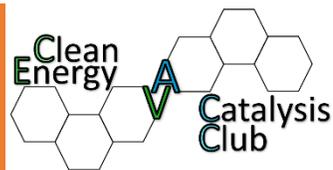


Virginia Clean Energy and Catalysis Club

2021 Summit (August 2nd, 2021)



Increased access to renewable resources has influenced new technological advances for more sustainable approaches to transform the energy, chemical, and materials. The Virginia Clean Energy and Catalysis Club (VA-CECC) is being organized to bring together Virginia researchers to disseminate recent advances in catalysis and clean energy fields through a monthly invited talk series and an annual summit. The VA-CECC strives to build collaborations among Virginia institutions and scientists, to provide opportunities for undergraduate and graduate researchers, and to develop fundamental science and engineering around sustainable solutions for our future energy needs.

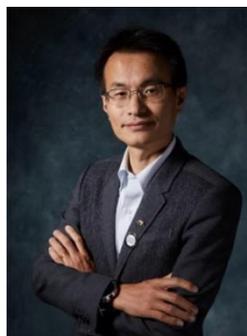
2021 Virtual Summit Registration Deadline: July 15th, 2021

Free registration: <https://uva.theopenscholar.com/2021virginiacleanenergycatalysis/activities>

Distinguished Lectureship Awards



Prof. Karen I. Goldberg
University of Pennsylvania
Vagelos Professor of Energy



Prof. Peidong Yang
University of California, Berkeley
S.K. and Angela Chan
Distinguished Professor of
Energy

Summit Presenters

Charles Machan, University of Virginia
Diana Iovan, Virginia Tech
Amanda Morris, Virginia Tech
Ian Harrison, University of Virginia
Peter Njoki, Hampton University
Feng Lin, Virginia Tech
Ayman Karim, Virginia Tech

Michael Norris, University of Richmond
Tarek Abdel-Fattah, Christopher Newport University
Adelina Voutchkova-Kostal, George Mason University
Ashleigh Baber, James Madison University
Rama Balasubramanian, Roanoke College
Chris Paolucci, University of Virginia
Weining Wang, Virginia Commonwealth University

Organizers

T. Brent Gunnoe, University of Virginia (Email: tbg7h@virginia.edu)
Sen Zhang, University of Virginia (Email: sz3t@virginia.edu)
Ram B. Gupta, Virginia Commonwealth University (Email: rbgupta@vcu.edu)
Hongliang Xin, Virginia Tech (Email: hxin@vt.edu)
Huiyuan Zhu, Virginia Tech (Email: huiyuanz@vt.edu)



VA Clean Energy and Catalysis Club (VA CECC) Summit 2021

Agenda

August 2, 2021, Monday (Eastern Standard Time)

8:00 am - 8:15 am	Opening Remark Melur K. "Ram" Ramasubramanian (UVA VPR) and T. Brent Gunnoe
8:15 am - 8:45 am	Distinguished Lecturer Karen Goldberg , University of Pennsylvania
8:50 am - 9:15 am	Charles Machan, University of Virginia
9:20 am - 9:45 am	Michael Norris, University of Richmond
9:50 am - 10:00 am	Coffee Break
10:00 am - 10:25 am	Diana Iovan, Virginia Tech
10:30 am - 10:55 am	Tarek Abdel-Fattah, Christopher Newport University
11:00 am - 11:25 am	Adelina Voutchkova-Kostal, George Washington University
11:30 am - 11:55 am	Amanda Morris, Virginia Tech
12:00 pm - 1:00 pm	Lunch Break
1:00 pm - 1:25 pm	Rama Balasubramanian, Roanoke College
1:30 pm - 1:55 pm	Ashleigh Baber, James Madison University
2:00 pm - 2:25 pm	Peter Njoki, Hampton University
2:30 pm - 2:55 pm	Ian Harrison, University of Virginia
3:00 pm - 3:05 pm	Coffee Break
3:05 pm - 3:30 pm	Feng Lin, Virginia Tech
3:35 pm - 4:00 pm	Chris Paolucci, University of Virginia
4:05 pm - 4:30 pm	Weining Wang, Virginia Commonwealth University
4:35 pm - 5:00 pm	Ayman Karim, Virginia Tech
5:05 pm - 5:35 pm	Distinguished Lecturer Peidong Yang , University of California, Berkeley
5:40 pm - 7:30 pm	Dinner Break
7:30 pm - 8:00 pm	Shimadzu Equipment Introduction
8:00 pm - 9:30 pm	Poster Session

