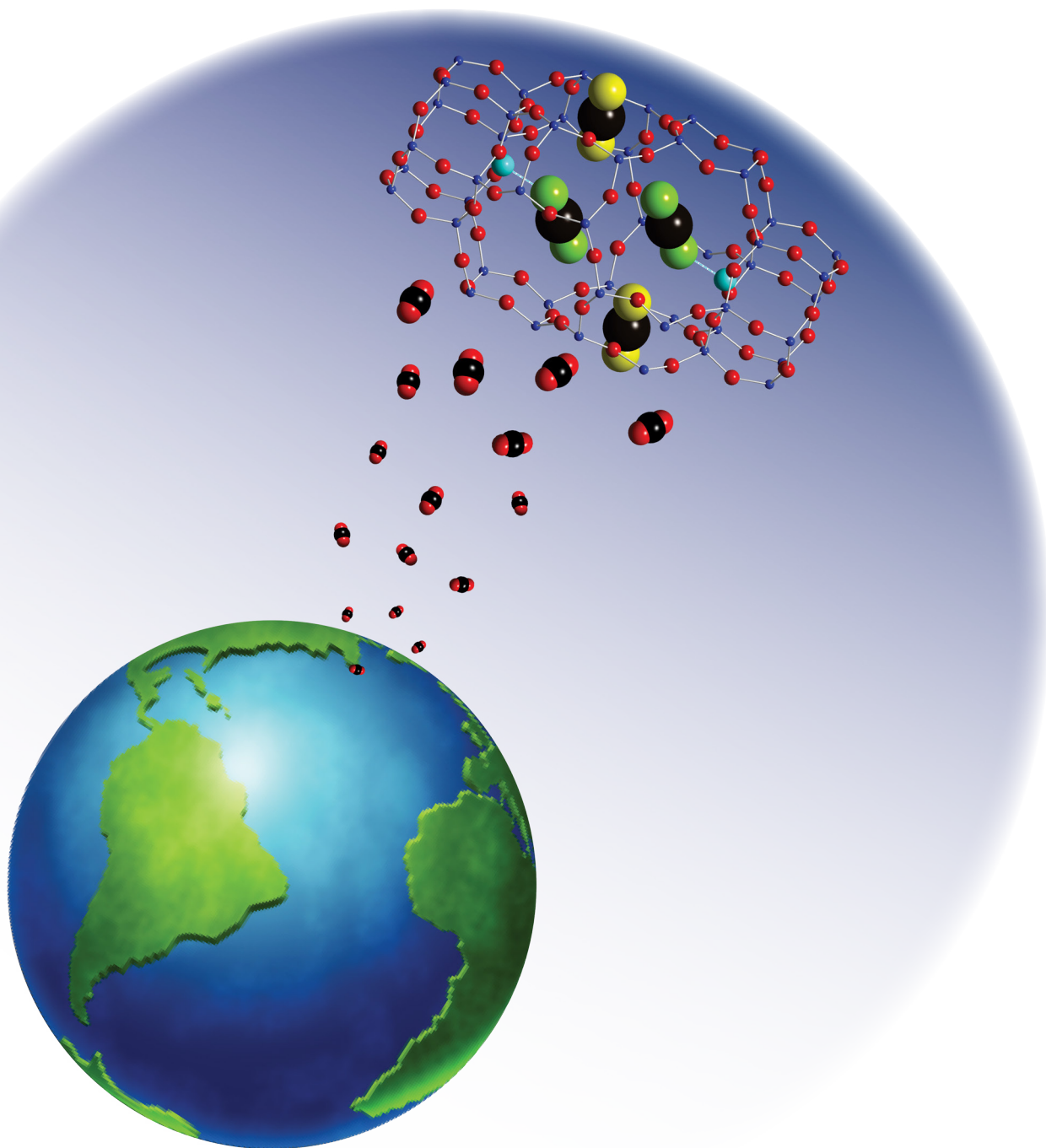


CENTER FOR CATALYTIC SCIENCE & TECHNOLOGY



Front cover image:

CO₂ captured in Zeolite (2014), design concept by Trong Pham, Ph.D. and Prof. Raul Lobo.



Raul F. Lobo

Claire D. LeClair Professor of Chemical & Biomolecular Engineering
and Director of Center for Catalytic Science & Technology

Dear Friends and Colleagues:

This has been a year full of interesting and important developments at the Center for Catalytic Science and Technology. Among the notable achievements are the recognition of Professors Joel Rosenthal and Feng Jiao with the CAREER award by the National Science Foundation, as well as an important grant by the National Institute of Health to Donald Watson. Through their work and energy, this group of young chemists and chemical engineers are changing and invigorating the research portfolio and the group dynamics between students and faculty at the center.

Feng Jiao has made a number of important discoveries in electrocatalysis and electrochemical systems. For example, he has developed new routes for the synthesis of mesoporous metal sulfides that are very flexible in terms of the composition of the materials that can be produced. This development opens the door to exploration of the electrochemical properties of many new metal sulfides that were before unknown in their mesoporous form. Feng has also discovered a new silver-based electrocatalysts for the selective CO₂ reduction in aqueous environments. In parallel and independently, Joel Rosenthal's group has discovered novel bismuth oxide electrocatalysts that are not only inexpensive and abundant, but also excellent for CO₂ reduction. This discovery is particularly important because conceptually this is a catalyst that has been neglected by the electrochemistry community and the origin of its properties is still incompletely understood.

In addition, two new important discoveries in electrocatalytic systems by the group of Prof. Yushan Yan are also notable. His group has found new efficient catalysts for the water oxidation reaction that are based on a special form of Ni hydroxide. Secondly, in collaboration with Prof. Jingguang Chen (at Columbia U. and a previous CCST director) they also discovered a non-precious ternary metallic catalyst (CoNiMo) for the hydrogen oxidation reaction in basic aqueous solutions. Together, these materials further the performance of fuel cells based on hydroxide exchange membranes instead of proton exchange membranes.

Professor Vlachos' group has made important advances in the understanding and development of catalysts for the conversion of sugars into fuels and chemicals. In particular, his group has developed a number of catalysts/solvent systems for the partial hydrogenation of hydroxymethyl furfural and furfural that rely on the use of a hydrogen donor solvent to reduce these molecules into dimethyl furan and methyl furan with high selectivity. These catalysts contain metal and Lewis acid sites (such as Ru/RuO₂ combinations) that work cooperatively to hydrogenate and dehydrate precursors and that let them carry out complementary reactions for both alcohol dehydrogenation and hydrogenation/dehydration of HMF intermediates. These catalysts and the ideas that lead to their application are valuable contributions to our understanding of biomass processing and suggest a plethora of options to improve both catalytic performance and overall selectivity.

Interest in catalysis has remained very high among incoming graduate students, and this can also be gleaned from the quantity and quality of the research described in this report. This is one of the great advantages to being part of the CCST and bodes well for our ability to continue conducting first-rate research at the CCST in the future. This research report summarizes the research conducted in the last 18 months at the CCST by our graduate students, postdocs and faculty and it is a testament to their dedication to high quality and impactful science across the board. We remain committed to pursue industry-relevant academic research and look forward to collaborations with industry on all aspects of catalysis. If you have any comments or inquiries about this report or our ongoing research activities, you are welcome to contact me or visit our offices in Colburn Laboratory.

The challenges to the field of catalysis change in response to changes in the availability of raw materials such as natural gas and natural-gas liquids, and to the constraints imposed by the environmental effect of human activities. We look forward to meeting these evolving challenges and to contribute to the progress and impact of catalysis in our society. I hope you enjoy reading this report and learn about our efforts to contribute to the science and practice of catalysis.

Raul F. Lobo C

About CCST

Recognizing the central role of catalysis in industrial practice, the Center for Catalytic Science and Technology was founded at the University of Delaware in 1978. The Center has pioneered multidisciplinary research in the scientific and engineering principles of catalysis. Over the last two decades, the Center has provided research opportunities in all aspects of catalysis to more than 300 students and postdoctoral fellows in the academic departments, Chemical Engineering and Chemistry & Biochemistry, which it spans. The hallmark of the Center's research continues to be its strong connection to industrial practice. These ties have been forged through a number of mechanisms, including the Center's Industrial Sponsors Program, industrially supported grant and contract research, collaborative projects with industrial scientists and engineers, and industrial sabbaticals and exchanges of research personnel. The Center's laboratories, virtually all newly constructed or renovated since 1993, and wide range of research instrumentation represent one of the foremost facilities for catalysis research in academia.



Douglas J. Buttrey

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Synthesis of complex oxides and alloys, composition-structure-property relationships in catalytic and electronic materials; high-resolution electron microscopy

BUTTREY GROUP

Observation of Sublattice Disorder of the Catalytic Sites in a Complex Mo-V-Nb-Te-O Oxidation Catalyst using High Temperature STEM Imaging, D. A. Blom, L. Allard, T. Vogt, and D. J. Buttrey, Topics in Catalysis. Published online 15 July 2014 - DOI 10.1007/s11244-014-0278-4.

Orthorhombic Mo₃VO_x Catalyst Most Active for Oxidative Dehydrogenation of Ethane Among Related Complex Metal Oxides, T. Konya, T. Katou, T. Murayama, S. Ishikawa, M. Sadakane, D. Buttrey, W. Ueda, Catal. Sci. Technol. 3 (2), 380 – 387 (2013).

Synthesis, Structural Characterization, and Physical Properties of the Early Rare-Earth Metal Digermanides REGe_{2-x} ($x \approx 1/4$) [RE = La-Nd, Sm]. A Case Study of Commensurately and Incommensurately Modulated Structures, J. Zhang, P. H. Tobash, W. D. Pryz, D. J. Buttrey, N. Hur, J. D. Thompson S, J. L. Sarrao, and S. Bobev, Inorg. Chem., 52 (2), 953–964 (2013).

Energy Storage in Electrochemical Cells with Molten Sb Electrodes, A. Javadekar, A. Jayakumar, R. J. Gorte, J. M. Vohs, D. J. Buttrey, Journal of The Electrochemical Society 159, A386 (2012).

Characteristics of Molten Metals as Anodes for Direct Carbon Solid Oxide Fuel Cells, A. Jayakumar, A. Javadekar, R. Küngas, D. J. Buttrey, J. M. Vohs, R. J. Gorte, ECS Transactions 41 (12), 149-158 (2012).



Wilfred Chen

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Engineering of protein scaffolds for biofuel production, disease diagnostic and treatment, drug discovery, and the environmentally-friendly biosynthesis, including the

application of scaffolds for biosensor development

CHEN GROUP

Bactericidal activity of elastin-like polypeptide biopolymer with polyhistidine domain and silver,

Kishore K. Krishnani, Wilfred Chen, and Ashok Mulchandani, Colloids and Surfaces B: Biointerfaces, 119, 66-70, 2014.

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Rahul D. Sheth, Mi Jin, Bharat V. Bhut, Jia Liu, Jongchan Lee, Rieble Siegfried, Zhengjian Li, Wilfred Chen, Steven M. Cramer, Biotechnol. Bioeng., 111, 1595-1603, 2014.

Biomolecular Scaffolds for Enhanced Signaling and Catalytic Efficiency,

Rebecca Chen, Qi Chen, Heejae Kim, Ka-Hei Siu, Qing Sun, Shen-Long Tsai and Wilfred Chen, Curr. Opin. Biotechnol., 28, 59-68, 2014.

