Elucidation of Electrocatalysis to Understand Photocatalytic Overall Water Splitting

Kazuhiro Takanabe

The climax of photocatalytic overall water splitting in powder suspension form is the simultaneous occurrence of electrocatalytic hydrogen evolution and oxygen evolution. In order for a semiconductor powder to achieve both reactions, the chemical potential at the surface should be shifted negatively and positively at the redox sites. It is however difficult to quantitatively describe such potentials of the powder suspension system. Knowledge transfer from electrocatalytic measurement to photocatalysis is effective to estimate the difficult-to-measure potentials of the photocatalytic system. This contribution discusses the effectiveness of electrocatalytic measurements to understand photocatalytic behavior, mainly focusing on hydrogen evolution catalysis and water-forming back reaction.

Successful photocatalytic overall water splitting is achievable when the water-forming back reaction from H₂ and O₂ to form H₂O does not prevail. Although decoration of hydrogen evolution catalysts on the semiconductor powder is often essential to achieve high photocatalytic efficiency, the same catalyst surfaces often introduce the thermodynamically-favorable back reaction. We show that the suppression of the back reaction is achievable when the semiconductor powder is decorated with highly dispersed noble metal catalysts, such as Pt species, with tungsten carbide nanoparticles, or with hydrogen-evolving catalysts covered with membrane-function layers, such as CrOₓ, MoOₓ, and SiOₓ. To elucidate the catalytic rates for both forward (hydrogen evolution) and backward (water formation) reactions, electrocatalytic measurements are effectively utilized where the potential of the catalysts is determined.

In a similar way, the importance of electrolyte identity is evaluated mainly at near-neutral pH by effectively comparing electrocatalysis and photocatalysis. It is well accepted that buffering action is considered inevitable especially at high rates, but our elucidation pins down such effects quantitatively, dividing the functions into solution resistance, concentration overpotential, and kinetic contribution in a photocatalytic system. Such electrolyte engineering may lead to the discovery of new reaction environments for water electrolysis in more benign conditions and more towards membrane-less systems.
as efficient methods to convert the energy stored in chemical bonds into usable power. At each step of the fuel cycle, high performance catalysts are essential. Transition metal phosphides (TMPs) have proven to be highly active and stable catalysts and are of great interest for the hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) and carbon dioxide reduction to hydrocarbon fuels. However, a detailed understanding of the role of phosphorous is still emerging, and even for the case of HER the performance has previously lagged behind that of the Pt benchmark.

We presented a detailed theoretical and experimental study in which we synthesize nanocrystalline CoP, particles with highly uniform size, allowing a systematic comparison of performance. The phosphorous rich CoP and CoP2 TMPs, as oppose to Co2P, are highly effective and selective catalyst toward HER and ORR. In fact CoP2 exhibits Pt-like performance at small overpotential of 390 mV to achieve -10 mA/cm2 and long term stability. The role of P in promoting catalysis must be understood by considering multiple effects: reducing the number of tightly bound multi-covalent H adsorption sites, increasing the surface disorder, and increasing the Co-H bond length. We will present both data from our recent publication (Adv. Mater. 2018, 30, 1705796) as well as our new results for high-performance CoP2 HER catalysts. The conclusions drawn from this study will be highly relevant to the broader energy catalysis community, and the study of TMP catalysts in particular.

9:30 AM ET08.01.04
Defect-Engineered Interface Assembly for Efficient Electrocatalyst Kishwar Khan and Zhengtang Luo; Hong Kong University of Science & Technology, Kowloon, Hong Kong.

The expansion of economical, effective, and durable electrocatalysts for the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), and hydrogen evolution reaction (HER) have significant importance aimed at numerous electrochemical devices, such as fuel cells, water electrolyzer, and rechargeable metal-air batteries. Heteroatom-doped catalyst has arisen as one of the best emergent candidate to replace the metal based marketable catalyst for electrochemical reactions. But, their delicate structure parameters to optimize the catalytic capability, and atomic-level mechanistic understanding are still a challenging issue. Herein, we advocate the assembly of separate single atoms of Ni and Fe (SSAs-NiFe) dual sites, anchored in defects engineered graphene (DG) substrate prepared by a facile nitrogen (N) elimination procedure from an N-doped precursor by an adsorption-calcination strategy. The concept of defect mechanism, exhibited the topological defect (e.g. multiple pentagon—octagon— pentagon or pentagon—heptagon—pentagon rings) correspondingly appeared in carbon atoms combination that avoid dislocations and disclinations. We believe that these specific combination of carbon atom rings in defective substrate with the decoration of Ni and Fe SSAs can provide more active sites, better electrical conductivity, and lowest energy barrier during catalytic reaction. We used the combination of high resolution transmission electron microscopy/high-angle annular dark field (HAADF) images established in scanning transmission electron microscopy (STEM) for studying the atomic structure of Ni and Fe isolated atoms on DG. At very low resolution (1nm) the individual atoms Ni and Fe in the field of view is detected through S/TEM, and resolved in graphene lattices. The electron energy loss spectroscopy (EELS) atomic spectra are used to identify the Ni/Fe SSAs in DG. The chemical insights structure of the material are examined by pre-edge peaks in X-rays absorption near edge structure (XANES) spectra. We demonstrated the electrocatalytic performance of SSAs-NiFe-DG hybrid material in acidic/alkaline mediums, and found it very active and stable trifunctional electrocatalyst for ORR, OER and HER. This work offers new prospects and underscores the importance of identifying the active species for multiple reactions catalysts and demonstrates how such knowledge can be applied to develop better multifunctional catalysts.

9:45 AM ET08.01.05
Carbon Nanodots as Efficient Photosensitizers for “Green” Solar Fuel Production Demetra S. Achilleos, Hatice Kasap and Erwin Reisner; Christian Doppler Laboratory for Sustainable SynGas Chemistry, Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK., University of Cambridge, Cambridge, United Kingdom.

The accelerated consumption of fossil fuels and the emerging ecological concerns, due to the alarming concomitant rise in greenhouse gas emissions, emphasize the need for the society to move towards renewable “green” resources. Photocatalysis is a promising approach for mitigating simultaneously both the energy and environmental concerns, since it allows the storage of the abundant solar energy in high energy density fuels, such as H2 (120 MJ/kg), in benign aqueous media. However, the development of economically sustainable processes for this purpose, creates the pressing need for new photosensitizers and catalysts of low cost and toxicity, which however maintain substantial performances. Carbon dots (CDs) can efficiently serve as photosensitizers for this purpose since they fulfill all these requirements. In particular, CDs are hydrophilic nanoparticles of low toxicity, which can be synthesized at low cost, and show optimum photocatalytic properties upon suitable design synthesis. In this work, we focus on the synthesis of CDs from naturally abundant and inexpensive biopolymers of various compositions and nanoarchitectures, which bestow the derived photosensitizers with distinctive photocatalytic performances. These light harvesters when combined with noble-metal free molecular catalysts in aqueous-based photocatalytic systems, not only allow for substantial “green” fuel synthesis but also simultaneously facilitate waste oxidation. Such substrates which originate from numerous resources and are abundantly available at no cost, serve as electron donors to quench the photogenerated holes and maintain the photocatalytic stabilities of the systems. The use of waste materials for this purpose, eliminates the need for additional sacrificial reagents, traditionally used in great excess, which add to the overall cost of the processes, and often result in by-products which need to be disposed. We anticipate that this approach, could be a breakthrough in the development of scalable, economically and environmentally sustainable photocatalytic systems, which could efficiently serve the increased energy needs of our societies.

References

10:00 AM BREAK

10:30 AM ET08.01.06
Designing Semiconductor Photoelectrodes for Integrated Photo-Electrochemical Water Splitting Lianzhou Wang; University of Queensland, St Lucia Brisbane, Queensland, Australia.

Semiconducting materials hold the key for efficient photocatalytic and photoelectrochemical water splitting. In this talk, we will give a brief overview of our recent progresses in designing semiconductor metal oxides materials for photoelectrochemical energy conversion including photocatalytic solar fuel
generation. In more details, we have been focusing the following a few aspects; 1) band-gap engineering of layered semiconductor compounds including layered titanate, tantalate and niobate-based metal oxide compounds for visible light photocatalysis, and 2) two-dimensional nanosheets/nanoplates of TiO₂, Fe₂O₃, WO₃, BiVO₄ as building blocks for new photoelectrode design. 3) the combination of a high performance photoelectrode BiVO₄ with perovskite solar cells can lead to unassisted solar driven water splitting process with solar-to-hydrogen conversion efficiency of >6.5%. The resultant material systems exhibited efficient visible light photocatalytic performance and improved power conversion efficiency in solar energy, which underpin important solar-energy conversion applications including solar fuel generation and simultaneous environmental application.

11:00 AM DISCUSSION TIME

11:15 AM ET08.01.08
Highly Dispersed Ruthenium Oxide Hydrate as an Efficient Cocatalyst for Z-Scheme Water Splitting

Hajime Suzuki¹, Shinnosuke Nitta², Osamu Tomita¹, Masanobu Higashi², Akinori Sacki¹ and Ryu Abe¹,²,³,¹
Department of Applied Chemistry, Graduate school of Engineering, Osaka University, Suita, Japan; ²Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan; ³JST-CREST, Kyoto, Japan.

Photoduced water splitting using semiconductor materials has attracted much attention owing to its potential for clean H₂ production from abundant solar light. To achieve practically high efficiency of H₂ production under solar light irradiation, it is indispensable to utilize a wide range of the solar light spectrum up to the visible region, as well as to achieve a high quantum efficiency in the photocatalytic process. Introducing two-step photoexcitation (i.e., Z-scheme) in water splitting has been recently proven as one of the most promising strategies for harvesting a wider range of visible light. In this system, the water-splitting reaction is broken up into two stages: one for H₂-evolution, and the other for O₂-evolution. These are combined using a shuttle redox couple in solution. In Z-scheme water splitting systems with an IO₃⁻/I⁻ redox couple, the reduction of IO₃⁻ on O₂-evolving photocatalysts via a six-electron process often represents the rate-determining step of the overall process, and therefore necessitates effective cocatalysts such as PtO₂ and RuO₂. However, these cocatalysts cannot be loaded onto thermally unstable materials via conventional impregnation processes involving calcination. In the present study, we introduce a new Ru-based cocatalyst that can be loaded without calcination and effectively promotes the reduction of IO₃⁻ on various photocatalysts, including non-oxide materials. The results reveal for the first time that the Ru species adsorbed via simple stirring of photocatalyst particles such as WO₃ in an aqueous RuCl₃ solution effectively trigger O₂ generation in the presence of IO₃⁻ as electron acceptor; moreover, the O₂ evolution rate on the present Ru-loaded WO₃ sample was much higher than that obtained with conventional RuO₂-loaded WO₃. The structural analysis indicates that the Ru species adsorbed on WO₃ are highly dispersed and characterized by octahedral RuO₄ environments similar to those found in RuO₂·nH₂O. Time-resolved microwave conductivity (TRMC) measurement confirmed that the loaded Ru species (most likely analogous to RuO₂·nH₂O) effectively capture the photogenerated electrons. In electrochemical measurement, the Ru species exhibit higher activity in the reduction of IO₃⁻ than anhydrous RuO₂, whereas RuO₂ exhibits much higher activity for the oxidation of water than RuO₂·nH₂O. The newly developed Ru-based cocatalyst was also applicable to thermally unstable materials such as H₂WO₄ and Ta₂N₅, thus enabling them to generate O₂ in the presence of IO₃⁻.

11:30 AM ET08.01.09
Photocatalytic Applications from Visible-Light Responsive Metal-Organic Framework Systems

Kyriakos Stylianou; EPFL Valais, Sion, Switzerland.

Solar to hydrogen (H₂) energy conversion represents the Holy Grail of energy science and technology. For decades, numerous materials have been developed and used as photocatalysts for this purpose. However, their inadequate visible light absorbance, poor stability and fast charge recombination have prevented their wide, industrial-scale deployment. Additionally, the use of noble metal-based co-catalysts and the toxicity of the majority of electron donors employed in these photocatalytic systems limit the profitability of this technology. This study aims to tackle these issues using a two-fold strategy. Firstly, we systematically studied the impact of different transition metal-based co-catalysts towards the photocatalytic water reduction, when they are physically mixed with the visible-light active MIL-125-NH₂. All co-catalyst/MIL-125-NH₂ photocatalytic systems were found to be highly stable after photocatalysis, with some systems exhibiting high hydrogen (H₂) evolution rates of >2000 μmol h⁻¹ g⁻¹. Secondly, we investigated how different electron donors affected the stability and H₂ generation rate of the best photocatalytic system and found that triethylamine fulfills both requirements. We then replaced the electron donor with dyes that are commonly used as simulant organic pollutant, with the aim of integrating the visible-light driven H₂ evolution with dye degradation in a single process. This is the first study where a metal-organic framework (MOF) system is used for this dual-photocatalytic activity under visible light illumination and our proof-of-concept approach envisages a sustainable waste-water remediation process driven by abundant solar energy, while H₂ is produced, captured and further utilized. [1]


11:45 AM ET08.01.10
Inductive and Electrostatic Promotion of Carbon Dioxide Reduction at Metal Macrocycles

Karthish Manthiram; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Electrochemical reduction of carbon dioxide at ambient conditions can enable local, modular synthesis of chemicals. Diverse catalysts have been explored for this process, including heterogeneous extended solids and molecular complexes. Among the molecular complexes, cobalt tetapyrrole macrocycles are among the most active and selective for converting carbon dioxide into carbon monoxide, a critical chemical intermediate. These complexes are prone to aggregation as they are planar, leading to favorable pi-pi interactions, which can obscure their intrinsic turnover frequencies for carbon dioxide reduction. We demonstrate methods by which the intrinsic turnover frequencies of these catalysts can be measured, revealing activities that are orders of magnitude higher than when measured in their aggregated states. These kinetic-limited catalysts enable detailed mechanistic studies, which reveal the molecular-level details of how carbon dioxide is reduced through either electron transfer or concerted proton-electron transfers. We have also identified the inductive and electrostatic contributions to catalysis at the active site, providing design principles for developing more active molecular complexes for carbon dioxide reduction.
Non-noble-metal, thin-film oxides are widely investigated as promising catalysts for oxygen evolution reactions (OER). A key challenge for gaining insight into mechanisms for thin-film photo- and electro-catalytic OER function lies in resolving the interplay between intrinsic catalytic activity of catalytic sites and the electronic structure and charge transport properties of the thin-film OEC. Transition metal (oxy)hydroxides show linked electron-proton conductivity which confers a volume rather than a surface area dependent activity to the films. This is understood to arise from homogeneously distributed and accessible catalytic sites though out the film, and with the catalytic current densities determined by the product ($k_{\text{cat}} k_{\text{H,e}}$) of the catalytic rate, $k_{\text{cat}}$, and electron-proton conductivity, $k_{\text{H,e}}$. As a result, understanding OER function for transition metal (oxy)hydroxide requires the structural basis for both catalysis and electron-proton conductivity to be addressed.

We have investigated amorphous cobalt oxide films electrochemically formed in the presence of borate (CoBi) and phosphate (CoPi) as a means to resolve structural and electronic factors that underlie OER performance in cobalt (oxy)hydroxides. CoPi and CoBi share a common cobaltate domain building block, but differ significantly in OER performance that has been proposed to derive from different electron-proton charge transport properties. In this report, we provide a comparison of CoBi and CoPi OER performance and bulk electronic properties, and correlate these to the electronic and structural properties measured at the atomic scale using a combination of soft X-ray absorption (XAS), resonant X-ray emission (RXES), resonant inelastic X-ray scattering (RIXS), and resonant vibrational Raman scattering (RR) techniques. This combination of analytical approaches show CoPi and CoBi to have characteristic differences in electronic structure measured at the atomic scale that provide a basis for understanding enhanced conductivities for CoBi compared to CoPi as thin film OEC. In particular, the results show that the cobaltate domains for these OEC differ in the content of tetrahedral Co(II) “defect” sites, the extent of oxygen-mediated metal-metal delocalization, and mesoscale ordering that can be understood to combine and support enhanced electron-proton conductivity in CoBi compared to CoPi. More generally, this work demonstrates opportunities to use the combination of soft XAS, RXES, RIXS for investigating the interplay between intrinsic catalytic activity of catalytic sites and the electronic structure and charge transport properties of thin-film catalysis.

2:00 PM ET08.02.02

Dinuclear Heterogeneous Catalyst on Metal Oxides for Solar Water Oxidation
Yanyan Zhao1, Ke. R. Yang2, Xingxu Yan1, Zechao Wang1, Sufeng Cao1, Yifan Ye1, Qi Dong1, Xizi Zhang1, James Thorne1, Kelly Materna1, Antonios Tripalis1, Sirine Fakra2, Shasha Zhu1, Xiaoyan Zhong1, Peng Wang1, Xiaoping Pan1, Jinghua Guo1, Maria Flynnzi-Stephanopoulos1, Gary W. Brudvig2, Victor Batista2, Dunwei Wang1; 1Boston College, Chestnut Hill, Massachusetts, United States; 2Yale University, New Haven, Connecticut, United States; 3University of California–Irvine, Irvine, California, United States; 4Tsinghua University, Beijing, China; 5Tufts University, Medford, Massachusetts, United States; 6Lawrence Berkeley National Laboratory, Berkeley, California, United States; 7Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Jülich, Germany; 8Nanjing University, Nanjing, China.

Atomically dispersed catalysts refer to substrate-supported heterogeneous catalysts featuring one or a few active metal atoms that are separated from one another. They represent an important class of materials ranging from single atom catalysts (SACs) and nanoparticles (NPs). While SACs and NPs have been extensively reported, catalysts featuring two atoms with well-defined structures are poorly studied. The difficulty in synthesizing such structures has been a critical challenge. Here we present preparing dinuclear heterogeneous catalysts (DHCs) by a facile photochemical method that produces catalytic centers consisting of two iridium metal cations, bridged by O and bound to a support. Direct evidence unambiguously supporting the dinuclear nature of the catalysts anchored on metal oxides is obtained by aberration-corrected scanning transmission electron microscopy. In addition, different binding modes have been achieved on two metal oxides with distinguishable surface oxygen densities and interatomic distances of binding sites. Side-on bound DHCs was demonstrated on iron oxide where both Ir atoms are affixed to the substrate and the other one is dangling was observed on WO3. Evidence supporting the binding modes was obtained in situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy. The resulting catalysts exhibit high activities toward H2O photooxidation. Density functional theory calculations provide additional support for atomic structure, binding sites modes on metal oxides, as well as insights into how DHCs may be beneficial for solar water oxidation reactions. The results have important implications for future studies of highly effective heterogeneous catalysts for complex chemical reactions.

2:15 PM ET08.02.03

Bismuth Substituted Strontium Cobalt Peroxides for Catalyzing Oxygen Evolution
Yanyan Zhao1, Ke. R. Yang2, Xingxu Yan1, Zechao Wang1, Sufeng Cao1, Yifan Ye1, Qi Dong1, Xizi Zhang1, James Thorne1, Kelly Materna1, Antonios Tripalis1, Sirine Fakra2, Shasha Zhu1, Xiaoyan Zhong1, Peng Wang1, Xiaoping Pan1, Jinghua Guo1, Maria Flynnzi-Stephanopoulos1, Gary W. Brudvig2, Victor Batista2, Dunwei Wang1; 1Boston College, Chestnut Hill, Massachusetts, United States; 2Yale University, New Haven, Connecticut, United States; 3University of California–Irvine, Irvine, California, United States; 4Tsinghua University, Beijing, China; 5Tufts University, Medford, Massachusetts, United States; 6Lawrence Berkeley National Laboratory, Berkeley, California, United States; 7Ernst Ruska-Centre for Microscopy and Spectroscopy with Electrons, Jülich, Germany; 8Nanjing University, Nanjing, China.

