

Energy Transition Focus Topic

Room A212 - Session TL+2D+HC+SS-MoA

Surface Reaction Mechanisms in Energy Conversion (ALL INVITED SESSION)

Moderators: Marie Turano, Loyola University Chicago, Sarah Zaccarine, Colorado School of Mines

1:40pm **TL+2D+HC+SS-MoA-1 Selective Photo-driven Organic Reactions on the Surfaces of Colloidal Quantum Dots**, Y Jiang, K McClelland, C Rogers, Emily Weiss, Northwestern University **INVITED**

Colloidal quantum dots present a unique opportunity not only to power chemical reactions with sunlight but to control those chemical reactions through various templating strategies. This talk will explore demonstrations of chemo-, regio-, and stereoselective reactions photocatalyzed by quantum dots.

2:20pm **TL+2D+HC+SS-MoA-3 Single-Atom Alloy Catalysts: Born in a Vacuum, Tested in Reactors, and Understood In Silico**, Charles Sykes, Tufts University **INVITED**

In this talk I will discuss a new class of metallic alloy catalysts called *Single Atom Alloys* in which precious, reactive metals are utilized at the ultimate limit of efficiency.¹⁻⁵ These catalysts were discovered by combining atomic-scale scanning probes with more traditional approaches to study surface-catalyzed chemical reactions. This research provided links between the atomic scale surface structure and reactivity which are key to understanding and ultimately controlling important catalytic processes. Over the last five years the concepts derived from our surface science and theoretical calculations have been used to design *Single Atom Alloy* nanoparticle catalysts that can perform industrially relevant reactions at realistic reaction conditions in collaboration with Maria Flytzani-Stephanopoulos at Tufts. For example, alloying elements like platinum and palladium with cheaper, less reactive host metals like copper enables 1) dramatic cost savings in catalyst manufacture, 2) more selective chemical reactions, 3) reduced susceptibility to CO poisoning, and 4) higher resistance to deactivation by coking. I go on to describe very recent theory work by collaborators Stamatakis and Michaelides at UCL that predicts reactivity trends of 16 different *Single Atom Alloy* combinations for important reaction steps like activation of H-H, C-H, N-H, O-H and C=O bonds. This project illustrates that the field of surface science is now at the point where it plays a critical role in the design of new heterogeneous catalysts.

References:

- [1] Kyriakou et al. *Science* **335**, 1209 (2012).
- [2] Marcinkowski et al. *Nature Materials* **12**, 523 (2013).
- [3] Lucci et al. *Nature Communications* **6**, 8550 (2015).
- [4] Liu et al. *JACS* **138**, 6396 (2016).
- [5] Marcinkowski et al. *Nature Chemistry* **10**, 325 (2018).

3:00pm **TL+2D+HC+SS-MoA-5 Understanding Fundamental Energy Conversion Mechanisms: How Surface Science Can Help**, Ulrike Diebold, Institute of Applied Physics, TU Wien, Austria **INVITED**

As we move to a more sustainable society, current energy conversion schemes need to be improved and novel ones designed. The relevant charge transfer processes and chemical transformations all occur at interfaces, so insights into fundamental mechanisms are needed to provide a scientific basis for these developments.

Using the frontier tools of surface science, I will discuss how we can directly inspect charge transfer to molecules, investigate the influence of the local environment on the reactivity of active sites, or probe the acidity of individual hydroxyls. Together with first-principles computations such experiments give crisp and clear insights into surface processes. I will also discuss the steps that are necessary to transfer the knowledge gained from model systems to more complex environments.

4:00pm **TL+2D+HC+SS-MoA-8 Atomically-defined Model Interfaces in Energy-related Catalysis, Electrochemistry, and Photoelectrochemistry**, Jörg Libuda, University Erlangen-Nuremberg, Germany **INVITED**

The transformation between chemical energy, solar energy, and electrical energy occurs at interfaces. Therefore, functional interfaces are the key to the development of new materials in energy technology and energy-related catalysis. In our work, we explore model systems, which provide

detailed insight into the chemistry and physics at such functional interfaces. Complex, yet atomically-defined model systems are studied both under 'ideal' surface science conditions and under 'real' conditions, i.e., in contact with gases, liquids, in electrochemical, and in photoelectrochemical environments. We illustrate the approach in three examples from our recent research.[1-5]

First, we consider new noble-metal-efficient catalysts for fuel cell applications.[1] We show that precious noble metals such as Pt can be anchored to nanostructured oxide supports. The resulting materials show very high noble metal efficiency and high stability. Surface science studies on model catalysts provide insight into the functionality of these systems. Electronic metal support interactions modify the reactivity of the catalytic surfaces but also stabilize sub-nanometer-sized Pt nanoparticles against sintering and deactivation.

Secondly, we report on the development of atomically defined model systems for oxide-based electrocatalysts, which can be studied under true operation conditions, i.e., in liquid environments and under potential control. We describe how such model electrodes are prepared by surface science methods and, subsequently, are studied in liquid electrolytes preserving their atomic structure. We investigate the role of particle size effects and identify the origin of metal-support interactions.

In the third part, we scrutinize the role of organic-oxide hybrid interfaces in energy transformation. Particularly fascinating are organic layers of molecular photoswitches, which provide an extremely simple solution for solar energy conversion and storage. We show that it is possible to assemble fully operational solar-energy-storing hybrid interfaces by anchoring tailor-made norbornadiene photoswitches to atomically defined oxides. Interestingly, the activation barrier for energy release in these systems is not affected by the anchoring reaction. Finally, we demonstrate that solar energy storage and release in such systems can also be controlled electrochemically with high reversibility.

- [1] A. Bruix, et al., *Angew. Chem. Int. Ed.*, **53**, 10525 (2014)
- [2] Y. Lykhach, et al., *Nat. Mater.* **15**, 284 (2016)
- [3] O. Brummel et al., *ChemSusChem* **9**, 1424 (2016)
- [4] O. Brummel et al., *J. Phys. Chem. Lett.*, **8**, 2819 (2017)
- [5] F. Faisal et al., *Nat. Mater.*, **17** 592 (2018)

4:40pm **TL+2D+HC+SS-MoA-10 Controlling Ultrafast Photochemical Reactions in Photocatalysis**, Annemarie Huijser, University of Twente, The Netherlands, The Netherlands **INVITED**

The transition from fossil to renewable energy is one of the most important challenges of our society. Solar devices are widely considered as a highly promising option, as the energy provided by the sun to the earth by far exceeds global needs. We are investigating the use of nanostructured materials for application in solar energy conversion. The overall efficiency relies on the complex interplay of many elementary process, occurring at different time scales and also dependent on the nanostructure. In this presentation I will show how a combination of methods for ultrafast spectroscopy can shed light on the nature of photoinduced processes and provide mechanistic information valuable for the design of novel materials.

