Surface Science
Room 209 CDE W - Session SS-TuA

Heterogeneous Catalysis I

Moderators: Zbynek Novotny, Paul Scherrer Institute, Switzerland, **Dario Stacchiola**, Brookhaven National Laboratory

2:15pm **SS-TuA-1 Interstellar Catalysis - a Route to Molecular Complexity in Space**, ***Liv Hornekaer,*** Aarhus University, Denmark **INVITED**

Interstellar molecular clouds, the regions where new stars and planetary systems form, are home to surprisingly complex chemistry. In spite of the very low temperatures and pressures characterizing these clouds more, than 330 different molecules have so far been detected. Nanoscale interstellar dust grains and polycyclic aromatic hydrocarbons are expected to play a dominant role as catalysts for the low temperature reactions resulting in the formation of these molecules. Their catalytic effect is not only ascribed to a lowering of reaction barriers, but also to their role in dissipating the energy released in the reaction. In some cases, the "catalysts" are even seen to increase the reaction barriers, while still enabling the reaction to proceed by providing energy dissipation pathways. The last 20 years have seen major advancements in our understanding of interstellar reactions, specifically with regards to simple molecules, however, the degree of chemical complexity attainable via such reactions is still under exploration. Recently it was shown that the simplest amino acid, glycine, can form under interstellar conditions. In this case a non-diffusive reaction mechanism was proposed. A more detailed quantum dynamical understanding of low temperature solid state radical-radical reactions could provide the answer to the question of whether the molecular building blocks of life – amino acids, DNA bases, sugars and fatty acids – can form in interstellar space, even before the formation of stars and planets. To answer this question, we recreate interstellar conditions in the laboratory and employ the full toolbox of surface science to study heterogenous catalytic reactions on interstellar dust grain analogue surfaces. As an example scanning tunneling microscopy measurements allows us to directly image low temperature ice cluster formation, as well as low temperature reaction products with single molecule detection efficiency.

2:45pm **SS-TuA-3 Kinetics and Dynamics of CO Oxidation on Rhodium Surfaces**, ***Dan Killelea,*** Loyola University Chicago

The ability to obtain velocity distributions of molecules desorbing from surfaces with both high temporal precision and angular resolution provide newfound insight into both the kinetics and the dynamics of the CO oxidation reaction and subsurface emergence.

I will discuss our observations of CO oxidation by co-adsorbed and absorbed oxygen on Rh(111) and how the velocity distribution shifts in comparison to the thermally-dominated desorption pathways found for surface-adsorbed oxygen. In addition, the role of systematic defects will be covered for both the oxidation reaction and surface oxidation. I will discuss these observations and their potential impacts in oxidation reactions in heterogeneously catalyzed reactions over transition metal surfaces.

3:00pm **SS-TuA-4 The Effects of Alkane Structure, Cluster Size, and Cluster Composition on Activity of Pt_n and Pt_nGe_m Catalysts for Cracking and Dehydrogenation**, ***Autumn Fuchs,*** *Scott Anderson,* University of Utah; *Avital Isakov, Anastassia Alexandrova,* University of California at Berkeley

The high temperature dehydrogenation, cracking, and coking chemistry of n-butane and isobutane, catalyzed by sub-nanometer Pt_n/alumina and Pt_nGe_m/alumina catalysts will be presented.The mechanisms are explored by temperature programmed desorption (TPD) experiments with size-selected clusters deposited on alumina supports, and detailed DFT calculations.The calculations probe cluster geometric and electronic structures, including the effects of both Ge and carbon addition, and examine binding and activation of the C4 alkanes and alkenes.N-Butane is observed to dehydrogenate efficiently on Pt catalysts with and without Ge.For pure Pt_n, there is some coking initially, but the coking decays over time and the dehydrogenation activity increases slightly, i.e., coking is self-limiting and does not deactivate Pt_n for n-butane dehydrogenation.With Ge present, there is essentially no coking for n-butane, even in the initial reaction.In contrast, isobutane on pure Pt_n/alumina catalysts simply cokes with hydrogen evolved, with no significant alkene or diene products.Ge addition to the Pt_n does suppress coking for isobutane, resulting in C_4H_8 product formation, but only for the the Pt_7-based catalyst (Pt_7Ge_2/alumina).In addition, we find that both 2- and isobutene coke badly on Pt_n/alumina, deactivating the catalysts, and that coking is suppressed by Ge addition.This work was supported by the Air Force Office of Scientific Research (AFOSR FA9550-19-1-0261).

