ChemCatBio
Chemical Catalysis for Bioenergy

Advanced Catalyst Synthesis and Characterization (ACSC) Project

Thermochemical Conversion

Susan Habas (NREL), Theodore Krause (ANL), Kinga Unocic (ORNL)

March 5, 2019

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- **Catalytic Upgrading of Biochemical Intermediates** (NREL, PNNL, ORNL, LANL, NREL*)
- **Catalytic Upgrading of Indirect Liquefaction Intermediates** (NREL, PNNL, ORNL)
- **Catalytic Fast Pyrolysis** (NREL, PNNL)
- **Electrocatalytic and Thermocatalytic CO_2 Utilization** (NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

- **Advanced Catalyst Synthesis and Characterization** (NREL, ANL, ORNL, SNL)
- **Catalyst Cost Model Development** (NREL, PNNL)
- **Consortium for Computational Physics and Chemistry** (ORNL, NREL, PNNL, ANL, NETL)
- **Catalyst Deactivation Mitigation for Biomass Conversion** (PNNL)

Industry Partnerships (Directed Funding)

- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

Cross-Cutting Support

- **ChemCatBio Lead Team Support** (NREL)
- **ChemCatBio DataHUB** (NREL)

ACSC Goal Statement

Project Goal: *Provide fundamental insight leading to actionable recommendations* for critical research challenges by leveraging world-class synthesis and characterization capabilities across multiple DOE National Laboratories

			Relevance
ChemCatBio Catalysis Projects	**Baseline**	**Future Target**	**Critical Research Challenge**
Catalytic Upgrading of Indirect Liquefaction Intermediates (IDL)	C_4 recycle conversion **22%**	**40%**	***Increase dehydrogenation activity***
Catalytic Fast Pyrolysis (CFP)	C-efficiency **33%**	**40%**	***Reduce coke formation***
Catalytic Upgrading of Biochemical Intermediates (CUBI)	Condensation yield **42%**	**50%**	***Improve C–C coupling selectivity***
Electrocatalytic and Thermocatalytic CO_2 Utilization (CO_2U)	Overpotential for C_{2+} **750 mV**	**600 mV**	***Reduce overpotential***

Project Outcome: *Accelerated catalyst and process development cycle* enabling demonstrated performance enhancements in half the time

Quad Chart Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/30/2019
- Percent complete: 80%

	Total Costs Pre FY17	**FY 17 Costs**	**FY 18 Costs**	**Total Planned Funding (FY 19-Project End Date)**
DOE Funded	–	$777 K	$1.3 M	$1.6 M
Project Cost Share				

Partners: National Laboratories: NREL (30%), ANL (34%), ORNL (34%), SNL (3%)

Universities: Purdue University, University of Kansas

Barriers addressed

Ct-E. Improving Catalyst Lifetime

Ct-F. Increasing the Yield from Catalytic Processes

Ct-G. Decreasing the Time and Cost to Develop Novel Industrially Relevant Catalysts

Objective

Address critical research challenges central to the ChemCatBio catalysis projects by leveraging the unique synthesis expertise and advanced characterization capabilities across multiple DOE National Laboratories to shorten the catalyst and process development cycle by half

End of Project Goal

Synthesize rationally designed multi-metal modified zeolite catalysts based on insights from advanced characterization and computational modeling to tune the paraffin to olefin (P:O) ratio to enable targeted fuel properties between (1) a fuel product suited to aviation gasoline having a $C_{5\text{-}7}$ P:O ratio >7.0, and (2) a fuel product suited to automobile gasoline having a $C_{5\text{-}7}$ P:O ratio <4.0.

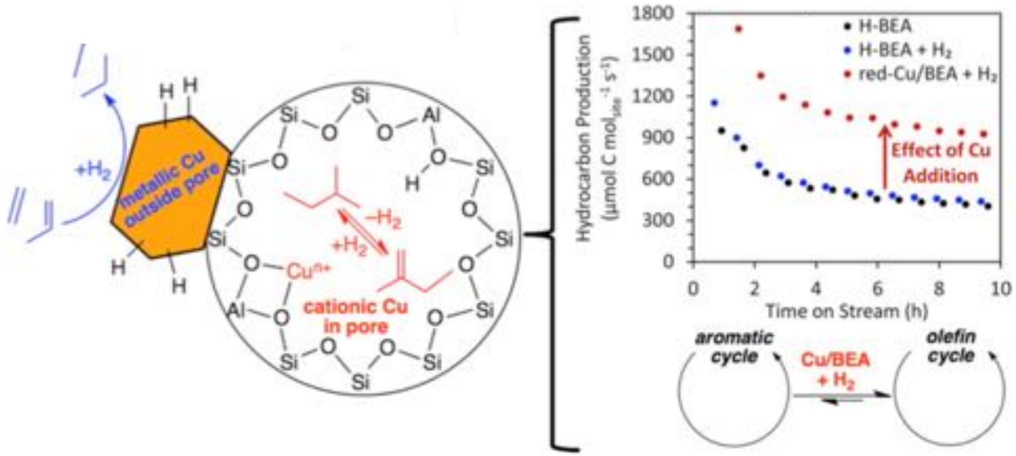
1. Project Overview – Based on Successful Collaboration

Cross-cutting enabling technologies supported by BETO in FY16

Consortium for Computational Physics and Chemistry
CCPC

Catalyst Cost Model Project
CCM, Now CatCost

Project specific access to Advanced Photon Source
APS at ANL

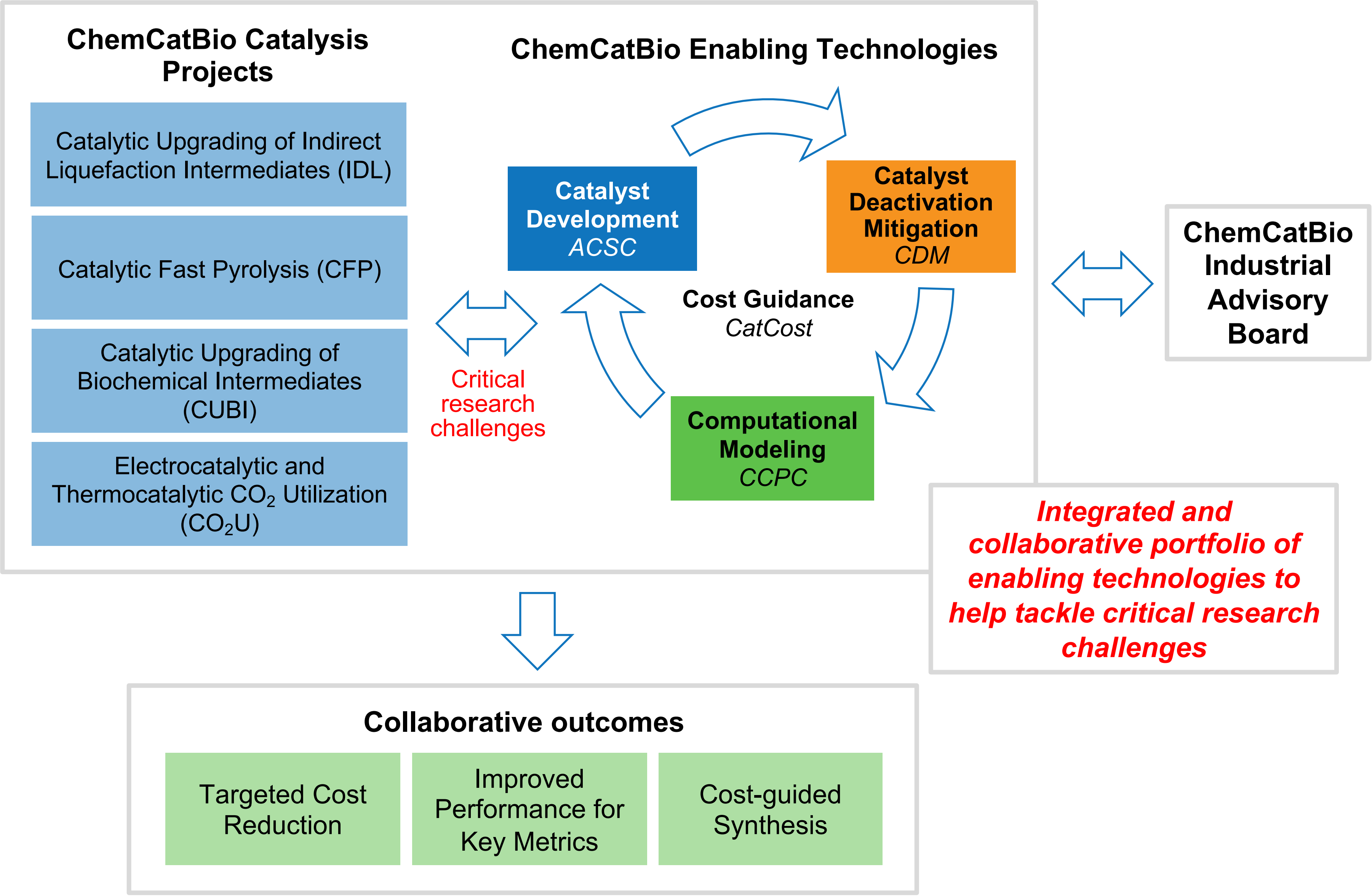


Schaidle et al. *ACS Catal.*, **2015**, *5*, 1794

Advanced characterization closely coupled with experiment led to a reduction in modeled MFSP of $1.06/GGE

Highly successful collaboration identified a need for access to advanced characterization across all projects

1. Project Overview – ACSC as an Enabling Technology



ChemCatBio Catalysis Projects

- Catalytic Upgrading of Indirect Liquefaction Intermediates (IDL)
- Catalytic Fast Pyrolysis (CFP)
- Catalytic Upgrading of Biochemical Intermediates (CUBI)
- Electrocatalytic and Thermocatalytic CO_2 Utilization (CO_2U)

