

## O 101: Poster Session VIII: Oxides and insulators: Adsorption and reaction of small molecules

II

Time: Thursday 13:30–15:30

Location: P

O 101.1 Thu 13:30 P

**Probing structural changes upon carbon monoxide coordination to single metal adatoms** — ●PAUL T. P. RYAN<sup>1,2,3</sup>, MATTHIAS MEIER<sup>3,4</sup>, ZEDENEK JAKUB<sup>3</sup>, JAN BALAJKA<sup>4</sup>, JAN HULVA<sup>3</sup>, DAVID J. PAYNE<sup>2</sup>, TIEN-LIN LEE<sup>1</sup>, CESARE FRANCHINI<sup>4</sup>, FRANCESCO ALLEGRETTI<sup>5</sup>, GARETH S. PARKINSON<sup>3</sup>, and DAVID A. DUNCAN<sup>1</sup> — <sup>1</sup>Diamond Light Source, Didcot, OX11 0QX UK — <sup>2</sup>Department of Materials, Imperial College London, SW7 2AZ UK — <sup>3</sup>Institute of Applied Physics, TU Wien, Austria — <sup>4</sup>Faculty of Physics and Center for Computational Materials Science, University of Vienna, Austria — <sup>5</sup>Physics Department E20, Technical University of Munich, 85748 Garching, Germany

The application of highly accurate, but yet computationally cheap, density functional theory (DFT) calculations allows for the fine tuning of catalyst development. However, it is necessary to have stringent benchmarks against which these calculations are tested. In this work, the adsorption height of Ag adatoms on the Fe<sub>3</sub>O<sub>4</sub>(001) surface after exposure to CO was determined using normal incidence X-ray standing waves. CO coordinated Ag adatoms (Ag<sup>CO</sup>) were found to be pulled out of the surface to an adsorption height of 1.15 ± 0.08 Å, compared to the previously measured height of 0.96 ± 0.03 Å for bare Ag adatoms[1]. Utilising DFT+vdW+U calculations with the substrate unit cell dimension fixed to the experimental value, the predicted adsorption height for Ag<sup>CO</sup> was 1.16 Å, in remarkably good agreement with the experimental results. [1] M. Meier et. al., *Nanoscale* 10, 2226 (2018)

O 101.2 Thu 13:30 P

**Polarons in single atom catalysts: case study of Me<sub>1</sub>=[Au<sub>1</sub>,Pt<sub>1</sub>,Rh<sub>1</sub>] on TiO<sub>2</sub>(110)** — ●PANUKORN SOMBUT<sup>1</sup>, LENA HAAGER<sup>1</sup>, MARLENE ATZMUELLER<sup>1</sup>, ZEDENEK JAKUB<sup>1</sup>, MICHELE RETICCIOLI<sup>2</sup>, MATTHIAS MEIER<sup>1,2</sup>, GARETH S. PARKINSON<sup>1</sup>, and CESARE FRANCHINI<sup>2,3</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien, Vienna, Austria — <sup>2</sup>University of Vienna, Vienna, Austria — <sup>3</sup>Università di Bologna, Bologna, Italy

Identification of the exact local environment of a single-atom catalyst (SAC) on metal oxide surfaces is crucial for understanding the reactivity as well as the catalytic properties of such systems. On TiO<sub>2</sub>(110), the stability and reactivity of adsorbed adatoms is further complicated by the presence of Oxygen vacancies and associated polaron charge, as both can affect the energetic, electronic configuration and local geometry of adsorbed adatoms. In this work the adsorption of group 9 to 11 transition metal adatoms (Rh, Pt and Au) are computationally studied by means of density functional theory (DFT, plus on-site Hubbard U), and compared with results obtained by experimental surface techniques such as scanning tunneling microscopy (STM), for Rh<sub>1</sub>, and with available literature (Au<sub>1</sub> and Pt<sub>1</sub>). Despite the many works on this subject, it is still unclear why Au and Pt are experimentally observed to adsorb in the O vacancy, contrary to Rh. By investigating the most stable adsorption site, oxidation state and the intermingled interaction among adatoms, O vacancies and polarons our data attempt to decipher the physical and chemical origin of the observed trend and to provide a conclusive interpretation of the puzzling observation.

O 101.3 Thu 13:30 P

**Direct assessment of the acidity of individual surface hydroxyls on In<sub>2</sub>O<sub>3</sub>(111)** — ●MARGARETA WAGNER<sup>1,2</sup>, BERND MEYER<sup>3</sup>, MARTIN SETVIN<sup>1,4</sup>, MICHAEL SCHMID<sup>1</sup>, and ULRIKE DIEBOLD<sup>1</sup> — <sup>1</sup>TU Wien, Vienna, Austria — <sup>2</sup>CEITEC BUT, Brno, Czech Republic — <sup>3</sup>FAU Erlangen-Nürnberg, Erlangen, Germany — <sup>4</sup>Charles University, Prague, Czech Republic

Non-contact atomic force microscopy is a versatile tool to investigate properties of individual atoms or molecules. Here we report a novel approach to determine the acidity of individual surface hydroxyls, which is directly linked to the proton affinity (PA) of the involved O atoms. The PA – the tendency to gain or lose a proton – is crucial e.g. in acid-base catalysis and the electro- and photocatalytic splitting of water.

