ChemCatBio
Chemical Catalysis for Bioenergy

Advanced Catalyst Synthesis and Characterization (ACSC) Project

Susan Habas, Theodore Krause, Kinga Unocic

BETO Peer Review

March 6, 2023

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

Project Overview – Target-Driven Goals and Outcomes

Project Goal: *Provide actionable insights into catalyst development challenges* under realistic process conditions by leveraging world-class synthesis and characterization capabilities across multiple DOE National Laboratories.

Catalytic Technology Projects	Baseline		Future Target	Outcome: Catalyst Development Challenges
Upgrading of C1 Building Blocks C1	Regeneration temperature 450 °C	⇨	<300 °C	Enable compatibility of regeneration temp. with dual catalyst system
Upgrading of C2 Building Blocks C2	Loss of Lewis acid sites < 60%	⇨	< 30%	Mitigate impact of steam on catalyst stability
Catalytic Upgrading of Pyrolysis Products CFP	External re-carburization > 24 h	⇨	< 6 h	Limit irreversible catalyst deactivation for *in situ* regeneration
Catalytic Upgrading of Biochemical Intermediates CUBI	Deactivation rate due to alkali impurities 10%	⇨	1%	Reduce impact of alkali impurities

Project Impact: *Accelerated catalyst and process development cycle* leading to a reduction in time required for Catalytic Technology projects to meet transportation decarbonization targets.

Project Overview – Enabling Capability Within ChemCatBio

Catalytic Technology Projects

- Upgrading of C1 Building Blocks, **C1**
- Upgrading of C2 Building Blocks, **C2**
- Catalytic Upgrading of Pyrolysis Products, **CFP**
- Catalytic Upgrading of Biochemical Intermediates, **CUBI**
- Electrocatalytic CO_2 Utilization, **CO_2U**

Catalyst development challenges

ChemCatBio Enabling Capabilities

- Catalyst Development **ACSC**
- Catalyst Deactivation Mitigation **CDM**
- Computational Modelling **CCPC**

ChemCatBio **Industrial Advisory Board** and **Accelerator Partners**

Johnson Matthey Inspiring science, enhancing life

IBM

micromeritics

Accelerator Partners

Integrated and collaborative portfolio of enabling capabilities to help catalyst development challenges

Collaborative outcomes

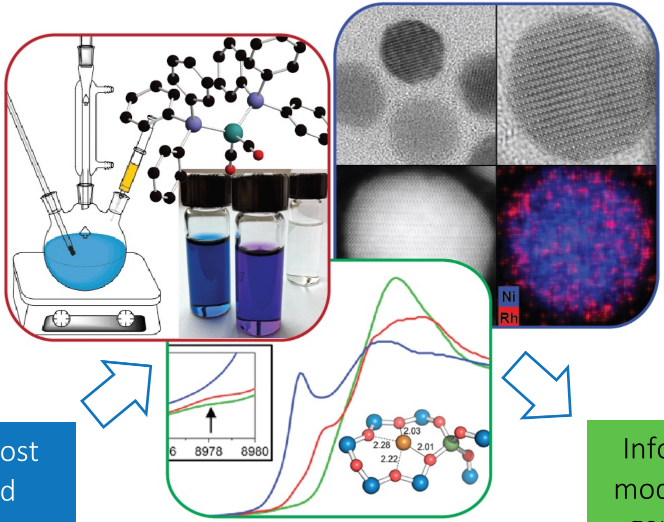
Targeted Cost Reduction	Improved Performance for Key Metrics	Cost-guided Synthesis

Project Overview – Providing Complementary Efforts

World-class synthesis and characterization capabilities provide insight into catalysts under realistic conditions

Dedicated synthetic effort for next-generation catalysts through innovative syntheses

NREL
NATIONAL RENEWABLE ENERGY LABORATORY



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-gen catalysts and de-risk scale up

CCPC
Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Project Overview – Capabilities Portfolio

Advanced Spectroscopic Characterization

- Overall coordination environments and oxidation states of metal atoms with *in-situ/operando* X-ray absorption spectroscopy at the DOE Office of Science User Facility, **Advanced Photon Source**
- Surface composition and chemical state by X-ray photoelectron spectroscopy
- Active sites and surface species including coke by *in-situ/operando* infrared, Raman, and UV-visible spectroscopies
- Crystalline structure by *in-situ/operando* X-ray diffraction

Advanced Spatially Resolved Imaging and Characterization

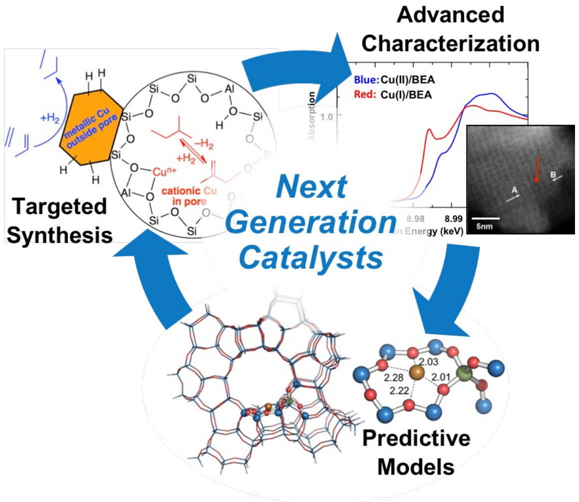
- Spatially-resolved structures and chemical composition by *in-situ/operando* sub-Ångström-resolution STEM imaging and spectroscopy at the DOE Office of Science User Facility, **Center for Nanophase Materials Sciences**, and Materials Characterization Center
- Topography and composition by scanning electron microscopy and spectroscopy
- Quantitative chemical composition by X-ray photoelectron spectroscopic mapping
- 3D elemental distribution by atom probe tomography
- Pore structure by 3D X-ray tomography

Advanced Catalyst Synthesis

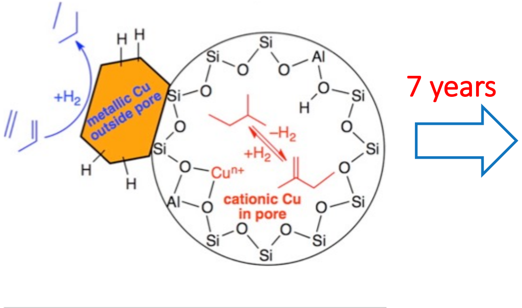
- Metal-modified oxides/zeolites with controlled atomic sites, nanostructures, and mesostructures
- Metal carbides, nitrides, phosphides via thermolysis of molecular precursors
- Scalable solution synthesis of nanostructured materials with controlled morphology, composition, and crystalline phase
- Manipulation of catalyst surface chemistry to control active site properties
- Industrially-relevant synthesis, processing, and characterization approaches for early-stage development of engineered catalysts

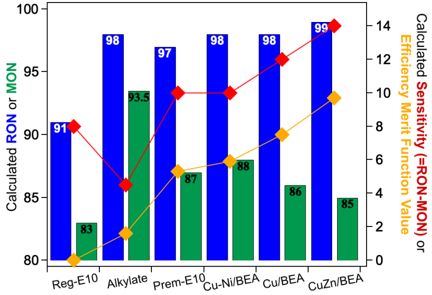
A primary mission is adaptation and demonstration of new capabilities to meet the needs of ChemCatBio Catalytic Technology projects

1. Approach – Catalyst and Process Development Cycle



Baseline: *Complete* Development Cycle (**C1**, last review)





- 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
- Evaluate *performance improvements* with ChemCatBio Catalytic Technology projects

Challenge: Quantify *Accelerated* Development Cycle (**C2**, this review)

- Leverage capabilities, expertise, and models for metal-modified zeolites
- Next-generation Cu-Zn-Y/BEA with increased C_{3+} olefin selectivity for ethanol to distillates process
- Target: *Half the time*

Leverage knowledge, capabilities, and expertise, to reduce the time required for Catalytic Technology projects to meet transportation decarbonization targets

1. Approach – Supporting ChemCatBio

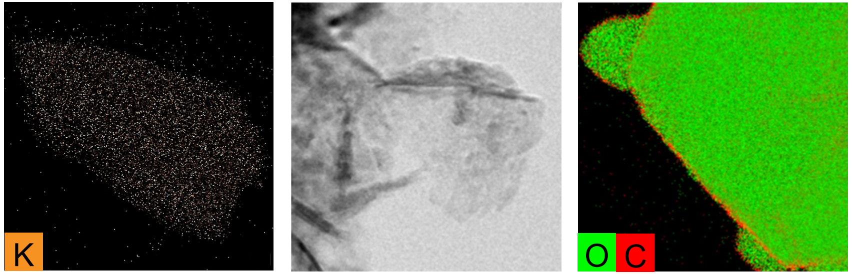
Direct engagement with *all* of the ChemCatBio Catalytic Technology projects

- Adapting and demonstrating **new capabilities** to meet specific needs of the catalysis projects
- Providing insight into the working catalyst structure through a 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

Ongoing focus on foundational research

- Tackling **overarching research challenges** to enable rapid response to new catalyst development challenges
- Identified based on needs of catalysis projects, Steering Committee, Industrial Advisory Board