Join Virtual Meeting:

<https://virginia.zoom.us/j/97758546396?pwd=RW9UUmYzZ1pWWW1vVHNZakJVOXlzZz09>

Meeting ID: 977 5854 6396

Passcode: 350341

Find your local number: <https://virginia.zoom.us/j/97758546396>

Instruction for Poster Session:

The poster session will be held in the two poster rooms of the Gather.town space (should be easy to find them by wandering around).

Gather.town is a web-based app that essentially allows you to wander around a virtual space and interact with objects and people (the latter via Zoom-like video conferencing). **A few important notes about gather:** Chrome is the recommended and only supported browser. Others can be used, but no guarantee that there will not be bugs. You can also go to <https://gather.town/> and try out a demo (“live walkthrough” is best but the office demo will work too.)

Link at Gather.town:

<https://gather.town/app/semIFQ36Gan0VuVj/VA%20CECC%20Summit%202021>

Password: VACECC

The organizers will have all posters up there by August 1, 2021. All students who will be presenting can simply stand in the front of poster and wait for people to show up (a video conference with the poster displayed should automatically start, or you may need to press “X”).

All poster presenters need to send poster electronic files (pdf or ppt) to Perrin Godbold (pmg2vy@virginia.edu) by 5 pm, Saturday, July 31, 2021 (EST).

Distinguished Lectureship

Developing Alternatives to Oil as Feedstocks for our Chemicals and Liquid Fuels



Prof. Karen Goldberg
University of Pennsylvania,
Philadelphia, PA,
United States

As we move to decarbonize our energy landscape, we must not only develop viable liquid fuels for the future, but we must also re-envision our chemical industry and economy. The carbon-based chemicals from which we make our medicines, detergents, plastics, fibers and almost everything we use on a daily basis are today derived from petroleum. Fundamentally new pathways from different carbon resources must be developed to successfully transition to a sustainable future. The Goldberg group is pursuing new strategies and reactions to make other carbon sources, e.g. natural gas and carbon dioxide, viable for production of our chemicals and liquid fuels. This talk will highlight the design of organometallic catalysts to promote reactions such as the selective partial oxidation of light alkanes to alcohols and olefins and the reduction of carbon dioxide to methanol.

Biography

Dr. Karen Goldberg received her A.B. degree from Barnard College of Columbia University in New York City. As an undergraduate, she pursued research projects with Professor Roald Hoffmann at Cornell University, Professor Stephen Lippard at Columbia University, and Drs. Tom Graedel and Steven Bertz at AT&T Laboratories. She then went on to the University of California at Berkeley where she earned her Ph.D. in Chemistry working with Professor Robert Bergman. Following a postdoctoral year with Professor Bruce Bursten at The Ohio State University, she joined the faculty at Illinois State University, a primarily undergraduate institution in Normal, IL, in 1989. In 1995, she moved to the University of Washington (UW) as Assistant Professor of Chemistry. She was awarded tenure at UW and rose through the ranks to full Professor. In 2007 she became the first Raymon E. and Rosellen M. Lawton Distinguished Scholar in Chemistry, and in 2010 she became the first Nicole A. Boand Endowed Professor of Chemistry. She served as Director of the first National Science Foundation-funded Phase II Center for Chemical Innovation (CCI), the Center for Enabling New Technologies through Catalysis (CENTC) from 2007-17. In 2017, she moved to the University of Pennsylvania as a Vagelos Professor of Energy Research and became the inaugural Director of the Vagelos Institute of Energy Science and Technology (VIEST). In 2018, Professor Goldberg was elected to the National Academy of Sciences.

