Surface Science
Room 305 - Session SS-WeM

Heterogeneous Catalysis

Moderators: Gengnan Li, Argonne National Laboratory, **Joerg Libuda**, Friedrich-Alexander-University Erlangen-Nürnberg (FAU)

8:00am **SS-WeM-1 Molecular Systems for Reversible Hydrogen Storage: Atomistic-Level Insights*, Swetlana Schauermann,*** Kiel University, Germany **INVITED**

Heterogeneous catalysts based on bimetallic single atom alloys (SAA) play a significant role in numerous technical processes. The fundamental working principles of these systems, however, remain poorly understood, especially the aspects related to the nanoscopic nature of bimetallic particles and the associated structure-reactivity relationships. In this study, we developed well-defined SAA catalysts consisting of Pd atomically dispersed in Cu nanoparticles prepared under ultra-high vacuum conditions on model Al_2O_3/NiAl(110) support.[1] Employing a unique combination of surface sensitive techniques – scanning tunning microscopy (STM), infrared reflection absorption spectroscopy (IRAS), molecular beams – and density functional theory (DFT) calculations, we performed detailed structural characterization of these systems at the microscopic level. We demonstrate that Pd disperses atomically in Cu nanoparticles and becomes partly negatively charged. Importantly, these Pd/Cu nanostructured systems show an outstanding catalytic performance in selective dehydrogenation of butanol and exhibit 100 % selectivity toward butanal over a broad range of Pd loadings – the property that cannot be reproduced employing simplified single crystalline Pd/Cu(111) counterparts.

In the second part, the catalytic decomposition of 2-propanol to acetone over Co_3O_4(111) catalyst will be addressed with the specific focus on the role of water and its derivatives in the reaction mechanism and the overall catalytic activity.[2] Pre-treatment of this catalyst with water at elevated temperatures (573 K) was shown to result in a substantial increase in the acetone formation rate. Combined STM and IRAS studies revealed that this procedure leads to the formation of isolated hydroxyls involving a lattice oxygen atom, which play a key role in H abstraction, both from molecular 2-propanol and from the propoxy reaction intermediate, leading to efficient formation of the target product acetone. Our results suggest that the isolated O_sH group is substantially more efficient hydrogen acceptor than the adsorbate-free lattice oxygen O_s.

1. *"Pd/Cu single atom alloys for selective alcohol dehydrogenation: from single crystalline to nanostructured model catalysts"*, P. A. Fredersdorff et al, Angew. Chem. Int. Edit. **(2026)** 65, e21885
2. *"Promoting role of isolated surface hydroxyls on selective dehydrogenation of 2-propanol to acetone over Co_3O_4 catalyst: a mechanistic study."*J. Smyczek et al, ACS Catalysis **(2025)** 15, 19268

8:30am **SS-WeM-3 When Interfaces Break Scaling: Metal–Ceria Catalysts for Selective Methane Conversion*, Maria Veronica Ganduglia-Pirovano, Pablo G. Lustemberg, Estefanía Fernández-Villanueva,*** Instituto de Catálisis y Petroleoquímica-CSIC, Spain

The selective activation of methane under mild conditions remains one of the central challenges in heterogeneous catalysis. Metal–oxide interfaces, particularly those formed between transition metals and ceria (CeO_2), provide a unique platform to control both activity and selectivity by coupling metal reactivity with the redox flexibility of the oxide support.

In this contribution, we present recent advances in the understanding and design of metal–ceria catalysts for methane conversion, combining DFT+U simulations with operando and in situ characterization (AP-XPS, XRD, XAFS) and catalytic testing. We show that low metal loadings (Ni, Co, Pt, Pd) on ceria generate highly active interfacial sites, where electron transfer to Ce 4f states stabilizes oxidized metal species, enabling methane activation at unusually low temperatures and efficient methane dry reforming under mild conditions. These systems deviate from conventional linear scaling relationships, demonstrating that nanostructured metal–oxide interfaces can overcome intrinsic activity–selectivity limitations.[1]

Building on this concept, we highlight recent results on the direct conversion of methane to methanol under mild conditions. In particular, $PdAu/CeO_2$ catalysts enable selective methane oxidation using water as the sole oxidant, achieving high methanol selectivity (~80% at 500 K). The alloy–oxide interface plays a decisive role: isolated Pd sites at the PdAu–ceria interface promote methane activation and water dissociation, while Au suppresses over-oxidation pathways leading to methanol decomposition. This synergistic interplay effectively tunes Pd reactivity, balancing activity and selectivity.[2]

These findings establish a unifying picture in which metal–oxide and alloy–oxide interfaces act as tunable active sites that decouple elementary steps and break traditional scaling constraints. This provides a rational framework for designing catalysts capable of selectively converting methane into value-added chemicals under technologically relevant conditions.

