O 59: Oxide and Insulator Interfaces II

Time: Wednesday 15:00–17:30 Location: MA 144

O 59.1 Wed 15:00 MA 144

Multitechnique characterization of rhodium single atoms on rutile TiO$_2$(110) — •Moritz Eder, David Rath, Jiri Pavelec, and Gareth S. Parkinson — Institute of Applied Physics, TU Wien, Vienna, Austria

Single-atom catalysis (SAC) has emerged as a prominent research topic in the last decade. The goal is to minimize the noble metal content on metal oxide surfaces by utilizing isolated atoms as active sites. A persistent challenge in the field is the characterization of these single atoms on the surface and showing that they are the dominant sites. Generally, there are few suitable analytical techniques for this on powder catalysts.

We will show a comprehensive surface science approach to the problem. Using isolated rhodium carbonyls on titania as an example, we characterize these single sites using x-ray photoelectron spectroscopy (XPS), temperature-programmed desorption (TPD), and a newly designed infrared reflection absorption spectroscopy (IRAS) apparatus to get the bigger picture. We compare the results to studies on powder catalysts in the literature and show that multitechnique approaches are imperative for characterizing single-atom catalysts.

O 59.2 Wed 15:15 MA 144

Crystal-facet-dependent surface transformation dictates the oxygen evolution reaction activity in lanthanum nickelate — •Achim Füngerlings[1], Marcus Wohlgemuth[2], Denis Antipin[3], Emma van der Minne[4], Ellen Marijn Kiens[4], Javier Villalobos[3], Marcel Risch[3], Felix Gunkel[2], Christoph Bäumer[4], and Rossitza Pentcheva[1] — [1]Department of Physics and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Duisburg, Germany — [2]Peter Gruenberg Institute and JARA-FIT, Forschungszentrum JuelichGmbH, Juelich, Germany — [3]Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany — [4]MESA+ Institute for Nanotechnology, Faculty of Science and Technology,University of Twente, Enschede, Netherlands

We present a combined experimental and theoretical study of the (001), (110) and (111) facets of LaNiO$_{3-\delta}$ electrocatalyst for water oxidation using electrochemical measurements, X-ray spectroscopy, and density functional theory calculations with a Hubbard U-term. We reveal that the (111) overpotential is $\approx 30-60$ mV lower than for the other facets. While a surface transformation into oxyhydroxide-like NiOO(H) may occur for all three orientations, it is more pronounced for (111). A structural mismatch of the transformed layer with the underlying perovskite for (001) and (110) influences the ratio of Ni^{2+} and Ni^{3+} to Ni^{4+} sites during the reaction and thereby the binding energy of reaction intermediates, resulting in the distinct catalytic activities of the transformed facets.

O 59.3 Wed 15:30 MA 144

How single water molecules adsorb on the calcite(104)-(2x1) surface — Jonas Heggemann[1], Yashasvi Ranawat[2], Jie Huang[2], Adam S. Foster[2], and •Philipp Rahe[1] — [1]Universität Osnabrück, Germany — [2]Aalto University, Finland

Calcite, the most stable polymorph of calcium carbonate and one of the most abundant minerals in the earth's crust, is critically involved in fluid-based dissolution-precipitation processes [1]. The hydrated (104) surface has intensively been studied [2], still, it was only very recently established that the pristine calcite(104) surface expresses a (2x1) reconstruction [3] that is lifted by water adsorption [4].

Here, we investigate the adsorption of single water molecules on calcite(104)-(2x1) by a combination of high-resolution atomic force microscopy (AFM) at 5K using CO-functionalised tips, density functional theory (DFT), and AFM image calculations. From DFT, we find two structurally similar but energetically different adsorption geometries. The excellent agreement between experimental and simulated AFM images confirms the presence of these two structures und unravels microscopic details of the water/calcite system. Our study clarifies the interaction of single water molecules with this most important mineral.

[1] A. Putnis, Rev. Min. & Geochem. 70, 87 (2009)

[2] P. Fenter et al., J. Phys. Chem. C 117, 5028 (2013)

[3] J. Heggemann et al., J. Phys. Chem. Lett. 14, 1983 (2023)

[4] J. Heggemann et al., Phys. Chem. Chem. Phys., Adv. Art. (DOI: 10.1039/d3cp01408h), (2023)

O 59.4 Wed 15:45 MA 144

Physisorption of a small aromatic hydrocarbon: Benzene on In$_2$O$_3$(111) — Andreas Ziegler[1], Matthias Preidl[2], Michael Schmid[2], Ulrike Diebold[2], Bernd Meyer[1], and •Margareta Wagner[2] — [1]FAU-Erlangen-Nürnberg, Germany — [2]TU Wien, Austria

In$_2$O$_3$ is a complex oxide material with a large unit cell and its (111) surface features different combinations of bulk-like and undercoordinated In and O atoms with 3-fold symmetry. Thus, small molecules can choose their adsorption site(s) from a variety of electronically and chemically different configurations.

