

## O 82: Fundamentals of Catalysis II

Time: Thursday 15:00–17:45

Location: H5

O 82.1 Thu 15:00 H5

**Embedding of cluster superlattices to prevent sintering** — ●TOBIAS HARTL, MORITZ WILL, PANTELIS BAMPOULIS, and THOMAS MICHELY — II. Physikalisches Institut, Universität zu Köln

Deposition of a metal, for example Ir, Pt, or W, on the moiré of Gr on Ir(111) leads to a well-ordered cluster superlattice [1]. These clusters are tunable in size, from a few up to hundreds of atoms each, and are of interest for catalysis due to their size dependent properties. However, their use is limited by their low thermal stability against sintering, which for the system under concern takes place by cluster diffusion and coalescence (Smoluchowski ripening) and starts around 500 K. Sintering destroys cluster order, broadens the size distribution and greatly reduces the cluster number density.

Here we explore embedding of an Ir cluster superlattice on Gr/Ir(111) into a matrix of elemental carbon. With increasing deposited amount of carbon, a conformal carbon coverage of the metal clusters establishes. As evidenced by scanning tunnelling microscopy, the embedding process does not affect the order of the cluster superlattice. Most important, sintering of the clusters by Smoluchowski ripening is suppressed up to the highest investigated temperatures of 1350 K.

[1] N'Diaye, AT. et al., *New Journal of Physics*, 2009

O 82.2 Thu 15:15 H5

**Graphene-coating of Platinum nanoparticles** — ●MARTHA SCHEFFLER, GEORGIOS PANTAZIDIS, and LIV HORNEKAER — Department of Physics and Astronomy, Aarhus University, Denmark

Despite the great potential that has been reported for core-shell metal-metal nanoparticles in catalytic processes and biomedical applications, similar reports on graphene-coated nanoparticles are lacking. Graphene coatings prevent nanoparticles from sintering, increase the temperature stability, and can prevent corrosive species from blocking the catalytically active sites. For some single crystal systems, graphene coatings have been shown to have beneficial effects, improving reaction efficiency.

We will present our measurements on graphene-coated Platinum nanoparticles. We synthesized Pt nanoparticles of tens of nm in diameter under UHV conditions using an HOPG support. Via chemical vapor deposition using ethylene, we produced a graphene coating on these nanoparticles that is tested on its catalytic and reactive properties. We use scanning tunneling microscopy to describe the shape and size of the nanoparticles as well as the topography of the graphene layer.

O 82.3 Thu 15:30 H5

**Dehydrogenation of Liquid Organic Hydrogen Carriers on Supported Pd Model Catalysts: Carbon Incorporation under Operation Conditions** — ●RALF SCHUSTER<sup>1</sup>, FABIAN WAIDHAS<sup>1</sup>, MANON BERTRAM<sup>1</sup>, HENNING RUNGE<sup>2</sup>, SIMON GEILE<sup>2</sup>, SIMON CHUNG<sup>2</sup>, VEDRAN VONK<sup>2</sup>, HESHMAT NOEI<sup>2</sup>, YAROSLAVA LYKACH<sup>1</sup>, FLORIAN BERTRAM<sup>2</sup>, ANDREAS STIERLE<sup>2</sup>, and JÖRG LIBUDA<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, D-22607 Hamburg

Hydrogen and carbon, formed during the dehydrogenation and unselective decomposition of liquid organic hydrogen carriers (LOHCs) under reaction conditions, may diffuse into the bulk of the catalyst and, thus, change its activity and selectivity. We studied the influence of hydrogen and carbon on a sapphire-supported Pd nanoparticle (NP) model catalyst under reaction conditions (500 K, 1 bar) by high-energy grazing incidence X-ray diffraction. In pure H<sub>2</sub> at 300 K, the Pd NPs show a continuous transition from the  $\alpha$ -PdH to  $\beta$ -PdH phase with increasing H<sub>2</sub> partial pressures, while the miscibility gap is narrowed in comparison to bulk Pd. With increasing temperature, the hydrogen uptake decreases and at 500 K, no hydride phase is formed. Surface carbon, formed by decomposition of the LOHC at 500 K, diffuses into the NP bulk. Our studies show that this formation of bulk carbon is efficiently suppressed in the presence of H<sub>2</sub>. This highlights the importance of controlling the partial pressure of H<sub>2</sub> during dehydrogenation of LOHCs over Pd-based catalysts in real hydrogen release units.