Catalyst stability challenges



Inorganic contaminants | *Impact of water* | *Carbon deposition*

Balance overarching catalyst development challenges with specific needs of catalysis projects

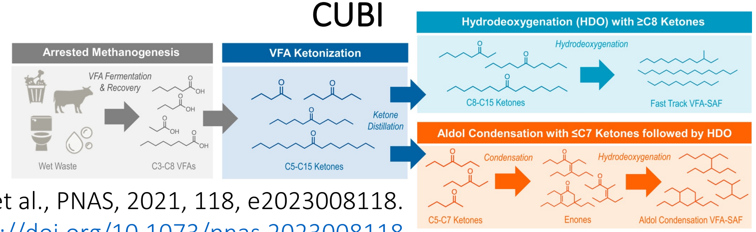
1. Approach – Multiple Modes of Interaction

How to work with the ACSC

- *Overarching challenges* are collectively tackled with other enabling capabilities each cycle
- *Project-specific milestones* with at least one collaboration maintained throughout project cycle
- *Immediate needs* are rapidly responded to via demonstrated capabilities and expertise

Evaluated biogenic impurities on catalyst surface

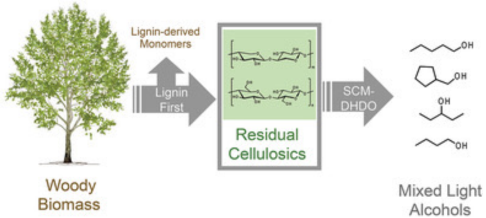
CUBI



N. A. Huq, et al., PNAS, 2021, 118, e2023008118. https://doi.org/10.1073/pnas.2023008118

Identified uniform distribution of metal elements

CUBI



H. Nguyen, et al., Adv. Sustainable Syst., 2022, 6, 2100310. https://doi.org/10.1002/adsu.202100310

Enables significant and rapid impact to ChemCatBio Catalytic Technology projects

1. Approach – Management of Evolving Needs of Catalytic Technology Projects

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 and visualizations: ChemCatBio **DataHub**

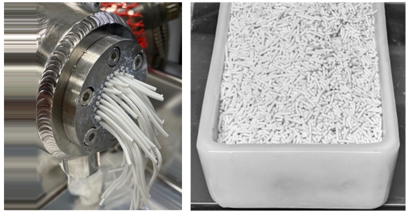
Active Management

Develop and demonstrate new capabilities

Go/No-Go Decision

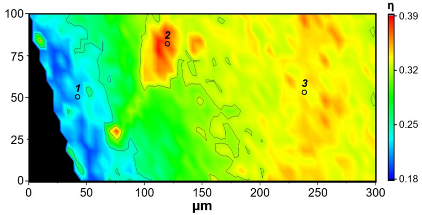
Annual Evaluation of New/Existing Capabilities

Engineered catalyst synthesis



Enable transition from research to engineered catalyst forms

Micro X-ray absorption spectroscopy



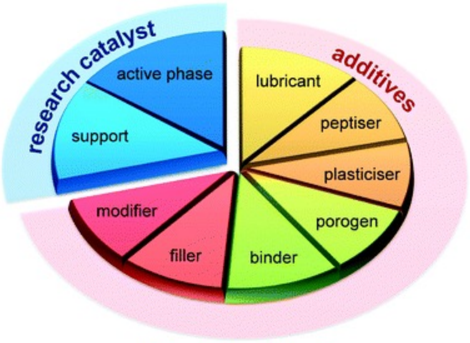
Spatially resolved compositional and structural analysis for catalyst composites (i.e., extrudates, MEAs)

Adaptation, demonstration, evaluation of new capabilities is integral to each Go/No-go decision

1. Approach – Responding to New Targets

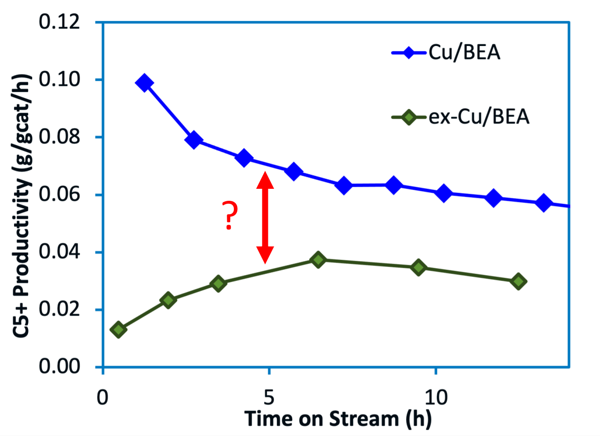
Challenge: Enable evaluation of catalytic performance of realistic engineered catalysts and develop structure-property relationships with engineered forms

Multicomponent formulation with additives and structural components required for commercial operation



Engineered catalyst

Mitchell, et al., *Chem. Soc. Rev.*, 2013, 42, 6094.
https://doi.org/10.1039/C3CS60076A



Binders, porosity, and/or changes in active site structures can impact catalytic performance

*Industry-informed **engineered catalyst synthesis capability and expertise** housed within ACSC project and funded by Catalytic Technology projects*

Projected Outcome: Reduces commercialization risks by addressing non-trivial transition from research to engineered catalyst forms

Responsive to previous Peer Review feedback and FY23 BETO goals

1. Approach – Risk Analysis and Mitigation

Risk Analysis		Mitigation Approaches
Limited acceleration of catalyst and process development cycle	→	Quantified successful acceleration of cycle through Go/no-go decision in previous cycle (**C1**, **C2**, **CCPC**)
New catalyst materials do not meet target metrics or are not scalable	→	Commercially-available catalysts as baseline materials with/without synthetic modifications. Scalability and cost evaluated via engineered catalyst capability and CatCost™
Minimal or slow impact of catalyst synthesis and characterization on Catalytic Technology projects	→	Multiple modes of interaction enabling significant and rapid impact, and focus on overarching challenges, project-specific milestones, immediate needs
Engineered catalysts do not meet target metrics	→	FY24 Go/no-go decision to meet activity and selectivity targets within 15% for an engineered catalyst relative to research powder catalyst (**C1**, **CDM**, **CCPC**)

Reduction in risks associated with meeting decarbonization targets and commercializing technologies

2. Progress and Outcomes – Demonstrated Catalyst Development Cycle (C1, Previous review)

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

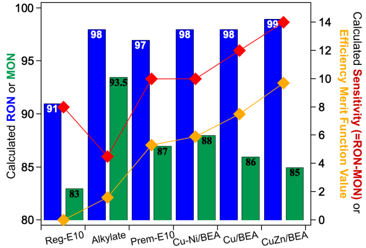
Outcome: Next-gen catalysts increased C_4 dehydrogenation >2-fold, bimetallics tuned paraffin to olefin ratio from 6.5 – 19

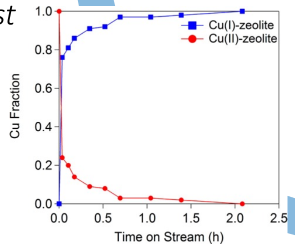
Catalyst	Active site
CuO/SiO₂	CuO particles
Cu/SiO₂	Cu(0) particles
H-BEA	Brønsted acid
ox-IE-Cu/BEA	Ionic Cu(II)-zeolite
red-IE-Cu/BEA	Ionic Cu(I)-zeolite

Synthesized catalysts with active sites in working catalyst

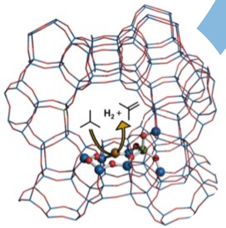
Targets: Ga, Zn, Ni, Co identified as potential next-generation ionic species to maximize dehydrogenation

Evaluated cost-normalized performance improvements, C1, CatCost^{TM}

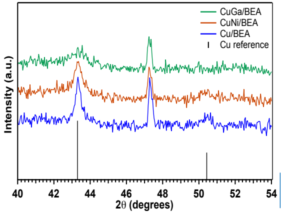




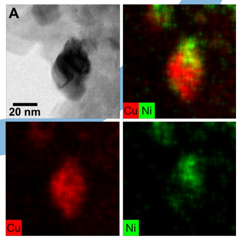
Identified Cu(I) as active site for dehydrogenation



Predictive model for dehydrogenation, CCPC



Synthetic control of speciation in bimetallic catalysts



Determined speciation in working catalysts

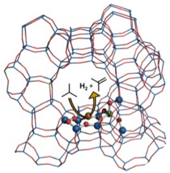
Success in the critical research challenge of improving fuel properties through catalyst design

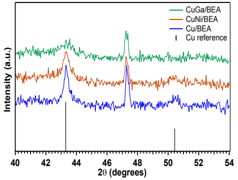
2. Progress and Outcomes – Quantified Catalyst Development Cycle (C1)

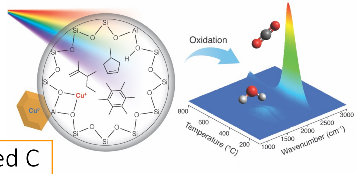
Goal: Identify active site(s) in Cu/BEA for dehydrogenation in the DME to hydrocarbons reaction to decrease product paraffin to olefin ratio (i.e., increase olefin selectivity) from a baseline of 9.4