Critical research challenges

ChemCatBio Enabling Technologies

Catalyst Development
ACSC

Catalyst Deactivation Mitigation
CDM

Computational Modeling
CCPC

Cost Guidance
CatCost

ChemCatBio Industrial Advisory Board

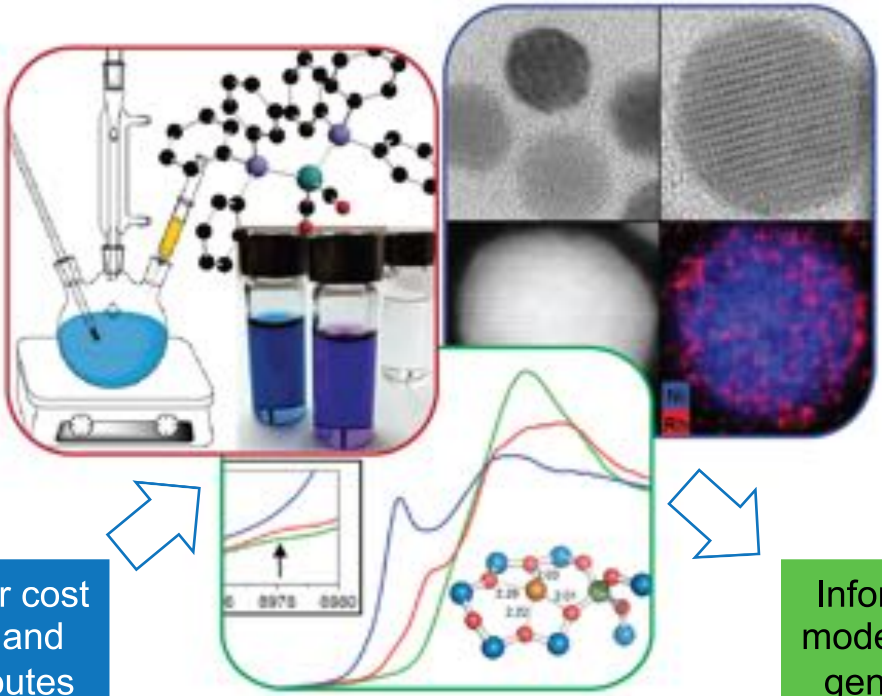
Integrated and collaborative portfolio of enabling technologies to help tackle critical research challenges

Collaborative outcomes

- Targeted Cost Reduction
- Improved Performance for Key Metrics
- Cost-guided Synthesis

1. Project Overview – ACSC Provides Complementary Efforts

World-class synthesis and characterization capabilities provide insight into working catalysts



Dedicated synthetic effort for next-generation catalysts through innovative syntheses

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Sandia National Laboratories

Advanced *spatially resolved* imaging and characterization

OAK RIDGE
National Laboratory

Identify lower cost precursors and synthesis routes

CatCost

Advanced spectroscopic techniques for *bulk and surface* structural and chemical characterization

Argonne
NATIONAL LABORATORY

OAK RIDGE
National Laboratory

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Inform computational models to predict next-generation catalysts

CCPC

1. Project Overview – ACSC Capability Portfolio

Advanced Spectroscopic Characterization

- Overall coordination environment and oxidation states in working catalyst with *in-situ/operando* XAS at APS
- Surface composition, site occupancies and distributions by neutron scattering at SNS
- Surface composition and chemical state by *in-situ/operando* XPS at KU
- Active sites and surface species including coke by *in-situ/operando* DRIFTS and Raman
- Crystalline structure by *in-situ/operando* X-ray diffraction (XRD)

Advanced Spatially Resolved Imaging and Characterization

- Spatially-resolved structures and chemical composition by *in-situ/operando* sub-Ångström-resolution STEM imaging and spectroscopy at MCC and CNMS
- Topography and composition by scanning electron microscopy and spectroscopy
- Quantitative chemical composition by XPS mapping
- 3D elemental distribution by APT
- Pore structure by 3D X-ray tomography

Advanced Catalyst Synthesis

- Metal-modified oxides/zeolites with controlled atomic sites, nanostructures and mesostructures
- Metal carbides, nitrides, phosphides
- Nanoscale materials with controlled size, morphology, composition
- Controlled surface modification
- Metal organic frameworks with independently tunable acidity and pore size

A primary mission of the ACSC is the development and demonstration of new capabilities to meet the needs of the ChemCatBio catalysis projects

2. Approach – Project Management

ACSC Project Structure

Task 1: Advanced Spectroscopic Characterization

PI: Theodore Krause (ANL)

Task 2: Advanced Spatially Resolved Imaging and Characterization

PI: Kinga Unocic (ORNL)

Task 3: Advanced Catalyst Synthesis

Lead PI: Susan Habas (NREL)

Sample handling: Designated liaisons for mature collaborations

Data management: ChemCatBio Datahub

Active Management

Monthly webinars and annual onsite meeting

Joint Milestones with ChemCatBio catalysis projects

Develop *and* demonstrate new capabilities

FY18 Go/No-Go Decision

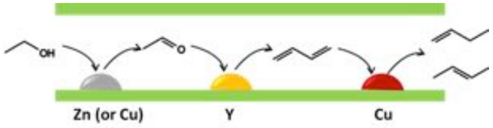
Identify capabilities to be integrated or removed

Based on current needs of ChemCatBio catalysis projects

Annual Evaluation of New/Existing Capabilities

Neutron scattering characterization

Establish metal site occupancies and distributions

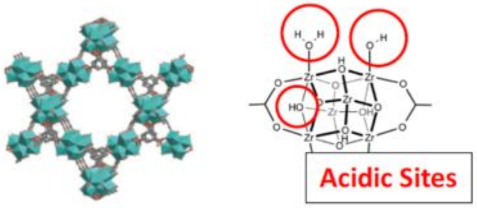


Target: Increase C_{3+} olefin selectivity from 87% to 92%

Spallation Neutron Source

Oak Ridge National Laboratory

Metal organic framework (MOF) catalyst synthesis

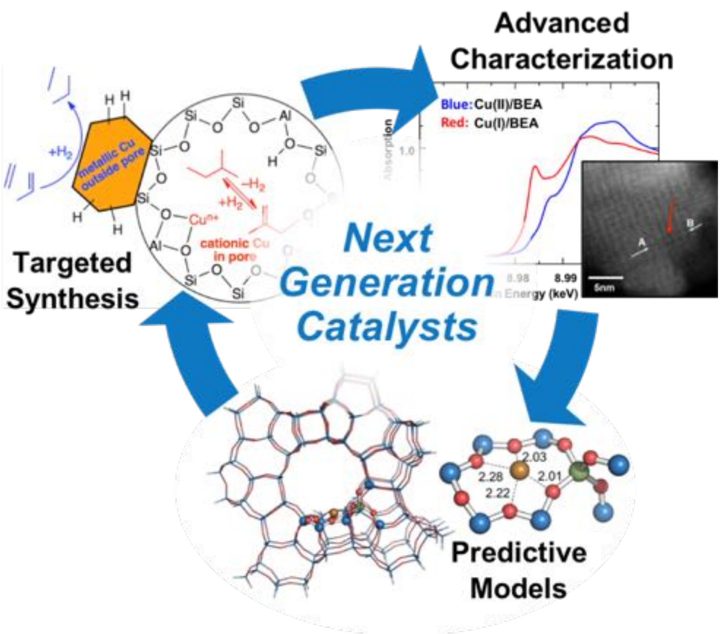


Tailor acid site characteristics and pore size to enhance C–C coupling

Sandia National Laboratories

2. Approach – Catalyst and Process Development Cycle

- **Identify** active site structures in *working catalysts* under realistic conditions
- **Inform** computational modeling to *predict active site structures* with enhanced performance
- **Develop** *next-generation catalysts* with predicted structures
- **Verify** *performance improvements* with ChemCatBio catalysis projects



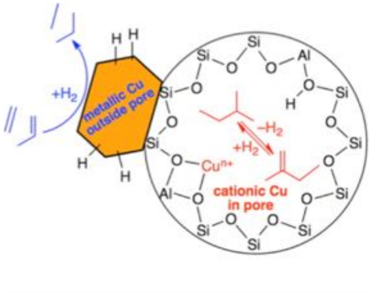
Advanced Characterization

Targeted Synthesis

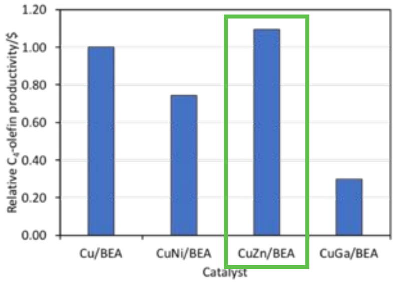
Next Generation Catalysts

Predictive Models

Baseline: *Complete* Development Cycle



3 years



Successful FY18 Go/No-Go Decision

Challenge: Assessing *Accelerated* Development Cycle

- Leverage capabilities, expertise, and models for metal-modified zeolites
- Next-generation Cu-Zn/Y-BEA with increased C_{3+} olefin selectivity (87 to 92%)
- Target: 1.5 years

Success Factor: Provide fundamental insight leading to actionable recommendations and acceleration of the catalyst and process development cycle

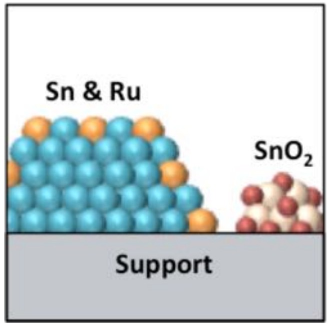
2. Approach – Supporting ChemCatBio

Catalysis projects

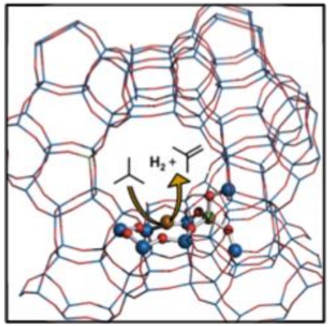
- Adapting and demonstrating new capabilities to meet specific needs of the catalysis projects
- Providing insight into working catalyst structure through focus on *operando/in-situ* techniques
- Handling complex chemistries by synthesizing model catalyst systems based on the working catalyst
- Developing joint milestones with the catalysis projects to foster frequent and consistent interaction

Foundational research

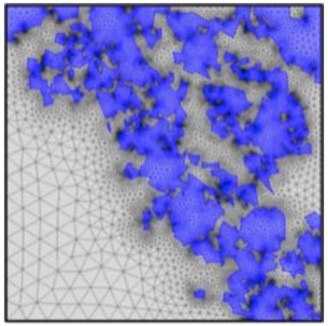
- Tackling *overarching research challenges* to enable rapid response to new critical research questions



Atomic-scale interface characterization



Metal-zeolite active site identification



Structure-stability relationship development

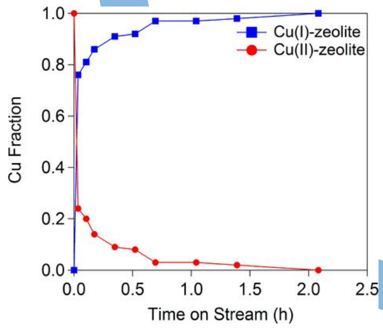
Balance overarching research challenges with specific needs of catalysis projects