This work builds on a close and highly fruitful collaboration with José A. Rodriguez and his team at Brookhaven National Laboratory.

References

[1] Lustemberg, P. G. et al. *J. Phys. Chem. Lett.* **11**, 9131−9137 (2020)

[2] Fernández-Villanueva, E. et al. *Angew. Chem. Int. Ed.* **127**, e202505716 (2025)

8:45am **SS-WeM-4 Supported Ni-Cu Catalysts for the Selective Dehydrogenation of Liquid Organic Hydrogen Carriers*, Donna Chen, Nirmal Phuyal, Mengxiong Qiao, Biplab Budhathoki,*** University of South Carolina

Hydrogen is a promising source of clean and renewable energy, but a major challenge lies in its storage and transportation. The use of liquid organic hydrogen carriers (LOHC) enables hydrogen storage in organic molecules that are liquids at room temperature and therefore suitable for transportation through existing petroleum infrastructure. The methylcyclohexane (MCH) toluene pair has been used for the catalytic cycle of hydrogenation to store hydrogen and dehydrogenation to release hydrogen. While inexpensive and efficient catalysts are already available for hydrogenation, there is still the need for the development of selective dehydrogenation catalysts that inhibit deactivation due to carbon fouling. In this work, Cu-Ni clusters deposited on a rutile TiO_2(110) support are studied as catalysts for selective dehydrogenation. Methylcyclohexene (MCE) is used as a surrogate probe molecule to investigate the surface chemistry of MCE in ultrahigh vacuum since MCE adsorbs more strongly on Ni surfaces than MCH. Temperature programmed desorption (TPD) experiments for MCE on pure 2 ML Ni clusters show that nonselective decomposition to H_2 and surface carbon is the main reaction pathway; the evolution of CO at high temperature from the recombination of surface carbon and lattice oxygen from the titania support is used to quantify the extent of nonselective decomposition. In contrast, MCE reaction on 2 ML Cu clusters results in little overall dehydrogenation activity although a small amount of toluene is evolved. For 2 ML Ni clusters modified by the deposition of 0.25 ML of Cu, the amount of toluene produced is increased by a factor of 3 compared to pure Cu, but the extent of nonselective decomposition is still comparable to what is observed on pure Ni, indicating that Cu-Ni alloying and site blocking do not completely suppress MCE decomposition. However, the deposition of a small coverage of Ni (0.1 ML) on 2 ML Cu clusters results in 100% selectivity to toluene and a toluene yield that is seven times greater than on pure Cu. Increasing the Ni coverage to 0.25 ML lowers toluene production and leads to the initial onset of nonselective decomposition.The high toluene selectivity for the 0.1 ML Ni on 2 ML Cu clusters is attributed to the formation of a dilute alloy in which the Ni ensembles are not large enough to promote nonselective decomposition, but the desired reaction pathway of dehydrogenation to toluene is facilitated. These results demonstrate that controlling Ni ensemble size in Cu–Ni dilute alloys is an effective strategy for developing selective, coke-resistant dehydrogenation catalysts.

9:00am **SS-WeM-5 Surface Structure, Stability, and Catalytic Reactivity of Metal Nanoparticles Supported on Tantalum Oxide*, Ravi Ranjan, Francisco Zaera,*** University of California - Riverside

The surface structure, thermal stability, and catalytic behavior of copper (Cu) and platinum (Pt) nanoparticles (NPs) supported on tantalum oxide (TaO_x/Ta) thin films have been investigated using reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD), with carbon monoxide (CO) as the probe molecule.