● Catalyst development *pre-ChemCatBio* 4 years ● Catalyst development 3 years ● Durability and regeneration 1 year ● Technology maturation 7.5 years

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

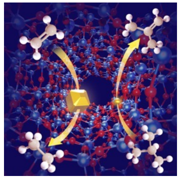


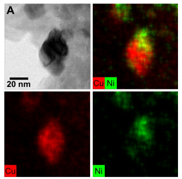


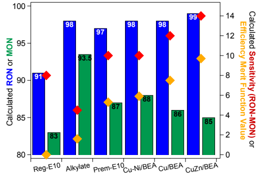


Timeline:

- FY13 – Initiated C1-ANL collaboration; Identified baseline Cu/BEA via screening
- FY15 – Published initial Cu/BEA report
- FY16 Q3 – Synthesized model catalysts to study active sites
- Q4 – Identified Cu(I) active site for dehydrogenation
- FY17 – Founded ChemCatBio; Initiated ACSC
- Q1 – Developed predictive dehydrogenation model
- Q4 – Demonstrated 10-15x scale
- FY18 – Demonstrated >1000x scale (TCF fund)
- Q4 – Demonstrated 7x dehydrogenation with predicted species
- FY19 Q2 – Synthetically controlled bimetallic speciation
- Q3 – Determined speciation in working catalysts; Identified C speciation to inform regeneration
- Q4 – Demonstrated control over P/O ratio (6.6-19) and fuel properties; Demonstrated 300 h TOS
- FY20 Q1 – Determined Cu species reduce regeneration severity
- Q2 – Licensed technology







Established catalyst and process development cycle as a baseline for comparison

2. Progress and Outcomes – Accelerated Catalyst Development Cycle (C2)

Goal: Identify active sites for conversion of ethanol to olefins to increase the C_{3+} olefin selectivity for the Cu-Zn-Hf/BEA catalyst from a baseline of 62%

- Catalyst development: 1.75 years
- Durability and regeneration: 1.75 year
- Technology maturation: 2.75 years

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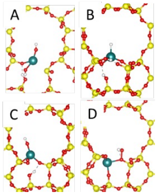
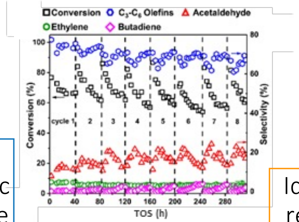
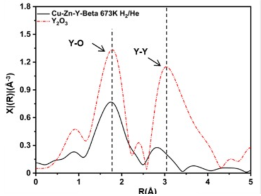
- FY17 — Founded ChemCatBio; Initiated ACSC
- FY18 Q1 — Initiated C2-ACSC collaboration; Developed baseline Cu-Zn-Hf/BEA with 62% C_{3+} olefin selectivity
- Q2 — Identified ionic Cu as active site for hydrogenation and Y to minimize dehydration
- Q4 — Developed Cu-Zn-Y/BEA catalyst
- FY19 Q1 — Identified isolated Cu, Zn, and Y sites in working catalyst
- Q2 — Developed predictive model based on isolated sites; Determined that minimization of Al sites and alternative Lewis acid sites can increase olefin selectivity
- Q3 — Demonstrated 89% C_{3+} olefin selectivity by synthetic optimization based on single site identification and support impact
- Q4 — Demonstrated 300 h TOS; Identified Cu sintering at extended TOS
- FY20 Q3 — Technology licensed
- FY21 Q1 — Identified Cu redispersion during regeneration
- Q4 — Optimize regeneration

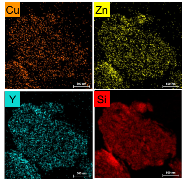
Argonne National Laboratory
NREL National Renewable Energy Laboratory
Oak Ridge National Laboratory

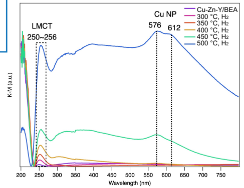


CCPC
Consortium for Computational Physics and Chemistry
U.S. Department of Energy







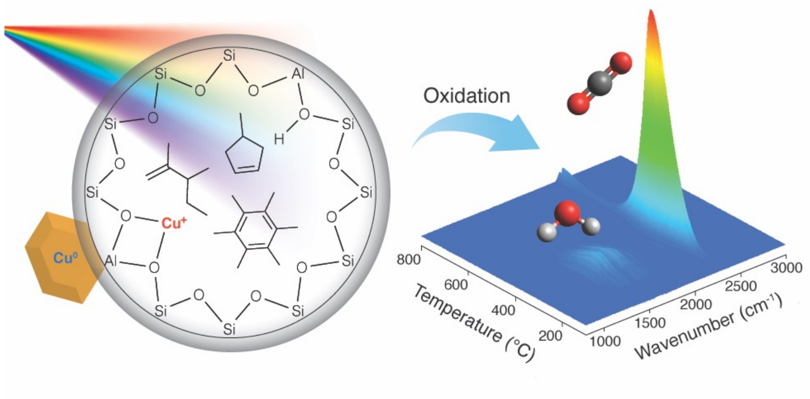


4x reduction in time between characterization of baseline catalyst and development of next-gen catalyst

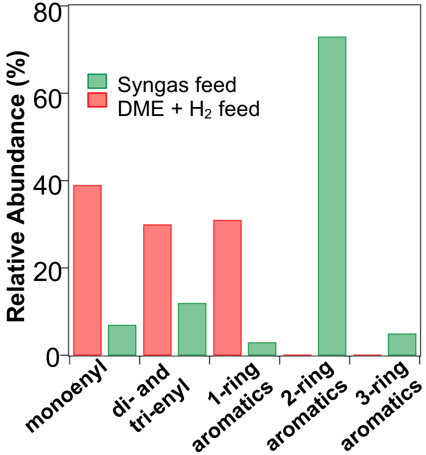
2. Progress and Outcomes – Catalyst Regeneration Challenges (C1)

Challenge: Develop regeneration process for syngas to hydrocarbons (STH) CZA-Cu/BEA catalyst system compatible with CZA temp. limit (ca. 300 °C)

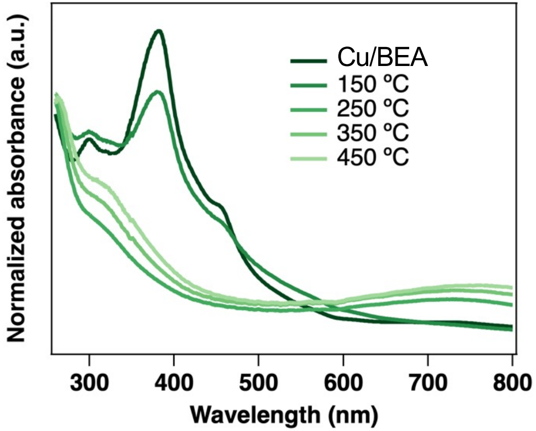
Leverage knowledge, expertise, and capabilities to study recurring themes of deactivation and regeneration



Q. Wu, A. T. To, et al., *Appl. Catal. B*, 2021, 119925.
https://doi.org/10.1016/j.apcatb.2021.119925



More multi-ring aromatics observed with syngas feed compared to DME feed



Cu oxide activates O_2 leading to carbon removal at significantly lower temperature

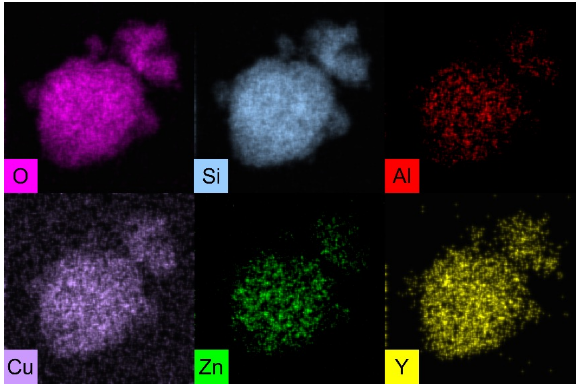
Outcome: Low temp. (250 °C) oxidative regeneration enabled full recovery of multi-component catalyst activity after 50 h TOS

Complementary spectroscopic characterization techniques to provide complete insight

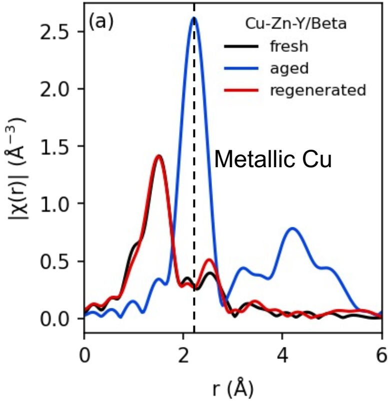
2. Progress and Outcomes – Catalyst Regeneration Challenge (C2)

Challenge: Identify deactivation mechanisms of Cu-Zn-Y/BEA during ethanol to C_{3+} olefins conversion

