A general synthetic method for MPO₄ (M=Co, Fe, Mn) frameworks using deep-eutectic solvents --- Feng Jiao et al.
The Center for Catalytic Science and Technology (CCST) continues to be a leader in catalysis research with substantial efforts in new catalyst discovery, the application of state-of-the-art characterization techniques, and the development of novel computational methods. You have probably noticed the rapid growth in the number of scientific journals devoted to all aspects of catalysis research across the globe. I am glad to report that the CCST’s research has a prominent presence in these new publications as well as the more established catalysis journals.

This publication describes some of our most important discoveries reported in 2011-2012, and shows a sample of the intense research activities conducted at the CCST. Our research environment remains dynamic and highly interactive. We continue to attract first-rate students who recognize that CCST is a place that not only fosters innovation, but also nurtures the innate research capacity of the students.

I would like to extend a warm welcome to our newest colleague, Wilfred Chen, the Gore Professor of Chemical Engineering at the University of Delaware (UD). Wilfred joined the Department of Chemical and Biomolecular Engineering at UD in 2011. Prior to joining Delaware, he was professor in the Chemical and Environmental Engineering Department at the University of California, Riverside. Wilfred’s research focuses on the development of the next generation of biomolecular tools needed for biofuel production including biocatalysts. We believe the future will see an increased synergy between biocatalysis and classical catalysis in order to meet future technological challenges. We are excited that Wilfred will play a key role in leading CCST in this direction.

I also extend my gratitude to the Eastman Chemical Company for sponsoring our 2012 Spring Seminar Series that featured distinguished seminar speakers who gave enlightening presentations, and also for sponsoring the Eastman Chemical Student Award. This year’s award will be presented to Weiting Yu during our Annual Research Review for her important discoveries in the reforming of small oxygenates on bimetallic and carbide surfaces. Last year’s award recipient was Mike Salciccioli.

We encourage you to contact us with questions or comments, and we hope you will visit our center either in person or via our web site (www.che.udel.edu/ccst). We look forward to continuing fruitful collaborations with each of you—our institutional partners, industrial sponsors and scientific colleagues.

With best regards,

Raul Lobo
CCST Director

Industrial Sponsors Program
Our Industrial Sponsors Program embodies the principal mechanisms for industry-university cooperation as they have evolved over the Center’s three decades of operation. The tangible benefits of such cooperation are many and include joint research programs, publications, and patents, as well as significant opportunities for support through established industry-university cooperative research funding mechanisms.

Benefits of Sponsorship
CCST sponsors benefit from the full portfolio of the Center’s research activities including a number of programs designed to provide early access to nonproprietary research:

Access to CCST Facilities
- Sample analysis
- Discounted rates for experiments
- Use of CCST software

Faculty Expertise
- Consultation by CCST faculty

Recruitment
- Recruitment of outstanding students

Research Programs and Activities
- Invitation to the Center’s annual research review at which the results of ongoing research programs are presented by center faculty and students
- Annual report of the Center’s research activities and accomplishments

CCST Seminars
- Invitation to Center seminars by catalysis experts from around the world

FROM THE DIRECTOR

Raul F. Lobo
Chemical & Biomolecular Engineering

RESEARCH INTERESTS
Synthesis, characterization and discovery of novel microporous materials and structure property relationships in catalysts and adsorption.
Welcome new CCST Faculty, Wilfred Chen

Mark A. Barteau
Chemical & Biomolecular Engineering
RESEARCH INTERESTS
Surface science and catalysis by metal oxides and metals; acid-base catalysis; application of density functional theory to surface reactions; self-assembly of inorganic materials; scanning probe microscopies

Feng Jiao
Chemical & Biomolecular Engineering
RESEARCH INTERESTS
Energy storage and conversion, advanced lithium-ion batteries, solar energy harvesting, and synthesis of nanostructure materials

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

Michael T. Klein
Chemical & Biomolecular Engineering
www.che.udel.edu/klein
RESEARCH INTERESTS
Chemical Reaction Engineering with special emphasis on the kinetics of complex systems

Jingguang Chen
Chemical & Biomolecular Engineering
RESEARCH INTERESTS
Synthesis and characterization of metal carbides and bimetallic alloys as low-cost catalysts and electrocatalysts.

Raul F. Lobo
Chemical & Biomolecular Engineering
RESEARCH INTERESTS
Synthesis, characterization and discovery of novel microporous materials and structure property relationships in catalysts and adsorption.

