

# **International Workshop on Clean Energy and Catalysis and Sixth Penn State-Dalian Joint Energy Workshop**

**Sponsored by PSU-DUT Joint Center for Energy Research**



**October 10-12, 2018  
Dalian University of Technology  
Dalian, China**

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*Promoting global cooperation in clean energy research and education*



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PENN STATE AND DALIAN UNIVERSITY OF TECHNOLOGY  
**Joint Center for Energy Research**



**宾州-大连联合能源研究中心**

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# **Agenda for the International Workshop on Clean Energy and Catalysis and Sixth Penn State-Dalian Joint Energy Workshop**

**Dalian University of Technology (DUT)  
October 10-12, 2018, Dalian, China**

## Wednesday, 10 October, 2018

Arrival and check-in (shuttle from the airport to Bayshore Hotel will be provided)

18:00--20:00 Welcome dinner at *Shining Pearl Seafood* Restaurant

## Thursday, 11 October, 2018 – AM & PM

### Meeting Room of the State Key Laboratory of Fine Chemicals, DUT Campus

8:10 Pick up of international delegation members from the lobby of Bayshore Hotel

8:50 Arrival of international delegation members in the Meeting Room of the State Key Laboratory of Fine Chemicals, DUT Campus

### Opening Session Chair: Dr. Chunshan Song, PSU-DUT JCER

09:00 to 9:05

Opening Remarks and Introduction by **Dr. Chunshan Song** (Co-Director, PSU-DUT JCER)

09:05 to 09:10

Welcome Speech by DUT Leader, **vice President and Prof. Shan Yao** (Professor of Materials Engineering at DUT)

09:10 to 09:30

**Group photo of DUT and PSU leaders, faculty and student participants**

### Session #2 Chair: Dr. Xinwen Guo, DUT

09:30 to 09:55

**Dr. Gary L. Haller** (*Professor of Department of Chemical & Environmental Engineering, Yale University, USA*)

**A Perspective on “Isomerization and  $\beta$ -scission reactions of alkanes on bifunctional metal-acid catalysts: Consequences of confinement and diffusional constraints on reactivity and selectivity”**

09:55 to 10:20

**Dr. Chuan Shi** (*Professor of Department of Chemistry at DUT*)

### **Strong Metal Support Interactions Tuning the Catalytic Performance**

10:20 to 10:45

**Dr. Yi Liu** (*Professor of Chemical Engineering at DUT*)

## **Molecular Sieve Membrane: Microstructure Control, Dimension Manipulation and Application Extension**

10:45 to 11:05

**Coffee break**

### **Session #3 Chair: Dr. Anfeng Zhang, DUT**

11:05 to 11:30

**Dr. Robert M. Rioux** (*Professor of Chemical Engineering and Professor of Chemistry at the Pennsylvania State University*)

### **Solvent Effects in Solid Acid Catalyzed Reactions**

11:30 to 11:55

**Dr. Guanghui Zhang** (*Associate Professor of Department of Chemical Engineering at DUT*)

**Seeing the Catalytically Active Phases/Sites with *in situ* Spectroscopy**

11:55 to 13:50

**Lunch Session Onsite**

**Poster Session**

**13:50 to 14:00 Break**

### **Session #4 Chair: Dr. Keyan Li (DUT)**

14:00 to 14:25

**Dr. Donghai Wang** (*Professor of Mechanical Engineering and Chemical Engineering at PSU*)

### **Harnessing Materials for Electrochemical Energy Storage**

14:25 to 14:50

**Dr. Yujiang Song** (*Professor of Chemical Engineering at DUT*)

### **Advanced Electrocatalysts of Polymer Electrolyte Membrane Fuel Cells**

14:50 to 15:15

**Dr. Hong Yang** (*Professor of Department of Mechanical Engineering, The University of Western Australia, Australia*)

## **Mesoporous 2D ZSM-5 Zeolites – Structure and Catalytic Performances**

15:15 to 15:40

**Dr. Zhongkui Zhao** (*Professor of Chemical Engineering at DUT*)

## **Photocatalytic Hydrogen Evolution & Clean Synthesis of Fine Chemicals under Visible Light Irradiation**

15:40 to 16:00

**Coffee break**

### **Session #5 Chair: Dr. Guanghui Zhang (DUT)**

16:00 to 16:25

**Dr. Michael J. Janik** (*Professor of Chemical Engineering at PSU*)

***Intermetallics enable Rational Control of Catalytic Active Site Nuclearity and Composition***

16:25 to 16:50

**Dr. Xiaowa Nie** (*Associate Professor of Chemical Engineering at DUT*)

***CO<sub>2</sub> Conversion to Hydrocarbons and Alcohols: Insight from DFT combined with Experiment***

16:50 to 17:15

**Dr. Li Gong** (*Associate Professor of Department of Chemistry, University of Science and Technology of China*)

***Mechanistic explanation/studies of NB selective reduction to PHA tuned by alkane amine coating***

17:15 to 17:40

**Dr. Anjie Wang** (*Professor of Chemical Engineering at DUT*)

***Ni<sub>3</sub>P as a High-Performance Catalytic Phase for Hydrodeoxygenation***

17:40 to 17:50 Closing Remarks

**Dr. Xinwen Guo** (*Vice Dean, Faculty of Chemical, Environmental and Biological Science and Technology*)

17:50 to 18:30 Transportation for international delegation members and DUT Faculty Members to *Shinning Pearl Seafood* restaurant for joint dinner

18:30 to 21:30 Dinner

## Friday 12 October, 2018 AM & PM

### Session #6: Individual PSU, Yale, UWA-DUT /Meetings

08:30 to 11:30

**Individual DUT faculty members pick up international delegation members from Bayshore Hotel**

**Individual DUT-International faculty group discussion and laboratory tour  
Action items and plans for potential collaborations**