In this work we study benzene, the smallest organic aromatic hydrocarbon, on bare and hydroxylated In$_2$O$_3$(111). We find that benzene adsorbs in the vicinity of a high-symmetry site of the surface lattice, with three molecules per unit cell in symmetry-equivalent sites. Hydroxylating the In$_2$O$_3$(111) surface blocks the preferred adsorption site of the benzene molecules. Still, one molecule can be accommodated in the less-favorable high-symmetry spot of the surface lattice, creating an array of well-spaced single benzene molecules. Both systems are studied with temperature programmed desorption (TPD) and noncontact atomic force microscopy (ncAFM); density functional theory (DFT) calculations and molecular dynamics (MD) simulations provide further insights into the adsorption and mobility of the molecules.

O 59.5 Wed 16:00 MA 144

Bare and Pd-doped ceria thin films prepared by ALD and EBE for hydrogen detection — •Yuliia Kosto[1], Paulina Kapuscik[2], Rudi Tschammer[1], Dominic Guttmann[1], Ewa Mankowska[2], Peter Matvija[3], Carlos Morales[1], Michal Mazur[2], Karsten Henkel[1], Iva Matolinova[3], Jaroslaw Domaradzki[2], and Jan Ingo Flege[1] — [1]BTU Cottbus-Senftenberg, Appl Phys & Semicond Spect, Cottbus, Germany — [2]Wroclaw Univ Sci & Technol, Fac Elect Photon & Microsyst, Wroclaw, Poland — [3]Charles Univ, Dept Surface & Plasma Sci, Prague , Czech

The need to store and use hydrogen safely as part of green economy based on renewable energy evokes a necessity to reliably detect it at ambient conditions. The majority of currently used sensors are working at elevated temperatures (200-500 °C). In this work, we demonstrate that ceria films deposited on a commercial electrode by atomic layer deposition (ALD) and electron beam evaporation (EBE) electrically respond to hydrogen (from 20 to 500 ppm) at much lower temperatures (50-200 °C). The results reveal that <1.5 nm thin Pd adlayer increases the electrical response by several orders of magnitude for both ceria films. The NAP-XPS study under changing oxidative/reductive atmospheres sheds light on the mechanism of Pd-CeOx thermal activation and the role of the deposition technique in the reactivity of the oxide.

O 59.6 Wed 16:15 MA 144

Infrared spectroscopic investigations of the interaction between formic acid and ceria surfaces — •Zairan Yu, Shuang Chen, Alexei Nefedov, Christof Wöll, and Yuemin Wang — Institute of Functional Interfaces(IFG),Karlsruhe Institute of Technology(KIT), Eggenstein-Leopoldshafen, 76344, Germany

Formic acid (HCOOH) as a simplest carboxylic acid with carboxylate functional group is involved in a wide variety of industrial processes. Ceria shows excellent catalytic activity in numerous reactions due to the unique redox properties and high oxygen storage capacity. Given the great complexity of nanostructured ceria catalysts, a surface science study based on well-controlled model systems is required to provide reliable and comprehensive reference data. In this work, we present a systematic IR study of the interaction between HCOOH and CeO2 surfaces of both single crystals and nanoparticles using a sophisticated UHV apparatus dedicated to IRRAS experiments at grazing incidence on monocrystals and FTIR transmission measurements for powders. The polarization-resolved IRRAS revealed that the dissociative adsorption of HCOOH occurs on both oxidized and reduced CeO2(111) surfaces, giving rise to formate species in different adsorption configurations. The reliable reference IRRAS data acquired for ceria single-crystal surfaces allowed us to unambiguously assign the IR bands observed on ceria powder samples. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation)-Project-ID 426888090-SFB 1441.

O 59.7 Wed 16:30 MA 144

Selective reduction of α-Fe$_2$O$_3$ (0001) by hydrogen adsorption and incorporation — •Muhammad Munawar and Rossitza Pentcheva — Department of Physics, University of Duisburg Essen, Germany.

The reduction of iron oxides using hydrogen as a reducing agent may be an alternative route towards the production of green steel. In this context, we perform DFT+U calculations to explore the initial adsorption and incorporation of hydrogen in the near surface region of hematite (0001). Starting with the Fe-O$_3$-Fe termination, which is stable in a wide range of oxygen chemical potentials, we vary the H concentration and distribution in the surface layers. The adsorption energy per H indicates that incorporation of H on the surface or in the near-surface region is favored, in contrast to incorporation in bulk hematite. H binds to an oxygen ion, while simultaneously an Fe^{3+} in the vicinity turns into Fe^{2+}, leading to a pronounced distortion of the lattice. The extent of localization of the donated electron depends on the layer where H is incorporated, suggesting a varying mobility of excess electrons. We find that the bandgap decreases with increasing hydrogen concentration at the surface, whereas a semiconductor-to-half metal transition is observed when H is incorporated in deeper layers.

