Fundamental Discoveries in Heterogeneous Catalysis Focus Topic
Room 321 - Session HC+AS+SS-TuA

Bridging Gaps I: Structural and Dynamic Effects in Catalysis

Moderator: Dan Killelea, Loyola University Chicago

2:20pm **HC+AS+SS-TuA-1 Fundamental Studies of C1 Catalysis on Metal-oxide and Metal-Carbide Interfaces*, Jose Rodriguez,*** Brookhaven National Laboratory **INVITED**

The transformation of CO_2 and CH_4 into alcohols or other hydrocarbon compounds is challenging because of the difficulties associated with the chemical activation of this highly stable molecules by heterogeneous catalysts. Pure metals and bimetallic systems used for this task have usually trouble binding CO_2 or CH_4 and, thus, low catalytic activity. Here, we will discuss a series of in-situ studies investigating different mechanisms or approaches for C-O and C-H bond activation. They illustrate the advantages of metal-oxide and metal-carbide interfaces when aiming at the conversion of CO_2 or CH_4 into methanol. CeOx/Cu(111), Cu/CeOx/TiO_2(110) and Cu/TiC(001) exhibit an activity for the $CO_2 \rightarrow CH_3OH$ conversion that is 2-3 orders of magnitude higher than that of a benchmark Cu(111) catalyst. In the Cu-ceria and Cu-TiC interfaces, the combination of metal and oxide (or carbide) centers affords complementary chemical properties that lead to special reaction pathways for methanol synthesis. Metal-oxide and metal-carbide interfaces also can be tune for the activation and conversion of CH_4.

3:00pm **HC+AS+SS-TuA-3 Atomic Scale Studies of Chromium Species on Iron Oxide Surfaces*, Moritz Eder,*** TU Wien, Austria*; P. Sombut,* University of Vienna, Austria*; C. Wang, L. Puntscher, A. Rafsanjani-Abbasi, M. Meier, J. Pavelec, G. Franceschi, M. Riva,* TU Wien, Austria*; C. Franchini,* University of Vienna, Austria*; M. Schmid, U. Diebold, G. Parkinson,* TU Wien, Austria

Chromium (Cr) ferrite catalysts are industrially employed for the water gas shift reaction in order to provide large amounts of molecular hydrogen.[1] However, the European REACH legislation demands that hexavalent Cr be banned from all catalysts used in industrial processes due to its toxicity. Consequently, alternative metals are sought to fulfill the role of Cr species in the corresponding compounds.[2] It is therefore necessary to obtain a fundamental understanding and characterization of Cr on iron oxides.

In this talk, we present the investigation of Cr species on Fe_3O_4(001) by means of STM and XPS at room temperature. We show the behavior during exposure to water gas shift reactants (i.e., CO and H_2O) and upon high temperature treatment. The latter is of utmost importance since the water gas shift reaction is conducted at temperatures up to 500°C.[1] The results are compared to the behavior of other transition metals and discussed with respect to implications for applied catalysis.[3]

[1] Häussinger, Lohmüller, Watson, *Hydrogen, 2. Production*. In: Ullmann's Encyclopedia of Industrial Chemistry, 2011

[2] Glassner, *Int. Surf. Technol.***14**, p. 36, (2021)

[3] Bliem, Pavelec, Gamba, McDermott, Wang, Gerhold, Wagner, Osiecki, Schulte, Schmid, Blaha, Diebold, Parkinson, *Phys. Rev. B* **92**, p. 075440 (2015)

3:20pm **HC+AS+SS-TuA-4 Investigation of CO Oxidation on Oxygenated Rh(111) Surfaces with RAIRS*, Elizabeth Jamka,*** *D. Killelea,* Loyola University Chicago

Surface IR spectroscopy is a quantitative technique that also provides information about the binding sites and chemical environments of the adsorbed CO molecules. In this research we are able to interface a FTIR to the ultra-high vacuum (UHV) chamber as a non-destructive and highly sensitive surface analysis technique. Because IR measurements can be performed in UHV conditions, interference from atmospheric species are avoided, while enabling investigation of catalytic systems, like carbon monoxide (CO) to carbon dioxide (CO_2) on Rh(111). To determine the reactivity of the various oxide phases, the oxidation reaction of CO to CO_2 on oxidized Rhodium (Rh) will be utilized as a probe reaction. Studying CO oxidation on different Rh surfaces will provide atomic level information regarding oxidation reactions, progressing the understanding of various surface phases relevant to many Rh catalyzed processes. This research focuses on CO sticked to clean Rh(111), (2x1)-O/Rh(111), and (2x1)-O + RhO_2/Rh(111). Via FTIR, these and other reaction sites of CO oxidation will be investigated to determine reaction pathways or mechanisms.