- (1) Catalysis/chemical energy conversion (Chuan Shi, Guanghui Zhang, Zhongkui Zhao, Yi Liu, Anjie Wang and Xiaowa Nie to pick up Gary L. Haller, Mike Janik, Rob Rioux, and Chunshan Song, Li Gong; this group may be divided, for separate meeting/group discussion/lab visit )

DUT faculty members	- - - - -	International
Anjie Wang and Guanghui Zhang	-	Gary Haller
Chuan Shi	-	Robert Rioux
Yujiang Song	-	Donghai Wang
Xinwen Guo and Anfeng Zhang	-	Hong Yang
Xiaowa Nie	-	Michael Janik
Zhongkui Zhao and Yi Liu	-	Chunshan Song

- (2) Electro-chemical energy (Yujiang Song to pick up Donghai Wang for separate meeting/group discussion/lab visit)
- (3) 2D Zeolite synthesis and application (Anfeng Zhang, Xinwen Guo to pick up Hong Yang, for separate meeting/group discussion/lab visit)

11:40 to 13:30

**Lunch** (International Delegation members - DUT faculty groups)

DUT faculty members accompany international delegation members to the Meeting Room of the State Key Laboratory of Fine Chemicals by **14:00**

### Session #7: DUT-International Faculty Members Panel Discussion Facilitated by Dr. Chunshan Song

14:00 to 16:00 **Dr. Gary L. Haller** (*Professor of Department of Chemical & Environmental Engineering, Yale University, USA*)

**A Brief History of Catalysis**

16:00 to 17:30

**Panel discussions by DUT and PSU faculty members**

**Meeting Room of the State Key Laboratory of Fine Chemicals, DUT**

How to further advance the DUT-PSU/ UWA collaboration?

Exchange of PSU/Yale/UWA and DUT students and faculty for collaboration

Joint efforts for potential international grants applications

**18:40- Dinner**

# **Abstract and Biosketch**



## Overview of the PSU-DUT Joint Center for Energy Research

### Chunshan Song

*EMS Energy Institute, Departments of Energy & Mineral Engineering, and of Chemical Engineering  
PSU-DUT Joint Center for Energy Research, The Pennsylvania State University ([csong@psu.edu](mailto:csong@psu.edu))*

This presentation gives an overview of the PSU-DUT Joint Center for Energy Research which was officially established between Penn State and DUT in April 2011. Significant progress has been made in collaborative research and education between Penn State and DUT through the efforts of faculty and graduate students in a number of research areas. Presidents of both universities have made mutual visits to the partner institutions. Five PSU-DUT Joint Energy Workshops have been organized, both in DUT and PSU with participation from both universities. Collaborative research between faculty members of the two universities in clean energy and environment-related research topics have already resulted in ~110 peer reviewed journal articles. More collaborative research and education efforts are expected to result from the present Workshop.



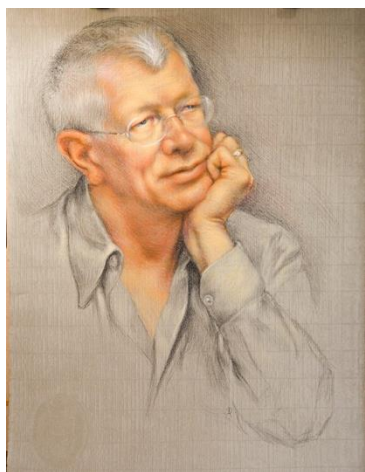
Dr. Chunshan Song is the Director of the EMS Energy Institute, and a Distinguished Professor of Fuel Science and Professor of Chemical Engineering. He also serves as the Associate Director of the Penn State's Institutes for Energy and the Environment and the Co-Director of PSU-DUT Joint Center for Energy Research at Pennsylvania State University (PSU). He is internationally known for his contributions to clean fuels, catalysis, and CO<sub>2</sub> capture and utilization research. He has over 340 refereed publications in leading journals, 8 patents, 9 books and 28 book chapters. He has delivered 60 plenary or keynote lectures at international conferences and 270 invited lectures worldwide. He has received many awards such as Henry Storch Award in Fuel Science and Fellow of ACS from American Chemical Society. He has held numerous leadership positions with professional societies and international conferences. Dr. Song's current research interests include catalysis and adsorption for fuel processing, desulfurization of fuels and bio-gas, reforming of hydrocarbons and bio-fuels for hydrogen production and fuel cells, CO<sub>2</sub> capture, CO<sub>2</sub> conversion and utilization, shape-selective catalysis for chemicals, synthetic clean fuels from coal, heavy oil and biomass.

## A Perspective on “Isomerization and $\beta$ -scission reactions of alkanes on bifunctional metal-acid catalysts: Consequences of confinement and diffusional constraints on reactivity and selectivity”

Gary L. Haller

Department of Chemical & Environmental Engineering, Yale University, USA ([gary.haller@yale.edu](mailto:gary.haller@yale.edu))

An in press paper, G. Noh et al., *J. Catal.* (2018), <https://doi.org/10.1016/j.jcat.2018.03.033>, as titled above, is a seminal study in catalysis. The micro pores or nano-structured voids of zeolites are classically known to influence catalytic selectivity by molecular constraint of the transport of reactants and/or products or by size constraints on the transition state. The latter concept originally hypothesized an increasing activation barrier as the size of transition state approached the size of the zeolite pores (voids). This concept has recently been refined to account for van der Waals interaction that may stabilize the transition state as its size and shape approach a good fit to the void; this is labeled confinement. Varying the size and shape of zeolite pores (voids) generally affects both diffusional transport and confinement but most studies focus on one or the other and avoid the entanglement. G. Noh et al. not only recognizes the entanglement of diffusive and confinement properties of zeolites but treats both quantitatively. The case study is of the bifunctional metal-acid isomerization and cracking on n-heptane where the metal function is the dehydrogenation and hydrogenation to olefins and the acid function is the structural isomerization to methylpentenes and dimethylpentenes, where the latter also undergoes cracking. Somewhat surprisingly, the van der Waals interaction energies, evaluated by DFT-converged transitions states for FAU, SFH, BEA and MFI zeolites that have acid sites of similar strength, are similar. The marked differences in selectivity among aluminosilicate frameworks reflect instead diffusional enhancements of secondary transformation. The conceptional and mathematical framework, developed and used for n-heptane isomerization on bifunctional metal-acid catalysts, is general and may be applied to other reactions on other microporous catalysts.