The distribution and on-demand use of electrical energy from sustainable resources requires storage technologies that are cost effective and involving earth-abundant elements [1-2], such as storing solar energy in form of chemical bonds by water splitting or CO2 reduction. The efficiency of these storage technologies is, however, severely limited by the catalysis of the oxygen evolution reaction (OER) [3], which is characterized by slow kinetics and the need for precious metal catalysts such as RuO2 and IrO2 [4]. The development of the efficient electrocatalysts for OER composed of earth-abundant materials is therefore crucial for the large-scale implementation of these technologies. Here we employ the recently reported inductive effect [5] associated with metal substitution to examine the redox potentials and OER activity of cobalt-based perovskites, where bismuth-substituted strontium cobalt perovskite, Bi$_x$Sr$_{1-x}$CoO$_3$, showed a low Tafel slope (~30 mV/decade) and pH dependence on RHE scale implying the decoupling of proton and electron transfer during one of the OER steps. The enhanced OER kinetics of Bi$_x$Sr$_{1-x}$CoO$_3$ relative to other active catalysts such as SrCoO$_3$,...
can be attributed to the presence of electronegative strong Lewis acid Bi\(^{3+}\) ions which can influence the surface charge facilitating deprotonation kinetics, and also enhance oxide stability by having lowered O\(p\) band center of Bi\(_2\)Sb\(_2\)O\(_6\) relative to the Fermi level via partial Co reduction and inductive effect. This work demonstrates a novel design strategy for enhancement of the OER activity and stability of oxide catalysts by the inductive effect induced by metal substitution to enable efficient and sustainable energy storage.

References:


2:30 PM ET08.02.04

Ultrathin Amorphous Iron-nickel Boride Nanosheets for Highly Efficient Electrocatalytic Oxygen Production

Jean Marie Vianney Nsanzimana and Xin Wang; Nanyang Technological University, Singapore, Singapore.

Electrochemical Hydrogen production has gained great interest over the past decades as a cleaner, higher purity and sustainable production technology for carbon-neutral alternative fuel sources. However, poor oxygen evolution reaction (OER) thermodynamic up-hill reaction limits the efficiency of \(\text{H}_2\) production from water electrolysis and photoelectrolysis routes to large-scale energy storage. Thus, it is crucial to develop efficient and low-cost material to boost the sluggish kinetics step of four-electron OER process. The state-of-the-art are the precious metal-based catalyst which suffers from higher cost and makes them lesser desirable for industrial applicable scale. Thus, developing low cost, durable, earth-abundant, and high-performance non-precious metal electrocatalyst for oxygen evolution reaction (OER) is a cornerstone for energy technologies. Despite a well-documented approach for synthesizing metal borides, it is recently that the application as promising OER electrocatalyst has emerged. Furthermore, the synergetic effect had been reported for multimetals borides materials which were found to be the most OER among the reported metal borides materials. Additionally, an improvement in metal borides based catalyst had been reported when supported on a higher conductive substrate such as graphene. A cost-effective and efficient electrocatalyst for oxygen evolution reaction during water electrolysis is highly desired. In an effort to develop an economical material for replacing precious metal-based catalysts, a novel and self-standing, amorphous ultrathin nanosheets of bimetallic iron-nickel boride (FeNiB NNS) on Ni foam is presented, which displays better oxygen-evolving activity compared to precious metal catalyst RuO\(_2\). In 1.0 M KOH electrolyte, it requires an overpotential of only 237 mV to reach a current density of 10 mA/cm\(^2\) with a small Tafel slope of 58 mV/dec and shows prominent longterm electrochemical stability. The synergistic effect between highly abundant catalytically active sites on 3D porous substrate, improved electron transport and proton transport arising from the presence of highly negative boron, and high conductivity of the substrate results in an outstanding electrocatalytic activity. The advanced catalytic activity, facile electrode fabrication, and low cost makes it a potential oxygen evolving material which may be extended to other energy conversion and storage technologies.

References:


2:45 PM ET08.02.05

CoSb\(_2\)O\(_6\) as a Stable Oxygen Evolution Catalyst in Acidic Media

Taylor A. Evans and Kyoung-Shin Choi; Chemistry, University of Wisconsin-Madison, Madison, Wisconsin, United States.

The electrochemical generation of hydrogen fuel via water reduction requires a counter reaction, typically the oxidation of water. This four electron, kinetically complex reaction has been intensely studied in basic media using a variety of inexpensive metal oxide materials (NiO\(_x\), FeO\(_x\), CoO\(_x\), etc.). However, in acidic media these catalysts have been shown to be unstable and degrade rapidly. While noble metal oxides, such as RuO\(_2\) and IrO\(_2\), are able to provide water oxidation in a stable manner with relatively low overpotentials in acidic media, their scarcity and high cost leave significant room for the development of inexpensive novel catalysts. Antimony (V) oxides are expected to be stable under oxidizing conditions in acidic media on account of their high oxidation state and low solubility in acid. In this presentation, the investigation of CoSb\(_2\)O\(_6\) as a stable water oxidation catalyst is reported. Synthesized through a facile electrochemical method, CoSb\(_2\)O\(_6\) films are demonstrated to be stable in acidic media while applying the necessary potentials for water oxidation. CoSb\(_2\)O\(_6\) opens the door as a possible replacement for noble metal oxide catalysts and encourages the investigation of other transition metal antimony oxide materials for use as water oxidation catalysts in acidic media.

3:00 PM BREAK

3:30 PM ET08.02.06

Porous Transition Metal Oxides for Selective Oxidations

Steven L. Suib\(^1\), \(^2\), \(^3\); \(^1\)Chemistry, University of Connecticut, Storrs, Connecticut, United States; \(^2\)Chemical and Biomolecular Engineering, University of Connecticut, Storrs, Connecticut, United States; \(^3\)Institute of Materials Science, University of Connecticut, Storrs, Connecticut, United States.

This presentation will focus on synthesis, characterization, and applications of novel microporous and mesoporous materials. Such microporous metal oxide materials have crystalline walls, high thermal stability, and monomodal pore size distributions. These systems can be made for most elements throughout the periodic table. They have unique catalytic activity in a number of reactions including selective oxidations, total oxidations, coupling reactions, water splitting, one pot Wittig reactions, dehalogenations, and others. A key focus is on the mechanisms of these selective oxidation reactions. The role of reactive oxygen species in these reactions is of considerable interest. This presentation will focus on synthesis, characterization, and selective catalytic oxidations applications using both microporous and mesoporous materials. Reactive oxygen species can be detected with a variety of methods. In situ methods to observe these species have been developed. How such reactive oxygen species are important in selective oxidation reactions will be discussed.

4:00 PM ET08.02.07
Advanced Structural Characterization of Ni-NW Catalysts Showing Enhanced OER Electroactivity

Sagar Prabhudev1, Minghui Hao2, Sebastien Garbarino2, Daniel Guay2 and Gianluigi A. Botton1; 1McMaster University, Hamilton, Ontario, Canada; 2INRS, Montreal, Quebec, Canada.

Hydrogen is arguably one of the most promising energy carriers which can mirror all the appealing attributes of electricity. To answer whether it can meet the global demand for energy while at the same time also be an effective clean and sustainable energy carrier, however, requires a low-cost and environmentally friendly means of production. Although Electrolytic methods of producing Hydrogen provide an attractive pathway to producing Hydrogen renewably (e.g., from water), they further entail employing electrolyzer systems such as the Anionic Polymer Electrolyte Membrane Water Electrolyzers that are yet to be optimized for their Oxygen Evolution Reaction (OER) kinetics.

In this work we discuss a new class of Ni-Nanowire Catalysts that were found to exhibit a significant decrease in the OER Overpotential (~200 mV) at 10 mA cm⁻² current densities. With the use of advanced electron microscopy tools for structural and compositional characterization we provide insights into their entire synthetic pathway, where a template-assisted electrodeposition procedure first formed the Ni-filled Aluminium Anodic Oxide (AAO) membranes, from which the usable pristine 1D Ni nanowires were then recovered by electrochemical dissolution of the AAO in 1M KOH. A detailed analyses of their SEM and high-resolution TEM images reveals that the as-received AAO membrane bears a close resemblance to the hexagonal assembly of pore arrangement, which is still preserved even in the case of pristine Ni NWs that are recovered in the final synthetic step. More importantly, a detailed analyses of the NW micrographs post electrochemical testing using advanced image processing methods suggests that the hexagonal assembly can be further retained, thus highlighting the electrochemical stability observed in this 1D Ni-NW catalysts.

Similar to the above analyses performed with TEM-imaging, we performed a detailed investigation of the NW compositions using electron energy loss spectroscopy (EELS). For this we analyzed the variation in the Ni-L2,3 and O-K elemental edges at very high spatial resolution, sufficient to determine the local compositional variations between the NW core/shell regions. Our results indicate that the NW surfaces form an oxide layer over the metallic core, which seems to be still preserved even after exposing to extensive electrochemical characterization (29.4 at.% vs. 26.7 at.% before and after, respectively).

In order to deduce the thermodynamic phase of the oxide layer formed (i.e., NiO vs. Ni(OH)₂) in the two samples (NWs pre-/post- treatment in 1M KOH), we further estimated their Ni-L3/L2 white-line intensity ratios over the core- and surface- regions. Our results indicate that the L3/L2 ratio in the shell-region for the Pristine is comparable to the Ni(OH)₂ state, and there is no apparent changes in the chemical state of Ni following the extensive electrochemical characterization.

4:15 PM ET08.02.08

Origin of High Activity of Mn₃O₄ Nanoparticle in Oxygen Evolution Reaction—An Atomic-Resolution STEM/EELS Study

Chun-Yu Lin and Zhenhai Xia; Materials Science and Engineering, University of North Texas, Denton, Texas, United States.

Clean energy technologies such as fuel cells, rechargeable metal-air batteries, and water splitting, are promising for future energy sources owing to their nature of no pollution and greenhouse gas emission. The key reactions in these technologies are the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) that generate power. The state-of-the-art electrocatalyst in OER is RuO₂ and in ORR is Pt, but their high cost and poor durability hindered their application in clean energy technologies. Zeolitic imidazolate frameworks (ZIFs), a subclass of metal organic frameworks (MOFs), mainly composed of a transition metal (TM) center and organic ligands, exhibits the excellent ability as electrochemical catalysts in clean energy conversion and storage. However, their ligand or coordination of metal ions must be modified to enhance their catalytic activities. To rationally design the ZIF catalysts, we have calculated the OER and ORR activities of TM-ZIFs and found an intrinsic descriptor which can describe the catalytic activities of the TM-ZIFs by density-functional theory (DFT) method. Our DFT calculations show that the unsaturated metal sites show high catalytic activities comparable to that of RuO₂ / Pt electrocatalyst. This theoretical result was confirmed by the experiment.

4:45 PM ET08.02.10

Mechanistic Investigations of Alkaline Hydrogen Electrocatalysis via Kinetic Modeling and Single-Crystal Voltammetry

Maureen Tang, Joshua Snyder, Saad Intikhab and Luis Rebollar-Tercero; Drexel University, Philadelphia, Pennsylvania, United States.

It has long been recognized that the reaction rates of the hydrogen oxidation and hydrogen evolution reactions (HOR /HER) are up to 200 times slower in basic than acidic electrolytes, even though the surface intermediate of adsorbed hydrogen is independent of solution pH [1]. The mechanistic origins of this difference have been hotly debated in the literature. In this work, we investigate possible explanations for the effect of pH by combining single-crystal voltammetry with microkinetic modeling and electroanalytical methods. We specifically determine the viability of the proposed ‘bifunctional mechanism’, in which slow water dissociation is overcome by mediation of adsorbed hydroxide [2].
Our previous work [3] has shown that on Pt(110) either a direct (hydroxide-as-spectator) or indirect (hydroxide-mediated) Volmer step can describe the measured reaction thermodynamics, but that only the direct Volmer step is consistent with realistic adsorption energies. Furthermore, increasing hydroxide adsorption strength via the electrolyte cation decreases kinetics, as observed by the dependence of peak-potential splitting on scan rate. Comparison with theory shows that this observation is consistent only with the direct mechanism. These results strongly suggest that adsorbed hydroxide serves as a competitive spectator in the alkaline Volmer step, and that the bifunctional HOR/HER mechanism plays only a minor role at best. The inability of the bifunctional mechanism to describe experimental data is further reinforced by investigating a two-site model recently proposed in the literature [2], in which oxophilic ruthenium or nickel sites are responsible for facilitating water dissociation. We find that such chemical dissociation steps result in anomalous trends with potential, and that oxophilicity has no effect on hydrogen coverage or HER/HOR rates. Comparison with experiment strongly indicates that the observed bifunctional mechanism is unrelated to hydroxide binding strength [4]. Overall, our work resolves a long-standing paradox in electrocatalysis and surface science by determining that oxophilicity is not an accurate descriptor for alkaline hydrogen electrocatalysts. Other parameters, such as water orientation and non-covalent interactions, must play a greater role in overall activity. Efforts to identify and measure these parameters are ongoing.


SESSION ET08.03: Catalytic CO2 Reduction
Session Chairs: Yu Han and Yugang Sun
Tuesday Morning, November 27, 2018
Hynes, Level 3, Room 306

8:00 AM ET08.03.01
2D-Derived Catalysts for Efficient CO2 Electroreduction F. Pelayo Garcia de Arquer, Oleksandr Bushuyev, Phil De Luna, Cao-Thanh Dinh, Ali Seifitiokaldani, Mahshud Saimadinov, Chih-Shan Tan, Li Na Quan, Andrew H. Proppe, Md. Golam Kibria, Shana Kelley, David Sinton and Edward H. Sargent; University of Toronto, TORONTO, Ontario, Canada.

The electrochemical reduction of CO2 into fuels and chemicals is an attractive route to store renewable electricity. Efficient CO2 reduction catalysts need to yield high activity, high selectivity, and low overpotential, simultaneously. The design of catalysts that exhibit tailored properties such as favourable facets for a given reaction, number of active sites, and oxidation state, is challenging: catalyst can undergo an extensive reconstruction under high productivity operating conditions such as high current densities, reducing potentials, and variable pH. Earth-abundant transition metals such as tin, bismuth, and lead have been proven stable and product-specific, but exhibit limited partial current densities. We present a strategy that employs bismuth oxyhalides as a template from which 2D bismuth-based catalysts are derived. The BiOBr-templated catalyst exhibits a preferential exposure of highly active Bi (110) facets, which we track in operando using grazing-incidence wide-angle X-ray scattering (GIWAXS) and X-ray absorption spectroscopy (XAS). The templated catalyst exhibit an enhanced CO2 reduction reaction selectivity to over 90% Faradaic efficiency for formic acid that is sustained up to stable facets, which we track in operando using grazing-incidence wide-angle X-ray scattering (GIWAXS) and X-ray absorption spectroscopy (XAS). The templated catalyst exhibit an enhanced CO2 reduction reaction selectivity to over 90% Faradaic efficiency for formic acid that is sustained up to stable current densities of 200 mA cm−2. This represents more than a twofold increase in the production of the energy-storage liquid formic acid compared to previous best Bi catalysts.

8:15 AM ET08.03.02

Electrochemical transformation of CO2 into energy-dense fuels may prove key towards the realization of economically viable, renewable fuels. However, the rational design of CO2 reduction catalysts guided by well-grounded chemical intuition or first-principles computational approaches, have so far been met with limited success. To address this important question of how to activate a molecule as stable and unreactive as CO2 and convert it into complex hydrocarbons, there may be no better place to look than biological systems capable of CO2 activation, for crucial guidance and inspiration.

Recent findings have demonstrated the utility of MoS2 and MoSe2 edge sites in catalyzing the transformation of CO2 to CO. Although this is a promising start, CO is not an easy product to work with industrially nor to transport due to its gaseous nature. Meanwhile, a close look of formate dehydrogenase (FDH), the key enzyme in formate metabolism which catalyzes the reversible two-electron oxidation of formate or reduction of CO2, reveals a catalytic center that is defined by Mo4+/5+ or W5+/6+ coordination with sulfide ligands (from molybdopterin prosthetic groups and cysteine residues) and a selenocysteine side chain. Translation of these chemical moieties, which are recognized as integral to the FDH's architecture and functions, into solid-state semiconductor devices, would suggest that the inclusion of Se ions in Mo/WS2 semiconductors as a dopant may promote the preferred generation of liquid formate, rather than gaseous CO, from CO2. In this project, we want to explore interstitial Se doping of W/MoS2 materials as potential CO2 reduction cathodes, with the ultimate goal of generating reduced liquid hydrocarbon products.

8:30 AM *ET08.03.03
Coupling Solar Energy into Catalytic CO2 Conversion Yuqiie Xiong; Department of Chemistry, University of Science and Technology of China, Hefei, China.

Considering the excessive emission of atmospheric carbon dioxide (CO2) caused by the combustion of fossil fuels, the sunlight-driven CO2 reduction into higher energy chemicals, such as carbon monoxide, formic acid, methanol or methane, offers a more promising approach to alleviate both global warming and energy crisis. Designing new photocatalytic materials for improving the photoconversion efficiency is a promising route to achieve this goal. Despite the invention of a large number of catalytic materials with well-defined structures, their overall efficiency in photocatalysis is still quite limited as the three key steps - light harvesting, charge generation and separation, and charge transfer to surface for redox reactions - have not been substantially improved. To improve each step in the complex process, there is a major trend to develop materials based on inorganic hybrid structures, in which surface and interface engineering holds the promise for boosting the overall efficiency. In this talk, I will demonstrate several different approaches to designing inorganic hybrid structures with improved photocatalytic performance via surface and interface engineering. It is anticipated that this series of works open a new window to rationally designing inorganic hybrid materials for photo-induced applications.
9:00 AM - ET08.03.04

Development of Semiconductor-MOF Ternary Photocatalyst Toward Intensified Charge Carrier Density and Molecule Activation in Heterogeneous Photocatalysis

Xiang He and Wei-Ning Wang; Virginia Commonwealth University, Richmond, Virginia, United States.

Heterogeneous photocatalysis, such as carbon dioxide (CO2) photoreduction, is a promising engineering approach to reduce atmospheric CO2 levels and simultaneously convert CO2 into hydrocarbon fuels. Among the numerous catalysts for CO2 photoreduction, semiconductors have been studied intensively because of their low cost, easy availability, nontoxicity, and exceptional chemical stability. However, the semiconductor-based CO2 photoreduction still suffers from low efficiency and poor selectivity, mainly due to low charge carrier density and weak ability to activate the adsorbed CO2 molecules. Towards addressing the aforementioned long-standing issues in CO2 photoreduction (i.e., low charge carrier density and inefficient CO2 activation), we herein report a rational development of MOF-based ternary nanocomposites composed of TiO2/Cu2O heterojunction and CuO(BTC)2, where the roles of semiconductor heterojunction and MOF in charge transfer and CO2activation are systematically explored. Specifically, the nanocomposites were synthesized via facile and rapid self-assembly of TiO2/Cu2O nanoparticles within microdroplets, followed by in situ growth of CuO(BTC)2 on the TiO2/Cu2O surface, where part of CuO serves as the sacrificial metal source. The unique ternary TiO2/CuO/CuO(BTC)2 composite possesses heterojunction and abundant coordinatively unsaturated copper sites, which results in not only increased charge carrier density but also efficient activation of CO2 molecules, therefore leading to high CO2 conversion efficiency and preferential formation of CH4. With systematic measurements (e.g., gas chromatography, photoluminescence spectroscopy, X-ray photoelectron spectroscopy, and time-resolved in-situ diffuse reflectance infrared Fourier transform spectroscopy), a plausible pathway of CO2 activation and subsequent reduction in this ternary system was proposed. The outcome of this work provides new insights in rational design of MOFs-based hybrid nanomaterials for efficient CO2 photoreduction.

9:15 AM - ET08.03.05

Photocatalytic and Optoelectronic Studies of SnS2: Thin Film by Controlled Implantation of Carbon Ions

Tadesse Billo Reta1, Indrajit Shown,2 Wei-yen Woor1, Rui-San Chen1, Chih-Hao Lee1, Li-Chyong Chen1 and Kuei-Hsien Chen1; 1Institute of Atomic and Molecular Sciences, Academia Sinica, Nangang, Taiwan; 2Department of Physics, National Central University, Taoyuan, Taiwan; Graduate Institute of Applied Science and Tech. National Taiwan University of Science and Technology (NTUST), Taipei, Taiwan; 4Department of Engineering and System Science, National Tsing Hua University, Hsinchu, Taiwan; 5Center for Condensed Matter Sciences, National Taiwan University, Taipei, Taiwan.

