

## O 20: Oxides II: Structures, Interactions and Reducibility

Time: Monday 15:30–18:30

Location: WIL B321

O 20.1 Mon 15:30 WIL B321

**From UHV to ambient conditions: Water on  $\text{In}_2\text{O}_3(111)$**  — HAO CHEN<sup>1,2</sup>, MATTHIAS A. BLATNIK<sup>1</sup>, FRANCESCA MIRABELLA<sup>1</sup>, GIADA FRANCESCHI<sup>1</sup>, MICHELE RIVA<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, JAN ČEČHAL<sup>3</sup>, BERND MEYER<sup>4</sup>, ULRIKE DIEBOLD<sup>1</sup>, and •MARGARETA WAGNER<sup>1,3</sup> — <sup>1</sup>Inst. of Applied Physics, TU Wien, Wien, Austria — <sup>2</sup>State Key Laboratory of Catalysis, CAS, iChEM, Dalian Inst. of Chem. Phys., Chin. Acad. of Science, Dalian, China — <sup>3</sup>CEITEC, Brno University of Technology, Brno, Czech Republic — <sup>4</sup>ICMM/CCC FAU Erlangen-Nürnberg, Erlangen, Germany

We study the interaction of water with the  $\text{In}_2\text{O}_3(111)$  surface, employing surface science techniques (TPD, XPS, non-contact AFM and STM as well as DFT calculations). The adsorption is investigated as a function of coverage, i.e., from single water molecules to multilayers, in UHV, at pressures present in the ambient and as a liquid. The saturation coverage at 300 K in UHV is three dissociated molecules per unit cell, visible as propeller-shaped bright protrusions in STM. Their internal structure is revealed by nc-AFM, showing in total six objects: 3 OH groups sharing a surface oxygen and 3 residual hydroxyl groups; TPD shows 3 desorption peaks above 300 K resulting from different desorption barriers for the recombining water molecules. After the interaction with liquid water also molecular water species are found on  $\text{In}_2\text{O}_3(111)$ .

O 20.2 Mon 15:45 WIL B321

**Direct Assessment of the Proton Affinity of Individual Surface Hydroxyls with AFM and DFT** — •BERND MEYER<sup>1</sup>, MARGARETA WAGNER<sup>2</sup>, MARTIN SETVIN<sup>2</sup>, MICHAEL SCHMID<sup>2</sup>, and ULRIKE DIEBOLD<sup>2</sup> — <sup>1</sup>Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg, Germany — <sup>2</sup>Institute of Applied Physics, TU Wien, Austria

The state of protonation/deprotonation of individual surface sites has far-ranging implications in all areas of chemistry. However, common experimental measurements of surface acidity are integral techniques which give only average quantities integrated over the whole surface. Here we show that an OH-functionalized tip of an atomic force microscope (AFM) can be used for quantitative insights into the acidity of individual surface OH groups. The chosen model oxide,  $\text{In}_2\text{O}_3(111)$ , offers four types of surface O atoms with distinct properties, each giving rise to a characteristic force–distance curve after protonation. Density-functional theory (DFT) calculations demonstrate a linear correlation between the force minimum and the proton affinity of the surface hydroxyls. By benchmarking the calculations to known proton affinities and  $\text{p}K_a$  values of gas-phase molecules, the force minima provide a direct measure of proton affinity distributions and  $\text{p}K_a$  differences at the atomic scale.

## Invited Talk

O 20.3 Mon 16:00 WIL B321

**Polarons in oxide surfaces** — •CESARE FRANCHINI — University of Vienna & University of Bologna

In this talk I shall discuss recent advances in the modelling and simulation of polaron effects in transition metal oxide surfaces by first principles and machine learning approaches: polaron formation and mobility, polaron-induced surface reconstruction, polaron-adsorbates interaction and competition between localized and delocalized carriers in quantum paraelectrics.

arXiv:1902.04183 DOI: 10.1007/978-3-319-50257-1\_52-1

O 20.4 Mon 16:30 WIL B321

**$\text{ZrO}_{2-\delta}$  thin films: Oxygen-deficient, but not reduced** — PETER LACKNER, SABRINA MAYR, JOSEF REDINGER, ULRIKE DIEBOLD, and •MICHAEL SCHMID — Institute of Applied Physics, TU Wien, Vienna, Austria

