STM) study concerning the kinetics of the self-metalation reaction of 2H-tetraphenylporphyrins (2HTPP) on Cu(111) with and without peripheral cyano functionalization. The corresponding self-metalation reaction, in which the free base porphyrins metalate with Cu atoms from the substrate, has been studied intensively for 2HTPP on Cu(111) in the past [1-3]. Surprisingly, we observed a strong decrease of the self-metalation rate directly correlating to the degree of functionalization with peripheral cyano groups, opposed to the expected trend for a metalation in solution. Statistical analysis of isothermal STM time series allows for the estimation of corresponding changes in the activation energy of the self-metalation for the different porphyrin species. The origin of this phenomenon will be discussed in respect to different binding motifs and the intramolecular conformation of the porphyrins. This work was funded through DFG FOR 1878 (funCOS) under grant MA 4246/2-1. [1] K. Diller et al., *J. Chem. Phys.*, 136 (2012) 014705 [2] S. Dietze et al., *Ang. Chem. Int. Ed.* 51 (2012) 10898 [3] H. Marbach, *Acc. Chem. Res.*, 48 (2015) 2649

O 78.12 Wed 18:15 Poster A

Reactivity of benzene on a sulfur-passivated Pt(111) surface — JOHANN STEINHÄUER, PHILIPP BACHMANN, UDO BAUER, FLORIAN SPÄTH, FABIAN DÜLL, HANS-PETER STEINRÜCK, and ●CHRISTIAN PAPP — Lehrstuhl für Physikalische Chemie II, FAU Erlangen-Nürnberg, Egerlandstr.3, 91058 Erlangen, Germany

Poisoning of catalysts with sulfur is a major issue in large scale applications. One very efficient poison for catalysts is sulfur, which leads to the blocking of reactive sites and a strong reduction of the total adsorption capacity. Interestingly sulfur is also used as a promoter in the dehydrogenation reaction of hydrocarbons. To understand the particular influence of sulfur in this reaction, we studied the effect of sulfur contamination on the reaction behavior of benzene on a Pt(111) single crystal with Temperature Programmed Desorption (TPD) and synchrotron based high-resolution XPS. In these studies, the sulfur coverages were varied up to 0.3 ML, obtained by adsorbing H₂S and subsequent annealing to 500 K. We followed the reaction of benzene on Pt(111) as a function of sulfur coverage. For sulfur-poisoned surfaces we find the desorption of benzene occurs at slightly lower temperatures of about 400 K. On the sulfur free Pt(111) surface also the reaction

and decomposition is found at higher temperatures of 435 and 640 K, respectively. This effect of sulfur on the reaction was also found in TPD measurements. Sulfur leads to a shift of the desorption peaks to lower temperatures with increasing sulfur coverages. Thereby indicating a decreased binding energy between catalyst and substrate or a deactivation of active sites on the catalyst through sulfur poisoning.

O 78.13 Wed 18:15 Poster A

Model Catalytic Studies of Liquid Organic Hydrogen Carriers: Dehydrogenation of Indole, Indoline and Octahydroindole on Pt(111) — PHILIPP BACHMANN¹, JOHANN STEINHÄUER¹, FLORIAN SPÄTH¹, FABIAN DÜLL¹, UDO BAUER¹, MARLENE SCHEUERMEYER², PETER WASSERSCHIED², HANS-PETER STEINRÜCK¹, and •CHRISTIAN PAPP¹ — ¹Lehrstuhl für Physikalische Chemie II, FAU Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany — ²Lehrstuhl für Chemische Reaktionstechnik, FAU Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen, Germany

Indole derivatives are considered promising Liquid Organic Hydrogen Carriers (LOHC) for renewable energy storage. Using X-ray photoelectron spectroscopy (XPS) and Temperature Programmed Desorption (TPD), we investigated low temperature adsorption, and dehydrogenation during heating of the hydrogen-lean indole, as well as the hydrogen-rich indoline and octahydroindole on Pt(111). For all three molecules, we find deprotonation of the NH bond above 270 K. For the hydrogen-rich carrier molecules indoline and octahydroindole we find that this deprotonation is accompanied by dehydrogenation via an indole intermediate, resulting in an indolide species above 300 K. For octahydroindole, we also find a side reaction yielding small amounts of a π -allyl species between 170 and 450 K. Above 450 K, decomposition of the remaining indolide species takes place.[1]

[1] M. Schwarz, P. Bachmann et al., Chem. Eur. J., 2017, 23, 14806-14818.

O 78.14 Wed 18:15 Poster A

Observing oxide surface reactivity at high temperatures: FastSTM on Fe₃O₄(001) — •ALEXANDER BOURGUND, BARBARA A. J. LECHNER, UELI HEIZ, and FRIEDRICH ESCH — Department of Chemistry & Catalysis Research Center, Technical University of Munich, Lichtenbergstr. 4, D-85748 Garching

Magnetite as a highly abundant oxide material shows a rich surface chemistry and is a well-known support for nanoparticles in catalysis [1]. While its surface dynamics have been studied extensively with con-

ventional Scanning Tunneling Microscopy (STM) and other techniques [1-3], little is known about these surface processes at the atomic scale when studied at elevated temperatures, with the required high temporal resolution. We present results on magnetite Fe₃O₄(001) surface dynamics taken with a specially developed FastSTM add-on module [4] that boosts the temporal resolution of our commercial STM up to 12 frames/s. In particular, we resolve subsurface diffusion of iron atoms and their exchange with the bulk at temperatures up to 800 K and provide additional insight into the high-temperature transition [3]. Furthermore, we observe surface etching under reducing or wet conditions, as well as growth in an oxygen atmosphere. The reactivity of the surface can be enhanced by deposition of Pt₁₀ clusters that lower the reaction onset temperature.

References: [1] G. S. Parkinson, *Surf. Sci. Rep.* 2016, 71, 272. [2] R. Bliem et al., *Angew. Chem. Int. Ed.* 2015, 54, 13999. [3] N. C. Bartelt et al., *Phys. Rev. B* 2013, 88. [4] F. Esch et al., *Rev. Sci. Instrum.* 2011, 82, 53702 and NFFA project JRA1.

O 78.15 Wed 18:15 Poster A

Analysis and interpretation of TPD measurements of organic molecules — •KAROLINA STOIBER, PETER DEIMEL, JULIAN LLOYD, FRANCESCO ALEGRETTI, JOACHIM REICHERT, HARTMUT SCHLICHTING, and JOHANNES V. BARTH — Physics Department, Technical University of Munich, James-Frank-Straße 1, 85748 Garching, Germany

In surface science, thermal programmed desorption (TPD) is one of the most traditional measuring techniques for the investigation of adsorbed species. Typically, a well-defined substrate covered with the molecules under investigation is heated up with a constant heating rate. Depending on kinetic parameters and the arrangement on the surface, desorption occurs at distinct temperatures with characteristic rates, until the substrate is depleted. Moreover, the interpretation of TPD spectra requires additional information gathered from methods like scanning tunnelling microscopy (STM). We realized a setup consisting of a TPD chamber flanged to a STM unit and a controlled ion beam deposition (CIBD) system to investigate large functional molecules and their assemblies on clean substrates. The TPD chamber provides a STM-compatible sample holder which can be cooled down to liquid nitrogen temperatures and heated up to some 1500 K for measuring. A quadrupole mass spectrometer, with a Feulner cup enhancing the desorbing flux of molecules, monitors the desorption rate. Together with the recorded temperature, binding energies and preexponentials of bisphenol A and diethylstilbestrol on Cu(111) are extracted and the TPD spectra are simulated with analytical and Monte Carlo methods.