3. Technical Accomplishments – Metal-Zeolite Active Sites (IDL)

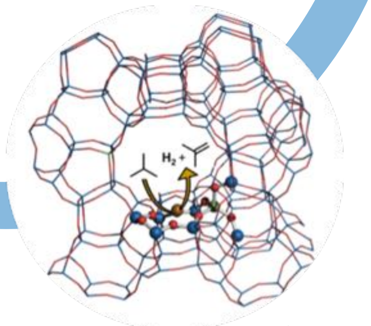
Challenge: Identify active site for alkane dehydrogenation and enable tunable control paraffin to olefin ratio from DME

Catalyst	Active site
CuO/SiO_2	CuO particles
Cu/SiO_2	Cu(0) particles
H-BEA	Brønsted acid
ox-IE-Cu/BEA	Ionic Cu(II)-zeolite
red-IE-Cu/BEA	Ionic Cu(I)-zeolite

Synthesized catalysts with active sites in working catalyst

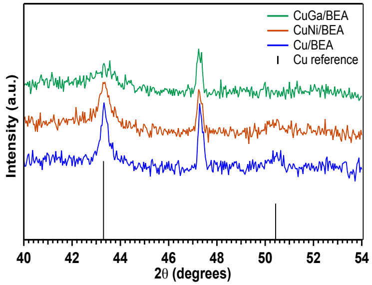


Identified Cu(I) as active site for dehydrogenation

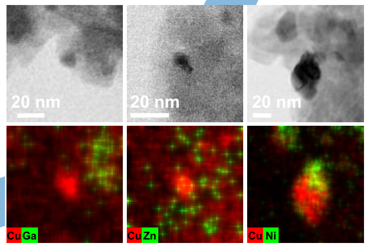


Predictive model for dehydrogenation CCPC

Outcome: Ga, Zn, Ni, Co identified as targets for next-generation catalysts to maximize dehydrogenation

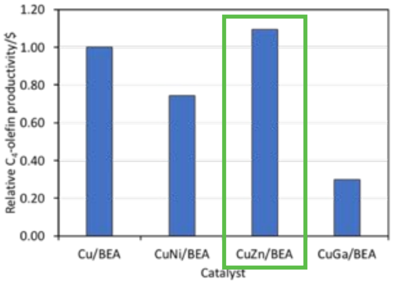


Synthetic control of speciation in bimetallic catalysts



Determined speciation in working catalysts

Verified cost-normalized performance improvements IDL, CatCost



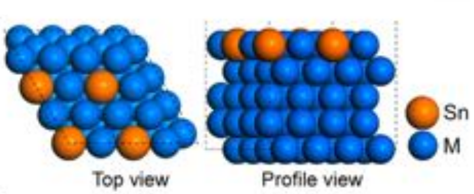
Outcome: Next-generation catalysts increased C_4 dehydrogenation > 2-fold, and bimetallic formulations tuned P:O ratio from 5.5 to 4.4

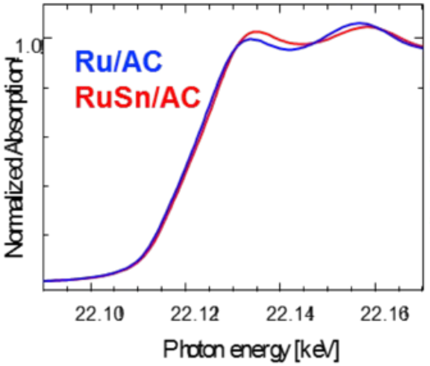
Demonstrated utility of complete catalyst and process development cycle

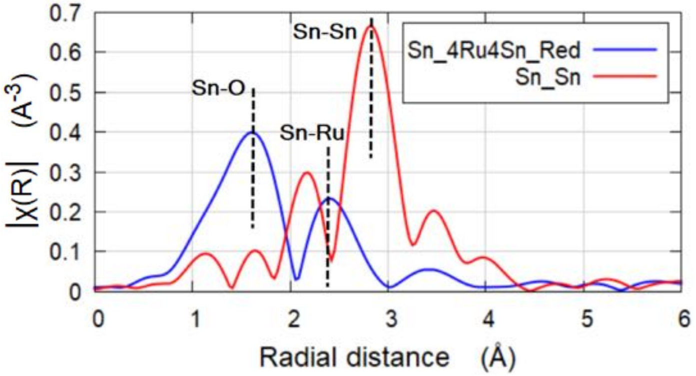
3. Technical Accomplishments – Atomic Scale Interfaces (CUBI)

Challenge: Increasing catalyst lifetime during aqueous phase succinic acid reduction to 1,4-butanediol

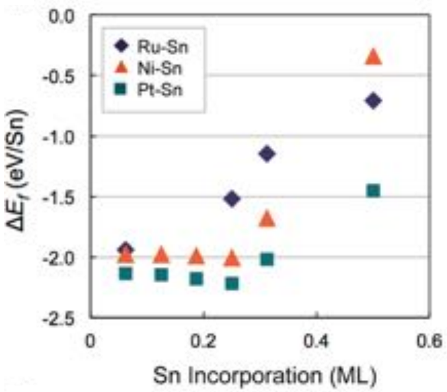
Structural model by CCPC to identify stable bimetallic configurations

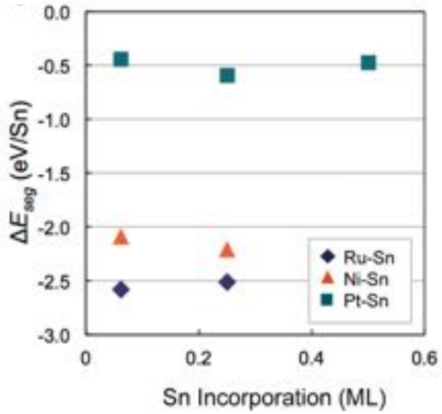


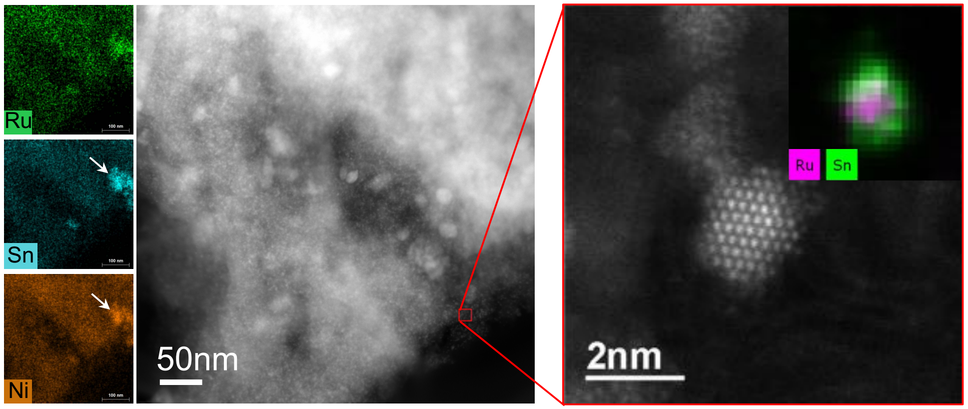




Working catalyst contains metallic Ru and oxidic Sn







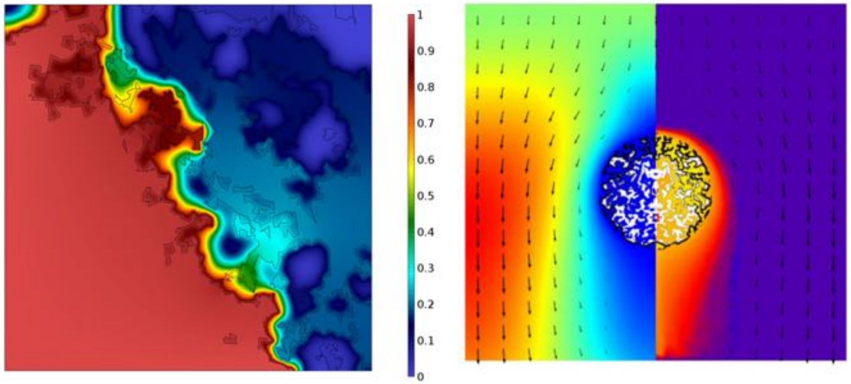
Co-localization of Ru and Sn with Ni-Sn formation from leaching leading to deactivation

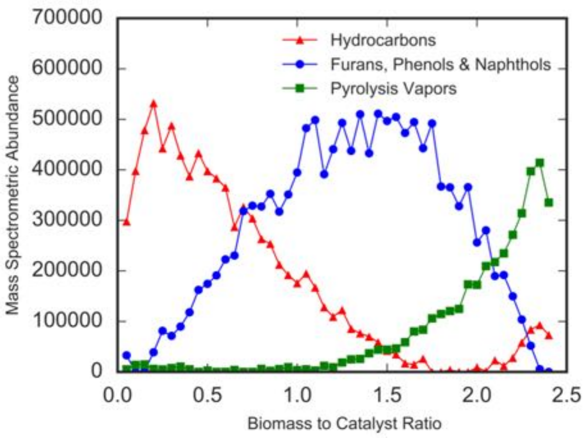
Outcome: Computationally-predicted targets based on working catalyst structure for increased catalyst lifetime

3. Technical Accomplishments – Structure-Stability Relationships (CFP)

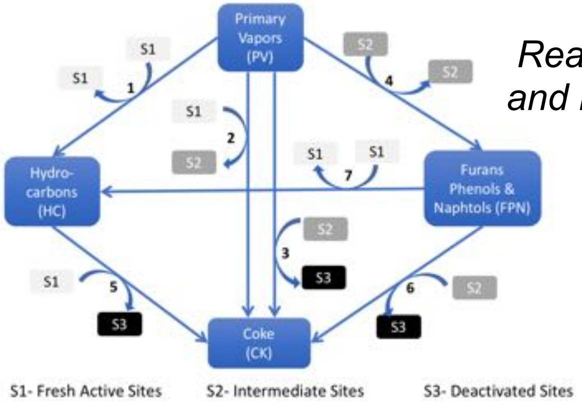
Challenge: Determine what catalyst features can be modified to minimize carbon losses to coke (8.3 wt% of dry biomass) during *ex-situ* CFP