Energy Transition Focus Topic

Room A212 - Session TL+MS+VT-TuM

Implications of Implementation: Making Energy Transition a Reality (ALL INVITED SESSION)

Moderators: Margaret Fitzgerald, Colorado School of Mines, Natalie Seitzman, Colorado School of Mines

8:00am **TL+MS+VT-TuM-1 The Energy Transition: Science and Technology Development Aspects, Richard M.C.M. van de Sanden**, DIFFER, Eindhoven University, The Netherlands, Netherlands **INVITED**

The Paris climate agreement requires a decarbonization of our energy infrastructure leading to a CO₂ neutrality by 2050. Therefore renewable energy generation by means of wind or from solar radiation through photovoltaics or concentrated solar power will continue to increase its share in the energy mix. Intermittency (due to e.g. day/night cycle), the regional variation of these energy sources, and penetration of renewable energy into other sectors than electricity (e.g. the chemical industry) requires means to store, transport and convert energy on a large scale. A promising option is the synthesis of chemicals and synthetic fuels (easily deployable within the present fossil fuels infrastructure) from raw feedstock using renewable energy. A truly circular economy requires that the raw materials are the thermodynamically most stable molecules such as water (H₂O), carbon dioxide (CO₂) and nitrogen (N₂) to produce base chemical feedstock, such as e.g. hydrogen, hydrocarbons and ammonia. In this talk I will discuss the opportunities this transformation of the chemical industry provides. Furthermore, I will highlight the science and technology challenges, the catalytic materials, processes and systems developments needed that can provide compatibility of renewable energy driven chemistry with e.g. intermittency and localized production.

8:40am **TL+MS+VT-TuM-3 Electrochemical CO₂ Reduction Across Scales: From Fundamental Mechanisms to Practical Applications, Wilson Smith**, Delft University of Technology The Netherlands, The Netherlands **INVITED**

Electrocatalytic CO₂ reduction has the dual-promise of neutralizing carbon emissions in the near future, while providing a long-term pathway to create energy-dense chemicals and fuels from atmospheric CO₂. The field has advanced immensely in recent years, taking significant strides towards commercial realization. While catalyst innovations have played a pivotal role in increasing the product selectivity and activity of both C₁ and C₂ products, slowing advancements indicate that electrocatalytic performance may be approaching a hard cap. Meanwhile, innovations at the systems level have resulted in the intensification of CO₂ reduction processes to industrially-relevant current densities by using pressurized electrolytes, gas-diffusion electrodes and membrane-electrode assemblies to provide ample CO₂ to the catalyst. The immediate gains in performance metrics offered by operating under excess CO₂ conditions goes beyond a reduction of system losses and high current densities, however, with even simple catalysts outperforming many of their H-cell counterparts. Using recent literature as a guidepost, this talk will focus on some of the underlying reasons for the observed changes in catalytic activity, and proposes that further advances can be made by shifting additional efforts in catalyst discovery and fundamental studies to system-integrated testing platforms.

9:20am **TL+MS+VT-TuM-5 Perspectives on the Research and Development of Nanomaterials for Hydrogen Production, Marcelo Carmo**, Forschungszentrum Jülich, Germany **INVITED**

Hydrogen is often considered the best means by which to store energy coming from renewable and intermittent power sources. With the growing capacity of localized renewable energy sources surpassing the gigawatt range, a storage system of equal magnitude is required, such as the production of electrolytic hydrogen by water electrolysis. Despite of more than 100 years of experience in alkaline electrolysis systems, and thousands of plants installed all over the world, only a few systems or industries remain, providing the state-of-the-art of this technology today. This is due to the fact that the cost of electrical energy has always remained as an uncomfortable barrier, with electrolytic hydrogen costs not being able to compete with the costs for the production of hydrogen by conventional steam reforming of fossil fuels. Nevertheless, today, increased interest can be observed for PEM water electrolysis technology, and over the past 20 years, new companies and projects have appeared, with new leaders being consequently established in this growing niche. The reason is that PEM electrolysis provides a sustainable solution for the production of hydrogen, and is well suited to couple with energy sources

such as wind and solar. The advantages of PEM electrolysis over alkaline electrolysis together with novel R&D approaches can potentially reduce the investment costs of PEM electrolyzers. We expect that in the following years, frontier advancements on PEM electrolysis systems will appear, demonstrating a true capacity to ultimately establish hydrogen as a key player in the energy market, and contribute to a future hydrogen economy.

11:00am **TL+MS+VT-TuM-10 Impacts and Adaptation Strategies in Ethiopia, Aschale Dagnachew Siyoum**, Xavier University of Louisiana

This paper highlights climate change and variability and its impact and adaptation strategies in Ethiopia. Due to low adaptive capacity and high sensitivity of socio economic systems, climate vulnerability is worsening over the last few decades in Ethiopia. Available evidences showed that since 1960, the mean annual temperature of the country has risen by about 1.3°C with an average rate of 0.28°C per decade imposing a significant challenge on food security, water availability, energy supply, poverty reduction and sustainable development efforts of the nation. Ethiopia has responded to the increasing impact of climate change and variability through developing relevant adaptation strategies, plans and policies largely focused on decreasing vulnerability in many different sectors including agriculture and food security, water resources, forestry, and health. To tackle the impact of climate change, the government has approved the National Adaptation Program of Action (NAPA) in 2007 which includes projects that focused on promoting drought insurance program, strengthening drought and flood early warning systems, developing small-scale irrigation and water harvesting schemes in arid, semi-arid, and dry sub-humid areas, and realizing food security through a multi-purpose large-scale water development project. Results, however, shows that although some progress has been made in addressing the impacts of climate change and variability, adaptation measures implemented over the last few decades were generally ineffective resulting in increasing losses as more and more people occupy vulnerable areas. This requires a sustained effort to further plan and implement the right mix of climate change adaptation strategies to address vulnerability to biodiversity and humanity to the increasing impacts of climate change. Addressing the impact of climate change requires a good understanding of the nexus between climate change adaptation measures and sustainable development as well as knowledge of climate change adaptation tools and techniques, which when used properly can minimize the total damage to life and property.

11:20am **TL+MS+VT-TuM-11 Developing and Scaling Up the Manufacturing of Thin Film Materials for the Future of Energy Production, Storage, and Reduction, Ken Nauman**, Von Ardenne North America **INVITED**

The world, and thus the economy, are clearly dependent on energy and in particular electricity. Production of electricity is ever increasing while the desire to create cleaner sources becomes a higher priority to reduce the environmental impact. The transition to electricity for mobility in transportation and communication relies on new technology to improve market penetration. Thus, the three key aspects of electricity in our modern society are: generation, storage, and saving. In order to make the energy transition a profitable reality, companies that develop technology will have to reduce the cost of energy production and storage while also considering how to lower energy usage. This talk will cover these key aspects from the perspective of an equipment and process technology company. Companies such as Von Ardenne that develop thin film materials have focused on these topics to reduce the CapEx and CoO for our customer's factories. This includes processes for Thin Film Photovoltaics and Crystalline Photovoltaics, along with emerging cell architectures, to reduce the cost of electricity generation while reducing overall CO₂ production. Our company also works on leading material science in battery and fuel cell technology to increase storage capacity and cost of storing energy. Finally, other technology development is focused on saving energy with low-e coatings for glass and plastics. This presentation will review the history of the technological development as well as the latest trends, economics, and status of market leading performance in manufacturing products related to generating, storing, and saving electricity.