Gary L. Haller is Henry Prentiss Becton Emeritus Professor of Engineering and Applied Science. He received his PhD in Physical Chemistry in 1966 from Northwestern University and after a post-doctoral year at Oxford University, was a member of the Yale faculty 1967-2015. At Yale, he served as Departmental Chair, Chair of the Council of Engineering, Deputy Provost for Engineering and Physical Sciences, and Master of the Jonathan Edwards College. He is currently Director of the Henry Koerner Center for Emeritus Faculty at Yale. Professor Haller has held several visiting positions including Oxford University, Universite Catholique de Louvain, Belgium, Universidad del Sur, Argentina (United Nations consultant), University of Edinburgh, Technical University of München (current), New York University, and the National Bureau of

Standards (now National Institute of Standards and Technology). He was co-editor (now senior editor for Perspectives and Mini-reviews) of the *Journal of Catalysis* and a member of several editorial boards, including that of the *Yale Alumni Magazine*. He has been an active industrial consultant for more than 15 companies and is author or co-author of more than 250 publications, one book and eight industrial patents.

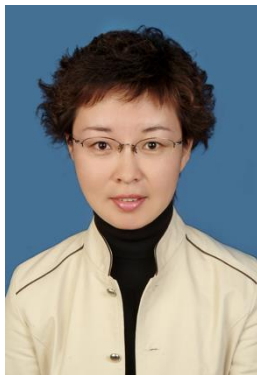
## Strong Metal Support Interactions Tuning the Catalytic Performance

Chuan Shi

*Department of Chemistry at Dalian University of Technology*

Our research interests focus on **Nanocatalysis and Plasma assisted catalysis**. Nanomaterials have received much interest by virtue of their excellent properties suited for applications in various fields such as electronic, pharmaceutical, biomedical, cosmetic, energy, and catalysis. Physical, chemical, and biological properties of materials in nano-scale differ in fundamental from those of individual atoms and molecules or bulk materials. The extremely small size of the particles maximizes surface area exposed to the reactant, allowing more reactions to occur. We investigate the nanocatalysis on: (i) Supported nano-gold catalysts; (ii) Nano-sized transition metal nitrides/carbides/phosphides. We focus on the size dependent of nano-particles on catalysis, as well as the specific properties of nanomaterials for catalysis, i.e. noble like chemical properties. Meanwhile, hybrid plasma-catalyst systems have proven to be very efficient in VOC oxidation, automobile catalysis and water purification. However, no matter which kind of system is being used, the problem associated with the plasma-catalysis approach is the relatively high energy cost required to remove very low concentrations of pollutants. Therefore we propose a tandem “Non-thermal plasma-pulse” regeneration process which combines with the enrichment of low-concentration air pollutants on the catalysts at room temperature. Plasma is only applied for a very short time compared with the operating time for air pollutant enrichment, providing an energy-efficient method for the synergy of plasma and catalysis.

Transition metal carbides (TMCs) are known to display catalytic properties similar with those of noble metals. The high activity of TMCs compared with their parent metals originates from a modification of the electronic properties from the addition of carbon, which in turn affects the binding strength and the reactivity of adsorbates. In the present talk, special interest will be focused on employing TMCs as a substrate to load another metal and the strong interactions between the admetal and the carbide. Several reactions involved will be discussed, including dry reforming of methane, water gas shift and reverse water gas shift reactions [1,2]



Dr. Chuan Shi is a Professor of Chemistry at Dalian University of Technology. She began his appointment at DUT in April, 2004. Her research interests are nanocatalysis and plasma assisted catalysis. Current activities address mainly on environmental catalysis, including automotive catalysis, VOC catalytic removal and small molecules of CH<sub>4</sub> and CO<sub>2</sub> activation and conversion. Her works have got the financial supports from National Science Foundation of China, and some research results have been published in Science, Appl. Catal. B-Environmental, AICHE Journal, Green Chemistry and ACS Catalysis etc. Dr. Chuan Shi has been awarded as New Century Excellent Talents in University and Outstanding Young Teachers of Liaoning province.

## Molecular Sieve Membrane: Microstructure Control, Dimension Manipulation and Application Extension

Yi Liu

State Key Laboratory of Fine Chemicals, Dalian University of Technology, China

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Owing to their high adjustability in both pore apertures and functionality, molecular sieve membranes have offered unprecedented opportunities for efficient separations. Nevertheless, challenging tasks facing high quality MOF membrane fabrication remains the trade-off phenomenon between permeability and selectivity. Herein we try to solve this issue by microstructure control and dimension manipulation of molecular sieve membranes.

Preferred orientation as an important microstructural parameter has proven to exert significant influence on the separation performances of molecular sieve membranes. Herein a facile, efficient and green approach was developed to prepare highly *b*-oriented MFI zeolite membranes and *c*-oriented NH<sub>2</sub>-MIL-125(Ti) MOF membranes, respectively. A novel Air-Liquid Interface-Assisted Self-Assembly (ALIAS) method was invented to guarantee the formation of highly *b*-oriented MFI and *c*-oriented NH<sub>2</sub>-MIL-125(Ti) seed monolayers; while proper thermal treatment of the precursor solution and microwave-assisted heating were employed to warrant the desired in-plane epitaxial growth. Both molecular sieve membranes showed significantly reduced mass transfer barrier and enhanced ion/gas selectivity.