Distinguished Lectureship

The Chemistry of Making Semiconductor Nanowires for Artificial Photosynthesis



Prof. Peidong Yang
University of California, Berkeley,
CA, United States

Semiconductor nanowires, by definition, typically have nanoscale cross-sectional dimensions, with lengths spanning from hundreds of nanometers to millimeters. These subwavelength structures represent a new class of semiconductor materials for investigating light generation, propagation, detection, amplification, modulation as well as energy conversion and storage. After more than two decades of research, nanowires can now be synthesized and assembled with specific compositions, heterojunctions, and architectures. This has led to a host of nanowire photonic and electronic devices. Nanowire also represents an important class of nanostructure building blocks for photovoltaics as well as direct solar-to-fuel conversion because of their high surface area, tunable bandgap, and efficient charge transport and collection. In this talk, I will present a brief history of nanowire research for the past 25 years and highlight the synthesis of nanowires using well-defined chemistry. These semiconductor nanowires are then used for artificial photosynthesis, where solar energy is converted and stored in chemical bonds in a solar driven CO₂ fixation process.

Biography

Dr. Peidong Yang is a Chemistry professor, S. K. and Angela Chan Distinguished Chair Professor in Energy at the University of California, Berkeley. He is a senior faculty scientist at Materials and Chemical Sciences Division, Lawrence Berkeley National Laboratory. He is a member of both the National Academy of Sciences and the American Academy of Arts and Sciences. Prof. Yang is known particularly for his work on semiconductor nanowires and their photonic and energy applications including artificial photosynthesis. He is the director for California Research Alliance by BASF and the Kavli Energy Nanoscience Institute at Berkeley. Dr. Yang received his B.A. in Chemistry from the University of Science and Technology in China in 1993. He then received his Ph.D. in Chemistry from Harvard University in 1997, and did his postdoctoral fellowship at the University of California, Santa Barbara. Soon after, he joined the faculty at the University of California, Berkeley. He is the recipient of Global Energy Prize, MacArthur Fellowship, E. O. Lawrence Award, ACS Nanoscience Award, MRS Medal, Baekeland Medal, Alfred P. Sloan research fellowship, the Arnold and Mabel Beckman Young Investigator Award, National Science Foundation Young Investigator Award, MRS Young Investigator Award, Julius Springer Prize for Applied Physics, ACS Pure Chemistry Award, and Alan T. Waterman Award. He is the 2014 Thomas Reuters Citation Laureate for Physics.

Cr Complexes for the Electrocatalytic Reduction of Carbon Dioxide



Prof. Charles Machan
University of Virginia,
Charlottesville, VA, United
States

The steady increase in anthropogenic carbon dioxide (CO₂) emissions and corresponding atmospheric concentrations continues to generate interest in using CO₂ as a liquid fuel and commodity chemical precursor. The conversion of CO₂ has the dual benefit of addressing its associated negative environmental effects and the diminishing supply of petrochemical feedstocks. Relative to later transition metals, chromium is underrepresented in molecular and heterogeneous catalysts for CO₂ conversion as a result of selection bias based on previous successes with metals like iron, cobalt, and nickel. With an appropriate redox-active framework, molecular chromium species are capable of producing carbon monoxide from CO₂ with high selectivity and activity. At the heart of efficient reductive transformations are proton-coupled electron transfer (PCET) reactions, where electrons and protons move in a concerted way to mitigate kinetic and thermodynamic penalties. Mechanistic understanding of these reactions can inform the design of optimized catalyst structures with improved activity and selectivity for specific products. Molecular systems are well-positioned to provide a better understanding of these reactions because of the relative fidelity with which they can be characterized, as well as the possibility for systematic testing of structure-function relationships through iterative molecular design.

Toward understanding the role of energy, proton, and electron source on the selectivity of CO₂ reduction



Prof. Michael Norris
University of Richmond,
Richmond, VA, United
States

Our research seeks to use renewable energy sources to reduce CO₂ to liquid fuels that can be incorporated into our current energy infrastructure. The challenge of CO₂ reduction is often framed as a fight with thermodynamics since CO₂ is such a “stable” molecule. However, aside from single electron reduction of CO₂ to make a radical, the thermodynamics are not insurmountable, and are actually more favorable for making methanol than products such as CO and formate. It seems promising then that a multitude of catalysts exist that affect the 2e⁻ reduction of CO₂ to CO and/or formate with high efficiency. Unfortunately, there are far fewer systems that reduce CO₂ to methanol (or methane) as significant kinetic barriers exist to these more highly reduced products. Systems capable of overcoming the kinetic barriers to produce methanol selectively have mostly relied on mechanisms in which hydrides are transferred to CO₂; either through hydrogenation reactions or sacrificial borane or silane donors. We have been working to understand the role that the delivery of reducing equivalents and protons play on the production of methanol from CO₂ reduction in order to logically design systems that can ultimately be regenerated with electricity. As opposed to just focusing on catalyst design, our investigations have centered on the roles of various other components, such as amines for activation of CO₂, Lewis acids that can cooperatively activate CO₂, hydride sources that vary in both hydricity and oxidized byproducts, and the delivery of electrons through electrochemical or photochemical means.