Photocatalytic conversion of CO2 into useful products using solar energy is one of promising technique to tackle both energy and global environmental challenges. Recently, several semiconductor photocatalyst including metal oxide and chalcogenide materials have been attracted enormous interest in the gas phase CO2 reduction via artificial photosynthesis. Irrespective of versatile applications, SnS2 is not well explored in photocatalytic CO2 reduction applications. Recent experimental study has demonstrated that carbon doping significantly tuning the electronic properties of bulk SnS2 and showing enhanced photocatalytic CO2 reduction. However, the influence of different percentage of carbon doping into 2D SnS2 layer structure together with optoelectronic behavior by a controlled process remains unaddressed. In this study, we report the synthesis and characterization of 2D SnS2/C thin film grown via chemical vapor transport method. The as grown thin film was implanted with carbon ions with the energy of 5 keV to form SnS2-C composite films with different concentration of carbon. The 6 wt % carbon implanted SnS2-C thin film exhibits high photocatalytic activity and product selectivity towards gas phase photocatalytic CO2 reduction under visible light. The SnS2-C thin film has produced CH3CHO as a major product which is 6 times higher than pristine SnS2 thin films. The improved photocatalytic activity and selectivity can be ascribed to band structure changes and pronounced charge-transfer taking place between SnS2 and carbon. The mechanism of interfacial charge transfer was studied using wavelength dependent photocurrent studies under CO2 and water vapor environments. The incorporation of carbon in SnS2 has improved the photocatalytic performance by more than 100 times of the as synthesized SnS2. The detail characterization and experimental results with the future perspective of this study will be presented.

9:30 AM - ET08.03.06

Heterogeneous Multi-Shelled Hollow Spheres for Efficient Photocatalytic Reduction of Carbon Dioxide

Dan Wang, Feifei You and Dan Mao; State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China.

A significant increase of CO2 in the atmosphere has a profound impact on global climate change, which has become a central challenge of the 21st century. Photocatalytic reduction of CO2 into chemical fuel is an appealing strategy to resolve greenhouse gas emissions and alleviate the energy crisis. The efficiency of CO2 conversion relies on the catalytic sites and microstructure of photocatalyst. In this work, we successfully synthesized SnS2SnO2 heterogeneous multi-shelled hollow spheres by the sequential templating approach. Multi-shelled hollow structures not only have the characteristics of the large specific surface area and high loading capacity; more importantly, they have multiple adjustable shells and inter-shell spaces, enabling sequential light reflection and scattering, which greatly improve the light-harvest capability and light conversion efficiency. These unique features make them promising candidate for photocatalytic reduction of CO2. The SnS2SnO2 multi-shelled hollow spheres exhibited an enhanced efficiency and good stability for photocatalytic reduction of CO2 to CO. Photocatalytic activity of SnS2SnO2 multi-shelled hollow spheres is increased with the shell number significantly. As a result, the quadruple-shelled SnS2SnO2 hollow spheres steadily photocatalyzed CO2 to CO at a rate of 50 μmol g-1 h-1 under AM 1.5 G simulated solar irradiation, and the rate can maintain 72 hours without decline. This work paves the way for enhancing photocatalytic performance by structural design of the emerging materials.

10:00 AM BREAK

10:30 AM - ET08.03.07

Designing Nanostructured Materials for Electrochemically Recycling Carbon Dioxide

Michael B. Ross and Peidong Yang; University of California, Berkeley, California, United States.

Electrochemical carbon dioxide (CO2) recycling enables the synthesis of high-value fuels and chemicals using renewable energy. Doing so requires the development of catalysts that both efficiently and selectively reduce CO2 into desirable products. Nanomaterials are particularly powerful for doing so due to their high surface areas, tunable chemical and physical properties, and unique reactivities that can differ from the bulk. Thus the synthesis, characterization, and integration of nanostructured electrocatalysts for CO2 reduction is a promising strategy for realizing breakthrough performance. Synthesis gas (syngas), a mixture of H2 and CO, can be converted into a variety of fuels and chemicals using established industrial processes that require different syngas compositions. Here we will describe the synthesis, characterization, and catalytic properties of nanostructured electrocatalysts that are versatile and modular, and which also provide dynamic access to a wide variety of desirable syngas compositions. Strategies for generating multi-carbon products will also be discussed.

11:00 AM - ET08.03.08

Controlled Selectivity of CO2 Reduction via Electrochemical Potential Modulation

Kevin Kimura, Jin Suntich and Tobias Hanrath; Cornell University, Ithaca, New York, United States.

Electrochemical carbon dioxide (CO2) recycling enables the synthesis of high-value fuels and chemicals using renewable energy. Doing so requires the development of catalysts that both efficiently and selectively reduce CO2 into desirable products. Nanomaterials are particularly powerful for doing so due to their high surface areas, tunable chemical and physical properties, and unique reactivities that can differ from the bulk. Thus the synthesis, characterization, and integration of nanostructured electrocatalysts for CO2 reduction is a promising strategy for realizing breakthrough performance. Synthesis gas (syngas), a mixture of H2 and CO, can be converted into a variety of fuels and chemicals using established industrial processes that require different syngas compositions. Here we will describe the synthesis, characterization, and catalytic properties of nanostructured electrocatalysts that are versatile and modular, and which also provide dynamic access to a wide variety of desirable syngas compositions. Strategies for generating multi-carbon products will also be discussed.
We present the product distribution of the CO₂ reduction reaction (CO₂RR) when the driving force is a pulse of electrochemical potential. The use of renewable electricity to convert CO₂ into energy-dense fuels and high-valued feedstocks is an enabler of many sustainable energy and chemical technologies. The CO₂RR offers a pathway to achieve this goal using electrochemistry. However, the CO₂RR suffers from poor selectivity, especially on Cu, despite its ability to produce hydrocarbons (such as methane, ethylene, etc.). In this presentation, we present a strategy for manipulating the CO₂RR selectivity by applying the CO₂RR driving force ("overpotential") as pulses. By applying pulses of overpotential with controlled duration and magnitude, we demonstrate that the CO₂RR selectivity can improve >97% of faradaic efficiency (FE) with respect to the competing hydrogen evolution reaction, and the selectivity toward methane can be as high as 83% FE. We will discuss the possible mechanism for why the temporal control of the overpotential pulse can lead to the CO₂RR selectivity control and the possible implications on the timescale of the competing pathways in the CO₂RR.

11:15 AM ET08.03.09
Transition Metal Single Atom Electrocatalysts for Selective CO₂ Reduction in Water—From Identification to Scaling-up Haotian Wang1, 2

The development of highly selective and earth-abundant electrocatalysts for CO₂ reduction is becoming increasingly important for renewable energy applications. The challenge here is the strong competition from water reduction, as well as the low selectivity towards a desired product. In this talk I will introduce the rational tuning of electronic properties of catalytic materials for their significantly improved CO₂ reduction performance. By dispersing transition metals into isolated single atoms with electronic structures significantly different from their bulk counterparts, we can dramatically suppress the competing hydrogen evolution and deliver an ultra-high CO₂ reduction selectivity of more than 95% under ambient conditions in water. I will also talk about the successful scaling-up of both the catalytic materials synthesis as well as the CO₂ reduction current density while maintaining ultra-high CO selectivity.

11:30 AM ET08.03.10
Rational Design of Terrace, Step and Corner Sites of The Metal or Bimetallic Catalysts for Hydrogenation and Hydrodeoxygenation of Biomass-Derived Platform Molecules Shelaka Gupta, Tuvin Suver Khan, Md. Imteyaz Alam and M. Ali Haider; Chemical Engineering Department, Indian Institute of Technology Delhi, New Delhi, India.

Deoxygenation and valorization of biomass-derived platform molecules was studied using ring-opening (RO), decarboxylation, hydrogenation and hydrodeoxygenation (HDO) reactions. The platform molecules studied here included cellulose-derived lactones, furans, 2-pyrones and lignin-derived phenolic compounds.

Study on the conversion of lactones was focused to understand the mechanism of RO and decarboxylation reaction. More specifically, oxocarbenium ions were proposed as an intermediate to play an important role in controlling the rate of RO step. The mechanism of RO and decarboxylation reaction in 2-pyrones is an interesting case, where the reaction in partially saturated 2-pyrones followed a retro-Diels-Alder (rDA) route. Both solvents and substituents were expected to influence the rDA reaction of partially saturated 2-pyrones, which was studied using density functional theory (DFT) simulations. 6-aminopyrone (6PP) was suggested as a potential platform chemical, which may be obtained directly from the fermentation of waste lignocellulosic biomass. On RO and decarboxylation, 6PP was converted to C₆ linear ketones which are proposed as precursors for jet and diesel range fuels. All of these catalytic transformations of 6PP can be integrated with the upstream fermentation of biomass to form a unique bio- and chemo-catalytic process for providing high value fuels and chemicals. However, biogenic impurities present in ppm levels (<100 ppm) along with the fermentation-derived molecules pose a detrimental effect to heterogeneous catalyst stability. Interaction of such impurities with the metal catalyst surface was studied using DFT simulations. Bi-metallic alloy of NiAu was proposed as a more stable surface for hydrogenation reactions.

Catalytic hydrogenation reaction carried out on the Pd catalyst was an interesting case to further explore the influence of catalyst particle size and morphology on the selectivity of a desired product. Detailed mechanistic studies were carried out on Pd (111) and Pd (100) surfaces using DFT calculations to corroborate experimental finding. Since Pd (111) are the majority (~70%) sites, high selectivity observed towards the partially hydrogenated product (cyclohexanone) in the experiments is thought to be from the Pd (111) surface. Contrary to this prevalent thought, on using a combined theoretical and experimental approach, Pd (111) surface was demonstrated to selectively produce the cyclohexanol. Surprisingly, Pd (100), the minority (~25%) sites were selectively producing cyclohexanone. These results lead to the development of a comprehensive understanding on facet-dependent selectivity control in phenol hydrogenation on the Pd catalyst. Final reaction in this sequence was HDO of biomass-derived furan compounds, wherein the synergistic interaction of Zn with the Pd catalyst was studied using DFT simulations. Zn was shown to participate in C-O bond activation step while Pd surface participated in the hydrogenation step.
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2:15 PM ET08.04.02

Membrane Coated Electrocatalysts for Stable, Active and Selective Electrocatalysis

Daniel Esposito, Chemical Engineering, Columbia University, New York, New York, United States.

Conventional electrocatalysts used in fuel cells and electrolyzers are comprised of metallic nanoparticles that are attached to a conductive electrode support that allows for the transfer of electrons between an external circuit and the electrocatalyst/electrolyte interface. Typically, these nanoparticles are partially or fully exposed to a bulk liquid or gaseous phase to facilitate mass transfer of reactants and products. In contrast, this presentation describes recent studies on an emerging class of electrocatalysts for which the active metal electrocatalysts are completely encapsulated by ultrathin layers of permeable oxides that can exhibit membrane-like properties. These so-called membrane coated electrocatalysts (MCECs) offer many potential advantages over conventional electrocatalysts, including the ability to simultaneously mitigate degradation, alter reaction selectivity, and improve reaction kinetics at the buried interface between the overlayer and active catalyst. This talk will describe three case studies of silicon oxide (SiOx)-encapsulated Pt electrocatalysts that separately demonstrate the ability of the SiOx overlayer to enhance catalyst stability, activity, and selectivity. Of particular interest to the last two studies are the task of developing a deeper understanding of the buried interfaces of MCECs, which represent confined environments where structure can, in principle, be tuned to alter reaction energetics and selectivity for a wide variety of electrochemical reactions.

References


2:45 PM ET08.04.03

Colloidal Hexagonal Copper Phosphide Cu3P Nanosheets for Selective and Low-Overpotential CO2 Electroreduction to Ethylene

Hui Li1, Peng Won2, Dominique S. Iuliano2, Zachary D. Hoed3, Minfang Chi1, Lin Jiang2, Yequin Qu2 and Scott M. Geyer1, Chemistry, Wake Forest University, Winston-Salem, North Carolina, United States; 2Department of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen, China; 3Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory (ORNL), Oak Ridge, Tennessee, United States; 4Institute of Functional and Soft Materials (FUNSOM), Soochow University, Suzhou, China.

Electrochemical CO2 reduction provides a fascinating pathway to produce valuable carbon-based fuels, but limited by low conversion efficiency, high overpotential for certain selectivity, and sluggish reaction rate. Herein, we report that colloidal hexagonal copper phosphide nanosheets (Cu3P NSs) show a remarkable onset potential of -0.33 V vs. RHE and achieves a maximum Faradaic efficiency of 62% at -0.88 V vs. RHE for selective CO2–to–C2H4 in a 1:1 volume ratio of EMIM–BF4 ionic liquid and H2O electrolyte. By contrast, Cu3P and Cu nanoparticles (NPs) tend to selectively reduce CO2 to CH4 and CO/CH4, respectively. DFT calculation reveals that the delocalized P atoms enhance the stabilization of CO* intermediate and the stepped facets of (211) on nanosheets favor C-C coupling step rather than the low-index (111) facets on nanoparticle. Moreover, only ~8% decay for a high partial C2H4 current density of 20.6 mA cm−2 at -1.0 V vs. RHE during 24 h stability test is observed on Cu3P NSs.

3:00 PM ET08.04.04

2-pyridinylidene as an Active Catalytic Intermediate for CO2 Reduction on p-GaP Photoelectrodes—Lifetime and Selectivity

Shenzhen Xu1 and Emily Carter2, Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey, United States; 2School of Engineering and Applied Science, Princeton University, Princeton, New Jersey, United States.

The active intermediate responsible for the highly selective reduction of CO2 to methanol at p-GaP photoelectrodes is currently under debate. Adsorbed 2-pyridinylidene (2-PyH*), produced from a two-electron reduction and protonation of adsorbed pyridine (Py*), was recently proposed by Carter and coworkers to be a key intermediate that facilitates hydride transfer (HT) to CO2 to produce formate. However, the lifetime of 2-PyH*, most likely controlled by the rate of 2-PyH* to CO2 protonation to form adsorbed dihydropyridine (DHP*), is still in question. In this work, we prove evidence for the transient existence of 2-PyH* on a p-GaP surface by comparing the activation energy for HT to CO2 to those predicted for 2-PyH* being protonated to form either DHP* or Py*/H2 via a hydrogen evolution reaction (HER). We predict that 2-PyH* situated next to an adjacent surface hydroxide (OH*) will be the most effective intermediate leading to CO2 reduction on p-GaP. Predicted high barriers of HER (via either 2-PyH* or H*) also explain the high selectivity toward CO2 reduction observed in experiments.

3:15 PM BREAK

3:45 PM ET08.04.05

Facet-Controlled Palladium Nanocrystals for Selective Catalysis

Younan Xia; Georgia Institute of Technology, Atlanta, Georgia, United States.

Facet-sensitive reaction, the activity and selectivity of a heterogeneous catalyst can both be enhanced by controlling the type of facet and thus the arrangement of atoms on the surface of nanocrystals. This concept, however, could not be materialized until recently when it became possible to synthesize facet-controlled nanocrystals, including those with high-index facets. In addition, the size of a facet-controlled nanocrystal determines the surface-to-bulk atomic ratio and the proportions of different types of atoms (e.g., vertex, edge, vs. face). In this talk, I will use palladium (Pd) as an example to illustrate how facet-controlled synthesis has enabled the development of catalysts with enhanced activity and selectivity toward an array of reactions, including formic acid oxidation and selective hydrogenation.

4:15 PM ET08.04.06

Morphological Effects of In Situ Reduction of Cuprous Oxide Interfaces for the Electrochemical CO2 Reduction Reaction

Hamed Mehrabi1, James M. Lowe2 and Robert H. Coridan1, 2, Microelectronics-Photonics, University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States; 2Chemistry and Biochemistry, University of Arkansas–Fayetteville, Fayetteville, Arkansas, United States.

Copper-based electrodes have shown uncommon promise for catalyzing the electrochemical reduction of CO2 to a variety of high-value products. Cuprous oxide (Cu2O) is a particularly interesting starting material, as it can be reduced in situ to generate active Cu metal sites on the surface. In recent work, we have demonstrated that the electrochemical properties and nanoscale morphology of photoelectrodeposited Cu2O can be modified by the illumination conditions during growth. Photogenerated electrons have sufficient energy to induce the formation of Cu metal nano-inclusions in a predominantly Cu2O
matrix. The presence of Cu disrupts the micro-crystalline growth observed in Cu$_2$O electrodeposited without illumination. Here, we will describe the experiments that study the effects of photodoping on electrodeposited Cu$_2$O electrodes for the CO$_2$ reduction reaction. The transition from oriented microcrystals to disordered nanocrystalline films with increasing light intensity during growth has a significant effect on the reduction of the electrode surface. This alters the dynamics and electrochemical behavior of the electrode for CO$_2$ reduction. We will also explore how chemical modifications to the surface, such as the thermal oxidation of the Cu nano-inclusions or the addition of a co-catalyst, can affect the branching ratios and dynamics of electrocatalysis. The work outlined here helps to inform further use of electrodes prepared by the in situ reduction of Cu$_2$O for this application.

4:30 PM ET08.04.07
Controlling Proton and Electron Transfer to Molecular Electrocatalysts for Enhanced Selectivity
Christopher Barile, Rajendra Gautam and Jason Mennel;
University of Nevada, Reno, Reno, Nevada, United States.

The O$_2$ reduction reaction and the CO$_2$ reduction reaction are both central to important renewable energy devices. Since both reactions require the transfer of multiple electrons and protons, they can proceed by a variety of mechanisms depending upon the relative rates of these transfer events. We have developed electrode architectures that enable the modulation of proton and electron transfer kinetics to molecular catalysts such that the selectivity of catalysts can be improved. These electrodes are comprised of a metal-centered catalyst such as a Cu-triazole or an Fe-porphyrin attached via a self-assembled monolayer (SAM), which is then covered by a proton-permeable membrane. By altering the identity of the SAM, the kinetics of electron transfer to the bound catalyst can be tuned. Changing the proton permeability of the membrane enables control over the kinetics of proton transfer to the catalyst.

One of the major challenges in designing catalysts for both the O$_2$ and CO$_2$ reduction reactions is selectivity. Using a membrane-modified electrode, we demonstrate that the selectivity of a Cu-based O$_2$ reduction catalyst can be improved by controlling proton transfer rates such that the catalyst produces exclusively water. In contrast, the same Cu catalyst produces ~10% deleterious H$_2$O$_2$ side product when proton transfer is unregulated. We also explore how altering proton and electron transfer kinetics affects the selectivity of molecular CO$_2$ reduction catalysts.

4:45 PM ET08.04.08
Electrochemical CO$_2$ Reduction to CO on Au—Isolating the Intrinsic Activity of the Most Common Crystal Facets
Brian J. Seger, Stefano Mezzavilla1,2, Han E. Stephens2 and Ib Chorkendorff1;
1Technical University of Denmark, Kongens Lyngby, Denmark; 2Department of Materials, Imperial College London, London, United Kingdom.

Due to the drastic drop in renewable electricity prices, electrochemical CO$_2$ reduction has received renewed interest. While CO$_2$ reduction can lead to a wide variety of products, almost all go through a CO intermediate, thus understanding the 2 electron transfer reaction of CO$_2$ to CO is important not just for CO production, but also for products such as ethylene, ethanol, methane and others. Au has been shown to be the most active electrocatalyst for CO production, however major fundamental knowledge on this reaction has yet to be discovered. While most works focus on highly active nanocrystalline Au electrodes, there has yet to be a comprehensive study on the intrinsic electrochemical activity of individual Au facets.

This talk will discuss our work on the electrochemical conversion of CO$_2$ to CO on single crystal Au <100>, <111>, <110>, and <211> facets as well as polycrystalline Au. Our results show a 25 fold difference between the least and most active crystal facets. All facets follow approximately the same Tafel slope between the tested potentials of -0.6 V to -0.8 V vs. RHE. Pb underpotential deposition (UPD) was used to deposit a monolayer of Pb on the Au gold surface to determine surface area. However, the potential at which Pb UPD deposits is facet dependent. By setting a correct potential we could selectively deposit lead on a given facet. While Pb UPD favored depositing on the most active sites, we still could gain fundamental catalysis knowledge. On polycrystalline Au, 20% of a monolayer of Pb yielded a 50% decrease in CO production, but only a 30% decrease in H$_2$ production. 50% of a Pb monolayer on Au yielded a 95% decrease in CO production, but only a 50% decrease on H$_2$ production. The decrease in CO production as a function of Pb coverage indicated that not only could we passivate the most active sites, but also that the facet dependent activity was quite different for CO production versus the competing H$_2$ evolution side reaction.