Creation of artificial cellulosomes on DNA scaffolds by zinc finger protein-guided assembly for efficient cellulose hydrolysis,

Qing Sun, Bhawna Madan, Shen-Long Tsai, Matthew P. DeLisa, and Wilfred Chen, Chem. Comm., 50, 1423-1425, 2014.

Positional assembly of enzymes on bacterial outer membrane vesicles for cascade reactions,

Miso Park, Qing Sun, Fang Liu, Matthew P. DeLisa, and Wilfred Chen, PLOS one, 9, e97103, 2014.

Quantitative assessment of in vivo HIV protease activity using genetically engineered QD-based FRET probes,

Lakshmi N Cella, Payal Biswas, Marylynn V. Yates, Ashok Mulchandani, Wilfred Chen, Biotechnol. Bioeng., 111, 1082-1087, 2014.

Engineering protein modules for diagnostic applications,

Daniel Blackstock, Miso Park, Qing Sun, Shen-Long Tsai, and Wilfred Chen, Curr. Opin. Chem. Eng., 2, 416-424, 2013.

Microbial biosensors: Engineered microorganisms

as the sensing machinery, Miso Park, Shen-Long Tsai, and Wilfred Chen, Sensors, 13, 5777-5795, 2013.



Douglas J. Doren

Chemistry & Biochemistry

RESEARCH INTERESTS

Theoretical and computational methods with applications to materials science, surface science, catalysis and solvation

DOREN GROUP

Formation and Growth of Molecular Clusters

Containing Sulfuric Acid, Water, Ammonia, and

Dimethylamine, DePalma, JW; Doren, DJ; Johnston, MV, Journal of Physical Chemistry A 118, 5464 (2014)

Binding of styrene on silicon (111)-7 x 7 surfaces

as a model molecular electronics system, Weiland, CR; Yang, L; Doren, DJ; Menning, CA; Skliar, D; Willis, BG; Chen, JGG; Opila, RL, Journal of Vacuum Science & Technology A 30, 031401 (2012)

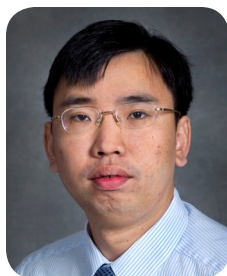
A perspective on the modeling of biomass

processing, Guo, N; Caratzoulas, S; Doren, DJ; Sandler, SI; Vlachos, DG, Energy & Environmental Science 5, 6703 (2012)

Structure Analysis and Photocatalytic Properties

of Spinel Zinc Gallium Oxonitrides,

Boppana, VBR; Schmidt, H; Jiao, F; Doren, DJ; Lobo, RF, Chemistry-A European Journal 17, 12417, (2012)



Feng Jiao

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Energy storage and conversion, advanced lithium-ion batteries, solar energy harvesting, and synthesis of nanostructure materials



Michael T. Klein

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Chemical Reaction Engineering with special emphasis on the kinetics of complex systems

JIAO GROUP

A General Synthetic Approach for Ordered Mesoporous Metal Sulfides, Yonemoto, B. T., Hutchings, G. S., & Jiao, F.* *Journal of the American Chemical Society* 136, 8895-8898 (2014). doi:10.1021/ja504407e

Environmental In Situ X-ray Absorption Spectroscopy Batteries for Rechargeable Lithium-Oxygen Batteries, Hutchings, G. S., Rosen, J., Smiley, D. L., Goward, G. R., Bruce, P. G., & Jiao, F.*, *Journal of Physical Chemistry C* 118, 12617-12624 (2014). doi:10.1021/jp5017399

Nanostructured Mg-modified LiMnPO₄ Matrix as High-rate Cathode Materials for Li-ion Batteries, Lu, Q., Hutchings, G. S., Zhou, Y., Xin, H., Zheng, H., & Jiao, F.*, *Journal of Materials Chemistry A* 2, 6368-6373 (2014). doi:10.1039/C4TA00654B

A Selective and Efficient Electrocatalyst for Carbon Dioxide Reduction, Lu, Q.,# Rosen, J.,# Zhou, Y., Hutchings, G. S., Kimmel, Y. C., Chen, J. G., & Jiao, F.*, *Nature Communications* 5:3242 (2014). doi:10.1038/ncomms4242 (#: equal contribution)

Synthesis, Structural Characterization, and Electrochemical Performance of Nanocast Mesoporous Cu-/Fe-based Oxides, Jiao, F.,* Yen, H., Hutchings, G. S., Yonemoto, B. T., Lu, Q., & Kleitz, F.*, *Journal of Materials Chemistry A* 2, 3065-3071 (2014). doi:10.1039/C3TA14111J

Enhancing photocatalytic oxygen evolution activity of cobalt-based spinel nanoparticles, Zhang, Y., Rosen, J., Hutchings, G. S., & Jiao, F.*, *Catalysis Today* 225, 171-176 (2014). doi:10.1016/j.cattod.2013.08.009

invited contribution

KLEIN GROUP

A novel simplification approach for large-scale structural models of coal: 3D molecules to 2D lattices. 3. Reactive lattice simulations, Energy and Fuels, Alvarez, Y. E.; Moreno, B. M.; Klein, M. T.; Watson, J. K.; Castro-Marciano, F.; Mathews, J. P., DOI: 10.1021/ef4001105, Publication Date (Web): April 18, 2013.

Modeling Aqueous-Phase Hydrodeoxygenation of Sorbitol over Pt/SiO₂-Al₂O₃, Brian M. Moreno, Ning Li, Jechan Lee, George W. Huber, and Michael T. Klein, *RSC Adv.*, 2013, 3 (45), 23769 - 23784

Molecule-based Modeling of Heavy Oil, S. R. Horton, Z. Hou, B. M. Moreno, C. A. Bennett and M. T. Klein, *SCIENCE CHINA Chemistry*, 1-8, DOI: 10.1007/s11426-013-4895-8

Reaction and Catalyst Families in the Modeling of Coal and Biomass Liquefaction Kinetics, Horton, Scott; Klein, Michael T., *Energy Fuels* 2014, 28, 37–40.

Discrimination between Free-Radical and Concerted Pyrolysis Mechanisms, Brian Matthew Moreno, Amy L Quach, Michael N Merves, and Michael T Klein, *Energy Fuels*, 2014, 28 (7), pp 4256–4259.



Raul F. Lobo

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Synthesis, characterization and discovery of novel microporous materials, and structure property relationships in catalysts and adsorption



Joel Rosenthal

Chemistry & Biochemistry

RESEARCH INTERESTS

Energy storage and conversion, solar energy harvesting, catalysis, electrochemistry, photochemistry, chemical detection arrays and inorganic synthesis

LOBO GROUP

Catalysis by Confinement: Enthalpic Stabilization of NO Oxidation Transition States by Microporous and Mesoporous Siliceous Materials, Artioli, N., Lobo, R.F. and Iglesia, E., *J. Phys. Chem. C*, 2013, 117, 20666-20674.

Analysis of visible-light-active Sn(II)-TiO₂ Photocatalyst, Boppana, V.B.R., Jiao, F., Newby, D. Jr., Laverock, J., Smith, K.E., Juma, J.C., Hutchings, G., Lobo, R.F., *Phys. Chem. Chem. Phys.*, 2013, 15, 6185-6189.

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Low Temperature Catalytic NO oxidation over Microporous Materials, Loiland, J.L. and Lobo R.F., *J. Catal.*, 2014, 311, 412-423.

ROSENTHAL GROUP

Efficient Reduction of CO₂ to CO with High Current Density Using in Situ or ex Situ Prepared Bi-Based Materials, Medina-Ramos, J., DiMeglio, J. L., & Rosenthal, J., *J. Am. Chem. Soc.*, 2014, 136, 8361-8367. doi:10.1021/ja501923g

Reduction of CO₂ using a rhenium bipyridine complex containing ancillary BODIPY moieties, Teesdale, J. J., Pistner, A. J., Yap, G. P. A., Ma, Y.-Z., Lutterman, D. A., & Rosenthal, J. (2014), *Cat Today*, 2014, 225, 149-157.

Selective Conversion of CO₂ to CO with High Efficiency Using an Inexpensive Bismuth-Based Electrocatalyst, DiMeglio, J. L., & Rosenthal, J., *J. Am. Chem. Soc.*, 2013, 135, 8798-8801. doi:10.1021/ja4033549

On-Surface Cross Coupling Methods for the Construction of Modified Electrode Assemblies with Tailored Morphologies, Amber A. S. Gietter, Rachel C. Pupillo, Glenn P. A. Yap, Thomas P. Beebe, Joel Rosenthal and Donald A. Watson, *Chem. Sci.* 2013, 4, 437-443. (DOI:10.1039/C2SC21413J)

Synthesis, Photophysics, Electrochemistry and Electrogenated Chemiluminescence of PEG-Modified BODIPY dyes in Organic and Aqueous Solutions, Alexander B. Nepomnyashchii, Allen J. Pistner, Allen J. Bard and Joel Rosenthal *J. Phys. Chem. C* 2013, 117, 5599-5609. (DOI:10.1021/jp312166w)

Synthesis, Electrochemistry and Photophysics of a Family of Phlorin Macrocycles that Display Cooperative Fluoride Binding, Allen J. Pistner, Daniel A. Lutterman, Michael J. Ghidui, Ying-Zhong Ma and Joel Rosenthal, *J. Am. Chem. Soc.* 2013, 135, 6601-6607. (DOI:10.1021/ja401391z)



Andrew V. Teplyakov

Chemistry & Biochemistry

RESEARCH INTERESTS

Experimental and computational surface and thin film chemistry, diffusion barriers, nucleation, growth, self-assembly, surface modification.



Klaus H. Theopold

Chemistry & Biochemistry

RESEARCH INTERESTS

Homogeneous catalysis, coordination polymerization of olefins, activation of dioxygen by novel oxidation catalysis

TEPLYAKOV GROUP

Structurally Different Interfaces between Electrospark-Deposited Titanium Carbonitride and Tungsten Carbide Films on Steel, Miller, T.; Pirolli, L.; Deng, F., Ni, C. and Teplyakov, A. V., Surf. Coat. Technol. 2014, DOI: 10.1016/j.surfcoat.2014.07.076.

Attachment Chemistry of PCBM to a Primary-Amine-Terminated Organic Monolayer on a Si(111) Surface, Miller, T. and Teplyakov, A. V., Langmuir, 2014, 30, 5105-5114.

Thermal Transformations of 2-Chlorophenol on a Surface of ZnO Powder Catalyst, Gao, J. and Teplyakov, A. V., Catal. Today 2014, <http://dx.doi.org/10.1016/j.cattod.2013.12.053>.

Nitroxidation of H-terminated Si(111) Surfaces with Nitrobenzene and Nitrosobenzene, Tian, F., Cui, Y. and Teplyakov, A. V., J. Phys. Chem. C 2014, 118(1), 502-512.

A. V. Formation of Copper Nanoparticles on ZnO Powder by a Surface-Limited Reaction, Kung, H. and Teplyakov, J. Phys. Chem. C 2014, 118(4), 1990-1998.