The testcase of this study is the stoichiometric In<sub>2</sub>O<sub>3</sub>(111) surface, which has four inequivalent surface O atoms O<sub>s</sub>(α-δ). Water dissociation leads to a pair of OH groups: the surface O<sub>s</sub>H(β) and the water O<sub>W</sub>H. The remaining surface O atoms O(α, γ, δ) can be protonated

via manipulation with the tip. We probe the strength of their H bond with a functionalized tip of a nc-AFM via *F*(*z*)-spectroscopy and find quantitative agreement with density-functional theory (DFT) calculations. By relating the results to known PAs of gas-phase molecules, we can calibrate our data and determine the PA of different surface sites of In<sub>2</sub>O<sub>3</sub>(111) with atomic precision. Measurements on hydroxylated TiO<sub>2</sub> and zirconia extend our method to other oxides. The trends of the site-specific PA values agree well with the expectations based on area-averaging techniques.

O 101.4 Thu 13:30 P

**Signatures of oxygen vacancies in O1s core level shifts** — ALVARO POSADA-BORBON, NOEMI BOSIO, and ●HENRIK GRÖNBECK — Chalmers University of Technology, Gothenburg, Sweden

Density functional theory calculations are used to investigate O1s surface core level shifts for MgO(100), ZnO(10-10), In<sub>2</sub>O<sub>3</sub>(111) and CeO<sub>2</sub>(111). Shifts are calculated for the pristine surfaces together with surfaces containing oxygen vacancies and dissociated H<sub>2</sub> and H<sub>2</sub>O. Pristine surfaces show small negative shifts with respect to the bulk components and oxygen vacancies are found to have minor effects on the O1s binding energies of neighboring oxygen atoms. OH-groups formed by H<sub>2</sub> or H<sub>2</sub>O dissociation yield binding energies shifted to higher energies as compared to the oxygen atoms in the bulk. The results exemplify the difficulties in assigning core-level shifts and suggest that assignments of shifts in O1s binding energies to neighboring oxygen vacancies for the explored oxides should be reconsidered.

O 101.5 Thu 13:30 P

**Thermal stability and CO-induced mobility of single Pt adatoms supported on the α-Fe<sub>2</sub>O<sub>3</sub>(1102) surface** — ●ALI RAFSANJANI-ABBASI<sup>1</sup>, FLORIAN KRAUSHOFER<sup>1</sup>, MORITZ EDER<sup>2</sup>, JIRI PAVELEC<sup>1</sup>, LENA HAAGER<sup>1</sup>, GIADA FRANCESCHI<sup>1</sup>, MICHELE RIVA<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, ULRIKE DIEBOLD<sup>1</sup>, and GARETH S. PARKINSON<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien, Wiedner Hauptstraße 8-10/E134, 1040 Wien, Austria — <sup>2</sup>Chair of Physical Chemistry, TU München, Lichtenbergstraße 4, 85748 Garching, Germany

Pt-based catalysts are the most efficient catalysts for the hydrogen evolution reaction and are also widely used for photocatalytic and CO-oxidation reactions. However, the high cost of Pt and its susceptibility to carbon monoxide poisoning are two drawbacks on its role as a catalyst. Downsizing catalyst clusters to single atoms is an effective way to reach maximum efficiency, and so-called "Single-Atom Catalysis" is now an important field of research [1]. Nevertheless, stabilization of single Pt atoms on a support without compromising catalytic activity is still a key challenge.

Here, we present a study of the thermal stability and CO-induced mobility of single Pt atoms on the α-Fe<sub>2</sub>O<sub>3</sub>(1102) surface, at elevated temperatures and in a CO-containing environment. Thermally-induced and CO-induced sintering of the Pt single atoms are traced by means of STM and XPS. In addition, in time-lapse series the mobility and rearrangement of single Pt adatoms have been determined with varying carbon monoxide pressure in the background.