Past decades witnessed significant progress made in 2D layered molecular sieve membranes. Layered double hydroxides (LDHs) as a representative of 2D layered materials possessed highly uniform and adjustable interlayer galleries, making them superb candidates for high performance separation membranes. With a facile *in situ* hydrothermal method, herein we prepared well-intergrown LDH membranes with diverse microstructures and excellent gas separation performances. Moreover, our recent research indicated that LDH buffer layers could further serve as efficient perch, active nucleation center and metal sources of MOF grains to solve a series of issues encountered in high quality MOF membrane synthesis.

In addition to separation applications, we further explored potential applications of LDH and MOF membranes in anti-corrosion. DC polarization test demonstrated that anti-corrosion performances of both LDH and MOF-modified Al plates were significantly enhanced.



Yi Liu received Ph.D. degree from Dalian Institute of Chemical Physics, Chinese Academy of Sciences in 2012. During 2012 and 2014 he was elected as an Alexander von Humboldt Research Fellow and worked at Leibniz Universität Hannover with Prof. Juergen Caro. Since 2015, he worked as a postdoctoral fellow at Kyoto University with Prof. Susumu Kitagawa. Currently he is a professor of Dalian University of Technology. His research interests mainly include zeolite, MOF and 2D molecular sieve membranes with potential applications in gas separation, pervaporation and desalination. He is the principal investigator of several projects such as the National Natural Science Foundation of China. He has published ~30

papers in peer-reviewed journals including *J. Am. Chem. Soc.*, *Angew. Chem. Int. Ed.* and *Adv. Mater.*.

## Solvent Effects in Solid Acid Catalyzed Reactions

Robert M. Rioux<sup>1,2</sup>

<sup>1</sup>*Department of Chemical Engineering and* <sup>2</sup>*Department of Chemistry, The Pennsylvania State University, 165 Fenske Laboratory, University Park, PA 16802-4400*

Brønsted acid catalysts are deactivated by the presence of water in liquid phase reactions. With the pervasiveness of water in biomass valorization reactions, the development of water tolerant acid catalysts is an important step in the path to economically viable production of fuels from biomass. Modification of a catalyst surface with hydrophobic groups is thought to improve tolerance to water by inhibiting the access of water to the active site. However, these hydrophobic groups can have undesirable side effects. Hydrophobic groups modify the solvation environment of the active site; if kinetically relevant reactants, intermediates and transition states are solvated to different degrees by the new environment, the rate of reaction will be altered. We have successfully synthesized increasingly hydrophobic alkyl-modified SBA-15-supported propylsulfonic acid catalysts and confirmed the increased hydrophobicity of the modified catalysts relative to the parent sulfonic acid grafted silica by solution calorimetry. We have observed alkyl groups (Me, Pr, Hex) have a detrimental effect on catalyst activity towards esterification of acetic acid, relative to the unmodified catalyst. Furthermore, we have shown that modification with alkyl groups does not improve water tolerance. Despite the presence of hydrophobic alkyl groups, water is able to access the active site and subsequently deactivate the catalyst. The hydrophobicity of the alcohol (solvent) does not appear to influence this behavior. Activation enthalpies demonstrate there is a net destabilization of the catalytic proton relative to the rate determining transition state when solvated by alkyl groups. In the presence of 3 M water, the influence of the alkyl groups disappears, with all catalysts exhibiting the same activity and activation enthalpy. We demonstrated the negative influence of surface hydrophobicity in heterogeneous Brønsted acid catalysts. Differential solvation of kinetically relevant species leads to a reduction in catalyst activity. The surface hydrophobicity does not improve water tolerance since the catalyst architecture does not maintain high chemical potential proton in the hydrophobic phase.

In separate work, we demonstrate the impact of solvent on the adsorption of pyridine on Brønsted solid acids (zeolites) using isothermal titration calorimetry (ITC). In a single experiment, ITC can yield the various thermodynamic parameters associated with titrant-Brønsted acid interactions, such as enthalpy, entropy, free energy and binding stoichiometry. ITC experiments demonstrate that the choice of the solvent strongly affects the apparent adsorption thermodynamics of pyridine on ZSM-5. The apparent adsorption enthalpy of pyridine on HZSM-5 varies from -20 kJ/mol in DMSO to -100 kJ/mol in n-heptane, in comparison to -175 kJ/mol determined by gas-phase calorimetry. A Born-Haber cycle is constructed for each solvent to rationalize the apparent adsorption thermodynamics in four different solvents.



Robert (Rob) M Rioux is the Friedrich G. Helfferich Professor of Chemical Engineering and Professor of Chemistry at the Pennsylvania State University. Prior to joining the Pennsylvania State University, he was a National Institutes of Health Postdoctoral Fellow at Harvard University in the Department of Chemistry and Chemical Biology. He received his Ph.D. in physical chemistry from the University of California, Berkeley in 2006 and a B.S. and M.S. degree in chemical engineering from Worcester Polytechnic Institute and the Pennsylvania State University, respectively. At Penn. State faculty, he has received a number of awards, including a DARPA Young Faculty Award, an Air Force Office of Scientific Research Young Investigator Program Award, a NSF CAREER Award and a 3M Non-Tenured Faculty Award. His group's current research focus is on the development of spatially- and temporally-resolved spectroscopic techniques for imaging catalytic chemistry, single molecule methods to understand single molecule/particle catalytic kinetics and dynamics, elucidating reaction mechanisms

in nanoscale systems, including catalyst synthesis, development of solution calorimetric techniques to understand catalytic processes at the solid-liquid interface and the development of base-metal catalysts for chemoselective chemical transformations.