Semiconductor surface functionalization for advances in electronics, energy conversion, and dynamic systems, Bent, S. F. and Teplyakov, A. V., J. Vac. Sci Technol. A, 2013, 31(5), 050810-1-12. Invited Review Article for the Special AVS 60th Anniversary Issue, awarded top 20 most downloaded articles in JVST.

A. V. Silicon surface functionalization targeting Si-N linkages, Tian, F. and Teplyakov, Langmuir 2013, 29(1), 13-28. Invited Feature Article, Image featured on the cover of the journal.

THEOPOLD GROUP

The Direct Oxidative Addition of O₂ to a Mononuclear Cr(I) Complex Is Spin Forbidden, Dai, F., G.P.A. Yap, and K.H. Theopold, Journal of the American Chemical Society, 2013. 135(45): p. 16774-16776.

A well-defined model system for the chromiumcatalyzed selective oligomerization of ethylene, Monillas, W.H., et al., Dalton Transactions, 2013. 42(25): p. 9198-9210.

An electron transfer series of octahedral chromium complexes containing a redox non-innocent alpha-diimine ligand, Shen, J., et al., Chemical communications (Cambridge, England), 2014. 50(73): p. 10626-9.

Chromium Mediated Reductive Coupling of Isonitrile Forms Unusual Heterocycles, Shen, J., G.P.A. Yap, and K.H. Theopold, Journal of the American Chemical Society, 2014. 136(9): p. 3382-3384.

Binding and activation of small molecules by a quintuply bonded chromium dimer, Shen, J., G.P.A. Yap, and K.H. Theopold, Chemical Communications, 2014. 50(20): p. 2579-2581.

Improved syntheses, and structural and electronic characterization of carboxamide-substituted Tp(CONHPh,Me) and Tp(CONHt-Bu), Me ligands, Sirianni, E.R., et al., Acta Crystallographica Section C-Crystal Structure Communications, 2013. 69: p. 947-953.

Deprotonation of coordinated ethylene may start Phillips catalysis, Theopold, K.H., Proceedings of the National Academy of Sciences of the United States of America, 2014. 111(32): p. 11578-11579.

New Complexes of Chromium(III) Containing Organic pi-Radical Ligands: An Experimental and Density Functional Theory Study, Wang, M., et al., Inorganic Chemistry, 2013. 52(8): p. 4472-4487.



Dionisios G. Vlachos

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Multiscale simulation, reacting flows, reaction mechanism development, catalyst design, microreactors, portable power, energy, crystal growth, nanomaterials, zeolites,

membranes, separations

VLACHOS GROUP

A DFT study of furan hydrogenation and ring opening on Pd(111), S. Wang, V. Vortnikov, and D. G. Vlachos, *Green Chem.* 16(2), 736-747, (2014).

Tungsten carbides as selective deoxygenation catalysts: experimental and computational studies of converting C3 oxygenates to propene, H. Ren, Y. Chen, Y. Huang, W. Deng, D. G. Vlachos, and J. G. Chen, *Green Chem.* 16(2), 761-769, (2014).

Liquid Phase Catalytic Transfer Hydrogenation of Furfural Over Ru/C Catalyst, P. Panagiotopoulou, and D. G. Vlachos, *Appl. Catal. A: General* 480, 17-24, (2014).

Aqueous-Phase Fructose Dehydration Using Brønsted Acid Zeolites: Catalytic Activity of Dissolved Aluminosilicate Species, J. S. Kruger, V. Nikolakis, and D. G. Vlachos, *Appl. Catal. A: General* 469, 116-123, (2014).

Cascade of Liquid-Phase Catalytic Transfer Hydrogenation and Etherification of Hydroxymethylfurfural to Potential Bio-diesel Components over Lewis Acid Zeolites, J. Jae, E. Mahmoud, R. F. Lobo, and D. G. Vlachos, *ChemCatChem* 6(2), 508-513, (2014).

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Donald A. Watson

Chemistry & Biochemistry

RESEARCH INTERESTS

Transition-metal catalysis; organic synthesis; alternative energy chemistry

WATSON GROUP

Rational Design of a Second Generation Catalyst for Preparation of Allylsilanes Using the Silyl-Heck Reaction, McAtee, J. R.; Yap, G. P. A.; Watson, D. A., *J. Am. Chem. Soc.*, 2014, 136, 10166-10172.

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The First Example Of Nickel-Catalyzed Silyl-Heck Reactions: Direct Activation Of Silyl Triflates Without Iodide Additives, McAtee, J. R.; Martin, S. E. S.; Cinderella, A. P.; Reid, W. B.; Johnson, K. A.; Watson, D. A., *Tetrahedron*, 2014, 70, 4250-4256.

Renewable Production Of Phthalic Anhydride From Biomass-Derived Furan And Maleic Anhydride, Mahmoud, E.; Watson, D. A.; Lobo, R. F., *Green Chemistry*, 2014, 16, 167-175.

Silyl-Heck Reactions for the Preparation of Unsaturated Organosilanes, Martin, S. E. S.; Watson, D. A., *Synlett*, 2013, 24, 2177-2182.

Preparation of Vinyl Silyl Ethers and Disiloxanes via the Silyl-Heck Reaction of Silyl Ditriflates, Martin, S. E. S.; Watson, D. A., *J. Am. Chem. Soc.*, 2013, 135, 13330-13333.

Selective Formation of Secondary Amides via the Copper-Catalyzed Cross-Coupling of Alkylboronic Acids with Primary Amides, Rossi, S. A.; Shimkin, K. W.; Xu, Q.; Mori-Quiroz, L. M.; Watson, D. A., *Organic Letters* 2013, 15, 2314-2317.

On-Surface Cross Coupling Methods for the Construction of Modified Electrode Assemblies with Tailored Morphologies, Gietter, A. A. S.; Pupillo, R. C.; Yap, G. P. A.; Thomas P. Beebe, J.; Rosenthal, J.; Watson, D. A., *Chemical Science* 2013, 4, 437-433.

Elucidation of Diels-Alder Reaction Network of 2,5-Dimethylfuran and Ethylene on HY Zeolite Catalyst, Do, P. T. M.; McAtee, J. R.; Watson, D. A.; Lobo, R. F., *ACS Catalysis* 2013, 3, 41-46.

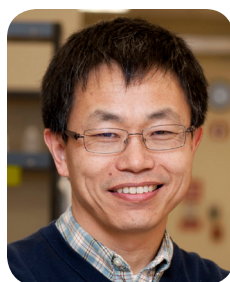


Bingjun Xu

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Rational catalyst design and mechanistic studies for biomass upgrade, in-situ spectroscopies for electrochemical interfaces and electrocatalysis



Yushan Yan

Chemical & Biomolecular Engineering

RESEARCH INTERESTS

Electrochemical energy devices; membranes and catalysts for fuel cells, electrolyzers, redox flow batteries, and solar hydrogen; and zeolite thin films for semiconductor and aerospace applications

XU GROUP

Electrochemical Energy Engineering: A New Frontier of Chemical Engineering Innovation, S. Gu, B. Xu, Y. Yan, *Annu. Rev. Chem. Biomol. Eng.*, 5, 2014, 429.

Predicting gold-mediated catalytic oxidative-coupling reactions from single crystal studies, B. Xu, R. Madix, C. Friend, *Acc. Chem. Res.* (2014)

Low-temperature, manganese oxide-based thermochemical water splitting cycle, B. Xu, Y. Bhawe, M. Davis, *Proc. Natl. Acad. Sci.* 109, 9260, (2012)

Dual-function of alcohols in gold-mediated selective coupling of amines and alcohols, B. Xu, R. Madix, C. Friend, *Chem. Euro. J.* 18, 2313, (2012)

Activated metallic gold as an agent for direct methoxycarbonylation, B. Xu, R. Madix, C. Friend, *J. Am. Chem. Soc.* 133, 20378, (2011)

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Achieving optimum selectivity in oxygen assisted alcohol cross-coupling on gold, B. Xu, R. Madix, C. Friend, *J. Am. Chem. Soc.* 132, 16571, (2010)

Oxygen-assisted cross-coupling of methanol with alkyl alcohols on metallic gold, B. Xu, J. Habrich, C. Freyschlag, R. Madix, C. Friend, *Chem. Sci.* 1, 310, (2010)

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YAN GROUP

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DOUGLAS J. BUTTREY

Synthetic Studies and Improved Structural Refinement of M1 Phase in Mo-V-Te-Nb-O Catalysts for Selective Oxidation and Ammoxidation of Propane

The Mo-V-Nb-Te-O mixed metal oxides are widely considered as the most efficient catalytic system for selective ammoxidation and oxidation of propane to acrylonitrile and acrylic acid, respectively. Acrylonitrile is among the top 25 chemical intermediates produced worldwide, though it is currently produced primarily from propene. PTT Asahi has recently opened the first propane-process plant for acrylonitrile production using the Mo-V-Nb-Te-O catalyst, enabling lower production costs than the conventional propene process. Two phases have been identified as the effective components of this new catalyst: an orthorhombic active phase (M1) and pseudo-hexagonal promoter phase (M2).

Two methods are often used for synthesis of the M1/M2 catalyst: the hydrothermal method and the slurry method. Both approaches involve mixing metal precursors in aqueous solutions as the first step. While the hydrothermal approach requires an autoclave, the slurry method requires only drying and calcination at ambient pressure. In addition to the M1 and M2 phases, a variety of minor impurities frequently accompany the desired phases. Since the impurities have simpler structures with smaller unit cells compared with the primary phases, these are often undetected. These may include $\text{TeMo}_5\text{O}_{16}$, V-substituted Mo_5O_{14} , Mo-substituted V_2O_5 and Te metal. The formation of $\text{TeMo}_5\text{O}_{16}$ is favored at relatively high slurry pH, whereas the formation of V-substituted Mo_5O_{14} is significantly affected by the heating rate of calcination. The formation of the V-substituted Mo_5O_{14} phase can be related to Te loss during the heat treatment. Mo-substituted V_2O_5 is always formed in small quantities when V is in excess, and can be removed by washing the product with concentrated H_2O_2 .

An improved structural model of M1 has been developed using simultaneous Rietveld refinement of synchrotron and neutron diffraction data [1] based on several improvements to the old model. These model improvements were motivated by feedback from aberration-corrected transmission electron microscopy. In addition, low-level impurity phases identified and included in the analysis. Much of the improvement results accounting for small amounts of the Mo-substituted V_2O_5 -type impurity phase. The improved refinement of the M1 model indicates that V preferentially occupies the linking sites (S1, S2, S3, S4, and S7 in Fig. 1) in the structure, consistent with the site contrast analysis based on previous HAADF imaging results. Bond valence sum results suggest that the oxidation state of V in the bulk contains significant 4+ valence, although it indicates that some linking sites (S3, S4, and S7 in Fig. 1) have a d^0/d^1 mixed configuration due to the presence of Mo^{6+} with V^{5+} . Based on electroneutrality considerations, it is apparent that the d0 site concentration in sites S3, S4, and S7 closely matches the vanadium occupancy. Therefore, we believe that the vanadium in these sites is d^0 (V^{5+}) and the molybdenum is d1 (Mo^{5+}). It is and expected that surface V^{5+} species are needed in the active sites for propane activation.

