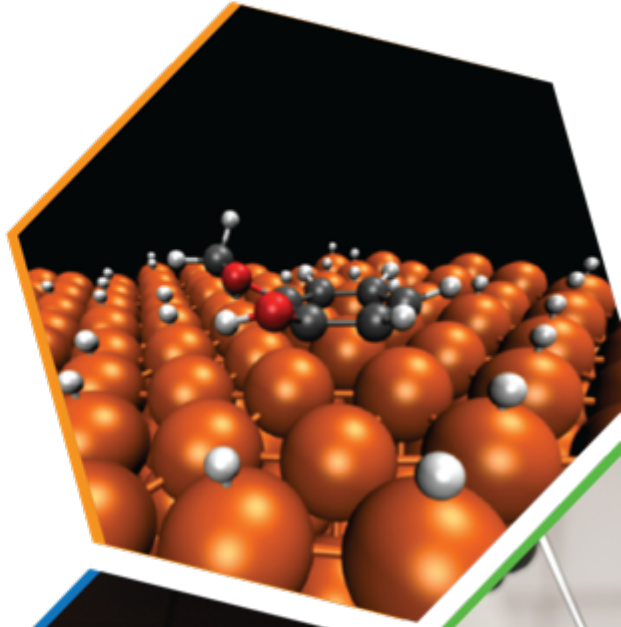
ChemCatBio
Chemical Catalysis for Bioenergy



Advanced Catalyst Synthesis and Characterization (ACSC) Project

WBS 2.5.4.304/303/305

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

March 11, 2021

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)
- Upgrading of C1 Building Blocks (NREL)
- Upgrading of C2 Intermediates (PNNL, ORNL)
- Catalytic Fast Pyrolysis (NREL, PNNL)
- Electrocatalytic CO_2 Utilization (NREL)

Enabling Capabilities

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

Industry Partnerships *(Phase II Directed Funding)*

- Opus12 (NREL)
- Visolis (PNNL)
- Sironix (LANL)

Cross-Cutting Support

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

Project Overview – Target-Driven Goals and Outcomes

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

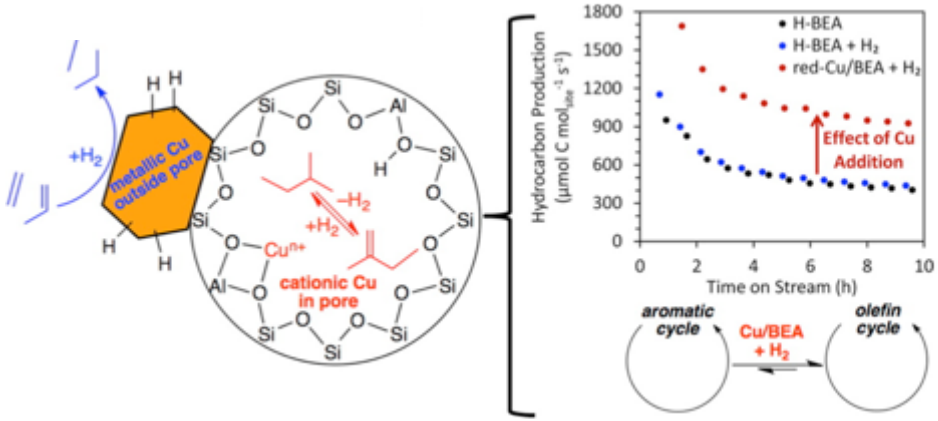
ChemCatBio Catalysis Projects	Baseline	Future Target	Impact: Critical Catalysis Challenge
Upgrading of C1 Building Blocks **C1**	Regeneration temperature **>600 °C**	**<500 °C**	Efficient regeneration leading to prolonged catalyst lifetime
Catalytic Upgrading of Pyrolysis Products **CFP**	TOS before regeneration **2.5 h**	**>7 h**	Reduce deactivation rate via informed catalyst synthesis
Catalytic Upgrading of Biochemical Intermediates **CUBI**	Deactivation rate due to alkali impurities **10%**	**1%**	Reduce impact of alkali impurities
Upgrading of C2 Building Blocks **C2**	Recovery of C_4 formation rate **45%**	**>60%**	Mitigate deactivation and inform regeneration