Funding within IMPRS SUSMET and computational time at Leibniz Rechenzentrum are acknowledged

O 59.8 Wed 16:45 MA 144

Extended support structure dictates the reactivity of model single-atom catalysts for dissociative oxygen adsorption — •Faith J. Lewis, Ali Rafsanjani-Abbasi, Matthias Meier, Michael Schmid, Ulrike Diebold, and Gareth S. Parkinson — Institute of Applied Physics, TU Wien, Vienna, Austria

A goal of single-atom catalysis (SAC) is to find a support that stabilizes single metal adatoms in geometries that make them catalytically active.[1] For this to be possible, the adatoms must be able to change their coordination state by forming and breaking bonds. Iron oxides are popular supports used in SAC because of their low cost, chemical stability, and non-toxicity.[2] Given its ubiquity in catalysis, platinum is an attractive metal to be used in SAC.

I will discuss the similarities and differences between Pt adatoms on hematite, α-Fe$_2$O$_3$(012)-(1x1), and magnetite, Fe$_3$O$_4$(001). Scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) were used to characterize these surfaces and how Pt atoms bind to them. In both cases, Pt is 2-fold coordinated to lattice oxygen atoms, but the reactivity differs. Interestingly, we find that the second coordination sphere plays an important role defining the reactivity to molecular oxygen.

1. Kraushofer, F., Single Atom Catalysis: Insights from Model Systems, Chemical Reviews, 2022. 122, 18, 14911-14939.
2. Parkinson, G.S., Iron oxide surfaces. Surface Science Reports, 2016. 71(1): p. 272-365.

O 59.9 Wed 17:00 MA 144

Calculating core-level binding energies of small molecules on Fe$_3$O$_4$(111) — Pauline Schütt[1,2,3], Heshmat Noei[2], Wernfried Mayr-Schmölzer[1], Andreas Stierle[2,3], and •Gregor Vonbun-Feldbauer[1] — [1]Institute of Advanced Ceramics, TU Hamburg, Germany — [2]DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg, Germany — [3]Fachbereich Physik, Universität Hamburg, Germany

The identification of species adsorbed on surfaces, especially under reactive conditions, is crucial for a better understanding and subsequent optimization of processes in various applications ranging from heterogeneous catalysis to hybrid nanocomposites. Here, various small organic and inorganic carbon compounds adsorbed on a magnetite (111) surface are studied computationally using Density Functional Theory (DFT). These molecules on magnetite surfaces are highly relevant, for example, in Fischer-Tropsch synthesis. After geometry optimization and a stability analysis for selected molecules, the core-level binding energies of the oxygen and carbon atoms involved are calculated using different approximations within DFT. The different approaches are compared. The results are rationalized and connected with experimental X-ray photoemission spectra to support the identification of species.

O 59.10 Wed 17:15 MA 144

Surface Structure of Vicinal Magnetite and the Adsorption of Formic Acid — •Marcus Creutzburg[1], Heshmat Noei[1], Vedran Vonk[1], Wernfried Mayr-Schmölzer[2], Gregor Vonbun-Feldbauer[2], and Andreas Stierle[1,3] — [1]Centre for X-ray and Nano Science (CXNS), Deutsches Elektronen-Synchrotron DESY, Hamburg — [2]Institut für Keramische Hochleistungswerstoffe, Technische Universität Hamburg — [3]Fachbereich Physik, Universität Hamburg

The study of vicinal magnetite (Fe$_3$O$_4$) surfaces, with regularly ordered terraces and steps, and their interaction with carboxylic acids is one approach towards an atomic understanding of the oxide/organic interface in complex nanomaterials and active facets during catalytic reactions. In this contribution a (112)-oriented magnetite single crystal is studied using various experimental techniques complemented by DFT calculations. We can show using LEED and STM that this surface is stable after UHV preparation and presents (001)- and (111)-oriented nanosized terraces, confirmed by SXRD. Formic acid (HCOOH) is typically used as a probe molecule and as a representative for larger carboxylic acids. FT-IRRAS reveals that three different formate species are present on the surface after adsorption of formic acid: bidentate bridging on the (001) facets and chelating and quasi-bidentate on the (111) facets, similar to the respective planar surfaces [1,2]. Polarization-dependent FT-IRRAS reveals that the majority of formate is adsorbed across the step edges. [1] Arndt et al., Comm. Chem. 2(92) (2019) [2] Creutzburg et al., J. Phys. Chem. Lett. 12(15) (2021)