

## O 93: Heterogeneous Catalysis: Experiment

Time: Thursday 15:00–17:00

Location: TRE Phy

## Invited Talk

O 93.1 Thu 15:00 TRE Phy  
**Oxygen and Oxide Cluster Functionalized Graphene for Model Catalytic Studies** — ●ZDENEK DOHNALEK — Pacific Northwest National Laboratory, Richland, WA, USA

Well-defined, monodispersed catalysts supported on oxidized carbon nanotubes and nanosheets are a promising class of new materials for heterogeneous catalysis. We have chosen graphene (Gr) supported on Ru(0001) as a surface science model and employed scanning tunneling microscopy to investigate its functionalization with oxygen atoms (AOs) and ceria and titania nanoclusters. On Ru(0001), Gr forms a Moiré structure with a periodicity of 3 nm with three distinct regions: C ring atop Ru, on HCP and FCC. At room temperature, AOs are found preferentially within the FCC regions. At 400 - 500 K, the AOs move primarily within the FCC regions or away from the metastable HCP regions. The high-resolution time-lapse data is used to assign the AO adsorption configuration to the on-top terminally-bound groups rather than the expected bridge-bonded epoxy species. For ceria and titania nanoclusters we find that they are anchored at the intrinsic defects in Gr. The thermal evolution of the cluster size distribution suggests that the sintering proceeds via diffusion and aggregation of entire clusters. To follow the cluster redox properties we examined their oxygen storage and release in an oxygen atmosphere at elevated temperature (550 - 700 K). Under oxidizing conditions, oxygen intercalation under the Gr layer is observed for ceria but not titania. Time-dependent studies demonstrate that the intercalation starts in the vicinity of the ceria clusters and extends until a completely intercalated layer is observed.

## Invited Talk

O 93.2 Thu 15:30 TRE Phy  
**Oxide model interfaces from ultrahigh vacuum conditions to liquid environments** — ●JÖRG LIBUDA — Friedrich-Alexander-Universität Erlangen-Nürnberg

Oxide-based hybrid interfaces are at the heart of many functional materials: Organic films on oxides find applications in molecular electronics and solar energy conversion; metal nanoparticles on oxides are used in heterogeneous catalysis and electrocatalysis. Studies on atomically-defined model hybrid interfaces can provide detailed insights into their chemical and physical functionalities.

Model electrocatalyst are prepared by deposition of active metals on ordered oxide films. Surface science studies of such systems in UHV provide a detailed understanding of electronic metal-support interactions, reaction mechanisms and catalytic activities. Recently, we showed that UHV-born model systems may preserve their atomic structure when used as electrocatalysts in liquid environments. This allows us to explore electrocatalytic reactions at complex atomically-defined model interfaces.

Model organic-oxide hybrid interfaces are prepared by anchoring of organic molecules, e.g. porphyrines, on ordered oxide surfaces. Exemplifying anchoring reactions with carboxylates, we explore the molecular orientation, metalation and the formation kinetics. Strong structure dependencies are observed for the film stability which are rationalized on the basis of the cation arrangement at the surface. Finally, we discuss the role of water and hydroxyl groups in molecular anchoring, both under UHV conditions and in liquid environments.

O 93.3 Thu 16:00 TRE Phy  
**In operando study on MnOx thin films during electrocatalytic water oxidation using soft x-ray absorption and emission spectroscopy** — ●MARYAM N. SHAKER<sup>1,2</sup>, MARC F. TESCH<sup>1</sup>, SHANNON A. BONKE<sup>3</sup>, ALEXANDR SIMONOV<sup>3</sup>, LEONE SPICCIA<sup>3</sup>, and EMAD F. AZIZ<sup>1,2</sup> — <sup>1</sup>Helmholtz Zentrum Berlin — <sup>2</sup>Freie Universität Berlin — <sup>3</sup>School of Chemistry, Monash University, Clayton, VIC, 3800, Australia

Manganese oxides (MnOx) are promising candidates to act as catalysts for the water oxidation half reaction, which is mandatory to produce hydrogen from water. To systematically understand what drives the catalytic efficiency of MnOx a comprehensive knowledge about its electronic structure is necessary. A powerful tool to study the electronic structure of transitions metal oxides is soft X-ray spectroscopy. However, such studies are usually restricted to ex situ measurements unable to unambiguously identify structural and electronic changes of the material occurring at working conditions, i.e. applying a potential.

Here, we present an in operando study using X-ray absorption spectroscopy (XAS) and resonant inelastic X-ray scattering (RIXS) at the Mn L-edge of electrodeposited MnOx films while applying potentials in a systematic fashion. Clear, potential dependent spectral changes related to variations in the Mn oxidation state were observed. The XAS spectra taken in operando are compared to ex situ XAS measurements and will be discussed with respect to in operando RIXS measurements revealing distinct changes in the structure of the occupied valence state, which play a key role for all catalytic reactions.