O 82.4 Thu 15:45 H5

**Spectroscopic Insights to Liquid Rh-Ga Alloys for Effective Propane Dehydrogenation** — ●HAIKO WITTKÄMPER, NARAYANAN RAMAN, MATHIAS GRABAU, SVEN MAISEL, NICOLA TACCARDI, JONAS DEBUSCHEWITZ, TANJA BAUER, MINGJIAN WU, MARCO HAUMANN, ANDREAS GÖRLING, ERDMANN SPIECKER, JÖRG LIBUDA, PETER WASSERSCHIED, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)

We present a study of Rhodium as active metal for selective alkane dehydrogenation. It becomes a very active, selective and stable propane dehydrogenation catalyst when incorporated in a matrix of liquid gallium on oxidic support particles. The remarkable properties of this catalyst are attested to the atomic dispersion of the active transition metal in liquid gallium nano-droplets, which is indicated by temperature dependent HRTEM. The observed temperature-dependence of the selectivity of the catalyst is due to the dissolution/precipitation of Rh-rich intermetallic phases, leading to the Rh enrichment/depletion of the liquid Ga phase as is demonstrated by temperature dependent XPS studies of Rh-Ga alloy model systems. Based on ab initio molecular dynamics simulations and density functional calculations of a possible reaction site a mechanism for the system is proposed that goes in line with what we previously proposed for similar supported catalytically active liquid metal solutions such as Pt-Ga and Pd-Ga.

O 82.5 Thu 16:00 H5

**Supported catalytically active liquid metal solutions: Preparation and characterization of Pd-Ga and Pt-Ga model systems on modified HOPG** — ●MIROSLAV KETTNER<sup>1</sup>, SVEN MAISEL<sup>2</sup>, CORINNA STUMM<sup>1</sup>, MATTHIAS SCHWARZ<sup>1</sup>, CHRISTIAN SCHUSCHKE<sup>1</sup>, ANDREAS GÖRLING<sup>2</sup>, and JÖRG LIBUDA<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, FAU Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany — <sup>2</sup>Lehrstuhl für Theoretische Chemie, FAU Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen, Germany

Single atom catalysts merge attractive properties of homogeneous and heterogeneous catalysts, such as atomically defined active sites, high selectivity, and high metal utilization. Recently, the concept of supported catalytically active liquid metal solutions (SCALMS) proved effective in creating such isolated active sites by diluting an active metal in a low melting point metallic matrix. To explore the properties of such systems under surface science conditions, we have prepared model systems for Pd-Ga and Pt-Ga SCALMS by physical vapor deposition of Pd/Pt and Ga in ultrahigh vacuum onto highly oriented pyrolytic graphite (HOPG) pre-modified by Ar<sup>+</sup> bombardment. We investigated the growth behavior, the morphology, the surface chemistry, and the stability of Pd-Ga and Pt-Ga alloys on HOPG by combining AFM and IRAS experiments with DFT calculations. The results prove the single atom character of the active sites in Ga-rich alloys. Thus, the Ga-rich nanoalloy systems prepared on modified HOPG present a well-suited model to study the adsorption and reaction on SCALMS by surface science methods.

O 82.6 Thu 16:15 H5

**Atomic oxidation of supported CoTPP films** — ●JAKOB HAUNS, ARTUR BÖTTCHER, and MANFRED M. KAPPES — Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

Thin Co-Tetraphenylporphyrin films, CoTPP, were grown on HOPG under UHV conditions by applying the low-energy cluster beam deposition technique (LECBD, [1]). The oxidation has been performed by exposing the films kept at room temperature to a beam of nearly-thermal oxygen atoms at a constant flux. UPS based analysis of the valence band revealed a gradual quenching of the HOMO state ( $E_B \sim 1.8$  eV). The oxygen conditioned evolution of all relevant CoTPP core states supported by DFT calculations of the most stable oxides enables to follow the oxidation pathways. The sublimation of the oxidized CoTPP films has been studied by monitoring the mass spectra of the volatile species during heating the sample (MSTDS, [1]). The emission of oxidized multilayers proceeds within a broad temperature interval (450–850K). It is dominated by a series of CoTPP-O<sub>n</sub> oxides ( $0 \leq n \leq 5$ ) which implies that an intact CoTPP is capable to adopt up to five oxygen atoms. In contrast, the sublimation of a CoTPP monolayer deposited on preoxidized HOPG gives rise to a completely different product spectrum indicating that the substrate uniquely participates

in the reaction.