Energy Transition Focus Topic

Room A226 - Session TL+AS+SS+TF-TuA

Breakthroughs and Challenges in Applied Materials for Energy Transition (ALL INVITED SESSION) & Panel Discussion

Moderators: Jason Avila, U.S. Naval Research Laboratory, Devika Choudhury, Argonne National Laboratory

2:20pm TL+AS+SS+TF-TuA-1 Interface Science and Engineering for Energy-Water Systems, *Seth Darling*, Argonne National Laboratory **INVITED**

Driven by climate change, population growth, development, urbanization, and other factors, water crises represent the greatest global risk in the coming decades. Advances in materials represent a powerful tool to address many of these challenges. Understanding—and ultimately controlling—interfaces between materials and water are pivotal [1]. In this presentation, we will lay out the challenges and present several examples based on materials science strategies for addressing applications in water. In each instance, manipulation of interfacial properties provides novel functionality, ranging from selective transport to energy transduction to pollution mitigation.

[1] J. Appl. Phys. 124 (2018) 030901

3:00pm TL+AS+SS+TF-TuA-3 Atomic Dynamics of Noble Metal Surface in Gases Revealed by Time Resolved Environmental Transmission Electron Microscopy, *Seiji Takeda, N Kamiuchi, R Aso, H Yoshida, T Tamaoka*, Osaka University, Japan **INVITED**

The surface of noble metals in gas has been extensively studied in the field of surface science. The surface has been investigated in both ultra high vacuum and various gases of high pressure and under various stimuli, for instance the illumination of intense light, the electric and/or magnetic field and the irradiation of charged particles. A microscopy study is potentially useful to provide us with the imaging data on the surface in real space and time at the resolution that is available in a microscopy apparatus to use. Among various methodologies for microscopy, atomic resolution environmental transmission electron microscopy has advanced greatly in the time resolution recently, allowing us to explore the dynamic surface and to elucidate the mechanism of the dynamic phenomena that are related to various energy transition processes. We show recent our studies, including the self-activated surface dynamics of gold catalysts in reaction environments [1] and the unexpected gas (nitrogen) -solid (palladium) transition [2] that is occurring on the surface under a strong electrostatic field. We demonstrate that the surface dynamics that is associated with the energy transition processes needs to be visualized at atomic scale for understanding the electronic excitations behind the surface dynamics.

References

[1] N. Kamiuchi et al., Nat. Commun. 9 (2018) 2060.

[2] T. Tamaoka, R. Aso et al., Nanoscale (2019) .

4:20pm TL+AS+SS+TF-TuA-7 Totally Organic and Organic-Inorganic Hybrid Batteries, *Burak Esat*, Fatih University, Turkey, Rutgers University; *S Bahceci, S Akay*, Fatih University, Turkey; *A Momchilov*, Bulgarian Academy of Science, Bulgaria

We hereby represent novel polymers and reduced graphene oxide with pendant electro-active groups such as TEMPO and quinones.

The first example of polymers with pendant anode-active groups studied in our group is a polymethacrylate derivative carrying anthraquinone moieties (pMANtrq). This anthraquinone based anode-active material has proven to show a quite good reversible electrochemical reduction behavior in both aqueous and non-aqueous electrolytes in our studies. pMANtrq|1M LiClO₄ in EC:DEC=1:1|Li battery system has been constructed. The initial discharge capacity of the cell obtained was 151 mAh/g when cycled between 4.2 and 1.2V at 0.25C rate and 79.2 mAh/g when cycled between 4.0 and 1.5V at 0.3C rate during subsequent cycles.

This material was also used in an aqueous battery, pMANtrq |5M KOH aq.|LiMn₂O₄ . Although an initial discharge capacity of 37.7 mAh/g was obtained, it deteriorated quickly due to the solubility of the reduced form of the polymer in this electrolyte system. This is the first reported example of such organic-inorganic hybrid battery.

An anode material based on reduced graphene oxide (RGO) functionalized with anthraquinone is also investigated and a battery against Li metal

revealed a quite reversible capacity of 200 mAh/g based on the weight of electro-active anthraquinone moieties when cycled between 3.2 and 1.8 V at 0.3C rate. The energy density was found to be around 450 mWh/g.

We have also synthesized and characterized polyacetylene polymers with pendant TEMPO radicals which are electrochemically oxidizable in a reversible manner at around 3.5-3.6V vs. Li. These materials have been proven to be cathode-active materials for rechargeable batteries. We have demonstrated that a mixture of Tempo radical polymer with LiMn₂O₄ (1:1) can be used as a hybrid cathode material. Typically, this polymer may be expected to act as a polymeric electro-active binder and a stability improver for the inorganic cathode-active material.

Studies toward construction of all organic batteries using these anode and cathode materials are currently in progress.

4:40pm TL+AS+SS+TF-TuA-8 Electrochemical Strategies for Designing Interfaces of Battery Materials, *Betar Gallant*, Massachusetts Institute of Technology **INVITED**

Future generations of energy-storage devices require advances beyond state-of-the-art materials and redox systems. Rechargeable batteries, specifically today's Li-ion batteries, have largely been dominated by transition metal oxide cathodes; advanced conversion systems with higher theoretical energy densities, such as Li-S and Li-O₂, have received significant attention as "beyond Li-ion" batteries, but have their own challenges and limitations. Looking at the periodic table invites one to wonder, "Is there more beyond sulfur and O₂?" This talk will focus on challenges and opportunities related to a different chemical family: fluorine, or more specifically, active fluoride. Fluoride-containing additives, electrolytes, solid electrolyte interphases (SEI), and intercalation materials represent a recurring motif in many proposed next-generation battery chemistries, but current understanding of the behavior of fluorinated interfaces and materials remains largely phenomenological. In addition, controlling the incorporation of fluoride into materials still remains a major challenge owing to safety issues of fluorine and the intransigence of fluoride-containing precursors, hindering design in this space.

In this talk, I describe our group's exploration of several applications where fluoride-forming reactions can be harnessed and tailored for benefit in advanced batteries. First, I describe our efforts to develop high-energy density redox systems based on the electrochemical reduction of fluorinated gases. We show that fundamental knowledge and the experimental framework developed in the field of Li-O₂ batteries in recent years can be successfully translated to the development of new gas-to-solid conversion reactions with high energy densities. Next, I will discuss the opportunities presented by the ability to generate fluoride *in situ* in working batteries from these reactions, creating new possibilities to fluorinate interfaces in tailorable and precise ways. I will present our findings relevant to two examples where fluoride has been suggested to play a critical and enabling role: Li anode interfaces, and oxyfluoride-based intercalation cathodes. Using our gas-based fluorination architecture, we explore the fundamental role that fluoride plays in each of these applications. Finally, I will highlight future challenges and opportunities in the characterization of fluorinated materials.