To further utilize Pb UPD to isolate sites we reinvestigated one of our least active facets, Au <111>. Single crystals are never completely flat and thus there are always a small percentage of step sites. We used selective Pb UPD to deposit 4% of a monolayer in the attempt to passivate these sites. This led to a 50% decrease in CO activity, but the same H$_2$ evolution activity. Covering the Au <111> with 15% of a monolayer led to a 90% drop in CO activity, but the same H$_2$ evolution activity. These results suggest that the intrinsic activity of the least active facets is probably much lower than measured and the experimental results are actually dominated by a small number of highly active defect sites. While these results focus on Au, no single crystal is defect free. Thus these results may lead us to also question whether there are other situations where the non-optimal facets for a given reaction are actually much less active than originally thought.

SESSION ET08.05: Poster Session I: Carbon-Related Catalysis
Session Chairs: Gugang Chen, Yu Han, Yuyang Sun and Lin Wang
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B
Stable materials in the presence of CO2 and fuel exist but the performance is low. For surface reaction limited materials a catalyst must be applied on the gas-membrane interfaces to accelerate the kinetics, but catalyst agglomeration into large clusters at high temperatures reduces the long-term performance. In addition, carbon poisoning can deactivate or even detach the particles from the surface.

In this work, we use exsolution to grow Nickel (Ni) nanoparticles on the surface of a perovskite host. Exsolution has been shown to deliver well-distributed nanoparticles, while the anchored nature of the catalyst reduces agglomeration and carbon poisoning. To investigate exsolution, La0.85Ca0.1Fe0.95Ni0.05O3-δ pellets do not require any pre-reduction of the perovskite, but can rather take place in-situ at the onset of the reactions using pure CO2 on one side of the material and CH4 on the other. The onset of exsolution at different temperatures and CH4 concentrations was systematically examined. We show that no exsolution happens at 900°C, while exsolution is triggered at 950°C and 1000°C using an inlet CH4 mole fraction of 10% and 4%, respectively. At 1000°C, we observe an order of magnitude increase in the CO production rate (JCO), CH4 conversion and syngas yield compared to LCF at the same conditions. Lowering the temperature to 900°C after exsolving at 1000°C reduces JCO and the fuel conversion by 50%, however, the values are still 5 times higher compared to LCF.

Our results set the basis for extension of the concept to other energy related applications, such as solid oxide fuel/electrolysis cells and chemical looping, exsolution of other transition metals and for a broad range of different conversions of industrial interest.

**ET08.05.03**
Enhanced Hydrocarbon Trapping Over C-Oriented Array-Structured ZSM-5 Integrated on Cordierite Junjie Feng1,2, Jie Chen1,2, Avinash M. Dongare1,2 and Puxian Gao1,2,1 Materials Science and Engineering, University of Connecticut, Storrs, Connecticut, United States; 2Institute of Material Science, University of Connecticut, Storrs, Connecticut, United States.

Compared to traditional wash-coated powder-form catalysts, array ensembles of one-dimensional (1D) nanostructures possess stronger gas-solid phase interaction, larger surface area and enhanced materials utilization efficiency [1, 2]. Unlike a layer of ZSM-5 film (MFJ framework) grown on cordierite[3], array-structured ZSM-5 with c-orientation was synthesized by a secondary-growth hydrothermal method. Although the BET surface area and pore size distribution were similar with traditional film, the hydrocarbon trapping efficiency over as-synthesized ZSM-5 arrays was significantly improved. The higher extent of the exposed a- and b- planes to reactant molecules could facilitate the catalytic reactions and adsorptions by improving the mass transportation. The novel ZSM-5 array-structure could provide a promising class of structured devices for hydrocarbon trapping and separation. Furthermore, first-principles Density Functional Theory (DFT) calculations are performed to investigate the AI substitution site preference on the ZSM structure, as well as the adsorption energetics of the reactant molecules.

**ET08.05.04**
Sulfur Segregation and Surface Site Vacancy Compensation During Methanol to Methoxy Reactions on MoS2 Prescott E. Evans1, Hae K. Jeong1, Zahra Hooshmand2, Duy Le2, Takat B. Rawal2, Sahar N. Alviilla4, Ludwig Bartels3, Taltat S. Rahman3 and Peter Dowben1; 1Duques University, Gyeongsang, Korea (the Republic of); 2University of Central Florida, Orlando, Florida, United States; 3University of Nebraska–Lincoln, Lincoln, Nebraska, United States; 4University of California, Riverside, Riverside, California, United States.

Coverage dependent, sulfur vacancy defect formation on the MoS2(0001) basal plane resulting from the adsorption of methanol on MoS2 and its subsequent conversion into methoxy, was investigated utilizing scanning tunneling microscopy, photoemission, photoluminescence, and modeled by density functional theory (DFT). The adsorption of methanol on MoS2 at 110 K followed by annealing near 350 K or the adsorption of methanol on MoS2 at 350 K results in the formation of numerous point defects at the MoS2 basal plane. Larger patch defects, nominally ~2 nm in size as well as line defects on the MoS2 sample surface become increasingly apparent with multiple cycles of methanol exposure and annealing. X-ray spectroscopy studies of the exposure of MoS2 to methanol are consistent with a conversion to methoxy, and the production of defects, based on the reaction kinematics, and significant shifts in oxygen binding energies. Additionally, shifts in sulfur binding energy and temperature dependent sulfur to molybdenum integrated XPS intensity ratios near the critical 350 K formation temperature indicate sulfur segregation to the surface and compensation of surface vacancy sites. The experimental results indicate a small but persistent activation energy for the reaction consistent with DFT predicted energetics. The energy favorability of coinciding defect creation and methoxy formation is also suggested by DFT kinematics. A strongly bound methanol surface species is not favored on the defect free MoS2 surface.

**ET08.05.05**
Developing Descriptor of Keggin Heteropolyacid for Application in Biomass Conversion Catalysis Fiaz Ahmad, Tuvin Suvar Khan, Md. Inteyaz Alam, Kamal K. Pant and M. Ali Haider; Indian Institute of Technology Delhi, New Delhi, India.

Bio-renewable resources have great potential to supersede conventional fossil fuel to meet energy and chemicals demands. Nevertheless, most of the processes employed for biomass conversion essentially requires the presence of an acid catalyst for sustainable production of fuel and chemicals. In this context, catalysts belonging to the family of Heteropolyacid (HPA) are extensively used owing to their excellent activity in biomass conversion reactions. Although a wide range of HPAs have been classified based on their geometrical arrangements, Keggin HPA’s represented by general formulae [XM12O40]n+ have prevalence in industrial applications owing to their super acidic nature, high thermal stability at elevated temperatures in liquid phase reactions and ease of synthesis as compared to other HPA’s. In general, the central atom X can be either P, Si, Ge, B, or Al whereas the heterooatom M can be either Wn+ or Mo6+ or V in which 12 linked octahedra containing addenda atoms (M12O40) surrounds a central tetrahedron (XO4)+. Interestingly, the higher activity of Keggin HPA’s is attributed to the combined effect arising from their stability, acidity, and structural accessibility, nevertheless no conclusive evidence has been suggested for the rational design of Keggin HPA’s. Moreover, the effect of changing central atom X on the activity of Keggin HPA’s is yet to be explored. Therefore, we have employed both theoretical and experimental approaches to conclude deprotonation energy (DPE) as a suitable descriptor for rational design and selection of Keggin HPA’s. In this regard, Density functional theory (DFT) have been employed to calculate the DPE of known Keggin HPA’s with heterooatom W and Mo as well as propose the novel and futuristic catalysts by changing the central atom with elements from group 13-17 in the periodic table. Parallely, esterification reactions have been performed with biomass-derived levulinic acid to produce additives for “green gasoline” in the presence of phosphotungstic acid and phosphomolybdic acid to validate the theoretical results. Interestingly, it was found that activity of Keggin HPA’s is a direct function of their DPE and difference in DPE remained constant when same elements from group 13-17 of the periodic table were put as central atom X in each of the Keggin HPA’s with W6+ and Mo6+ heterooatom. Nevertheless, change in the central atom of the
The dispersing single atom catalysts have been developed recently and reveal highly catalytic activities. The materials of single transition metal embedded in nitrogen-doped graphene display great potential as the catalysts for many reactions. For example, single atomic Ru in nitrogen-doped graphene exhibits excellent activity for oxygen reduction reaction [1]; single Fe Co and Ni in Mn5C3 honeycomb shows tunable electrocatalytic activity in oxygen evolution reaction [2], and Fe dispersed on nitrogen-doped graphene has been demonstrated as an efficient electrocatalyst for CO2 reduction reaction [3]. In those systems, the single atom center contributes as the active site, while the interaction between the single atom and the substrate is crucial. In our study, we applied density functional theory (DFT) simulations to elaborate different nitrogen doping concentrations and configurations surrounding the metal center. The stability of graphene supported metal-nitrogen active center, the magnetic and catalytic properties have been explored. Take CO2 reduced into CO on Fe-N-graphene system as an example, our results show that the chemical environment around the single atom is critical, and the metal center and nitrogen atoms nearby determine the catalytic performance synergistically. Regulating single atom coordination tunes catalytic activity which will be instrumental for designing catalysts with the desired properties.


**ET08.05.06**

Deciphering Graphene Supported Metal-Nitrogen Active Center on CO2 Reduction Reaction—Structure, Magnetic and Catalytic Properties from First Principle Simulations Mingjie Liu, Guanqiang Wang1 and Qin Wu1; Brookhaven National Laboratory, Upton, New York, United States; 2College of Chemistry and Materials Science, Hubei Engineering University, Xiaogan, China.

In this work, we investigated the effect of the Pt-precursor, on the catalytic properties of the Pt/CoO2-NR catalysts for H2 production. The CoO2-1D support was synthesized by the hydrothermal method, using a (NaOH) solution 10 M as precipitating agent [1,2]. The active phase Pt 0.5% (w/w) was impregnated to the catalytic support CoO2-1D by impregnation method. The Pt/CoO2-1D catalysts were characterized by XRD, TPR, TEM and EDS. Afterwards, the activity and selectivity in the SRM reaction was evaluated using a commercial system RIG-100-ISRI in a temperature range of 200 - 450 °C at atmospheric 204 Pressure. The reaction products were analyzed using a Gow-Mac 580 Gas chromatograph with a thermal conductivity detector equipped with a two column system. The characterization results showed a specific surface area of 89 and 95 m2/g respectively for the support and the best Pt/CoO2-(Nit) catalyst. The XRD results showed the typical diffraction pattern of the fluorite cubic structure for CoO2 and a peak associated with Pt is not detected, which confirms a small particle size and a high dispersion of the metal. TPR profiles of the Pt/CoO2-(X) catalysts, showed peaks of H2 consumption associated with the reduction of PtOx to Pt0 at low temperature as well as, a partial reduction of surface ceria from Ce4+ to Ce3+, associated to the presence of the noble metal on the surface of the support [3]. Catalytic activity in the steam reforming methanol reaction, the Pt/CoO2-(Nit) catalyst exhibited a higher catalytic activity reaching a conversion yield of 99% at 350 °C, as well as higher H2 production. In addition, it exhibited a higher yield, as well as the lower production of CO and CH4. None of the synthesized catalysts exhibited a significant deactivation over the evaluated time period.

Authors gratefully acknowledge financial support from the ININ projects CA-607, CO-081 and CONACYT-SENER 226151.

References:


**ET08.05.07**

Pt/CoO2-1D Catalysts for Steam Reforming of Methanol Raul Pérez-Hernández1, Albina Gutiérrez Martínez1, Arturo Claudio-Piedras1, B.C. A. Alcántar-Vázquez2 and R. M. Ramírez-Zamora2; 1Instituto Nacional de Investigaciones Nucleares, Ocoyoacac, Mexico; 2Instituto de Ingeniería, Universidad Nacional Autónoma de México, Mexico, Mexico.

In the present work, two series of nickel catalysts with 4 wt. % of Ni loading were evaluated in the hydrogenation of naphthalene in order to elucidate the effect of surface acidity (Bromsted or Lewis) and preparation method used on the catalyst's activity and selectivity. On the one hand, two supports, SBA-15 silica and Al-SBA-15 with Si/Al molar ratio = 30, were synthesized by hydrothermal method in order to obtain 2D nanostructured supports with and without Brønsted acidity. On the other hand, Ni catalysts were prepared by the incipient wetness impregnation method using two different nickel precursors: nickel nitrate (NN) and a Ni-EDTA complex (ED). We were also interested in the effect of the preparation method on the nickel dispersion and the acidity of the prepared catalysts.

Prepared catalysts were labeled as: NiSBA(NN), NiSBA(ED), NiSBA(NN) and NiSBA(ED). Characterization of the catalysts was performed by nitrogen physisorption, powder X-ray diffraction, temperature programmed reduction, temperature programmed desorption of ammonia, infrared spectroscopy of adsorbed pyridine and high resolution transmission electron microscopy. Characterization results showed that both SBA-15 and Al-SBA-15 supports had attractive textural properties. However, the characteristic hexagonal pore arrangement of SBA-15 was not preserved in the Al-SBA-15 support. The IR of adsorbed pyridine allowed us to confirm and quantify the Brønsted (B) and Lewis (L) acid sites present in the NiSBA and NiSBA catalysts prepared from both precursors used, being the NiSBA(ED) catalyst the most acidic one. Catalytic activity of the catalysts in hydrogenation of naphthalene increased in the following order: NiSBA(NN) < NiSBA(ED) < NiSBA(ED) < NiSBA(ED). Acidity of the catalysts and the dispersion of the reduced Ni nanoparticles also affected the selectivity of the catalysts to decalins (completely saturated products). Both catalysts prepared using a Ni-EDTA complex (NiSBA(ED) and NiSBA(ED)) showed high selectivity to decalins, whereas those prepared from a nickel nitrate solution (NiSBA(NN) and NiSBA(ED)) were selective for tetralin production. Therefore, the nickel precursor used and the support’s acidity affected the activity and selectivity of the tested Ni catalysts.
Enhanced CO₂ Reduction in Lead-Free Perovskite Cs$_3$Sb$_2$Br$_9$ Nanocrystals—Performance and Selectivity

Chang Lu, Xiao Ma, Dominique S. Itanze, Hui Li and Scott M. Geyer; Wake Forest University, Winston Salem, North Carolina, United States.

The last decade has witnessed the burgeoning development of halide perovskite materials with a significant focus on solar and light-emitting diodes applications. However, halide perovskites have received less attention as a catalyst for energy application, for example, water splitting and CO₂ reduction reaction. Moreover, the development for Pb-free perovskite is highly desired for all applications. To this end, in our work, we developed a facile synthesis method for Sb-based halide perovskite nanocrystals (NCs). These exhibit structure uniformity and high thermal stability, with only a 2 % weight drop (attributed to the ligand loss) under 200 °C annealing. For solar driven CO₂ reduction the Cs$_3$Sb$_2$Br$_9$ produces 400 umol(CO)/g, a 40-fold more improvement in CO per gram compared to CsPbBr$_3$. Interestingly, the use of Pb-based perovskite also generates CH₄, which is not observed in Sb-based reaction batch, and we will present DFT calculation results to shed further light into the differences in reaction mechanism for the Pb-based and Sb-based system. This brings new insights into the emerging field of Pb-free perovskite alternatives and perovskite materials for catalytic applications.

Development of Catalytic La-Based Perovskite Redox Materials for Solar Thermochemical Conversion of CO₂ into Syngas

Rahul R. Bhosale and Gorakhnath Takalkar; Department of Chemical Engineering, Qatar University, Doha, Qatar.

The energy utilization of the world today is around 15TW and it is expected that it will raise up to 30TW by the year 2050. In addition to this, due to the excessive utilization of fossil fuels (for the production of required energy), the concentration of CO₂ in the environment increases rapidly. The production of syngas (which can be used as a precursor for the production of liquid transportation fuel) by using H₂O, CO₂, and solar energy provides a promising path to solve the issues associated with the utilization of fossil fuels and increase in the CO₂ concentration. Direct production of syngas via thermalysis of H₂O and CO₂ is possible, however it needs a very high temperature and chances of forming a gaseous explosive mixture of H₂ and O₂ is also very high. Utilization of solar driven metal oxide based catalytic thermochemical H₂O and CO₂ splitting cycle reduces the requirement of higher temperatures and avoids the formation of explosive gas mixture. Various non-volatile redox materials have been investigated towards the thermochemical production of solar fuel via H₂O and CO₂ splitting reactions. In addition to the ferrite and ceria based materials, recently the researchers are focused towards perovskite based redox materials as an active catalyst for the solar splitting process. In particular, La-based perovskite materials are of particular interest as they are capable of producing higher amounts of O₂ and H₂ at lower operating temperatures as compared to ceria and ferrites.

In this study, a variety of La-based perovskite materials were synthesized using combustion method and tested towards multiple H₂O/CO₂ splitting cycles using a high temperature thermogravimetric analyzer. It is very important to note that in most of the previous investigations the maximum number of cycles performed in case of La-based perovskites are 3 to 4. Hence, this study has a uniqueness that it tested the La-based perovskites in more than 50 thermochemical cycles.

Enhancement of CO₂ Reduction Activity Under Visible Light Irradiation Over Zn-Based Metal Sulfoles by Combination with Ru-Complex Catalysts

Tomiko M. Suzuki¹, Tomoaki Takayama¹, Shunsuke Sato¹, Akhide Iwase², Akihiko Kudo² and Takeshi Morikawa¹; ¹Toyota Central R&D Labs Inc, Nagakute, Japan; ²Tokyo University of Science, Tokyo, Japan.

The reduction of CO₂ to obtain useful energy-rich chemicals utilizing photocatalysts has attracted attention as a potential means of artificial photosynthesis operating under sunlight irradiation. Although the use of powdered systems for CO₂ reduction is challenging owing to the inherent difficulty in achieving the highly selective reaction of CO₂, in solution, the system is attractive as a practical cost-effective system to utilize sunlight [1]. In this regard, we have demonstrated visible light-induced selective reduction of CO₂ to HCOOH using metal-complex/semiconductor hybrid photocatalyst consisting of a Ru-complex and a p-type metal oxide semiconductor particles (N-doped Ta₂O₅) in acetonitrile (MeCN)/triethanolamine (TEOA) solution with quantum efficiencies of 1.9% and more [2, 3]. Among various semiconductors, Zn-based sulfole are also attractive semiconductor for the hybrid photocatalyst, because ZnS possesses a relatively negative conduction band minimum (E_{CBM}) formed by the Zn 4s4p orbitals, which facilitates the electron transfer from the CBM of the semiconductor to the metal-complex.

In the present study, the powdered Zn-based sulfoles which were reported to be active for sacrificial H₂ evolution, were investigated in combination with various Ru-complex catalysts with regard to the promotion of visible light driven CO₂ reduction. Hybrid photocatalysts consisting of a Ru-complex and a semiconductor anchored by organic groups were prepared by an adsorption method. Photocatalytic CO₂ reduction was performed in MeCN/TEOA solution under visible light (≤410 nm) irradiation. The photocatalytic activities were largely dependent on the basic characteristics of the Ru-complex and the metal sulfole. The results demonstrate that several of semiconductors improve the photocatalytic CO₂ reduction selectivity of the hybrid system, and that n-type (AgIn₁₋ₓZnₓS) [4] and Zn₆Ni (Ni 0.2 mol%) [5] linked with a neutral Ru-complex containing phosphonate anchors ([Ru(dpbbpy)(CO)₂Cl₂, dpbbpy: 4,4'-diphosphonatel-2,2'-bipyridine) exhibited highest turnover number with above 100 after 16 h irradiation. The carbon source for the HCOOH evolved in the reaction over the hybrid photocatalysts was confirmed to be CO₃ based on ¹³C₂O₄ analyses [6].

These results suggest that Zn-based metal sulfole are potential candidates for use in powdered semiconductor/molten-complex systems for active and selective CO₂ photoreduction. Our results also suggest that future success in powdered Z-scheme systems utilizing water as an electron donor and protons source.

References


High Yield Preparation of Two-Dimensional Cu Nanocatalysts for Carbon Dioxides Reduction Reaction

Shutang Chen and Gugang Chen; Honda Research Institute USA Inc., Columbus, Ohio, United States.

