O 41: Heterogeneous Catalysis II

Time: Tuesday 14:00–15:15 Location: H8

O 41.1 Tue 14:00 H8

Oxide growth and oxide/metal interaction in $\mathbf{CeO}_x$/Ni(111) — •Dominic Guttmann, Raquel Sánchez-Barquilla, Carlos Morales, and Jan Ingo Flege — Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus 03046, Germany

Ni/ceria catalysts exhibit a high activity and selectivity for CO_2 methanation, making them very promising candidates for applications within a sustainable economy. The redox properties of cerium oxide allow it to readily switch between Ce^{4+} and Ce^{3+} states, facilitating CO_2 activation and conversion. We have studied the so-called strong metal-metal oxide interactions in the inverse catalyst configuration CeO_x/Ni(111) prepared by reactive molecular beam epitaxy in an oxygen atmosphere. Under specific growth conditions, the CeO_x (111)-oriented islands of different heights preferentially align in registry with the Ni(111) surface or are rotated azimuthally by ±10°, as observed by low-energy electron diffraction. Analysis by X-ray photoelectron spectroscopy reveals that during growth, partial oxidation of the Ni(111) surface leads to the formation of a NiO interface layer between the CeO_x islands and Ni substrate, resulting in a complex CeO_x(111)/NiO(111)/Ni(111) system with significant oxide-metal interactions. Finally, when we expose the system to H_2, O_2, and CO_2 atmospheres, we observe a complex behavior of the cerium and nickel oxidation states, which correlate with morphological changes in the oxide islands.

O 41.2 Tue 14:15 H8

Size-dependent nanoparticle sintering under catalytic reaction conditions — •Thomas Florian Keller[1,2], Christoph Seitz[1], Henning Runge[1], Vedran Vonk[1], and Andreas Stierle[1,2] — [1]Centre for X-ray and Nano Science CXNS, Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — [2]University of Hamburg, Department of Physics, Hamburg, Germany

Catalytic metal nanoparticles applied in heterogeneous gas phase catalysis are known to change their shape during the conversion. We elucidate the evolution of the height to diameter aspect ratios of a substantial number of PtRh alloy nanoparticles exposed to mild and harsh catalytic CO oxidation reaction conditions by correlative atomic force- and scanning electron-microscopy. The preferentially (111) oriented Pt rich nanoparticles supported on a (0001) Al_2O_3 single crystal surface were imaged as grown and after the exposure to the catalytic conditions. We utilized an image-registration based approach combined with one-by-one nanoparticle correlation to overcome single nanoparticle studies and ensemble averages. This approach permitted us to shed light onto the active size dependent sintering mechanism as e.g., particle migration and coalescence, and Ostwald ripening. While for mild catalytic conditions the aspect ratio is rather independent of the lateral nanoparticle size, for harsh conditions particles above an initial threshold diameter of around 45 nm tend to extraordinary grow on the cost of the surrounding smaller particles.

O 41.3 Tue 14:30 H8

High-throughput photocatalytic screening of lead-free halide perovskites with bayesian optimization for surface photovoltage — •Astita Dubey[1,2], Mahshid Ahmadi[2], Vladimir Shvartsman[1], Sergei Kalinin[2], and Doru Lupascu[1] — [1]Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, Universitätsstr. 15, 45141 Essen, Germany — [2]Institute for Advanced Materials and Manufacturing, Department of Materials Science and Engineering, The University of Tennessee Knoxville, Knoxville, TN 37996, USA

The development of lead-free, stable, and efficient catalysts for energy conversion necessitates rapid materials discovery. In this study, we employed Bayesian optimization (BO) to investigate a one-dimensional binary combinatorial library of zero-dimensional lead-free halide perovskites (A3Bi2I9 types) synthesized using a high-throughput automated pipetting robot. Structural analysis revealed hexagonal P6*/mmc symmetry throughout the library with pronounced variations in the lattice parameter c. Gaussian process-based BO identified the optimal composition featuring 49% cesium substitution, which demonstrated the best photocatalytic activity and stability attributed to the enhanced surface photovoltage and optimized anion vacancies. This composition achieved complete degradation of rhodamine B and methylene blue dyes within 15 and 20 minutes, respectively. The identified composition's stability, defect management and the most efficient photocatalytic activity among 96 compositions is promising for its further use in water splitting.

O 41.4 Tue 14:45 H8

Automatic Exploration of Catalytic Reaction Networks — •Hyunwook Jung, Johannes T. Margraf, Hendrik H. Heenen, and Karsten Reuter — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195, Berlin

The reaction network is a crucial element of first-principles microkinetics simulations, representing the connection between surface species and elementary reactions. Lacking systematic exploration methods, the reaction network is presently typically set up by human intuition. Especially for complicated processes such as syngas conversion, this is error prone and the absence of important species and reaction steps can be a source of sizable discrepancy between theoretical modeling and experiment. To address this problem, we introduce an automatic reaction network exploration scheme that starts with a fully enumerated, yet redundant reaction network, in which a reaction pathway is refined iteratively. The associated computational cost for extensive sampling of structures for both adsorption and activation energy calculations along the pathway is circumvented by simultaneously fine-tuning a MACE foundation model. Each trial reaction pathway is coupled with corresponding mean-field microkinetics and a detouring operation is attempted for the identified rate-limiting step. This procedure is repeated until user-defined criteria are reached. We demonstrate this automatic scheme on methanol synthesis at a Cu(111) surface.

O 41.5 Tue 15:00 H8

Functionalization of atomically defined Au step edges with N-heterocyclic carbenes for the electrocatalytic reduction of carbon dioxide — •Philipp Wiesener[1], Duong Tran[1], Ankita Das[2], Ying Pan[3], Nieves Lopez Salas[3], Frank Glorius[2], and Harry Mönig[1] — [1]Physikalisches Institut, Universität Münster, Münster, Germany — [2]Organisch-Chemisches Institut, Universität Münster, Münster, Germany — [3]Institut für Chemie, Universität Paderborn, Paderborn, Germany

N-Heterocyclic carbenes (NHCs) are versatile ligands allowing to tune the catalytic performance of metal surfaces and nanoparticles. In recent years, the understanding of molecular adsorption of a variety of NHC compounds on flat single crystalline surfaces has significantly advanced the knowledge about their extraordinary properties. In the present work, we use scanning tunneling microscopy (STM) and non-contact atomic force microscopy (nc-AFM) to investigate the adsorption of various NHCs on a Au(788) surface, featuring a high density of atomically defined step edges. Our results reveal that NHC nucleation is significantly more stable at the step edges than on flat terraces. Correlating sub-molecular imaging techniques with voltammetry, we demonstrate the formation of a macroscopically defined and catalytically active nanostructure for the CO_2 reduction reaction. Our results spotlight the important role and opportunities of step edge functionalization by NHC compounds to design highly efficient and selective catalysts with defined active sites.