O 32: Heterogeneous Catalysis I

Time: Tuesday 10:30–12:45 Location: H25

O 32.1 Tue 10:30 H25

Stability and reactivity of metal clusters on rutile $TiO_2(110)$ under near-ambient pressure conditions — •Marina Isabel de la Higuera Domingo, Florian Kraushofer, Matthias Krinninger, Friedrich Esch, and Barbara A. J. Lechner — Technical University of Munich, TUM School of Natural Sciences, Department of Chemistry, 85748 Garching, Germany

Clusters are widely recognized for their unique performance in heterogeneous catalysis as they exhibit discrete electronic states that lead to strongly size-dependent catalytic properties [1]. However, their application in industrial processes is often limited by their instability under reaction conditions. At elevated temperatures, clusters tend to sinter, which reduces their surface area and alters their catalytic behavior.

Reducible oxides, such as titania (TiO_2), are effective supports to stabilize clusters and tune their activity through encapsulation induced by the strong metal-support interaction (SMSI) [2]. While metal nanoparticles on TiO_2 are well-studied, much less is known about the dynamics of clusters, in particular at high temperatures and pressures. In the present work, we employ near-ambient pressure scanning tunneling microscopy (NAP-STM) to study the effect of reducing and oxidizing atmospheres on metal clusters on rutile $TiO_2(110)$. We will also delve into the influence of the sample stoichiometry on its reactivity at different ambient conditions [3].

[1] A.Beck, et al. Nat.Commun. 2020, 3220.
[2] S.J. Tauster. Acc. Chem. Res. 1987, 389-394
[3] F. Kraushofer, et al. Nanoscale 2024, 17825-17837

O 32.2 Tue 10:45 H25

Structural and chemical analysis of coexisting hexagoal and monoclinic phases of samarium oxide on Cu(111) — •Björn Riedel, lars Buss, Raquel Sanchez-Barquilla, and Jan Ingo Flege — Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Germany

The absence of in-depth spectroscopic and structural studies on model systems leads to a knowledge gap in understanding how the structure of samaria influences its chemical behavior. A multi-method approach has been employed to investigate the Cu(111)-supported Sm_2O_3 surface with high structural and chemical sensitivity by using low-energy electron microscopy (LEEM) in combination with X-ray absorption photoemission electron microscopy (XAS-PEEM) and other complementary methods such as micro-spot low-energy electron diffraction (μLEED) and X-ray photoelectron spectroscopy (XPS). Our measurements show the phase coexistence of small hexagonal A-$Sm_2O_3(0001)$ islands and monoclinic B-$Sm_2O_3(100)$ rectangular-shaped islands with different rotated rectangular domains. Furthermore, the redox properties of both Sm_2O_3 phases were studied by exposing the system to reducing (H_2) and oxidizing (CO_2) conditions, indicating a face-dependent reduction and oxidation behavior. Moreover, the monoclinic $Sm_2O_3(100)$ islands appear less stable as they change to the hexagonal phase during annealing. These results indicate a highly dynamic system that can easily be adjusted by adapting the growth conditions, such as growth temperature and oxygen partial pressure.

O 32.3 Tue 11:00 H25

Digital Catalysis: Accelerated Discovery through Human in the Loop — •Charles Pare[1], Aybike Terzi[2], Christian Kunkel[1], Frederik Rüther[2], Frederic Felsen[1], Robert Baumgarten[2], Esteban Gioria[2], Raoul Naumann d'Alnoncourt[2], Christoph Scheurer[1], Frank Rosowski[2,3], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]BasCat - UniCat BASF JointLab, Berlin — [3]BASF SE, Catalysis Research, Ludwigshafen

Catalyst promoters often form key components of stable and well-performing industrial heterogeneous catalysts. Yet, today's industrial catalysts often only benefit from one or two promoters. This can often be traced back to the laborious empirical research required to identify promising formulations that jointly act to improve catalyst performance. To overcome such hurdles, we implemented an accelerated catalyst discovery approach by globally exploring a large catalyst design space using only a limited number of experiments. Its pillars are an efficient Design-of-Experiment (DoE) planning, a fast parallelized testing protocol and an iterative incorporation of experimental feedback. New and competitive promoter chemistries for the non-oxidative propane dehydrogenation to propylene over supported Pt were discovered in a limited experimental campaign. The results show the potential of iterative DoE strategies for the data-efficient knowledge-generation and optimization in complex, academically and industrially relevant catalytic systems.