O 93.4 Thu 16:15 TRE Phy  
**Reactivity of quasi one-dimensional CoO<sub>2</sub> nanostructures on Ir(100)** — PASCAL FERSTL<sup>1</sup>, M. ALIF ARMAN<sup>2</sup>, JAN KNUDSEN<sup>2</sup>, EDVIN LUNDGREN<sup>2</sup>, LUTZ HAMMER<sup>1</sup>, and ●M. ALEXANDER SCHNEIDER<sup>1</sup> — <sup>1</sup>Lst. f. Festkörperphysik, FAU Erlangen-Nürnberg, Germany — <sup>2</sup>Division of Synchrotron Radiation Research, Lund University, Sweden

In this study we analyze the catalytic properties of quasi one-dimensional CoO<sub>2</sub> nanostructures grown on the Ir(100) surface [1], exemplified by the oxidation of hydrogen and CO. Due to the long range order of the system before and after the reactions it was possible to quantify the structural changes by means of full dynamical LEED analyses. Combining this detailed structural information with data obtained by HR-XPS, STM and TDS we were able to follow the processes during the reactions in situ on the atomic scale.

We thus identified the relevant species during the different stages of the two oxidation reactions. Further the observed structural changes hint at the importance of defects like grain boundaries for the reaction kinetics. In summary, the cobalt oxide nanostructures enable both reactions at temperatures lowered by 150 K – 200 K compared to the oxygen covered Ir(100)-(2×1)O surface [2] and therefore show high catalytic activity.

[1] P. Ferstl, et al., Phys. Rev. Lett. **117**, 046101 (2016); [2] P. Ferstl, et al., Phys. Rev. B **93**, 235406 (2016)

O 93.5 Thu 16:30 TRE Phy  
**Strong Metal-Support Interaction and Catalytic Edge-Effects for Controlling Electrical Transport Edge-Effects in Nanowires** — ●ALEX LORD<sup>1</sup>, PHILIP DAVIES<sup>2</sup>, JON EVANS<sup>1</sup>, and STEVE WILKS<sup>1</sup> — <sup>1</sup>Centre for Nanohealth, Institute of Life Sciences 2, Singleton Campus, Swansea University, Singleton Park, Swansea SA2 8PP, UK — <sup>2</sup>Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT, United Kingdom

Semiconductor nanowires grown by techniques catalyzed with metal nanoparticles present a bottom-up solution for new technological devices. Here, I will discuss a strong metal-support interaction (SMSI) that encapsulates the Au growth particle adding material to the edge-region of the interface between the catalyst and the ZnO nanowire. The electron microscopy evidence shows the process occurs at room temperature over a long time period and in ambient benign conditions. It is shown by directly correlating atomic-resolution electron microscopy to electrical transport measurements that the nature of the SMSI-diffused ZnO material at the interface edge creates a channel affecting the quantum-mechanical tunneling electron-transport. The results are confirmed by using the enhanced catalytic activity of the Au-ZnO interface edge to etch away the ZnO at the edge-region undercutting the metal nanoparticle. The microscopy analysis and transport measurements show this removes the support edge-region and eliminates the quantum-mechanical tunneling path. This work correlates catalytic edge-effects with electrical transport edge-effects found in metal-semiconductor electrical contacts.

O 93.6 Thu 16:45 TRE Phy  
**Electronic properties of Au nanoparticles on CeO<sub>2</sub> in the water-gas shift (WGS) reaction using operando X-ray absorption spectroscopy** — ●JOACHIM BANSMANN, GABRIELA KUCEROVA, ALI ABDEL-MAGEED, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Small Au nanoparticles (NPs) on ceria surfaces are important catalysts in the CO oxidation and water-gas shift (WGS) reaction. The activity and deactivation during time on stream (TOS) of those catalysts strongly depends on the nature (oxidic and/or reductive) of

pre-treatments. Here, we will concentrate on the oxidation state and the size of the Au nanoparticles after different pretreatments and during reaction using ex-situ characterization techniques (e.g. XPS) as well as operando methods such as XANES/EXAFS and diffuse IR spectroscopy (DRIFTS). Reductive pretreatments lead to metallic Au particles, whereas oxidic pretreatments results in partially oxidized Au NPs (depending on the temperature).

Employing operando X-ray absorption spectroscopy, we followed the

changes in chemical state and size of the Au particle during the water-gas shift reaction at 180°C. The results are discussed in comparison with the activity and deactivation of these catalysts considering also effects such as blocking of active sites by formation of carbonates and formates. Finally, we compare our findings with results obtained in the CO oxidation [1] using similar Au/CeO<sub>2</sub> catalysts.

[1] A. Abd El-Moemen et al., J. Catal. 341 (2016) 160