O 81: Catalysis and surface reactions II

Time: Thursday 10:30–12:15 Location: TRE/MATH

O 81.1 Thu 10:30 TRE/MATH

Pd/Cu single atom alloys for selective alcohol dehydrogenation: from single crystalline to nanostructured model catalysts — •Philipp Alexander Fredersdorff[1], Jan Smyczek[1], Carsten Schroeder[1], Paul Froehlich[1], Paul Kohlmorgen[1], Stephan Appelfeller[2], Konstantin Neyman[3], and Swetlana Schauermann[1] — [1]Institute of Physical Chemistry, University Kiel, 24118 Kiel, Germany — [2]MAX IV Laboratory, Lund University, 22100 Lund, Sweden — [3]Departament de Ciència de Materials i Química Física & Institut de Química Teòrica i Computacional (IQTC-UB), Universitat de Barcelona, Barcelona 08028, Spain

Single-atom alloy (SAA) catalysts offer atomic-level control of selectivity, yet structure reactivity relationships in realistic systems remain insufficiently understood. Here, we report the first preparation of well-defined Pd/Cu single-atom alloy nanoparticles under UHV on Al2O3/NiAl(110) and investigate their properties using IRAS CO titration, STM, and TPD. Temperature-dependent Pd de-aggregation shows the same behaviour as on Pd/Cu(111), with optimal incorporation at 550 K. Both de-aggregated materials catalyze the non-oxidative dehydrogenation of butanol, but only the nanostructured Pd/Cu-NP SAA achieves 100 percent selectivity, completely suppressing CO formation. A Pd-coverage-dependent analysis reveals that cluster formation rapidly decreases aldehyde selectivity on single-crystal Pd/Cu(111), whereas the newly developed nanostructured SAA catalysts maintain full selectivity across a wide Pd range.

O 81.2 Thu 10:45 TRE/MATH

Acetylene Cyclotrimerization to Aromatic Products on Coinage Metal Surfaces — Nipun T. S. K. Dewage[1], •Dennis Meier[1], Santu Biswas[2], Matthew M. Montemore[2], and E. Charles H. Sykes[1] — [1]Department of Chemistry, Tufts University, Medford, Massachusetts 02155, USA. — [2]Department of Chemical and Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, USA.

Benzene and toluene are indispensable chemical feedstocks used in products ranging from pharmaceuticals to building materials. They are primarily produced through petroleum cracking and reforming, which require high energy input, severe operating conditions, and lack 100% selectivity. As the chemical industry transitions from oil to shale gas as its primary hydrocarbon feedstock, interest is growing in alternative routes to synthesize aromatics. One promising approach is the cyclotrimerization of acetylene, which uniquely yields benzene with 100% selectivity on Ag(111) in ultra-high vacuum. However, this reaction requires more than a monolayer of acetylene to initiate benzene formation, necessitating high pressures that may limit industrial viability. In this work, we investigate strategies to enhance the activity of this reaction on coinage metal surfaces.

O 81.3 Thu 11:00 TRE/MATH

Automated Workflow for Kinetic Modeling in Heterogeneous Catalysis: A Case Study of the Ammonia Oxidation Reaction — •Emanuel Colombi Manzi, Hyunwook Jung, Hendrik H. Heenen, Vanessa J. Bukas, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Developing reliable kinetic models in computational catalysis is a big challenge, especially when involving large reaction networks with complex intermediates. Atomistic models built upon first-principles energetics, typically density-functional theory (DFT), are widely used today for elucidating catalytic mechanisms and trends. The cost of DFT calculations, however, makes these models far too expensive to thoroughly sample the many structural configurations that are possible for all relevant surface-bound intermediates. As a result, assumptions on the preferred geometry or surface binding site are commonly adopted based on chemical intuition. Here, we present a fully automated workflow that derives an entire microkinetic model without any *a priori* knowledge or heuristics about the preferred binding configurations. The approach is demonstrated on the kinetics of NH_3 oxidation over selected metal surfaces and alloys. Enabled by an efficient DFT-trained machine learned interatomic potential, an ensemble of low-energy adsorbate structures is identified through global optimization and all process barriers between them are systematically computed. Our simulations provide chemical insight beyond the limitations of standard DFT models and open the road for large-scale screening studies without the need of simplifying assumptions like scaling relations.