1. G. S. Parkinson, *Catal. Lett.* 149, 1137 (2019).

O 101.6 Thu 13:30 P

**Momentum for Catalysis: How Surface Reactions Shape the RuO<sub>2</sub> Flat Surface State** — VEDRAN JOVIC<sup>1,2</sup>, ARMANDO CONSIGLIO<sup>3</sup>, KEVIN E. SMITH<sup>4</sup>, CHRIS JOZWIAK<sup>1</sup>, AARON BOSTWICK<sup>1</sup>, ELI ROTENBERG<sup>1</sup>, DOMENICO DI SANTE<sup>3</sup>, and ●SIMON MOSER<sup>1,3</sup> — <sup>1</sup>Advanced Light Source, USA — <sup>2</sup>GNS Science, New Zealand — <sup>3</sup>Würzburg-Dresden Cluster of Excellence ct.qmat, Universität Würzburg, Germany — <sup>4</sup>Boston University, USA

The active (110) surface of the benchmark oxygen evolution catalyst RuO<sub>2</sub> spans a flat-band surface state (FBSS) between the surface projections of its Dirac nodal lines (DNL) that define the electronic properties of this functional semimetal. Monitoring well known surface adsorption processes of H<sub>2</sub>, O<sub>2</sub>, NO and CO by in-operando angle resolved photoemission spectroscopy, we selectively modify the oxidation state of individual Ru surface sites and identify the electronic nature of the FBSS: Stabilized by bridging oxygen O<sub>br</sub> p<sub>z</sub>, the FBSS disperses along <001> oriented chains of bridging Ru<sub>br</sub> 4d<sub>z<sup>2</sup></sub> orbitals,

collapses upon  $O_{br}$  removal, yet, remains surprisingly unaffected by the oxidation state of the undercoordinated 1f-cus-Ru species. This directly reflects in the ability of  $RuO_2$  (110) to oxidize CO and  $H_2$  along with its inability to oxidize NO, demonstrating the FBSS's active role in catalytic charge transfer processes at the oxygen bridge sites. Our synergetic approach provides momentum resolved insights to the interplay of a catalyst's delocalized electronic band structure and the localized orbitals of its surface reactants - a route towards a microscopic understanding of heterogeneous catalysis.

O 101.7 Thu 13:30 P

**Selective electrochemical reduction oxalic acid on anatase surfaces** — ●GERGELY JUHASZ — Tokyo Institute of Technology, Tokyo, Japan

Direct electrochemical reduction of carboxylic acids to alcohols is rare and has several potential applications such as raw material synthesis or energy storage. We studied the mechanism of the recently reported electrochemical reduction of oxalic acid on anatase nanoparticle surfaces. The questions we focused on were why the reduction occurs only on one of the carboxylic groups, what would be the necessary conditions to perform full 8 electron reduction, and why the reaction occurs only on anatase surfaces.

Calculations with DFTB methods revealed that the molecules can be reduced only on a carboxylic group that is not attached to the surface, and the other group works as an anchor and stays electrochemically inactive. This explains the preference for 4 electron reduction and the selectivity of the process. Further calculations showed that the majority of titanium-oxide surfaces prefer to bind both carboxylic groups of

the oxalic acid, therefore they remain electrochemically inactive.

O 101.8 Thu 13:30 P

**Surface reactivity to hydrogen of Ag- and Cu- modified CeO<sub>2</sub>** — ●STEFANIA BENEDETTI<sup>1</sup>, AVINASH VIKATAKAVI<sup>1,2</sup>, GIULIA RIGHI<sup>1,2</sup>, PAOLA LUCHES<sup>1</sup>, SERGIO D'ADDATO<sup>1,2</sup>, RITA MAGRI<sup>1,2</sup>, and ANNABELLA SELLONI<sup>3</sup> — <sup>1</sup>CNR, Istituto Nanoscienze, 41125 Modena, Italy — <sup>2</sup>Dipartimento di Fisica, Informatica e Matematica, Universita' di Modena e Reggio-Emilia, 41125 Modena, Italy — <sup>3</sup>Department of Chemistry, Princeton University, Princeton, New Jersey 08540, United States

In this work we investigate the  $H_2$  dissociation on Ag- and Cu- modified CeO<sub>2</sub> surfaces to increase oxide activity for application in catalytic reactions in electrochemical devices to replace Pt. We have followed by XPS the Ag oxidation state, the concentration of Ce<sup>3+</sup> ions, O vacancies, and OH- groups during thermal reduction cycles in  $H_2$  and in UHV of thin CeO<sub>2</sub> films. As expected, the reactivity of ceria toward  $H_2$  dissociation improves when Ag is included. However, thermal treatment under H exposure decreases the concentration of Ce<sup>3+</sup> ions in Ag-modified ceria with respect to pure oxide in the same conditions, while the number of surface O vacancies is larger for the Ag-modified surface [1]. Thanks to DFT calculations, we explain this behavior in terms of a reduction of the surface Ag, which acquires some of the extra electrons created by the O vacancies and the adsorbed H atoms. Results are compared to films with substitutional Cu atoms. In this case Ce<sup>3+</sup> concentration increases by a factor of 2 compared to pure oxide and activation temperature decreases to 570 K. [1] S. Benedetti et al., ACS Applied Materials & Interfaces, 2020, 12, 24, 27682-27690