O 81: Heterogeneous Catalysis III

Time: Thursday 10:30–12:30 Location: H6

O 81.1 Thu 10:30 H6

Cu Oxide Nanoparticles for Virus Inactivation — •Daniel Silvan Dolling[1,2], Miguel Blanco Garcia[1,2], Mona Kohantorabi[1], Mohammad Ebrahim Haji Naghi Tehrani[1,2], Jan-Christian Schober[1,2], Ming-Chao Kao[1,2], Jagrati Dwivedi[1], Arno Jeromin[1], Thomas F. Keller[1], Olof Gutowski[3], Dimitry V. Novikov[3], Andreas Stierle[1,2], and Heshmat Noei[1] — [1]Centre for X-ray and Nano Science CXNS, Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany — [2]Fachbereich Physik, Universität Hamburg, Jungiusstraße 11, 20355 Hamburg, Germany — [3]Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, 22607 Hamburg, Germany

TiO_2 is known to inactivate SARS-CoV-2 photocatalytically under UV light. Recently, it has been shown that Cu oxide on Titania shifts the photoactivty into the visible light region. The specific oxidation state of Cu is paramount for the photocatalyst efficiency. Here, we use single crystalline TiO_2 to investigate the effects of growth conditions of Cu nanoparticles (NPs). To this cause, we employ X-ray diffraction (XRD) and scanning electron microscopy (SEM), revealing a temperature-dependent morphology. Subsequently, we analyze the short- and long-term oxidation behavior with X-ray photoelectron spectroscopy (XPS) and scanning Auger microscopy (SAM). Finally, we investigate the interaction of the NPs with asparagine amino acid using reflection-absorption infrared spectroscopy (IRRAS) and grazing-incidence small-angle scattering (GISAXS).

O 81.2 Thu 10:45 H6

Charting Catalysis: Unveiling Regime Boundaries in Kinetic Phase Spaces Through Concentration Profiles — •Maryke Kouyate, Gianmarco Ducci, Frederic Felsen, Christian Kunkel, Karsten Reuter, and Christoph Scheurer — Fritz-Haber-Institut der MPG, Berlin

In an industrial context, optimizing process variables is a critical step in ensuring optimal performance of catalytic reactors. Selecting the relevant process variables not only aids in meeting precise requirements but also in streamlining reactions and thus saving time and costs. Robust kinetic rate laws capable of accurately describing experimental data allow for predictive modelling in reactor design, optimization, and control. Specialized profile reactors efficiently yield the required data to derive kinetic models by providing access to spatio-temporally resolved chemical information along the reactor axis. Depending on the range of experimental conditions and the catalytic reaction, the kinetic phase space can exhibit sub-regions of smooth kinetic behavior, separated by transitional regions characterized by sudden qualitative changes of the kinetic behavior. These kinetic phase transitions carry important information about the catalytic reaction network. To pinpoint distinct sub-regions and corresponding models within a kinetic phase diagram, we propose an automated system capable of systematically exploring the design space. This algorithm manages the experimental reactor and iteratively suggests new experiments through model-based design of experiments.

O 81.3 Thu 11:00 H6

Mechanistic Probes for Photocatalysis: Gas Phase Reactions of Tertiary Alcohols on Titania in a Micro-Photoreactor — •Martin Tschurl[1], Clara Aletsee[1], Paula Neumann[1], Ib Chorkendorff[2], and Ueli Heiz[1] — [1]Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany — [2]SurfCat Section for Surface Physics and Catalysis, Department of Physics, Technical University of Denmark, 2800 Kgs Lyngby, Denmark

The lack in mechanistic understanding still hinders the rational design of efficient photocatalyst for various applications. To gain more comprehensive insights into the fundamental effects in photocatalysis, we analyze the gas phase photoreactions of tertiary alcohols on titania powder in a micro-photoreactor in a well-defined environment under the exclusion of oxygen. The parallels of the observed reaction properties to studies performed on a rutile single crystal in vacuum suggest similar mechanistics, which is in contrast to the generally assumed reaction model under such conditions. Furthermore, the time resolution of the micro-reactor setup allows the determination of the alcohol surface coverage, which excludes the existence of liquid films and evidences a gas phase reaction. In addition to the scientific insights on photocatalysis on titania, these results demonstrate the use of tertiary alcohols as suitable probe reactants for mechanistic studies.