Wilfred Chen
Chemical & Biomolecular Engineering
RESEARCH INTERESTS
Cellular and metabolic engineering, synthetic biology for biofuel production, protein therapeutics, viral detection, drug discovery, protein purification.

S. Ismat Shah
Materials Science & Engineering
RESEARCH INTERESTS
Nanosctructured materials synthesis via PVD and CVD processes with applications to environmental catalysis and energy generation

Douglas J. Doren
Chemistry and Biochemistry
RESEARCH INTERESTS
Theoretical and computational methods with applications to materials science, surface science, catalysts and sorbation

Andrew V. Teplyakov
Chemistry and Biochemistry
RESEARCH INTERESTS
Experimental and computational surface and thin film chemistry, diffusion barriers, nucleation, growth, self-assembly, surface modification.

Yushan Yan
Chemical & Biomolecular Engineering
RESEARCH INTERESTS
His research focuses on new materials for fuel cells, energy storage and solar hydrogen generation and zeolite thin films for semiconductors and aerospace applications.

Dougliss F. Taber
Chemistry and Biochemistry
RESEARCH INTERESTS
Stereoselective synthesis of natural products, organometallic catalysis, computational organometallic chemistry

Klaus H. Theopold
Chemistry and Biochemistry
RESEARCH INTERESTS
Homogeneous catalysis, coordination polymerization of olefins, activation of oxygen by novel oxidation catalysis

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.

Donald A. Watson
Assistant Professor of Chemistry
RESEARCH INTERESTS
Transition-metal catalysis; organic synthesis; alternative energy chemistry

Yuslan Yen
Chemical & Biomolecular Engineering
RESEARCH INTERESTS
His research focuses on new materials for fuel cells, energy storage and solar hydrogen generation and zeolite thin films for semiconductors and aerospace applications.
RECENT PUBLICATIONS

BARTEAU GROUP


CHEN GROUP


DOREN GROUP

Binding of styrene on silicon (111)-7 x 7 surfaces as a model molecular electronics system, Weiland, CR; Yang, L; Doren, DJ; Menning, CA; Willis, JI; Zhao, Z.; Jiao, F.; Doren, DJ; Lobo, RF. Structure and Electronic Properties of Spinel Zinc Gallium Oxonitrides, Boppana, VBR; Schmidt, WA; Doren, DJ; Journal of Physical Chemistry B 115, 249-261 (2011).


LOBO GROUP


KLEIN GROUP


continued


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Insight into On-Wafer Crystallization of Pure-Silica-Zeolite Films through Nutrient Replenishment, Lew, Christopher M.; Liu; Yan; Kisailus, David; Kloster, Grant M.; Chow, Gabriel; Boyanov, Boyan; Sun, Minwei; Wang, Junlan; Yan, Yushan, Langmuir 27 7, pp. 3283-3285, APR 5 2011. Dynamic Hydrothermal Synthesis of a b-Oriented MFI Zeolite Film, Li Xianming; Wang Zhengo; Zheng Jie; Shao Shiqun; Wang Yinchao; Yan Yushan, Chinese Journal of Catalysis 32 2, pp. 217-223, FEB 2011. High-Performance Zeolite Membranes on Inexpensive Large-Pore Supports: Highly Reproducible Synthesis using a Seed Paste, Wang; Zhengo; Ge; Qiong; Gao; Jingsi; Shao; Jia; Liu, Chunjie; Yan, Yushan, ChemSusChem 4 11, pp. 1570-1573; 2011. Self-cross-linking for dimensionally stable and solvent-resistant quaternary phosphonium based hydroxide exchange membranes, Gu, Shuang; Cai, Rui; Yan, Yushan, Chemical Communications 47, 10, pp. 2856-2858, 2011.