Surface Science Division

Room A220-221 - Session SS+AS+HC+TL-ThM

Surface Science of Energy Conversion and Storage

Moderators: Steven L. Tait, Indiana University, Francisco Zaera, University of California, Riverside

8:00am SS+AS+HC+TL-ThM-1 Chemical and Electrochemical Stability of Perovskite Oxide Surfaces in Energy Conversion: Mechanisms and Improvements, *Bilge Yildiz*, Massachusetts Institute of Technology **INVITED**

A broad range of highly active doped ternary oxides, including perovskites, are desirable materials in electrochemical energy conversion, catalysis and information processing applications. At elevated temperatures related to synthesis or operation, however, the structure and chemistry of their surfaces can deviate from the bulk. This can give rise to large variations in the kinetics of reactions taking place at their surfaces, including oxygen reduction, oxygen evolution, and splitting of H₂O and CO₂. In particular, aliovalent dopants introduced for improving the electronic and ionic conductivity enrich and phase separate at the surface perovskite oxides. This gives rise to detrimental effects on surface reaction kinetics in energy conversion devices such as fuel cells, electrolyzers and thermochemical H₂O and CO₂ splitting. This talk will have three parts. First, the mechanisms behind such near-surface chemical evolution will be discussed. Second, the dependence of surface chemistry on environmental conditions, including temperature, gas composition, electrochemical potential and crystal orientation will be described. Third, modifications of the surface chemistry that improve electrochemical stability and activity, designed based on the governing mechanisms, will be presented. Guidelines for enabling high performance perovskite oxides in energy conversion technologies will be presented.

8:40am SS+AS+HC+TL-ThM-3 Mechanism of Oxygen Reduction Reaction on Nitrogen-doped Carbon Catalysts, *Junji Nakamura*, University of Tsukuba, Japan

Nitrogen-doped carbon materials are expected to be non-Pt catalysts for oxygen reduction reaction (ORR) in fuel cells. Among several types of nitrogen species in carbon materials, pyridinic nitrogen (nitrogen atom bound to two C atoms) has been found to create ORR active sites in our previous work¹. We then try to prepare catalytically active carbon surfaces covered with pyridinic nitrogen-containing aromatic molecules with high density. Recently we have reported model catalyst studies using HOPG (highly oriented pyrolytic graphite) electrode covered with pyridinic nitrogen-containing aromatic molecules (dibenz[a,c] acridine (DA) molecule and acridine (Ac)molecule)². The DA molecules form a two-dimensional ordered structure along the direction of the HOPG substrate by self-organization. Adsorbed DA on the HOPG surface shows high ORR activity in terms of specific activity per pyridinic nitrogen and is comparable to that of pyridinic-nitrogen-doped carbon catalysts. We study the mechanism of ORR taking place on the DA/HOPG model catalyst. In acidic reaction conditions, pyridinic nitrogen is protonated to pyridinium nitrogen (NH⁺) species. It is suggested that the adsorption of oxygen take place on a carbon atom in a DA molecule upon reduction of the NH⁺ species. Generally, the reduction of NH⁺ is difficult to proceed thermodynamically at higher potentials above 0 V vs RHE. However, in the presence of oxygen, the reduction of NH⁺ is possible by an energy gain due to simultaneous adsorption of oxygen. The supplied electron goes to pi system as SOMO electron upon reduction, which is responsible for the adsorption of oxygen. That is, the role of pyridinic nitrogen is to provide SOMO electron upon reduction of NH⁺ species.

References

- Guo D, Shibuya R, Akiba C, Saji S, Kondo T, Nakamura J, (2016). Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science*, 351, 361-365.
- Shibuya R, Kondo T, Nakamura J, (2018). Bottom-up design of nitrogen-containing carbon catalysts for the oxygen reduction reaction. *ChemCatChem* doi.org/10.1002/cctc.201701928

9:00am SS+AS+HC+TL-ThM-4 Copper Corrosion Inhibition Investigated on the Molecular Scale Using APXPS, *Bo-Hong Liu*, Lawrence Berkeley National Laboratory; *O Karshloğlu*, Lawrence Berkeley National Laboratory; *M Salmeron*, *S Nemšák*, Lawrence Berkeley National Laboratory; *H Blumh*, Fritz Haber Institute of the Max Planck Society, Germany

Copper has been used in a wide variety of applications. Though relatively inert, it corrodes when in contact with aqueous solutions/water vapor and corroding agents such as chlorine.¹ Benzotriazole (BTA) is a commonly used corrosion inhibitor to protect copper surfaces. A consensus regarding the mechanism of corrosion protection is that BTA complexes with surface copper atoms, resulting in a Cu(I)-BTA protective polymer layer.² UHV-based surface science studies clarified the structure of the BTA layer on copper single crystal surfaces at low dosage, as demonstrated by a very recent study combining DFT and spectroscopic techniques;³ however, the effect of environmental factors could not be well addressed by this approach. Here, we report an Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) study of the influence of water vapor and chlorine on well-defined Cu surfaces. To capture the material complexity of the corrosion phenomenon, we study copper single crystals as well as polycrystalline foils of metallic copper, cuprous oxide and cupric oxide. In this presentation, we will show that the water uptake of copper surfaces under humid condition is strongly influenced by the presence of a BTA layer. Also, a BTA layer blocks chlorine uptake in some conditions. Based on these experimental results, factors that influence the BTA inhibitory effect on copper corrosion are identified.

1. Atlas, D.; Coombs, J.; Zajicek, O. T., THE CORROSION OF COPPER BY CHLORINATED DRINKING WATERS. *Water Research* **1982**,16 (5), 693-698.
2. Finsgar, M.; Milosev, I., Inhibition of copper corrosion by 1,2,3-benzotriazole: A review. *Corrosion Science* **2010**,52 (9), 2737-2749.
3. Gattinoni, C.; Tsaousis, P.; Euaruksakul, C.; Price, R.; Duncan, D. A.; Pascal, T.; Prendergast, D.; Held, G.; Michaelides, A., Adsorption Behavior of Organic Molecules: A Study of Benzotriazole on Cu(111) with Spectroscopic and Theoretical Methods. *Langmuir* **2019**,35 (4), 882-893.

9:20am SS+AS+HC+TL-ThM-5 Analysis and Deliberate Modification of Electrochemical Interfaces, *Esther Takeuchi*, *K Takeuchi*, *A Marschilok*, Stony Brook University **INVITED**

Interfaces in electrochemical energy storage systems are critical in the transport of electrons and ions and are significant factors in electrochemical function, yet remain a challenge to fully understand. In lithium based systems, the interfaces or interphases often form spontaneously due to reactions of the active materials and the electrolytes. The interfaces formed due to these spontaneous reactions may prove beneficial as they provide needed protection inhibiting further and continuous reaction. However, the characteristics of the interface may also contribute to decreased ion transport and the accompanying increased effective resistance.

Conversion-type materials for next generation lithium ion systems are appealing due to the opportunity for multiple electron transfer within one metal center. However, implementation of conversion materials has been hindered by the phase transformations occurring during cycling as well as formation of a resistive solid electrolyte interphase (SEI). This presentation will explore the effective implementation of combinations of characterization techniques including the use of *ex-situ* and *operando* methods to provide insight into the formation, composition and deliberate modification of the SEI.