Another important finding resulting from the improved refinement is the oxygens bridging the S2, S4, and S7 metal

sites have anomalously large thermal parameters. Subsequent HAADF-STEM imaging experiments on the M1 phase have been performed to explore this further using a Protochips heating stage at Oak Ridge National Lab to observe the evolution of the structure with temperature [2]. At 780 K, substantial thermal motion is evident among the active site metals producing some blurring in the image, whereas the pentagonal ring sites remain clear. Figure 2 shows the room temperature image (top) and the 200°C image (bottom). This is consistent with the large thermal parameters of active site oxygens observed in the room temperature refinement, and indicates that the active site is highly dynamic at elevated temperatures.

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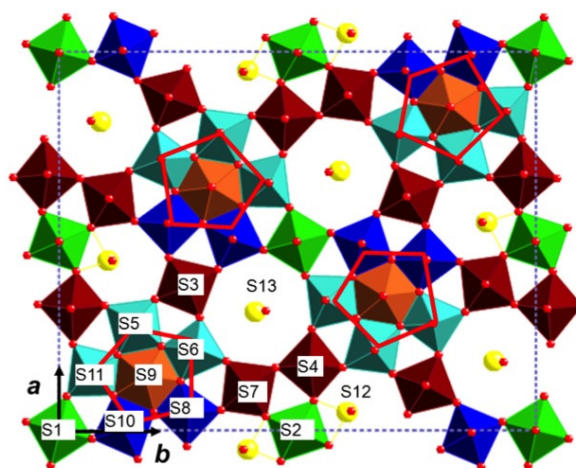


Figure 1. [001] projection of the M1 structure [1].

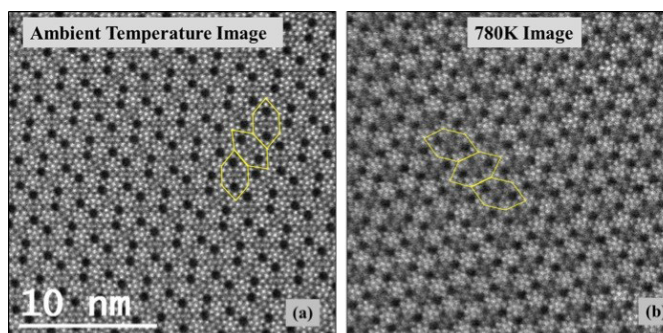


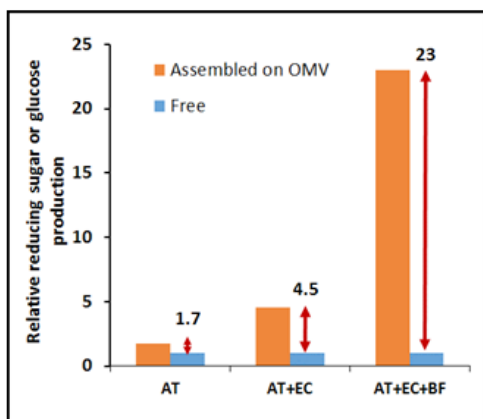
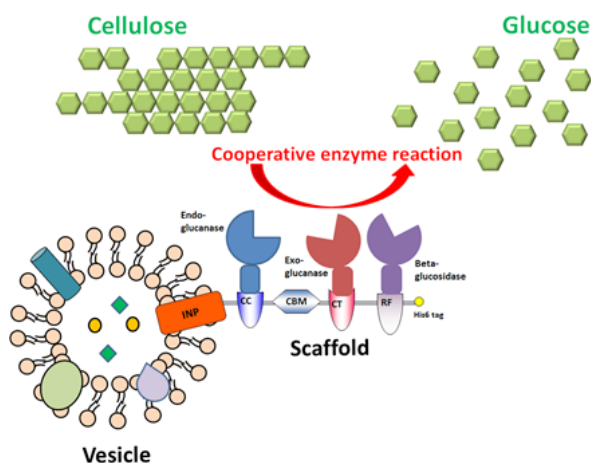
Figure 2. [001] HAADF-STEM image at (a) ambient temperature and (b) 780 K [2].

WILFRED CHEN

Positional Assembly of Enzymes on Bacterial Outer Membrane Vesicles for Cascade Reactions

The systematic organization of enzymes is a key feature for the efficient operation of cascade reactions in nature. My group has demonstrated a facile method to create nanoscale enzyme cascades by using engineered bacterial outer membrane vesicles (OMVs) that are spheroid nanoparticles (roughly 50nm in diameter) produced by Gram-negative bacteria during all phases of growth. By taking advantage of the fact that OMVs naturally contain proteins found in the outer cell membrane, we displayed a trivalent protein scaffold containing three divergent cohesin domains for the position-specific presentation of a three-enzyme cascade on OMVs through a truncated ice nucleation protein anchoring motif (INP). The positional assembly of three enzymes for cellulose hydrolysis was demonstrated. The enzyme-decorated OMVs provided synergistic cellulose hydrolysis resulting in 23-fold enhancement in glucose production than free enzymes.

This project was recently funded by NSF and we are in the process of assembling multiple enzymes on the same scaffold to create unique architectures such as synthetic 3D metabolons and multivalent OMV vaccines.



FENG JIAO

Nanoporous Materials for Catalysis

In the Jiao laboratory catalysis, materials science and electrochemistry, are integrated to address the exciting and critical scientific challenges in the field of energy conversion and storage. Breakthroughs in this field are crucial to tackle global warming by providing the society with clean, sustainable, and environmentally friendly energy solutions. Current research interests include heterogeneous catalysis, electrocatalysis, nanomaterials, and computational modeling.

Early this year, the Jiao group reported in Nature Communications the discovery of a nanoporous silver catalyst, which is able to electrochemically convert carbon dioxide into carbon monoxide in a very selective and efficient way.[1] The nanoporous structure creates an extremely large surface area for catalytic reaction and the curved internal surface generates a large number of highly active step sites for CO₂ conversion, resulting in an exceptional activity that is over 3000 times higher than that of the polycrystalline counterpart at a moderate overpotential.

More recently, Prof. Jiao and his team reported the first general synthetic method to prepare mesoporous transition metal sulfides with ordered porosity and crystalline walls. Transition metal sulfides range from metallic to large band-gap materials and are under investigation for a number of important applications such as batteries, fuel cells, catalysis, water purification, electrocatalysis, and solar cells. Mesoporous metal sulfides, with higher surface areas and accessible diffusion channels, could greatly enhance the performance for these processes. Unfortunately, only a small number of nanocast mesoporous metal sulfides have been reported.

One reason for this lack of success is the large volume contractions during the conversion of metal salt precursors to final metal sulfide products, resulting in isolated nanoparticles instead of ordered structures within the silica hard template. For example, based on the volume per iron atom of Fe(NO₃)₃·9H₂O (a common precursor for mesoporous metal oxide preparation) and pyrite FeS₂ a 90% volume contraction will occur during synthesis, making it very unlikely for iron sulfide crystallites to form a coherent ordered structure. To overcome this problem, the Jiao research group invented a

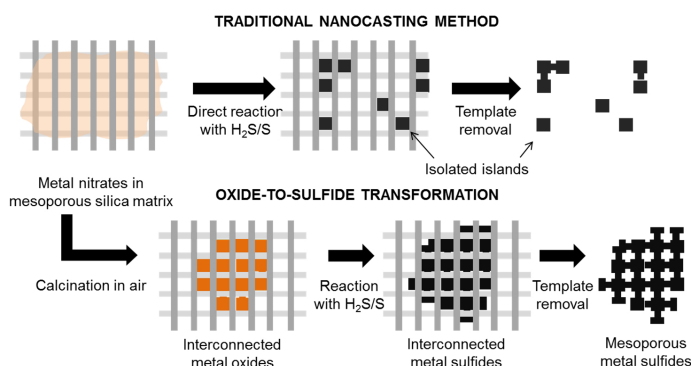


Figure 1. A schematic diagram of the "oxide-to-sulfide" method for ordered mesoporous metal sulfide synthesis.

new preparation methodology, which is coined as an “oxide-to-sulfide” conversion. The strategy is to first grow a metal oxide structure, using well understood methodologies, within the pore channels of the silica hard template. Once the well-ordered oxide has formed inside the mesoporous silica, a sulfidation reaction can be performed to convert the oxide crystal structure into a metal sulfide (Figure 1). By using this approach, a 58% volume expansion from $\alpha\text{-Fe}_2\text{O}_3$ to pyrite FeS_2 occurs. The expanding volume ensures the formed mesoporous particles will maintain their well-ordered architecture within the template. Then the template is removed, yielding previously inaccessible mesoporous metal sulfides, i.e. FeS_2 , CoS_2 and NiS_2 (Figure 2). The new mesoporous structures delivered enhanced activity compared to bulk structures

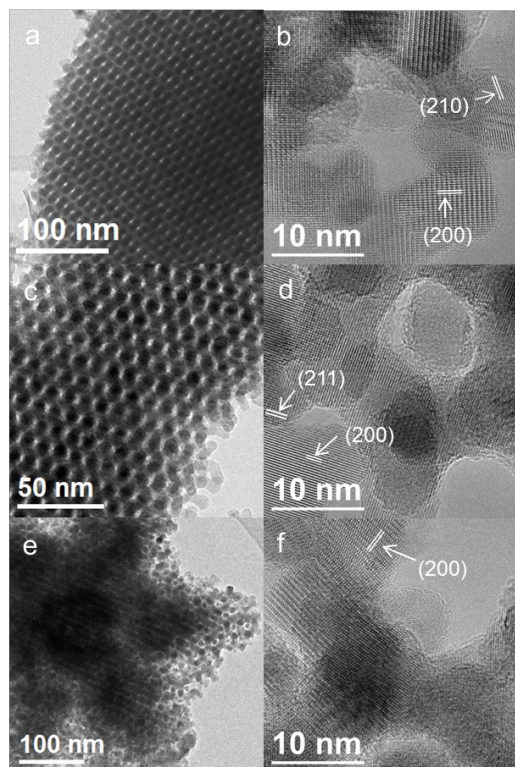


Figure 2. Transmission electron microscopy images of (a, b) mesoporous iron sulfide, (c, d) mesoporous nickel sulfide, and (e, f) mesoporous cobalt sulfide materials.

during the photocatalytic removal of methylene blue dye under visible light. Most importantly, the basic logic for “oxide-to-sulfide” transformations can be extended to make new mesoporous metal sulfide, phosphide, nitride and carbide materials. The new scientific discovery has been published in the Journal of the American Chemical Society and featured in the JACS spotlights.[2]

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MICHAEL KLEIN

Software Tools for the Construction of Detailed Kinetic Models

The worldwide energy transportation sector is almost entirely dependent on petroleum, a remarkable resource on which a highly sophisticated refining and vehicle infrastructure has grown. Given the capital value of the existing worldwide refining and transportation infrastructures, and the slow characteristic time for their change, it is likely that carbon-based resources, including unconventional feedstocks that will be upgraded for use with petroleum in the existing infrastructure, will be utilized for decades to come. Mathematical models of the chemistry of their upgrading and conversion will assist the commercial realization of these possibilities.

The considerable interest in molecule-based models of these chemistries is motivated by the need to predict both upstream and downstream properties. This is because the molecular composition is an optimal starting point for the prediction of mixture properties. The challenge of building these models is due to the staggering complexity of the complex reaction mixtures. There will often be thousands of potential molecular and intermediate (e.g., ions or radicals) species. Clearly, the use of the computer to not only solve but also formulate the model, would be helpful in that it would allow the modeler to focus on the basic chemistry, physics, and approximations of the model.