Cu NPs were prepared by vapor deposition at room temperature and under ultrahigh vacuum (UHV) conditions, and characterized by following the adsorption of CO at 77 K. Increasing deposition of Cu led to the growth of nanoparticles exhibiting distinct adsorption sites associated with the metal-oxide interface and different Cu surface facets. The Cu NPs remained stable under both UHV and high-pressure CO environments over a broad range of

temperatures.

Pt deposition onto TaO_x/Ta resulted in the gradual formation of NPs with predominantly one major CO adsorption feature. In contrast to the case of Cu, Pt NP growth was less structurally distinct, as indicated by the CO vibrational signatures. Pt nanoparticles remained stable in UHV up to approximately 500 K, above which subsurface migration into the oxide support was observed.

The catalytic properties of the Pt/TaO_x/Ta surfaces were further examined using acrolein hydrogenation as a model reaction. Reaction studies under atmospheric pressures, using a so-called high-pressure cell to directly transfer the surfaces from UHV to the catalytic reactor, revealed the formation of propanal, propanol, and allyl alcohol, demonstrating competing hydrogenation pathways involving both C=C and C=O. These findings provide molecular-level insights into how nanoparticle structure, stability, and metal-support interactions influence catalytic selectivity and reactivity under catalytic conditions.

9:15am **SS-WeM-6 CO Oxidation on Plasma-Activated Pd and PdAg Surfaces**, ***Pablo de Oliveira***, *Camilla Codeço, Marcos G. Menezes,* UFRJ, Brazil*; J.Anibal Boscoboinik,* BNL

Plasma-assisted surface treatments offer an attractive alternative to conventional sputter/annealing cycles for surface cleaning and activation, particularly in alloyed materials where preferential sputtering or thermal segregation may alter the near-surface stoichiometry. Here, we investigate how sequential oxygen and hydrogen plasma cycles modify the surface chemistry and CO oxidation activity of Pd-based systems. By combining ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), ambient-pressure infrared reflection–absorption spectroscopy (AP-IRRAS), and density-functional theory (DFT) calculations, we compare the reaction pathways on a Pd foil and a PdAg alloy under near-ambient conditions. While both systems exhibit CO oxidation even slightly above room temperature (373 K), they reveal a dependence on the CO:O_2 composition. On Pd foil, CO oxidation is mainly observed under balanced feeds (p_{CO} = p_{O2}), whereas the PdAg alloy sustains activity even under oxygen-rich conditions (p_{O2} = 2 x p_{CO}). This enhanced tolerance is attributed to the formation of hydride-like Pd species during the in situ, room temperature hydrogen plasma. DFT calculations further confirm that hydrogen dissociation is energetically favored on the PdAg alloy compared to Pd foil. The presence of hydride prevents the formation of PdO layers, enabling alternative low-energy pathways for CO oxidation. These results demonstrate that sequential plasma treatments can do more than clean Pd-based surfaces, actively tuning the active sites that govern CO oxidation in alloy catalysts.

9:30am **SS-WeM-7 Catalysis with Liquid Gallium Alloys**, ***Christian Papp***, Freie Universität Berlin, Germany **INVITED**

Recently, Supported Catalytically Active Liquid Metal Solutions (SCALMS) were shown to surpass conventional alkane dehydrogenation catalysts in both activity and stability, due to their liquid nature and the presence of catalytically active single atom sites. SCALMS consist of a liquid metal matrix (Ga) that dissolves a catalytically active transition metal (Pt, Rh, Pd, Ni). Binary SCALMS systems are the subject of extensive research on the fundamental level with the aim to reach optimal performance.

Here, we present an operando NAPXPS study of the dehydrogenation of simple alkanes on gallium-platinum SCALMS (Supported Catalytically Active Liquid Metal Solutions) catalyst systems. As an industrially relevant test reaction, the dehydrogenation reaction of propane was used. In the study we compare the activity of oxidized GaPt SCALMS and liquid / metallic GaPt SCALMS surfaces, using Near-Ambient Pressure X-ray Photoelectron Spectroscopy. From the study, we conclude that the oxide shows a lower activity as compared to the metallic liquid GaPt SCALMS model systems. Further, the gallium matrix reduces under reaction conditions and coke residues disappear.

Our study thus underscores the practical value of NAPXPS in tracking surface changes and electronic states during catalytic reactions. By exploring these differences, the study sheds light on the role of oxides on the catalytic performance. These findings contribute essential insights for optimizing catalyst design and improving effectiveness, offering a pragmatic approach to catalytic enhancement.

