

## O 40: Poster Tuesday: Adsorption and Catalysis

Time: Tuesday 18:00–20:00

Location: Poster D

O 40.1 Tue 18:00 Poster D

**Wetting Properties of Electrochemically Active Polycrystalline CuFeO<sub>2</sub>, CuMO<sub>2</sub> and CuFexM<sub>1-x</sub>O<sub>2</sub> Delafossite Porous Surfaces** — ROBERT A. WHEATLEY, MARTIN ROBLE, SEBASTIAN MOLINA, ●DIEGO DIAZ, SUSANA D. ROJAS, BIRGER SEIFERT, SASCHA WALLENTOWITZ, DONOVAN E. DIAZ-DROGUETT, and ULRICH G. VOLKMANN — Institute of Physics and CIEN-UC, Pontificia Universidad Catolica de Chile, Av. Vicuna Mackenna 4860, Santiago, Chile

Delafossite type ternary oxides are considered favorable catalytic/photo-catalytic materials for a range of chemical reactions. For water-based reactions, hydroxylation, a process connected to the wettability of the surface, can greatly influence catalytic activity of a metal oxide. We investigate the wetting properties of CuFeO<sub>2</sub>, CuAlO<sub>2</sub>, CuGaO<sub>2</sub> and composite CuFexM<sub>1-x</sub>O<sub>2</sub> Delafossite oxides synthesized using hydrothermal and solid state methods. The materials display significant variance in wetting properties, from highly hydrophobic CuFeO<sub>2</sub> as-grown powder, to complete wetting for porous cold-pressed pellets. After annealing treatments at relatively low temperatures  $T > 300$  degree C the surfaces displayed permanent superhydrophilicity and a rapid absorption of H<sub>2</sub>O droplets via intergranular porosity. Acknowledgements: CONICYT Fellowship (MR) and Anillo CONICYT-PIA ACT 1409.

O 40.2 Tue 18:00 Poster D

**Adsorption of Hydrogen Atoms on Aluminiumoxide** — ●MARTIN LIEBETRAU and JÖRG BEHLER — Universität Göttingen, Institut für Physikalische Chemie, Theoretische Chemie, Tammannstraße 6, 37077 Göttingen, Germany

The adsorption of atomic hydrogen is important in many fields, from heterogeneous catalysis and hydrogen storage to interstellar hydrogen on dust grains and nuclear fusion. Here, we report molecular dynamics simulations of high-energy hydrogen atom scattering at  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Employing a high-dimensional neural network potential, which allows us to include the full-dimensional thermal motion of the surface atoms, we are able to calculate a large number of trajectories with the accuracy of density-functional theory. Probing different kinetic energies and incident angles, we are able to characterize the interaction with the surface in detail.

O 40.3 Tue 18:00 Poster D

**Water splitting reactions at clean and water adsorbed lithium niobate surfaces** — ●CHRISTOF DUES<sup>1</sup>, WOLF GERO SCHMIDT<sup>2</sup>, and SIMONE SANNA<sup>1</sup> — <sup>1</sup>Institut für Theoretische Physik, Justus-Liebig-Universität Gießen, Heinrich-Buff-Ring 16, 35392 Gießen, Germany — <sup>2</sup>Department Physik, Universität Paderborn, Warburger Str. 100, 33098 Paderborn, Germany

Ferroelectric lithium niobate is a promising substrate for catalytic reactions. Yet, water splitting reactions aiming at hydrogen production are difficult to establish. Employing DFT and a simplified thermodynamic approach to calculate Gibbs energy differences, we present an efficient method to estimate the over-potentials related to the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) on both pristine LiNbO<sub>3</sub>(001) surfaces [1]. Our calculations show that the OER and HER over-potentials are lower on the negative (1.27 V) and positive (0.39 V) surface, respectively. The aqueous environment, simulated by water fragments adsorbed to the surface, changes the tendencies of the reactions: The OER over-potential becomes lower on the positive surface (1.07 V), and the HER over-potential at the negative surface (1.2 V).

