O 94: Oxides and insulators: Adsorption and reaction of small molecules

Time: Friday 9:30–12:30 Location: HSZ/0204

Invited Talk O 94.1 Fri 9:30 HSZ/0204

Surface Chemistry on Copper Oxides — •Dario Stacchiola — Brookhaven National Laboratory, Upton NY, 11720, USA

The chemical and electronic properties of copper combined with its large natural abundance lend this material to impact a wide range of technological applications, including heterogeneous catalysis. The reactivity of copper in its Cu1+ oxidation state makes this specific state relevant in various chemical reactions, but the facile redox properties of copper make the isolation of individual states for fundamental studies difficult. I will present our work on model systems including Cu2O/Cu(111) films, bulk Cu2O crystals and copper-based mixed-oxides used to study the interaction of Cu1+ with small molecules making use of in-situ surface science techniques. Advantages and disadvantages of each system are discussed and exemplified through case studies of chemical adsorption and reactivity studies

O 94.2 Fri 10:00 HSZ/0204

Calculating vibrational bands for formic acid on magnetite surfaces — •Gregor Vonbun-Feldbauer — Institute for Interface Physics and Engineering, TU Hamburg, Germany — Institute of Surface Science, Helmholtz-Zentrum hereon, Germany

Understanding the adsorption properties of organic molecules on oxide surfaces, such as their adsorption geometry, is crucial for optimising processes in various applications, ranging from heterogeneous catalysis to hybrid nanocomposites. In this study, the adsorption of formic acid on magnetite surfaces (001), (111) and (112) is examined using Density Functional Theory (DFT). The vibrational properties are then calculated and compared with experimental infrared spectroscopy data for single crystalline surfaces and nanoparticles. This enables adsorption geometries and modes to be identified.

O 94.3 Fri 10:15 HSZ/0204

Thermal CO_2 Activation and Carbonate Formation on $Fe_2O_3(012)$ — •Johannes Filzmoser, Moritz Eder, Florian Kraushofer, Jiri Pavelec, and Gareth Parkinson — Vienna University of Technology, Austria

The adsorption of CO_2 on hematite α-$Fe_2O_3(012)$ has been investigated in ultra-high vacuum (UHV) using temperature-programmed desorption (TPD) and infrared reflection absorption spectroscopy (IRAS). CO_2 adsorption on this surface exhibits complex behavior, resulting in multiple desorption features in TPD. For coverages up to one molecule per unit cell (0.5 molecules per Fe^{2+} cation), two desorption features centered around 150 K and 220 K increase concurrently with increasing coverage. IRAS shows that this behavior originates from a thermally activated conversion of weakly bound, physisorbed CO_2 into surface carbonate (CO_3^{2-}) species at temperatures above 100 K, a process that directly competes with molecular desorption. By supplying CO_2 at temperatures just below the carbonate desorption temperature, higher carbonate coverages can be obtained. These findings contribute to our understanding of CO_2 activation on $Fe_2O_3(012)$ and will be a prerequisite for surface reaction studies.

O 94.4 Fri 10:30 HSZ/0204

Redox dynamics of $Co_3O_4(111)$ during H_2S adsorption and decomposition — Jonas Hauner[1], Tomáš Skála[2], Nataliya Tsud[2], Fernando Stavale[3], •Yaroslava Lykhach[1], and Jörg Libuda[1] — [1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — [2]Charles University, Prague, Czech Republic — [3]Brazilian Center for Research in Physics, Rio de Janeiro, Brazil

The redox interactions between transition metal oxides and sulfur-containing compounds play a key role in catalytic processes and gas sensing technologies. We investigated the redox dynamics of $Co_3O_4(111)/Ir(100)$ model catalysts in response to the adsorption and decomposition of hydrogen sulfide (H_2S) using synchrotron radiation photoelectron spectroscopy (SRPES). Upon adsorption, H_2S partially dissociates to form a variety of species including sulfites, sulfides, chemisorbed H_2S, hydroxyl and sulfhydryl groups. Subsequent annealing in ultrahigh vacuum induces desorption and conversion of adsorbed species to sulfates. These transformations are accompanied by temperature-dependent redox processes which can be monitored as a function of Co^{3+}/Co^{2+} ratio. The obtained insights into H_2S–Co_3O_4 redox interactions offers a foundation for the rational design of cobalt oxide catalysts and sensors for H_2S detection and abatement.