Our recent work has led to the development of an automated capability to model development. Statistical simulation of feedstock structure casts the modeling problem in molecular terms. Reactivity information is then organized in terms of quantitative linear free energy relationships. The model equations are then built and coded on the computer. Solution of this chemical reaction network, in the context of the chemical reactor, provides a prediction of the molecular composition, which is then organized into any desired commercially relevant outputs. Of particular note is the Attribute Reaction Model approach that is useful when the number of desired components in the molecular mixture is constrained by the practical limits of hardware and software.

RAUL F. LOBO

Catalysis for Energy and the Environment

We envision a future in which catalysis plays an increasingly important role by enabling technologies that provide clean energy, technologies that deliver materials with minimal environmental impact, and technologies to abate pollutants and toxic molecules with increasing efficiency. New scientific knowledge, new principles of catalyst design and the discovery of new materials with hitherto unseen catalytic properties are needed to address these 21st century challenges.

Research in the Lobo group centers on these challenges by integrating catalyst synthesis, catalyst testing and structural and spectroscopic investigations of catalytic materials to elucidate the physicochemical requirements of the active sites, and to elucidate how chemical bonds are broken and formed in the right sequence to go from reactants to products. We investigate heterogeneous catalysts and reaction systems that are of industrial interest and that have the potential to impact clean energy technologies, improve raw material utilization and reduce emissions. Much of our work uses zeolites and other ordered microporous materials where we can leverage our extensive synthesis experience, well-defined active sites and our expertise in chemical kinetics and diffraction and spectroscopic techniques.

From biomass to fuels and chemicals

Biomass is a feedstock that can be tapped to decrease our dependence on fossil fuels for liquid fuel production and for production of commodity and specialty chemicals. We are interested in catalysts and processes that are effective for the hydrodeoxygenation of C5 and C6 sugars into furanic compounds, and in the use of these compounds to produce valuable chemicals. One example is the transformation of furan (derived from C5 sugars) and acrylic acid (from lactic acid) into benzoic acid. This transformation can be accomplished by a two-step reaction where furan and acrylic acid react to form a Diels Alder adduct as indicated.



Scheme 1

We have discovered that siliceous forms of zeolite beta, containing small amounts of hafnium, tin or zirconium are excellent catalysts for the formation of the Diels Alder adduct. The Hf, Sn and Zr metal cations act as Lewis acids that bind acrylic acid and activate it for reaction with furan. We are investigating the properties of these catalysts and a number of reactions where the Lewis acidic properties of these materials can be used to advantage.

Reduction of NO_x Emissions

Nitrogen oxides (NO_x) are harmful pollutants produced at high temperatures in internal combustion engines. The development of a system for NO_x removal from diesel engines is a topic of on-going interest and a number of copper-containing zeolite catalysts have proven to be effective for the selective catalytic reduction of NO_x using ammonia is the reducing agent. The rate-determining step in this reaction is the oxidation of NO into NO₂ and this has motivated a study of

the reaction mechanism of this oxidation. We initially targeted acid zeolites (without the Cu^{II} cations) and this has led to the interesting results depicted in Figure. There are two reaction regimes: at low temperature the reaction proceeds with a negative activation energy and the rate decrease up to ~425K; above this temperature rates increase rapidly with temperature evidencing the activation of a new reaction channel. Reaction rate orders are different as well being 2nd order in NO at low temperature and 1st order in NO at high temperature.

We are in the process of elucidating the reaction mechanisms of this NO oxidation, prior to incorporating Cu cations into the zeolite pores. These investigations promise to yield insights that can be used to improve catalyst performance and perhaps help identify new reactions where these oxidation reactions are important.

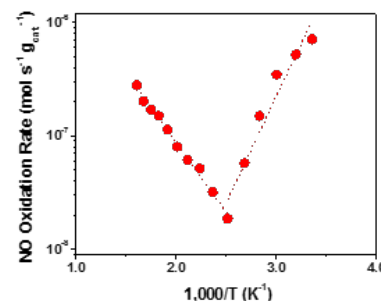


Figure X. Rate of NO oxidation over zeolite H-SSZ-13

Alkane activation and isomerization

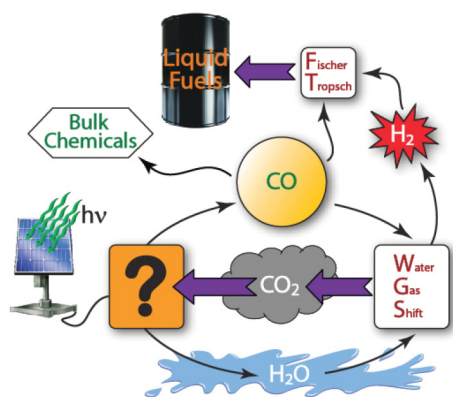
Hydraulic fracturing technology for the extraction of shale gas and shale oil has changed the prospects of the chemical industry in the US due to the availability of inexpensive natural gas (methane) that can be used as a source of energy or as source of hydrogen through methane reforming. Much of the shale gas is rich in natural gas liquids (ethane, propane *n*- and *iso*-butane) and in parallel with an increase in the supply of methane there will be an increase in the supply of C2-C4 hydrocarbons. This represents a great opportunity to produce commodity chemicals at low cost.

Our group is interested in developing new catalytic systems able to activate methane and natural gas liquids into more valuable products, particularly methanol, ethylene and propylene. The methane to methanol partial oxidation reaction is difficult because methanol is easier to oxidize than methane. A number of Cu-containing zeolites (Cu-ZSM-5 and Cu-mordenite) have shown promise for this reaction by conducting the process via a temperature cycle: the zeolite is first oxidized at high temperature, methane is then passed over the zeolites at lower temperatures forming adsorbed methoxide species and lastly, the methoxide species are desorbed by steam. We have discovered a number of zeolite structures and compositions that show similar and superior performance than ZSM-5 and mordenite as determined by the amount of methanol produced per Cu atom. We are studying this system to decrease the temperature needed for the oxidation step such that a practical reaction cycle can be developed.

We are also developing novel ethane and propane dehydrogenation catalysts based on new insights in hydrocarbon activation obtained from computational investigations carried out by the Vlachos group and from surface science experiments conducted by Prof. Jingguang Chen's group.

JOEL ROSENTHAL

The widespread implementation of intermittent renewable energy sources such as solar and wind requires the efficient storage of electron equivalents. The development of methods to store energy via the generation of chemical fuels in a carbon-neutral fashion represents one strategy to address this issue. A major thrust of our research program is dedicated to the catalytic conversion of the greenhouse gas carbon dioxide to versatile, energy-rich species via energetically uphill chemical processes. We are particularly interested in the development of systems for the sequestration and reduction of carbon dioxide to generate value added species such as synthetic petroleum. One potential energy storage scheme that generates fuel from CO_2 is shown here.



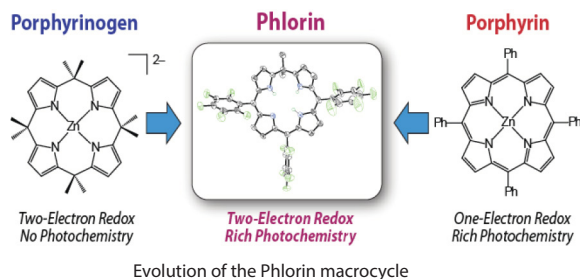
Energy conversion and CO_2 remediation

for the direct photochemical production of energy rich species such as H_2 from H_2O or hydrohalic acids. Accordingly, we are designing new porphyrinoid architectures that are capable of engendering a multielectron reactivity. This represents a major advancement over typical porphyrin architectures, which only allow for single electron reactivity. Through rational design, we seek to overcome the kinetic barriers of small-molecule activation while driving energy-storing endothermic reactions via the direct input of solar energy.

We have designed a new porphyrinoid macrocycle that is a hybrid cousin of the porphyrinogen and porphyrin. This new architecture is known as a Phlorin and we have shown that it is capable of supporting a complex multielectron redox chemistry while maintaining the rich photochemical properties intrinsic to most porphyrinoids. In addition to being able to recognize several different anionic species, the Phlorin is a suitable platform for binding of transition metal centers including cobalt and zinc. Current work is aimed at promoting energy-storing catalytic processes using these systems.

We are synthesizing Ni and Pd complexes supported by carbene and nitrogen based ligands to promote this chemistry. Electrochemical and other mechanistic studies are elucidating the molecular design principles that drive efficient CO_2 activation. We are also investigating homologous systems, which incorporate hydrogen bonding functionalities to assist the activation of CO_2 . Initial studies have shown that ditopic molecular clefts incorporating protonic functionalities can decrease the overall reorganization energy associated with formation of reduced CO_2 adducts and conversion to high-energy species. Our continuing work in this area is aimed at incorporating these molecular design principles into robust catalyst systems for liquid fuel production.

Development of New Molecular Scaffolds for Multielectron Photochemistry



In developing a research program centered on the molecular chemistry of renewable energy, we are pursuing new catalysts

ANDREW V. TEPLYAKOV

Covalently Attached Macromolecules on Semiconductor surfaces

We are interested in covalent binding of large molecules and nanoparticles onto solid substrates. Interfacing multifunctional molecules with semiconductor surfaces has a variety of applications; however, it is important to understand the selectivity of target surface reactions to produce the surface with desired functionality. In a recent work, a silicon surface modified with 1-amino-10-undecene was reacted with [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) in toluene. Two possible competing reactions for PCBM, via the ester group and by a direct attachment to the C₆₀ portion, are analyzed. The studies suggest that despite similarity of the energetics for those two reaction pathways, the predominant chemisorption occurs via the direct attachment of the C₆₀ cage to the primary amino-group of the functionalized silicon surface [1]. This work is important for sensing and organic photovoltaics. We have also investigated the biosensor model system designed based on a single-strand biotin-modified thiol-DNA attached to the silicon substrate. The binding of this thiol-DNA to the surface is performed through the crosslinker sulfo-succinimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate (SSMCC) attached to the 11-amino-1-undecene monolayer on Si(111) surface. Streptavidin-coated gold nanoparticles are used to test the reactivity of the surface and to examine the role of passivation in the entire scheme. The passivation of the remaining surface reactive sites is achieved via a reaction with 1-octadecanethiol (ODT) [2].

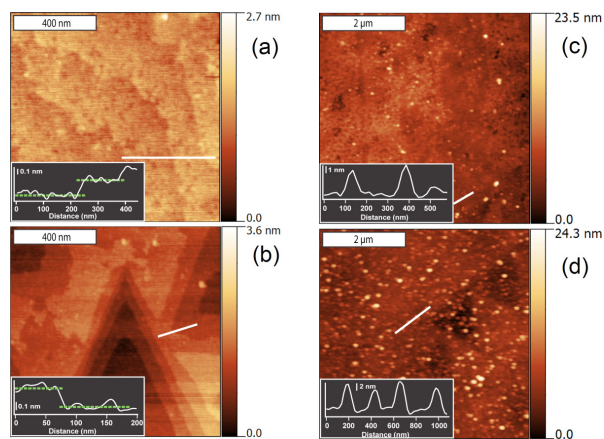


Figure 1. AFM images of: (a) H-terminated Si(111) wafer; (b) AUD-modified Si(111), (c) PCBM-terminated Si(111) wafer (exposure time 3 hours), (d) PCBM-terminated Si(111) wafer (exposure time 5 hours). The corresponding line profiles (white lines in each figure) are shown as an inset in each image [1].