O 81.4 Thu 11:15 H6

Selectivity trends in CO hydrogenation over transition metal surfaces — •David Degerman[1,2], Patrick Lömker[1], Markus Soldemo[1], Fernando Garcia-Martìnez[3], Robin Yoël Engel[1,2], Martin Beye[1,2,3], and Anders Nilsson[1,2] — [1]Department of Physics, Stockholm University, 114, 21, Stockholm, Sweden — [2]WISE - Wallenberg Initiative Materials Science for Sustainability, Department of Physics, Stockholm University, 114, 21, Stockholm, Sweden — [3]Deutsches Elektronen Synchrotron, DESY, Photon Science, Notkestraße, 22607, Hamburg, Germany

Understanding the selectivity of heterogeneously catalyzed CO hydrogenation is increasingly important for the transition towards a sustainable chemical industry. While theoretical studies yielded a model based on the competition of various elementary surface reactions, we need experimental observation of the surface's chemical state to verify the mechanistic origin of the selectivity. Here, we compare in-situ x-ray photoelectron spectra over operating single crystal catalysts (200 to 325 °C, 150 mbar) of Fe, Rh, Ni, Co and Cu and infer from the observed trends which mechanistic steps decides the product distribution for each material. In particular, we find that the chemisorption energies of C and O (commonly used descriptors for activity and selectivity) qualitatively predicts the rate-limiting step of catalysts, but fails when the reaction mechanism of Ni and Fe is fundamentally altered due to reaction-induced carburization. This work emphasizes that the complete chemical overview provided by photoemission spectroscopy is required to understand the selectivity of CO hydrogenation.

O 81.5 Thu 11:30 H6

Exploration of Explicit Solvation Effects in Heterogeneous Catalysis Using Machine Learning Interatomic Potentials — •Maciej Baradyn and Johannes T. Margraf — University of Bayreuth

The presence of solvent affects many aspects of modeling elementary reactions involved in heterogeneous catalysis, such as stabilization of adsorbed species, the nature of interaction with the surface, as well as energetics and reaction rates, to name just a few. Unfortunately, treating solvent effects in atomistic simulations is a great challenge, since the solvent adds many additional degrees of freedom to the calculation. In first-principles calculations, implicit solvation models are often used to approximately include these effects with moderate computational effort. However, they do not take into account the explicit solvent-surface and solute-solvent interactions, and are therefore known to fail, e.g. when hydrogen bonding is important. More importantly, the solvent molecules can sometimes play a decisive role in the reaction's mechanism (e.g. as proton shuttles), which cannot be captured by implicit models, where solvent is treated as a continuous medium. In this contribution, we explore the efficiency of machine learning potentials based on the MACE-MP-0 foundation model for describing explicit solvation at catalytic interfaces. These potentials are used to capture the kinetic and thermodynamic parameters of small organic molecules interacting with metallic surface in an explicit water bath. Implications for our understanding of the underlying catalytic reaction network and improved design of catalysts will be discussed.

O 81.6 Thu 11:45 H6

Reducibility of Sm-doped ceria islands on Ru(0001) — •Raquel Sanchez-Barquilla, Rudi Tschammer, Lars Buss, Carlos Morales, and Jan Ingo Flege — Applied Physics and Semiconductor Spectroscopy, BTU Cottbus-Senftenberg, Germany

The interaction between metal and oxide is critical when considering the hydrogenation of CO_2 to hydrocarbons. In this context, the inverse oxide/metal catalysis architecture allows for achieving better catalytic performance due to strong oxide-metal interactions. In particular, in cerium-based inverse catalyst systems, the Ce^{3+} cations have been demonstrated to play an active role in methanol synthesis, suggesting that the activity can be enhanced by promoting those through alloying with trivalent, catalytically active rare-earth metals, such as Sm.