[1] C. Dues, W. G. Schmidt and S. Sanna, *Water Splitting Reaction at Polar Lithium Niobate Surfaces*, submitted (2018).

O 40.4 Tue 18:00 Poster D

**Amorphous oxide surfaces and their reactivity towards water dissociation** — ●HANNAH SCHLOTT and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

Surface science studies on oxides mostly focus on the physical and chemical properties of single-crystal terminations. In nature, however, oxides are often amorphous and covered by hydroxyl groups and residual water. By using Car-Parrinello Molecular Dynamics (CPMD) and

a melt-quench procedure we have created a series of realistic amorphous oxide surface structures. A new technique has been applied which allows a direct preparation of amorphous surfaces without requiring a retrospective cleavage of the amorphous bulk. Simultaneously, other species, such as hydroxyl groups, can be incorporated seamlessly into the amorphous surfaces. The reliability of the method is demonstrated for the oxides ZnO, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. In a next step we analyzed the reactivity of the amorphous oxide surfaces towards water dissociation. For the example of amorphous ZnO we discuss typical water adsorption features and binding modes. Furthermore, we describe proton hopping events and chains of proton transfer reactions at the water/oxide interface.

O 40.5 Tue 18:00 Poster D

**Structure evolution of oxide-supported Pt nanoparticles under reaction conditions** — ●JUNJUN WANG, ALEXEI NEFEDOV, CHRISTOF WÖLL, and YUEMIN WANG — Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Noble metal nanoparticles (e.g. Pt) dispersed on oxide supports have attracted great interest due to their high catalytic activity for various chemical reactions. Despite extensive investigations, a thorough understanding of the structure-activity relationship remains still a major challenge. In this work, the structure evolution of oxide-supported Pt nanoparticles (NPs) under different conditions was monitored by temperature-dependent infrared (IR) spectroscopy using CO as a probe molecule in combination with grazing-emission XPS. For Pt/CeO<sub>2</sub> it was found that Pt NPs vary substantially in size and oxidation state depending on the reductive/oxidative conditions. The IR data together with high-resolution TEM results obtained for Pt/Al<sub>2</sub>O<sub>3</sub> catalysts revealed the presence of Pt particles/clusters with different shape and size ranging from isolated atoms to sub-nanometer clusters and ordered NPs. Our results allowed to gain deep insight into the structure evolution of various Pt species during the course of propane dehydrogenation reaction.

O 40.6 Tue 18:00 Poster D

**Lattice formation and binding of metal clusters to hexagonal boron nitride on Ir(111)** — ●MORITZ WILL<sup>1</sup>, NICOLAE ATODIRESEI<sup>2</sup>, VASILE CACIUC<sup>2</sup>, TOBIAS HARTL<sup>1</sup>, PANTELIS BAMPOULIS<sup>1</sup>, and THOMAS MICHELY<sup>1</sup> — <sup>1</sup>II. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany — <sup>2</sup>Peter Grünberg Institut (PGI) and Institute for Advanced Simulation (IAS), Forschungszentrum Jùlich and JARA, 52425 Jùlich, Germany

Moirés of two-dimensional materials on metal single crystal surfaces have a templating effect upon metal deposition from the gas phase, which can result in the formation of cluster superlattices. In particular, the moiré of hexagonal boron nitride (h-BN) on Ir(111) has been recently found to template Ir clusters into highly regular arrays with a thermal stability against sintering which far exceeds all other known substrates. [1]

Here we analyze the universality of the templating effect of h-BN/Ir(111) and compare the properties of other metal cluster arrangements to Ir clusters on h-BN/Ir(111). Scanning tunneling microscopy reveals cluster lattices of Pt can be grown with a number density per unit cell of  $n = 1$  at room temperature. Au cluster lattices reach  $n = 0.7$  for room temperature deposition, while for the case of Fe, deposition at 40 K enables superlattice formation with  $n = 0.7$ , stable at 300 K. Moreover, we analyze in detail for the case of Ir clusters the binding mechanism through selective hybridization of B and N atoms with the underlying substrate.