Intra- and extra-particle diffusion and convection models developed by CCPC

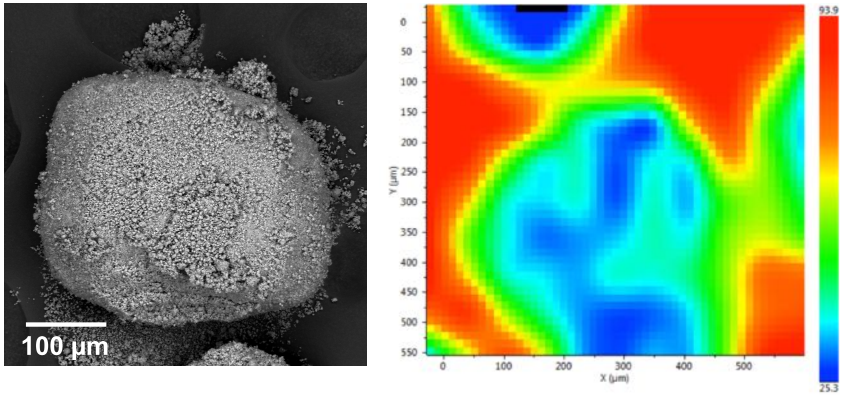




Zeolite deactivation correlated with coke formation



Reaction mechanism and kinetics for zeolite deactivation



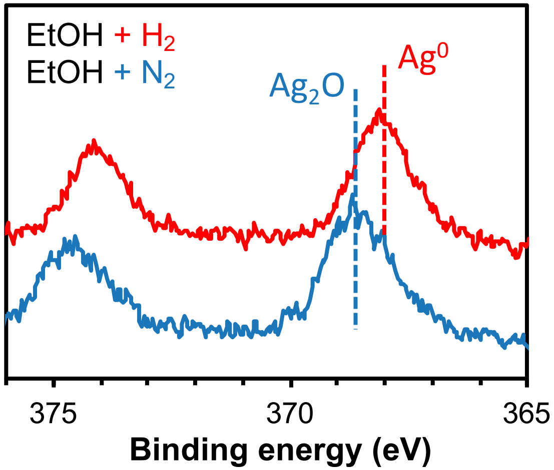
Quantify coke formation over multiple length scales in ***technical zeolites***

Outcome: Computationally-predicted targets for process conditions and key catalyst features to minimize coke formation

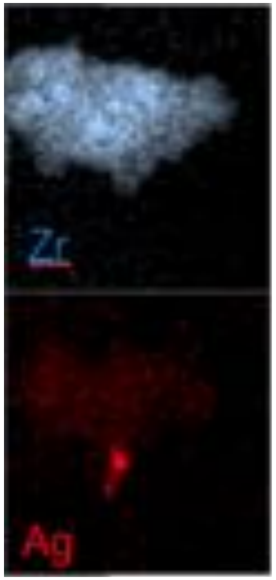
3. Technical Accomplishments – Structure-Stability Relationships (IDL)

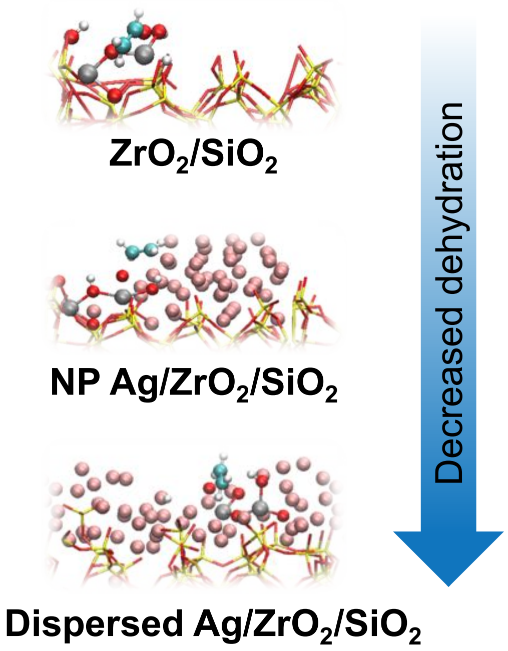
Challenge: Understanding the role of Ag in $Ag/ZrO_2/SiO_2$ to limit ethylene production and favor butadiene/butenes in ethanol to distillates process

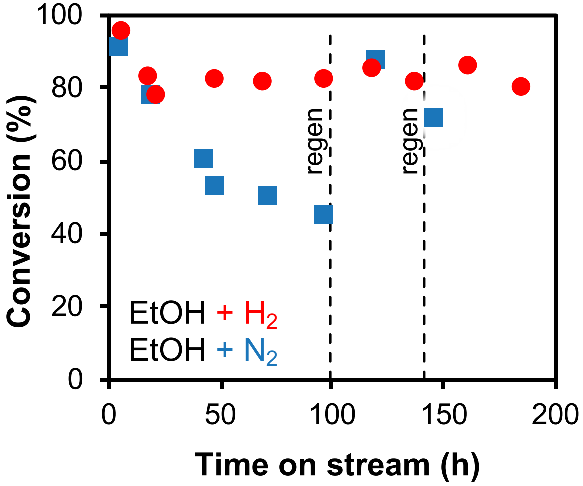
Relationship between Ag oxidation state and selectivity identified using operando XPS



Combined experimental/computation (CCPC) work suggests reducing Ag size limits dehydration to form ethylene







Co-fed H_2 forms reduced Ag, shifting products to butenes and improving catalyst lifetime

Outcome: Synthetic target identified requiring stabilization highly-dispersed Ag to minimize ethylene selectivity

4. Relevance – Bioenergy Industry

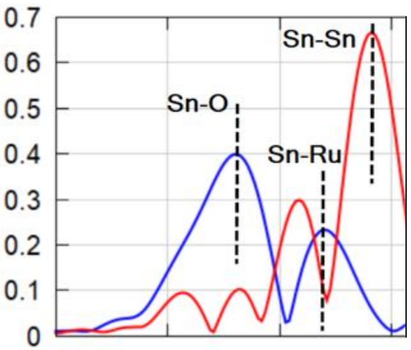
Direct interaction with industry

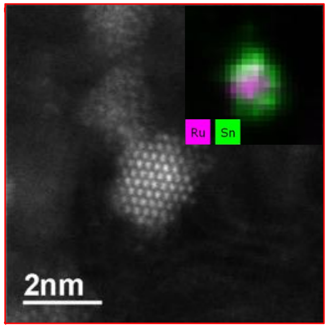
- Nearly **50% of industry collaborations** through current DFA projects are leveraging ACSC capabilities and expertise

Feedback from Industrial Advisory Board

- ChemCatBio needs to be world-class in synthesis and characterization
- It is important to develop tools and expertise for broad overarching challenges

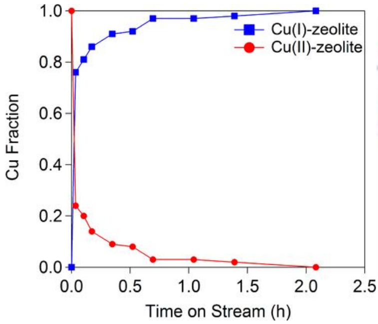
4. Relevance – Quotes from BETO MYP

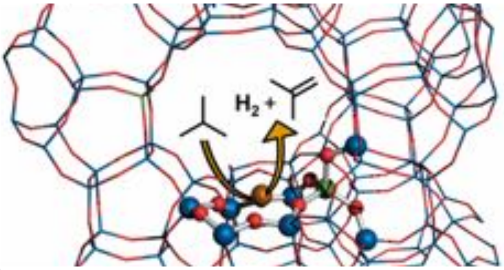




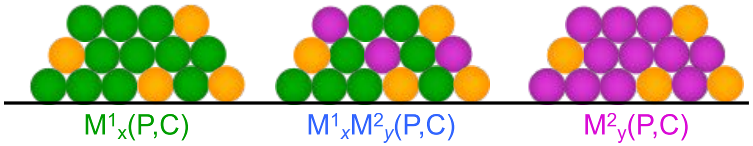
"Developing these processes should be coupled with efforts to obtain a better understanding of the causes of catalyst **poisoning and deactivation**"

"A better understanding of **catalytic active sites** and reaction mechanisms, across both low- and high temperature processes, can be obtained through advanced characterization techniques."

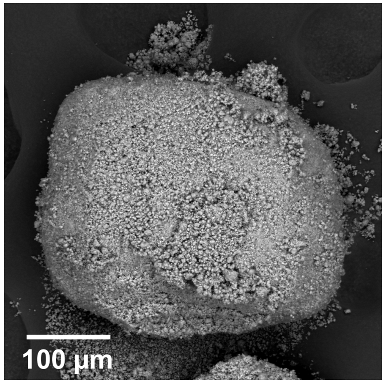


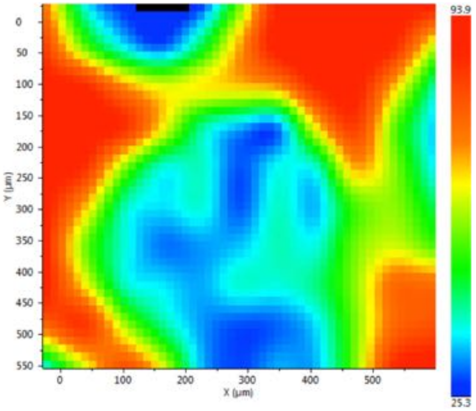


"Emerging technologies and processes may require the design and synthesis of **novel catalysts**."



The ACSC directly supports the 2022 verification by working with the CFP project to make "direct improvements to catalyst performance that **minimize the loss of carbon**"





4. Relevance – ChemCatBio

The ACSC is working with all of the ChemCatBio catalysis projects to *provide fundamental insight leading to actionable recommendations* for critical research challenges

			Relevance
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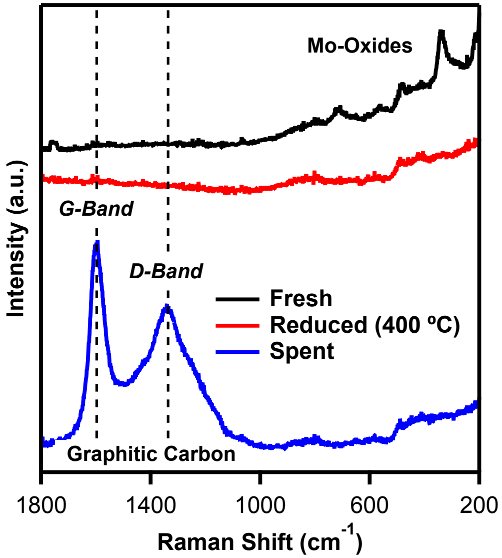
Electrocatalytic and Thermocatalytic CO_2 Utilization (CO_2U)	Overpotential for C_{2+} **750 mV**	**600 mV**	***Reduce overpotential***

Engagement with the ChemCatBio catalysis projects *accelerates the catalyst and process development cycle* enabling demonstrated performance enhancements in half the time