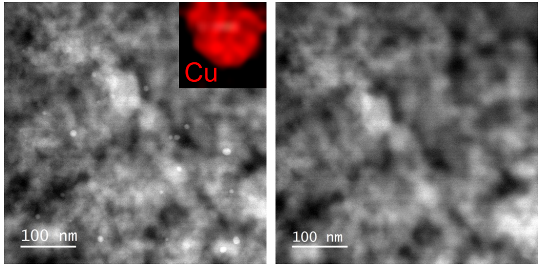
Zn and Y sites maintain atomic dispersion, but Cu begins to cluster at longer time on stream



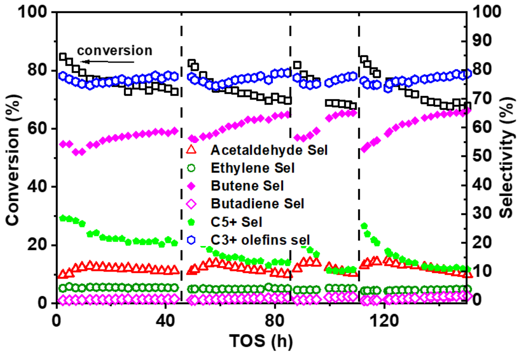
S. Purdy, et al., 2023, *In Preparation.*



Identified Cu sintering and redispersion as a function of reactive environment



H_2 400 °C, 1 h   Air 550 °C, 4 h



Applying knowledge, capabilities, expertise to provide rapid insight into Cu and C speciation during reaction/regeneration

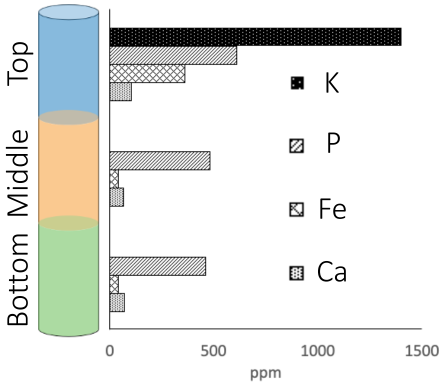
Outcome: An oxidative regeneration procedure that enabled full recovery of catalyst activity (85%) through Cu redispersion

Collaborative effort to provide comprehensive insight (C2, ACSC, CDM, CCPC)

2. Progress and Outcomes – Catalyst Deactivation (CFP, CDM, CCPC)

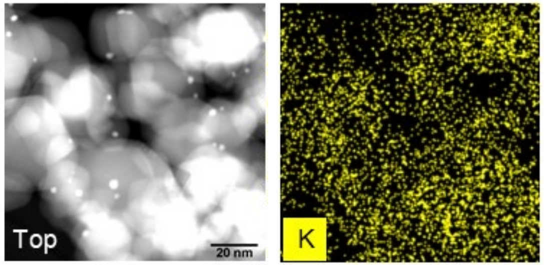
Challenge: Identify causes of catalyst deactivation during *ex situ* CFP over SOT 0.5 wt% Pt/TiO_2 catalyst

Spent catalyst from multiple bed locations following 4 cycles and 32 hours time on stream

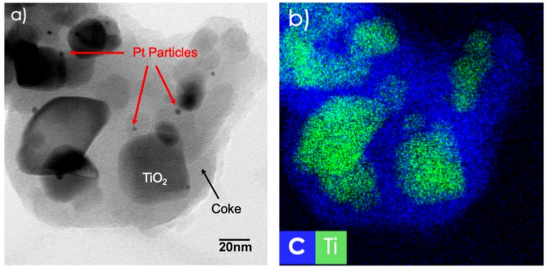


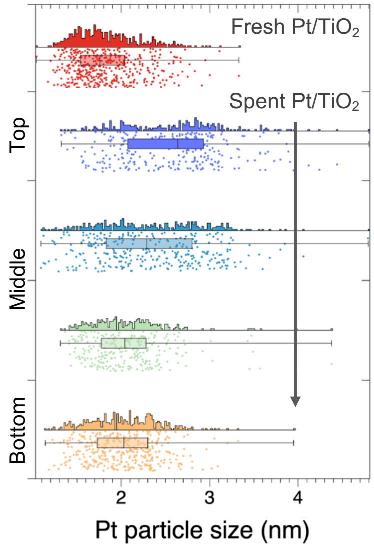
F. Lin, et al. *ACS Catal.*, 2022, 12, 465.
https://doi.org/10.1021/acscatal.1c02368

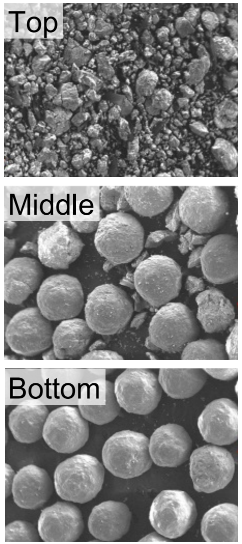
Spatially resolved distribution of K concentration correlated with deactivation mechanisms



Distribution of coke throughout bed informed regeneration requirements







Determined impact of temperature on Pt sintering/redistribution catalyst particle stability during reaction and regeneration

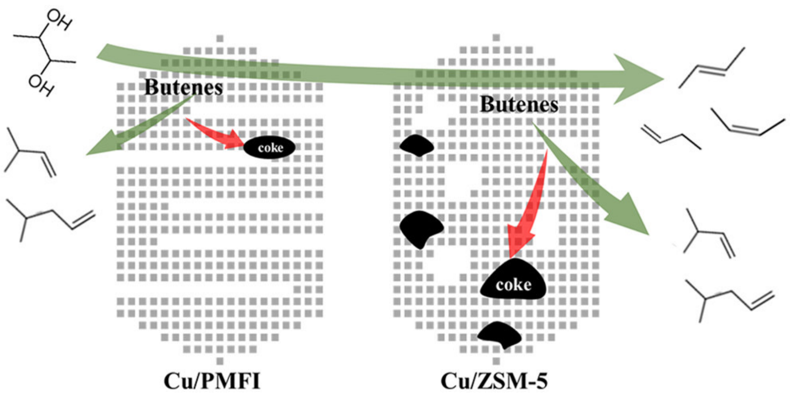
Outcome: Identified coking, K deposition, and temperature excursions, as causes of deactivation and developed regeneration procedure for full recovery of activity.

Leverage knowledge of coke formation, impurity deposition, and regeneration for zeolite CFP catalysts

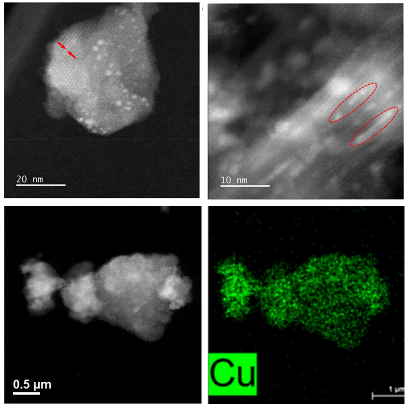
2. Progress and Outcomes – Catalyst Deactivation (CUBI)

Challenge: Determine deactivation mechanisms of Cu 2D pillared MFI catalyst for 2,3-butanediol to C_{3+} olefins process.

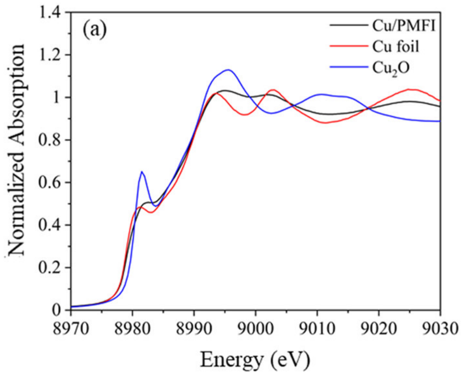
Compare Cu-modified diffusion-free 2D pillared MFI catalyst (Cu/PMFI) in comparison to mesoporous Cu/ZSM-5



S. Adhikari, et al., *ACS Sus. Chem. Eng.*, 2022, 10, 1664.
https://doi.org/10.1021/acssuschemeng.1c0767



Ordered mesoporous structure containing bimodal size distribution of Cu species on external surfaces and within interlayer spaces



In situ analysis indicates metallic Cu species associated with nanoparticles observed by microscopy as well as ionic Cu species

Outcome: Combination of metallic and ionic Cu species and hierarchically porous structure significantly reduced coking (>50%) and non-butene olefin formation.