Tuning the Reactivity of First-Row Transition Metals for C–H Bond Functionalization



Prof. Diana Iovan
Virginia Tech, Blacksburg,
VA, United States

Efficient conversion of simple hydrocarbon feedstocks into value-added products remains a major synthetic target. To this end, seeking to emulate the aerobic C–H hydroxylation function of cytochrome P450, metal-ligand multiple bond constructs have been extensively targeted for C–H bond functionalization. The Betley group has reported C–H amination catalysis using high-spin iron dipyrinato complexes, ascribing this reactivity to the unique electronic configuration of an isolated high-spin ferric iminyl. Our studies also highlighted the access to a di-iron bridging imido that can catalytically transfer the N-group into allylic and benzylic C–H bonds, emphasizing the importance of establishing a correlation between electronic structure and reactivity. With an interest in further expanding the avenues for C–H bond functionalization, my research group seeks to leverage metal-metal and metal-ligand cooperativity to manipulate the electronic structure and reactivity of earth-abundant, first-row transition metals. We aim to target bimetallic complexes to (1) explore a polarization-induced mechanism for C–H cleavage and (2) fundamentally understand electronic structure requirements of bioinspired dimeric oxo motifs for C–H hydroxylation.

Metal organic frameworks precursor for metal borides catalyst fabrication for hydrogen generation resections



Prof. Tarek M. Abdel-Fattah
Christopher Newport
University, Newport News,
VA, United States

Metal borides hold great promise in sustainable energy applications through their use as catalysts. This work describes efficient synthesis of nickel borides and the ability to improve the synthesis efficiency of nickel borides by first utilizing a nickel chloride precursor in a synthesis of a nickel metal organic framework. The preparation of nickel metal organic framework occurs at room temperature in aqueous solution. The comparison between the nickel precursor and the nickel metal organic framework to produce nickel borides is characterized by the kinetics of their hydrogen evolution reactions in aqueous solution at varying reaction conditions, by X-ray powdered diffraction (XRD) for crystallization prior to and after reduction, Thermogravimetric Analysis (TGA) for stability analysis of nickel metal organic framework and Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM-EDX) is conducted to confirm the composition of the framework and formation of nickel borides. Comparing between the nickel precursor alone and the nickel metal organic framework, activation energy of nickel borides formation was decreased from 62.6 kJ mol⁻¹ to 56.2 kJ mol⁻¹ and hydrogen evolution was significantly increased at higher temperatures of 303 K from 480 μ L min⁻¹ to 770 μ L min, respectfully. Optimal production of nickel borides and evolution of hydrogen was also found with more acidity conditions. XRD study confirmed the formation of nickel borides from nickel metal organic framework and revealed a complete reduction of framework after 24 hours while the diffraction of nickel borides from the metal precursor revealed impurities within the borides within this reaction time. SEM-EDX confirmed a 2:1 ratio of nickel to boron in the resulting nickel borides from the framework. This work shows a novel approach to a higher quality synthesis of nickel borides from synthesized nickel metal organic framework as a catalyst for hydrogen generation from solid feedstock.

Direct conversion of alcohols to long-chain hydrocarbons via tandem dehydrogenation-decarbonylative olefination



Prof. Adelina Voutchkova-Kostal
George Washington
University, Washington,
D.C., United States

Hydrogen-free upgrading of alcohols to liquid hydrocarbons using supported catalysts is desirable for producing drop-in fuel substitutes, but direct and atom-economical processes are yet to be reported. Here we describe an innovative alcohol upgrading and deoxygenation cascade that meets these criteria, producing only water, hydrogen and carbon monoxide. This hydrogen-free cascade is catalyzed by multifunctional Pd catalysts, whose supports offer diverse acid-base properties: primarily basic MgO, acidic γ -Al₂O₃ and Mg-Al hydrotalcite (HT) with a combination of Lewis acidic and basic sites. The impact of support selection on activity and selectivity offers insights into the design principles for next-generation catalysts for this process and related transformations.