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

Project Overview – Based on Successful Collaboration

Cross-cutting enabling capabilities 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

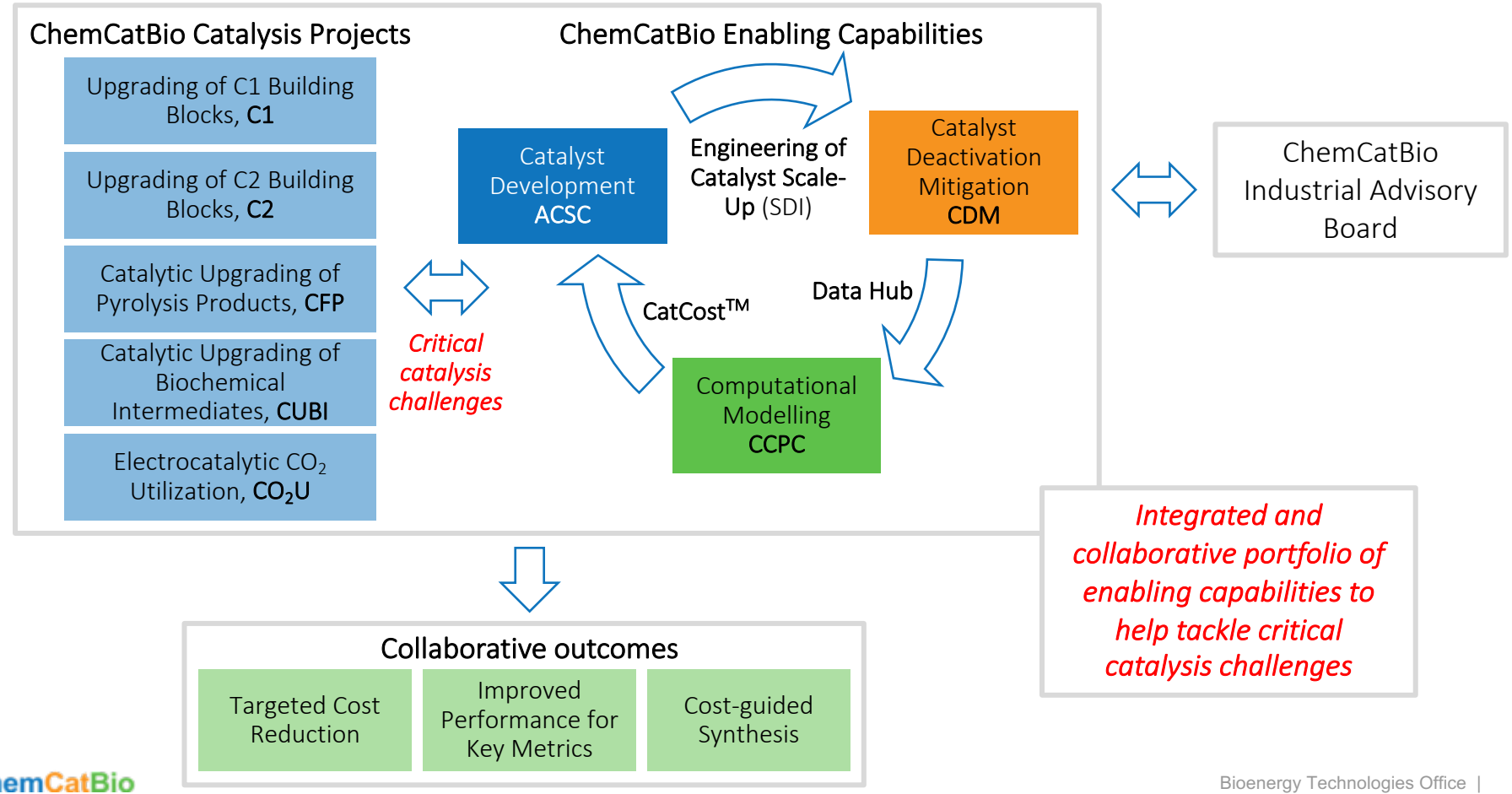


Schaidle et al., *ACS Catal.,* 2015, 5, 1794. https://doi.org/10.1021/cs501876w

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

Highly successful collaboration identified need for advanced characterization across all projects