11:00am SS+AS+HC+TL-ThM-10 An Investigation on Active Sites of La₂O₃ Catalyst for OCM Reaction: A Combined Study of *in situ* XRD, XPS and Online MS, *Yong Yang*, *C Guan*, *E Vovk*, *Z Liu*, *X Zhou*, *J Liu*, *Y Pang*, ShanghaiTech University, China

Oxidative coupling of methane (OCM) is a catalytic partial oxidation process that converts methane directly to valuable C₂ products (ethane and ethylene). Previous results suggested that the bulk structure change of the La₂O₃ catalyst was related to the performance of the reaction. In this work, a designed *in situ* XRD-MS coupled characterization setup coupled with online MS instrument are used for measuring both the reaction products and the bulk structure of the catalyst in real time and under simulated industrial conditions. This allows for the more detailed study in order to relate information from of bulk structure change vs. CO₂ related treatment and quantitative analysis of the reaction products, thus for a further connection and understanding of the conversion rate of CH₄ and the selectivity of C₂. The work presented focused on online characterization of the OCM reaction on La₂O₃ catalyst, covering different parameters including: 1. La₂O₃ pretreatment under different CO₂ concentrations, 2.

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Consecutive OCM reactions, comparing the behavior of a clean surface La_2O_3 catalyst with a La_2O_3 catalyst after OCM, 3. OCM performed after La_2O_3 has undergone pretreatment with pure CO_2 . Results indicate that carbonates formation on La_2O_3 is two step, surface carbonates formation at below 500°C and bulk formation at $500\text{--}700^\circ\text{C}$. *In situ* TPD performed in a high pressure gas cell (HPGC) and XPS measurement results confirm the above.

The results showed that bulk CO_3^{2-} formation under CO_2 exposure, results in higher light-off temperature of CO_2 and C_2 than the clean surface during OCM reaction. There is carbonate formation on commercial La_2O_3 during OCM reaction and CO_2 desorption after OCM reaction by *in situ* XRD-MS, and it influences the light-off temperature of CO_2 and C_2 up to 65°C higher than the clean surface. It is proposed that CO_3^{2-} may perform as a catalyst poison in this reaction. This result provides an important insight of the active site for OCM reaction. Based on this result, a brief XPS study of the carbonate free sample surface, which may be only prepared from the HPGC vacuum connected further reveals an oxide feature related with methane activation. Additional DFT calculations based upon the experimental data indicates a carbonation mechanism which occurs in the subsurface, which in turn could be related to La_2O_3 activity.

11:20am **SS+AS+HC+TL-ThM-11 Interaction of Amino Acids on Au(111) as Studied with EC-STM: From Islands to Magic Fingers**, J Phillips, K Boyd, I Baljak, L Harville, Erin Iski, University of Tulsa

With growing interest into origin of life studies as well as the advancement of medical research using nanostructured architectures, investigations into amino acid interactions have increased heavily in the field of surface science. Amino acid assembly on metallic surfaces is typically investigated with Scanning Tunneling Microscopy (STM) at low temperatures (LT) and under ultra-high vacuum (UHV), which can achieve the necessary resolution to study detailed molecular interactions and chiral templating. However, in only studying these systems at LT and UHV, results often tend to be uncertain when moving to more relevant temperatures and pressures. This investigation focuses on the Electrochemical STM (EC-STM) study of five simple amino acids (L-Valine, L-threonine, L-Isoleucine, L-Phenylalanine, and L-Tyrosine) as well as two modifications of a single amino acid (L-Isoleucine Ethyl Ester and N-Boc-L-Isoleucine), and the means by which these molecules interact with a Au(111) surface. Using EC-STM under relevant experimental conditions, the amino acids were shown to have a considerable interaction with the underlying surface. In some cases, the amino acids trapped diffusing adatoms to form Au islands and in other cases, they assisted in the formation of magic gold fingers. Importantly, these findings have also been observed under UHV conditions, but this is the first demonstration of the correlation *in situ* and was controlled via an applied external potential. Results indicate that an increase in the molecular weight of the amino acid had a subsequent increase in the area of the islands formed. Furthermore, by shifting from a nonpolar to polar side chain, island area also increased. By analyzing the results gathered via EC-STM at ambient conditions, fundamental insight can be gained into not only the behavior of these amino acids with varied side chains and the underlying surface, but also into the relevance of LT-UHV STM data as it compares to data taken in more realistic scenarios.

11:40am **SS+AS+HC+TL-ThM-12 Deposition and Structure of MoO_3 Clusters on Anatase TiO_2 (101)**, Nassar Doudin, Z Dohnálek, Pacific Northwest National Laboratory

Oxide clusters supported on metal oxide substrates are of great interest due to their importance in heterogeneous catalysis [1]. The nature and strength of the interactions between the metal oxide clusters and the support materials not only govern their structure and stability but also control the energetics of elementary steps that are critical for the overall activity [1]. Understanding the nature of the interactions is therefore important to tailor the supported metal oxide cluster systems to achieve the desired reactivity and selectivity. Here, we present a scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) study of the monodispersed MoO_3 clusters deposited by the sublimation of MoO_3 powder on anatase $\text{TiO}_2(101)$ surface at 300 K. After the deposition, the STM images of the lowest concentration of MoO_3 show that the clusters initially migrate over the surface and preferentially anchor at step edges before they start to aggregate on the terraces. Interestingly, the aggregates are mostly composed of three adjacent clusters, with a small concentration of monomers and dimers. Further exposures to MoO_3 increase the cluster coverage until a fully saturated over-layer is created with each clusters being are centered on top of the Ti sites. The adsorbed clusters appear as bright protrusions, with an apparent cluster height of approximately 1.5 Å

and diameter of about 8.5 Å. Since the cyclic $(\text{MoO}_3)_3$ trimers are known to be a dominant gas phase species resulting from the sublimation of MoO_3 [1], we propose that each cluster on the surface is a trimer. Annealing to 550 K results in a better-order of the $(\text{MoO}_3)_3$ layer, but further annealing to 650 K leads to three-dimensional clusters. The XPS results indicate that the $\text{Mo}(3d_{5/2})$ binding energy in as-deposited $(\text{MoO}_3)_3$ is characteristic of Mo^{6+} , and the oxidation state of Mo remains (+6) upon heating to 600 K. As such, this system may offers great promise as an ideal platform for reactivity studies on well-defined supported model transition-metal oxide catalysts.

[1] Zdenek Dohnálek et al. Royal Society of Chemistry 43, 7664–7680 (2014).