Tetraazamacrocyclic Metal-Organic Frameworks for Carbon Dioxide Utilization



Prof. Amanda J. Morris
Virginia Tech, Blacksburg,
VA, United States

Developing materials and methods to capture and convert carbon dioxide to useful chemicals and fuels is imperative considering the rapidly advancing impacts of global climate change. Metal-organic frameworks (MOFs) have emerged as potential platform material for both. For example, MOFs display the highest CO₂ sorption capacities known. Additionally, many research groups have demonstrated the ability of MOFs to reduce and/or utilize CO₂ in chemical reactions. Toward this goal, the Morris group has developed the VPI-100 series of MOFs, which incorporates a tetraazamacrocyle as the linker component. VPI-100-Cu and -Ni are competent catalysts for the addition of CO₂ to cyclic epoxides. These results coupled to a detailed mechanistic study of the interactions between the VPI-100 analogs (Zr and Hf) and both CO₂ and cyclic epoxides will be presented. The MOF displays a synergistic effect between the linker and the node imparting enhanced reactivity.

Superparamagnetic Properties of Nanophase Maghemite Catalytic Particles



**Prof. Rama
Balasubramanian
Roanoke College, Salem,
VA, United States**

Cylindrical nanostructures of graphene, carbon nanotubes (CNTs), have many interesting electronic and mechanical properties. In particular, Y-shaped single walled nanotubes (Y-SWNTs) are preferred for fabrication of nanoelectronic devices. We show that high density Y-SWNTs, with diameters less than 2 nanometers, can be grown directly using cation (Co/Cr) substituted maghemite nanoclusters as catalysts in a chemical vapor deposition chamber.

Catalytic nanoclusters of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and $\gamma\text{-(Fe}_{1-x}\text{M}_x)_3$, where M= Co/Cr and x=0, 2, 5 wt.%, were synthesized using a co-precipitation technique. Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) measurements showed that the catalytic clusters were approximately 100 nm aggregates. These aggregates were comprised of individual particulates of cation substituted maghemite, of size less than 10nm as evidenced by X-ray diffraction measurements. Transmission Mössbauer spectra at room temperature of catalyst clusters were dominated by presence of superparamagnetic doublet and broadened hyperfine fields, characteristic of ultrafine superparamagnetic iron oxide phase (SPION) with size less than 15 nm. Y-SWNTs were synthesized with catalytic decomposition of hydrocarbons on nanoclusters. The sizes of SWNT were measured using AFM and FE-SEM. The average tube diameter was measured to be 1.0 ± 0.2 nm and a decrease in particle size of catalytic nanoclusters generally resulted in a greater density of CNT with surface density ' ρ ' greater than 10 ($\text{n}/\mu\text{m}^2$). With the growth of single wall nanotubes, our results show that the superparamagnetic phase of the nanocatalyst clusters play a crucial role in the formation of multiple Y-branches, which is a promising candidate for building network of nanoelectronic transistors. The crystallographic, morphological and magnetic properties of the catalyst metal powders and the properties of the resulting SWNTs will be presented.

Controlling the selectivity of ethanol dehydrogenation with systematic TiO₂/Au(111) surface preparations



Prof. Ashleigh Baber
James Madison University,
Harrisonburg, VA, United States

The dry dehydrogenation of ethanol to form acetaldehyde, an important chemical feedstock, and hydrogen gas is a preferential pathway over the formation of water. Herein, we investigate the role of surface modifications on the selective oxidation of ethanol to acetaldehyde over the elimination reaction to form ethylene and water. Depending on the surface preparation conditions, Au(111) supported TiO₂ nanoparticles react with small alcohols to form either reduced and oxidized products. A systematic study of ethanol reactivity over several TiO₂/Au(111) surfaces elucidates the effect of surface conditions on the selectivity of the reaction between ethanol and TiO₂/Au(111). The reactivity of the surface for ethanol oxidation was altered by controlling the oxidation state of TiO_x ($x < 2$) and coverage of TiO₂. Atomic force microscopy (AFM) was used to study the structure of the Au(111) supported TiO₂ nanoparticles and ultrahigh vacuum temperature programmed desorption (TPD) was used to monitor the selectivity of the reaction between ethanol and TiO₂/Au(111). Low coverages of fully oxidized TiO₂ nanoparticles on Au(111) are active for the selective oxidation of ethanol to form acetaldehyde.