4:20pm **HC+AS+SS-TuA-7 Molecular Beam Surface Reaction Experiments with Chiral Molecules*, Tim Schäfer,*** Georg August University, Goettingen, Germany **INVITED**

Chirality is a feature of asymmetry describing the geometrical property of objects that cannot be mapped onto their mirror images like our hands as classic example. In chemistry, one observes chirality on the molecular level: two mirror images of chiral molecules (enantiomers) have only little difference in the structure, but this might cause a vast change in the biological activity.

Unfortunately, a fundamental understanding of chemical processes in chiral environments is challenging, as enantiosensitive detection methods must introduce chirality to distinguish enantiomers. Until recently, enantiospecific assignment of chiral gas phase molecules at low concentrations was not even possible. In the last decade, new enantiosensitive detection techniques have been invented based on photoionization of molecules (Photoelectron Circular Dichroism, PECD). Our group contributed to these advances by developing a unique technique that combines PECD with surface science. This approach allows the investigation of dynamics and kinetics of surface reactions of chiral molecules at the gas surface interface.

We use this technique for studies on heterogeneously catalyzed chiral surface reactions like the partial oxidation of olefins to epoxides on metal surfaces. For this, we combine PECD measurements with velocity resolved kinetics experiments, providing enantiosensitive information about reaction mechanisms at surfaces.

5:00pm **HC+AS+SS-TuA-9 A Local View on the Influence of Solvent and Product on the Reactivity of Surface-Catalyzed Reactions*, Karina Morgenstern,*** Ruhr Universität Bochum, Germany **INVITED**

Though largely influencing the efficiency of a reaction, the molecular-scale details of the local environment of the reactants are experimentally inaccessible hindering an in-depth understanding of a catalyst's reactivity, a prerequisite to maximizing its efficiency. We introduce a method to follow individual molecules and their largely changing environment during laser-induced reactions. The method is illustrated with a single-molecule resolution on two examples, the dissociation of halogenated benzene molecules adsorbed on ice [1] and of CO_2 on two catalytically relevant surfaces, Ag(100) and Cu(111)[2]. Dissociation of halobenzene is triggered by delocalized excess electrons. The adsorption on ice sufficiently lowers the energy barrier for the transfer between themolecular orbitals to facilitate dissociation of bromo- and chloro- but not of fluorobenzene at cryogenic temperatures.For the CO_2dissociation, we reveal how the reactant's surroundings evolve with progressing laser illumination and with it their propensity for dissociation. Our results shed light on the influence of solvent and products on reaction yields on the nanoscale.

[1]P. Auburger, I. Kemeny, C. Bertram, M. Lingges, M. Bockstedte, U. Bovensiepen, K. Morgenstern, Phys. Rev. Lett. 121, 206001 (2018)

[2] M. Vyshnepolsky, Z.-B. Ding, P. Srivastava, P. Tesarik, H. Mazhar, M. Maestri, K. Morgenstern, Angew. Chem. Int. Ed. 60, 18217-18222 (2021)

5:40pm **HC+AS+SS-TuA-11 Enhanced Catalytic Selectivity Due to Topographically Reduced Work Function of Carbon Nanospikes*, Arthur P. Baddorf,*** Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; A. Rondinone,* Center for Integrated Nanotechnologies, Los Alamos National Laboratory*; D. Hensley,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Carbon nanospikes show excellent Faradaic efficiency and selectivity for electrochemical conversion of technologically important reactions, including CO_2 to ethanol in the presence of Cu [1] and N_2 to ammonia in the presence of Li [2]. Rates are higher than for other aqueous electrochemical approaches, including other low-dimensional carbon nanomaterials such as nanotubes, fibers, and foams, and much greater than for flat carbon surfaces. The essential attribute appears to be the sharp spike topography at which electric fields are enhanced. Transmission electron microscopy images reveal that films consist of a high density of nanospikes each 50-80 nm in height and terminated with a sharp tip of radius ~1 nm, i.e. a very high curvature.

We have explored the electric fields at the nanospikes by measurements of the absolute work function in comparison that of other carbon geometries using ultraviolet photoemission spectroscopy (UPS). As samples were characterized after transfer through air, surface cleanliness was monitored with x-ray photoelectron spectroscopy (XPS). Annealing as-grown samples above 275 °C was required to produce a clean surface which has a 4.13 eV work function, a half volt lower than that of flat graphite. This reduction supports the idea that a strong electric field is generated by the nanospike topography which contributes to the electrochemical activity.

