O 23: Catalysis and surface reactions – Poster

Time: Monday 18:00–20:00 Location: P2

O 23.1 Mon 18:00 P2

Investigating Single Atomic Catalytic Sites within Metal- Coordinated Supramolecular Networks via Submolecular Imaging in correlation with Electrochemical Analysis — •Duong Tran[1], Philipp Wiesener[1], Ying Pan[2], Nieves López- Salas[2], and Harry Mönig[1] — [1]Physikalisches Institut, Universität Münster, Germany — [2]Department of Chemistry, Sustainable Materials Chemistry, Universität Paderborn, Germany

Metal-organic layers serve as an excellent platform for creating single-atom catalysts (SACs). This study focuses on a heat-induced deprotonation reaction of a melem precursor and the formation of a heptazine-based metal-organic network on an Au(111) substrate. To overcome thermal desorption challenges hindering chemisorption, we developed a vacuum reactor chamber with a high-flux evaporator for precursor deposition. The resultant heptazine-based Au-nitride network aligns with previous results on Cu(111) using the same precursors. In particular, the interaction of Au(111) atoms with dehydrogenated nitrogens results in a gold atom flexibly suspended between two nitrogen atoms, indicating promising active sites for oxygen reduction reaction (ORR). Scanning tunneling microscopy (STM), noncontact atomic force microscopy (nc-AFM) with an oxygen-terminated copper tip, and X-ray photoelectron spectroscopy (XPS) confirm the strong chemisorption and stability of the network. A comparison of the catalytic performance of heptazine-based metal-nitride networks on Au(111) and on Cu(111) under ambient conditions enhances the understanding of the ORR electrochemical applications.

O 23.2 Mon 18:00 P2

Support-Dependent Thermal Activation of Pt17 Clusters on HOPG and CeO2: For-mation of Active CO Oxidation Catalysts — Papri Chakraborty[1,2,3], •Johannes Seibel[2], Nicola Da Roit[4], Artur Böttcher[2], Ajai Raj Lakshmi Nilayam[1], Christian Kübel[1], Silke Behrens[4], and Manfred Kappes[1,2,3] — [1]Institute of Nanotechnology, KIT, 76344 Eggenstein-Leopoldshafen, Germany — [2]Institute of Physical Chemistry, KIT, 76131 Karlsruhe, Germany — [3]Institute of Quantum Materials and Technologies, KIT, 76344 Eggenstein-Leopoldshafen, Germany — [4]Institute of Catalysis Research and Technology, KIT, 76344 Eggenstein-Leopoldshafen, Germany

Atomically precise ligand-protected metal clusters are attractive precursors for heterogeneous catalysts, potentially allowing for the precise control of the initial active site composition. However, the transformation from the protected cluster to the active catalyst, specifically the removal of the ligand shell, remains a poorly understood process that depends heavily on the support material. Here, we present a comparative study of the thermal activation of $Pt_{17}(CO)_{12}(PPh_3)_8(NO_3)_2$ on inert graphite, on reactive ceria CeO2 surfaces and in gas phase. For this we combined thermal desorption spectroscopy with high-resolution mass and ion mobility spectrometry to map the decomposition pathway of the cluster. Additionally we probed clusters supported on CeO2 before and after CO oxidation catalysis with transmission electron microscopy. This revealed dissociation of clusters and dispersion of the Pt atoms on the oxide support under certain reaction conditions.

O 23.3 Mon 18:00 P2

From model to powder systems: Sm-doped ceria for CO_2 conversion. — •Raquel Sánchez-Barquilla[1], Sichen Liu[1], Alexander Contreras-Payares[2], Pablo G. Lustemberg[2], Dominic Guttmann[1], Carlos Morales[1], Fabian Rachow[1], Verónica Ganduglia-Pirovano[2], and Jan Ingo Flege[1] — [1]Brandenburg University of Technology, Cottbus-Senftenberg, Germany — [2]Instituto de Catálisis y Petroleoquímica, Madrid, Spain

Reducible oxides are crucial in many heterogeneously catalyzed redox reactions because they can store and release oxygen during the catalytic cycle. Among these, cerium oxide (CeO_2) stands out due to its facile transition between the Ce^{4+} and Ce^{3+} oxidation states. Furthermore, the Ce^{3+} cations have been suggested to provide the active sites for CO_2 activation. Consequently, the catalytic performance of ceria-based catalysts may be significantly enhanced by promoting and stabilizing these sites, e. g., by alloying with trivalent rare-earth (RE) metals that also form cubic sesquioxides (RE_2O_3), such as samarium.

Here, we present a model system composed of (111)-oriented Sm-doped ceria nanoislands studied using X-ray photoelectron spectroscopy under near-ambient pressure. We show that Sm is crucial for CO_2 activation. This activation is accompanied by a charge-transfer process that modifies the measured Ce^{3+}/Ce^{4+} ratio, as explained by density functional theory calculations. Once the reaction mechanism was established, we performed *operando* absorption spectroscopy on powder catalysts with different Sm/Ce ratios to examine the effect of Sm doping under more realistic conditions.