3:15pm **SS-TuA-5 Oxygen Passivation of Au Capped Niobium**, ***Van Do,*** *Helena Lew-Kiedrowska, Sarah Willson,* University of Chicago; *Chi Wang,* National Cheng Kung University (NCKU), Taiwan; *Steven Sibener,* University of Chicago

Nb is the highest temperature elemental superconductor; however, its application in particle accelerators and quantum computers is limited by growth of native surface Nb oxides. Au capping layers have been shown to prevent deleterious Nb oxide growth but Au morphology, kinetics, and degree of passivation at various coverages on Nb have not been fully investigated. This work characterizes the physical deposition and oxygen contamination of sub-ML to 10 ML Au coverages on Nb(100). We analyze the physical features and chemical states of the surface using Scanning Tunneling Microscopy, X-ray and UV Photoelectron Spectroscopy, and Auger Electron Spectroscopy. Preliminary results show that a post-deposition anneal as low as 350 C causes Au island formation at Sub-ML to 1 ML coverages, substantially exposing Nb to oxidation. Thus, understanding the effects of temperature and coverage on Au formation will be critical for revealing the optimal method to passivate Nb.

4:00pm **SS-TuA-8 Achieving Effective Catalysis by Transient Heating Using Mechanocatalysis and Pulsed Joule Heating**, ***David Sholl,*** *Zili Wu,* ORNL; *Carsten Sievers,* Georgia Institute of Technology; *Liangbing Hu,* Yale University **INVITED**

Transient heating can be a powerful approach to control the selectivity of catalytic reaction networks, especially for endothermic reactions where undesirable species can be formed under steady state conditions. Mechanocatalysis and pulsed Joule heating are two approaches where surface temperature changes of 500-1000 K can be achieved on millisecond timescales. This talk will discuss how a combination of experiments and computational simulations have been used to understand the reaction conditions that are accessible with these unconventional heating methods. Examples will include the use of computational modeling to probe temperature inhomogeneities in realistic models of carbon fiber supports during pulsed Joule heating and the use of single impact experiments and simulations to quantify heat delivery and chemical reactivity during mechanochemical depolymerization.

4:30pm **SS-TuA-10 Unraveling the Desorption Dynamics of Cyclic Hydrocarbons on Fe_3O_4(001): Insights from Temperature-Programmed Desorption**, ***Moritz Eder***[1], TU Wien, Austria; *Federico Loi,* J. Heyrovsky Institute of Physical Chemistry, Czechia; *Nail Barama, Faith Lewis, Margareta Wagner,* TU Wien, Austria; *Štefan Vajda,* J. Heyrovsky Institute of Physical Chemistry, Czechia; *Jiří Pavelec, Gareth Parkinson,* TU Wien, Austria

We investigate cyclic hydrocarbons — cyclohexane, cyclohexene, and benzene — on the magnetite Fe_3O_4(001) surface by means of temperature-programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), and x-ray photoelectron spectroscopy (XPS). Through a detailed analysis of the TPD profiles, we uncover distinct interaction mechanisms between these molecules and the Fe_3O_4(001) surface, shedding light on the role of molecular structure and surface chemistry. Despite the structural similarities, the adsorption energies and desorption orders and hence the interaction with the surface are different for each molecule. Furthermore, the desorption behavior differs from other surfaces previously investigated in the literature.[1,2] The results provide a deeper understanding of the substrate-surface interactions, with implications for catalytic applications, such as hydrocarbon upgrading, and the design of oxide-supported catalysts for energy and chemical industries.

[1] Smith, R. S., & Kay, B. D. (2018).Desorption kinetics of benzene and cyclohexane from a graphene surface. J. Phys. Chem. B, 122(2), 587-594.

[2] Chen, L., Zhang, S., Persaud, R. R., Smith, R. S., Kay, B. D., Dixon, D., & Dohnalek, Z. (2019). Understanding the binding of aromatic hydrocarbons on rutile TiO_2(110). J. Phys. Chem. C, 123(27), 16766-16777.

4:45pm **SS-TuA-11 Investigating the Stability and Reactivity of Subsurface Oxygen in Ag(111) Using Lattice-Gas Models, DFT, and Monte Carlo Simulations**, *Carson Mize, Lonnie Crosby, Bright Daniel,* ***Sharani Roy,*** University of Tennessee Knoxville

First-row atoms, such as hydrogen, carbon, and oxygen, not only adsorb on the surface of a solid but are small enough to diffuse into the near-surface or subsurface region. The percolation of adsorbates through the surface

[1] **JVST Highlighted Talk**

raises many fundamental questions, such as what conditions promote subsurface adsorption? Does the same adsorbate have different chemical properties in the subsurface compared to the surface? How do subsurface adsorbates influence chemical reactions on surfaces? To address these questions, we extended the theoretical framework of lattice-gas models to describe both coverage-dependent surface and subsurface adsorption in crystalline solids. Using this framework, we developed an all-site DFT-parameterized lattice-gas model for O/Ag(111) and integrated it with Monte Carlo simulations to calculate the thermodynamic distributions of atomic oxygen on the surface and in the subsurface of Ag(111). The results show that subsurface adsorption becomes thermodynamically favorable for oxygen coverages exceeding 0.375 ML. Furthermore, we applied the simulations to construct the first ab initio phase diagram of O/Ag(111) that shows the pressure and temperature ranges within which subsurface oxygen coexists with surface oxygen on Ag(111). Our results indicate that subsurface oxygen is present under the industrial conditions used for the catalytic partial oxidation of olefins on silver nanoparticles. Finally, we computed the reaction pathway for the conversion of ethylene to ethylene oxide on Ag(111) using DFT and found significant changes to the reaction barriers with increased oxygen coverage and the presence of subsurface oxygen.