Chemical Modification of Semiconductor surfaces

Semiconductor substrates are widely used in many applications. Multiple practical uses involving these materials require the ability to tune their physical (bandgap, electron mobility) and chemical (functionalization, passivation) properties to adjust those to a specific application. The goal of this research direction is to develop new strategies for manipulating the surface properties of semiconductor materials in a controlled way to control further functionalization [3,4] or deposition reactions for metalorganic precursors [5]. Our expertise allows us to selectively tune the chemical and physical properties of semiconductor surfaces

by an appropriate choice of elemental or III-V semiconductor, or by chemical modification. Computational investigations are used to reconstruct complex energy landscapes for such processes. Our approach focuses on chemical passivation, on molecular switches and on the use of a variety of functionalized self-assembled monolayers. The findings of these investigations will be relevant for future applications in molecular and nanoelectronics, sensing, and solar energy conversion.

Thin Solid Films as Hard Coatings

The main goal of this project is to develop molecular-level understanding, control, and predict chemical reactions relevant for the formation and properties of complex hard coatings based on carbides and nitrides of W, Ti, Ta. The applications of these coatings are numerous and include oil and gas and fracking technologies, where the coatings are required to withstand extreme thermal and chemical conditions. Our group has investigated a potential to use TiCN films that were initially developed for microelectronics as hard coatings and a number of very attractive properties can be obtained [6,7].

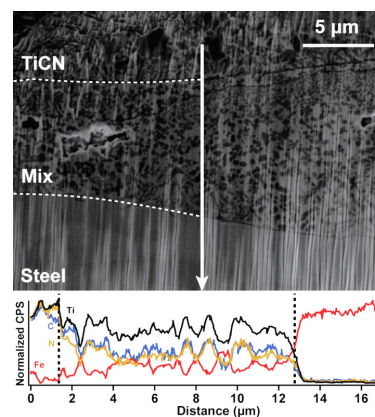


Figure 2. SEM cross-section for TiCN with linescan EDX. The white dashed line in the SEM image represents the WC coating-substrate interface. The red line shows relative Fe concentration in counts-per-second (CPS) along the linescan, the black line shows the relative Ti (CPS) along the linescan, the blue line shows the relative C (CPS) along the linescan, and the yellow line shows the relative N (CPS) along the linescan [7].

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Past investigations in my group has been directed at preparing homogeneous Cr(III) alkyls as model compounds for commercially used, and ill understood olefin polymerization catalysts – e.g., the union Carbide catalyst ($\text{Cp}_2\text{Cr}/\text{SiO}_2$) and the Phillips catalyst (Cr/SiO_2). More recently, inspired by the commercially practiced selective oligomerization of ethylene – in practice, trimerization of ethylene to 1-hexene – presumably dependent on low-valent chromium, we have investigated the preparation of highly reduced chromium compounds and evaluated their reactivity and potential as oligomerization catalysts. We generally seek to prepare well-defined homogeneous catalysts, which can be fully characterized and subjected to investigation of their reaction mechanisms.

Reduction of easily accessible halide precursors $[(\text{Ar})\text{nacnacCr}(\mu\text{-X})_2]$ ('nacnac' = β -diketiminate, $\text{X} = \text{Cl}, \text{I}$) has yielded the dinuclear complexes $[(2,6\text{-}^i\text{Pr}_2\text{Ph})\text{nacnacCr}^{\text{I}}]_2(\mu_2\text{-}\eta^6\text{:}\eta^6\text{-C}_6\text{H}_6)$ (**1**) and $[(2,6\text{-}^i\text{Pr}_2\text{Ph})\text{nacnacCr}^{\text{I}}]_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-N}_2)$ (**2**) and the mononuclear $(2,6\text{-}^i\text{Pr}_2\text{Ph})\text{nacnacCr}^{\text{I}}(\eta^2\text{-C}_2(\text{SiMe}_3)_2)$. Compound **2** features three-coordinate Cr^{I} with an 11-electron configuration. Gratifyingly, **2** was found to catalyze the selective trimerization of ethylene to 1-hexene. When a THF solution of it – coordinating solvent – is exposed to ethylene at ambient temperature and pressure, it steadily and selectively produces 1-hexene (see Figure 1).^[1] When the ethylene is used up, the only remaining organometallic product is the unusual dinuclear ethylene complex $[(2,6\text{-}^i\text{Pr}_2\text{Ph})\text{nacnacCr}^{\text{I}}]_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-C}_2\text{H}_4)$ (**3**, see Figure 2)

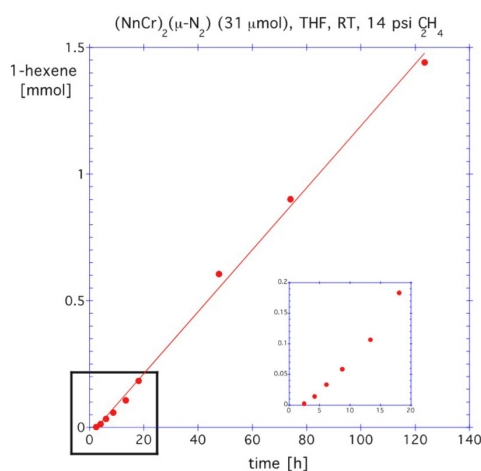


Figure 1. Formation of 1-hexene by selective trimerization of ethylene catalyzed by **2**.

We had proposed a potential catalytic cycle depending entirely on dinuclear intermediates – i.e., alternating between Cr(I) and Cr(II) – instead of the commonly accepted mechanism involving mononuclear intermediates. However, we have now ruled this out by showing that i) isolated **3** does not react with ethylene, and ii) the product forming step, a reductive

elimination of 1-hexene from a dinuclear hexenyl hydride is likely to face an unusually high activation barrier

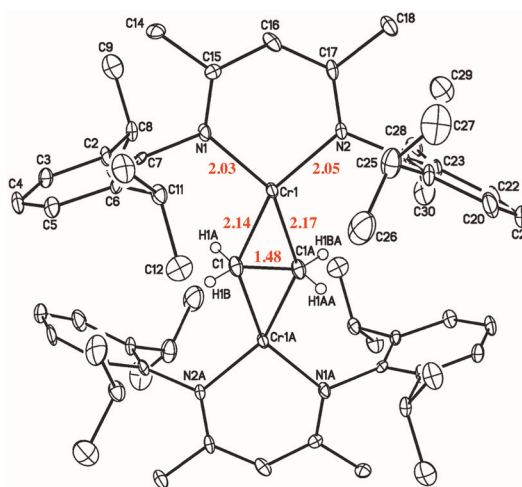


Figure 2. The molecular structure of ethylene complex **3** (selected interatomic distances in Å).

At this point, we are reconsidering the widely accepted mononuclear mechanism, and we have prepared relevant catalytic intermediates (e.g. chromocyclopentanes), and compounds that serve as close models for such species.^[1] We are in the process of investigating the catalytic properties of these compounds.

[1] W. H. Monillas, J. F. Young, G. P. A. Yap, K. H. Theopold, "A well-defined model system for the chromium catalyzed selective oligomerization of ethylene", *Dalton Trans.* 2013, 42, 9198.

DIONISIOS G. VLACHOS

The Vlachos group works at the interface of catalysis and reaction engineering. We perform multiscale simulations and kinetic experiments in vapor and liquid phase, in batch and continuous flow mode. We fabricate microreactors and put together devices. Major research thrusts are described next.

Predictive microkinetic modeling.

In our group we lead the construction of detailed reaction mechanisms for catalytic reactions of simple and complex chemistries along with their experimental validation. We employ first-principles density functional theory (DFT) calculations and develop DFT-based semi-empirical thermochemistry and kinetics methods for rapid parameter estimation in conjunction with high throughput reactor computing and experiments. Examples of reactions include dehydrogenation, hydrogenation, reforming, catalytic combustion, selective oxidation, water-gas shift, hydrodeoxygenation, isomerization, dehydration (Figure 1), and cycloaddition of both traditional feedstocks and renewables. We focus primarily on single metal and bimetallic supported catalysts, zeolites, and their combinations. Our models can predict the active site and effects of size, shape, and support.

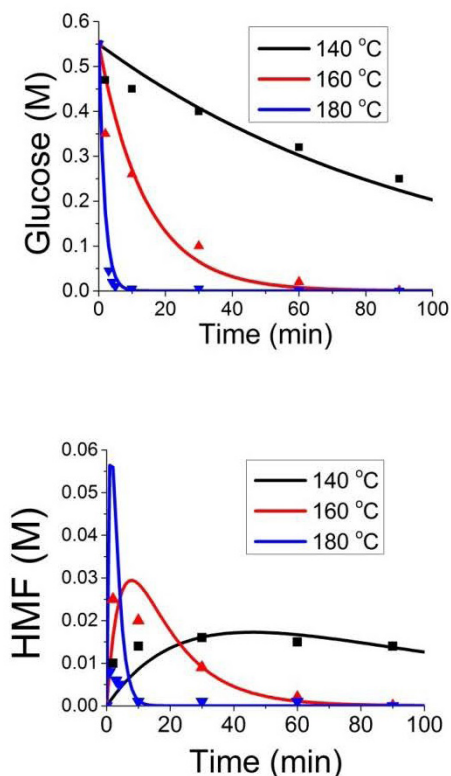


Figure 1. Example of microkinetic model prediction vs. experimental data of acid-catalyzed (HCl) dehydration of glucose to hydroxymethyl furfural (HMF).¹

Computation-driven Prediction of New Catalysts.

We develop a framework for multiscale model-based catalyst selection to improve activity, selectivity, and stability.

Our approach blends development of descriptor-based microkinetic models, execution of an optimization problem, and catalyst informatics. Alternatively, we combine mid-throughput experiments and catalyst informatics to come up with improved catalysts and by doing so to bypass the development of kinetic models (Figure 2). We have demonstrated experimentally the power of this framework for core-shell bimetallic catalysts in various chemistries including reforming, dehydrogenation, hydrodeoxygenation, and complete oxidation (Figure 2) and proved its feasibility for microporous acid catalysts.

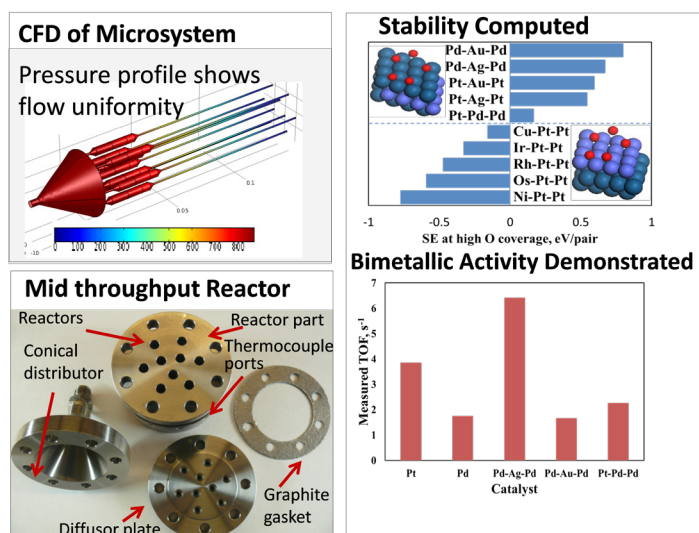


Figure 2. CFD design of mid throughput microreactor and picture of fabricated microreactor for high-precision kinetics.² Single metal catalysts are experimentally screened and numerous core-shell bimetallics are down selected using computational methods for activity and stability. Core-shell structures tested experimentally for propane total oxidation showing superior performance to Pt.³

Biomass processing.