Acknowledgement:

The research is funded by the DFG through SFB 1452 (Project number: 419654270).

11:00am **SS-WeM-13 Ni as a Promotor for Ethylene Epoxidation: Computation, Surface Science, and Reactor Studies**, ***Matthew Montemore***, Tulane University **INVITED**

Single-atom alloys have shown strong catalytic performance for several types of reactions, including hydrogenation reactions and alkane conversion. However, single-atom alloys have not been extensively studied for oxidation reactions, despite the critical importance of these reactions. The possibility that single-atom alloys could easily activate molecular oxygen but bind O relatively weakly makes them intriguing, as weakly bound O is likely to be quite reactive. In this work, we computationally designed single-atom alloys for oxidation, focusing on surfaces that can easily activate O_2 but give relatively weak O binding. We found several Ag-based single atom alloys that are predicted activate O_2 with very low barriers, in some cases near 0, while still binding O relatively weakly. In particular, NiAg stood out as a case with a very low barrier but relatively weak binding. Subsequent experimental synthesis and testing of single-crystal single-atom alloy surfaces shows that NiAg can activate O_2 and create relatively weakly bound O. Characterization with X-ray photoelectron spectroscopy, scanning tunneling microscopy, and temperature-programmed desorption gives strong fundamental insight into the interaction of these materials with oxygen and their state when exposed to oxygen and a reductant. Finally, NiAg nanoparticles were synthesized and tested, and show excellent performance for ethylene epoxidation. This work demonstrates the utility of integrated computational-experimental studies, and opens up the possibility of high-performance single-atom alloy catalysts for many oxidation reactions.

11:30am **SS-WeM-15 Tuning Oxygen Activation on Gold with RhAu Single-Atom Alloys**, ***Dennis Meier***, *Vinita Lal, E. Charles H. Sykes,* Tufts University

Selective oxidation reactions, such as olefin epoxidation and alkane oxidation, are large-scale industrial processes and are key to the more efficient conversion of natural gas into value-added products. Given the ongoing challenge of optimizing industrial chemical processes, there is a great need for highly selective catalysts. We investigated Au, which is known to be exceptionally selective for many oxidation reactions, but whose inability to efficiently activate O_2 limits reaction rates.

Density functional theory (DFT) predicted that small amounts of Rh guest atoms could overcome the low intrinsic activity of Au toward oxygen activation while preserving its high selectivity. We prepared RhAu single-atom alloys (SAAs), in which Rh atoms remain isolated in the Au surface, and probed their reactivity using a combination of temperature-programmed desorption (TPD), scanning tunneling microscopy (STM), and ambient-pressure X-ray photoelectron spectroscopy (AP-XPS). At comparable O_2 pressures and sample temperature, the RhAu systems show a significantly higher amount of Au-associated oxygen than clean Au, providing strong evidence that O_2 is activated at Rh sites and subsequently spills over onto the Au surface, which is the initial step for selective oxidation on Au. We further studied how the coordination environment of the guest atoms influences reactivity by comparing the (111) and (110) facets. The latter forms a (1×2) reconstruction that gives rise to undercoordinated surface sites. Using AP-XPS, we investigated the stability of RhAu SAAs at different temperatures and during exposure to CO and O_2. Together, these findings show that RhAu SAAs can overcome the low oxygen-activation activity of pure Au while retaining the potential for highly selective oxidation chemistry.

11:45am **SS-WeM-16 Reaction Product and Single-Atom Promotion of Acetylene Cyclotrimerization and Cross-Coupling on Ag(111)**, ***Nipun Kahagalla Dewage***, Tufts University*; Santu Biswas,* Tulane University*; Volkan Cinar, Dennis Meier,* Tufts University*; Matthew Montemore,* Tulane University*; Charles Sykes,* Tufts University

Benzene (C_6H_6) and toluene (C_7H_8) are irreplaceable chemical feedstocks used to produce pharmaceuticals, polymers, and materials. These aromatics are currently produced primarily through petroleum cracking and reforming processes, which require high energy input, harsh operating conditions, and lack full selectivity. As hydrocarbon feedstocks increasingly shift from oil to shale gas, alternative catalytic routes for the selective synthesis of aromatics are of significant interest. Acetylene (C_2H_2) cyclotrimerization is one promising pathway because it uniquely produces C_6H_6 with 100% selectivity on Ag(111). However, this reaction requires more than one monolayer (ML) of C_2H_2 on Ag(111) to initiate C_6H_6 formation, necessitating high reactor pressures that limit its practical applicability.