5:00pm **SS-TuA-12 Size and Proximity Dependent Electronic Metal-Support Interactions on Cu/TiO_2(110)**, *Lindsey Penland, H. H. Hirushan, N. Dissanayake,* ***Rachael Farber****,* University of Kansas

Electronic metal-support interactions (EMSI) are often cited as an origin of enhanced selectivity and efficiency of oxide-supported metal nanoparticle catalysts. While it is understood that tuning the oxide support defect density and metal nanoparticle size impacts the EMSI, it is unclear how such structural modifications attenuate the electronic landscape of the catalyst at the atomic scale. In this work, rutile TiO_2(110) was used as a strong Lewis acid oxide support to determine the spatially resolved electronic consequences of Cu nano-particle size on EMSI. Using a combination of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), the TiO_2(110) (1×1), (1×2), (1×3), and (2×2) surface reconstructions were characterized to reveal the relationship between the coordination number of Ti and the observed local density of states (LDOS). Following this characterization, sub-monolayer quantities of Cu were deposited on TiO_2(110) and annealed to either 100 °C, 300 °C, or 500 °C to promote Cu diffusion and aggregation. STS taken atop the Cu particles showed the emergence of electronic states within the bandgap of TiO_2(110). The intensity and position of these electronic states were strongly dependent on the size of the Cu particle. STS collected at the Cu/TiO_2(110) interface showed unique LDOS when compared to the LDOS of the Cu particle and the TiO_2(110), suggesting an attenuation of the electronic structure at the Cu/TiO_2(110) interface. This attenuation of the LDOS extended beyond the immediate Cu/TiO_2(110) interface, with the distance of attenuation related to the size of the Cu particle. These results highlight the real-space, heterogeneous electronic landscape of oxide-supported metal nanoparticle systems which may have significant implications for overall reactivity and selectivity.

5:15pm **SS-TuA-13 Steering Pt Cluster Dimensionality via Morphology and Surface Oxidation State of CeO2(111) Thin Films**, ***Johanna Reich****,* *Mina Soltanmohammadi,* Technical University of Munich, Germany*; Vedran Vonk,* Deutsches Elektronen-Synchrotron (DESY), Germany*; Sebastian Kaiser, Ueli Heiz,* Technical University of Munich, Germany*; Andreas Stierle,* Deutsches Elektronen-Synchrotron (DESY), University of Hamburg, Germany*; Friedrich Esch, Barbara A. J. Lechner,* Technical University of Munich, Germany

Ceria has recently returned into the focus of research thanks to the possibility to reversibly form and redisperse supported, catalytically active Pt clusters by controlling its morphology and redox state. In the present work, we systematically synthesize CeO_2(111) thin films to tune these parameters independently and investigate their influence on size-selected Pt_{20} cluster dimensionality and sintering behavior. First, we present recipes for atomically flat islands and closed CeO_2(111) films with a thickness up to 18 monolayers (ML), grown on Rh(111), and characterize them by means of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and low-energy electron diffraction (LEED). Remarkably, XRD and LEED show an epitaxially grown, crystalline, and relaxed film with cube-on-cube alignment. Bulk or exclusive surface reduction is achieved by ultra-high vacuum (UHV) annealing or room temperature (RT) CH_3OH dosing and annealing cycles, respectively. The methanol procedure forms oxygen vacancies only in the surface, without reducing the deeper layers of the film or introducing roughening. When deposited on a fully oxidized (Figure 1 (a,d)) versus a surface-reduced (Figure 1 (b,e)) support, Pt_{20} clusters show a strikingly different temperature-dependent dimensionality and sintering behavior. From STM images, we extract detailed cluster height distributions and coverages (Figure 1 (c,f)) and find that Ostwald ripening already sets in around 600 K on both, oxidized and reduced supports, without any indication for cluster diffusion and coalescence. Notably, at these temperatures, we obtain flat 2D clusters on the reduced support and 3D clusters on the oxidized support, where the atom detachment during sintering leads to the intermediate formation of Pt^{2+} species, in line with the redispersed single atoms at step edges observed in the literature [1-3].

References

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[2] F. Dvořák, M.F. Camellone, A. Tovt, N.D. Tran, F.R. Negreiros, M. Vorokhta, T. Skála, I. Matolínová, J. Mysliveček, V. Matolín, S. Fabris, Creating single-atom Pt-ceria catalysts by surface step decoration, Nat. Commun. 7 (2016).

[3] F. Maurer, J. Jelic, J. Wang, A. Gänzler, P. Dolcet, C. Wöll, Y. Wang, F. Studt, M. Casapu, J.D. Grunwaldt, Tracking the formation, fate and consequence for catalytic activity of Pt single sites on CeO_2, Nat. Catal. 3 (2020) 824–833.

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