Project Overview – Enabling Capability Within ChemCatBio

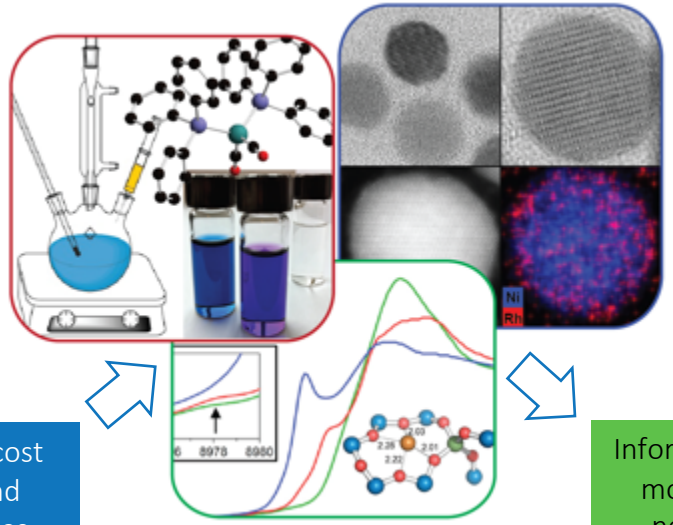


Project Overview – Providing Complementary Efforts

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



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
Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY

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 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

Argonne NATIONAL LABORATORY
OAK RIDGE National Laboratory
NREL NATIONAL RENEWABLE ENERGY LABORATORY

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 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

OAK RIDGE National Laboratory

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
- Collaboration with the **Engineering of Scale-up project** (SDI) for early-stage development of technical catalysts

NREL NATIONAL RENEWABLE ENERGY LABORATORY

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

1. Management – Evolving to Meet ChemCatBio Needs

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

Monthly meetings, annual face-to-face, project specific meetings

Joint Milestones with ChemCatBio catalysis projects

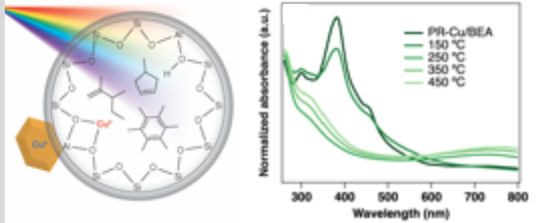
Develop and demonstrate new capabilities

FY21 Go/No-Go Decision

Identify capabilities to be integrated or removed

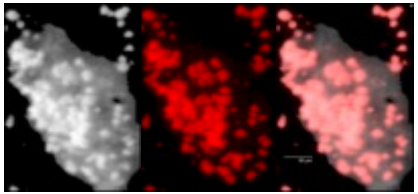
Annual Evaluation of New/Existing Capabilities

