O 63: Oxides and Insulator Surfaces: Adsorption and Reaction of Small Molecules II

Time: Wednesday 10:30–12:30 Location: H25

O 63.1 Wed 10:30 H25

Unravelling the Photocatalysis of Alcohol on Rutile(110) — •Philip Petzoldt, Lucia Mengel, Anna Lemperle, Moritz Eder, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Heterogeneous photocatalysis is a promising tool for the environmentally benign production of chemical fuels such as hydrogen. However, the structural complexity of state-of-the-art materials makes mechanistic investigations and, in consequence, the targeted design of new catalysts extremely challenging. We employ surface science methods to explore fundamental mechanisms in photocatalysis. In this contribution, we focus on the photocatalytic hydrogen evolution from alcohols over rutile(110) loaded with Pt cluster co-catalysts. Our experimental evidence reveals a new reaction mechanism, which substantially differs from the generally assumed model of independent redox reactions. By changing active sites for both the alcohol oxidation and the hydrogen evolution reaction, we further show that the overall photoactivity strongly depends on the equilibrium of a reaction network of several elementary photo- and thermal reaction steps. Our results provide new mechanistic insights into the photocatalytic hydrogen evolution from Pt loaded titania and illustrate the importance of a comprehensive understanding of the photocatalysts (surface) chemistry.

O 63.2 Wed 10:45 H25

Characterization of rhodium single atoms as dicarbonyls on TiO_2(110) — •Moritz Eder, Faith Lewis, Panukorn Sombut, Johanna Hütner, David Rath, Jan Balajka, Jiri Pavelec, and Gareth Parkinson — Institute of Applied Physics, TU Wien, Austria

Single-atom catalysts (SACs) have garnered significant attention in recent years due to their potential to minimize noble metal usage by isolating active atoms on metal (oxide) surfaces. However, stabilizing these single atoms remains a major challenge. Ligands, such as carbon monoxide, can stabilize single atoms by transforming them into surface-bound metal complexes, closely resembling the well-defined species in homogeneous catalysis. In this contribution, we present a comprehensive characterization of a ligand-stabilized single atom: a rhodium gem-dicarbonyl ($Rh(CO)_2$) bound to rutile TiO_2(110). Using XPS, TPD, scanning probe, and a newly developed IRRAS apparatus, we provide a detailed analysis of these sites. Our findings are contextualized through comparisons with theoretical models and insights from powder catalyst studies in the literature. This work demonstrates that multi-technique approaches are essential for the accurate characterization of single-atom catalysts, offering a deeper understanding of their structure and stability.

O 63.3 Wed 11:00 H25

Desorption of water from microcline (001) — Tobias Dickbreder[1,2], Florian Schneider[1], Lea Klausfering[1], Kim Noelle Dreier[1], Franziska Sabath[1,3], Adam S. Foster[4], Ralf Bechstein[1], and •Angelika Kühnle[1] — [1]Bielefeld University, 33615 Bielefeld, Germany — [2]University of Vienna, 1090 Vienna, Austria — [3]Max Planck Institute for Polymer Research, 55128 Mainz, Germany — [4]Aalto University, Finland and Kanazawa University, Kanazawa 920-1192, Japan

Feldspar minerals are highly abundant in the Earth's crust. They play a significant role in a plethora of geochemical processes, including, e.g., weathering and ice nucleation. For many of these processes, the interaction of water with the feldspar surface is decisive. However, little is known about binding and desorption of the first water layer on feldspar. Here, we present temperature-programmed desorption (TPD) experiments of water desorbing from the thermodynamically most stable cleavage plane of potassium-rich feldspar, microcline (001). From the interplay of these experimental data with density-functional theory (DFT) results we shed light onto the binding of the first water layer. Our work confirms previous theory results from literature and provides molecular-scale insights into the binding of water onto microcline (001).

O 63.4 Wed 11:15 H25

Cleaved feldspar surfaces under dry and humid conditions: an AFM study — •Luca Lezuo[1], Sandra Boigner[1], Rainer Abart[2], Michael Schmid[1], Ulrike Diebold[1], and Giada Franceschi[1] — [1]Inst. of Applied Physics, TU Wien, 1040 Wien, Austria — [2]Dep. of Lithospheric Research, Universität Wien, 1090 Wien, Austria

The Earth's surface is largely shaped by the interaction between water and the minerals of its crust. Feldspars, the most common aluminosilicates, are made of a framework of corner-sharing silica and alumina tetrahedra, enclosing cations such as potassium (K^+), sodium (Na^+), and calcium (Ca^{2+}). The chemical reactions at the feldspar-water interface contribute to geological processes such as erosion and weathering [1], clay formation [2], and ice nucleation [3], with implications for geology, agriculture, atmospheric chemistry, and climate science.

We exposed cleaved surfaces of different feldspars to air and Ar with defined humidity and examined the evolution of their mesoscale morphology with atomic force microscopy (AFM). Overlayers with distinct patterns develop over time. They remain stable after rinsing the surface with ultrapure water, suggesting a permanent alteration of the surface morphology. We attribute the distinct patterns to local chemistry differences and different cation leaching rates [1].