Zirconia ( $\text{ZrO}_2$ ) has a wide range of applications, as an engineering material, in solid-state electrochemistry (gas sensors, solid oxide fuel cells), and as a catalyst support. We have studied thin films ( $\approx 5$  ML) sputter-deposited in ultrahigh vacuum on metal substrates [1]. As-deposited films are slightly oxygen-deficient, which leads to a pronounced core level shift in x-ray photoelectron spectroscopy (XPS). This is caused by positively charged oxygen vacancies ( $\text{V}_{\text{O}}^{\bullet\bullet}$ ) shifting the electrostatic potential [2]. The XPS results indicate a preference for vacancy formation near the interface, in agreement with density func-

tional theory (DFT) calculations. Full oxidation of the films is possible via oxygen spillover from a metal [2]. The positive  $\text{V}_{\text{O}}^{\bullet\bullet}$ s present in the vicinity of the metal support have much lower formation energies than neutral  $\text{V}_{\text{O}}$ s. Thus, oxygen-deficient films can form on a metal under conditions where bulk  $\text{ZrO}_2$  would remain stoichiometric. Due to charge transfer from the  $\text{V}_{\text{O}}^{\bullet\bullet}$ s to the substrate, Zr can retain its preferred 4+ charge state. In other words, the Zr in metal-supported, oxygen-deficient  $\text{ZrO}_{2-\delta}$  films is not reduced.

[1] P. Lackner et al., Surf. Sci. 679, 180 (2019).

[2] P. Lackner et al., Phys. Chem. Chem. Phys. 21, 17613 (2019).

O 20.5 Mon 16:45 WIL B321

**High temperature reduction and reoxidation of cerium oxide on Cu(111)** — •LINUS PLEINES<sup>1</sup>, LARS BUSS<sup>1,4</sup>, TEVFIK ONUR MENTES<sup>2</sup>, FRANCESCA GENUZIO<sup>2</sup>, ANDREA LOCATELLI<sup>2</sup>, JAN INGO FLEGE<sup>4</sup>, and JENS FALTA<sup>1,3</sup> — <sup>1</sup>Institute of Solid State Physics, University of Bremen, Germany — <sup>2</sup>ELLETRA Synchrotron Light Source, Basovizza, Italy — <sup>3</sup>MAPEX Center for Materials and Processes, Bremen, Germany — <sup>4</sup>Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Germany

Cerium oxide is of great interest due to its technological importance in various electronic, optical and catalytic applications. The inverse model catalyst cerium oxide on Cu(111) shows a high activity for the production of methanol. For the production of methanol from  $\text{CO}_2$  and  $\text{H}_2$  oxygen vacancies, e.g. in form of reduced ceria, are necessary. The reduction of ceria may be achieved by exposure to  $\text{H}_2$  at elevated temperatures. We studied the interaction of  $\text{H}_2$  and  $\text{CO}_2$  with cerium oxide islands on a Cu(111) substrate with low-energy electron microscopy (LEEM) and x-ray absorption spectroscopy (XAS). From earlier studies the orientation of the  $\text{CeO}_x$  is known to be decisive for the catalytic activity. In our experiments both orientations are directly compared via growth of (100) and (111)  $\text{CeO}_x$  islands side by side on the same metal substrate, so that the same conditions prevail during the experiment. At high temperatures, exposure to  $\text{H}_2$  leads to partial reduction and exposure to  $\text{CO}_2$  leads to complete reoxidation of the cerium oxide. The (100) and (111) orientations show different reduction and reoxidation behaviours.

O 20.6 Mon 17:00 WIL B321

**Atomic structure of cubic ceria surfaces: an IR spectroscopic study** — CHENGWU YANG, •JUNJUN WANG, XIAOJUAN YU, ALEXEI NEFEDOV, STEFAN HEISSLER, CHRISTOF WÖLL, and YUEMIN WANG — Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344, Eggenstein-Leopoldshafen, Germany

Polar surfaces of solid ionic compounds exhibit unique physical and chemical properties but they are intrinsically instable due to a diverging electrostatic energy. A fundamental understanding of the compensation mechanisms is a key but challenging issue. Here, we present an atomic-level picture of the stabilization mechanisms governing the surface polarity compensation of cube-shaped ceria nanoparticles based on a thorough surface science study on polar  $\text{CeO}_2(100)$  single-crystal surfaces using primarily temperature and polarization-resolved infrared reflection absorption spectroscopy (IRRAS). The results obtained by IRRAS in conjunction with high-resolution transmission electron microscopy and density functional theory calculations reveal a multistep scenario for polarity compensation at the polar (100) surface of ceria.

O 20.7 Mon 17:15 WIL B321

**Copper Oxidation on Pt(111) - More than a Surface Oxide?** — •ALEXANDER GLOYSTEIN and NIKLAS NILIUS — Institute of Physics, Carl von Ossietzky University Oldenburg, Germany

LEED, STM and XPS have been used to monitor the growth of copper oxide thin films on a Pt(111) support. At 500 K preparation temperature, a monolayer oxide forms while most of the precipitated copper accumulates as Cu(111) at the Pt interface. Respective films are composed of distorted Cu-O six-rings and resemble the well-known '29' and '44' surface oxides formed via low-pressure oxidation of Cu(111). With increasing temperature, unreacted Cu mixes with the Pt top-layers, resulting in a well-ordered Cu<sub>3</sub>Pt surface alloy. In response to this substrate modification, the oxide film undergoes an order-disorder transition, in which an increasing number of 5-7 defects are inserted into the Cu-O honeycomb lattice, before it decays into isolated ox-

ide islands. Above 750 K annealing, uniform  $\text{Cu}_3\text{O}$  shamrock units that self-assemble into highly crystalline  $2\sqrt{3}$  domains become the dominant structural element of the film.