Operando DR-UV-vis spectroscopy



Rapid metal and carbon speciation at extended time on stream

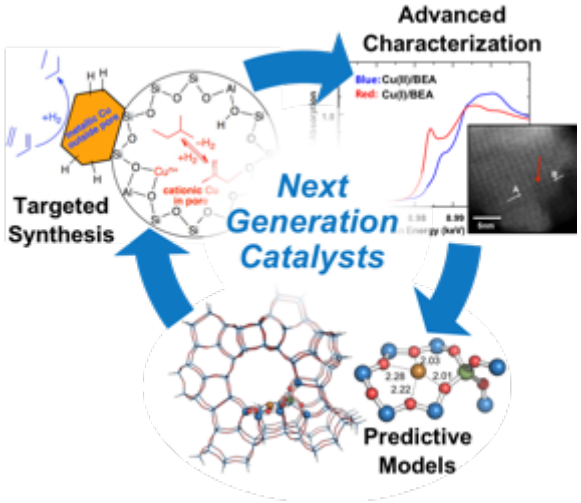
X-ray microprobe analysis



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

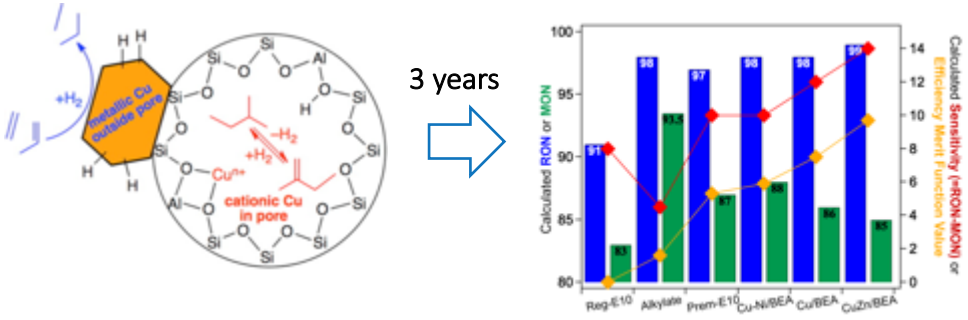
Based on the current and emerging needs of ChemCatBio catalysis projects

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

Baseline: *Complete* Development Cycle (**C1**, FY19)



Challenge: Assessing *Accelerated* Development Cycle (**C2**, FY21)

- Leverage capabilities, expertise, and models for metal-modified zeolites
- Next-generation Cu-Zn/Y-BEA with increased C_3–C_6 olefin selectivity for ethanol to distillates process
- **Target:** 1.5 years

Provide fundamental insight leading to actionable recommendations and acceleration of development cycle

2. Approach – Supporting ChemCatBio

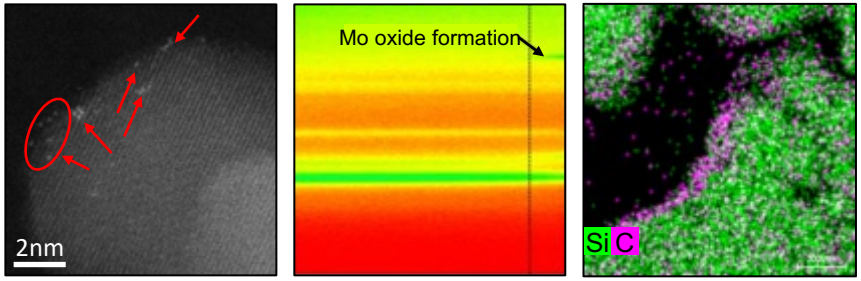
Direct engagement with *all* of the ChemCatBio catalysis projects

- 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

Ongoing focus on foundational research

- Tackling overarching catalysis challenges to enable rapid response to new critical catalysis challenges
- Needs of catalysis projects, Steering Committee, Industrial Advisory Board

Catalyst stability challenges



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

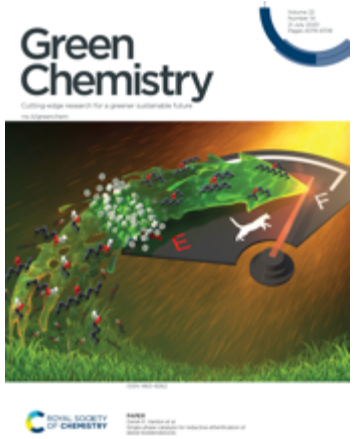
Balance overarching catalysis challenges with specific needs of catalysis projects

2. Approach – Multiple Modes of Interaction

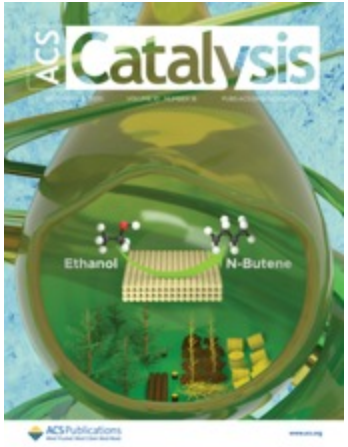
How to work with the ACSC

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

Identified active Ga species
CFP



Determined optimal Pd nanoparticle size
CUBI



Assessed surface carbon species
C2

K. Iisa, et al., *Green Chem.,* 2020, 22, 2403. https://doi.org/10.1039/C9GC03408K
G. R. Hafenstine, et al., *Green Chem.,* 2020, 22, 4463. https://doi.org/10.1039/D0GC00939C
V. L. Dagle, et al., *ACS Catal.,* 2020, 10, 10602. https://doi.org/10.1021/acscatal.0c02235