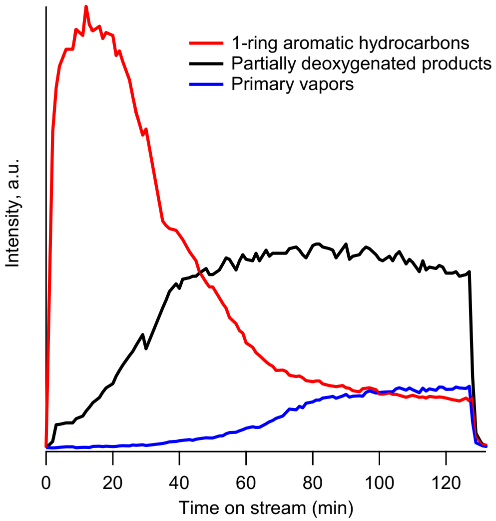
5. Future Work – Structure Stability Relationship (CFP)

Challenge: Directly measure active sites during *ex-situ* CFP to gain insight into active site evolution and deactivation mechanism

Surface carbon deposition leads to deactivation



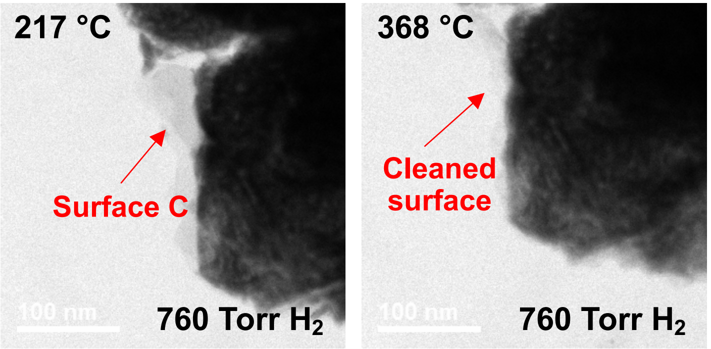
Regeneration requires costly and time-consuming ex-situ re-carburization



Apply expertise in *in-situ/operando* capability development to design/demonstrate analytical reactor system for active site quantification

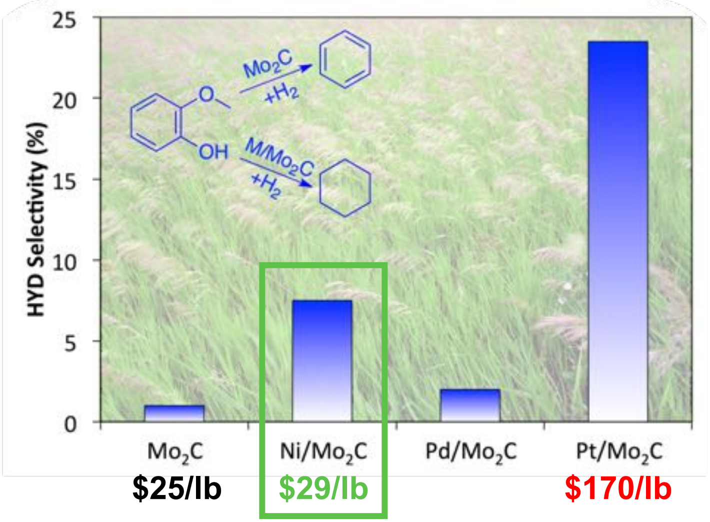
Projected Outcome: Decrease metal carbide deactivation during CFP and develop effective regeneration procedures to meet cost targets

In-situ/operando characterization to develop regeneration strategies



Surface carbon removal as CO/CO_2

Synthetic methodologies to manipulate properties associated with deactivation

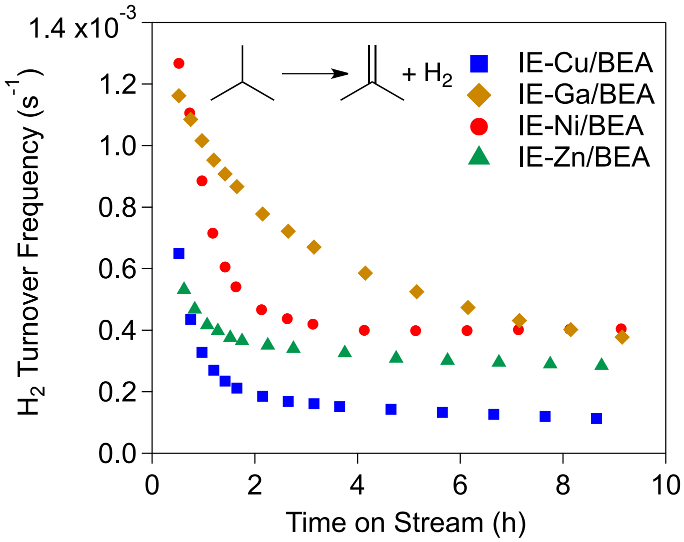


Metal modification to increase hydrogenation

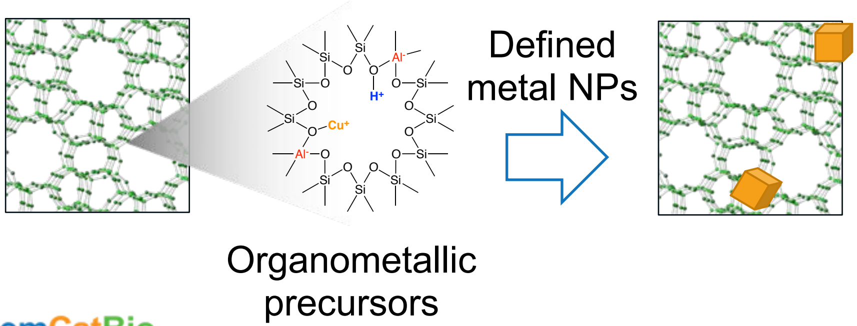
5. Future Work – Metal-Zeolite Active Sites (IDL)

End of 3-Year Goal: Rationally design bimetallic metal zeolite catalyst formulations with tailored dehydrogenation/hydrogenation activity

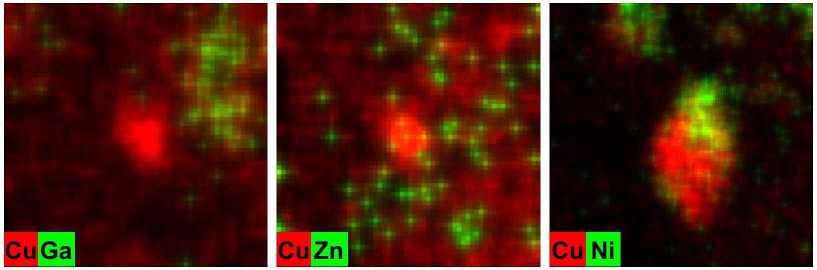
Identify precursors for key ionic species



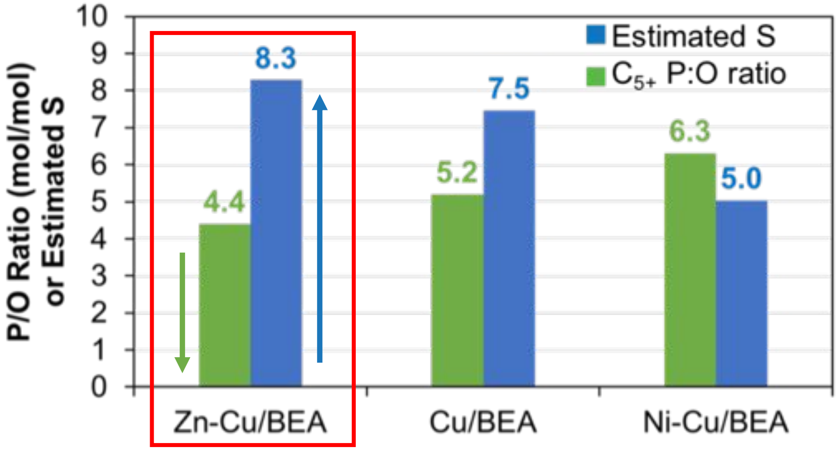
Synthetic strategies for tunable speciation



Advanced characterization to determine speciation in working catalyst



Control P:O ratio and fuel properties

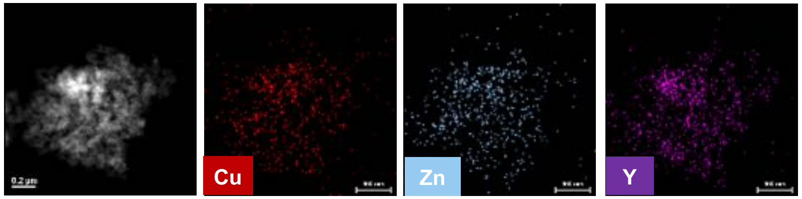


Projected Outcome: Enable targeted fuel properties between (1) aviation gasoline with C_{5-7} P:O ratio >7.0, (2) automobile gasoline with C_{5-7} P:O ratio <4.0

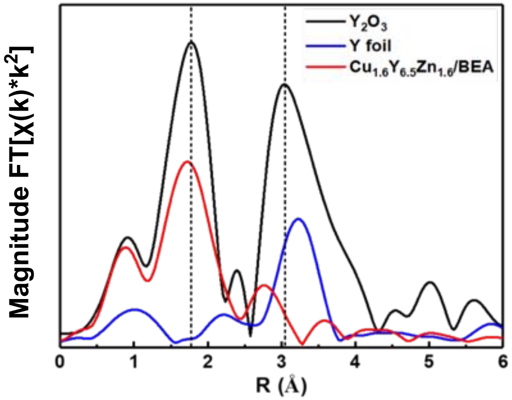
5. Future Work – Neutron Scattering (IDL)

Challenge: Can we rationally design next-generation catalyst for improved C_{3+} olefins production from ethanol?