O 94.5 Fri 10:45 HSZ/0204

Characterization of CO_2 adsorption configurations on stoichiometric, reduced and hydroxylated In_2O_3 — •Sarah Tobisch[1], Andreas Ziegler[2], Sarah Horak[1], Marco Knapp[1], Michele Riva[1], Michael Schmid[1], Ulrike Diebold[1], Bernd Meyer[2], and Margareta Wagner[1] — [1]TU Wien, Vienna, Austria — [2]FAU-Erlangen-Nürnberg, Erlangen, Germany

CO_2 reduction to methanol is a promising pathway towards a more circular economy, converting CO_2 into valuable fuels and feedstock for the chemical industry. In_2O_3-based catalysts have gained lots of attention in recent years due to their high selectivity towards methanol synthesis. Since catalytic reactions typically take place at the interface, it is important to understand how CO_2 molecules interact and adsorb on the surface on an atomic level.

In this work, the adsorption of CO_2 molecules was studied on three different $In_2O_3(111)$ surfaces: stoichiometric, reduced, and hydroxylated. We present atomically resolved non-contact AFM images which allow for the identification of the adsorption sites of all individual molecules. The CO_2-saturated, stoichiometric $In_2O_3(111)$ shows long range order, albeit breaking the three-fold symmetry of the surface. Missing contrast inversion in nc-AFM combined with XPS measurements result in the identification of physisorbed and carbonate species. DFT calculations confirm adsorption sites and orientation of the individual molecules. CO_2 shows similar motifs on the reduced surface but partly displaces the In adatoms. On the hydroxylated surface, the OH groups block adsorption of CO_2 and long-range order is not observed.

O 94.6 Fri 11:00 HSZ/0204

How chirality controls catalysis: Spin-dependent effects in the catalytic OER from first-principles — •Suryansh Suryansh[1], Rafael Gutiérrez[1], Arezoo Dianat[1], and Gianaurelio Cuniberti[1,2] — [1]Institute of Materials Science and Max Bergmann Center of Biomaterials, Dresden University of Technology, Dresden 01062, Germany — [2]Dresden Center for Computational Materials Science (DCMS), TU Dresden, 01062, Dresden, Germany

The evolution of a mixture of unpolarized electrons into an ensemble of spin-polarized electrons after passing through a chiral molecule such as DNA, proteins, or peptides is a well-established phenomenon attributed to the chiral-induced spin selectivity (CISS) effect. This effect has important implications for electrochemical water-splitting. Experiments have shown that chiral molecules enhance the oxygen evolution reaction (OER) by controlling the spin of electrons at the electrode surface when the electrode is coated with a monolayer of chiral molecules, a film of chiral polymer, or a chiral inorganic oxide. This enhancement is associated with facilitating the singlet-to-triplet spin transition of oxygen at the interface. However, the microscopic origin and physical mechanisms behind CISS-based water-splitting remain unclear. In this work, we investigate the electronic and magnetic properties of ferrimagnetic surfaces functionalized with chiral and achiral molecules using first-principles calculations. We compute the reaction energy barriers of the individual OER steps and analyze the spin-polarized electronic states near the Fermi level, providing theoretical insights into the mechanisms underlying spin-assisted water-splitting.

O 94.7 Fri 11:15 HSZ/0204

Tailoring the OER activity of Co_3O_4 surfaces by Mn and V-doping: insights from DFT+U calculations — •Palani Muthu Kumar and Rossitza Pentcheva — Department of Physics, University of Duisburg-Essen

The rational design of efficient electrocatalysts for sustainable energy conversion demands an atomistic understanding of how surface modifications influence the overall activity. Here we present a detailed DFT+U investigation of Mn- and V-doping on the oxygen evolution reaction (OER) activity at Co_3O_4 surfaces. Mn-doping at the surface octahedral sites on both A- and B-terminated $Co_3O_4(001)$, reduces the OER activity. Conversely, V-doping demonstrates termination-dependent behaviour: at the B-termination, V^{5+} in a surface octahedral site reduces the overpotential at $Co_{\rm oct}$ from 0.48 V to 0.43 V. At the A-termination, V^{4+} in a subsurface octahedral site leads to the lowest overpotential of 0.18 V at $Co_{\rm tet}$ reaction site, reversing the intrinsic activity trend where pristine Co_{tet} sites (0.74 V) are less active than Co_{oct2} (0.55 V) sites. For most studied cases, the deprotonation of *OH to *O is the potential-determining step. The enhanced catalytic activity of the V-doped A-termination originates from the modification of surface Co^{3+}(IS) to Co^{2+}, weakening the *OH binding energy and lowering the PDS by 0.56 eV. These findings show that selective doping effectively tunes electrocatalyst performance. The scope of the investigation is further extended to the $Co_3O_4(111)$ surface, thereby broadening the understanding of facet-dependent effects.