## Seeing the Catalytically Active Phases/Sites with *in situ* Spectroscopy

**Guanghai Zhang**

PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning 116024, China (gzhang@dlut.edu.cn)

Recent advances in model catalysis and in *in situ* spectroscopic methods now enable us to investigate a catalyst in its active state, i.e. while it is functioning. At PSU-DUT Joint Center for Energy Research, we are developing new *in situ* characterization capabilities both domestically and collaboratively. In this talk, two examples will be given. In the first example, various *ex situ* and *in situ* characterization techniques were used to identify the active ultra-small clusters and single atomic sites in g-C<sub>3</sub>N<sub>4</sub> supported Fe catalysts for advanced oxidation reactions. While in the second example, a clear subsurface electronic effect on supported 2 nm core-shell nanoparticles with atomically precise and high temperature stable Pt<sub>3</sub>Mn intermetallic surface is demonstrated by *in situ* synchrotron X-ray Diffraction, difference X-ray Absorption Spectroscopy and Energy Dispersive X-ray Spectroscopy, together with *ex situ* high-angle annular dark field scanning transmission electron microscopy and density functional theory calculations.



Dr. Guanghai Zhang is an associate professor at School of Chemical Engineering at Dalian University of Technology. He received his B.S. degree in chemistry at Nanjing Normal University in 2007, M.S. degree in organic chemistry in 2010 at the same university, and Ph.D. in organic chemistry in 2014 at Wuhan University. Before joining Dalian University of Technology in 2018, he carried out his post-doc research at Illinois Institute of Technology/Argonne National Laboratory, and subsequently at Purdue University. Dr. Zhang's research interest lies in heterogeneous catalysis, homogeneous catalysis, organometallic chemistry, and synchrotron-related X-ray spectroscopy. His current research focuses on the development of new catalytic materials for energy and environmental applications, especially on the catalytic conversion of small alkanes and carbon dioxide. Dr. Zhang is the co-author of over 50 referred publications (H-index is 18, web of science).

## **Harnessing Materials for Electrochemical Energy Storage**

Donghai Wang

Department of Mechanical and Nuclear Engineering,  
The Pennsylvania State University, University Park, PA, 16802

Electrochemical energy storage systems are key components of sustainable transportation systems and electrical grids, allowing for increased efficiency in energy use, full-fledged utilization of intermittent renewable energy sources (eg. wind, solar, wave, etc), superior power management – and, attendant on these, decreased greenhouse gas emissions and energy independence. Many of the foremost challenges in this area are materials-based – new materials are highly desirable to provide stable, high-energy, high-power energy storage for a variety of applications and conditions. The Energy Nanostructures Laboratory under Dr. Donghai Wang at Penn State is investigating many exciting new paths in pursuit of such energy breakthroughs. The majority are presently focused on development of battery materials, and cell design and fabrication –materials for next generation Li-ion battery and beyond Li-ion battery technology such as Li metal battery, Na-ion batteries, solid-state batteries. In this talk, I will present recent development in my group on new electrode materials that enable high performance Li metal batteries and solid-state batteries.



Dr. Donghai Wang is Professor at Department of Mechanical Engineering and Department of Chemical Engineering at The Pennsylvania State University. Before joining Penn State in 2009, he was a postdoc and subsequently became a staff scientist at Pacific Northwest National Laboratories where he developed functional materials for catalysis and energy storage techniques. He received a B.S. and Ph.D. degree in Chemical Engineering from Tsinghua University and Tulane University in 1997 and 2006, respectively. Dr. Donghai Wang's research interests have been related to design and synthesis of materials for a variety of applications. His recent research is focused on material development for energy conversion and storage technologies

such as batteries, supercapacitors, fuel cells and solar fuels. Professor Wang has authored and co-authored over 90 peer reviewed publications, more than 15 patents and patent applications, and 4 book chapters.

## **Advanced Electrocatalysts of Polymer Electrolyte Membrane Fuel Cells**

### **Yujiang Song**

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China, yjsong@dlut.edu.cn

Polymer electrolyte membrane fuel cell (PEMFC) as a clean and renewable technology may eventually tackle inter-correlated energy and environmental issues confronting us. Electrocatalysts are needed for the acceleration of the anode and cathode reaction of PEMFC, but remain as a challenge for both proton and hydroxide exchange membrane fuel cells. This talk will focus on several issues related to the electrocatalysts. Firstly, the low durability is a bottle-neck problem for non-noble metal electrocatalysts (NNMEs) toward acidic oxygen reduction reaction (ORR). The strategy adopted by my group will be presented for dealing with this problem. Next, the nature of the active sites of NNME toward alkaline ORR remains elusive. We propose that the activity should arise from the distortion of nitrogen-doped carbon. Finally, non-platinum electrocatalysts for alkaline hydrogen oxidation reaction (AHOR) will be discussed from the perspective of mechanism discrepancy and rational design and synthesis of electrocatalysts.



**Yujiang Song** was born in Benxi, P. R. China, in 1975. He received BS in chemistry (Northeast Normal University, 1997), MS in inorganic chemistry (Jilin University, 2000), and PhD in physical chemistry (University of New Mexico, 2004, US). In 2005–2007, he was a Postdoctoral Researcher at Sandia National Laboratories (SNL), US Department of Energy. He was a member of the Technical Staff at SNL from 2007 to 2009. He worked at Dalian Institute of Chemical Physics, Chinese Academy of Sciences from 2009 to 2014 as a group leader. Currently, he is a full professor at School of Chemical Engineering, Dalian University of Technology.

Dr. Song's research interests include low platinum and non-platinum electrocatalysts, scale-up production of electrocatalysts, fabrication technology of membrane electrode assembly, proton and hydroxide exchange membrane fuel cells, low-temperature direct biomass fuel cells, and H<sub>2</sub>O & CO<sub>2</sub> electrolyzers.



## Mesoporous 2D ZSM-5 Zeolites – Structure and Catalytic Performances

**Hong Yang**

*Laboratory for Functional Materials, Department of Mechanical Engineering, The University of Western Australia, Australia (hong.yang@uwa.edu.au)*

Microporous ZSM-5 zeolite is an important catalyst and adsorbent for many applications including petrochemical processing and fine chemical production. Ability to create hierarchical mesoporous structure in ZSM-5 has the promise to significantly enhance its performance and suitability in applications involving bulky molecules. This work reports a study on the formation of mesopores in ZSM-5 zeolite nanosheets. The work revealed that intercrystalline mesopores can be generated through the formation of self-interlocked cores of ZSM-5 nanosheet stacks. The formation of the mesoporous structure was found to be critically depended on the basicity and nature of the cations and anions in the precursor solutions, and dictated by the aggregation of the structure directing agent used. The work has also determined the required ternary composition domain that enables the formation of mesoporous ZSM-5 over a wide Si/Al ratio range, investigated the chemical activity and catalytic performance of the mesoporous ZSM-5 synthesized. The findings of this work pave a way for rational design and synthesis of mesoporous ZSM-5 materials with tailored structural and chemical properties for targeted applications.