Identify active sites with ACSC



STEM and EDS (ORNL)



EXAFS (ANL)

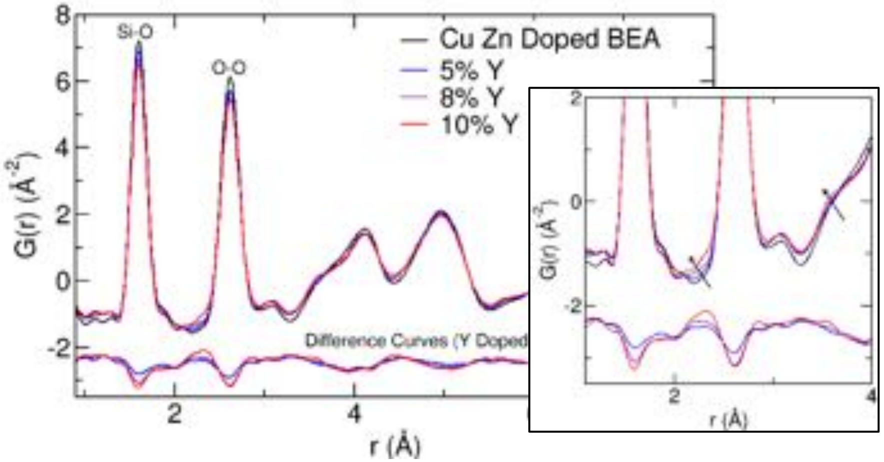
With ACSC (STEM and EXAFS):

- **Cu, Zn and Y are atomically dispersed**

Challenge: *how to find out the local metal bonding environment?*

Neutron Scattering

- **Demonstrated unique capability to identify metal local bonding**
- **Sensitive to Light Atom: H, C, O**
  - ○ Unique for biomass catalysis



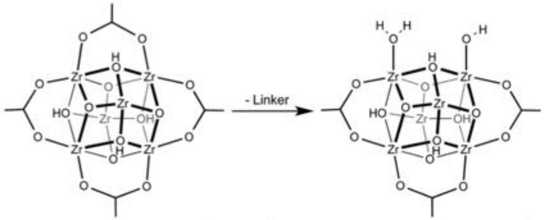
- Preliminary neutron pair distribution function (PDF) analysis shows sensitivity to metal sites
- Distinct local trends with increase in Y
- **Plan:** neutron scattering to further **elucidate the structure of active metal sites**

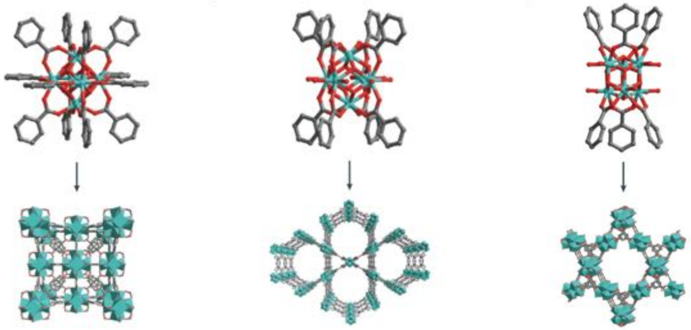
Projected Outcome: Enable the development of next-generation catalyst to increase C_{3+} olefin selectivity from 87% to 92%, increasing distillate yield and reducing MFSP.

5. Future Work – Metal-Organic Framework Catalysis (CUBI)

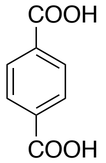
Challenge: Can we independently control the pore size and acid site characteristics using MOFs to control C–C coupling reactions?

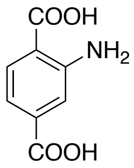
MOFs with tunable acid site concentrations and pore size





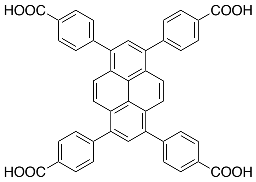
12-connected **8-connected** **6-connected**





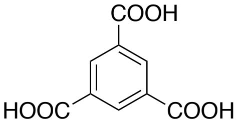
UiO-66 **UiO-66-NH$_2$**

(7 Å or 9 Å) pores



NU-1000

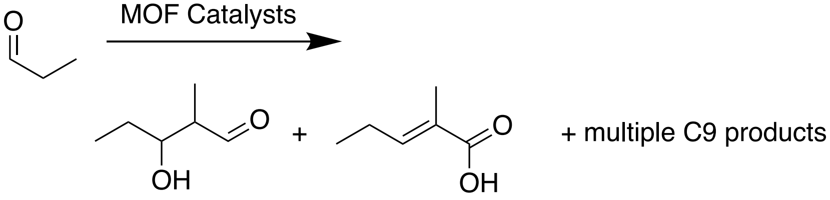
(30 Å and 15 Å pores)

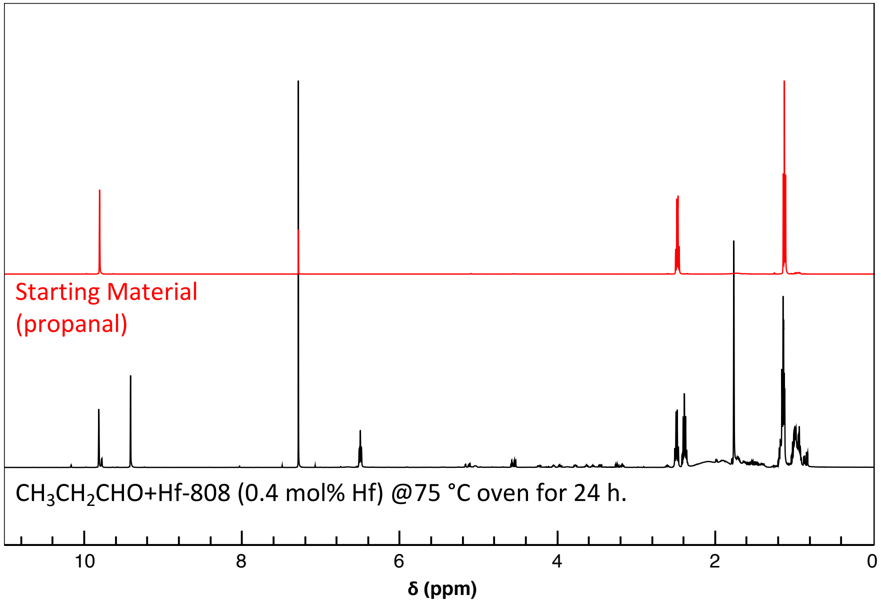


MOF-808(Zr, Hf)

(17 Å pores)

Zr-based MOFs are active for aldol reactions Reactivity is related to the number of acid sites per Zr$_6$ node





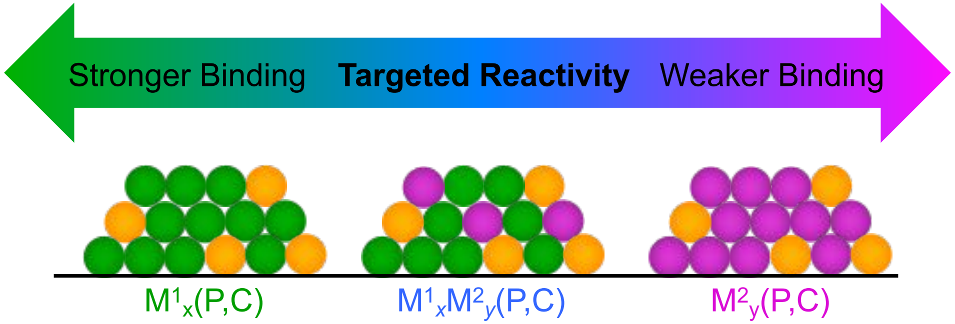
Projected Outcome: Improved selectivity and/or conversion for coupling reactions to produce at least 50 % 2-ethylhexanal (from current < 20%)

5. Future Work – Responding to New Project Needs

Electrochemical CO_2 Utilization

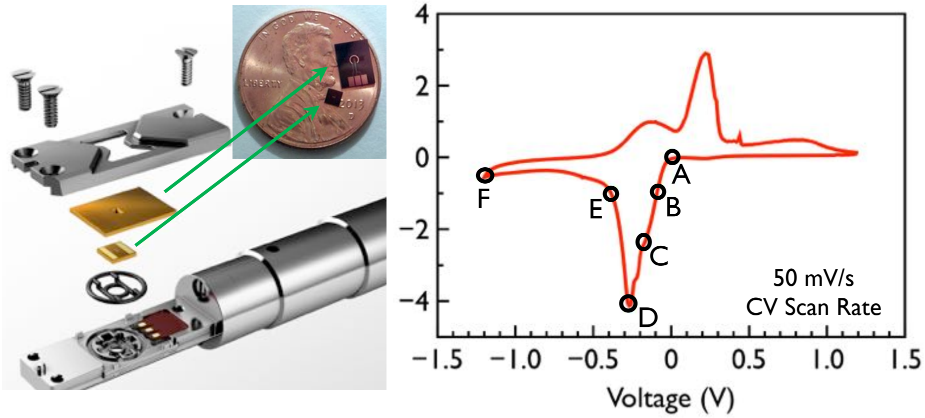
- Leverage capabilities and expertise
  - Existing ChemCatBio projects
  - National lab capabilities
  - Other EMNs
- Adapt and develop to meet needs of new projects

Tunable electrocatalyst systems



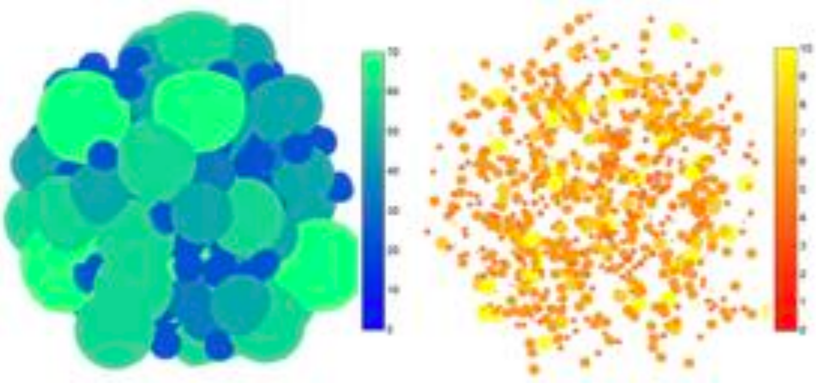
Mixed-metal phosphides and carbides (CFP)

Structure of working electrocatalyst



Electrochemical STEM (ORNL)

3D organization of working electrodes

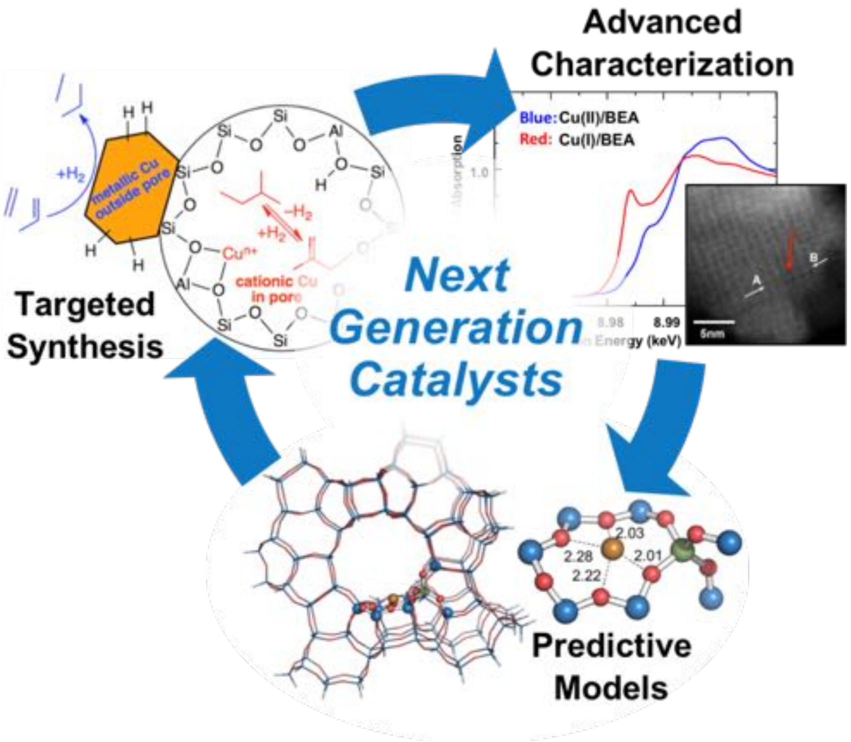


X-ray nanotomography (FCTO ElectroCat)