Cu-based nanostructures have been explored for catalyzing CO₂ electroreduction due to their lower working function and cost, and higher earth-abundancy. However, the practical application of CO₂ electroreduction reaction requires Cu catalysts hold a high percentage of CO₂ of exposed surface atoms, which can improve the utilization efficiency of catalysts and products selectivity. Here we reported a high temperature reduction method to prepare Cu nanosheets in hydrophobic system. The feeding molar ratio of triethanolamine/Cu ion precursors plays a critical role for the formation of Cu nanosheets. The shape of Cu nanosheets were controlled by adjusting the reaction interval, the types of Cu ion precursor, and the purity of triethanolamine. The size and thickness of Cu nanosheets are variable from 50 nm to 13 µm and 15 nm to 500 nm, respectively. Moreover, pure Cu nanosheets are stable in solution for more than three months. As a result of high percentage of Cu surface area, these nanosheets as catalysts have demonstrated the enhanced catalytic activity and selectivity to convert CO₂ to fuels.
Co-based bimetallic nitride flakes grown on n-doped carbon nanofibers (Co-M-N@NCNF, M = Ni, Mn, Fe) by employing transition metals such as Co, Mn, and Ni. Especially, transition metal nitrides such as Co4N are considered as a promising candidate material due to their superior electrical conductivity and chemical stability. Furthermore, bimetallic compounds can further induce oxygen-based catalytic activity by effective tuning of d-band structure.

Here, we proposed facile synthetic method for Co-based bimetallic nitride flakes grown on n-doped carbon nanofibers (Co-M-N@NCNF, M = Ni, Mn, Fe) by using Co-based bimetallic leaf like zeolite imidazolate framework (ZIF-L), which is composed of cobalt and other metal ions (Ni, Mn, Fe) with organic linkers. Firstly, electrospun Polyacrylonitrile (PAN) nanofibers were treated by NaOH for smooth growth of Co-based bimetallic ZIF-L. Followed by subsequent stabilization and nitridation process under ammonia gas, it converted to Co-M-N@NCNF. The Co-M-N@NCNF electrodes showed remarkable electrochemical properties for both oxygen evolution reaction (OER) and oxygen reduction reaction (ORR). We demonstrate enhanced catalytic activity of Co-M-N@NCNF for both OER and ORR in terms of overpotential, Tafel slope, and charge transfer. These are mainly attributed to the synergistic effects from Co-based bimetallic compounds with nitrogen atoms. Also, unique structure of active two dimensional flakes grown on one dimensional carbon nanofiber offered more exposed active sites and high surface area. The proposed strategy of ZIF-derived bifunctional nanomaterials provides prospects for developing highly active electrocatalysts in electrochemical energy devices.
Minimizing Energy Use for Surface Reactions by Using Both Light and Heat—Plasmonic Catalysts and Non-Plasmonic Catalysts Enabling Photocexcitation of Adsorbates

Chanyeon Kim and Hyeonjo Lee; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Many heterogeneous catalytic reactions occur at high temperatures, which may cause a large energy cost, poor safety, and thermal degradation of catalysts. Here, we propose a “light-assisted surface reaction”, which catalyze the surface reaction using both light and heat as an energy source. Plasmonic metal nanoparticles absorb light energy and release the energy through radiative or non-radiative channels. Surface catalytic reaction would take advantage of the non-radiative energy relaxation of plasmon with enhanced activity. Particularly, binary nanoparticles are interesting because diverse integration would be possible consisting of plasmonic part and catalytic part. Herein, we demonstrated ethanol dehydrogenation under light irradiation using Ag-Ni binary nanoparticles with different shapes, snowman and core-shell, as plasmonic catalysts. The surface plasmon formed in the Ag part enhanced the surface catalytic reaction that occurred at the Ni part, and the shape of the nanoparticles affected the extent of the enhancement. The surface plasmon compensated the thermal energy required to trigger the catalytic reaction. The absorbed light energy was transferred to the catalytic part by the surface plasmon through the non-radiative hot electrons.

Non-plasmonic conventional metal catalysts such as Ru, Rh, Pt, Ni, and Cu were tested for CO2 hydrogenation, and Ru showed the most distinct change upon light irradiation. CO2 was strongly adsorbed onto Ru surface, forming hybrid orbitals. The energy gap between the HOMO and LUMO was reduced significantly upon hybridization. Hot electrons could be generated by jumping the shortened energy gap upon light irradiation, enhancing CO2 dissociation. The light-assisted CO2 hydrogenation used only 37% of the total energy with which the CO2 hydrogenation occurred using only thermal energy. The CO2 conversion could be turned on and off completely with a response time of only 3 min, whereas conventional thermal reaction required hours to terminate the CO2 conversion. These unique features can be potentially used for on-demand fuel production with minimal energy input.

Investigating Light Enhanced Catalytic Lifetimes and Activities Over Plasmonic Au Catalysts in the CO Oxidation Reaction

Peter Novello1, Puni Varanasi1,2 and Jie Liu1; 1Duke University, Durham, North Carolina, United States; 2U.S. Army Research Office—Materials Science Division, Research Triangle Park, North Carolina, United States.

Light interacting with catalysts via surface plasmon resonances has the potential to dramatically improve catalytic reactions by photothermal heating and hot-electron transfer. This project investigates plasmonic light enhancement of the CO oxidation reaction over supported Au catalysts. Optimization of this reaction empowers removal of poisonous CO at room temperature which has the potential to improve human health. This reaction also features a negative activation energy which leads to a minimum in the temperature dependent conversion curve near 80 °C. Results show that catalytic activity around room temperature doubled under light and catalyst lifetimes increased by a factor of 5. From these results, an analysis of the relative magnitude of the photothermal catalytic enhancement and non-thermal catalytic enhancement effects were performed by utilizing the temperature dependent change from positive to negative activation energy. This demonstrated that the effect of photothermal heating is more substantial and that both effects enhance the reaction rate and improve catalytic lifetimes. From further experiments coupling light induced desorption of CO2 to the regeneration of catalytic activity, a mechanism for light enhancement on gold catalysis is proposed. Light reactivates the catalyst by removing surface carbonates which otherwise act as poison, allowing for dramatically increased catalytic activity and lifetime to demonstrate a new path for highly active CO oxidation.

Revelation of Active Sites for Room Temperature CO Disproportionation on a Gold Nanoparticle Driven by Electron Beam Excited Localized Surface Plasmon Resonance

Wei-Chang D. Yang1, 2, Canhui Wang1, 2, Lisa A. Fredin3, Henri Lezec1 and Renu Sharma1; 1CNST, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; 2Maryland NanoCenter, University of Maryland, College Park, Maryland, United States; 3Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Recent reports of hot electron-induced dissociation of small molecules, such as hydrogen1,2, demonstrate the potential of using plasmonic nanomaterials to convert light into chemical energy for low-temperature catalytic reactions. Theories have typically assumed that plasmonic catalysis is mediated by the optical excitation of energized electrons or holes through the dephasing of localized surface plasmon (LSP) modes on Au, Al, or Ag nanoparticle and subsequent charge transfer from the metal to the adsorbed gas molecules3. However, only a few hot electron experiments on gas-phase substrate has been reported to date.

Here, we exploit the LSP resonance of a triangular Au nanoprim excited by an electron beam to drive CO disproportionation (2CO + 2CO2) as a model reaction that typically takes place between 300 °C to 600 °C at room temperature, in an environmental scanning transmission electron microscope (ESTEM). Using in situ electron energy loss spectroscopy (EELS) mapping, combined with density functional theory (DFT) and electromagnetic boundary element method (BEM) calculations, we show that amorphous carbon deposits, resulting from the CO disproportionation reaction, occur only at selective sub-particle locations where preferred CO adsorption sites and plasmon modes antinodes are coincident. Low-loss and core-loss EELS are used to locate the maximum LSP resonance intensity excited by the electron beam and the adsorbed CO molecules, respectively, on a Au nanoprim. Amorphous carbon deposited on the cantilevered corner of a nanoprim, measured after CO is evacuated from the sample chamber, confirms that (a) CO molecules disproportionate at room temperature and (b) the location corresponds to where the CO adsorption probability and the intensity of the LSP antinode.

Reference:
studies of the optical properties of these nanostructures, we show that the flow of energy is strongly biased towards absorption (i.e., excitation of energetic charge carriers) in the thin Pt shell. We demonstrate the utility of these nanostructures for photocatalytic chemical reactions in the preferential oxidation of CO in excess H₂. The reactor studies conclusively show that photo-excitation of these nanostructures results in photo-chemical reactions on the Pt surface. We describe the fundamental physical reasons for the observed directed flow of energy and discuss how these discoveries impact the field of plasmonic catalysis.

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10:00 AM BREAK

10:30 AM *ET08.06.05
Rotational Spectroscopy for Characterization of Plasmonic Photocatalytic Reaction Products Naomi J. Halas1, Philip Christopher2 and Henry O. Everitt1; 1 Rice University, Houston, Texas, United States; 2Department of Chemical Engineering, University of California, Santa Barbara, California, United States; 3Army Aviation & Missile RD&E, Huntsville, Alabama, United States.

Rotational spectroscopy is introduced as a new in situ method for monitoring gas phase reactants and products during chemical reactions. Exploiting its unambiguous molecular recognition specificity and extraordinary detection sensitivity, rotational spectroscopy at terahertz frequencies was used to monitor the decomposition of carbonyl sulfide (OCS) over an aluminum nanocrystal (AlNC) plasmonic photocatalyst. The intrinsic surface oxide on AlNCs is discovered to have a large number of strongly basic sites that are effective for mediating OCS decomposition. The strength of rotational spectroscopy is witnessed through its ability to detect and distinguish isotopeologues of the same mass from an unlabeled OCS precursor at concentrations <1 nanomole or partial pressures <10 mTorr. These attributes recommend rotational spectroscopy as a compelling approach for monitoring gas-phase chemical reactants and products in real time.

11:00 AM *ET08.06.06
Sustainable Nanocatalysis—Plasmonic Silver Nanocubes and Cellulose Nanocrystals as Non-Innocent Support Audrey Moores; McGill University, Montreal, Quebec, Canada.

We explored the use of cellulose nanocrystals as a non-innocent support to generate metal/cellulose nanohybrids.1 We showed that, with Pd, we could afford active and enantioselective hydrogenation catalysts,2 while with Ru, extremely active and recyclable catalysts were accessed for the difficult reduction of amines under mild conditions.2 These nanocrystals in suspension could allow the direct synthesis of silver nanoparticles without the use of any additional oxidizing or reducing chemical.3

Besides, we have employed silver nanocubes for hydrogen activation and hydrogenation of ketones and aldehydes via irradiation at 405 nm, corresponding to the position of the plasmon band of the nanocubes.4 Exposure to other wavelengths, or absence of light failed to provide activity thus proving the plasmonic effect. Compared to other catalytic systems, the plasmonically activated catalyst provides access to primary and secondary alcohols using milder conditions, in a highly atom economical fashion. Plasmonic catalysis of the oxidation of aldehyde to carboxylic acid was also demonstrated.


11:30 AM ET08.06.07
Efficient Ammonia Synthesis via Light-Driven Thermal Gradients in Fixed-Bed Catalytic Reactors Xueqian Li1,2, Jie Liu1 and Henry O. Everitt1; 1 Chemistry, Duke University, Durham, North Carolina, United States; 2Physics, Duke University, Durham, North Carolina, United States; 3Army AMRDEC, Huntsville, Alabama, United States.

When the temperature of exothermic chemical reactions increases, thermodynamic equilibrium shifts away from producing products and towards retaining reactants. Unfortunately, for reactions with high activation barriers, the reaction rate can be extremely slow at the lower temperatures that favor products. Scalable industrial processes require both high reaction rates and high product yields and balancing these two represents the art of chemical engineering. A prominent example is the industrial Haber-Bosch process, which requires optimized catalysts, high temperatures, high pressures, and several recycling steps to achieve practical reaction rates and yields of ammonia, but at the cost of consuming up to 2% of the global energy produced annually. Here, we demonstrate how light-induced plasmonic heating can produce a controlled thermal gradient in a conventional Ru-based catalyst that simultaneously achieves both high reaction rates and high conversion yields in ammonia synthesis. Using continuous wave light emitting diodes, ammonia is copiously produced under ambient conditions without any external heating. Our results suggest that the optical control of thermal gradients in catalysts may become a universal strategy for simultaneously increasing reaction rates and conversion yields of many exothermic reactions.

11:45 AM ET08.06.08
Electrocatalytic CO₂ Reduction at Functionalized Cu Surfaces—Structure-Reactivity Relationships Between Organic Modifiers and Product Selectivity Aya K. Buckley1,2, F. Dean Toste1 and Francesca Maria Toma1,2; 1 Joint Center for Artificial Photosynthesis, Berkeley, California, United States; 2Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; 3Department of Chemistry, University of California, Berkeley, California, United States.

An efficient electrocatalyst for the reduction of CO₂ (CO₂R) would enable the conversion of a major contributor to global warming into valuable carbon-based products. Cu surfaces are unique in that they are the only single-metal system to catalyze the formation of multicarbon products from CO₂. However, the lack of selectivity of these Cu surfaces necessitates investigation into how their catalytic behavior may be adjusted.

The complexity of the catalyst/electrolyte interface poses challenges in identifying how a change in an electrocatalyst affects the observed CO₂R
selectivity. Therefore, we employ a methodical experimental approach that focuses upon identifying which parameters play an important role in determining CO2R selectivity.

First, we examined the effect of a series of organic modifiers on the CO2R selectivity of Cu. Oxide-derived Cu surfaces were functionalized with molecular and polymeric modifiers featuring a wide variety of structural characteristics, including neutral and cationic species, protic and aprotic species, and species bearing various functional groups. The product distribution of these surfaces in the CO2R reaction was characterized at -0.7 V vs. RHE, focusing upon the selectivity between CO, formic acid and H2. This allowed classification of the organic structures based upon the promoted product. Finally, each class of modifiers was examined and key, common structural characteristics of the modifiers were identified.

Through this systematic study, we demonstrate that the CO2R selectivity of a non-precious metal catalyst may be improved for CO, formic acid or H2 by changing the organic modifier applied. Selectivities of up to 76% CO or 62% formic acid were observed, and H2 selectivity was tuned from 97% down to 2%. In this presentation, we describe the structural characteristics of these modifiers that are key to changing the observed selectivity. These common features offer insights into the mechanism by which organic modifiers influence CO2R selectivity at the metal surface. We expect that the identified structure-reactivity relationships will illuminate important design principles for novel, selective CO2R electrocatalysts and organic structures for CO2R devices.

SESSION ET08.07: Characterization for Catalysis
Session Chairs: Yuzi Liu and Yugang Sun
Wednesday Afternoon, November 28, 2018
Hynes, Level 3, Room 306

1:30 PM *ET08.07.01
Quantitative Super-Resolution Imaging of Nanocatalysis
Peng Chen; Cornell University, Ithaca, New York, United States.

This talk will present our latest efforts in developing and using single-molecule super-resolution microscopy to map catalytic reactions on single nanoparticles at nanometer resolution and under operando conditions. Depending on available time, the topics may include: 1) cooperative communications within and between single nanocatalysts; 2) visualizing bimetallic effect within single nanocatalysts; and/or 3) mapping catalytic hotspots on plasmonic nanostructures.

2:00 PM *ET08.07.02
In Situ Characterization of Metal Surface Dynamics in Reaction Gas by Atomic Scale and Millisecond Resolution Environmental TEM
Seiji Takeda, Naoto Kamiuchi, Takehiro Tamaoka, Ryotaro Aso and Hideto Yoshida; Osaka Univ, Ibaraki, Japan.

Environmental transmission electron microscopy (ETEM) provides us with mostly static structural data of solid surfaces in reaction environments for a long time. However, given the recent advancement in TEM image detectors such as CMOS-based TEM cameras, the technique has started to progress in revealing the atomic dynamics that are correlated with catalytic reaction processes [1].

In this presentation, first we summarize the history of in-situ TEM in our research group briefly for the past decades. Second we show our recent time-resolved analyses with millisecond-resolution on the unexpected atomic dynamics on the surface of nanoporous gold (NPG) catalysts. The surface of NPG catalysts is structurally stabilized in pure oxygen environments, while the surface appears to be dynamically fluctuated with space and time in the reaction environment for the oxidation of CO at room temperature. Since the NPG catalysts inevitably include the residual impurity of Ag in addition to the majority of Au, it is concluded that the Ag atoms on the surface are oxidized to form stable Ag-O-Au atomic clusters in pure oxygen environment. It is also concluded that the self-activating atomic clusters are reduced and oxidized repeatedly in a reaction environment that, of course includes both oxygen and CO. Hence, the catalytically active structure in the gold catalysts (supported Au nanoparticle catalysts and NPG catalysts) can now be experimentally unified toward elucidating the fascinating catalysis mechanism of gold. We also show some recent challenges on the oxidation and reductions processes on the surfaces of related metals.

Though a chemical reaction is an extremely fast electronic phenomenon, the present study has clarified that the atomic dynamics occurring on the catalytically active surfaces can be observable by the advanced ETEM technique. Finally, to derive clearly the intrinsic natures of a specimen in a reaction environment by atomic scale and millisecond resolution ETEM, it is still indispensable to consider the influence of electron beam. We also discuss the related topics [2].


2:30 PM BREAK

3:30 PM *ET08.07.03
Investigation of Gas-Solid Reaction in Confined Space by In Situ TEM and Synchrotron X-Ray
Yuzi Liu; Argonne National Laboratory, Lemont, Illinois, United States.

The reaction between gas and solid is a great interest for material science. In more specific, materials transformation, gas molecules adsorption/desorption and chemical reaction on the surface are the most attractive topics. Here we use both transmission electron microscope (TEM) and synchrotron x-ray to study the gas-solid reaction with the material in gas environments in confined space (tween two SiN membranes with gap ~500nm) which allow the high energy electron beam and x-ray penetrating the system.

Firstly, the conventional and gas flow TEM were employed to study how the AgCl transformed to AgOx at different O2 partial pressure. It was found that the high energy electrons help to generate Cl vacancies which drive the AgCl reduction to Ag. The Ag was further oxidized to AgO because of the high energy electrons radicalized the O2, which is at very low partial pressure in TEM column. When AgCl particles were in the O2 rich condition, the same reduction process took place to generate Ag. But, Ag was oxidized to AgO due to the high O2 partial pressure. Clearly, there are two steps to transfer from AgCl to AgOx. AgCl transfers to Ag upon the response of Cl vacancies generation through high energy electron beam. Then, the Ag will be oxidized either to AgxO or AgO at very low or high O2 partial pressure respectively.
In this work, highly doped TiO$_2$:Ni$^2+$ (15 mol\%) nanoparticles are synthesized via sol-gel chemistry. The drying and annealing of the aged sol are shown to affect dopant occupancy. Therefore, this work addresses the phenomenon of spatially controlled dopant incorporation for controlled optical and photocatalytic separation of charge carriers, and the surface reaction kinetics. Commonly used bulk characterization techniques are often indifferent to surface vs. bulk States; 3Consiglio Nazionale delle Ricerche, Pisa, Italy; 4Chemistry, Caltech, Pasadena, California, United States. Massachusetts, United States; 3Walter Schottky Institute & Physics Department, Technische Universität München, Garching, Germany.

This work was performed at the Center for Nanoscale Materials, a U.S. Department of Energy Office of Science User Facility, and supported by the U.S. Department of Energy, Office of Science, under Contract No. DE-AC02-06CH11357.

4:00 PM ET08.07.04

Resolving the Atomic Details of Gas-solid Interfaces in Catalytic Materials Through In Situ Neutron Total Scattering Daniel Olds, Jue Liu and Kate Page; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Nanostructured and porous materials have widespread industrial applications in adsorption and catalysis, but experimental studies providing atomistic data regarding gas-sorbtion interactions under application-relevant conditions are limited. Current analytical methods give information about either the crystal structure or the macroscopic kinetics involved in these processes, but not their interplay.

We present a new sample environment for interrogating materials under precise gas-flow conditions using time-of-flight neutron scattering. This capability allows for simultaneous measurements of stroboscopic, isotope-contrast neutron total scattering and Steady-State Isotopic Transient Kinetic Analysis (SSITKA), thus providing material insight into both structural and kinetic details. We anticipate this sample environment will be useful in studies of gas-solid interfaces, hierarchical structure, molecular sieves, nanomaterials catalysis, and more.

The results of a commissioning study on nitrogen adsorption in calcium exchanged zeolite X will be presented. Together with theoretical considerations from Grand Canonical Monte Carlo simulation, we identify the location of a heterogeneous distribution of adsorption sites under operational conditions (1 atm, 30° C). We also highlight recent upgrades to the sample environment allowing for high-temperature studies (up to 800° C) of materials under gas flow, which is demonstrated with an in situ rxdex reaction study on ceria nanorods. This sample environment is presently available in the general user program on the NOMAD beamline at the Spallation Neutron Source (ORNL).