O 23.4 Mon 18:00 P2

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 are often key components of stable and efficient industrial heterogeneous catalysts, yet most commercial systems rely mostly on one or two promoters and predominantly leverage their isolated rather than their synergistic effects. This limitation frequently results from the laborious empirical research needed to identify formulations with jointly acting components that enhance performance. To address this challenge, we implement an accelerated catalyst discovery approach that adaptively explores a large catalyst design space using only a limited number of experiments. Its foundation lies in an efficient Design-of-Experiment (DoE), parallelized testing, and iterative integration of experimental feedback. New and competitive promoter chemistries for the non-oxidative propane dehydrogenation to propylene over supported Pt are discovered within a constrained experimental campaign. The results demonstrate the potential of adaptive DoE strategies for directed, data-efficient knowledge generation and optimization in complex catalytic systems of both academic and industrial relevance.

O 23.5 Mon 18:00 P2

Automatic Kinetic Equation Discovery from Experimental Data — •Maryke Kouyate, Gianmarco Ducci, Karsten Reuter, and Christoph Scheurer — Fritz-Haber-Institut der MPG, Berlin

Optimizing and controlling industrial catalytic processes requires effective kinetic models that are both robust and interpretable, capable of predicting how key operating variables affect reactor behavior. We introduce a model-based, adaptive design-of-experiments (DoE) framework that efficiently learns parsimonious, mechanistically meaningful rate expressions from data. At each step, it selects feed conditions to maximize expected information gain.[1,2] Profile reactors further boost per-run information by providing spatio-temporally resolved composition profiles along the reactor axis. Applied to CO oxidation on Pt, the framework automatically constructs a robust, chemically interpretable kinetic model that reproduces the characteristic mid-reactor transition in concentration profiles and reveals the need for a nonlinear term to capture the observed shift from CO poisoning to a non-poisoned regime.

[1] G. Ducci *et al.*, J. Chem. Phys. **162**, 114118 (2025).

[2] M. Kouyate *et al.*, J. Chem. Phys. (in press), DOI: 10.1063/5.0289751

O 23.6 Mon 18:00 P2

Structural development of new defective titanium carbon phosphorus hybrid composites by soft x-ray spectroscopy — •Hesham Hamad — City of Scientific Research and Technological Applications, Alexandria, Egypt — Elettra Sincrotrone Trieste, Trieste, Italy

The discovery of "black" TiO2 nanoparticles with enhanced solar absorption in the visible and near-infrared regions has sparked growing interest in solar energy applications. However, their properties remain incompletely understood. In this work, we explore a sustainable defective titanium*carbon*phosphorous (TCPH) hybrid nanocomposite for photocatalytic applications. TCPH was synthesized and applied in the degradation of methyl orange (MO) dye, a model organic pollutant. Characterization revealed the presence of Ti3+ species, oxygen vacancies, and a core-shell structure, along with a significant increase in surface area. These features enhance charge transport and separation, leading to excellent photocatalytic activity. X-ray photoelectron spectroscopy (XPS) confirmed the Ti3+ modifications in TCPH. To further probe its properties, synchrotron-based X-ray absorption fine structure (XAFS) spectroscopy was employed. This advanced technique provides insights into unoccupied and occupied states, particularly the O 2p and Ti 3d hybrid orbitals, revealing the electronic and crystalline structures of anatase, rutile, Ti metal, and TCPH. The combination of XAFS with complementary methods, including XRD, XPS, and HRTEM, enables a comprehensive understanding of TCPH's morphology, crystallinity, and local electronic structure.

O 23.7 Mon 18:00 P2

Cooperative Co-Fe Effect on the OER Activity of $CoFe_2O_4$ (100), (001) and (111) surfaces — Shohreh Rafiezadeh, •Aparna Chaitram, and Rossitza Pentcheva — Department of Physics, University of Duisburg-Essen, Duisburg

Water splitting, a key method for green hydrogen production, is limited by the sluggish anodic half process - the oxygen evolution reaction (OER) [1]. This necessitates finding efficient and affordable electrocatalysts which can reduce the overpotential. Using density functional theory calculations with an on-site Hubbard U term, we study the OER activity of the $CoFe_2O_4$ (001), (100), and (111) surfaces, exploring a wide range of potential active sites and the effect of solvation. The lowest overpotential of 0.20 V is found for an octahedral Co at the A-layer termination of the (100) surface, which contains both Fe and Co. This is attributed to the synergistic stabilization of the *OOH intermediate by binding to a neighbouring Fe site[2]. Remarkably, sites with higher catalytic activity are found to retain bulk like oxidation states. Our results show that such bonding configurations that break the OER scaling relationships reveal new routes to designing catalysts for water splitting.