Professor Hong Yang obtained her PhD from the University of Pennsylvania, USA in 1991. She then worked as a postdoctoral research fellow at the University of Western Australia (UWA) for three years before commencing her academic career in 1995 at the same university. She is now appointed Full Professor of Materials Engineering and Head of Department of Mechanical Engineering at UWA. Professor Yang serves as a member of international advisory committees of several international conference series and is a member of editorial board of Materials Technology: Advanced Performance Materials. She has a broad research interest in the area of functional and engineering materials, including materials thermodynamics, materials chemistry, materials synthesis, nano-functional and microporous materials for catalysis and energy conversion, nano-engineered bulk metallic materials and martensitic transformations in metals. Professor Yang also engages in industry research and her most recent industrial projects includes corrosion mitigation of subsea pipelines for oil and gas industry, waste to energy conversion from biomass, and value-added products from spent types. She has published over 100 research articles in SCI listed international journals with an H-index of 30.

## Photocatalytic Hydrogen Evolution & Clean Synthesis of Fine Chemicals under Visible Light Irradiation

**Zhongkui Zhao**

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China

The gradual depletion of fossil fuels and the resulted more and more heavy environmental crisis by the consumption of fossil fuels have become a global problem. Photocatalysis, driven by solar energy, especially by visible light, has attracted the increasing attention, including hydrogen evolution from water splitting, CO<sub>2</sub> reduction, ammonia synthesis, organic pollution degradation, and the emerging selective organic transformations. The design of an efficient, stable, environmentally friendly, and cheap photocatalyst is the key to the practical application of photocatalytic technology. In this presentation, I would highlight the recent advance from our advanced catalytic materials research group (ACM at DUT) in the photocatalytic hydrogen evolution and clean synthesis of fine chemicals under visible light irradiation. It contains 4 examples: 1) Fabrication of a novel porous defect-modified graphitic carbon nitride (P-DCN) via thermal polymerization of a freeze-dried crystalline mixture containing dicyandiamide (DCDA) and ammonium chloride (NH<sub>4</sub>Cl) under nitrogen atmosphere, which exhibits 26 times higher hydrogen evolution rate (HER) under visible light irradiation than traditional bulk g-C<sub>3</sub>N<sub>4</sub>, reaching 20.9 μmol h<sup>-1</sup>; 2) Preparation of highly efficient nitrogen deficient g-C<sub>3</sub>N<sub>4</sub> bunched microtubes via a KOH-assisted hydrothermal treatment of rodlike melamine-cyanuric acid (RMCA) supramolecular aggregates followed by thermal polymerization, showing 39 times higher HER than bulk g-C<sub>3</sub>N<sub>4</sub>; 3) A facile thermal post-treatment method for preparing cyano-decorated g-C<sub>3</sub>N<sub>4</sub> nanosheets, exhibiting 2.4 times higher activity than pristine CNNS for the visible light-driven oxidative coupling of benzylamine to imine, an industrially important transformation as a probe reaction; 4) We presents an efficient strategy for visible light-driven imine production through a photocatalytic non-oxygen coupling reaction of diverse amines dramatically boosted by hydrogen evolution over noble metal-free Ni/CdS nanoparticles. Thanks to the integrating effect, close to 100% conversion of benzylamine and 97% selectivity for imine with 21.4 mmol g<sup>-1</sup> h<sup>-1</sup> hydrogen evolution rate have been achieved at room temperature and ambient pressure.



Dr. Zhongkui Zhao is a Professor at Dalian University of Technology (DUT). He received his B.S. degree in 2000 and Ph. D degree in 2005 from Dalian University of Technology (DUT). He then worked as a Postdoctoral Research Associate at Ohio State University. He has appointed as a full professor of DUT since 2016. He is the head of the “Advanced Catalytic Materials” research group, DUT. In 2012, he was awarded the “Program for New Century Excellent Talents in University” by the Chinese Ministry of Education. Dr. Zhao is a visiting professor at Hebei University of Science & Technology. He is an author of more than 100 peer-reviewed papers on scientific journals and also one book, four book chapters and a patent. His current research activities are concentrated on the design, synthesis and modulation of novel catalytic materials mediated by functional molecules

and their applications for photocatalytic solar fuels conversion and organic synthesis, thermocatalytic highly efficient transformation of fossil fuel and biomass transformation, and clean synthesis of fine chemicals and intermediates, and electrocatalytic hydrogen evolution.

*Intermetallics enable Rational Control of Catalytic Active Site Nuclearity and Composition***Michael J. Janik**