We develop catalysts, kinetics (Figure 1), and processes for biomass processing and specifically for the conversion of ligno-cellulosic sugars to furans and a variety of chemicals and fuels, such as alkylated furans, aromatics, and diesel-size ethers. We attempt to understand solvent effects and how to select catalysts and solvents for specific processes.

References:

1. L. Yang, G. Tsilomelekis, S. Caratzoulas, and D. G. Vlachos, Mechanism of Brønsted-acid Catalyzed Glucose Dehydration. Submitted, (2014).
2. N. R. Peela, I. C. Lee, and D. G. Vlachos, Design and Fabrication of a High-Throughput Microreactor and Its Evaluation for Highly Exothermic Reactions. Ind. Eng. Chem. Res. 51(50), 16270-16277, (2012).
3. N. R. Peela, W. Zheng, I. C. Lee, A. M. Karim, and D. G. Vlachos, Core-Shell Nanocatalyst Design by Combining High-Throughput Experiments and First-Principles Simulations. ChemCatChem 5(12), 3712-3718, (2013).

DONALD A. WATSON

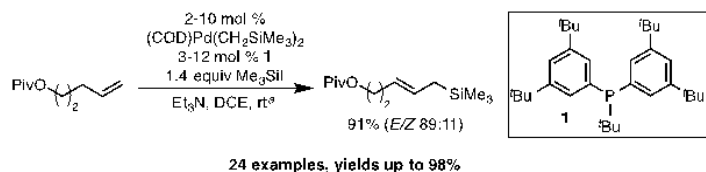
Our research program is broadly focused on the development of transition metal catalysts for applications in organic synthesis and alternative energy. We are developing catalytic methods that allow high-value organic molecules to be prepared from inexpensive and abundant starting materials. We are particularly interested in inventing new reactions for the stereocontrolled introduction of heteroatoms, such as silicon and nitrogen, in rapid fashion. We are also employing principles of catalyst design and organometallic catalysis to prepare novel materials for use as catalysts in alternative fuel preparation and energy storage.

For example, we are developing cross couplings of electrophilic silanes for the synthesis of allyl and vinyl silanes. Allyl and vinyl silanes are extremely important reagents in organic synthesis. Typical syntheses require multiple steps and involve highly functionalized starting materials. We recognized that a transition metal-catalyzed Heck-type process involving electrophilic silanes and alkenes would provide a single-step entry into both allyl and vinyl silanes from simple and abundant starting materials.

Our initial efforts (Angew. Chem. Int. Ed., 2012) focused on establishing the synthetic viability of the silyl-Heck reaction through the development of more reactive catalysts. Our studies revealed that palladium catalysts supported by tBuPPh₂ were uniquely active. This catalyst system enabled the silylation of numerous styrene and styrene-like heterocyclic compounds using Me₃SiH, providing trans-vinyl silanes in outstanding yields. Importantly, this catalyst allowed the use of limiting alkene and only modestly elevated temperatures (50 °C), allowing high functional group tolerance. This catalyst also enabled the previously unknown silylation of terminal alkenes bearing allylic hydrogen atoms (α -olefins) to provide allyl silanes with high allyl:vinyl selectivity and modest to good yields (Chemical and Engineering News in April 2012).

We have recently developed a second-generation catalyst that improves the yield of allyl silane (J. Am. Chem. Soc. 2014). Using a rational approach to ligand design, we have found that the larger and more electron-rich ligand **1** dramatically improved the results, giving allyl silanes often in near-quantitative yields (Scheme 1).

Scheme 1. Second-Generation Silyl-Heck Catalyst.



Recognizing that vinyl siloxyethers are highly useful in Hiyama cross-couplings, we have also developed conditions to prepare these valuable intermediates (J. Am. Chem. Soc., 2013). The silyl-Heck reaction provides a high yielding and completely

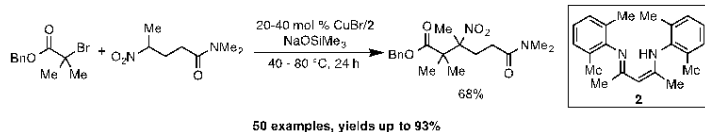
regioselective means of accessing these reagents from simple alkenes.

We have also demonstrated that silyl-Heck reactions can be carried out using nickel catalysis. These reactions allow the use of silyl triflates, which are more commercially abundant than silyl iodides but do not react under palladium-catalyzed conditions, and enable preparation of vinyl silanes with silyl groups larger than Me₃Si. This work recently appeared as an invited article in Tetrahedron.

We also have established catalytic reactions for the C-alkylation of nitroalkanes. Nitroalkanes are highly valuable intermediates in organic synthesis, but despite this vast reactivity, the seemingly simple alkylation of nitroalkanes with alkyl electrophiles (such as alkyl halides) has remained a highly challenging task; nitroalkanes undergo alkylation at oxygen, ultimately leading to aldehydes.

We discovered that the combination of CuBr and the easily accessed diketimine ligand (nacnac) successfully over-turn the inherent selectivity in the alkylation reaction and catalyzed the benzylation of nitroalkanes at carbon in high yield (J. Am. Chem. Soc., 2012). This process proved to be highly general with respect to both nitroalkane and benzyl bromide, as well as very functional group tolerant.

Scheme 2. Formation of β -Nitrocarbonyls via Copper-Catalyzed Alkylation of Nitroalkanes.



More recently we have reported a highly general entry into β -nitrocarbonyl compounds using a nearly identical catalyst system and readily available α -bromocarbonyls (Scheme 2, Org. Lett., 2014). This strategy is an attractive alternative to Mannich disconnections for making β -aminocarbonyl products, particularly because the nitro group is often available as a handle for further C–C bond-forming reactions. *We expect this new catalytic method will allow facile preparation of a variety of classes of biologically active compounds that are widely used in medicine and biology.*

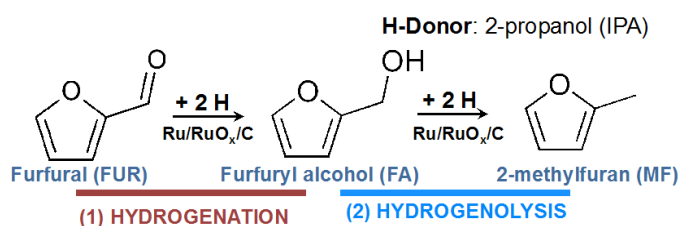
The surging global energy demand and the increasingly disruptive impact of climate change have set two general trends in motion: 1) the transition from carbon-intensive fossil fuels to carbon-neutral renewable fuels; and 2) the development of highly efficient energy conversion and storage devices. As an enabling technology, catalysis will play an increasingly important role in the global economy and the well being of the society.

The central theme of research in Xu Group is to develop efficient heterogeneous catalytic and electrocatalytic processes via rational design of (electro)catalysts. In-situ spectroscopies and isotopic labeling techniques are employed to achieve molecular understanding of the adsorption, and bond-forming processes on the catalysts surface. The new mechanistic insights are then applied to tailor catalysts for chemical and energy applications.

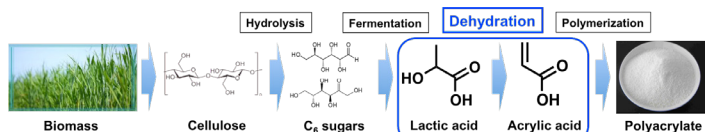
Upgrade biomass to fuels and chemicals

Non-food based lignocellulosic biomass is an abundant, accessible and carbon-neutral energy source, a key element to a renewable energy future. Through a series of catalytic steps, the complex biopolymers present in plants can be converted to liquid fuels and value-added chemicals. We aim to developing efficient catalysts for two specific reactions: 1) hydrodeoxygenation of oxygenated furanics, and 2) selective dehydration of lactic acid to acrylic acid.

Hydrodeoxygenation (HDO) of oxygenated furanics. The chemical versatility of oxygenated furanics such as 5-hydroxymethylfurfural (HMF) and furfural renders them as a platform from which many useful molecules can be derived. For example, the removal of the hydroxyl and carbonyl groups in these oxygenated furanics leads to reduced furanics such as 2,5-dimethylfuran (DMF) and 2-methylfuran (2-MF), which are valuable chemical intermediates and potential fuel additives. Vlachos and collaborators have identified Ru/RuO_x/C as an active and selective catalyst for this reaction via the catalytic transfer hydrogenation pathway. Through a series of carefully designed isotopic labeling experiments, we demonstrate that there are two key steps in the conversion of furfural to 2-MF: the hydrogenation step to furfuryl alcohol (FA) proceeds primarily via the MPV mechanism, whereas the subsequent hydrogenolysis step is likely to proceed via both direct hydrogenolysis and ring activation mechanism. The insight that the coexistence of metallic and Lewis acid sites is key to achieve high yield of 2-MF opens up the possibility of designing non-precious metal/Lewis acid composite catalysts for this reaction.

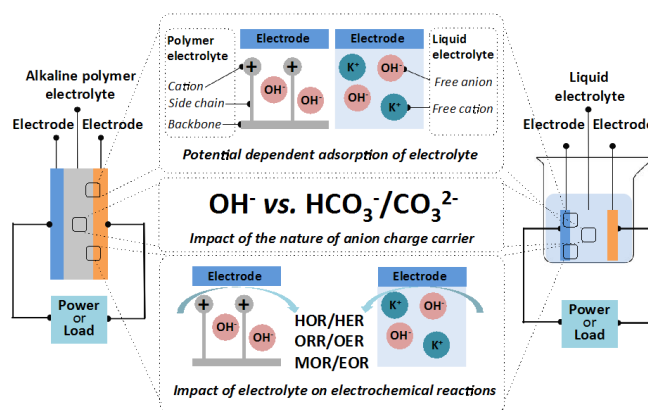


Selective dehydration of lactic acid to acrylic acid. Catalytic dehydration of lignocellulosic biomass-derived lactic acid has the potential to become an economical and renewable route to produce acrylic acid. Acrylic acid and its esters are key precursors for the polymer industry. The multifunctional nature of lactic acid and its esters indicates that very specific interactions between the α -hydroxyl group and the catalyst are needed. Through reactivity and in-situ transmission FTIR studies, we have shown that the sodium cations in faujasites zeolites can protect the carboxylic acid group by forming sodium lactates upon adsorption of lactic acid or its esters. The Bronsted acid sites formed in-situ are likely to play a key role in facilitating the dehydration reaction. We are in the process of developing bifunctional catalysts with both acid and base sites tailored to the selective dehydration reaction of lactic acid and its esters.