We acknowledge funding by DFG within CRC TRR 247.

[1] J. Rossmeisl, Z. W. Qu, H. Zhu, G. J. Kroes, and J. K. Nørskov, *J. Electroanal. Chem.* 607, 83 (2007).

[2] S. Rafiezadeh, A. Chaitram, R. Pentcheva, *ChemCatChem* (2025), DOI: 10.1002/cctc.202501290.

O 23.8 Mon 18:00 P2

Probing the active state of Cu(111) for plasma-catalytic CO_2 hydrogenation — •Luka Babić and Roland Bliem — ARCNL, Materials & Surface Science for EUVL, Science Park 106, 1098 XG Amsterdam, The Netherlands

Plasma catalysis combines the concept of heterogeneous catalysis with the activation of reactants by a plasma discharge. The activation of strong molecular bonds is expected to change the kinetics of challenging reactions such as the hydrogenation of CO_2 to methanol. This reaction proceeds in a mixed H_2/CO_2 plasma, which consists of a multitude of species, including radicals, atoms, and ions with energy stored in various states and degrees of freedom. The state of surfaces interacting with this complex mixture is poorly understood, even for well-defined single-crystalline model catalysts.

Here, we use in situ X-ray photoelectron spectroscopy (XPS) and residual gas analysis to disentangle reaction pathways and the evolution of a Cu(111) model catalyst surface during exposure to radicals generated in plasma. Optical emission spectroscopy (OES) is used to characterize plasma and to assess the species hitting the surface during the exposure. XPS reveals the formation of adsorbed oxygen, followed by Cu(I) and finally Cu(II) oxides. Carbon is fully absent during the reaction with neutral activated CO_2 species. Upon reduction by plasma-activated hydrogen, hydroxides are formed. Depending on the operating conditions, we thus expect the active surface of a Cu plasma catalyst to be either Cu hydroxide or Cu metal.

O 23.9 Mon 18:00 P2

Size selected Pt clusters on a CeO_2(111) support: mobility, reactivity and dimensionality — •Fabian Heisinger, Johanna Reich, Mina Soltanmohammadi, Rasmus Bischoff, Friedrich Esch, and Barbara A.J. Lechner — TU Munich, Germany

Ceria is a renowned material for its exceptional oxygen storage capacity with applications in catalysis. Central to this functionality are oxygen vacancies and their mobility. In interaction with metal catalyst particles, this reducible oxide is highly versatile, as we demonstrate for size-selected Pt clusters on a single-crystalline ceria film. We study oxidation reactions as a function of cluster size, dimensionality, support reduction, and gas environment. With conventional and fast STM, we directly observe the dynamics of surface vacancies and supported clusters to determine cluster shape changes related to defect density and sintering. We combine this cluster height and coverage monitoring with LEED and XPS to characterize the CeO_2 films in crystallinity, thickness, oxidation state, and Pt coverage. We demonstrate that the Pt cluster dimensionality during sintering can be steered by controlling the oxygen vacancy coverage on the support[1]. Through STM, we track the mobility of O vacancies in an effort to correlate their dynamics with cluster properties, and the cluster dynamics to unravel the influence of their shape on stability and catalytic activity. These dimensionality-tuned, size-selected clusters provide an ideal platform to study the structural dynamics of small metal clusters during an ongoing oxidation reaction.

[1] Reich, Johanna, et al. ACS catalysis 15 (2025): 18369-18382.

O 23.10 Mon 18:00 P2

Metal clusters on rutile TiO_2(110) as model catalysts: Stability and reactivity under near-ambient pressure conditions — •Jonathan Paul, Marina Isabel de la Higuera Domingo, Lorenz Falling, Florian Kraushofer, Matthias Krinninger, and Barbara A. J. Lechner — Technical University of Munich, TUM School of Natural Sciences, Department of Chemistry, 85748 Garching, Germany

Clusters frequently exhibit strongly size-dependent catalytic properties and have discrete electronic states, often leading to a particularly high activity in heterogeneous catalysis. However, at the elevated temperatures typically employed in industrial applications, clusters tend to sinter into larger particles, which can lead to a decrease in catalytic activity. Reducible oxide supports, such as titania (TiO_2), are effective materials for stabilizing clusters and can further modify their catalytic behavior through encapsulation effects induced by the strong metal-support interaction (SMSI).

Here, we employ near-ambient-pressure scanning tunneling microscopy (NAP-STM) to investigate how reducing, oxidizing and reaction atmospheres influence the stability, structural dynamics and geometry of Pt and Ni clusters supported on rutile TiO_2(110).[1] Structural insights obtained from microscopy are complemented by a highly sensitive sniffer setup for activity measurements, investigation of reaction mechanisms and determination of turnover frequencies.[2]

[1] F. Kraushofer, et al. J. Am. Chem. Soc. 2025, 39846-39859.

[2] J. Reich, et al. Top. Catal. 2024, 880-891.