Summary

Project Goal: *Provide fundamental insight leading to actionable recommendations* for critical research challenges by leveraging world-class synthesis and characterization capabilities across multiple DOE National Laboratories

- Integrated and collaborative portfolio of enabling technologies to help answer *critical research questions*
- Tackling *overarching research challenges* to enable rapid response to new critical research questions
- Demonstrated utility of *complete catalyst and process development cycle* for DME to hydrocarbons pathway



Project Outcome: *Accelerated catalyst and process development cycle* enabling demonstrated performance enhancements in half the time

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Vitalie Stavila
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ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

This work was performed in collaboration with the ChemCatBio Consortium, a member of the EMN

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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Argonne NATIONAL LABORATORY

CCPC

CatCost

NREL NATIONAL RENEWABLE ENERGY LABORATORY

Sandia National Laboratories

OAK RIDGE National Laboratory

KU THE UNIVERSITY OF KANSAS

PURDUE UNIVERSITY

Supplementary Information

ChemCatBio
Chemical Catalysis for Bioenergy

Publications

- Getsoian, U. Das, J. Camacho-Bunquin, G. Zhang, J. R. Gallagher, B. Hu, S. Cheah, J. A. Schaidle, D. A. Ruddy, J. E. Hensley, T. R. Krause, L. A. Curtiss, J. T. Miller, A. S. Hock, “Organometallic Model Complexes Elucidate the Active Gallium Species in Alkane Dehydrogenation Catalysts Based on Ligand Effects in Ga K-edge XANES”, Catal. Sci. Technol., 2016, 6, 6339.
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- J. A. Schaidle, S. E. Habas, F. G. Baddour, C. A. Farberow, D. A. Ruddy, J. E. Hensley, R. L. Brutchey, N. Malmstadt, and H. Robota, “Transitioning Rationally Designed Catalytic Materials to Real ‘‘Working’’ Catalysts Produced at Commercial Scale: Nanoparticle Materials”, Catalysis, RSC Publishing, 2017, 29, 213, DOI: 10.1039/9781788010634-00213.
- C. A. Farberow, S. Cheah, S. Kim, J. T. Miller, J. R. Gallagher, J. E. Hensley, J. A. Schaidle, D. A. Ruddy, “Exploring Low-Temperature Dehydrogenation at Ionic Cu Sites in Beta Zeolite to Enable Alkane Recycle in Dimethyl Ether Homologation”, ACS Catal., 2017, 7, 3662.
- K. A. Unocic, D. A. Ruddy, T. R. Krause, S. Habas, “In situ S/TEM Reduction Reaction of Calcined Cu/BEA-zeolite Catalyst”, Microsc. Microanal., 2017, 23, 944.
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- F. G. Baddour, V. A. Witte, C. P. Nash, M. B. Griffin, D. A. Ruddy, J. A. Schaidle, “Late-Transition-Metal-Modified β-Mo_2C Catalysts for Enhanced Hydrogenation During Guaiacol Deoxygenation” ACS Sus. Chem. Eng., 2017, 5, 11433.
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- K. A. Unocic, H. M. Meyer III, F. S. Walden, N. L. Marthe, W. C. Bigelow, L. F. Allard, “Controlling Water Vapor in Gas -Cell Microscopy Experiments”, Microsc. Microanal., 2018, 24, Suppl. 1, 286-287.
- K. A. Unocic, J.S. Choi, D.A. Ruddy, C. Yang, J. Kropf, J. Miller, T.R. Krause and S. Habas, “In situ S/TEM Reduction Reaction of Ni-Mo_2C catalyst for Biomass Conversion”, Microsc. Microanal., 2018, 24, Suppl. 1, 322-323.

Presentations

- S. Habas, F. Baddour, D. Ruddy, C. Nash, J. Schaidle, “A Facile Route to Nanostructured Metal Phosphide Catalysts for Hydrodeoxygenation of Bio-oil Compounds”, Frontiers in Biorefining Meeting, St. Simons Island, GA, November 11, 2016.
- K. Unocic, T. Krause, S. Habas, “Accelerated Catalyst Development for Emerging Biomass Conversion Processes”, Physical Sciences Directorate 2017 Advisory Committee Meeting, Oak Ridge, TN, February 9, 2017.
- S. Habas, “Advances in Nanoscale Metal Phosphide and Carbide Catalysts for Biomass Conversion Applications”, University of Kansas Department of Chemical and Petroleum Engineering Seminar, Lawrence, KS, November 16, 2017.
- J.-S. Choi, “Developing Molybdenum Carbide Catalysts for Fast Pyrolysis Bio-oil Upgrading”, Invited Lecture at the Catalysis Society of Metropolitan New York Monthly Meeting, Somerset, New Jersey, February 21, 2018.
- S. Habas, F. Baddour, D. Ruddy, J. Schaidle, “Advances in Nanoscale Metal Carbide and Phosphide Catalysts for Biomass Conversion Processes”, Invited Presentation, 255th American Chemical Society National Meeting and Exposition, New Orleans, LA, March 21, 2018.
- T. Krause, C. Yang, A. J. Kropf, J. T. Miller, D. Ruddy, J. Schaidle, S. Cheah, K. A. Unocic, S. Habas, “Accelerating the Development of Catalysts for Biofuel Production Through the Application of X-ray Absorption Spectroscopy”, Invited Presentation, 255th American Chemical Society National Meeting and Exposition, New Orleans, LA, March 21, 2018.
- K. A. Unocic, J.-S. Choi, D. A. Ruddy, J. Schaidle, T. R. Krause, C. Mukarakate, M. Xu, S. Habas, In situ S/TEM Closed-Cell Gas Reactions of Catalysts: Capabilities and Opportunities”, Invited Presentation, 255th American Chemical Society National Meeting and Exposition, New Orleans, LA, March 21, 2018.
- J.-S. Choi, K. A. Unocic, Z. Wu, H. Wang, A. H. Zacher, S. E. Habas, “Durability of Molybdenum Carbide Catalysts in Reductive Upgrading of Fast Pyrolysis Bio-oil”, Invited Presentation, 255th ACS National Meeting and Exposition, New Orleans, LA, March 21, 2018.
- S. Habas, “Advances in Nanoscale Catalysts for Conversion of Biomass to Renewable Fuels”, University of Southern California Department of Chemistry Seminar, Los Angeles, CA, March 27, 2018.
- ACSC Team, “Accelerating the Catalyst Development Cycle: Integrating Predictive Computational Modeling, Tailored Materials Synthesis, and in situ Characterization Capabilities Through the ChemCatBio Consortium”, ChemCatBio Consortium Webinar, June 27, 2018.
- K. A. Unocic, “Controlling Water Vapor in Gas-Cell Microscopy Experiments”, Microscopy & Microanalysis 2018 Meeting, Baltimore, MD, August 5-9, 2018. (Invited)

Responses to Feedback from 2017 Peer Review

- Focus on the correct catalyst-process combinations (cannot work on everything); support BETO projects
  - Collaborate closely with ChemCatBio catalysis projects and enabling technologies to meet the needs of the program
  - Identify overarching challenges (e.g., atomic scale interfaces, metal-zeolite active sites, structure-stability relationships)
- Ability to obtain sufficient amounts of catalysts; partner with industry for catalyst manufacture
  - Catalyst development on 1-100 g scale
  - Early-stage investigation into the impact of scaling with CatCost
  - Collaboration with Engineering of Scale-up project (ADO)
  - Existing industrial partnerships for larger scale catalyst synthesis
- Offer characterization capabilities outside of ChemCatBio to facilitate development
  - DOE user facilities, focus on publications, ChemCatBio Directed Funding Assistance projects

Responses to Feedback from 2017 Peer Review

- Post-mortem analysis of commercial catalysts is critically important for industrial partners
  - Investigating commercially available zeolites and metal modified zeolites for the CFP project, as well as Cu/BEA prepared using industrial equipment for the IDL project.
- Not much emphasis on catalyst synthesis and preparation
  - Two critical roles: (1) As an integral part of advanced characterization effort (e.g., model catalyst materials to identify active sites), (2) targeted catalyst materials (e.g., metal carbides with controlled hydrogenation activity and extended lifetime)
- Develop relationship with the high-field mass spectrometry group in Florida. There is a lack of sophisticated techniques for organic compound identification in the program.
  - Primary focus on catalyst material characterization
  - Demonstrated *in-situ* Raman spectroscopy, TGA-DSC-FTIR, NMR

Acronyms and Abbreviations

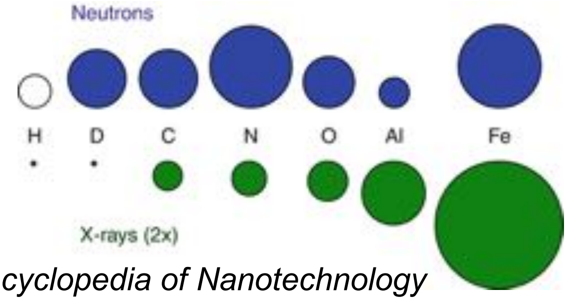
ACSC	Advanced Synthesis and Characterization
ADO	Advanced Development and Optimization
ANL	Argonne National Laboratory
APS	Advanced Photon Source (ANL)
APT	Atom Probe Tomography
BETO	Bioenergy Technologies Office
CCM	Catalyst Cost Model Development
CCPC	Consortium for Computational Physics and Chemistry
CDM	Catalyst Deactivation Mitigation for Biomass Conversion
CFP	Catalytic Fast Pyrolysis
ChemCatBio	Chemical Catalysis for Bioenergy Consortium
CNMS	Center for Nanophase Materials Sciences (ORNL)
CO_2U	Electrocatalytic and Thermocatalytic CO_2 Utilization
Cu/BEA	Cu-modified beta zeolite
CUBI	Catalytic Upgrading of Biochemical Intermediates
DME	Dimethyl ether
DOE	U.S. Department of Energy
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
EERE	Office of Energy Efficiency and Renewable Energy
EMN	Energy Materials Network
FCTO	Fuel Cell Technologies Office
GGE	Gallon gasoline equivalent
IDL	Catalytic Upgrading of Indirect Liquefaction Intermediates
LANL	Los Alamos National Laboratory
MCC	Materials Characterization Center (ORNL)
MFSP	Minimum fuel selling price
MYP	Multi-Year Plan
NETL	National Energy Technology Laboratory
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
SNL	Sandia National Laboratory
SNS	Spallation Neutron Source (ORNL)
STEM	Scanning transmission electron microscopy
wt%	Percentage by weight
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