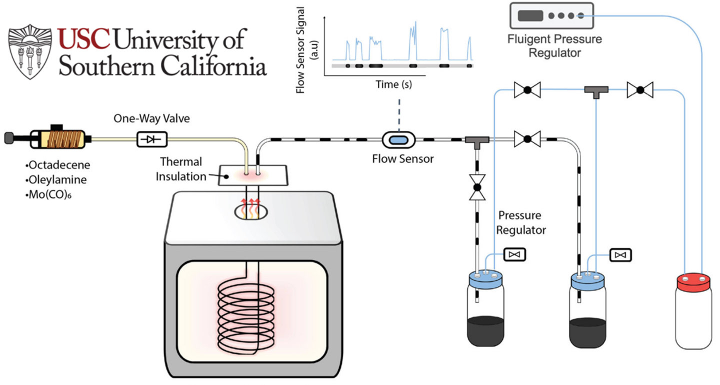
Catalyst design to mitigate deactivation and promote desired selectivity

2. Progress and Outcomes – Catalyst Synthesis

Challenge: Improve scalability of non-noble metal multifunctional carbide catalysts catalysts for CFP and CO_2 reduction (C1, CO_2 rich syngas)

Continuous flow synthesis of MoC_{1-x} enables rapid evaluation of variable space for target property of throughput

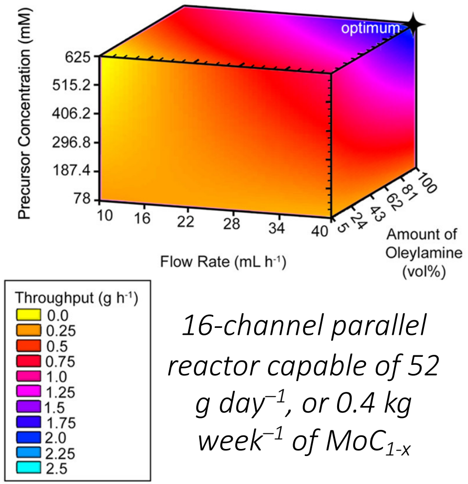
USC University of Southern California



L. R. Karadaghi, et al., *ACS App. Nano Mater.,* 2022, 5, 1966.
https://doi.org/10.1021/acsanm.1c02916

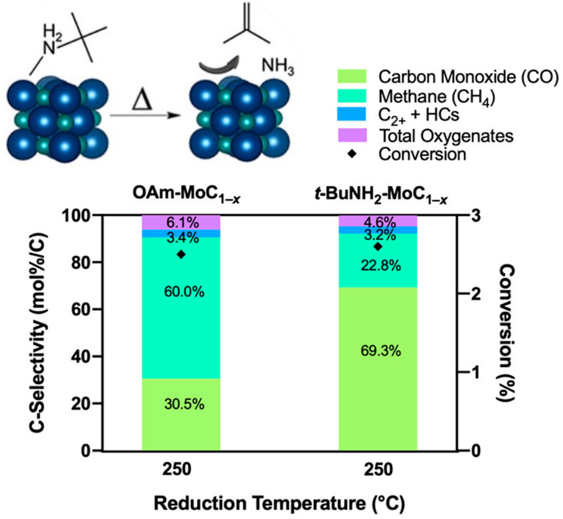
F. G. Baddour, et al., U.S. Patent Application 2021, 0309525 A1.

Statistical DoE with response surface methodology to optimize the throughput



16-channel parallel reactor capable of 52 g day^{-1}, or 0.4 kg week^{-1} of MoC_{1-x}

Surface ligand design to promote low temperature activation and desired reactivity



L. R. Karadaghi, et al., *Chem. Mater.,* 2022, 34, 8849.
https://doi.org/10.1021/acs.chemmater.2c02148

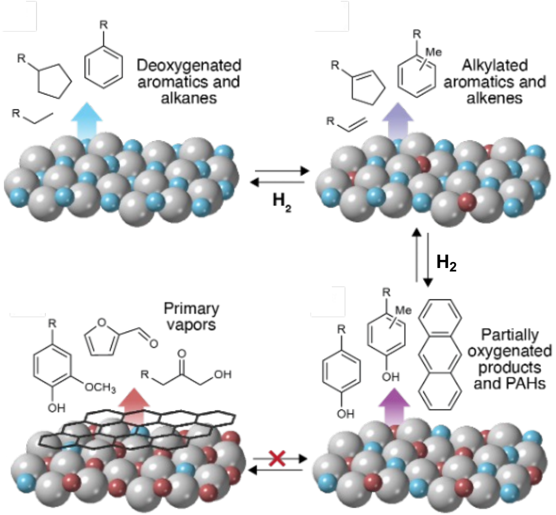
Outcome: 50x increase in throughput over lab-scale batch reaction with comparable CO_2 hydrogenation performance

Optimized throughput and pathway to scaling production to industrially relevant quantities

2. Progress and Outcomes – Deactivation of Metal Carbides (CFP, C1)

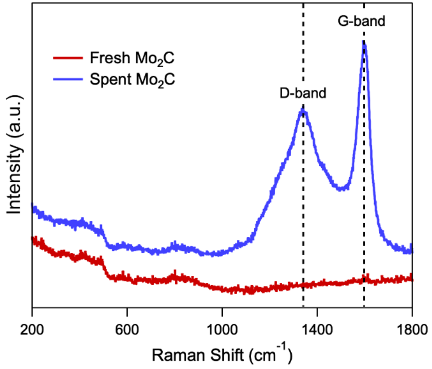
Challenge: Leverage knowledge of Pt/TiO_2 deactivation to determine mechanisms for CFP transition metal carbide catalysts

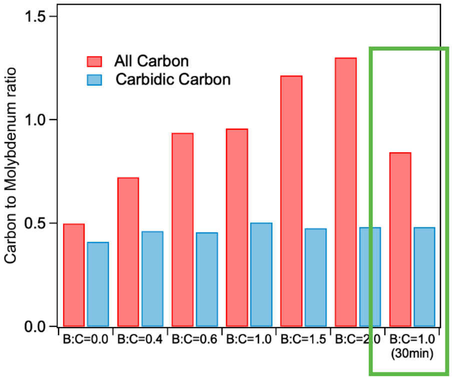
H_2 activation on metallic sites promote desorption of deactivating aromatic hydrocarbons preventing irreversible catalyst deactivation



C. Mukarakate, et al., *Chem. Catal.*, 2022, 2, 1819. https://doi.org/10.1016/j.checat.2022.06.004

Regeneration of metal carbide catalysts relied on costly high-temperature re-carburization



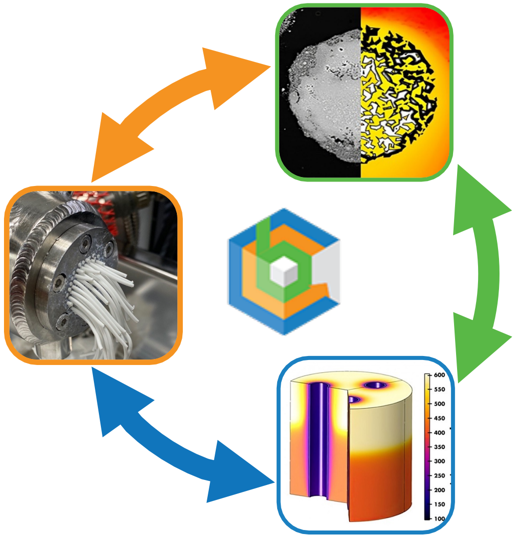


Characterization of carbon speciation during CFP and impact of H_2 on coke deposition from pyrolysis vapors

Projected Outcome: Fundamental understanding of deactivation mechanisms enabled increased catalyst lifetime and *in situ* regeneration

Enables application of tunable multifunctional metal carbide catalysts (Feedback from last Peer Review)

2. Progress and Outcomes – Future R&D



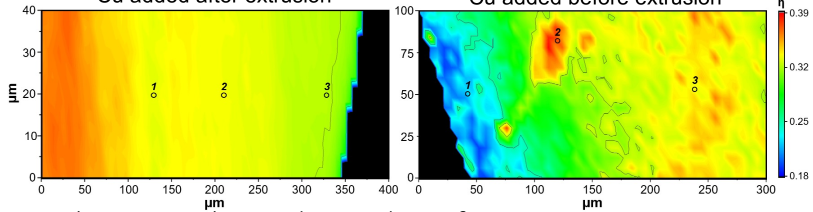
- **FY23:** Determine the impact of engineered catalyst formulation on Cu speciation and catalyst deactivation mechanisms (C1, CDM)
  - Correlate Cu speciation with differences in syngas to hydrocarbons (STH) catalytic performance and deactivation profile
  - Reduces the risk associated with assumptions for engineered catalyst performance
- **FY24:** Establish coke characteristics for at least two catalyst systems from different ChemCatBio catalytic technologies (CFP, C1, C2, CDM)
  - Multi-project effort to experimentally and computationally understand the deactivation and regeneration of engineered catalysts
- **FY24 Go/No-go:** Evaluate the ability of the computational and characterization approach to generate improved engineered catalysts
  - Target C_{4+} hydrocarbon yield, CO_2 selectivity and DME selectivity within 15% relative to powder Cu/BEA catalyst
- **End of Project Goal (FY25):** Develop a predictive model for engineered catalysts to reduce risk associated with engineered catalyst formulations when scaling reactor dimensions (C1, CCPC, CDM)
  - Correlates CO_2-rich STH performance with critical properties of engineered catalysts

Focus on engineered catalysts to reduce risks associated with commercialization

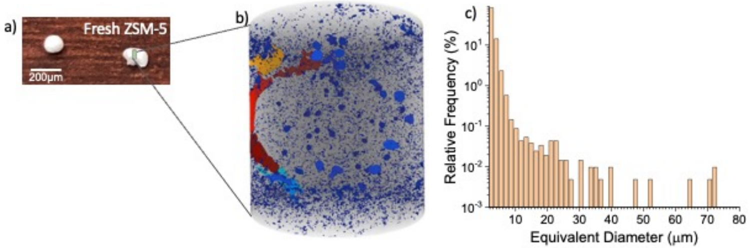
2. Progress and Outcomes – Future R&D

Challenge: Effectively measure active site characteristics, deactivation mechanisms, and regeneration of engineered catalysts