[1] J. Weippert, et al. *J. Phys. Chem. C* DOI:10.1021/acs.jpcc.8b01655

O 82.7 Thu 16:30 H5

**Defect dependent adsorption of tungsten oxide clusters on rutile TiO<sub>2</sub> surfaces for model (photo-)catalysis** — ●LARS MOHRHUSEN, MAXIMILIAN GREBIEN, and KATHARINA AL-SHAMERY — Carl von Ossietzky University of Oldenburg, Institute of Chemistry, Oldenburg, Germany

Rutile TiO<sub>2</sub> is one of the most intensively studied materials for heterogeneous thermal and photoinduced catalysis. In earlier publications, the importance of bulk and surface defects for the chemical reactivity of small molecules such as oxygen,<sup>[1]</sup> methanol<sup>[2]</sup> or benzaldehyde<sup>[3]</sup> has been demonstrated. In temperature programmed reaction spectroscopy (TPRS) and infrared reflection-absorption spectroscopy (IR-RAS), different reaction pathways such as the reductive coupling, deoxygenation to hydrocarbons and partial oxidation were significantly dependent on the defect density as well as the presence of different oxygen species.

The deposition of (oxidic) cocatalysts<sup>[4,5]</sup> is a common approach to address the (photo-)catalytic performance. However, a detailed understanding is often missing. Here, we present systematic studies on rutile TiO<sub>2</sub> (110) under well-defined ultra-high vacuum conditions illustrating the deposition of tungsten oxide clusters to control the defect density dependent adsorption and reactivity of small molecules.

[1] E. Lira et al., *J. Am. Chem. Soc.* 2011, 133, 6529. [2] M. Osmić et al., *J. Phys. Chem. C* 2018, DOI: 10.1021/acs.jpcc.8b02953 [3] P. Clawin et al., *Chem. Eur. J* 2014, 25, 7665. [4] C. Pang et al., *Chem. Rev.* 2013, 113, 3887 [5] J. Kim et al., *Catal. Today* 2007, 120, 186.

O 82.8 Thu 16:45 H5

**Adsorption and Interfacial Reactions of 2H-Tetraphenylporphyrin on Cobalt Oxide Thin Films** — ●DANIEL WECHSLER<sup>1</sup>, CYNTHIA FERNÁNDEZ<sup>2</sup>, QURATULAIN TARIQ<sup>1</sup>, NATALIYA TSUD<sup>3</sup>, KEVIN PRINCE<sup>3,4</sup>, FEDERICO WILLIAMS<sup>2</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, and OLE LYTKEN<sup>1</sup> — <sup>1</sup>Chair of Physical Chemistry II, University Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany — <sup>2</sup>Department of Inorganic, Analytical and Physical Chemistry, University of Buenos Aires, Buenos Aires C1428EHA, Argentina — <sup>3</sup>Eletra-Sincrotrone Trieste S.C.p.A., Strada Statale 14, km 163.5, 34149 Basovizza-Trieste, Italy — <sup>4</sup>IOM, Strada Statale 14, km 163.5, 34149 Basovizza-Trieste, Italy

Understanding the interactions between organic molecules and metal-oxide surfaces plays an important role in many nanotechnology devices.

We have studied the adsorption and interfacial reactions of 2H-tetraphenylporphyrin (2HTPP) with synchrotron-radiation X-ray photoelectron spectroscopy on cobalt- and oxygen-terminated Co<sub>3</sub>O<sub>4</sub> and CoO cobalt-oxide thin films. Already at 175 K, we find evidence for the formation of a metalated species, most likely CoTPP, on both surfaces. The degree of metalation increases with temperature on both surfaces until 575 K, at which point desorption is observed from the reducible cobalt-terminated Co<sub>3</sub>O<sub>4</sub> oxide, while decomposition is observed on the non-reducible oxygen-terminated CoO oxide.