4:15 PM ET08.07.05

Mechanisms of Photocatalytic H$_2$ Evolution on Co-Catalyst Loaded Semiconductors in the UHV Constantin A. Walenta1, 2, Sebastian Kollmannsberger1, Carla Courtois2, Rui Nuno Pereira3, Martin Stutzmann1, Martin Tscharl4 and Ueli Heiz1; 1Chemistry Department & Catalysis Research Center, Technische Universität München, Garching, Germany; 2Department of Chemistry & Chemical Biology, Harvard University, Cambridge, Massachusetts, United States; 3Walter Schottky Institute & Physics Department, Technische Universität München, Garching, Germany.

Despite of intense research efforts in the last decade, photocatalytic processes for the generation of renewable fuels are still lacking the requirements for successful application on industrial scale. Research strategies have so far been focused on material screening due to the complexity of the underlying processes. However, a deep fundamental understanding will ultimately allow us to implement knowledge-based improvements towards enhanced photocatalytic efficiencies, selectivities and stabilities.

In this work, we examine the reaction mechanism of photocatalytic alcohol reforming on a model system (co-catalyst loaded rutile TiO$_2$(110)). By judicious choice of surface preparation and catalyst loading, we are able to unravel the photochemical mechanism on an atomic scale. By changing the reaction conditions e.g. temperature, photochemical reaction steps of the isotopically labeled reactant can clearly be disentangled from chemical thermal reaction steps in the mechanisms. A detailed kinetic analysis reveals, that the photocatalytic reaction rate depends linearly on the photon flux, indicating that only one charge transfer of this two-step process is facilitated photochemically.

4:30 PM ET08.07.06

Ammonia Synthesis on the Fe(111) Surface—Reaction Mechanism and Kinetics Qi An1, Jin Qian2, Alessandro Fortunelli1, 2, Robert Nielsen4 and William Goddard4; 1University of Nevada, Reno, Reno, Nevada, United States; 2Materials Science, Caltech, Pasadena, California, United States; 3Consiglio Nazionale delle Ricerche, Pisa, Italy; 4Chemistry, Caltech, Pasadena, California, United States.

The Haber-Bosch (HB) process converting nitrogen gas (N$_2$) and hydrogen gas (H$_2$) into the ammonia (NH$_3$) consumes 1–2% of the world's energy supply and generates more than 300 million tons of carbon dioxide annually. It is essential to optimize the efficiency of HB process extensively to save energy consuming and to reduce CO$_2$ production. However, the reaction mechanisms of HB process at industrial conditions are not fully understood. Here, we employed density functional theory to predict reaction mechanisms and kinetics for NH$_3$ synthesis on Fe (111) surface which is more efficient for NH$_3$ synthesis than other surfaces such as (100) and (110). First of all, the free energies of all steps are predicted under experimental condition of 673 K and 20 atm and industry condition of 730 K and 200 atm. Then we built the free energy diagrams into a kinetic Monte Carlo model to predict the steady state catalytic rates and compare with single-crystal experiments. We predicted a turnover frequency (TOF) of 17.7 s$^{-1}$ per 2 × 2 site ($5.3 \times 10^9$ mol/cm$^2$/sec) under condition of 673 K and 20 atm. This agrees very well with single crystal experiment of TOF = 10 s$^{-1}$ per site.

4:45 PM ET08.07.07

Spatial Tailoring of Dopant Position in Solids for Enhanced Visible Light Photocatalytic Performance Pragathi Darapaneni1, Natalia da Silva Moura1, Darrell Harry2 and James A. Dorman1; 1Louisiana State University, Baton Rouge, Louisiana, United States; 2Chemical Engineering, Southern University, Baton Rouge, Louisiana, United States.

Transition metal (TM) doped semiconductor materials are extensively employed for light harvesting and photocatalytic applications to increase the charge mobility for better performance. The position and site occupancy of the dopant dictate the physical properties of these materials such as light absorption, separation of charge carriers, and the surface reaction kinetics. Commonly used bulk characterization techniques are often indifferent to surface vs. bulk dopant occupancy. Therefore, this work addresses the phenomenon of spatially controlled dopant incorporation for controlled optical and photocatalytic properties.

In this work, highly doped TiO$_2$:Ni$^{2+}$ (15 mol\%) nanoparticles are synthesized via sol-gel chemistry. The drying and annealing of the aged sol are shown to affect the segregation of NiO$_2$ onto the surface of TiO$_2$. Specifically, it is possible to control the dopant position by varying the moisture exposure time, indicating that the ambient water layer on the surface of TiO$_2$ plays an important role on surface energetics. The effect of moisture and annealing rate on the dopant position was systematically studied using steady-state and time-resolved methods (XRD, UV-Vis, Raman, TGA/DSC, and FTIR) to extract crystallization temperatures, optical absorption, bond formation, and surface hydroxyl concentration. XRD results show that the vacuum dried TiO$_2$:Ni$_2$ powders formed a doped anatase phase while the air dried powders formed segregated anatase and NiO phases upon annealing. Furthermore, rapid annealing of the air-dried TiO$_2$:Ni$_2$ powders formed a metastable anatase doped phase while slow annealing resulted in the segregation of NiO phase, which...
can also be observed in TGA/DSC. The annealing processes produce a shift from discrete peaks to a broad absorption based on the dopant position. The evolving local environment is probed via x-ray absorption spectroscopy (XAS) and High-Resolution TEM to elucidate the difference in the dopant local environment with photocatalytic performance using photoluminescence (PL) spectrometer. Moreover, the charge carrier recombination kinetics in these NPs can be investigated using time-resolved PL measurements to understand the modified reaction pathways. This ability to incorporate higher dopant concentrations while engineering the dopant position in nanostructures will assist in the development of improved photocatalytic devices. Finally, a similar trend of dopant segregation was observed with other first row TM doped TiO₂ powders upon slow annealing, suggesting that the segregation of TM dopants in TiO₂ is a function of the dopant size.

Selective Formation of Li₂O in a Lithium-Air Battery
Jaelyn Luneg, Livia Giordano and Yang Shao-Horn; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Although current electric vehicles rely on lithium-ion technology, lithium-ion batteries cannot provide a sufficiently far driving range at low cost [1]. Lithium-air batteries offer a promising alternative to conventional lithium-ion batteries due to their high theoretical energy density, close to that of gasoline. Although lithium peroxide is the discharge product typically observed in lithium-air batteries, lithium oxide is the preferred product with a specific capacity 1.3 times greater than that of lithium peroxide [2]. In addition, many electrolytes have been found to react significantly with lithium peroxide and with the superoxide ion, whereas lithium oxide may be less reactive with the electrolyte [3]. Because the free energies of reaction for lithium oxide and lithium peroxide are similar (~511 kJ/mol and ~571 kJ/mol respectively), it should be possible to design a catalyst that selectively forms lithium oxide at room temperature. Additionally, it is important that such a catalyst also reduces ORR/OER potential losses, which currently inhibit lithium-air battery efficiency.

To design a catalyst selective for lithium oxide formation, it is necessary to understand the reaction pathways for the growth of lithium oxide and lithium peroxide. While the reaction mechanism describing electrochemical growth of lithium peroxide has been well studied [4], much less is known about the initial nucleation of lithium peroxide or lithium oxide on the surface of a catalyst. In this study, the initial nucleation pathways for both lithium peroxide and lithium oxide are identified using the ruthenium dioxide (110) surface as a model catalyst. The lowest energy interfaces between lithium peroxide and lithium oxide and the ruthenium dioxide (110) surface are identified by employing a lattice matching algorithm. Density functional theory is then used to identify the charge and discharge pathways which offer the lowest overpotentials. Initial growth of lithium oxide on ruthenium dioxide (110) is found to have a discharge overpotential of 0.58 V, rate limited by adsorption of lithium ions. The removal of the final layer of lithium oxide on ruthenium dioxide (110) is found to have a charge overpotential of 0.44 V, rate limited by the desorption of oxygen. The effects on the charge/discharge overpotentials due to straining and doping the ruthenium dioxide (110) catalyst are studied to identify design principles for a catalyst that is both selective for lithium oxide formation and offers low ORR/OER overpotentials.


Computational High-Throughput Screening and Characterization of Catalytic Mass Activities of Tailored Pt Electrocatalysts for the Oxygen Reduction Reaction
Marlton Rück and Alessio Gagliardi; Department of Electrical and Computer Engineering, Technische Universität München, Munich, Germany.

Tailored Pt electrocatalysts harbor great potential to enhance the catalytic mass activity for the oxygen reduction reaction (ORR) in fuel cells [1]. Due to elaborate experimental synthesis and innumerable variations of nanostructures, computational high-throughput screening may highly promote the search for promising electrocatalysts. In our present work, we computationally screen through a plethora of distinct Pt nanostructures where an optimization algorithm tweaks the fine adjustment on the atomic-scale. Precise characterization of tailored electrocatalysts within feasible timescales is the critical step in high-throughput screenings. To this end, we employ our recently developed model [2] which rapidly predicts the catalytic mass activities of the screened nanostructures in absolute units of A/mg_Pt. Our study discloses nanostructures with high mass activities up to 3.86 A/mg_Pt. To further support experimental synthesis, we analyze the size dependence of the nanostructures on the catalytic mass activity. Summing up, our work comprises the crucial steps from screening and characterization to size dependence of tailored Pt electrocatalysts aiming at experimental and theoretical collaboration in nanoparticle synthesis.

Biomass Derived Nitrogen-Doped Powdered Activated Carbon for Efficient Electrocatalytic Production of Hydrogen Peroxide

For this purpose, there are various materials reported including carbon-based materials (g-C3N4, graphite, carbon nanotubes, graphene, graphite). Attempts have been made to prepare appropriate and cost-effective cathode materials to enhance the ORR activity and current efficiency for H2O2 electro-generation. We show examples of n type, p type, and ambipolar organic semiconductors performing photochemical oxygen reduction, both as semiconductor is in contact with oxygenated aqueous solution, the light driven 2-electron/2-proton redox cycle leads to photoreduction of oxygen to hydrogen peroxide. Herein we present our results show that the catalysts are featured with high density of single metal atoms supported on hierarchically porous carbon frameworks. They exhibited consistent with the pure CeO2 structure, confirming that the introduction of La did not give rise to the local formation of secondary phases. A shift in the peaks of the XRD patterns was observed with increasing La content up to approximately 7 mol%, suggesting the latter value is approximately the limit of the La solid solubility. Indeed, this was further confirmed by Energy Dispersive X-Ray Spectroscopy (EDS) spatially resolved chemical analysis, performed with subnanometer resolution by Scanning TEM (STEM). This revealed that the largest observed lanthanum concentration is equal to 7 mol%, in the sample with 10 mol% nominal lanthanum doping. Chemical mapping carried out using STEM-EDS also showed the La was homogeneously distributed throughout the CeO2 nanocubes for all investigated samples, thus proving the formation of an evenly La-doped structure.

Further characterisation is in progress to confirm that these lanthanum-doped nanocubes do enhance redox ability.

ET08.08.04
Atomically Dispersed Ectrocatalyts for High-Efficiency Ambient N2 Fixation Lili Han¹, Xijun Liu², Jun Luo² and Huolin Xin¹; ¹Brookhaven National Laboratory, Upton, New York, United States; ²Tianjin University of Technology, Tianjin, China.

NH3 synthesis by the electrocatalytic N2 reduction reaction (NRR) under ambient conditions is regarded as an appealing alternative to the industrial method that requires high temperature and pressure. Finding a material that can efficiently catalyze electrochemical N2 fixation at ambient condition is a subject of considerable current interest. Atomically dispersed catalysts with mononuclear metal complexes or single metal atoms anchored on supports would be a promising candidate, because of their maximum atom efficiency, unique catalytic performances, and the similarity of the metal coordination environment to the ligand fields in molecular catalysts. A series of cost-effective and optimized atomically-dispersed electrocatalysts for NRR will be reported. Our results show that the catalysts are featured with high density of single metal atoms supported on hierarchically porous carbon frameworks. They exhibited remarkable selectivity of NH3 formation and high NH3 yield rate at low applied potentials at room temperature. Moreover, the catalysts show negligible activity decay in an NRR electrolysis as long as 50,000 s. On the basis of our results and the previously reported work, a possible mechanism for NRR on the catalyst will be proposed to provide a fundamental insight into the high-efficiency NRR.

ET08.08.05

One of the biggest challenges of sustainable development is efficient solar energy harvesting and storage. Huge progress in photovoltaics enabled economically feasible solar-driven electricity generation, however an issue of the energy storage remains unresolved. One emerging possibility is photocatalytic oxygen reduction to the high-energy product hydrogen peroxide. Hydrogen peroxide is easier to store than hydrogen. Herein we present our recent work on photocatalysis and photoelectrocatalysis with organic semiconductors which efficiently produce hydrogen peroxide. When the organic semiconductor is in contact with oxygenated aqueous solution, the light driven 2-electron/2-proton redox cycle leads to photoreduction of oxygen to hydrogen peroxide. We show examples of n type, p type, and ambipolar organic semiconductors performing photochemical oxygen reduction, both as stand-alone photocatalysts and as components in photoelectrochemical cells. Many of these catalytic systems are stable and effective in a wide pH range from 1-12. This demonstration of efficient organic semiconductors as aqueous photocatalysts possibly opens new avenues for their catalytic applications.

ET08.08.06
Biomass Derived Nitrogen-Doped Powdered Activated Carbon for Efficient Electrocatalytic Production of Hydrogen Peroxide Yudong Xue¹, 2, 3, Shili Zheng¹ and Yi Zhang¹; ¹Institute of Process Engineering, Chinese Academy of Sciences, Beijing, China; ²Department of Chemical & Environmental Engineering, Yale University, New Haven, Connecticut, United States; ³University of Chinese Academy of Sciences, Beijing, China.

Recently, the market for hydrogen peroxide is expanding in various industrials, with the increasing importance of green chemistry. At present, hydrogen peroxide is synthesized by the so-called anthraquinone method at a large scale. The in-situ synthesis of H2O2 based on advanced technologies is attracting much interest as a simple H2O2 production method. Among them, electrochemical methods are environmental-friendly and effective for the direct generation of hydrogen peroxide with high production rate and simple process. Hydrogen peroxide can be electrochemical generated by the two-electron oxygen reduction reaction (ORR) on the surface of electrocatalysts. Considerable attempts have been made to prepare appropriate and cost-effective cathode materials to enhance the ORR activity and current efficiency for H2O2 electro-generation. For this purpose, there are various materials reported including carbon-based materials (g-C3N4, graphite, carbon nanotubes, graphene, graphite felt and carbon cloth), transition metal oxides (Nb2O5, CeO2, Fe2O3 and Co3O4) and precious metal nanomaterials. Development of low-cost carbon-based metal-free catalyst with high ORR catalytic activity and low cost is emerged as an effective strategy for the replacement of precious metal. As carbon-rich precursor, biomass has served as the raw material for the fabrication of carbon-based materials for a long time. With the choice of suitable activators, various works have reported that porous carbon derived from biomass can obtain well-defined micropore size distribution and an ultrahigh surface area. Activated carbon materials are applied into the development of catalyst in energy storage/conversion devices. Furthermore, considering the advantages of nitrogen doping for the enhancing of electrocatalytic activity, nitrogen-rich biomass and their derivatives have been recently chosen as promising precursors for nitrogen-doping carbon catalysts. As a typical low-cost and easily obtained nitrogen-rich biomass resource, Ramie is widely distributed in the east and south of China as textile, feeding and paper raw materials. We developed nitrogen-doped powered activated carbon under appropriate temperature with high surface area from ramie biomass as a highly efficient electrocatalyst for hydrogen peroxide production. Electrochemical characterizations revealed that the as-prepared catalyst showed superior ORR selectivity through a two-electron pathway and extraordinary long-term stability. The nitrogen atoms on the catalyst surface was derived from the biomass and deconvoluted by XPS techniques, which is the important factor for the enhancement of electrocatalytic performance. The present work paves a way for the development of biomass-derived carbon material for electrochemical applications.

ET08.08.07
Development of Photocatalysts Based on the Fe-Ti-O System—An Efficient Combination for Artificial Photosynthesis Renato V. Goncalves; Physics, University of Sao Paulo, Sao Carlos, Brazil.
Conversion of solar energy to hydrogen fuel by artificial photosynthesis is considered one of the most important technologies breakthroughs to solve environmental and energy problems. Artificial photosynthesis process was inspired by photosynthesis in nature and has been studied since the pioneer work reported by Fujishima and Honda in 1972. The main challenge of artificial photosynthesis reactions is the development of efficient and robust semiconductor-based photocatalysts with suitable band structures to absorb visible light and generate electrons and holes into their conduction and valence bands, respectively, with potential for overall water splitting. Very recently, Fe2TiO5 (FTO) structure has been the most widely studied Fe–Ti–O combination material with pseudobrookite structure to overcome the challenges of the reaction. Herein, we prepared several approaches for the development of Fe2TiO5 photocatalysts for split water in H2 and O2 using visible light. The FTO has a bandgap of around 2.0 eV, with adequate electronic and structural properties for the reaction of artificial photosynthesis to produce H2 and O2 efficiently.

ET08.08.08

We synthesized Ce-substituted LaFeO3 perovskite-type oxides (LCFO) via Pluronic F127-assisted hydrothermal process. Obtained LCFOs exhibited several micrometer-sized spherical morphology. Crystal structure of LCFO was pure LaFeO3 perovskite structure with small amount of cerium because lanthanum ions were perfectly substituted by cerium ions. Increasing the ratio of Ce to La ions, however, it was found that cerium oxides were formed by unsubstituted Ce ions. The catalytic properties of LCFOs were evaluated by the efficiency of selective catalytic reduction of nitric oxide with ammonia (NH3-SCR). Pure LaFeO3 oxide (LFO) showed poor catalytic performance for NH3-SCR, which is consistent with previous studies. On the other hand, NO conversion efficiencies were significantly enhanced in LCFO samples, especially in pure phased LCFO. Furthermore, the LCFO catalyst with single crystal structure exhibited high resistance against SO2 gas. This results indicated the substituted Ce ions generated new type of active sites with enhanced catalytic activity and SO2 tolerance.

ET08.08.09
Mediated Photoelectrochemical Oxidation of Water on WO3 by Silver (II) Taehwa Jeon, Damián Monllor-Sátoea, Gun-hee Moon, Wooyul Kim, Hyung-il Kim, Hyunwoong Park and Won Yong Choi; 1Division of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang, Korea (the Republic of); 2School of Energy Engineering, Kyungpook National University, Daegu, Korea (the Republic of); 3School of Engineering, Universitat Ramon Llull, Barcelona, Spain; 4Department of Civil and Environmental Engineering, Yonsei University, Seoul, Korea (the Republic of); 5Department of Chemical and Biological Engineering, Sookmyung Women's University, Seoul, Korea (the Republic of).

Ag(I) is a common electron scavenger used in photocatalysis for promoting oxidative pathways through photogenerated holes, preventing deleterious electron-hole recombination. Although its straightforward reduction to metallic state (i.e., Ag0), it can also capture holes to generate the highly reactive Ag(II) species, provided the proper reactive conditions are given. In this contribution, we demonstrate, for the first time, mediated photoelectrochemical oxidation of water and concurrent oxygen evolution by the Ag(I)/Ag(II) redox cycle with high efficiencies. In the presence of Ag(I), photoelectrochemical (PEC) performance of WO3 electrodes was enhanced (biased at 1.23 V vs. RHE) in a mild acidic nitrate medium (pH 5) in terms of steady-state photocurrent (>4-fold), and O2 evolution (>4-fold) and its Faradaic efficiency (40% without Ag(I) vs. 75% with Ag(I)). During the PEC reaction, the electrolyte solution acquires a brown color, caused by the formation of Ag3NO3 complex. Upon turning both potential bias and light off, photocurrent drops to zero whereas O2 evolution continues over ~10 h (homogeneous water oxidation) leading to the overall Faraday efficiency of 100%, and simultaneously the electrolyte is gradually bleached. This confirms the Ag(I)-complex-mediated water oxidation which occurs during the PEC and the unbiased dark periods. This phenomenon is found neither in the Ag(I)-free PEC reactions nor in the photocatalytic (i.e., bias-free) reactions with Ag(I). The various spectroscopic analyses (UV-Vis, XRD, XPS, SEM/EDS, HR-TEM/EELS, etc.) suggest that Ag3+AgO core-shell structure and AgNO3 complexes play the heterogeneous and homogeneous water oxidation reactions, respectively.