O 32.4 Tue 11:15 H25

Synergistic effect of oxygen and water on the environmental reactivity of 2D layered GeAs — •Luca Persichetti[1], Giacomo Giorgi[2], Luca Lozzi[3], Maurizio Passacantando[3], Fabrice Bournel[4], Jean-Jacques Gallet[4], and Luca Camilli[1] — [1]University of Rome Tor Vergata, Italy — [2]University of Perugia, Italy; — [3]University of L'Aquila, Italy — [4]Sorbonne Université, CNRS, Paris, France

GeAs is a fascinating 2D material with compelling properties stemming from its intrinsic anisotropy. However, it reacts strongly with air, forming a Ge-oxide layer that affects its optoelectronic properties, such as contact resistance and refractive index. Investigating GeAs reactivity under realistic device conditions, including humid O2 and water exposure, is therefore crucial.

At the TEMPO beamline of Soleil, near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) was employed to study GeAs in the presence of oxygen and water. Results showed minimal reactivity with dry O2 and de-aerated water, while slight humidity (Rw = 0.5%, T = 20°C) in an O2 atmosphere significantly enhanced reactivity. Density functional theory calculations confirmed this synergistic effect, revealing a highly exothermic formation energy for the simultaneous chemisorption of O2 and H2O, compared to the adsorption of each molecule individually.

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O 32.5 Tue 11:30 H25

A comparative DFT+U study of the oxygen evolution reaction at infinite-layer, brownmillerite and perovskite nickelates — •Achim Füngerlings and Rossitza Pentcheva — Department of Physics, University of Duisburg-Essen, Duisburg, Germany

We present a detailed DFT+U investigation of rare earth nickelates $R\mathrm{NiO}_x(001)$, $R = \mathrm{La}, \mathrm{Nd}$; $x = 2, 2.5, 3$ as anode materials for the oxygen evolution reaction (OER). In these materials the Ni reaction sites at the surface exhibit different coordination, i.e. square-planar in the infinite layer ($x = 2$, IL), fivefold coordination at the (001) perovskite surface ($x = 3$) and both fourfold and fivefold coordination at the brownmillerite surface ($x = 2.5$, BM). Voltammetry measurements find a lower onset potential for the catalytically much more active infinite layer compared to the perovskite counterparts.[1] Moreover, x-ray diffraction measurements suggest that the infinite layer gradually transform into brownmillerite during OER.[1] Our calculations confirm a lower overpotential for both the infinite layer and brownmillerite phases over the respective perovskite phase. The results reveal that the oxidation state of surface Ni has a more profound effect on the catalytic activity than the coordination number, with Ni^{2+} (found at the IL and the fivefold coordinated BM site) leading to lower (0.53, 0.56 V for R=La; x=2, 2.5) and Ni^{3+} (at the fourfold coordinated site in BM and the fivefold coordinated site at the perovskite surface) leading to higher overpotentials (0.67, 0.68 V for R=La; x=2.5, 3).

[1] M. Osada, A. Füngerlings, R. Pentcheva, and H. Y. Hwang, to be submitted.

O 32.6 Tue 11:45 H25

How does lanthanum promote cobalt for ammonia synthesis in Co/La_2O_3 catalysts? — •Clara C. Aletsee, Lau H. Wandall, Ke Zhang, Oliver Christensen, Jens K. Nørskov, and Ib Chorkendorff — Physics, Technical University of Denmark

The interest in developing catalysts for ammonia synthesis, operating under milder reaction conditions than the Haber-Bosch process, has increased in the last decades. Cobalt, typically unreactive, can be activated for ammonia synthesis through the addition of lanthanum in metallic or oxidized form.[1,2] To obtain a comprehensive understanding of the promotion mechanism, we investigate the ammonia formation over Co particles on La_2O_3 by combining experiments with theory. For this, we synthesized defined model catalyst, consisting of mass-selected Co nanoparticles, deposited on La_2O_3 films generated by magnetron sputtering. Their catalytic activity was tested at 1 bar and 350-500°C in a UHV-compatible reaction cell.[3] Catalyst states before and after reaction were analyzed by X-ray photoelectron spectroscopy and low-energy ion scattering. The results, combined with previous findings on the Co/LaN system,[2] suggest that the reaction proceeds on La-promoted Co steps due to spin-mediated effects supported by theoretical calculations.[4] We further demonstrate that the activity of the Co/La_2O_3 can be partially recovered after air exposure.