Microwave-Assisted Synthesis of Copper-Based Nanoparticles for Catalysis



Prof. Peter Njoki
Hampton University,
Hampton, VA, United States

Multimetallic nanoparticles have gained interest due to their synergistic effect and structure-property relationship at the nanoscale. This presentation focuses on the synthesis of copper-based nanoparticles via microwave irradiation method. We choose copper because it is inexpensive, has physical properties that include high electrical conductivity, and is a valuable constituent in heterogeneous catalysis. Nevertheless, copper is susceptible to oxidation leading to loss in activity and applicability. To overcome this drawback, we have combined copper with other metals. For example, we successfully synthesized copper-silver nanoparticles by reacting aqueous solutions of copper (II) nitrate hemi(pentahydrate) and silver nitrate with sodium acrylate (reducing/capping agent) via microwave irradiation. When silver ions were reduced on preformed copper nanoparticles at hydrothermal temperature (160 °C), spherical copper-silver nanoparticles were formed. Simultaneous reduction of copper ions and silver ions at 160 °C produced octahedral and rods-shaped copper-silver nanoparticles. The morphology and composition were examined by scanning transmission electron microscopy - energy dispersive spectroscopy and X-ray photoelectron spectroscopy. Future work will focus on exploration of electrocatalytic activities towards CO₂ reduction reactions.

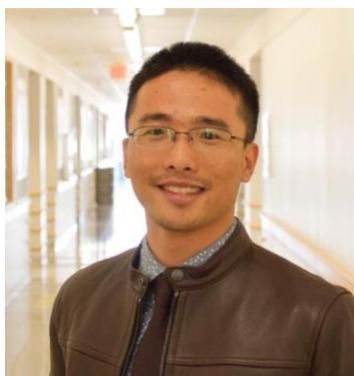
Alkane Activation at Pt & Rh Surfaces: Effects of Dynamics, van der Waals Interactions, and Steps



Prof. Ian Harrison
University of Virginia,
Charlottesville, VA, United
States

The initial C-H bond cleavage of C₁-C₉ alkanes on Pt (111) and methane on Rh (111) has been examined using effusive molecular beam techniques. Beam studies provide opportunities to study gas-surface reactivity and energy transfer under a relatively broad range of thermal equilibrium and non-equilibrium conditions. Molecular translational energy directed along the surface normal is found to be about twice as effective as vibrational energy in promoting the reactivity of methane. The transition states of larger alkanes are stabilized by van der Waals interactions with the surface. Though alkane reactivity on the Pt (111) surface is dominated by (111) terrace site reactivity, methane reactivity on Rh (111) indicates that Rh step sites are not readily poisoned by C accumulation and can contribute substantially to the overall methane reactivity at temperatures of catalytic interest.

Degradation and Reformation of Electrocatalyst Surfaces under Operating Conditions



Prof. Feng Lin
Virginia Tech, Blacksburg,
VA, United States

The electrode-electrolyte interfacial reactivity and stability govern the efficiency and lifetime of electrochemical devices, especially under aggressive reaction conditions such as high temperature, high potential, and corrosive environments. Modulating the metal-oxygen bonding environment at the electrode surface offers an effective path towards enhancing the interfacial reactivity. However, the high interfacial reactivity can trigger undesired interfacial reactions that lead to local structural changes, phase segregation and dissolution, and ultimately the complete degradation of the pre-designed electrode surface. The rational design of a highly active and stable electrocatalyst is largely hindered by this dilemma. Understanding how the electrocatalyst-electrolyte interface transforms under operating conditions can generate mechanistic insights into identifying the catalytically active motif and establishing methods to circumvent the dilemma by repairing the degraded structure. Using metal hydroxide oxygen evolution electrocatalysts as a platform, our operando synchrotron spectroscopic and microscopic analyses demonstrate that the interfacial degradation can be reversible between catalytic oxidation and reduction potentials. Such reversibility allows us to develop an intermittent reduction method to revivify the catalytic activity under operating conditions, enhancing catalyst durability.