ChemCatBio
Chemical Catalysis for Bioenergy

U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

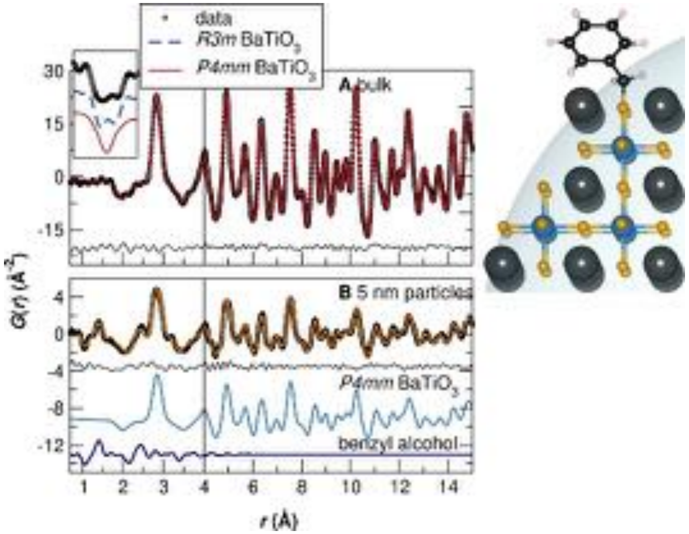
Neutron Advantages

Sensitive to Light Atom and Neighboring Atom Species



M. Laver, *Encyclopedia of Nanotechnology* (2012), 2437-2450.

Sensitive to Surface Species of Nano and Porous Materials



K. Page, Th. Proffen, M. Niederberger, and R. Seshadri, Probing local dipoles and ligand structure in BaTiO3 nanoparticles, *Chem. Mater*. 22 (2010), 4386-4391.

Chemical Specificity through Isotope Substitution

J. E. Enderby, D.M. North, P. A. Egelstaff, Partial structure factors of liquid Cu-Sn *Phil. Mag.*14 (1966) 131.

Also:

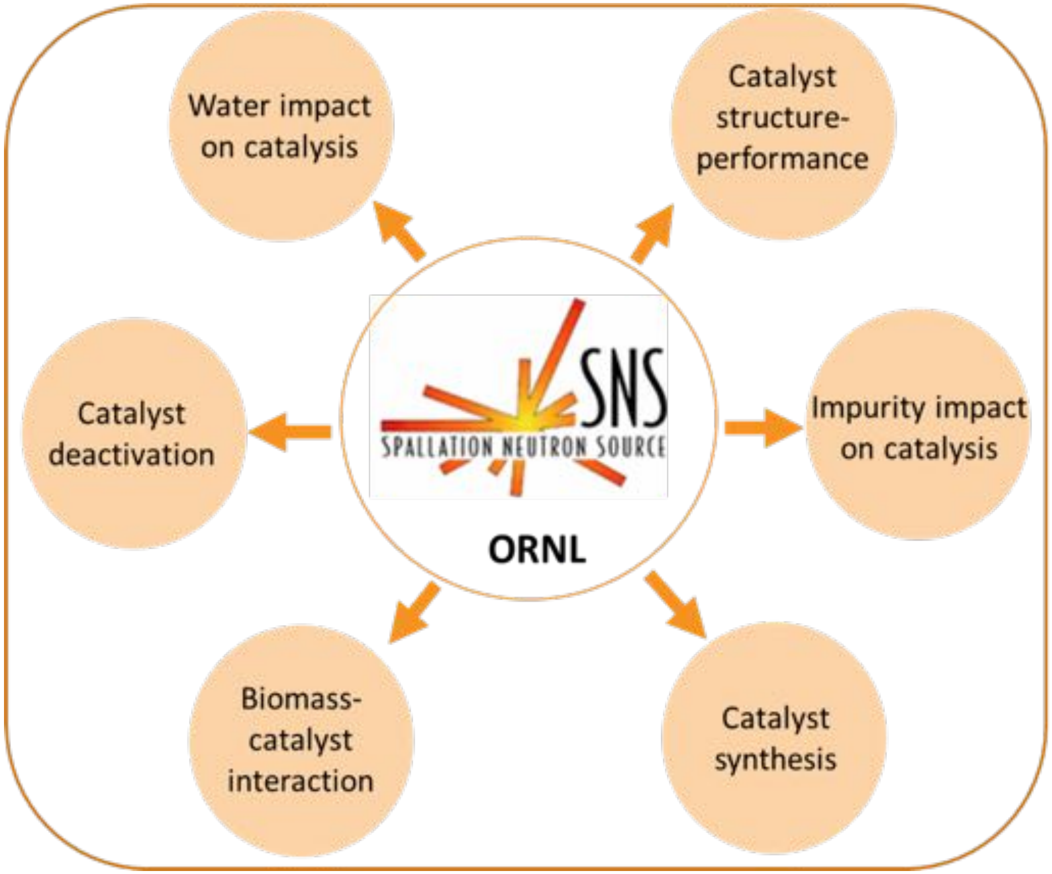
Nondestructive

Great Penetration of Sample Environments

Neutron scattering to address unique biomass catalysis challenges

Spallation Neutron Source (SNS) at ORNL

- One-of-a-kind research facility that provides the **most intense pulsed neutron beams** in the world, provides the **state-of-the-art experiment stations** to help address biomass catalysis challenges



Unique for biomass catalysis:

1) **Sensitive to light atoms** (H, D, C, N, O) – great for biomass molecules detection
2) **Sensitive to neighboring atoms** (e.g., Ni-Co, Cu-Zn)
3) **Sensitive to surface species** on catalyst, useful to identify surface molecular structures
4) **Great penetration of sample environment**
    - *in situ/operando* analysis
5) **Nondestructive analysis**
    - suitable for beam sensitive samples (e.g., zeolites)

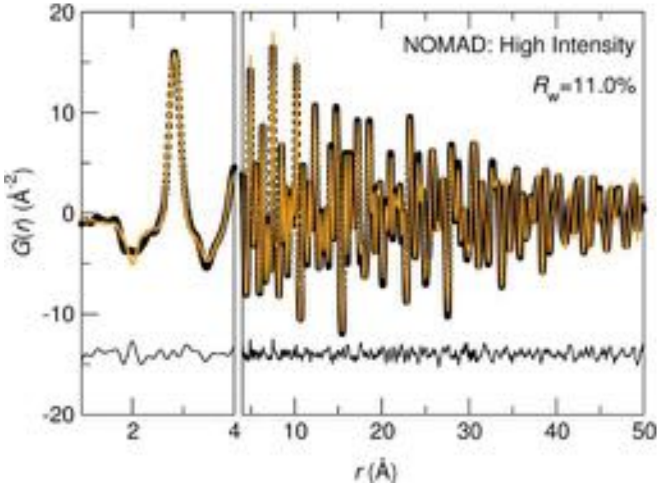
Specific Neutron Capabilities for Catalysis at ORNL

Neutrons (and X-rays) can help to understand heterogeneous materials from the atomic- to mesoscales, validating and advancing material concepts and models, also as a function of T, P, x, *etc*.

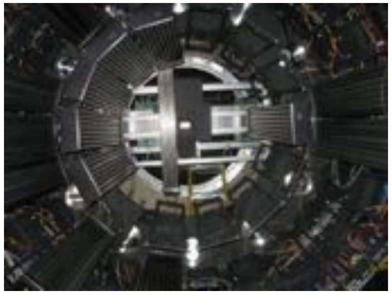
- **N/X PDF (NOMAD,** X-ray counterparts): Identity, phase fractions, and sizes/correlation length scales of amorphous, nanostructured, and crystalline species; study gas-solid components and their interfaces; relevant to adsorption processes, reactions, poisoning of catalytic surfaces, regeneration of catalysts, etc.
- **Neutron vibrational spectroscopy (VISION)**: characterizes molecular vibrations in a wide range of crystalline and disordered materials over a broad energy range (> 5 to < 600 meV); identifying and quantifying chemical species and dynamic behaviors in solutions or solids, and at interfaces, including hydrogen bonding, molecules adsorbed on surfaces and porous materials, etc.
- **N/X Diffraction (POWGEN, NOMAD**, X-ray counterparts): Identity and phase fractions of crystalline components; cation and anion site ordering
- **N/X Small Angle Scattering**: characterize larger length-scale structural features, porosity and chemical inhomogeneity, particulate/agglomerate growth

TOF Diffraction and Total Scattering at SNS

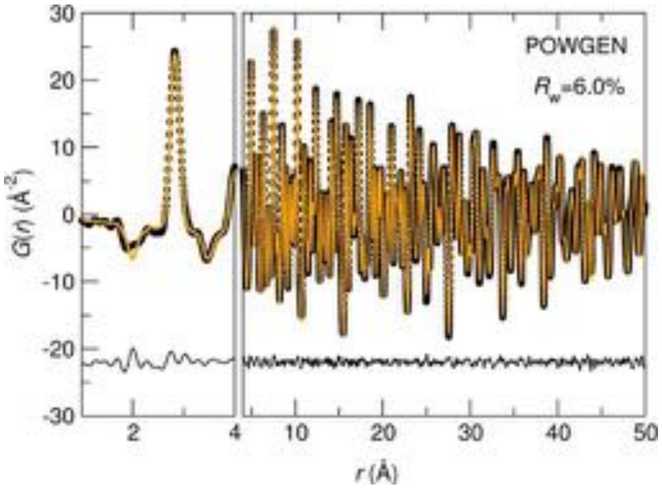
Pair Distribution Function (PDF) methods follow local atomic bonding configurations, intermediate structure, and correlation length scale- *regardless of a material's long range structure*



NOMAD data can be collected for **100 mg** of sample in a 3 mm quartz capillary in **~1 hour**.



***high intensity** diffraction and PDF for small samples and in situ studies on amorphous, nanostructured, and crystalline materials*



POWGEN data can be collected for **~10 g** of sample in a 6 mm vanadium canister in **~3 hours**

***high resolution** diffraction and PDF of crystalline materials*

Mail-in programs available on both instruments