Surface Science
Room 209 CDE W - Session SS-TuA
Heterogeneous Catalysis I

Moderators: Theo Kitsopoulos, University of Mississippi, **Matthew Gebbie**, University of Wisconsin - Madison

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,*** 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 Surface Modifications Induced by H_2 and H_2O Exposure on Cu-Doped Cerium Oxide***, Paola Luches,* Nanoscience Institute, National Research Council, Italy*; Avinash Vikatakavi,* Department of Physics, Informatics and Mathematics - University of Modena and Reggio Emilia, Italy*; Eleonora Spurio, Samuele Pelatti,* Nanoscience Institute, National Research Council, Italy*; Silvia Mauri, Mario Rivera-Salazar, Edvard Dobovičnik,* Istituto Officina dei Materiali, National Research Council, Italy*; Sergio D'Addato,* Department of Physics, Informatics and Mathematics, University of Modena and Reggio Emilia, Italy*; Piero Torelli,* Istituto Officina dei Materiali, National Research Council, Italy*; Stefania Benedetti,* Nanoscience Institute, National Research Council, Italy

Cerium oxide is a relevant material in catalysis due to the relative stability of Ce cations in two oxidation states, 4+ and 3+, and to the related ability to reversibly store and transport O atoms. The replacement of a minority of Ce cations with lower-valence metal ions was shown to induce a decrease of O vacancy formation energy and enhance the catalytic activity of the material.

To unravel the specific mechanisms that determine the surface functionality of Cu-doped ceria, we exposed ceria films with different dopant concentration to ambient pressure of H_2 and H_2O at different temperatures and we detected the surface modifications by X-ray absorption near-edge spectroscopy (XANES). The measurements were performed at the APE-HE beamline of the ELETTRA synchrotron radiation source, using a reaction cell with an ultrathin membrane that confines the gas flux in a narrow region extremely close to the sample surface. Ce M_{45}-edge and Cu L_{23}-edge spectra were measured during thermal treatments in H_2 and H_2O at ambient pressure, using the total electron yield detection mode to enhance surface sensitivity. Gas chromatography was used to correlate the observed surface spectroscopic modifications with the reaction products obtained.

Pure ceria showed a progressively increasing relative intensity of the Ce^{3+}-related features with increasing temperature in H_2 pressure. In Cu-doped films, as the Cu concentration increases, the same treatment led to a progressively higher intensity of the Ce^{3+}-related features (Fig. 1b and c). This evidence, combined with the evolution of the Cu oxidation state and with gas chromatography, suggested that at moderate temperatures H_2 dissociation is favored by the presence of Cu^{1+} sites, and at high temperatures water is desorbed from the surface with the uptake of oxygen from cerium oxide [1].

The modifications of the same materials upon H_2O exposure and the effect of irradiation with laser light at 375 nm wavelength were also investigated. Also in this case the Cu dopant ions were found to be active in modifying the electronic structure of CeO_2, and in enabling more efficient hydrogen production at lower temperatures, as compared to the pure oxide.

Reference:

[1] A. Vikatakavi, S. Mauri, M.L. Rivera-Salazar, E. Dobovičnik, S. Pelatti, S. D'Addato, P. Torelli, P. Luches, S. Benedetti, *Role of Metal Dopants in Hydrogen Dissociation on Cu:CeO_2 and Fe:CeO_2 Surfaces Studied by Ambient-Pressure X-ray Absorption Spectroscopy*, ACS Appl. En. Mater., 7, 2746-2754 (2024).

5:00pm **SS-TuA-12 Simultenous Electron Spectroscopy and X-Ray Scattering on Model Ceria Catalysts***, Baran Eren,* Weizmann Institute of Science, Israel **INVITED**

Heterogeneous catalysis is a timely and critical research field in basic and applied energy sciences, due to its potential to provide solutions to global environmental issues. However, there is still a lack of a profound understanding of the molecular and structural processes at the interfaces between solids and reactant gases. A detailed understanding of the correlation between the chemistry, structure, and function in these materials requires a multimodal investigation. Over the past few years, scientists at the at the Advanced Light Source, the Berkeley synchrotron facility, have developed a unique setup attached to an X-ray beamline where chemically-sensitive ambient pressure X-ray photoelectron spectroscopy (APXPS) and structure-sensitive grazing incidence X-ray scattering (GIXS) experiments can be performed simultaneously. Here, we showcase that this tool can provide mechanistic insights that are unparalleled in the literature.

This novel approach allows us to probe the changing surface and bulk chemistry, and surface and bulk structure of the model ceria catalysts in the presence of H_2 and CO_2 gases. In addition to the method itself, the electron density, surface chemistry, and roughness trends observed in ceria during the reaction will be discussed in this talk.Access to such a variety of data from working catalysts in a single experiment can have far-reaching implications, because changes in surface roughness, ability to store hydrogen in the bulk in various forms, and the chemical state of the surface, which all depend on the reactive environment, can directly affect the catalyst performance.

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