Effects of Water on the Formation and Degradation of Pd(II) Cations in Zeolites



Prof. Christopher Paolucci
University of Virginia,
Charlottesville, VA, United
States

Metal-exchanged zeolites, though often exhibiting enhanced resistance to sintering in comparison to other supported metal cation counterparts, may gradually deactivate due to agglomeration of metal atoms. This phenomenon is of particular importance for Pd-exchanged CHA zeolites, whose ability to adsorb NO at low temperatures make it a promising candidate for emissions control. Here, employing density functional theory (DFT) calculations, and first-principles thermodynamic modeling, we follow the life cycle of Pd cations in CHA zeolites and the critical role of H₂O throughout.

Computational modeling, and X-ray absorption and infrared spectroscopies demonstrate that Pd cations are solvated by H₂O below 573K, forming four-fold coordinated square planar complexes detached from the zeolite framework, akin to homogeneous Pd complexes. These H₂O-solvated complexes exhibit higher NO desorption temperatures than their dehydrated counterparts, inhibit CO adsorption, and have the same coordination environment across zeolites of varying topology.

Once NO desorbs, CO and H₂O cause Pd cations to aggregate and form metallic Pd clusters that oxidize to PdO nanoparticles, leading to a loss in NO adsorption capacity. To determine the conditions where Pd cations can be regenerated we formulated computational phase diagrams that predict how nanoparticle size, gas conditions, and zeolite composition affect interconversion of PdO to cations. We demonstrate through modeling and experiment that small nanoparticles can be regenerated to cations at much lower temperatures than large particles. Finally, we show that, contrary to prior proposals, H₂O inhibits regeneration of PdO nanoparticles to Pd cations, and higher water pressures can actually promote nanoparticle formation.

Rational Design of MOFs-based Photocatalysts Towards Addressing Environmental Challenges



Prof. Wei-Ning Wang
Virginia Commonwealth
University, Richmond, VA,
United States

Metal-organic frameworks (MOFs) have attracted much attention in the past decades owing to their amazing properties, including rich surface chemistry, flexible structure, superior surface area, and tunable porosity. Endorsed by those features, MOFs find a variety of applications, such as gas capture and separation, catalysis, drug delivery, and sensing. MOFs are conventionally synthesized via wet-chemistry methods, which, however, suffer from long reaction durations, inhomogeneous mixing, and limited batch processes. To address the above issues, we have developed a microdroplet-based nanomanufacturing process to fabricate MOFs-based functional materials with controlled hierarchical nanostructures in the rapid, continuous, and scalable manner. Further, we have also developed strategies to integrate MOFs with semiconductors to form hybrid photocatalysts to tackle various environmental challenges, such as CO₂ photoreduction and water treatment. The quantitative mechanisms of gas adsorption, activation, and charge transfer within the hybrid nanostructures were explored by various in-situ techniques, such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), photoluminescence (PL) spectroscopy, and X-ray photoelectron spectroscopy (XPS), coupled with density functional theory (DFT) calculations.

Catalysis on Precious Metals in the Subnanometer Regime: New Properties and Reaction Pathways



Prof. Ayman M. Karim
Virginia Tech, Blacksburg,
VA, United States

Supported noble metal catalysts are extensively used in industry and their catalytic performance is strongly affected by particle size and shape. In the last decade, supported single atoms and clusters in the subnanometer size regime have attracted a lot of interest since they maximize the metal utilization and have also shown extraordinary catalytic properties for many reactions. However, to tailor the catalyst properties for specific reactions and determine possible limitations, there is a need to understand, on the atomic scale, the origin of activity and selectivity in the subnanometer regime.

In this talk, I will present my group's efforts in understanding the role of metal nuclearity and electronic properties in catalyzing model oxidation, hydrogenolysis and selective hydrogenation reactions. Using a suite of advanced characterization techniques (aberration-corrected electron microscopy, microcalorimetry, in-situ and in-operando DRIFTS, XPS, EXAFS and HERFD-XANES) complemented by DFT calculations and detailed kinetics measurements, the catalyst structural and electronic properties are identified and correlated with the reaction kinetics. The talk will cover how the metal nuclearity and strong interaction with the support in the subnanometer regime have a strong effect on the reaction mechanism, for CO oxidation, butane hydrogenolysis and selective hydrogenation of acetylene. The results will be discussed in relation to scaling and Brønsted-Evans-Polanyi relationships.