Adapting and demonstrating new capabilities

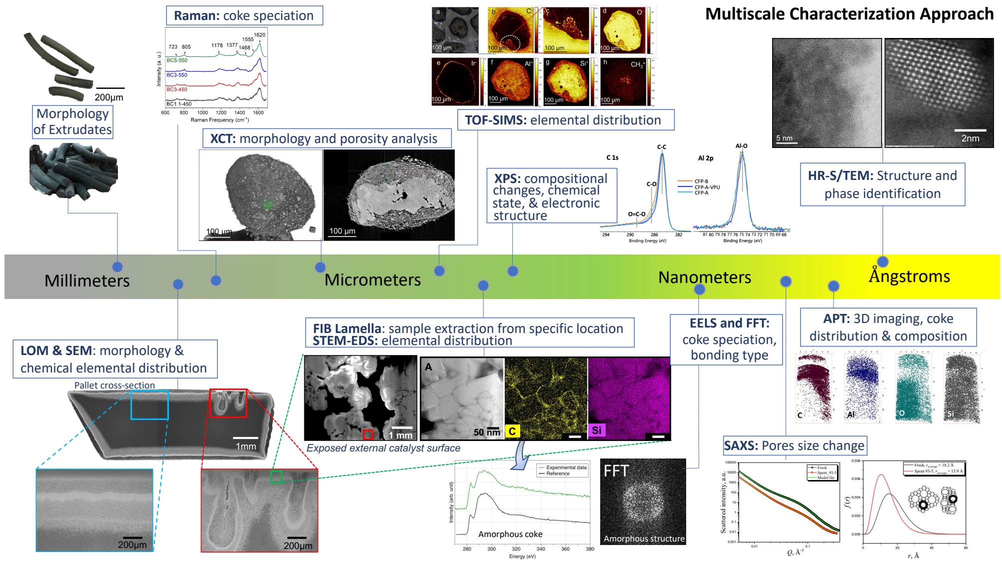


In-house synthesized extrudates for C1 project



Commercial spray-dried catalyst for CFP project

Leveraging previous experience with DFOs and Catalytic Technology projects characterizing engineered catalysts across multiple length scales



Outcome: Inform engineered catalyst development and process conditions, reducing commercialization risks associated with engineered catalyst operability

Building knowledge, capabilities, and expertise for spatially-resolved characterization of engineered catalysts

3. Impact – Reaching the Bioenergy Industry

Direct interactions with industry

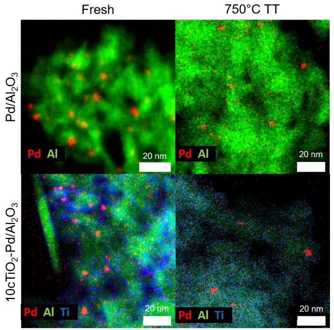
- Nearly *50% of industry collaborations* through current and previous DFO projects leverage ACSC capabilities and expertise

Feedback from Industrial Advisory Board

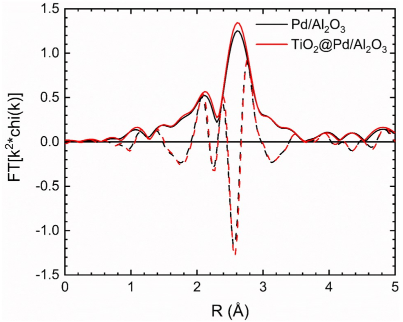
- ChemCatBio needs to be ***world-class*** in synthesis and characterization
- It is important to develop tools and expertise for broad *overarching challenges*

Challenge: Identify the origin of enhanced hydrogenation activity for TiO_2-coated Pd catalyst

Demonstrated co-location of TiO_2 and Pd nanoparticles



Determined Pd electronic structure was not altered by TiO_2

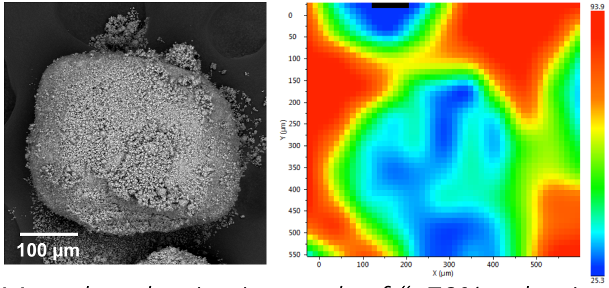


W. W. McNeary, et al., *ACS Catal.*, 2021, 11, 8538.
https://doi.org/10.1021/acscatal.1c02101

Outcome: Determined that enhanced activity was due to ensemble effects from partial TiO_2 coverage of Pd

Providing capabilities and expertise that are responsive to industry needs

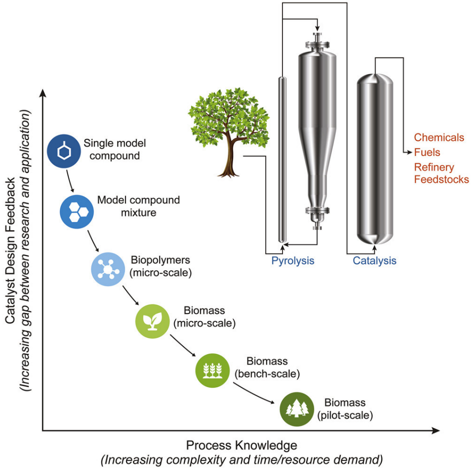
3. Impact – Enabling BETO Goals

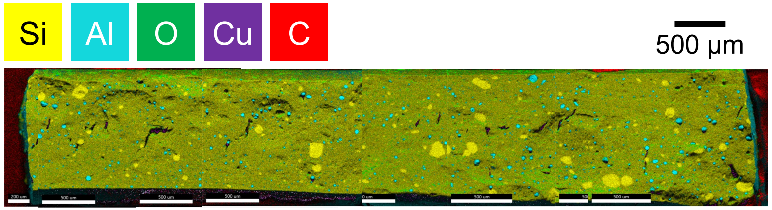


Meet decarbonization goals of ">70% reduction in GHG emissions compared to a petroleum incumbent by the end of the three-year cycle"

"Identify and research novel catalysts for hydrodeoxygenation and hydrodenitrification processes on bio-derived intermediates."
– DOE SAF Grand Challenge Roadmap

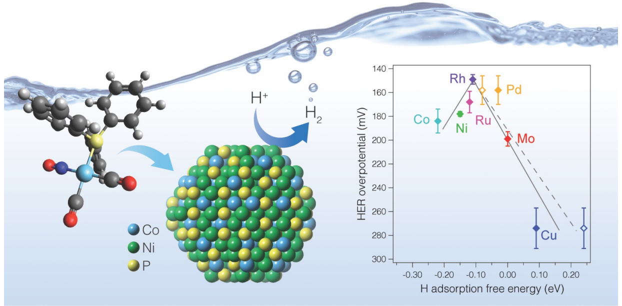
C. Mukarakate, et al., *Chem. Catal.*, 2022, 2, 1819.
https://doi.org/10.1016/j.checat.2022.06.004





"By the end of the three-year cycle projects must use engineered catalyst forms relevant to the industrial application." – BETO 2023 Lab Call

C. A. Downes, et al., *Chem. Mater.*, 2022, 34, 6255.
https://doi.org/10.1021/acs.chemmater.2c00085



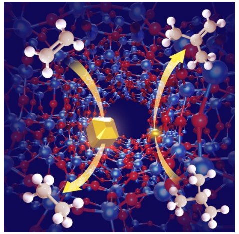
"R&D and industrial engagement on incorporating novel reductants such as renewable electrons and photons. Strategies and technologies that enable use of waste CO_2 to improve system yields." – DOE SAF Grand Challenge Roadmap

Supporting decarbonization of transportation sector by enabling R&D towards commercialization of SAF

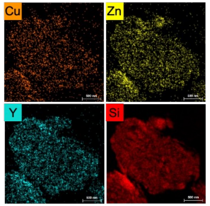
3. Impact – Providing Knowledge, Capabilities, and Expertise

Within ChemCatBio and BETO

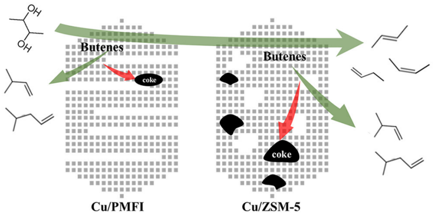
Developing capabilities and expertise that span multiple projects



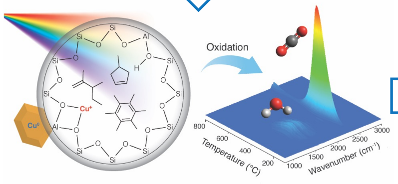
*Precise understanding of active sites in Cu/BEA (**C1**)*



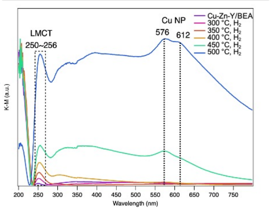
*Extended to Cu-Zn-Y/BEA (**C2**)*



*Rapid insight into Cu/pillared zeolite (**CUBI**)*



*Informed targeted regeneration of Cu/BEA (**C1**)*



*Extended to regeneration of Cu-Zn-Y/BEA (**C2**)*

Outcome: Acceleration of the catalyst and process development cycle for bioenergy applications

Externally to the catalysis community

- 18 peer reviewed publications since last review
- 8 external presentations by PIs since last review
- Industry engagement with 5 Directed Funding Opportunities
- Webinar on Accelerating the Catalyst Development Cycle
- New capabilities and expertise available at DOE Office of Science User Facilities

Positioning ChemCatBio as a Central Hub of Knowledge for the Bioenergy Community

3. Impact – Target-Driven Goals and Outcomes

Project Goal: *Provide actionable insights into catalyst development challenges* under realistic process conditions by leveraging world-class synthesis and characterization capabilities across multiple DOE National Laboratories.