[1] Will, M., et al., ACS Nano (2018)

O 40.7 Tue 18:00 Poster D

**A microscopy approach to investigating the energetics of small supported metal clusters** — BARBARA A J LECHNER, FABIAN KNOLLER, ALEXANDER BOURGUND, ●SEBASTIAN KAISER, UELI HEIZ, and FRIEDRICH ESCH — Department of Chemistry & Catalysis Research Center, Technical University of Munich, Lichtenbergstr. 4, D-85748 Garching

We present examples of cluster dynamics observed via fast scanning tunneling microscopy (FastSTM). To that purpose, we have boosted the temporal resolution of our commercial STM up to 16 frames per

second with a specially developed add-on electronics module [1], allowing us to match the frame rate to surface dynamics observed at elevated temperatures. On the example of small Pd clusters supported on a hexagonal boron nitride nanomesh on Rh(111), we observed a range of different dynamics [2]. Cluster diffusion within a nanomesh pore changes with adsorbate size: While atoms diffuse along the rim of the pore, a small cluster experiences a corrugation in the potential energy landscape and jumps between six sites around the pore center. The difference can be explained by the additional internal degrees of freedoms of a cluster. Furthermore, we monitored the reversible switching between two structural isomers of Pd clusters in situ.

[1] F. Esch, C. Dri, A. Spessot, C. Africh, G. Cauero, D. Giuressi, R. Sergo, R. Tommasini, G. Comelli, *Rev. Sci. Instrum.* 2011, 82, 53702.

[2] B. A. J. Lechner, F. Knoller, A. Bourgund, U. Heiz, F. Esch, J. *Phys. Chem. C* 2018, 122, 22569.

O 40.8 Tue 18:00 Poster D

#### **In-Situ Magnesium Thin Film Nanoscale Hydrogenography**

— •JULIAN KARST, FLORIAN STERL, HEIKO LINNENBANK, MARIO HENTSCHEL, and HARALD GIESSEN — 4th Physics Institute and Research Center SCoPE, University of Stuttgart, Germany

During the hydrogenation of Magnesium (Mg), a phase change from the metallic Mg to dielectric magnesium hydride (MgH<sub>2</sub>) occurs, rendering it highly interesting for switchable optical systems. In such active systems, the nanoscale hydrogen diffusion mechanism is clearly of utmost importance, yet, so far, the details are not well understood.

To this end, we perform scattering-type scanning near-field optical microscopy to image the phase transition from Mg to MgH<sub>2</sub> on the nanometer scale in an in-situ environment. Additionally, we perform

nanoFTIR spectroscopy and identify a phonon resonance which aids in our experimental scheme. The resonance causes a very high material contrast between Mg and MgH<sub>2</sub> in 2D near-field scattering phase images.

Our results reveal that the phase transition is nucleated at grain boundaries. From these sites, the hydrogenation front progresses into the adjoining nanocrystallites. Most interestingly, the hydrogenation seems to saturate before the entire film is hydrogenated, leaving areas of metallic Mg within the dielectric MgH<sub>2</sub>. Our results constitute an important step forward in the understanding of the hydrogen loading process in Mg and are expected to help improving the diffusion kinetics as well as the efficiency of hydrogen storage in a variety of metals.

O 40.9 Tue 18:00 Poster D

#### **Methane clathrate hydrates study using molecular dynamics simulations** — •ANOOP KISHORE VATTI and LAXMAN KUMAR KUNDARAPU — Manipal Institute of Technology, Manipal, Karnataka, India

Gas clathrates are found copiously in permafrost region. In natural gas reservoirs or gas processing field, hydrates are formed by the chemical combination of the water and gas (precisely methane) at temperature above the freezing point of water. Gas clathrates are crystalline solids composed of water (ice) and gas (Methane/Ethane/Propane/CO<sub>2</sub>). The most common hydrate structure i.e. sI (structure I) is investigated. These cubic structure forms a combination of polyhedral cages (water) hosting the guest molecule (methane). We performed classical molecular dynamics (MD) simulations to understand the behaviour of gas hydrates using various water models (SPC/TIP3P/TIP4P) under extreme pressure. The structural properties and accuracy of the various water models be discussed.