Understanding electrochemical interfaces via in-situ spectroscopy

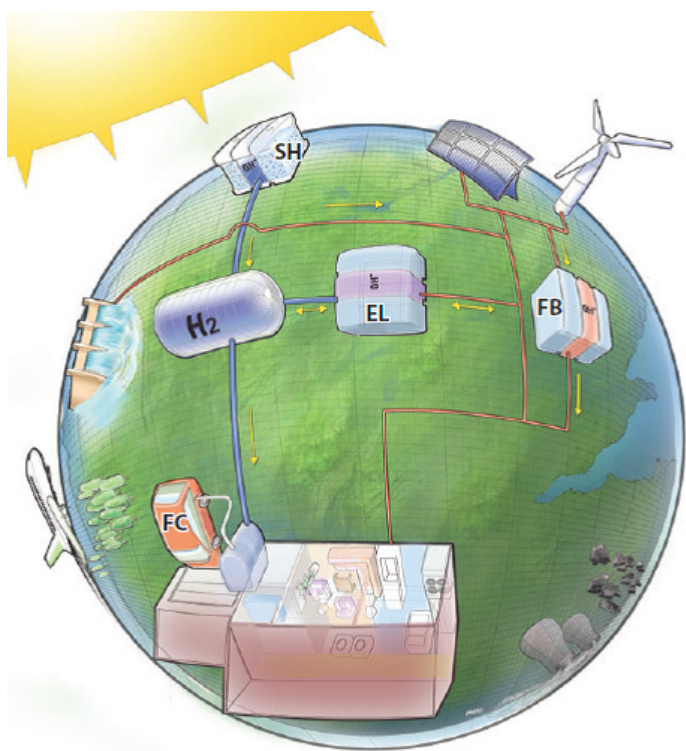
The electrochemical interface is the place where the key components of electrochemical reactions converge, interact and diverge. The multifunctional character of electrochemical interfaces leads to the (over)emphasis on optimizing individual components of electrochemical interfaces, with the assumption that optimal performance can be achieved by individual component optimization. However, liquid and polymer based electrolytes in many cases lead to different catalysts performance under otherwise identical conditions, strongly suggesting cations attached to the polymer electrolytes adsorb and interact with electrocatalysts, reactants and intermediates quite differently compared to that of solution. Understanding the processes occurring at the interfaces at the molecular level are necessary steps towards the rational design of highly efficient electrochemical interfaces, and electrochemical devices. We are in the process of developing in-situ surface sensitive spectroscopic tools to probe the interaction between polymer electrolytes and its impact on key electrochemical reactions such as hydrogen oxidation reaction (HOR), oxygen reduction reaction (ORR) and alcohol oxidation reactions (AOR).



YUSHAN YAN

Nanostructured Materials for Energy, Environment, and Electronics

One of the grand challenges facing humanity today is a safe, clean, and sustainable energy system where combustion is no longer the dominant method of energy conversion. We propose that electrochemical energy conversion could set the foundation for such an energy system. We further suggest that a simple switch from an acid to a base membrane coupled with innovative cell designs may lead to a new era of affordable electrochemical devices, including fuel cells, electrolyzers, solar hydrogen generators, and redox flow batteries. With this vision as a goal, we have been working on developing new polymer hydroxide exchange membranes and *nonprecious metal catalysts* for durable and affordable fuel cells and electrolyzers. We have also designed new redox flow batteries that can couple redox pairs and electrolyte pHs that were impossible to integrate in a single cell.



An integrated, safe, clean, and sustainable electrochemical energy system based on fuel cells (FCs), solar hydrogen generators (SHs), electrolyzers (ELs), and redox flow batteries (FBs). With minor variations, all the aforementioned electrochemical devices share the same basic three-layer structure: electrode/membrane/electrode. Gu, Xu, Yan Annu. Rev. Chem. Biomol. Eng. 2014. 5:429–54

FACULTY HIGHLIGHTS

Douglas J. Buttrey

- Plenary Speaker for the 3rd International Symposium on Advanced Electron Microscopy for Catalysis (EMCat2014), Seon Monastery, Bavaria, 3-6 September, 2014
- Invited Speaker for the 6th Irsee Symposium on Selective Oxidation Catalysis, Irsee, Germany, 2013.
- Keynote Speaker for the 7th World Congress on Oxidation Catalysis, Saint Louis, MO, 2013
- Scientific Committee for the 7th World Congress on Oxidation Catalysis, Saint Louis, MO, 2013
- Visiting Professor, African University of Science and Technology (AUST), Abuja Nigeria, Summer 2013

Wilfred Chen

- Biotechnology Progress Award for Excellence in Biological Engineering Publication, 2012
- Fellows, American Institute for Medical and Biological Engineering (AIMBE), 2011
- Gore Professor of Chemical Engineering, January 2011-Present

Feng Jiao

- National Science Foundation CAREER Award, 2014
- "A General Synthetic Approach for Ordered Mesoporous Metal Sulfides", Journal of the American Chemical Society, 2014

Raul F. Lobo

- Plenary Speaker at the International Zeolite Conference, Moscow, 2013
- Named Claire de Le Clare Professor, 2014
- Two Top 50 Most Cited Articles in Catalysis Journals (Elsevier), 2013
 - » "The ammonia selective catalytic reduction activity of copper-exchanged small-pore zeolites", 2011
 - » "Investigation into the shape selectivity of zeolite catalysts for biomass conversion", 2011

Joel Rosenthal

- Alfred P. Sloan Research Fellow in Chemistry, 2014
- NSF CAREER Award, 2014
- Camille and Henry Dreyfus Environmental Chemistry Mentor, 2014
- Division of Inorganic Chemistry – Undergraduate Research Mentor Award, 2014
- Presidential Symposium Speaker at 248th ACS National Meeting & Exposition, San Francisco, CA, August, 2014

- Named a 2013 "Mover and Shaker" by The Catalyst Review, Volume 26, Issue 12, December 2013

Andrew V. Teplyakov

- "Semiconductor surface functionalization for advances in electronics, energy conversion, and dynamic systems", 2013
- "Silicon surface functionalization targeting Si-N linkages", Langmuir 2013
- Invited LaMattina Lectureship at the Department of Chemistry, University of New Hampshire (Durham, NH), 2014

Yushan Yan

- Outstanding Alumni Lecture, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 2011
- Distinguished Engineering Professor, University of Delaware, 2011

Dionisios G. Vlachos

- Renewable Chemicals and Fuels from Biomass, Gordon Research Conference, Catalysis: From Art to Science, New London, NH, 2014
- Modern catalytic technologies for converting biomass to renewable fuels and chemicals, Plenary lecture for the conference, Advanced Materials, Energy and Sustainability, 64th Canadian Chemical Engineering Conference (CSCHE 2014), Niagara Falls, Ontario, 2014
- Heteroepitaxial materials in the energy arena: self-assembly, control, and emergent properties, 2014-2015 ICI Distinguished DB Robinson Lectureship Series at the University of Alberta, Department of Chemical and Materials Engineering, 2014.
- Multiscale Simulation of Chemical Reactions and Reactors: Combinatorial Complexity, Uncertainty, and Emergent Behavior, 2014-2015 ICI Distinguished Lecture, DB Robinson Lectureship Series at the University of Alberta, Department of Chemical and Materials Engineering, 2014
- Insights into the Interplay of Lewis and Brønsted Acid Catalysts in Glucose and Fructose Conversion to 5-(Hydroxymethyl)furfural and Levulinic Acid in Aqueous Media. J. Am. Chem. Soc. 135(10), 3997-4006, (2013)
- Cascade of Liquid-Phase Catalytic Transfer Hydrogenation and Etherification of Hydroxymethylfurfural to Potential Bio-diesel Components over Lewis Acid Zeolites. ChemCatChem 6(2), 508-513, (2014)
- N. R. Peela, W. Zheng, I. C. Lee, A. M. Karim, and D. G. Vlachos, Core-Shell Nanocatalyst Design by Combining High-Throughput Experiments and First-Principles Simulations. ChemCatChem 5(12), 3712-3718, (2013)

FACULTY & STUDENT NEWS

Two Novel CO₂ Reduction Catalysts Discovered by CCST Faculty

This past year was an exciting year in the development of effective catalysts for the reduction of CO₂ into CO in the presence of water.

Joel Rosenthal in the Department of Chemistry and Biochemistry developed an inexpensive bismuth-based catalyst that can utilize electricity generated from solar energy to convert carbon dioxide, a major greenhouse gas, into chemical fuels. They have further developed these catalysts to make them easier and safer to prepare. At this point, the group has increased their activity such that they can now be used to convert CO₂ and renewable energy to conventional fuels with rates and efficiencies that are better than those displayed by traditional precious metal catalysts such as gold and silver.

The work is published in a paper in the *Journal of the American Chemical Society* (JACS), "Efficient Reduction of CO₂ to CO with High Current Density Using in Situ or ex Situ Prepared Bi-Based Materials," co-authored by postdoctoral researcher Jonnathan Medina-Ramos and Ph.D. student John DiMeglio.

The development of efficient and robust cathode materials that can promote the rapid conversion of CO₂ to CO is a key step on the road to the storage and conversion of renewable energy inputs to liquid carbon-based fuels. Initially Rosenthal group faced the problem that the process used to prepare the bismuth-based material involved the use of highly acidic solutions, which are corrosive and therefore incompatible with many energy storage platforms. Now, as reported in the JACS paper, they have discovered that an organic solvent, rather than caustic hydrochloric acid, can be used to form a thin-film catalyst directly on an inexpensive carbon or metal electrode.

Feng Jiao's group, in the Department of Chemical and Biomolecular Engineering, recently developed a highly selective silver catalyst also capable of electrochemically converting carbon dioxide to carbon monoxide with 92 percent efficiency and reported this finding in *Nature Communications*. He has recently received the CAREER Award from NSF that provides new funding for exploring the use of bimetallic catalysts for converting carbon dioxide (CO₂) to carbon monoxide (CO).

Bimetals are materials composed of two separate metals that, when joined together, interact to produce properties not achievable with a single metal. In a previous report, Jiao used computational modeling to identify bimetallics for producing hydrogen fuel. He will use a similar approach to pinpoint combinations of metals useful for electrochemically reducing CO₂ to CO.

He also will develop new structural characterization methods and monitor the bimetal's surface reactions in real time using X-ray absorption spectroscopy and electrochemical liquid transmission electron microscopy. This will create experiential evidence to explain what's happening on the metal's surface.

2014 Eastman Chemical Student Award

Nima Nikbin was the recipient of the 2013 Eastman Chemical Student Award. Nima's work deals with the applications of quantum chemical calculations and theoretical chemistry to the analysis of catalysis problems of biomass derived molecules. He has investigated the difficult problem of understanding the molecular basis for catalytic activity and selectivity in the liquid phase for molecules as complex as fructose. This award recognizes his research accomplishments and the breath of his research activities. As a result of this award, Nima will give a summary of recent research results at the next CCST Annual Research Review and will receive a plaque and a gift at the Annual Review.



Nima Nikbin, recipient of the 2013 Eastman Chemical Student Award. Pictured above (l-r) is Professor Raul Lobo, Nima Nikbin, and Eastman Representative, Zhufang Liu.

CCST's advisory board provides feedback on past accomplishments and suggestions on future research directions. We extend our sincere appreciation to our board members for their time and assistance in this important endeavor.

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