[1] Brantley and White, Chem. Weath. Rates of Sil. Min. (2018)
[2] Bleam., Clay Min. and Chem., 87-146 (2017)
[3] Atkinson, et al., Nature 498, 355-358 (2013)

O 63.5 Wed 11:30 H25

Tracking the redox cycle of CeO_2 by Infrared spectroscopy via a titration of the defect states by O_2 adsorption. — •Lachlan Caulfield, Eric Sauter, Hicham Idriss, and Christof Wöll — Karlsruhe Institute of Technology

CeO_2 is probably the most stable reducible metal oxide known. It is the main component of automobile three-way catalysts and is the chief prototype for the thermochemical water splitting to H_2 and O_2 reaction as well as for CO_2 thermal reduction to CO. This is largely due to the relative stability of the $Ce4f_1$ electron formed upon the removal of surface oxygen atoms during the reduction process. While these are commonly studied by photoelectron spectroscopy (XPS Ce3d or UPS Ce4f), less attention in general has been given to the Ce^{3+} (2F5/2 to 2F7/2) spin orbit transition of this process that appears in infrared spectroscopy at ca. 2150 cm^{-1}. In this work we have monitored the formation of these transition on reduced polycrystalline CeO_2 exposed to molecular O_2 as a function of temperature using the DRIFT technique. Results have shown that there is a linear relationship between the disappearance of the observed electronic transition at ca. 2130-2160 cm^{-1} and the IR signal of the superoxo (O^{2-}). species upon exposure of the reduced surface to different partial pressures of O_2. Moreover, it was found that the oxidation process is irreversible: the spin-orbit transition signal does not recover upon the removal of adsorbed oxygen species. Work in progress to track the catalytic activity of these adsorbed O_2 species and spin-orbit transition by probe molecules suitable for the redox cycle.

O 63.6 Wed 11:45 H25

Nucleation of TMDAH on CoO nanoislands on Au(111) — •Jonas Hauner, Nikolai Sidorenko, Hanna Bühlmeyer, and Jörg Libuda — Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

Atomic layer deposition (ALD) has recently received considerable attention as a promising method to precisely grow thin films of a wide variety of materials. This work focuses on the ALD of HfS_2 on oxide substrates. In specific, we report on the nucleation behavior of the ALD precursor tetrakis(dimethylamido)hafnium(IV) (TMDAH) on cobaltoxide nanoislands on Au(111). The samples were prepared by deposition of Co in oxygen atmosphere and subsequent deposition of TMDAH. We investigated the adsorption of TMDAH by scanning tunneling microscopy (STM) and infrared absorption reflection spectroscopy (IRAS). At 300 K, TMDAH nucleates at OH groups at the CoO surface by means of a Brønsted acid-base reaction. At 400 K, the mechanism changes and involves a Lewis acid-base reaction due to the lack of OH groups on the substrate. Presaturation of the substrate with H_2O further modifies the reaction mechanism of nucleation.

O 63.7 Wed 12:00 H25

Maghemite (γ-Fe_2O_3): From Bulk Phases to (001) Oriented Surfaces

— •Muhammad Munawar[1,2] and Rossitza Pentcheva[1] — [1]Department of Physics and Center for Nanointegration (CENIDE), Universität Duisburg-Essen, Lotharstr. 1, 47057 Duisburg, Germany — [2]International Max Planck Research School on Sustainable Metallurgy, Max-Planck-Straße 1, 40237, Düsseldorf, Germany

Maghemite (γ-Fe_2O_3) finds applications across a wide range of fields, including spintronics, magnetic recording, and nano-medicine, to name a few. It can be derived from the magnetite (Fe_3O_4) structure by introducing Fe vacancies in the B layers containing octahedral Fe ions and oxygen. A stoichiometric phase is achieved by tripling the cubic cell along the c-axis, resulting in a charge-transfer insulator with band gap of 1.90 eV. Phonon dispersion indicates that the cubic structure is stable without imaginary frequency modes. *Ab initio* molecular dynamics (AIMD) simulations confirm the stability at 300 K. Additionally, we explore the stability of the (001) surface within the framework of *ab initio* thermodynamics. The A and B layer terminations are favored at oxygen-poor and oxygen-rich conditions, whereas at intermediate oxygen chemical potentials, a 0.5A layer termination is stabilized. While the A termination exhibits only a minor band gap change, a significant decrease occurs for the B-layer termination due to reduction of magnetic moments and Fe-O bonds up to 0.21 Å. These surfaces serve as a starting point to explore the mechanism of hydrogen adsorption and reduction of the material in view of green steel production.

O 63.8 Wed 12:15 H25

New insights into CO adsorption on TiO_2(110): Enhanced IRAS characterisation

— •Nail Barama, Moritz Eder, Igor Sokolović, Michele Reticcioli, David Rath, Michael Schmid, Ulrike Diebold, Jiri Pavelec, and Gareth Parkinson — Institute of Applied Physics, TU Wien, 1050 Vienna, Austria

TiO_2(110) serves as a model system for investigating surface reactivity and catalytic behavior, with CO adsorption commonly employed as a probe molecule. While previous IR spectroscopy studies identified two distinct adsorption sites for low coverages, regular Ti sites, and Ti sites near oxygen vacancies[1,2], recent work based on DFT and microscopy suggests the existence of additional adsorption configurations influenced by the polaronic nature of the substrate[3]. In this contribution, we present experimental results obtained using our custom-built reactivity and infrared reflection absorption spectroscopy (IRAS) setup[4]. This design, optimized for detecting small concentrations of adsorbates on metal oxide surfaces, delivers high-resolution spectra with a high signal-to-noise ratio, allowing us to observe new features. Our data reveal multiple CO adsorption configurations on TiO_2(110), which agrees with STM observations from a recent study[3]. References: [1] Xu, M. et al. Angew. Chem. Int. Ed. 51, 4731-4734 (2012). [2] Petrik, N. G. & Kimmel, G. A. J. Phys. Chem. Lett. 3, 3425-3430 (2012). [3] Reticcioli, M. et al. Phys. Rev. Lett. 122, 016805 (2019). [4] Rath, D. et al. Rev. Sci. Instrum. 95, 065106 (2024).