O 20.8 Mon 17:30 WIL B321

**Ab-initio studies of the (110) surface terminations of rutile  $\text{VO}_2$**  — ●JAKUB PLANER, FLORIAN MITTENDORFER, and JOSEF REDINGER — Vienna University of Technology, 1040 Vienna, Austria

Vanadium dioxide is a promising candidate for fast electronic or optical switching. These applications are based on an insulator-to-metal transition which occurs at 340 K and is accompanied by the structural change from a monoclinic to a rutile phase.

Despite the potential usability of the  $\text{VO}_2$ , many open questions remain with respect to its surface structure. We will therefore discuss properties of the rutile  $\text{VO}_2$  (110) surface under varying oxygen partial pressure, and compare our results to recent experimental findings. Although standard GGA functionals (PBE) offer an appropriate description of the structural properties of the rutile and monoclinic phase, the surface properties such as surface energy or stability of surface reconstructions are not captured well. Advanced functionals such as meta-GGA approaches (SCAN) implemented in the Vienna Ab initio Simulations Package (VASP) thus have been employed to overcome these shortcomings.

It is experimentally found that the  $\text{VO}_2$  surfaces contain more oxygen than the bulk. This is in agreement with the previous study focused on the oxygen adsorption on the (110) surface. However, our work shows different oxygen-rich tetrahedral surface terminations that are related to the vanadium pentoxide (001) monolayer, in agreement with the STM results.

O 20.9 Mon 17:45 WIL B321

**First-Principles Study of Lithium Oxide Surfaces and Crystallites for Lithium-Oxygen Batteries** — ●BEHNAZ RAHMANI DIDAR and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

$\text{Li-O}_2$  batteries are a promising alternative to Li-ion batteries as they theoretically provide the highest possible specific energy density. In this type of battery,  $\text{O}_2$  anions produced in the cathode react with Li cations produced from the oxidation of the Li anode, thus forming  $\text{LiO}_2$ , and more prominently,  $\text{Li}_2\text{O}_2$ , as discharge products.  $\text{Li}_2\text{O}_2$  is an electronic insulator and its precipitation on the cathode is thought to be the main limiting factor in achieving high capacities. SEM and TEM observations reveal crystallite morphologies of  $\text{Li}_2\text{O}_2$  com-

pounds, rather than uniform layers covering the electrode surface. The shapes and crystallite morphologies of  $\text{LiO}_2$  and  $\text{Li}_2\text{O}_2$  particles, may all affect the capacity, rechargeability and generally the electrochemistry of the cell. The precise morphologies and their effects, however, remain largely undetermined. We use DFT calculations and *ab initio* thermodynamics to study the stability of these oxide surfaces, and their crystallite morphologies. Surface-state analyses are also employed to gain insight into the electronic structure of these oxides.

O 20.10 Mon 18:00 WIL B321

**Structure and properties of Cs ions grown on  $\text{ZnO}/\text{Ag}(111)$**  — ●TING-CHIEH HUNG and KARINA MORGENSTERN — Chair of Physical Chemistry I, Ruhr-University of Bochum, Bochum, Germany

Zinc oxide ( $\text{ZnO}$ ) is a broad direct bandgap semiconductor, which is widely used as a catalyst. Therefore, the properties of  $\text{ZnO}$  and interaction between  $\text{ZnO}$  and molecules have been investigated extensively. However, the microscopic views and properties of the adsorbed molecules and ions interacting on  $\text{ZnO}$  ultrathin layers supported by metal substrates have remain unexplored. To understand the interaction between water molecules and ions on  $\text{ZnO}$  ultrathin layer, we first investigated the structures and properties of the caesium (Cs) ions grown on  $\text{ZnO}(0001)/\text{Ag}(111)$  model system. From scanning tunneling microscopy (STM) images we found that the Cs ions are grown only on the  $\text{ZnO}$  layer by following its moiré pattern [1]. Further STM results will be presented in this talk.

[1] Q. Pan et al, Catalysis Letters, 2014, 144(4), 648-655.

O 20.11 Mon 18:15 WIL B321

**Hydrogen Atom Scattering at Aluminium Oxide** — ●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 via hydrogen storage to nuclear fusion. Here, we report molecular dynamics simulations of high-energy hydrogen atom scattering at the  $\alpha\text{-Al}_2\text{O}_3(0001)$  surface. 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 at a small fraction of the computational costs. Probing different kinetic energies, surface temperatures and incident angles, we are able to characterize the scattering process in detail.