Contamination of the spiked surface raises the work function above that of the clean nanospikes. Work function values following exposure increased to 4.19 eV for hydrocarbons, 4.30 for air, 4.42 for water, and 4.48 for oxygen. Blunting the spikes, by exposure to an oxygen plasma, argon sputtering, or annealing to 800 °C results in a work function close to that of flat graphite, 4.62 eV. An unusual double onset in the UPS secondary electron intensity is observed after absorbing hydrocarbons on clean nanospikes. This double onset has not been reported on metal surfaces and appears to be unique to carbon substrates. The energy difference between the two onsets, about 0.4 eV is close to that of a typical C-H stretch in hydrocarbons suggesting the lower energy onset may originate in inelastic scattering of photoelectrons.

* This work was supported by Center for Nanophase Materials Sciences (CNMS), which is a US Department of Energy, Office of Science User Facility at Oak Ridge National Laboratory.

[1] Y. Song, et al., Chemistry Select 1 (19), 6055 (2016).

[2] Y. Song, et al., Sci. Adv. 4(4)(2018).

6:00pm **HC+AS+SS-TuA-12 HC Graduate Student Finalist Talk: Enhanced Descriptor Identification and Mechanic Understanding for Catalytic Activity using Data-Driven Framework: A Case Study of CO Hydrogenation over Cu-Based Single Atom Alloys***, **Wenjie Liao,*** Stony Brook University/Brookhaven National Laboratory*; P. Liu,* Brookhaven National Laboratory and State University of New York at Stony Brook

Accurate identification of descriptors for catalytic activities has long been essential to the in-depth mechanic study of catalysis and recently to set the basis for catalyst screening. However, commonly used derivative-based local sensitivity analysis methods suffer from low accuracy in predictability. This study reports an enhanced approach to accurately identifying the descriptors from a kinetic dataset using the machine learning (ML) surrogate model. The CO hydrogenation to methanol over Cu-based single atom alloys was taken as a case study.

Our model captures not only the contribution from individual elementary steps (i.e., first-order descriptors), but also the interaction between relevant steps within a reaction network (i.e., second-order descriptors), which was found to be essential for accuracy. As a result, six effective descriptors are identified, which are accurate enough to ensure the trained gradient boosted regression (GBR) model for well prediction of the methanol turn-over-frequency (TOF) over metal (M)-doped Cu(111) model surfaces (M = Au, Cu, Pd, Pt, Ni). More importantly, going beyond the purely mathematic ML model, the catalytic role of each identified descriptor can be revealed by using the model-agnostic interpretation tools, which enhances the mechanic insight into the promoting effect of alloying. The trained GBR model outperforms the conventional derivative-based methods in terms of both predictability and mechanic understanding.

The proposed data-driven framework allows one to identify key descriptors beyond rate-limiting steps while clearly depicting how each identified key descriptor would affect the catalytic activity when more than one activation energies were tuned. This approach can be applied to other reactions and catalysts, which opens alternative possibilities toward accurate descriptor-based rational catalyst optimization

Author Index

Bold page numbers indicate presenter

— B —
Baddorf, A.: HC+AS+SS-TuA-11, **1**
— D —
Diebold, U.: HC+AS+SS-TuA-3, 1
— E —
Eder, M.: HC+AS+SS-TuA-3, **1**
— F —
Franceschi, G.: HC+AS+SS-TuA-3, 1
Franchini, C.: HC+AS+SS-TuA-3, 1
— H —
Hensley, D.: HC+AS+SS-TuA-11, 1
— J —
Jamka, E.: HC+AS+SS-TuA-4, **1**
— K —
Killelea, D.: HC+AS+SS-TuA-4, 1
— L —
Liao, W.: HC+AS+SS-TuA-12, **2**
Liu, P.: HC+AS+SS-TuA-12, 2
— M —
Meier, M.: HC+AS+SS-TuA-3, 1
Morgenstern, K.: HC+AS+SS-TuA-9, **1**
— P —
Parkinson, G.: HC+AS+SS-TuA-3, 1
Pavelec, J.: HC+AS+SS-TuA-3, 1
Puntscher, L.: HC+AS+SS-TuA-3, 1
— R —
Rafsanjani-Abbasi, A.: HC+AS+SS-TuA-3, 1
Riva, M.: HC+AS+SS-TuA-3, 1
Rodriguez, J.: HC+AS+SS-TuA-1, **1**
Rondinone, A.: HC+AS+SS-TuA-11, 1
— S —
Schäfer, T.: HC+AS+SS-TuA-7, **1**
Schmid, M.: HC+AS+SS-TuA-3, 1
Sombut, P.: HC+AS+SS-TuA-3, 1
— W —
Wang, C.: HC+AS+SS-TuA-3, 1