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Insight into On-Wafer Crystallization of Pure-Silica-Zeolite Films through Nutrient Replenishment, Lew, Christopher M.; Liu; Yan; Kisailus, David; Kloster, Grant M.; Chow, Gabriel; Boyanov, Boyan; Sun, Minwei; Wang, Junlan; Yan, Yushan, Langmuir 27 7, pp. 3283-3285, APR 5 2011. Dynamic Hydrothermal Synthesis of a b-Oriented MFI Zeolite Film, Li Xianming; Wang Zhengo; Zheng Jie; Shao Shiqun; Wang Yinchao; Yan Yushan, Chinese Journal of Catalysis 32 2, pp. 217-223, FEB 2011. High-Performance Zeolite Membranes on Inexpensive Large-Pore Supports: Highly Reproducible Synthesis using a Seed Paste, Wang; Zhengo; Ge; Qiong; Gao; Jingsi; Shao; Jia; Liu, Chunjie; Yan, Yushan, ChemSusChem 4 11, pp. 1570-1573; 2011. Self-cross-linking for dimensionally stable and solvent-resistant quaternary phosphonium based hydroxide exchange membranes, Gu, Shuang; Cai, Rui; Yan, Yushan, Chemical Communications 47, 10, pp. 2856-2858, 2011.

RESEARCH
PHOTOCATALYTIC OXYGEN EVOLUTION
Faculty: Feng Jiao (Chemical & Biomolecular Engineering) Graduate students: Self Vusil, Gregory Hutchings (Chemical & Biomolecular Engineering) Oxygen evolution from water is the critical reaction for solar fuel production, because a solar-driven system needs a high flux, clean and abundant source that is capable of completing the redox cycle for producing either hydrogen (from H2O) or carbonaceous fuels (from CO2) on a timescale. In our lab, we recently demonstrated that the morphology and crystal structure have negligible effect on the photocatalytic properties of MnO2-based oxygen evolution catalysts, which else turnover rate is proportional to its surface area (i.e. MnO2 sites available on the surface). To further enhance the turnover frequencies (TOF) that limited by surface area, surface active site with a higher TOF rate compared with MnO2 is required. Along this direction, we introduce K+ doped MnO2 catalysts into oxygen evolution reaction. By doping MnO2 with K+, we create Mn2+ sites on the surface of mixed manganese oxides. Our preliminary data show that more than one order higher oxygen evolution rates per surface Mn were observed. In order to explore the origin of the enhancement in oxygen evolution activity, detailed structural characterizations have been performed and the results indicate that Mn2+ sites generated by K+ doping may be responsible for the high TOFs.

CoPO4 structures. Water usually plays a critical role in organic template decomposition and accelerates phase transition in cobalt phosphate system. The charge disposition and the size of the decomposing organic template have delicate influence on the coordination behaviors of different metal ions. Judicious choice of atomic solvent is important to prepare different transition metal phosphates. Among all the as-synthesized MPO4 compounds, four new metal phosphate frameworks, MnPO4-DFT, DEL-1, DEL-2 and DEL-3, are reported for the first time. This work provides us a new synthetic approach for design and preparation of transition metal phosphate materials, which opens great opportunities in many important applications.

NANOPOROUS METAL PHOSPHATES
Faculty: Feng Jiao (Chemical & Biomolecular Engineering) Graduate students: Bryan Yonenoto, (Chemical & Biomolecular Engineering) Recently, ionothermal synthesis was introduced to the preparation of zeolite and metal-organic frameworks by Morris and his co-workers. The utilization of ILs and DES as solvents to replace traditional aqueous solutions in material synthesis offers new opportunities in synthesis of inorganic solids with unique frameworks, which cannot be obtained through other methods due to highly ionic environment under synthetic conditions. Recently, we have successfully developed a general synthetic approach to synthesize a wide range of transition metal phosphate frameworks via ionothermal synthesis. Using the choline chloride/ N,N’-dimethylurea DES yields a layer CoPO4 structure (DEL-1) that phase changes to the 12-member ring DEL-2 structure. It was demonstrated that DEL-2 can further phase change to ABW (8-member ring) and HEX (6-member ring) frameworks with longer reaction times. At low temperature (10-10°C) only DEL-1 is observed, so higher temperatures are necessary to produce 3-D
For over a quarter of a century the hydrogen-terminated Si(111) single-crystalline surface has been the gold standard as a starting point for silicon surface modification chemistry. However, creating a well-defined and stable interface based on Si–N bonds has remained elusive. Despite the fact that azides, nitro compounds, and amines do lead to the formation of surface Si–N, each of these modification schemes produces additional carbon- or oxygen-containing contaminants that affect the interface properties for any further modification protocols. We describe the preparation of a Si(111) single-crystalline surface has the been characterized by infrared spectroscopy and X-ray photoelectron spectroscopy. This analysis was supplemented with DFT calculations. This newly characterized surface will join the previously established H–Si(111) and Cl–Si(111) surfaces as a general starting point for the preparation of oxygen- and carbon-free interfaces, with numerous potential applications.