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Designing selective metal catalysts is challenged by identifying the active site in a heterogeneous distribution of local structures and compositions. Site isolated catalysts can help to define active site requirements for a given reaction by exposing a single active site composed of a controlled number of metal atoms in a specific arrangement. This talk will discuss our collaborative theory and experimental work (with the Rioux group at Penn State) to use intermetallic structures to design selective hydrogenation catalysts. Intermetallic compounds can isolate a small number of active atoms in an inert matrix of a second metal, with long range periodic atomic order and resistance to surface segregation. We have identified the Pd-Zn  $\gamma$ -brass phase as a starting point to study the catalytic effect of active site nuclearity, a key parameter in selective catalyst design. The prototypical Pd<sub>8</sub>Zn<sub>44</sub> structure contains only isolated Pd atoms, but as the Pd concentration is increased by Zn substitution (Pd<sub>8+x</sub>Zn<sub>44-x</sub>, x = 1-3), a fixed number of Pd-Pd-Pd trimers are formed. Density functional theory calculations were used to establish the structure of these trimer sites on the surface, and predict that these sites will be active for acetylene hydrogenation but inactive to ethylene hydrogen. To prove this transition from monomer to trimer sites is catalytically impactful, H-D exchange and ethylene hydrogenation are used as probe reactions. The reaction kinetics of Pd<sub>8</sub>Zn<sub>44</sub> for both reactions are distinct from the other Pd-Zn catalysts and this discrepancy is consistent with first principle calculations on model monomer and trimer Pd sites. The trimer containing Pd<sub>9</sub>Zn<sub>43</sub> and Pd<sub>10</sub>Zn<sub>42</sub> have ~1000 times higher activity compared to trimer-free Pd<sub>8</sub>Zn<sub>44</sub>, but the latter leads to net ethylene gain by only semi-hydrogenating acetylene, consistent with theoretical predictions. The Pd-Zn  $\gamma$ -brass phase also provides flexibility in modifying the composition of the active sites through incorporation of a third metal (Pt, Ni, Au or Ag). Rietveld refinement and DFT calculations suggest that Ni group elements form Pd-Pd-M clusters while Cu group elements can form Pd-M'-Pd clusters. Several Pd-M alloys involving these metals (notably Au, Cu and Ag) are known to be selective hydrogenation catalysts. We further share DFT predictions and microkinetic modeling towards designing active catalysts for alkene hydrogenation in the presence of aromatics.



**Speaker Bio:** Dr. Janik is a Professor of Chemical Engineering at Pennsylvania State University. His research interests are in the use of computational methods to understand and design materials for alternative energy conversion systems. Current activities address a wide-range of energy technologies including fuel cells and electrolysis, heterogeneous catalysis, and organic electronics. Research methods emphasize atomistic simulation using quantum chemical methods and kinetic modeling. Janik is affiliated with the Penn State Energy Institute, PSU-Dalian University of Technology Joint Center for Energy Research, the PSU Institutes of Energy and the Environment, and the Battery and Energy Storage Technology Center. He also holds the title of Visiting Professor at Dalian University of Technology. The Janik group currently includes 9 graduate students, 5 undergraduate students, and a post-doctoral research associate.

Dr. Janik is also the Undergraduate Program Coordinator for the Chemical Engineering Department. Dr. Janik received his B. S. in Chemical Engineering from Yale University and his Ph.D. degree at the University of Virginia. He has co-authored approximately 135 papers, and co-edited the book "Computational Catalysis" (with Aravind Asthagiri), published by the Royal Society of Chemistry in 2013.

*CO<sub>2</sub> Conversion to Hydrocarbons and Alcohols: Insight from DFT combined with Experiment*

Xiaowa Nie

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Fe-based catalysts have shown good performance for the CO<sub>2</sub> hydrogenation via reverse water–gas shift (RWGS) and Fischer–Tropsch (F-T) synthesis. The iron carbide, especially Hägg-carbide, is commonly considered as the active species for catalyzing the hydrogenation of CO to hydrocarbons in F-T synthesis which might also be catalytically active for CO<sub>2</sub> hydrogenation. Our recent experimental work demonstrates that the bimetallic combinations of Fe with small amounts of transition metals such as Co, Ni, Cu, and Pd, together with a K promoter, led to significantly higher activities for olefin-rich hydrocarbons. Designing selective Fe catalysts for CO<sub>2</sub> conversion to hydrocarbons is challenging because multiple iron phases were detected in experiment including metallic Fe, carbide and oxidized iron. Identifying the active sites, reaction pathways, and kinetic controlling factors are crucial steps for catalyst evaluation which can be accessed by theoretical calculations combined with experiments. On one side, this talk will discuss our computational work on investigating the mechanism and catalyst composition/structure-pathway-activity/selectivity relationship for CO<sub>2</sub> hydrogenation to hydrocarbons (C<sub>1</sub> and C<sub>2</sub>) over Fe carbide and Fe-Cu bimetallic catalysts. DFT and microkinetic studies are used to discuss the activity and selectivity and the results are compared to our experimental work. On the other side, we will also discuss our recent progress on CO<sub>2</sub> hydrogenation to methanol over Pd-Cu bimetallic catalysts from DFT and experimental studies. The reaction mechanism was deeply studied, and the important effect of bimetal alloy structure and water on CO<sub>2</sub> conversion and methanol selectivity was uncovered. DFT studies demonstrated that the stepped PdCu(111) surface is more active for H<sub>2</sub> and CO<sub>2</sub> adsorption and activation than the flat PdCu<sub>3</sub>(111) surface and the PdCu-type catalyst will be superior for methanol synthesis. The energetically favorable pathway goes through: CO<sub>2</sub>\*→HCOO\*→HCOOH\*→H<sub>2</sub>COOH\*→CH<sub>2</sub>O\*→CH<sub>3</sub>O\*→CH<sub>3</sub>OH\* on PdCu(111). The presence of small amount of H<sub>2</sub>O can alter the “H-transfer” pathway and the rate-limiting step, and reduce the kinetic barriers for CO<sub>2</sub> conversion to methanol. Our experimental collaborator at Penn State successfully synthesized the PdCu(111)-rich and PdCu<sub>3</sub>(111)-rich alloys and the catalytic experiments confirmed that the catalyst that rich in PdCu(111) alloy has higher methanol selectivity. With respect to the effect of H<sub>2</sub>O, the catalytic experiment demonstrated that on the PdCu(111)-rich catalyst, when the water vapor concentration was 0.03 mole, the selectivity of methanol was significantly increased (~52%). However, on the PdCu<sub>3</sub>(111)-rich alloy phase, we did not observe the promotion effect of H<sub>2</sub>O. The experimental results are consistent with DFT calculations. This work provides new idea and opens avenue for future optimal design of highly selective catalysts for carbon dioxide hydrogenation.