ET08.08.10
Loading Effect of Various Metal Oxide Colloids as an Electron Mediator on Visible-Light-Responsive Photocatalyst Particles in Photocatalyst Panels for Z-Scheme Water Splitting Hiromasa Tokudome1,2, Sayuri Okunaka1,2, Shingo Oozu1,2, Qian Wang1, Takashi Hisatomi3 and Kazunari Domen3,4; TOTO Ltd, Chigasaki-city, Japan; 2Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), Chiyoda-ku, Japan; 3Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Bunkyo-ku, Japan; 4Center for Energy & Environmental Science, Shinsu University, Nagano, Japan.

Photocatalytic water splitting utilizing abundant sunlight including visible light is an active area of research focused on providing a renewable hydrogen. In the past two decades, a lot of visible light responsive photocatalysts have been developed to oxidize water and/or reduce water, but only a few were known to overall split water into H2 and O2 in the stoichiometric amount. On the other hand, Z-scheme system is known to realize overall water splitting using two kinds of visible light responsive photocatalyst particles, which are active for either for H2 or O2 evolution, without/with appropriate mediators such as redox ions or conductive materials. We recently developed a Z-scheme-type photocatalyst panel consisting of mixed films of two visible-light-active photocatalysts (La, Rh-doped SrTiO3 and Bi2O3, for H2 and O2 evolution) and a colloidal electron mediator (gold or indium-tin-oxide) on a glass substrate. It showed relatively high activity with a solar-to-hydrogen energy conversion efficiency of 0.1%1,2). In this study, we prepared a Z-scheme-type photocatalyst panel composed of Bi2O3 and Rh-doped SrTiO3 loaded with various metal oxide colloids as a low-cost and scalable electron mediator and examined the water splitting activity. It demonstrated relatively high activity with a solar-to-hydrogen energy conversion efficiency of 0.1%1,2). This study, we prepared a Z-scheme-type photocatalyst panel composed of Bi2O3 and Rh-doped SrTiO3 loaded with various metal oxide colloids as a low-cost and scalable electron mediator and examined the water splitting activity.


ET08.08.11
Improvement of Z-Scheme Water Splitting Activity on Nano ITO-Mediated Printable Photocatalyst Panels by Loading Co-Catalyst Sayuri Okunaka1,2, Hiromasa Tokudome1,2, Qian Wang1, Takashi Hisatomi3,4 and Kazunari Domen3,4; 1TOTO Ltd, Chigasaki-city, Japan; 2Japan Technological Research Association of Artificial Photosynthetic Chemical Process (ARPChem), Chiyoda-ku, Japan; 3The University of Tokyo, Bunkyo-ku, Japan; 4Shinsu University, Nagano, Japan.

Photocatalytic water splitting has been widely investigated as a potential method to produce hydrogen from renewable solar energy. Although two types of semiconductor-based systems (heterogeneous system and photoelectrochemical system) have extensively been studied for photo-induced water splitting so
far, it is necessary to develop a scalable, versatile and cost-effective system for the practical application. Photocatalyst panels, wherein semiconductor particles are fixed on substrates such as glass, have a wide range of visible light, it is necessary to employ narrow bandgap materials and/or introducing Z-scheme mechanism. Recently, the authors’ group reported that the composite-type photocatalyst panels, which composed of La, Rh-codoped SrTiO3 as the hydrogen evolution photocatalyst (HEP), Mo-doped BiVO4 as the oxygen evolution photocatalyst (OEP) and gold (Au)/indium-tin-oxide (ITO) nanocolloids as the electron mediator, for Z-scheme water splitting.1) These panels were prepared by using simple screen-printing method. The obtained printable panels evolved hydrogen and oxygen from pure water in the stoichiometric ratio under visible light irradiation and showed relatively high activity with a solar-to-hydrogen energy conversion efficiency (STH) of ca. 0.1%.1,2)

In this study, we investigated the effect of co-catalyst loading on the photocatalytic water splitting activity of the printable ITO nanocolloids-mediated photocatalyst panels. The water splitting activity of these panels was changed by changing the metal species and loading amount of co-catalyst. By loading appropriate co-catalyst, the water splitting activity was greatly enhanced and achieving 0.4% STH, which is four times greater than photocatalyst panels without co-catalyst loading.

ET08.08.12
Real Time Imaging of Nucleation, Growth and Corrosion Behaviors of Electrocatalsysts Hao Shan, Yanling Ma, Fenglei Shi, Tao Deng and Jinhbo Wu; Shanghai Jiao Tong University, Shanghai, China.

The core-shell catalysts with atomic layered surface Pt through liquid phase atomic layer deposition has been proven to be one of the most promising oxygen reduction (ORR) electrocatalysts with high activity and low consume of Pt.1-5 It is important to directly observe how the atomic layers grow via in situ technique. On the other hand, corrosion is a major and unavoidable challenge for the degradation of properties of multimeatal core-shell electrocatalysts during electrocatalysis, which restricts the practical application of this type electrocatalysts severely.6-8 Therefore, it has been an urgent issue to understand the evolution and mechanism of corrosion of Pt-based core-shell catalysts during the reaction with an aim to the effective utilization of the catalysts.8

In this presentation, we will first report a 3D growth mechanism for the formation of core–shell nanostructures involving a hybrid process with initial island growth and surface diffusion. The desired surface structure can be achieved by adjusting the competition between island deposition and surface diffusion. Therefore, we will show the corrosion behavior of Pd@Pt core-shell electrocatalysts in the etching solution, which depends on the effects of geometry and surface defect.10-11 Finally, we can demonstrate the capability of electrochemistry inside of TEM, showing both the oxidative etching and the re-deposition behaviors during the cyclic voltammetry in TEM.

References:

ET08.08.13
A Double-Anionic Oxides Based Organic-Inorganic Hybrid Compound for Simultaneously Catalytically Oxidative and Hydrolytic Decontamination of Chemical Warfare Agent Simulants Jufang Hu1, 2; 1Beijing Institute of Nanoenergy and Nanosystems, Academy of Sciences, Beijing, China; 2College of Optoelectronic Engineering, Shenzhen University, Shenzhen, China.

Rapid transformation of chemical warfare agents (CWAs) to environmentally benign products is a significant issue, and considerable efforts have been devoted to the catalytic removal of CWAs. Although many homogenous and heterogeneous catalysts for CWA removal have been developed, a broad-spectrum and simultaneous hydrolysis catalyst (for nerve agent removal) and oxidation catalyst (for mustard removal) is fairly needed. In this work, an organic-inorganic hybrid compound, H12(CH3)12[N2(PNb6O19)(V5O12)(3H2O)(2)][H2O] (1), based on two different anionic oxide fragments (also known as polyoxometalates, primarily constituted by Mo, W, Nb centers and oxo ligands), was hydrothermally synthesized, structurally thoroughly characterized, and catalytically tested with the broad-spectrum reactivity in the decontamination of chemical warfare agents. Compound 1 crystallizes in the tetragonal I-4 space group and contains bicapped polyoxometalate (PNb6O19) and tetranuclear polyoxovanadate, which are independent on each other, a complex rarely seen in polyoxometalate chemistry. Interestingly, compound 1 effectively catalyzes both hydrolysis of the nerve agent simulants, diethyl cyanophosphonate (DECP), and selective oxidation of the sulfur mustard simulants, 2-chloroethyl ethyl sulfide (CEES) under mild conditions. In particular, in the oxidative decontamination system 100% CEES was transformed selectively to nontoxic 2-chloroethyl ethyl sulfone and vinyl ethyl sulfide using nearly stoichiometric 3% aqueous H2O2 with a turnover frequency (TOF) of 16000 h-1. The catalytic performance is maintained even after ten runs and CEES is completely decontaminated in 3 mins without formation of the highly toxic sulfone by-product. The combination of polyoxoniobates and polyoxovanadates give this compound those noteworthy catalytic properties, and a three-step oxidative mechanism is proposed.

References:

ET08.08.14
Continuous Hydrothermal Synthesis of Catalytic Metal Oxide Nanoparticles in Supercritical Water Elizabeth G. Rasmussen, Brian R. Pinkard, Justin Davis, John C. Kramlich, Per G. Reinhall and Igor V. Novoselov; Mechanical Engineering Department, University of Washington, Seattle, Washington, United States.

Metal oxide nanoparticles have been studied at length for their catalytic properties in many industries including chemical manufacturing, energy-related
applications and environmental remediation. Given these advances in their applications, the tunable synthesis is of great interest, especially regarding control of crystal structure. In this study, iron oxide (Fe2O3) and zinc oxide (ZnO) nanoparticles were synthesized using a continuous-flow supercritical water reactor. The products were characterized for both size and crystalline structure by transmission electron microscopy (TEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Additionally, Raman spectra samples taken showed a decreased presence of the toxic organic solvent Dimethylformamide (DMF) showing advancement in completely eliminating such reagents in final products. Thus, the process presented can be compatible for green and sustainable chemistry in a way that reduces the environment load. The optimization of this technique is discussed and its advancement forward of the current bounds of continuous hydrothermal synthesis for catalysts applications is reviewed.

ET08.08.15
Intermetallic Pt-Mn/C Nanoparticles as ORR Electrocataysts

Mahdi Ahmadi and Héctor D. Abruña; Cornell university, Ithaca, New York, United States.

The sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode remains as one of the main challenges for commercial viability of alkaline exchange membrane fuel cells (AEMFCs). It is therefore, of great interest to explore the development of electrocatalysts with superior activity and stability relative to the conventional carbon supported Pt nanoparticles (NPs).

In this work, we have studied the effects and evolution of structure and surface composition of Pt-Mn NPs on their electrocatalytic activity for the ORR in alkaline media. Pt-Mn NPs were synthesized using solvothermal methods and were supported on C via impregnation. An ordered intermetallic phase was obtained by heat treatment. We have investigated the crystalline structure of these NPs using X-ray diffraction (XRD) and their size, morphology and composition using TEM/STEM, EELS and EDX. Cyclic voltammetry (CV) and rotating disk electrode (RDE) voltammetry were used to assess their electrocatalytic activity and stability.

The Pt-Mn NPs were electrochemically dealloyed in acidic media, through potential cycling, leading to the formation of a ~1 nm thick Pt shell on an ordered Pt/Mn core. Enhanced mass and specific activity resulted by such electrochemical dealloying. The stability of the electrocatalyst was tested after 4,000 potential cycles in alkaline media following the DOE protocol (0.6–1.0 V vs reversible hydrogen electrode). In alkaline media, Mn surface segregation ensued, leading to a lower electrocatalytic activity when compared to the freshly dealloyed catalyst.

Descriptive from scaling relations are at the forefront of theoretical studies in the search for effective catalyst design principles and in the prediction of catalytic activity from first principles. We propose an intuitive and widely applicable structural descriptor for transition metal oxides from first principles. We demonstrate that our descriptor can provide the bridge between the structural, the electronic, and the energetic properties for TMO surfaces. We then use it to accurately predict C-H activation energies with low deviations from DFT calculations. By building upon the compositional diversity of the perovskites, we further establish some descriptors to correlate with the key reaction steps of methane activation on the oxide surfaces. From the analysis of first and second C-H activation energies and their correlation with the hydrogen adsorption energy on a variety of ABO3 perovskites, general trends emerge that an optimal range of hydrogen adsorption energy strikes the right balance between easy first C-H activation and difficult second C-H activation energies to avoid further oxidation.

9:00 AM *ET08.09.02
First-Principles Study of n-butane Monomolecular Cracking on Zeolites and 2D Bilayer Aluminosilicate Models—Reaction Mechanism and Effects of Spatial Confinement

Mengen Wang1,2; Jianguang Zhong1, Anibal Boscoakin1 and Deyu Lu1; 1Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 2Materials Science and Chemical Engineering, Stony Brook University, Stony Brook, New York, United States.

Zeolites are nanoporous industrial catalysts (e.g. consisting of [AlO4] and [SiO4] tetrahedra) with catalytically active sites located inside the channels and nano-cages, rendering them inaccessible for surface science measurements. Two-dimensional (2D) ultrathin (~0.5 nm) bilayer aluminosilicate films consisting of hexagonal prisms with acidic hydroxyl groups exposed on the surface have been synthesized on Ru(001) surface as a zeolite model system to study gas molecule adsorption1 and chabazite (CHA)-based catalysts2,3. DFT studies were performed to investigate the dehydrogenation and monomolecular cracking of n-butane molecules over the acidic hydroxyl groups of aluminosilicate films. Intrinsinc energy barriers of dehydrogenation, terminal and central C=C bond cracking on aluminosilicate films were found to be ~0.6 eV higher than those of the bulk CHA. We further investigated the effects of the zeolite channel and cage sizes on the n-butane adsorption and monomolecular cracking for six different 3D nanoporous zeolite frameworks (TON, MEL, VFI, FER, CHA, and MEL). We found that as the confinement of straight channels or nano-cages decreases, n-butane adsorption becomes weaker and intrinsic energy barrier for terminal C=C cracking increases. The 2D bilayer film surface, which may be considered as zeolite cages at the infinite cage size limit, has the smallest adsorption energy and highest intrinsic energy barrier. Comparison of the reaction pathway of n-butane terminal C=C cracking in 3D nano-cages and on bilayer aluminosilicate film surface revealed that the decrease of the intrinsic energy barriers in bulk zeolites is caused by the stabilization of the transition states in the 3D nano-cages.


Research is carried out in part at the Center for Functional Nanomaterials and the Scientific Data and Computing Center, a component of the Computational Science Initiative at Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-SC0012704. This research used resources of the NERSC, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.
The selective dehydrogenation of alcohols to carbonyl compounds is an important class of reaction as aldehydes and ketones produced are essential intermediates in the chemical process industry. This process can be made environmentally sustainable by integrating it with the renewable biomass-derived feedstock and employing a non-oxidative process, which prevents catalyst inhibition due to water formation and suppresses over-oxidation of products. To gain insights into the non-oxidative dehydrogenation (NODH) of biomass derived alcohols over transition metal catalysts, a microkinetic model (MKM) using ethanol as a model molecule has been developed. Previously, a similar study has been conducted to understand the hydrodeoxygenation trends. The NODH of ethanol was first demonstrated by Church and Joshi in 1951, wherein Cu catalyst was employed with Co and Cr as promoters. Since then, catalysts mostly based on Cu have been utilized for NODH of alcohols. The NODH of ethanol may proceed via the initial C-H, O-H, C-O or C-C bond scission leading to the production of acetaldehyde, hydrogen, ethane, carbon monoxide, water and methane. For the production of aldehydes and ketones, the process should be made selective for acetaldehyde and hydrogen production. At the reaction conditions of 473K and 10% reactant conversion, the activity trend for acetaldehyde production from ethanol followed the order; Pt > Cu > Pd > Co > Ni > Ag > Au > Rh > Ru > Re. At these conditions, Pt showed the highest activity (TOF = 10^5 s^-1), followed by Cu (TOF = 10^4 s^-1). As Cu is the cheaper metal, therefore, it is widely used for this process. Followed by acetaldehyde, ethane was the other major product formed. However, all the metals except Au and Ag were selective towards aldehyde production. From the coverage analysis done in the MKM, it was determined that the surface of Cu was covered with the intermediate, CH$_3$CHO on Cu. Inspired from this fact, a bimetallic catalyst was proposed wherein Cu with Pt was combined with a metal having low C-H activation barrier (such as Ni, Pd, Pt, Rh). These bimetallic alloys were found to show higher reactivity (TOF > 10^4 s^-1) as compared to Cu for aldehyde formation. Earlier experimental studies on ethanol NODH over the bimetallic NiCu measured lower activation barrier of 45 kJ/mol, than that of Cu catalyst (Ea = 70 kJ/mol) and increased catalyst stability owing to lesser Cu sintering in the presence of Ni.

With growing demands of fossil fuel, advanced technologies of exhaust treatment are getting more concern in order to control the deteriorating air pollution from vehicles and factories. A series of nanoarray-based manganese oxide catalysts were developed by one-pot hydrothermal synthesis to fabricate nanorod arrays on the cordierite honeycomb substrates. Compared to monolithic catalysts with a traditional alumina support, nanoarray-based monolithic catalysts possess advantages, e.g. efficient open surfaces, reduced usage of porous supports, low pressure-drop, less agglomeration of nanoparticles. Copper manganese oxide (CuMn$_2$O$_4$) nanosheets were introduced to enhance the oxidative activity for hydrocarbons. The CuMn$_2$O$_4$ nanosheets coated nanoarray-based catalyst, Na-CuMn$_2$O$_4$, shows efficient 90% propane (C$_3$H$_8$) conversion at around 400 °C, which is 50 °C and 75 °C lower than CuMn$_2$O$_4$ wash-coated catalyst (WC-CuMn$_2$O$_4$) and Pd loaded catalyst (WC-Pd), respectively. The benefit of nanoarray morphology was demonstrated by correlating the variation of surface area to the reactivity. The incorporation of cobalt ions was found to increase the specific surface area and thus enhance C$_3$H$_8$ conversion of CuMn$_2$O$_4$. The CuMn$_2$O$_4$/Mn$_2$O$_3$ nanoarray-based monoliths are promising types of emission control devices.

Selective oxidation of CH$_4$ to high-value industrial chemicals such as CO or CH$_3$OH remains a challenge. Photocatalytic reactions hold great promise for practical applications but have been poorly studied. Existing demonstrations of photocatalytic CH$_4$ oxidation exhibit limited control over the process selectivity, with CO as the most common product. The yield of CO or other hydrocarbons is too low to be of any practical value. In this work, we show that highly selective production of CO by CH$_4$ oxidation can be achieved by a photocatalytic (PEC) approach. Moreover, our results revealed that the selectivity toward CO also depends on the substrate types and applied potentials. Based on the experimental results, we proposed a reaction mechanism that involves synergistic effects by adjacent Ti sites on TiO$_2$. Spectroscopic characterization and computational studies provide critical evidence to support the mechanism. Furthermore, the synergistic effect was found to parallel heterogeneous CO$_2$ reduction mechanisms. Our results not only present a new route to selective CH$_4$ oxidation, but also highlight the importance of mechanistic understandings in advancing heterogeneous catalysis.
Bimetallic nanoparticles have attracted a lot of attention because they show multiple functionalities and prominent catalytic activity, selectivity as well as thermal and/or chemical stability over their monometallic counterparts. Due to synergistic effects, modified electronic and/or geometric surface structures, high catalytic activities and selectivities have been achieved for chemical reactions even if one of the constituents is less or even inactive. Although the controllable synthesis of nanoparticles has developed rapidly over the recent years, more accurate control over nucleation and growth stages is needed for bimetallic nanocrystals. Since bimetallic nanocrystals are composed of different metal atoms, the composition and atomic distribution not only influences the final nanoparticle architecture but also the catalytic properties. The catalytic performance is highly sensitive to the nature of atomic ordering (i.e., random alloy, intermetallic compound) even if the overall composition and stoichiometry are the same. Here, we address the synthesis of bimetallic Pt/Sn-based nanoparticles with tunable composition and structure by exploiting the beneficial properties of ionic liquids (ILs). Small nanoparticles are obtained in a one-pot synthesis by reducing the metal salt precursors with triethylborohydride in the IL. The weakly coordinating IL anions and cations directly control particle nucleation and growth processes enabling nanoparticle synthesis without addition of stabilizing additives or strongly coordinating capping molecules. The nanoparticles form sols of very high colloidal stability in the IL, which is particularly interesting in view of their use as quasi-homogeneous catalysts. The composition and structure of the nanoparticles is tailored by the nature of the metals salt precursors, their initial molar ratio and the nature of the IL. Investigations by X-ray diffraction, X-ray photoelectron spectroscopy and transmission electron microscopy reveal the formation of random-type alloy or intermetallic nanoparticles. The catalytic performance of the bimetallic nanoparticles is evaluated in hydrogenation reactions. The selective hydrogenation of cinnamaldehyde, for example, is used to probe the catalytic performance of the Pt/Sn nanoparticles, demonstrating the effect of tuning the catalytic activity and selectivity to the α,β-unsaturated cinnamic alcohol is achieved for the Pt/Sn-based nanoparticles.