O 81.4 Thu 11:15 TRE/MATH

Adsorption of CO and CO_2 on MgO(100) single-crystal surfaces investigated by polarization-resolved IRRAS — •Wangtao Li, Zairan Yu, Alexei Nefedov, Christof Wöll, and Yuemin Wang — Institue of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

MgO, a low-cost alkaline metal oxide material, is widely used in heterogeneous catalysis. Comprehensive understanding of MgO-based catalysts requires reliable reference data from surface science studies on MgO model systems. Here, we present polarization-resolved reflection absorption spectroscopy (IRRAS) data obtained for CO and CO_2 adsorption on MgO(100) single-crystal surfaces using a sophisticated UHV apparatus (THEO). The low-temperature (67 K) and temperature-dependent IRRAS results provide deep insights into the interaction of CO and CO_2 with MgO(100). The p- and s-polarized IRRAS data enable detailed analysis of vibrational frequencies, adsorption configurations, and binding energies of different species bound to distinct surface sites including defects. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - Project-ID 426888090 - SFB 1441.

O 81.5 Thu 11:30 TRE/MATH

Experimental Modelling of Ti-based (Photo-)Catalysts for the Activation of Greenhouse Gasses — •Lars Mohrhusen — Carl von Ossietzky Universität Oldenburg, Germany

Sustainable catalysts are key materials for future energy technologies and the activation of greenhouse gasses via thermal and photocatalysis. To replace critical raw materials such as (noble) metals in (photo-)catalysts, we combine low-dimensional (semi-)metallic structures such as point defects or 2D materials with oxides to hybrid materials. Combined insights from spectroscopy, microscopy and reactivity studies on well-defined model systems under UHV or so-called operando conditions gains a comprehensive atomistic picture.[1−3]

Selected examples for such Ti-based materials relevant for solar photocatalysis will be presented. Therein, the activation of greenhouse gas molecules (esp. N_2O and CO_2) on Ti^{3+} and Ti^{2+} defects will be illuminated.[3,4] While such gases interact weakly with defective rutile TiO_2 in UHV, higher pressures of CO_2 combined with the presence of water as an H donor were found to enable a rich reduction chemistry along multiple parallel pathways in operando-XPS.[4] In addition to oxides, nanostructured 2D titanium disulphide (TiS_2) as well as conjugated organic polymers on metal and oxide surfaces represent potential candidates for photocatalytic applications.[5]

[1] L. Mohrhusen et al., J. Phys. Chem. C 2022, 126, 48, 20332. [2] L. Mohrhusen et al., Small 2024, 2405715. [3] L. Mohrhusen K. Al-Shamery, Catal. Lett. 2023, 153, 2, 321. [4] J. Klimek, et al. under review [5] N. Kruse et al. Small 2025, 38, e06023.

O 81.6 Thu 11:45 TRE/MATH

Studying low surface area photocatalysts at ambient pressure in a microreactor — •Paula Neumann[1], Clara Aletsee[2], Martin Tschurl[1], 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

While driving reactions with solar light is an ambitiously pursued goal, current approaches often suffer from low efficiencies due to missing knowledge about reaction dynamics on the catalysts surface. Here, the application of highly defined photocatalysts may allow deeper mechanistic insight but their low surface area imposes high demands on detection sensitivity for studying reactions at ambient conditions. Our gas-phase microreactor enables time-resolved investigation of planar photocatalysts by mass spectrometry in a well-defined reaction environment. Using the photo-oxidation of alcohols on a titania photocatalyst as a model system we show how reaction mechanisms first established in the ultra-high vacuum transfer to conditions of 1000 mbar. Disentangling the mechanistics of alcohol photochemistry might be a crucial step towards improving hydrogen formation as an important energy carrier as well as opening up pathways for the production of higher-value chemicals.

O 81.7 Thu 12:00 TRE/MATH

Model-Free Reconstruction of Local Kinetic Information on Catalytic Surfaces from Operando Profile Measurements — •Jinyi Zhou[1], Mishai Avila[2], Daniel Runge[3], Lukas Thum[4], Heinz Junkes[1], Michael Geske[2], Christian Merdon[3], Frank Rosowski[2,5], Karsten Reuter[1], Christoph Scheurer[1], and Sebastian Matera[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]BasCat - UniCat BASF JointLab, TU Berlin — [3]Weierstraß-Institut, Berlin — [4]Helmholtz-Zentrum Berlin — [5]BASF SE, Catalysis Research, Ludwigshafen, Germany

Operando characterization experiments are typically strongly affected by transport effects, which can cause strong local variations of reactivity and concentration on the catalytic surface. We present a framework that allows one to obtain this local kinetic information from a measured concentration profile away from the active surface, without assuming any specific kinetic model. Utilizing Green's functions of the transport operator and a function space formulation of the inverse problem, the approach allows robust reconstruction from finite, noisy data. We apply this approach to a compact profile reactor, where concentration is measured along the axis of a channel flow with catalyst deposited on the channel walls. Using synthetic data, we demonstrate that the approach has the potential to resolve sub-millimeter variations in surface reactivity with modest computational and experimental footprints. Additional challenges that need to be overcome in order to fully exploit this potential for high accuracy when using experimental data will be discussed.