O 94.8 Fri 11:30 HSZ/0204

Towards Understanding the Photoreactivity of SrTiO3 through Studies in Ultra-High Vacuum — •Anna Lemperle, Philip Petzoldt, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany

Strontium titanate is renowned for its photocatalytic water splitting capabilities. However, the catalytic mechanism remains elusive. A promising approach to obtain insights into structure-reactivity relations is to investigate well-defined single crystal model catalysts under ultra-high vacuum conditions. This contribution discusses first results on the thermal and photoreactivity of water and oxygen on the bare strontium titanate (100) surface. Experiments combining temperature programmed desorption and studies under illumination point to a high importance of the dynamic behaviour of bulk and surface oxygen for the reactivity of strontium titanate (100).

O 94.9 Fri 11:45 HSZ/0204

Methanol photodecomposition on $TiO_2(110)$ under UV illumination studied with vibrational SFG spectroscopy in ambient conditions — •Milad Salarinasab[1], Julian Andreas Hochhaus[1], Anas Akhtar[2], Kristina Tschulik[2], Carsten Westphal[1], Zhe Wang[1], and Ahmed Ghalgaoui[1] — [1]Department of Physics, TU Dortmund University, Otto-Hahn-Str. 4a, Dortmund, 44227, Germany — [2]Analytical chemistry II, Ruhr-Universität Bochum, Universitätsstrasse 150, 44801 Bochum, Germany.

Methanol is widely used as a model system for photocatalysis on TiO_2 surfaces, but many earlier investigations were performed in UHV and therefore do not reflect real catalytic conditions. To address this gap, we studied methanol photodecomposition on $TiO_2(110)$ under realistic ambient conditions using vibrational sum frequency generation (SFG) spectroscopy. By recording spectra in the C-H stretch region, we followed CH_3, CH_2, and methoxy species during UV illumination and monitored how these surface species evolve in real time.

The SFG signals show clear differences from the reaction pathways commonly described in vacuum studies. Most importantly, we identify a new photodecomposition route that becomes active only under realistic conditions combined with UV excitation. This finding provides new insight into methanol chemistry on $TiO_2(110)$ and helps connect surface science studies with photocatalytic behavior in practical environments.

O 94.10 Fri 12:00 HSZ/0204

Bridging the Gap: Interpreting Photocatalysis Under Ambient Conditions Based on Findings from Surface Science — •Martin Tschurl, Philip Petzoldt, Lucia Mengel, Paula Neumann, Anna Lemperle, and Ueli Heiz — Chair of Physical Chemistry, Technical University of Munich, Lichtenbergstr. 4, 85748 Garching, Germany

The interpretation of heterogenous photocatalytic reactions is usually closely linked to electrochemistry. Based on a qualitative, exclusively thermodynamic picture, it normally focuses on the properties of photon-generated charge-carriers. However, some years ago in ultra-high vacuum (UHV) studies, we discovered that for the heavily studied Pt-titania system, a fundamentally different reaction mechanism governs the photocatalytic conversion of alcohols. This mechanism underscores the critical role of surface chemistry - an aspect often neglected in the interpretation of applied photocatalysts. In this presentation, we will interpret systems operating under ambient conditions based on insights gained from UHV experiments. This way, we also demonstrate merit of surface science studies for a comprehensive understanding of photocatalysis.

O 94.11 Fri 12:15 HSZ/0204

Molecular Dynamics Simulation of Impingment of Atomic Oxygen on Alumina and Silica Surfaces — Stephen Hocker, Hansjörg Lipp, Aahmed Kassem, Ricco Isele, Leonidas Simitsis, and •Johannes Roth — Institute for Functional Matter and Quantum Technologies (FMQ), University Stuttgart, Germany

Atomic oxygen (AO) impinging on satellite surfaces in very low earth orbit (VLEO) transfers momentum and energy, leading to material degradation and drag forces. To be able to counteract these effects, we investigate the impact mechanisms of AO on alumina (Al2O3) and silica (SiO2) surfaces. In this talk we give an overview of our activities: Using molecular dynamics (MD) simulations with classical force fields, we study material stability, angular distributions of reflected particles, and adsorption rates. Our findings indicate that bare Al2O3 does not degrade under AO impacts but accumulates oxygen due to adsorption processes. The angular distribution of reflected particles is highly dependent on the surface structure and the angle of incidence, with a higher ratio of specular reflection observed on smoother surfaces and at larger incidence angles. This is confirmed by the few experimental results available. We further present first results of the impingement of AO on SiO2 surfaces obtained with the same method. Here we study especially the influence of different interactions. The talk is completed with an outlook on the role of specific interactions in general.