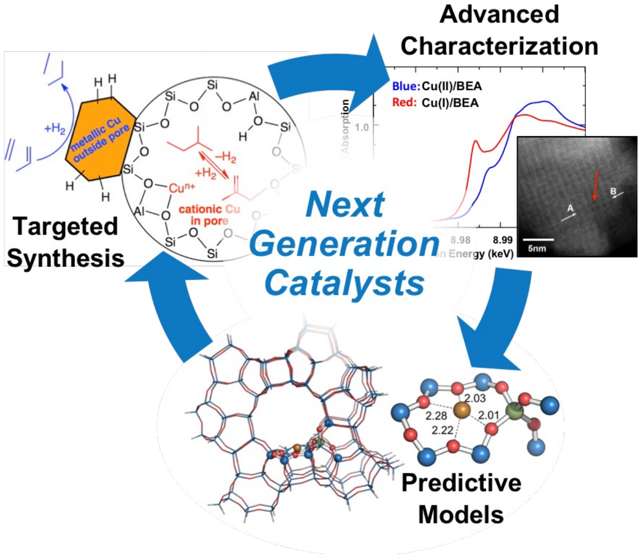
Catalytic Technology Projects	Baseline	Future Target	Outcome: Catalyst Development Challenges
Upgrading of C1 Building Blocks **C1**	Regeneration temperature **450 °C**	**<300 °C**	Enable compatibility of regeneration temp. with dual catalyst system
Upgrading of C2 Building Blocks **C2**	Loss of Lewis acid sites **< 60%**	**< 30%**	Mitigate impact of steam on catalyst stability
Catalytic Upgrading of Pyrolysis Products **CFP**	External re-carburization **> 24 h**	**< 6 h**	Limit irreversible catalyst deactivation for *in situ* regeneration
Catalytic Upgrading of Biochemical Intermediates **CUBI**	Deactivation rate due to alkali impurities **10%**	**1%**	Reduce impact of alkali impurities

Project Impact: *Accelerated catalyst and process development cycle* leading to a reduction in time required for Catalytic Technology projects to meet transportation decarbonization targets.

Summary

Project Goal: *Provide actionable insights into catalyst development challenges* under realistic process conditions by leveraging world-class synthesis and characterization capabilities across multiple DOE National Laboratories.

- Developed cohesive portfolio of Enabling Technologies that has successfully tackled catalyst development challenges
- Demonstrated acceleration of the catalyst and process development cycle for ethanol to C_{3+} olefins pathway
- Leveraging knowledge, capabilities, and expertise for engineered catalysts to reduce commercialization risks



Project Impact: *Accelerated catalyst and process development cycle* leading to a reduction in time required for Catalytic Technology projects to meet transportation decarbonization targets.

Quad Chart Overview

Timeline

- Project start date: 10/1/2022
- Project end date: 9/30/2025

	FY23 Planned	Total Award
DOE Funding	$510K (NREL) $530K (ANL) $452.5K (ORNL)	$1.53M (NREL) $1.59M (ANL) $1.38M (ORNL)
Project Cost Share*	None	None

TRL at Project Start: 1-3
TRL at Project End: 1-3

Project Goal

Provide actionable insights into catalyst development challenges under realistic process conditions to accelerate catalyst and process development cycle and reduce time required to to meet transportation decarbonization targets.

End of Project Milestone

Develop predictive model for engineered catalysts correlating CO_2-rich syngas to hydrocarbons (STH) performance with critical properties of engineered catalysts to reduce risk associated with engineered catalyst formulations when scaling reactor dimensions.

Funding Mechanism

2023 BETO National Laboratory call

Project Partners

- ChemCatBio Catalytic Technology projects
- University of Southern California
- Purdue University

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Jeffrey Miller

ChemCatBio Chemical Catalysis for Bioenergy

Energy Materials Network U.S. Department of Energy

This work was performed in collaboration with the Chemical Catalysis for Bioenergy (ChemCatBio) Consortium, a member of the Energy Materials Network (EMN)

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Additional Slides

Responses to FY21 Peer Review Comments

- Continue to clarify how the ACSC contributes to accelerated catalyst and process development cycle. It was good to hear 1/2 the development cycle time stated.
  - We agree with the reviewers that the ACSC project should continue to clarify how we contribute to acceleration of the catalyst and process development cycle, and we have now quantified this acceleration with the Upgrading of C2 Building Blocks project as a Go/No-go decision in comparison to our previous collaboration with the Upgrading of C1 Building Blocks project, which served as a baseline for the complete development cycle.
- Transition metal carbides have great potential for replacing noble metal-based CFP catalytic materials. A strategy for regeneration under mild conditions would be a nice impact and another non-noble metal system should be proposed as an alternative.
  - We have continued to evaluate metal carbide catalysts as replacements for noble metal-based materials through new synthesis approaches and by developing a strategy for regeneration under mild conditions based on a fundamental understanding of catalyst deactivation. Additionally, we are leveraging our understanding of catalyst deactivation and regeneration to evaluate non-noble metal zeolite catalyst materials across multiple projects.
- The ACSC should consult the TEA team on estimating the financial impact of this work on MFSP. It could also be beneficial if the ACSC could consider sustainability and affordability when developing catalyst synthesis. The team should continue to strive to find experimental ways to speed up characterization and synthesis. This is why the close cooperation with the CCPC is paramount to introduce the learning algorithms into the approach where experimental characterization can take more of a validation role in the future.
  - We agree with these comments and have continued to strengthen our collaborations with the TEA team through the Catalytic Technology projects to ensure that our efforts have a measurable impact that considers costs, as well as to incorporate catalyst cost estimations using the CatCost™ tool into early-stage catalyst synthesis decisions. Similarly, we have developed joint milestones with the CCPC to move towards predictive models that can further accelerate catalyst and process development, which will be a focus of the current research cycle for engineered catalysts.

Publications (Since last review)

1. L. R. Karadaghi, A. T. To, S. E. Habas, F. G. Baddour, D. A. Ruddy*, R. L. Brutchey*, "Activating Molybdenum Carbide Nanoparticle Catalysts under Mild Conditions Using Thermally Labile Ligands", *Chem Mater.,* 2022, online. https://doi.org/10.1021/acs.chemmater.2c02148
2. K. A. Unocic*, N. LiBretto, A. T. To, J. A. Kropf, D. A. Ruddy, T. R. Krause, L. F. Allard, S. E. Habas, "Revealing the Reaction Behavior of $Co_{0.86}Mn_{0.14}O$ under H_2 using *in situ* Closed-Cell Gas Reaction S/TEM", *Microsc. Microanal.,* 2022, 28, 1884. https://doi.org/10.1017/S1431927622007395
3. B. Talukdar, H. M. Meyer III, C. Mukarakate, K. Iisa, M. B. Griffin, S. E. Habas, K. A. Unocic*, "Deactivation study on zeolite materials using XPS and STEM characterization", *Microsc. Microanal.,* 2022, 28, 2472. https://doi.org/10.1017/S1431927622009461
4. C. Mukarakate*, K. Iisa, S. E. Habas, K. A. Orton, M. Xu, C. Nash, Q. Wu, R. M. Happs, R. J. French, A. Kumar, E. M. Miller, M. R. Nimlos, J. A. Schaidle*, "Accelerating catalyst development for biofuel production through multiscale catalytic fast pyrolysis of biomass over Mo_2C", *Chem Catal.,* 2022, 2, 1819. https://doi.org/10.1016/j.checat.2022.06.004
5. C. A. Downes, K. M. Van Allsburg, S. A. Tacey, K. A. Unocic, F. G. Baddour, D. A. Ruddy, N. J. LiBretto, M. M. O'Connor, C. A. Farberow, J. A. Schaidle*, S. E. Habas*, "Controlled Synthesis of Transition Metal Phosphide Nanoparticles to Establish Composition-Dependent Trends in Electrocatalytic Activity", *Chem. Mater.* 2022, 34, 6255. https://doi.org/10.1021/acs.chemmater.2c00085
6. M. J. Cordon, J. Zhang, N. "River" Samad, J.W. Harris, K. A. Unocic, M. Li, D. Liu, and Z. Li, Ethanol conversion to C4+ olefins over bimetallic copper- and lanthanum-containing Beta zeolite catalysts, *ACS Sustainable Chem. Eng.,* 2022, 10, 5702. https://doi.org/10.1021/acssuschemeng.1c07442

Publications (Since last review, cont.)