References

The active and stable catalysis of methane dry reforming relies upon the ability of the material to inhibit carbon formation. Central to this is the ability of a catalyst support to remove oxygen from the acidic carbon dioxide gas, storing or transporting this oxygen, before releasing it to oxidise an adsorbed CH₄ intermediate species (Djinović et al., 2012). For the first time, an aerosol method was used to mix lanthanum with cobalt/alumina materials to improve support basicity. Double flame spray pyrolysis was used to synthesise heterogeneous mixtures of cobalt oxide, alumina and lanthanum oxide. Lanthanum loadings of up to 15 wt% were investigated at two separate nozzle distances (11 and 18cm). The lanthanum content in the materials and the nozzle distance separating the flames were both found to have a key influence over material composition and properties.

The structure of the supported cobalt catalysts was characterised by high-resolution transmission electron microscopy, X-ray diffraction, XANES, carbon dioxide temperature programmed desorption, X-ray photoelectron spectroscopy and hydrogen temperature programmed reduction. Catalytic activity and stability for methane dry reforming was determined via testing in a fixed bed reactor over a temperature range of 500-800 °C, while catalyst activity was determined at a fixed temperature of 700 °C for 48 hours.

The addition of La to the system gave rise to the substitution of La³⁺ into the Al₂O₃ lattice, as shown by high-resolution transmission electron microscopy and XANES. Hydrogen temperature programmed reduction showed that doping with La and increasing the nozzle distance limited CoAl₂O₄ spinel formation and facilitated the production of readily reduced Co species. The addition of La also resulted in an increase in material basicity, independent of nozzle distance, lending the catalysts a strong resistance to carbon formation.

Methane conversion and catalyst stability at 700 °C were enhanced via the addition of La. Maximum methane conversions of 89-93% were observed for the two samples with the greatest (15 wt%). This remarkable conversion is very promising when compared to the other Co-based dry reforming catalysts. Additionally, the catalysts with 15 wt% La loading showed no sign of catalyst deactivation or carbon formation, indicating high selectivity towards the desired reaction.

SESSION ET08.10: Selective Catalysis-Industrial Perspective
Session Chairs: Gugang Chen and Yugang Sun
Thursday Afternoon, November 29, 2018
Hynes, Level 3, Room 306

1:30 PM *ET08.10.01
Surfactant-Mediated Patterned Growth of Atomically Thin Transition Metal Dichalcogenides Avetik Harutyunyan; Honda Research Institute USA Inc, Columbus, Ohio, United States.

Atomically thin transition metal dichalcogenides (TMD) with diversity of their compositions, crystallographic structures, "sandwich" heterostructures and tunability open unique opportunity to create new catalytic activities for various applications. Yet, capitalizing this potential demand controllable growth of patterned monolayers over larger areas on arbitrary surfaces without interfering with their intrinsic properties. Therefore, developing facile growth pathway that provides lithography-free direct patterned monolayers on various substrates is of central importance. To this end, understanding the fundamental science of how additives nucleate and enhance the growth of TMD monolayers becomes essential since they can facilitate monolayered growth, their properties and selection of the substrates. We find that alkali metal halide salt additive behaves as a surfactant in the growth of TMD monolayers by chemical passivation of the edges that reduces the strain and thereby kinetically transfer 3D island growth mode into layered growth mode. This insight allows the growth of TMD monolayers with desirable patterns on predefined location of the various substrates using pre-deposited salt layer as a water-removable template. The discovery of surfactant-mediated growth pathway not only enables substrate diversity but also provides opportunity to exploit lithography-free patterned TMD monolayers.

2:00 PM *ET08.10.02
Material Discovery and Design Principles for Stable, High Activity Perovskite Cathodes for Solid Oxide Fuel Cells Ryan Jacobson, Tam Mayeshiba, John Booske and Dane Morgan; University of Wisconsin–Madison, Madison, Wisconsin, United States.

The discovery of new materials with high oxygen reduction reaction (ORR) catalytic activity and high thermodynamic stability under typical cathode operating conditions are crucial for the development of improved solid oxide fuel cell (SOFC) and related technologies. We have used high-throughput density functional theory (DFT) methods enabled by the MAterials Simulation Toolkit (MAST)[1] with multicomponent phase stability analysis using the Python Materials Genomics (Pymatgen)[2] toolkit, to screen a wide composition space of 2145 perovskite materials (chemical formula Aₓ₋ₓBiₓLaₓSrₓCoₓFeₓO₃) for candidates that have high surface exchange coefficient k* and are thermodynamically stable under typical SOFC operating conditions.

Recent computational work has demonstrated there exists a linear relationship between the calculated bulk O p-band center and experimental surface exchange coefficient (k*) values for numerous perovskites.[3] Therefore, the O p-band center is a useful descriptor for k*, which is strongly correlated with overall ORR activity for perovskite materials.[3] We have employed a three-stage screening procedure to down-select promising candidate materials. Candidate materials were eliminated if they had (i) Predicted k* less than the commercial SOFC cathode material (La, Sr)CoO₃, (ii) Calculated thermodynamic phase instability > 47 meV/atom (calculated value of (La, Sr)CoO₃ above the convex hull under SOFC operating conditions, and (iii) Electronic structure that had a nonzero electronic bandgap and thus likely to have poor electronic transport. This computational search has yielded 52 promising materials with good predicted stability in typical SOFC operating conditions and predicted k* values similar or better than leading ORR perovskite catalysts.[4] We have also analyzed trends in predicted k* and stability to suggest material design principles based on compositional doping to maximize both the stability and catalytic activity.
References:


2:15 PM ET08.10.03
Reactive Metal-Support Interaction in 2D MXene Zhe Li and Yue Wu; Iowa State University, Ames, Iowa, United States.

The reactive metal-support interaction (RMSI) offers electronic, geometric and compositional effects that can be used to tune catalytic active sites. Generally, supports other than oxides are disregarded as candidates for RMSI. In this presentation, we will discuss an example of non-oxide based RMSI between Pt and Nb:C, MXene, a recently developed, two-dimensional (2D) metal carbide. The surface functional groups of the 2D carbide can be reduced, and a Pt-Nb surface alloy is formed at a moderate temperature (350 °C). Such an alloy exhibits weaker CO adsorption than monometallic Pt. Water-gas shift (WGS) reaction kinetics reveal that the RMSI stabilizes the nanoparticles and creates alloy-MXene interfaces with higher H2O activation ability compared to a non-reducible support or a bulk niobium carbide. This RMSI between Pt and the niobium MXene support can be extended to other members of the MXene family and opens new avenues for the facile design and manipulation of functional bimetallic catalysts.

2:30 PM ET08.10.04
Electride Concept in Intermetallic LaTMSi (TM=Sc,Fe,Co,Ru) for Catalytic Ammonia Synthesis Jiazheng Wu, Yutong Gong, Junjie Wang, Masaaki Kitano and Hideo Hosono; Tokyo Institute of Technology, Yokohama, Japan.

An electride is a compound in which electrons serve as anions. Due to the weakly bound nature of the anionic electrons, electrides exhibit a variety of interesting properties, such as low work function, which enables an easy electron donation to materials with high work functions. Therefore, recently, these materials have been successfully employed as promoters to catalysts for ammonia synthesis [1]. Importantly, the reaction bottleneck was shifted from the sluggish N2 dissociation to NH3 formation, providing an alternative route to synthesize ammonia beyond the industrial Haber-Bosch process. However only few electrides have been discovered so far and most of them are chemically unstable in the presence of air and water, so the exploration of new electrides and the concept of electride are urgent issues for both chemical interests and catalytic applications in the materials society.

In the present presentation, we show that LaTMSi, (TM=Sc, Mn, Fe, Co, Ru) are new electride candidates and show robust chemical stability in ambient conditions. [2,3] LaScSi contains multiple types of symmetry-distinct interstitial voids accommodating tiered electron anions. [2] When loaded with Ru, it shows outstanding activity for ammonia synthesis under mild conditions (0.1 MPa, 400°C), with its turnover frequency (TOF=0.1 s^-1) one order of magnitude higher than those of oxide-based Ru catalysts. When Sc is replaced by Mn, Fe, Co or Ru, the transition metal atoms become activation centers and the compounds show a self-promotion behavior with high catalytic activity without loading additional metals. As with other electrides, these compounds show reversible hydrogen storage ability, and electron anions (H vacancies) exchange with H anions rapidly, providing many activated H for the catalytic reactions. Importantly, the transition metal atoms, implanted into the lattice, are activated and work effectively to cleave the N≡N triple bonds and modify the rate-determining step from the N2 dissociation to NH3 formation. The good catalytic performance will be interpreted on a basis of the electride concept and a “hot-atom” mechanism by combining the experimental observations and theoretical simulations.

References


2:45 PM ET08.10.05
Developing Fe-Based Electrocatalysts for Ambient Ammonia Synthesis Lin Hu, Jun Wang and Xiaofeng Feng; University of Central Florida, Orlando, Florida, United States.

Considering the limited supply of fossil fuels, there is an urgent need to use renewable energy to drive NH3 production, as the current Haber-Bosch process for NH3 synthesis is energy-intensive and consumes 3–5% of the world’s natural gas production. Electrochemical NH3 synthesis may provide a promising strategy, which can enable sustainable, distributed production of NH3 when powered by solar- or wind-generated electricity. However, the development of such a process has been impeded by the lack of efficient catalysts for the N2 reduction reaction (N2RR) under ambient conditions. Many catalysts show a Faradaic efficiency <1% for N2RR under ambient conditions. Here, we report the development of Fe-based electrocatalysts for N2RR with a Faradaic efficiency of up to 8.29%. An Fe/Fe3O4 sample was prepared by in situ reduction of a pre-oxidized Fe foil in 0.1 M phosphate buffer solution (PBS). The resulting Fe/Fe3O4 catalyst shows greatly enhanced activity and selectivity for N2RR under ambient conditions than the original Fe foil, achieving a Faradaic efficiency of 8.29% for NH3 production at -0.3 V vs RHE in the 0.1 M PBS electrolyte, which is around 120 times higher than that of the Fe foil. The high selectivity is enabled by an enhancement of the intrinsic N2RR activity as well as an effective suppression of the undesired hydrogen evolution reaction. Comparisons with Fe/Fe oxide samples prepared at different pre-oxidation temperatures indicate that the N2RR activity may depend on the ratio of Fe and Fe oxide. In addition, the N2RR selectivity of the Fe/Fe3O4 catalyst is superior to that of the Fe, FeOx, and FeO nanoparticles, which provides new insights into the understanding and development of efficient, cost-effective electrocatalysts for ambient NH3 synthesis.

3:00 PM BREAK

3:30 PM *ET08.10.06

Producing petrochemicals and fuels with minimal capital investment and operating cost requires maximizing the formation of target molecules, while minimizing the formation of unrecoverable side product under the economic operating conditions with uninterrupted operation.

One approach to understand what is required to attain the theoretically attainable performance is to lay out the elementary steps of the systems and identify thermodynamic limitations and sources of deficiencies. In this presentation we show how the material and process approaches are adopted to help circumvent the thermodynamic limitations and improve efficiencies of the elementary steps and overall process in petrochemical production.
Highly Active and Stable Carbon Nanosheets Supported Iron Oxide Nanocatalysts for Fischer-Tropsch to Olefins Synthesis

Yunyun Zhou1, 2, Sittichai Natesakhat1, 3, Thuy Duong Nguyen Phan1, 2, Douglas Kaufman1, Christopher Marin1, Huolin Xin1, Eli Stavitski5, Klaus Attenkofer5, Yijie Tang1, Yisong Guo6, Iradwikanari Waluyo5, Amitava Roy7, Jonathan Lekse1, John Baltrus1, Christopher Matranga1 and Congjun Wang1, 2; 1National Energy Technology Laboratory, Pittsburgh, Pennsylvania, United States; 2AECOM, Pittsburgh, Pennsylvania, United States; 3Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania, United States; 4Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, United States; 5National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, New York, United States; 6Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States; 7Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana, United States.

Fischer-Tropsch to olefins (FTO) synthesis has drawn significant attention due to the high demand of light olefins as building blocks for the chemical industry, the desire to reduce the dependence on petroleum cracking for these chemicals, and the need for improving environmental sustainability. Iron-based catalysts have emerged as promising FTO catalysts because of their low cost and excellent catalytic performances. We have designed a promising nanocatalyst of porous interconnected carbon nanosheets supported iron oxide nanoparticles for FTO synthesis. The catalysts demonstrate an extremely high iron time yield (FTY) of 1882 μmolCO/gFes with 41% selectivity for light olefins and excellent stability (>100 h time on stream). Our FTY value is found to be one of the highest FTYs and in particular, is 50 to ~1300 times higher compared with those catalysts exhibiting similar light olefins selectivity reported in literature. Misbacher characterization demonstrates the presence of catalytically active iron carbide species after FTO reaction. ex situ XAFS measurements reveal that the carbon nanosheets support stabilizes metallic iron during the initial catalyst reduction step, which leads to more carbon uptake under FTO reaction conditions to more efficiently form highly active iron carbide phase. In contrast, a control sample with carbon nanotubes as the catalyst support exhibits oxidized iron in the catalyst after removal from H2 reduction pretreatment, suggesting substantially reduced stabilizing effect of carbon nanotubes towards supported metallic iron nanoparticles. This results in inefficient formation of iron carbide species under FTO conditions. Additional EXAFS results further confirm the buildup of iron carbide phase as a function of time on stream in the carbon sheets supported catalysts, whereas a much smaller portion and negligible growth of iron carbide phase was observed in the carbon nanotube supported catalysts under the same reaction conditions.

Hydrocracking Catalyst Optimization for Upgrading Heavy, Polyaromatic Oil Fractions

Mark Kaminsky1, Sarah Kobusilj1, Tatiana Pilyugina1, Karemuddin Shaik2, Limhui Ding2 and Essam Al-Sayed3; 1Aramco Services Co., Cambridge, Massachusetts, United States; 2Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia; 3Technical Services Dept., Aramco Services Co, Houston, Texas, United States.

Introduction

Changes in global supply and demand for fuels versus chemicals has increased the incentive to better control how much of each is produced from a barrel of crude oil. In addition, as the value of crude oil increases, there is incentive to improve the efficiency of upgrading a barrel of crude, in particular the bottom of the barrel resid. Such highly aromatic resid fractions, which used to end up in petroleum coke or asphalt, are being upgraded to more valued products with new catalytic and process advances. This is partly driven by further restrictions on the burning of petroleum coke, which makes delayed coking less desirable. Hydrogen addition, via hydrocracking, avoids the production of such petroleum coke from the resid fractions, transforming them into more useful fuel and chemical products.

Discussion

This talk will describe two aspects of hydrocracking catalyst development to upgrade heavier crude oil fractions. In the first part, we will present results on the development of a multifunctional hydrocracking catalyst, comprising both homogeneous organometallic and heterogeneous zeolite components. The homogeneous components are oil soluble organometallic compounds of Mo or Fe that are designed to transform in situ into unsupported nanoparticle metal sulfides that hydrocrack the large asphaltene molecules, which tend to foul heterogeneous zeolitic pores. The mesoporous zeolites will then more effectively hydrocrack the smaller products of the asphaltene and maltene cracking, in order to make chemicals/fuels with less pore plugging. However, with time on stream, the nanoparticles might sinter and become less active. We will present results on the sintering rates of the Mo and Fe nanoparticles at various conditions in the presence of zeolites. Since the nanoparticles and zeolite crystals are both in the same hydrocracking reactor, it is important to understand their interaction under reaction conditions via characterization of the used catalytic materials. Such catalyst characterization will shed light on the interaction and deactivation mechanisms of these catalyst species.

In the second part of our hydrocracking catalyst development we will present data on the synthesis of nano-sized Beta zeolite crystals and the effect of zeolite crystal size and shape on hydrocracking activity. Details of the synthesis method for preparation of the nano-sized Beta will be presented in addition to activity studies using a highly aromatic LCO (Light Cycle Oil) feedstock for the hydrocracking reaction.

Electroreduction of Oxygen at Nanostructured Methanol Tolerant Cathodes for Mixed-Reactant Direct Methanol Fuel Cells

Mark F. Kaminsky1, Sarah Kobusilj1, Tatiana Pilyugina1, Karemuddin Shaik2, Limhui Ding3 and Essam Al-Sayed1; 1Aramco Services Co., Cambridge, Massachusetts, United States; 2Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia; 3Technical Services Dept., Aramco Services Co, Houston, Texas, United States.

Energy sources for all kind of electronic devices are under constant pressure to achieve higher efficiency levels by increasing the energy density and decreasing both volume and weight while reducing the cost of portable power sources at the same time [1]. Mixed-reactant microfluidic direct methanol fuel cells (MR-μDMFCs) represent a promising power supply alternative for electronic portable devices in the future, due to their simplicity of design, fabrication and operation. Theoretically, they can achieve higher energy density in comparison with other DMFCs. The main challenge arises from the need for selective electrocatalysts [2]. The synthesis of cathode materials with high mass specific activity towards the oxygen reduction reaction (ORR) and no activity towards the methanol oxidation reaction (MOR) is crucial for the development and commercialization of MR-μDMFC.

In the present work, we report a two-step synthesis by pulsed laser deposition (PLD) of two Pt-based catalysts having a layer onto layer structure. For the two catalysts, first an ultra-low loading Pt layer is deposited directly on carbon nanotubes and further coated with a porous Ag layer or a porous MnOx layer, obtaining Ag/Pt/CNTs and MnOx/Pt/CNTs, respectively. According to the physicochemical characterization, these layers don’t present electronic interaction with each other. The resulting binary materials exhibit electrocatalytic activity similar to Pt towards the ORR in alkaline media. The XPS spectra reveal that the ORR on both Pt/CNTs and MnOx/Pt/CNTs, is carried out through a 3.9 electron transfer mechanism, while on Ag/Pt/CNTs, the transfer is about 3.7 electron. Interestingly, the bilayer cathodes show no activity for the MOR. Furthermore, those materials demonstrate to be tolerant to methanol concentration as high as 5 M. The results suggest that the superficial Ag and MnOx components discriminate between the molecular volume of O2 and MeOH. Lastly, in order to compare the performance of the methanol-tolerant cathodes in a fuel cell, the materials are tested in a passive, air-breathing MR-μDMFC in conditions close to real application.

Commercialization of polymer electrolyte membrane (PEM) fuel cell materials has been of a great interest over the past decade. At the cathode side, the oxygen reduction reaction (ORR) is the key reaction where sluggish kinetics is present, for which Pt remains the catalyst of choice. In order to leapfrog the current limits to Pt use, three main objectives have to be achieved. First, is a reduction of Pt loading; second, is an enhancement of the mass activity per Pt atom; and third is an increase the catalyst durability. Herein, we demonstrate the dual role of single graphene layer, both as a growth template and as a protective cap for 2D Pt monolayers catalysts, where all three objectives can be achieved.

Using iterative under potential deposition (UPD), atomic layers of Pt catalyst are grown on top of a single layer graphene. X-ray absorption spectroscopic (XAS) and scanning transmission electron microscopy (STEM) analyses show that Pt growth is dictated by the graphene-templated epitaxy. Pt/graphene intimacy induces a localized compressive strain on Pt monolayers ranges 3-10%, owing to structural defects, with an overall compressive strain of 3.5% according to extended x-ray absorption fine structure (EXAFS) analysis. In addition, cyclic voltammetry (CV) analysis shows fully-wetted Pt monolayers coverage of graphene under-layer with only a ~1 nm ultra-thin layer of Pt, while ripening was suppressed as shown through STEM images. Atomic Force Microscopy (AFM) analysis demonstrates that Pt monolayers prefer to follow Frank-van der Merwe growth (i.e. layer-by-layer growth mode) rather than Volmer-Weber growth (i.e. island growth mode), where root mean square (rms) of surface roughness remains quite similar while increasing Pt loading is increased.

Pt/graphene hybrid catalysts show superior catalytic activity for ORR relative to the graphene-free counterparts or state of the art Pt commercial catalyst. A combination of the graphene-imposed compressive strain and electron transfer, push the Pt d-band center up, lowering the overpotential needed for ORR to occur. Furthermore, the graphene/Pt cap hybrid shows the graphene protecting Pt MLs from both dissolution and from ripening, with almost no Pt loss after 5000 fuel cell operating cycles. Our demonstration of a graphene-Pt hybrid opens the door for graphene/metal or metal/graphene architectures with potential applications in, and not limited to, energy, thermo-electric and electronics field.