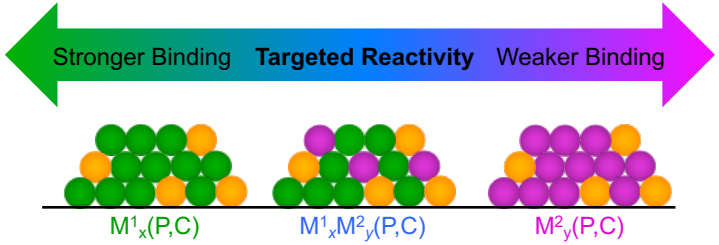
Enables significant and rapid impact to ChemCatBio Catalysis projects

2. Approach – Responding to New Project Needs

Electrochemical CO_2 Utilization

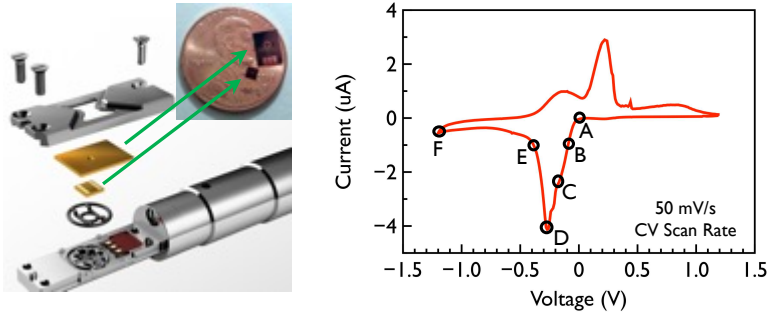
- Leverage capabilities and expertise
  - Existing ChemCatBio projects
  - National lab capabilities
  - Other EMN Consortia

Tunable electrocatalyst systems



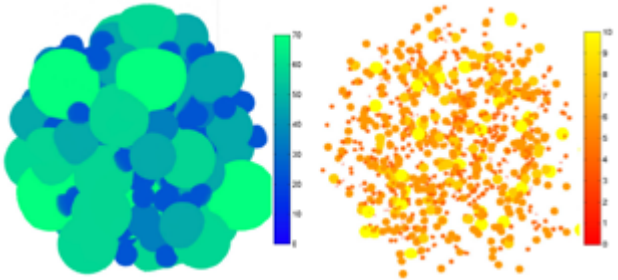
Mixed-metal phosphides and carbides (CFP)

Structure of working electrocatalyst



Electrochemical STEM (ORNL)

3D organization of working electrodes



X-ray nanotomography (FCTO ElectroCat)

Adapting and developing capabilities to meet needs of new projects

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

opus 12

Vertimass
Transformative fungible biofuels.

Johnson Matthey
Inspiring science, enhancing life

FORGE NANO

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Feedback from Industrial Advisory Board

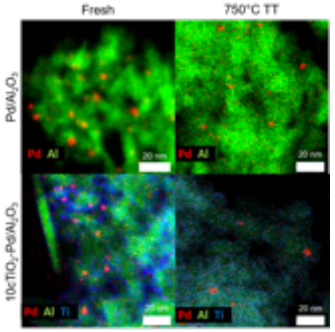
- ChemCatBio needs to be *world-class* in synthesis and characterization
- It is important to develop tools and expertise for broad *overarching challenges*

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

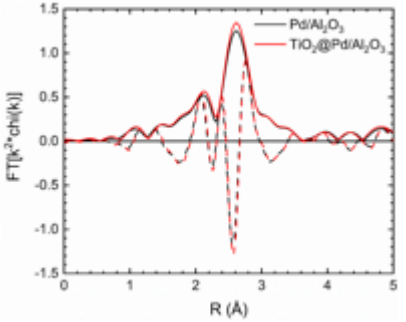
Johnson Matthey
Inspiring science, enhancing life