[1]S. I. Miyahara *et al.*, *ACS Omega* 7, 24452-24460 (2022). [2]K. Zhang *et al.*, *Science* 383, 1357-1363 (2024). [3]K. Zhang *et al.*, *Rev. Sci. Instrum.* 94, 114102 (2023). [4]A. Cao *et al.*, *Nat. Commun.* 13, 2382 (2022).

O 32.7 Tue 12:00 H25

U-Ce charge transfer in epitaxial $Ce_{1-x}U_xO_2$ films grown on Ru(0001): consequences for thermochemical water splitting — •Carlos Morales[1], Rudi Tschammer[1], Thomas Gouder[2], Hicham Idriss[3], and Jan Ingo Flege[1] — [1]Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology, Cottbus, Germany — [2]European Commission, Joint Research Centre (JRC), Karlsruhe, Germany — [3]Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Reducible metal oxides are crucial in applications like catalysis and solar energy conversion. Among these, cerium oxide (CeO_2) stands out for its stability and activity, yet its reduction requires high energy. Ceria doping or mixing with other elements has been proven successful in increasing the conversion from Ce^{4+} to Ce^{3+}. Uranium cations are the most suitable candidates: substituting a fraction of Ce^{4+} by U^{4+} results in a charge transfer that promotes the formation of Ce^{3+} and U^{5+} states. The fundamental study of the charge transfer process requires model systems, as heat and mass transfer limitations are largely absent compared to polycrystalline powders. By in-situ X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED), we explored the redox properties and structural stability of epitaxial (111)-oriented $Ce_{1-x}U_xO_2$ on Ru(0001). The as-grown films, prepared by reactive direct current sputtering from metallic targets, show a high Ce^{4+} to Ce^{3+} conversion, reversible upon reducing-oxidizing cycles. The experimental results are discussed in the light of density function theory (DFT) calculations.

O 32.8 Tue 12:15 H25

Accelerating Surface Adsorption Energy Prediction with Machine Learning Foundation Models — •Karlo Sovic[1,2] and Johannes T. Margraf[2] — [1]University of Zagreb Faculty of Science — [2]University of Bayreuth

Determining the adsorption energies of molecular adsorbates on surfaces is critically important in heterogeneous catalysis, as well as in many other fields of materials science and chemistry. Understanding the nature and strength of adsorbate-surface interaction leads to a more rational design of efficient catalysts and improvements in their performance. While accurate first-principles calculations have brought about a revolutionary advance in our ability to predict properties and design materials *in silico*, high computational costs and poor scaling limit their application in exploring complex real-world materials. Machine-learning interatomic potentials offer a solution to this materials exploration problem. In particular, the recent emergence of pre-trained foundation models offers a data-efficient route to obtain accurate models via fine-tuning. To showcase their efficiency and performance, extensive computational research has been conducted using a fine-tuned MACE-MP-0 model to study the adsorption of glycerol on various metallic surfaces in the gas phase. This talk will present the methodology for investigating the global minima of complex adsorbate molecules on various metal surfaces, determining their respective adsorption energies, and exploring various reaction mechanisms on adsorbent's surface through computational approaches.

O 32.9 Tue 12:30 H25

Role of Co-Catalyst Loading in the Photoreforming of Tertiary Alcohols at Ambient Pressure on Titania P25 — •Paula Neumann, Clara Aletsee, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Efficient semiconductor photocatalysts are usually modified with a so-called co-catalyst, a metal particle which is commonly assumed to promote charge separation, but whose exact role remains elusive. To elucidate the influence of platinum particles loaded onto a titania powder catalyst we investigated the photoconversion of tertiary alcohols in our gas phase-photoreactor at ambient conditions. Different to its usual interpretation but in accordance with UHV studies we show that the co-catalyst facilitates the recombination of surface hydrogen. Thereby, a second reaction pathway is opened up where a C-C coupling product forms on the titania surface. Hence, identifying the mechanistics of alcohol photochemistry is not only providing insights into hydrogen formation but it also sheds light onto complex alkyl coupling reactions.