The project is supported by the DFG trough FOR 1878 (funCOS).

O 82.9 Thu 17:00 H5

**Artificial Leaf, catalysis of oxygen evolution with the doping of hematite** — ●HUU CHUONG NGUYỄN<sup>1</sup>, FELIPE ANDRÉS

GARCÉS-PINEDA<sup>1</sup>, MABEL DE FEZ FEBRÉ<sup>1</sup>, JOSÉ RAMÓN GALÁN-MASCARÓS<sup>1,2</sup>, and NÚRIA LÓPEZ<sup>1</sup> — <sup>1</sup>Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona (Spain) — <sup>2</sup>Catalan Institution for Research and Advanced Studies (ICREA), Passeig Lluís Companys, 23, Barcelona 08010, Spain

A-LEAF is a project of the European Commission for developing an efficient and economically viable photoelectrocatalytic cell (PEC). The goal is to recycle CO<sub>2</sub> to fuel like an artificial leaf. The two most important reactions in a PEC are CO<sub>2</sub> reduction and oxygen evolution reaction (OER). These processes are energetically costly and but can be improved with catalysis. There are several possible strategies for optimisations. One of them is by doping a material to reduce the energy barrier and improve the kinetics. In this talk, we will present the general framework of A-LEAF, the basic concepts and theory of catalysis, Density Functional Theory, CO<sub>2</sub> reduction and oxygen evolution with a practical example; the doping of hematite as a model catalyst for the OER. Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) is a non-toxic, cheap and abundant material. Doped with redox or non-redox active species, it presents very different performances and catalytic pathways. Using both experimental and theoretical techniques, we will show how doping with non-redox and redox dopants differs, how Proton-Coupled-Electron-Transfer is involved and how this affects the global catalytic performance.

O 82.10 Thu 17:15 H5

**Near-Surface Doping of Rutile RuO<sub>2</sub> for Optimizing the Oxygen Evolution Reaction** — ●MANUEL J. KOLB<sup>1,2</sup> and FRANK ABILD-PEDERSEN<sup>1,2</sup> — <sup>1</sup>SLAC National Laboratory, Stanford, USA — <sup>2</sup>Stanford University, Stanford, USA

The electrochemical oxygen evolution reaction plays a fundamental role in the current limitations to the efficiency and viability of hydrogen-oxygen-based fuel cells. Recent experimental and theoretical work [1,2] on the pre-oxygen-evolution region of the RuO<sub>2</sub>(110) voltammogram found evidence for the existence of stable dioxygen species, in contrast to earlier theoretical calculations [3]. Based on this new information we investigated the possibilities of doping RuO<sub>2</sub>(110) with a variety of metal dopant atoms and their influence on the adsorption energies of these oxygen-related species.

[1] R. Rao et al, *Energy & Environmental Science*, 2017, 10, 2626-2637 [2] K. Stoerzinger et al, *ACS Energy Lett.*, 2017, 2(4), 879-881 [3] I. Man et al, *ChemCatChem*, 2011, 3, 1159-1165

O 82.11 Thu 17:30 H5

**Electrical and Protonic Conductivity of Surface Modified Porous Yttria-Stabilized Zirconia (YSZ) Thin Films** — ●ERDOGAN CELIK and MATTHIAS T. ELM — Center for Materials Research, Justus-Liebig-University Gießen, Germany, Heinrich-Buff-Ring 16, 35392 Gießen

Porous yttria-stabilized zirconia (YSZ) thin films were prepared using pulsed laser deposition in order to investigate the influence of the high surface area on the electrical transport properties. Electrochemical impedance spectroscopy was carried out as a function of temperature, oxygen activity and humidity of the surrounding atmosphere. At high humidity protons on the surface of the porous YSZ thin films lead to an increased conductivity, especially at low temperatures. By coating the porous YSZ films with a titania (TiO<sub>2</sub>) film of only a few nanometers, the protonic contribution to the conductivity at low temperatures is completely suppressed revealing the large influence of the surface on the transport properties of porous materials.