**Bio:** Dr. Xiaowa Nie is an Associate Professor of Chemical Engineering at Dalian University of Technology (2015-present). Her research interests are using computational methods to understand the mechanism and design of materials for heterogeneous catalysis and energy conversion. Current research focuses on addressing fundamental questions in CO<sub>2</sub> conversion to hydrocarbons and alcohols over Fe- and Cu-based catalysts by using density functional theory (DFT) calculations combined with experiments. Dr. Nie received her B. S. degree in Applied Chemistry from Liaoning Normal University in 2006 and her Ph.D. degree at Dalian University of Technology in 2011. She did postdoc research at Ohio State University (2011-2014)

and Georgia Institute of Technology (2014-2015). She published over 30 papers and delivered more than 20 conference talks. She received the “Outstanding Young Researcher Award” of the 15<sup>th</sup> International Conference on CO<sub>2</sub> Utilization (ICCDU) in 2017 and “Outstanding Postdoctoral Research Award” at Ohio State University in 2012.

## Mechanistic explanation/studies of NB selective reduction to PHA tuned by alkane amine coating

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Adsorbed organic modifiers can alter selectivity of metal catalysts by modifying reactant, intermediate, or product adsorption affinities and configurations. Herein, we show how alkylamine self-assembled monolayers with varying surface densities can be used to tune selectivity to desired hydrogenation products of nitrobenzene (NB) reduction on a Pt (111) catalyst. Nitrobenzene is a toxic environmental pollutant with deleterious health effects, and its selective conversion to valuable chemicals can both convert this pollutant and improve catalytic process efficiency. Density functional theory (DFT) calculations demonstrate that the selectivity of NB reduction to phenylhydroxylamine (PHA) is achieved by controlling the surface crowding, with specific sites exposed for the selective reduction of NB on the Pt (111) surface through the selection of alkylamine modifier surface density. Surface crowding forces NB and subsequent reaction intermediates to bind with their long axis vertical to the Pt (111) surface, increasing the selectivity to the desired product, PHA. This surface crowding serves both to enhance selectivity and provide insight into the reaction mechanism of NB reduction.



Doctor Li Gong is a junior faculty in the College of Environment at Zhejiang University of Technology. Her current research efforts are in interfacial chemical reactions in remediation of groundwater and efficient catalysts design for water pollutant control. Dr Gong has been published as the first or the co-first author on Nature Communications, Applied Catalysis B: Environmental, Water Research. Dr. Gong was a visiting scholar at the Pennsylvania State University in 2016-2017. She received her Ph.D. in 2018 from Department of Chemistry at the University of Science and Technology.

## Ni<sub>3</sub>P as a High-Performance Catalytic Phase for Hydrodeoxygenation

Anjie Wang

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Bio-oils produced by pyrolysis or liquefaction of lignocellulosic biomass are promising alternative sources for the production of fuels. Bio-oils have a high oxygen content (45~50 wt%), which leads to undesired properties such as high viscosity, low thermal stability, low heating value and immiscibility with petroleum fractions. Converting bio-oils to fuels requires the reduction of the oxygen content. Hydrodeoxygenation (HDO) is regarded as the most promising route for this task. Mo- or W-based sulfide catalysts, which are industrially important hydrotreating catalysts in refineries, are active for HDO, showing high performance in removing oxygen from bio-oils. However, these metal sulfide catalysts suffer from progressive deactivation during HDO of bio-oils, due to the loss of sulfur in the catalytic phase. On the other hand, the lost sulfur species will contaminate the hydrotreated products. As a result, non-sulfide catalysts, including precious metals, base metals, metal carbides, metal nitrides, and metal phosphides, have been considered as potential HDO catalysts for upgrading bio-oils.

Metal phosphides exhibit not only high catalytic activity in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), but Ni<sub>2</sub>P supported on MCM-41 showed also excellent activity in HDO of phenol. Since a large fraction of water is present in bio-oils and water is also the by-product in HDO of bio-oils, it is of significant importance to investigate the effects of water on the structure and performance of nickel phosphides under HDO conditions.

Recently, we discovered that Ni<sub>2</sub>P was not stable in aqueous phase HDO of phenol whereas Ni<sub>3</sub>P was more active and significantly stable in phenol HDO both in aqueous phase and in organic phase.



Dr. Anjie Wang is a professor of Catalysis at Dalian University of Technology. He received his Ph.D. degree in Coal Chemical Engineering from Dalian University of Technology in 1991. After graduation, he joined the faculty of Department of Catalysis at School of Chemical Engineering, Dalian University of Technology. He is currently a member of Chinese Catalysis Society, Director of Liaoning Key Laboratory of Petrochemical Technology and Equipment, and Director of The R&D Center for Microchannel System in Chemical Engineering of Dalian University of Technology. He visited Tokyo University of Agriculture and Technology for one year as a visiting scholar from 1999-2000 (Prof. Toshiaki Kabe), worked with Prof. Roel Prins in ETH Zurich as a guest professor for six months in 2004, collaborated with Prof. Chunshan Song in Pennsylvania State University as a visiting professor for six months in 2007, and worked with Prof. Johannes Lercher in PNNL for three months as a guest professor in 2011. His

research interests include heterogeneous catalysis involved in clean fuel production (hydrodesulfurization, hydrodenitrogenation, hydrodeoxygenation, oxidative desulfurization), plasma catalysis, mesoporous and meso-microporous materials, microchannel reactors for continuous production of fine chemicals and nano-sized metal oxides. He has published over 200 peer-reviewed research articles, and co-authored a textbook “Introduction to Heterogeneous Catalysis” (Imperial College Press, World Scientific Publishing Co. Ltd) with Profs. Roel Prins and Xiang Li in 2016 and a textbook “Chemical Reaction Engineering” (Chemical Industry Press, in Chinese) with Profs. Shouchen Zhang and Xiang Li in 2018.