12:00pm **SS+AS+HC+TL-ThM-13 Ionic Conducting Nanostructures Tailored on Porous Mixed Conduction Composite Electrodes for Enhancement of Oxygen Reduction Reaction**, Jong-Eun Hong, D Joh, S Kim, H Ishfaq, Korea Institute of Energy Research, Republic of Korea; C Jung, J Park, DGIST, Republic of Korea; S Lee, H Kim, T Lim, S Park, R Song, Korea Institute of Energy Research, Republic of Korea; K Lee, DGIST, Republic of Korea

With decrease in the operation temperature of solid oxide fuel cells, the oxygen reduction reaction (ORR) in the cathodes, which is sluggish, plays an important role in improving the electrochemical performance. Much effort has given to facilitate the ORR by the applications of cathode surface modification using active catalysts, nano-particle cathodes, and advanced cathode materials. In particular, the cathode surface modification with a reactive electro-catalyst has been appeared to increase the electrode reactivity and thus to decrease the polarization resistance to the oxygen reduction reaction. Infiltration of electro-catalysts has been widely utilized to tailor the cathode microstructures as it is a facile method. In this study, one-step infiltration using an *in-situ* sol-gel process was applied to modify porous mixed conducting composite cathodes, and the impact of surface microstructure tailoring on the electrochemical performances was investigated. The precursors of Sm- and Nd-doped ceria (SNDC), whose ionic conductivity is even higher than that of Gd-doped CeO_2 (GDC), were infiltrated into the cathode by using an ultrasonic spray nozzle to produce fine and uniform droplets. The infiltrated samples then experienced an *in-situ* heat-treatment after repeating the ultrasonic spraying and drying processes and were submitted for electrochemical measurements. The detailed results on the microstructure evolution and electrochemical properties of the specimens prepared using the ultrasonic spraying infiltration are presented, and the elucidation of the results are discussed.

2D Materials

Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA

Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications

Moderator: Mark Edmonds, Monash University, Australia

2:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-1 Molecular Layers on Nanoporous Gold Electrodes, Elizabeth Landis**, College of the Holy Cross
Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials, Paul Brown**, American Society for Engineering Education; *S Fischer, J Kofacz, C Spillmann, D Gunlycke*, U.S. Naval Research Laboratory

Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

3:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?, Vladimir Korolkov**, Oxford Instruments-Asylum Research; *S Chulkov, M Watkins*, University of Lincoln, UK; *P Beton*, The University of Nottingham, UK

Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces^{1,2} and bulk polymers³.

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular

contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model⁴ to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

¹Korolkov et al., Nat. Chem., 2017

²Korolkov et al., Nat. Comm., 2017

³Korolkov et al., Nat. Comm., 2019

⁴Hapala et al., Phys. Rev. B 90, 085421

3:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds, Jangyup Son**, University of Illinois at Urbana-Champaign; *N Buzov*, University of California at Santa Barbara; *S Chen*, University of Illinois at Urbana-Champaign; *D Sung*, Sejong University, Republic of Korea; *H Ryu*, Seoul National University, Republic of Korea; *J Kwon*, Yonsei University, Republic of Korea; *S Kim, J Xu*, University of Illinois at Urbana-Champaign; *S Hong*, Sejong University, Republic of Korea; *W King*, University of Illinois at Urbana-Champaign; *G Lee*, Seoul National University, Republic of Korea; *A van der Zande*, University of Illinois at Urbana-Champaign

Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF₂) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-6 Functionalization of MoS₂ with Halogens, G Copetti**, IF-UFRGS, Brazil; *E Nunes*, IQ-UFRGS, Brazil; *G Soares*, IF-UFRGS, Brazil; *Cláudio Radtke*, IQ-UFRGS, Brazil

Transition metal dichalcogenides (TMDs) with lamellar structures similar to that of graphite have received significant attention because some of them are semiconductors with sizable bandgaps and are naturally abundant. This offers opportunities for fundamental and technological research in a variety of fields including catalysis, energy storage, sensing, and electronic devices. In order to TMDs fulfill their potential, a precise control i) of surface functionalization and ii) of the number of stacked TMD monolayers are mandatory. Surface functionalization was shown to play a key role in

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tuning photoluminescence properties of MoS₂, formation of controllable and low defect density dielectric/MoS₂ interfaces obtained by atomic layer deposition, and etching of MoS₂ layers. Halogenation is one of the most promising functionalization techniques of TMDs. MoS₂ etching with atomic layer control was already achieved by chlorine adsorption associated with Ar⁺ sputtering. Moreover, doping techniques to tune the conductivity and photoemission properties of MoS₂ are essential. Previous works have already shown that incorporation of F-containing species in MoS₂ leads to doping, as well as other interesting properties such as tunable ferromagnetic ordering. In this work, we performed first principal calculations with the density functional theory (DFT) to gain insight into the effect of MoS₂ exposure to halogens. Results evidenced different reactivities while comparing F and Cl, as well as MoS₂ surfaces with variable amounts of defects. These results were explored experimentally. Bulk exfoliated MoS₂ as well as CVD-grown monolayer MoS₂ samples were used. Chlorination was achieved by irradiating the samples with UV light in Cl₂ flux. Prior to chlorination, sputtering of the MoS₂ with Ar ions is performed to induce S removal. X-ray Photoemission Spectroscopy measurements and Rutherford Backscattering Spectrometry showed that S vacancies play a fundamental role in the chlorination process, with vacancy concentration dictating the balance between etching of the MoS₂ layer and Cl incorporation. Fluorination was performed by exposing the samples to pulses of XeF₂. Different degrees of fluorination are achieved by varying exposure time. S is removed and F is incorporated without any loss of Mo. Chemical displacement on the Mo 3d and S 2p XPS peaks was observed after both halogenations processes. These results can clarify the mechanisms of Cl and F incorporation. Finally, the halogenation techniques proposed can be simple and useful methods to adapt the MoS₂ properties for future applications.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study***, *Tao Jiang, D Le, T Rahman*, University of Central Florida

Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO₂ towards ethanol formation, in the reaction pathway of which the crucial step for forming C₂ bond, i.e. reaction of adsorbed species CH₃* and CO* to form CH₃CO*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS₂ functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH₃* and a CO* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C₂ species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya, A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS₂ activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers**, *Woo-Kyung Lee, J Pietron, D Kidwell, J Robinson, C McGann, S Mulvaney*, U.S. Naval Research Laboratory

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the

electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is $6.2 \times 10^4 \Omega\text{-cm}$, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA). We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-9 Sensor for Breath and Skin Diagnostics**, *Pelagia I Gouma*, The Ohio State University

Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-10 Symmetry Controlled Adsorption of Diiodobenzene on MoS₂**, *Zahra Hooshmand*, University of Central Florida; *P Evans, P Dowben*, University of Nebraska - Lincoln; *T Rahman*, University of Central Florida

In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS₂(0001). The intensity ratio of iodine to molybdenum measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS₂(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS₂, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS₂(0001).

* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA-11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS₂ and 2D-MoS₂ Catalysts**, *Mihai Vaida*, University of Central Florida

Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H₂ molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS₂ and MoS₂. Crystalline 2D-TaS₂ and 2D-MoS₂ with surface area of 1 cm² are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling

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microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS₂ occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS₂, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methylidyne radical (CH), which subsequently react with other CH radical to produce acetylene (C₂H₂).

Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room A213 - Session HC+SS+TL-ThA

Reaction Pathways and Addressing Challenges for Energy Production in the 21st Century & Heterogeneous Catalysis Graduate Student Award Presentation

Moderators: Sanjaya Senanayake, Brookhaven National Laboratory, Arthur Utz, Tufts University

2:20pm **HC+SS+TL-ThA-1 High Resolution XPS to Identify C_nH_y Surface Species on a Cobalt Model Catalyst: New Experimental Evidence for the Importance of Alkylidyne as Growth Intermediates in Fischer-Tropsch Synthesis**, *Kees-Jan Weststrate*, Syngaschem BV, Netherlands; *D Sharma, D Garcia Rodriguez, M Gleeson*, DIFFER, Eindhoven University, The Netherlands, Netherlands; *H Fredriksson, H Niemantsverdriet*, Syngaschem BV, Netherlands

Supported cobalt catalysts find their most widespread application in low temperature Fischer-Tropsch synthesis (FTS), a process in which C-C bond forming reactions produce long chain saturated hydrocarbon chains from synthesis gas, a mixture of CO and H₂. The versatile FTS process may very well continue to play a role in future energy scenarios: synthesis gas can be derived from any carbon-containing source, e.g. biomass or even CO₂ may be used. These renewable carbon sources offer a sustainable alternative to replace petroleum as the principal feedstock of chemicals and liquid transportation fuels.

The FTS reaction mechanism can be ranked among the most complex in the chemical industry. CO and H₂ are converted into long chain hydrocarbons in a sequence of bond-breaking and bond-making steps that are catalyzed by metals such as cobalt, ruthenium and iron (the latter is active in the carbide form). As the steady state concentration of chain growth intermediates is below the detection limits of in-situ spectroscopies simplified model studies are needed to elucidate the mechanism by which long hydrocarbon chains grow on the cobalt catalyst surface. Since chains grow on a surface that is packed with CO, it is of crucial importance to consider how CO spectators influence the reactivity of hydrocarbon adsorbates. We use a Co(0001) single crystal surface as a model system to study how C_nH_x adsorbates react on a cobalt surface, both in ultrahigh vacuum (~10⁻¹⁰ -10⁻⁷ mbar) as well as at near-ambient pressure (~0.1 mbar). By using the high resolution available of x-ray photoemission spectroscopy at the SuperESCA beamline of ELETRA (Trieste, Italy), and the unique opportunity to combine these qualities with measurements at near-ambient pressure at the HIPPIE beamline of MAX IV (Lund, Sweden), we were able to elucidate the reaction mechanism by which carbon-carbon bonds form on a cobalt surface. We find that CO's presence is of essential importance: It promotes hydrogenation of acetylene, HC≡CH [the most stable C₂H_{rad} without CO] to ethylidyne, ≡C-CH₃, a facile reaction that occurs around 250 K. Ethylidyne dimerization around 310 K produces 2-butyne (H₃C-C≡C-CH₃), a strongly bound alkyne adsorbate that hydrogenates to 2-butene (g) above 400 K. Extrapolated to FTS, the findings speak in favour of the alkylidyne chain growth mechanism: long chain alkylidynes (≡C-R), stabilized by the presence of CO spectators, react with a methylidyne (≡CH_{ad}) monomer to produce a 1-alkyne (R-C-CH) adsorbate. Partial hydrogenation of the 1-alkyne product is promoted by CO_{ad} and produces the alkylidyne species needed for the next CH insertion step.

2:40pm **HC+SS+TL-ThA-2 Beam Reflectivity Measurements of Carbon Dissolution on Nickel Single Crystal Catalysts**, *Eric High, D Tinney, A Utz*, Tufts University

The interaction of carbon with metal catalysts is of significant interest. In methane steam reforming, the build-up of carbon in the nickel subsurface

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leads to a gradual reduction in reactivity on the surface and ultimately results in deactivation of the metal catalyst. Additionally, the initial dissolution and subsequent reemergence of carbon from the subsurface are key steps in the growth of well-ordered graphene on nickel substrates via chemical vapor deposition (CVD). Researchers have previously used Auger and X-ray photoelectron spectroscopy to investigate the dynamics of carbon dissolution into nickel surfaces. We instead employ beam reflectivity measurements to monitor the process of carbon diffusion into the nickel subsurface in real-time. We will present data collected via exposure of a Ni(997) single crystal to supersonically expanded CH₄ molecules at surface temperatures above 600 K. We observe significant changes in the reaction profile by increasing surface temperature as the rate of dissolution approaches the reactive flux of the high energy gas molecules. We use these results to further develop kinetic models for methane reactivity as a function of surface coverage as well as carbon diffusion into the stepped nickel crystal. The major parameters from these models include the site-blocking coverage and its subsequent dependence on surface temperature as well as an updated measure of the barrier to diffusion for the C/Ni system.

3:00pm **HC+SS+TL-ThA-3 Fundamental Research Opportunities to Advance Energy Technologies**, *Bruce Garrett*, Department of Energy

INVITED

The U. S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences (BES) supports fundamental research in chemical and materials sciences to provide the foundations for new energy technologies and to support DOE missions in energy, environment, and national security. This presentation will discuss opportunities for fundamental research to impact DOE's energy mission "to catalyze the timely, material, and efficient transformation of the nation's energy system and secure U.S. leadership in energy technologies" with a focus on the way we generate, store and use energy nationally. I will provide an overview of BES strategic planning over the past decade that identified priority research directions for advancing energy applications, highlight key scientific advances in these areas, and discuss some future opportunities for modern science, particularly studies of interfacial processes, to accelerate the transformation of the U. S. energy portfolio.

4:00pm **HC+SS+TL-ThA-6 Oxidation and Redox-Mediated Transformation of a Tb₂O₃ Thin Film from the Cubic Fluorite to Bixbyite Structure**, *Christopher Lee, J Weaver*, University of Florida

The terbium oxides, a member of the rare earth oxide family, exhibit favorable properties in selective oxidation catalysis due to the high mobility of oxygen stored and released within the lattice. Of particular note is the ease of structural rearrangement into highly stable, well-ordered intermediates between the Tb₂O₃ and TbO₂ stoichiometries in addition to a continuum of nonstoichiometric states. As opposed to ceria, which stabilizes strongly in the CeO₂ stoichiometry, thin film terbium is very stable in the Tb₂O₃ stoichiometry and can exist in an oxygen deficient cubic fluorite arrangement (CF-Tb₂O₃) as well as the bixbyite structure (c-Tb₂O₃).

We discovered a redox-mediated mechanism for the transformation of thin film CF-Tb₂O₃(111)/Pt(111) to c-Tb₂O₃(111)/Pt(111) in ultrahigh vacuum (UHV). Low energy electron diffraction (LEED) and temperature programmed desorption (TPD) shows that repeated oxidation and thermal reduction to 1000 K transforms an oxygen deficient cubic fluorite Tb₂O₃(111) thin film to the well-defined bixbyite, or c-Tb₂O₃(111) structure. In addition, TPD measurements show the development of several distinct O₂ desorption peaks arising from the oxidation of c-Tb₂O₃ domains to the stoichiometrically-invariant ι -Tb₇O₁₂ and δ -Tb₁₁O₂₀ phases and demonstrates the more facile oxidation of c-Tb₂O₃ relative to CF-Tb₂O₃. We present evidence that nucleation and growth of c-Tb₂O₃ domains occurs at the buried TbO_x/CF-Tb₂O₃ interface, and that conversion of the interfacial CF-Tb₂O₃ to bixbyite takes place mainly during thermal reduction of TbO_x above ~900 K and causes newly-formed c-Tb₂O₃ to advance deeper into the film. The avoidance of low Tb oxidation states may facilitate the CF to bixbyite transformation via this redox-mechanism.