7. L. R. Karadaghi, M. S. Madani, E. M. Williamson, A. T. To, S. E. Habas, F. G. Baddour, J. A. Schaidle, D. A. Ruddy, R. L. Brutchey*, N. Malmstadt, Throughput Optimization of Molybdenum Carbide Nanoparticle Catalysts in a Continuous Flow Reactor Using Design of Experiments, *ACS Appl. Nano Mater.,* 2022, 5, 1966. https://doi.org/10.1021/acsanm.1c02916
8. C. P. Nash, D. P. Dupuis, A. Kumar, C. A. Farberow, A. T. To, C. Yang, E. C. Wegener, J. T. Miller, K. A. Unocic, E. Christensen, J. E. Hensley, J. A. Schaidle, S. E. Habas*, D. A. Ruddy*, "Catalyst design to direct high-octane gasoline fuel properties for improved engine efficiency", *Appl. Catal. B,* 2022, 301, 120801. https://doi.org/10.1016/j.apcatb.2021.120801
9. S. Adhikari, J. Zhang, K. A. Unocic, E. C. Wegener, P. Kunal, D. J. Deka, T. Toops, S. S. Majumdar, T. R. Krause, D. Liu, Z. Li*, "Direct 2,3-Butanediol Conversion to Butene-Rich C_{3+} Olefins over Copper-Modified 2D Pillared MFI: Consequence of Reduced Diffusion Length", *ACS Sus. Chem. Eng.,* 2022, 10, 4, 1664. https://doi.org/10.1021/acssuschemeng.1c07670
10. H. Nguyen, N. A. Huq, D. Stück, S. M. Tifft, D. R. Conklin, A. J. Koehler, W. W. McNeary, G. M. Fioroni, C. Hays, E. D. Christensen, I. McNamara, A. Bartling, R. Davis, K. A. Unocic, D. R. Vardon*, "Supercritical Methanol Solvolysis and Catalysis for the Conversion of Delignified Woody Biomass into Light Alcohol Gasoline Bioblendstock", *Adv. Sustainable Syst.,* 2022, 6, 2100310. https://doi.org/10.1002/adsu.202100310
11. F. Lin, Y. Lu, K. A. Unocic, S. E. Habas, M. B. Griffin, J. A. Schaidle, H. M. Meyer III, Y. Wang, H. Wang*, "Deactivation by Potassium Accumulation on a Pt/TiO_2 Bifunctional Catalyst for Biomass Catalytic Fast Pyrolysis", *ACS Catalysis,* 2022, 12, 465. https://doi.org/10.1021/acscatal.1c02368
12. K. A. Unocic*, D. K. Hensley, F. S. Walden, W. C. Bigelow, M. B. Griffin, S. E. Habas, R. R. Unocic, L. F. Allard, "Performing In Situ Closed-Cell Gas Reactions in the Transmission Electron Microscope", *J. Vis. Exp.,* 2021, 173, e62174. https://doi.org/10.3791/62174

Publications (Since last review, cont. 2)

13. X.Huo, D. R. Conklin, M. Zhou, V. Vorotnikov, R. S. Assary, S. C. Purdy, K. Page, Z. Li, K. A. Unocic, R. I. Balderas, R. M. Richards, D. R. Vardon*, "Catalytic activity and water stability of the MgO(111) surface for 2-pentanone condensation", *Appl. Catal. B,* 2021, 294, 120234. https://doi.org/10.1016/j.apcatb.2021.120234
14. J. Zhang, E. C. Wegener, N. River Samad, J. W. Harris, K. A. Unocic, L. F. Allard, S. Purdy, S. Adhikari, M. J. Cordon, J. T. Miller, T. R. Krause, S. Cheng, D. Liu, M. Li, X. Jiang, Z. Wu, Z. Li*, "Isolated Metal Sites in Cu–Zn–Y/Beta for Direct and Selective Butene-Rich C_{3+} Olefin Formation from Ethanol", *ACS Catal.,* 2021, 11, 9885. https://doi.org/10.1021/acscatal.1c02177
15. W. W. McNeary, S. A. Tacey, G. D. Lahti, D. R. Conklin, K. A. Unocic, E. C. D. Tan, E. C. Wegener, T. Eralp Erden, S. Moulton, C. Gump, J. Burger, M. B. Griffin, C. A. Farberow, M. J. Watson, L. Tuxworth, K. M. Van Allsburg, A. A. Dameron, K. Buechler, D. R. Vardon*, "Atomic Layer Deposition with TiO_2 for Enhanced Reactivity and Stability of Aromatic Hydrogenation Catalysts", *ACS Catal.,* 2021, 11, 8538. https://doi.org/10.1021/acscatal.1c02101
16. M. J. Cordon, J. Zhang, S. C. Purdy, E. C. Wegener, K. A. Unocic, L. F. Allard, M. Zhou, R. S. Assary, J. T. Miller, T. R. Krause, F. Lin, H. Wang, A. J. Kropf, C. Yang, D. Liu, Z. Li*, "Selective Butene Formation in Direct Ethanol-to-C_{3+}-Olefin Valorization over Zn–Y/Beta and Single-Atom Alloy Composite Catalysts Using *In Situ*-Generated Hydrogen", *ACS Catal.,* 2021, 11, 7193. https://doi.org/10.1021/acscatal.1c01136
17. N. A. Huq, G. R. Hafenstine, X. Huo, H. Nguyen, S. M. Tifft, D. R. Conklin, D. Stück, J. Stunkel, Z. Yang, J. S. Heyne, M. R. Wiatrowski, Y. Zhang, L. Tao, J. Zhu, C.S. McEnally, E. D. Christensen, C. Hays, K. M. Van Allsburg, K. A. Unocic, H.M. Meyer, Z. Abdullah, D. R. Vardon, "Toward net-zero sustainable aviation fuel with wet waste–derived volatile fatty acids", *PNAS,* 2021, 118, e2023008118. https://doi.org/10.1073/pnas.2023008118
18. Q. Wu, A. T. To, C. P. Nash, D. P. Dupuis, F. G. Baddour, S. E. Habas*, D. A. Ruddy*, "Spectroscopic insight into carbon speciation and removal on a Cu/BEA catalyst during renewable high-octane hydrocarbon synthesis", *Appl. Catal. B,* 2021, 119925. https://doi.org/10.1016/j.apcatb.2021.119925

Patents (Since last review)

1. F. G. Baddour, S. E. Habas, B. E. Petel, A. Yung, “Fluidic Systems and Methods for the Manufacture of Nanoparticles”, U.S. Patent Application 18/173,317, February 23, 2023.
2. F. G. Baddour, A. Kumar, K. M. Van Allsburg, D. A. Ruddy, S. E. Habas, A. Royappa, B. E. Petel, C. T. Nimlos, “Metal Carbides and Methods of Making the Same”, U.S. Patent Application 2021/0309525 A1, October 7, 2021.

Presentations (since last review)

1. K. A. Unocic, N. LiBretto, A. T To, J. A. Kropf, D. A. Ruddy, T. R. Krause, L. F. Allard, S. E. Habas, Revealing the Reaction Behavior of $Co_{0.86}Mn_{0.14}O$ under H_2 using in situ Closed-Cell Gas Reaction S/TEM, Microscopy and Microanalysis 2022, July 31-August 4, 2022, Portland, OR, USA. (In person)
2. Invited presentation, S. E. Habas, "Scalable solution synthesis approaches to tailored nanostructured catalysts", 2022 Annual Spring Symposium for the Catalysis Club of Chicago, Rosemont, IL, May 6, 2022. (In person)
3. "From in situ to operando closed cell gas reaction STEM: Challenges and opportunities", *In-situ/Operando* TEM Techniques for Advanced Nanomaterial Characterization Workshop, CCEM McMater University, March 31 - April 1, 2022.
4. "Investigation of deactivation mechanisms in Pt/TiO_2 catalyst using advanced and operando STEM", American Chemical Society Spring Meeting, San Diego, CA, March 20-24, 2022.
5. Invited presentation, S. E. Habas, "Nanostructured metal phosphide catalysts for renewable carbon conversion processes", 2020 International Chemical Congress of Pacifichem Basin Societies, Honolulu, HI, December 16, 2021. (Virtual)
6. Invited Colloquium, K. A. Unocic, "*Operando* STEM - Simulating Reaction Conditions via In Situ closed-cell gas-reaction Microscopy", Department of Materials Science and Engineering, The Ohio State University, Columbus, OH, November 17, 2021.
7. Invited presentation, K. A. Unocic, M. Griffin, J. Schaidle, S. E. Habas, F. S. Walden, R. R. Unocic and L. F. Allard, "Practical Aspects of Performing Quantitative EELS Measurements of Gas Compositions in Closed-Cell Gas Reaction S/TEM," Microscopy and Microanalysis 2021 Meeting, Virtual Meeting, August 1-5, 2021.
8. Invited presentation, S. E. Habas, "Nanostructured metal phosphide catalysts for renewable carbon conversion processes", ACS Spring Meeting, ACS Award in Inorganic Nanoscience Symposium Honoring Richard Leo Brutchey, Virtual , April 12, 2021.