HETEROGENEOUS CATALYST CONVERTS BIOMASS-DERIVED FURANS TO PARA-XYLENE FOR RENEWABLE PLASTICS WITH VERY HIGH YIELD

Biomass naturally produces furan chemical structures (five-member rings), such as 5-hydroxymethylfurfural (HMF) or dimethylfuran (DMF), when undergoing catalytic reactions. However, most of the polymers and products currently used, including packaging, clothing, and computers, require six-member ring structures. Engineers at the University of Massachusetts and University of Delaware have shown that the furan ring can be converted to a six-carbon aromatic chemical, such as p-xylene, at high yield (>75%). P-xylene is the main component in polyethylene terephthalate (PET) plastics which make up plastic bottles, adhesives, insulation and substrates in solar cell devices. This discovery bridges the gap between biomass and current petroleum-based products. The same technology can potentially be applied to most of the aromatic chemicals currently produced from non-renewable resources.

REVEALING PYROLYSIS CHEMISTRY FOR BIOFUELS PRODUCTION

Vlachos Group (Department of Chemical and Biomolecular Engineering, University of Delaware) and Tsapatsis Group (Department of Chemical Engineering, University of Massachusetts)

Next-generation biofuels production utilizes high temperatures (>1000 °F) to convert all parts of a plant to molecules similar in size to those found in fuels. A series of complex processes fracture large biomolecules containing millions of atoms into much smaller molecules with higher energy density and reactivity. While this chemical deconstruction is critical to biofuels production, for decades the fundamental chemical reactions controlling this transformation have been unknown. Researchers at the Catalysis Center for Energy Innovation (CCEI) have unmasked the complex chemistry of high-temperature biomass conversion. A novel thin film technique was developed which utilizes extremely small samples (approximately the thickness of a human hair) for precise control of the deconstruction process. Next a small molecule was identified that gives the same product distribution as cellulose and can be used to mimic the complexity of the biopolymer. These advanced experiments were then coupled with first principles simulations at very high temperatures to understand for the first time the underlying mechanisms of conversion of raw cellulose to fuels and chemicals. These findings can enable development of fundamental chemistry models for optimization of large scale deconstruction of biomass.

THE MAGIC OF TIN: CONVERTING HEMICELLULOSE BUILDING BLOCKS TO FURFURAL IN AQUEOUS MEDIA

Lobo, Sandner, and Vlachos Groups (Department of Chemical & Biomolecular Engineering, University of Delaware) and Tsapatsis Group (Department of Chemical Engineering and Materials Science - University of Minnesota)

Hemicellulose makes up a large fraction of lignocellulosic biomass. The majority of hemicellulose consists of C5 sugars (pentoses), such as xylose. Biological routes, such as conversion of xylose by yeast or micro-organisms, have not been met with much success. As a result, the key C5 furan, furfural, is currently made from xylose by sulfite acid heat treatment at high temperatures and is stripped away by steam. This is an energy intensive process, similar to the first industrial furfural production process established by Quaker Oats in 1921. CCEI researchers at the University of Delaware have recently introduced the Sn-beta zeolite as a Lewis acid to selectively isomerize xylose to xyulose in water at low temperatures. Xylulose is then dehydrated using a Bronsted catalyst to furfural. It was demonstrated that it is possible to combine two heterogeneous catalysts to achieve furfural yields approaching 90% under certain conditions using a reactive separation scheme. CCEI researchers at the University of Minnesota have further demonstrated that the Sn-beta catalyst does its magic for aldol to keto sugar isomerization, further enriching the portfolio of heterogeneous Lewis catalyzed chemistry in water introduced by the CCEI researchers in 2010.

The introduction of selective and active heterogeneous bifunctional catalysts for the transformation of xylose to furfural can be a transformative technology in efficiently utilizing hemicellulose.

Schematic representation of xylose isomerization using the Sn-beta zeolite and the xylose dehydration using a Bronsted acid catalyst.

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

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Joel Rosenthal
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Andrew V. Teplyakov
- American Chemical Society Delaware Section Award, 2012.
- Organizer of the Surface Science Session at the EAS, 2012.

Dion Vlachos

Yushan Yan
- 27th Outstanding Alumni Lecture, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 2011.
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