Here, we present a low-energy and X-ray photoemission electron microscopy (LEEM/XPEEM) investigation that shows how the reducibility of $CeO_2(111)$ islands on Ru(0001) is highly enhanced when doped with Sm. After post-annealing with Sm, intensity-voltage (I-V) LEEM curves show an immediate reduction of the islands at the surface. Exposure to low H_2 pressures efficiently reduces the islands to a (3×3) superstructure formed by ordered oxygen vacancies, as evidenced by characteristic IV-LEEM spectra and low-energy electron diffraction patterns. Furthermore, annealing at high temperatures shows the further reduction of the Sm-ceria islands, with features characteristic of the hexagonal $Ce_2O_3(0001)$ phase. While this reduction takes about one hour for pure ceria, this transition is virtually immediate for the Sm-doped ceria islands at comparable conditions.

O 81.7 Thu 12:00 H6

Interaction of single cobalt co-catalyst atoms with the $SrTiO_3$(001) surface — •Aji Alexander[1], Pankaj Kumar Samal[1], Llorenç Albons[1], Jan Škvára[1], Dominik Wrana[2], Viktor Johánek[1], Josef Myslivecek[1], and Martin Setvin[1] — [1]Department of Surface and Plasma Science, Charles University, Prague, Czech Republic — [2]Marian Smoluchowski Institute of Physics, Jagiellonian University, Krakow, Poland

Perovskite surfaces attract attention in the catalysis community due to their promising chemical properties, ability to separate electron-hole pairs for light harvesting, and ferroelectricity in various phases. Understanding metal clusters, specifically their electronic structure and atomic utilization efficiency, is crucial for developing more efficient and sensitive catalysts.

This work focuses on the atomic structure of doped $SrTiO_3(001)$ perovskite surface and the potential to modify its catalytic activity by the presence of extrinsic metals, with the main focus on cobalt. Combined STM/AFM, LEED, and XPS show a combination of cobalt clustering and dispersion within an ordered reconstruction. We will highlight how cobalt interacts with perovskite surfaces at different reducing conditions and explain the various phases of the supported cobalt as a function of temperature.

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O 81.8 Thu 12:15 H6

Machine Learning Assisted Realistic Description of Mo-V Mixed Oxide Surfaces — •Kyeonghyeon Nam, Y. Song, L. Masliuk, T. Lunkenbein, A. Trunschke, K. Reuter, and C. Scheurer — Fritz-Haber-Institut der MPG, Berlin

The activity and selectivity of realistic heterogeneous catalysts can be noticeably altered by subtle changes in factors such as bulk composition, dopants, defects, and reaction conditions. These effects are intricately interrelated. To systematically unravel them, we aim to understand their impact on the evolution of catalyst surfaces. Specifically, we focus on the M1 structural modification of $(Mo,V)O_x$ and $(Mo,V,Te,Nb)O_x$ as selective catalysts for the oxidative dehydrogenation of ethane to ethylene.

The large primitive cell of the M1 catalyst poses challenges for a detailed study of its surface terminations using conventional first-principles calculations. To overcome this, we trained machine learning interatomic potentials (MLIPs) using a staged training method from motifs to surfaces. By combining density-functional tight-binding (DFTB) calculations with simulations employing MLIPs, such as molecular dynamics and *ab initio* thermodynamics (AITD), we elucidated the influence of niobium and tellurium doping on enhanced surface structure stability and catalytic activity during the thermal activation. This was supported by experimental *quasi-operando* scanning transmission electron microscopy (STEM) images.