Further oxidation of a well-ordered c-Tb₂O₃ film provides evidence of the sequential phase stabilization of ι -Tb₇O₁₂, δ -Tb₁₁O₂₀, and α -TbO_{2-x} stoichiometric structures along with lower temperature peaks corresponding with more weakly-bound surface oxygen. Oxidation at temperatures between 300-500 K reveals an apparent Arrhenius activation barrier of ~7.4 kJ/mol for the initial conversion of c-Tb₂O₃ to ι -Tb₇O₁₂. Furthermore, oxidation at 100 K creates an additional oxygen species stable at lower temperatures that has a much more pronounced effect on oxidation of the film surface over the bulk of the film. The ability to control

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the surface termination of the $\text{TbO}_x(111)$ thin films along with selectively creating surface bound oxygen species provides the structural basis necessary to clarify the partial oxidation mechanisms associated with terbia-based catalysis.

4:20pm **HC+SS+TL-ThA-7 Discrimination of Surface Storage and Mechanistic Pathways Using Dynamic Pulse Response Experiments**, Y Wang, M Kunz, Idaho National Laboratory; G Yablonsky, Washington University in Saint Louis; **Rebecca Fushimi**, Idaho National Laboratory

Pulse response experiments in a pure diffusion reactor significantly increase the number of gas/solid collisions for probing kinetic interactions but maintain straightforward transport modeling by avoiding gas phase dynamics. Using inverse-diffusion methods [1] the millisecond time-dependence of the reaction rate can be calculated as it responds to the forced concentration dynamic. More importantly, in this experiment the gas and surface concentrations are decoupled and their influence on the transformation rates of reactants and products can be studied.

Vacuum pulse response studies of ammonia decomposition on polycrystalline Fe, Co and a CoFe bimetallic preparation were conducted to investigate the microkinetic features that lead to very distinct global performance [2]. We present dynamic atomic accumulation; a new measure used to characterize the ability of a complex surface to regulate adsorbed species. We find Fe can support hydrogenated species with a longer surface lifetime than either CoFe or Co. From the time-dependence of the rate we find Co can support two mechanistic pathways for H_2 production. The quantitative rate, gas and surface concentration data of microkinetic reaction steps explain why materials with cobalt perform better at a global level.

1. Redekop, E.A., et al., *The Y-Procedure methodology for the interpretation of transient kinetic data: Analysis of irreversible adsorption*. Chem. Eng. Sci., 2011. **66**(24): p. 6441-6452.

2. Wang, Y., et al., *Transient Kinetic Experiments within the High Conversion Domain: The Case of Ammonia Decomposition*. Catalysts, 2019. **9**(1): p. 104.

4:40pm **HC+SS+TL-ThA-8 Nuclearity Effects in Supported Zinc and Gallium Catalysts for Alkane Dehydrogenation**, **Susannah Scott**, University of California at Santa Barbara **INVITED**

The selective dehydrogenation of alkanes to alkenes is an important process in the valorization of shale gas liquids and in the production of on-demand olefins. Ga- and Zn-modified aluminosilicates have been extensively studied as catalysts for these reactions. In the presence of Brønsted acid sites (BAS), the olefins undergo subsequent aromatization to more valuable BTX. The nuclearity of the metal active sites, the proximity between the metal sites and the BAS, and the nature of the support, may influence the catalytic activity but detailed structure-property relationships are difficult to ascertain in conventional catalysts with many types of sites. The reactions of GaMe_3 and ZnMe_2 with the hydroxyl-terminated surfaces of dehydrated silica and alumina, as well as with the internal and external surfaces of H-ZSM-5, are particularly simple. They generate methane and isolated dimethylgallium and methylzinc sites. K-edge X-ray absorption spectra, analyzed via inspection of the wavelet transform EXAFS (WT-EXAFS) and curvefitting of the Fourier transform EXAFS (FT-EXAFS), reveal that the silica and zeolite materials contain dinuclear grafted sites, regardless of the thermal pretreatment of the support, while alumina gives dispersed mononuclear grafted sites. Differences in reactivity and stability appear to originate in these structural variations.

5:20pm **HC+SS+TL-ThA-10 Fundamental Insights into Hydrocarbon Conversion Mechanisms in Lewis and Brønsted Acid Zeolites using Temporal Analysis of Products**, **Hari Thirumalai**¹, J Rimer, L Grabow, University of Houston

The surge in natural gas production has incentivized the search for processes that can utilize methane and light olefin derivatives in the manufacture of useful products such as benzene, toluene and xylene (BTX). These are important commodity chemicals that are used as fuel additives and as raw materials in the synthesis of specialty chemicals. Industrial demand is met through processes such as the synthesis of BTX through dehydroaromatization of light olefins or through alkylation of aromatics, typically with the use of zeolites as catalysts. Complex reaction mechanisms determined by the presence of a hydrocarbon pool dominate hydrocarbon chemistry and are challenging to study. These challenges hinder the in-depth understanding of the role of the catalyst and its eventual design for tailored applications.¹

In this work, we use the transient kinetics technique, temporal analysis of products (TAP), to probe hydrocarbon conversion and upgrade in the transient regime of reaction. TAP experiments help probe the intrinsic kinetics of reactant conversion in a well-defined Knudsen transport regime under high-vacuum conditions. We studied the dehydroaromatization of ethylene and the methylation of toluene as case-studies for hydrocarbon conversion reactions. The precise control of reactant molecules entering the reactor and responses recorded by a high-resolution mass spectrometer at the reactor outlet in the dehydroaromatization of ethylene suggest that a Lewis acid such as Ag^+ or Ga^{3+} in the zeolite accelerate the retention of long lived carbonaceous species in the zeolite, thus attaining the autocatalytic arene cycle more rapidly. Pulse responses provide qualitative evidence that olefins are strongly bound to the metal-exchanged zeolite samples with delayed desorption, enhancing the rate of hydrocarbon conversion and carbon retention. Finally, experiments investigating the methylation of toluene to xylene provide valuable information on competitive binding of reactants to the zeolite acid sites and the ensuing primary reactions that drive the reaction.

Overall, our experiments under semi-idealized conditions help provide insight into the crucial primary reactions that initiate the hydrocarbon pool mechanism, thus elucidating the role of extra-framework species such as Ag^+ or Ga^{3+} and their synergy with the Brønsted acid sites in hydrocarbon conversion. The fundamental understanding gained from these experiments will be crucial in deciphering the role of the different zeolitic active sites in model hydrocarbon conversion reactions.

References

1. Hsieh, M. F., Zhou, Y., Thirumalai, H., Grabow, L. C., & Rimer, J. D. ChemCatChem, (2017), 9(9), 1675-1682.

¹ Morton S. Traum Award Finalist

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