To understand and overcome this limitation, C_2H_2 cyclotrimerization on Ag(111) was investigated using Temperature-Programmed Desorption

(TPD), 12 K Scanning Tunneling Microscopy (STM), and Density Functional Theory (DFT). Coadsorption experiments with isotopically labeled benzene (C_6D_6) reveal that C_6D_6 promotes acetylene conversion to 20% at coverages of ≥0.6 ML. STM and DFT show that attractive C_2H_2-C_6D_6 interactions and increased molecular packing stabilize the key C_4 transition state involved in the rate-limiting step, making C-C coupling competitive with C_2H_2 desorption. In addition, coadsorption of C_2H_2 and propyne (C_3H_4) was examined to explore heterocoupling pathways for toluene (C_7H_8) formation. While coupling occurs at ≥1 ML total coverage with higher C_3H_4:C_2H_2 ratios, reaching a maximum at 1.5:1, C_6H_6 remains the dominant product (95%), with C_7H_8 forming only in minor quantities (5%). Guided by mechanistic insights from DFT, we further demonstrate that introducing chromium (Cr) dopant atoms into Ag(111) to form a Cr single-atom alloy dramatically alters the free energy landscape of C_2H_2 cyclotrimerization. This enables C_6H_6 formation at C_2H_2 coverages below 0.1 ML while maintaining the 100% selectivity of Ag(111) at Cr coverages ≤2%.

Together, these findings provide mechanistic insight into product-promoted C_2H_2 cyclotrimerization and C_2H_2-C_3H_4 coupling on Ag(111). They also demonstrate that CrAg(111) single-atom alloys can enable selective aromatic formation, offering a potential pathway for upgrading shale-gas-derived $C_{2,3}$ hydrocarbons into high-value aromatics without requiring high reactor pressures.

12:00pm **SS-WeM-17 Selective Hydrogenation of Styrene to Ethylbenzene Over a Pd/Cu(111) Single Atom Alloy Surface***, Mohammad Rahat Hossain, Michael Trenary,* University of Illinois - Chicago

Selective hydrogenation of alkynes and alkenes is central to industrial catalysis, yet direct spectroscopic identification of surface intermediates under realistic pressure conditions remains challenging. Here, we investigate styrene hydrogenation on a Pd/Cu(111) single-atom alloy (SAA) surface using polarization-dependent reflection absorption infrared spectroscopy (PD-RAIRS), Auger electron spectroscopy (AES), and kinetic analysis under ambient-pressure conditions. A 0.03 ML Pd/Cu(111) surface selectively hydrogenates styrene to ethylbenzene while suppressing aromatic ring hydrogenation. Time-resolved RAIRS measurements reveal the disappearance of styrene vibrational features at 909, 991, 1018, and 1637 cm^{-1} and the growth of ethylbenzene bands at 1033, 1066, 1329, 1385, and 1462 cm^{-1}, accompanied by aliphatic C–H stretching modes below 3000 cm^{-1}. A transient surface feature at ~1385 cm^{-1} is assigned to a benzylic σ-bound intermediate, consistent with β-selective hydrogenation of the vinyl group. Kinetic measurements show approximately first-order dependence on H_2 and near-zero-order dependence on styrene, supporting a Langmuir–Hinshelwood-type mechanism involving facile styrene adsorption and kinetically relevant hydrogenation steps. Repeated reaction cycles lead to carbon accumulation detected by AES, with carbon coverage increasing from ~45% to ~65%; however, catalytic activity persists despite the formation of a thin carbonaceous overlayer. These findings demonstrate that Pd/Cu(111) SAAs provide atom-efficient and highly selective hydrogenation catalysts while enabling molecular-level insight into hydrocarbon hydrogenation and carbon overlayer formation under elevated-pressure conditions.

Author Index

Bold page numbers indicate presenter