FORGE NANO

Demonstrated co-location of TiO_2 and Pd nanoparticles



Determined Pd electronic structure was not altered by TiO_2

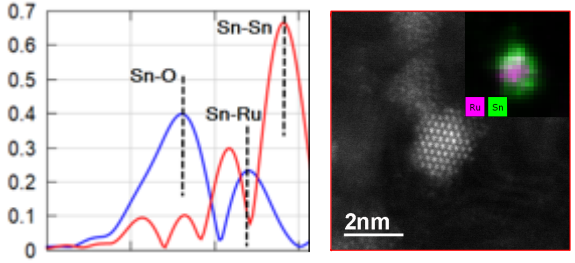


W. W. McNeary, D. R. Vardon, et al., *ACS Catal. Submitted.*

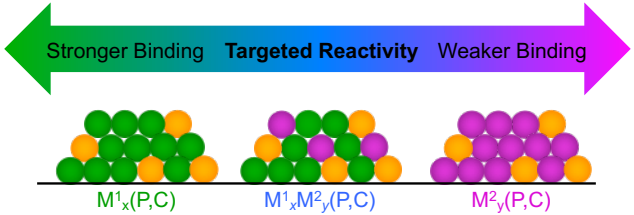
Outcome: Determined that enhanced activity was due to ensemble effects from partial TiO_2 coverage of Pd

Providing capabilities and expertise that are responsive to industry needs

3. Impact – Enabling BETO Goals

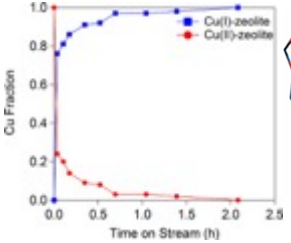


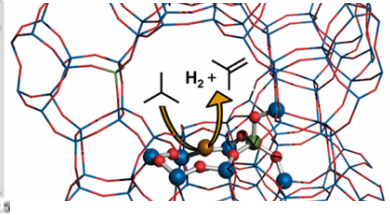
"Developing these processes should be coupled with efforts to obtain a better understanding of the causes of catalyst poisoning and deactivation"



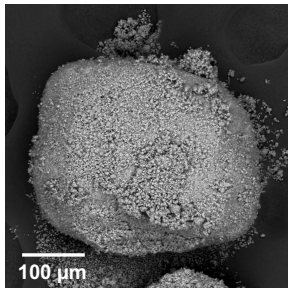
"Emerging technologies and processes may require the design and synthesis of novel catalysts."

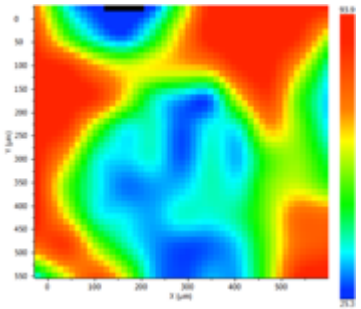
"A better understanding of catalytic active sites and reaction mechanisms, across both low- and high temperature processes, can be obtained through advanced characterization techniques."





The ACSC "identifies catalysts and process conditions that increase overall yield" by "direct improvements to catalyst performance that minimize the loss of carbon"



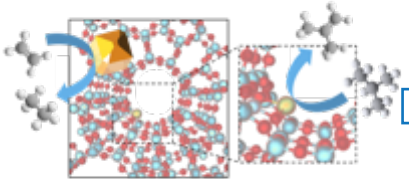


Derisking bioenergy processes through catalyst development and characterization

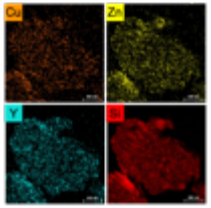
3. Impact – Providing Capabilities and Expertise

Within ChemCatBio and BETO

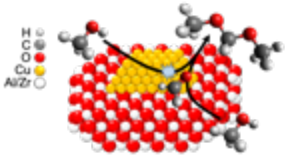
Developing capabilities and expertise that span multiple projects



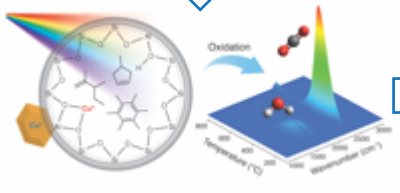
*Precise understanding of active sites in Cu/BEA (**C1**)*



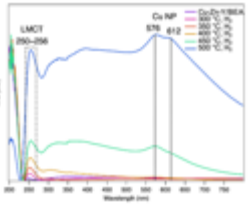
*Extended to Cu-Zn-Y/BEA (**C2**)*



*Rapid insight into Cu/metal oxides (**Co-Optima**)*



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

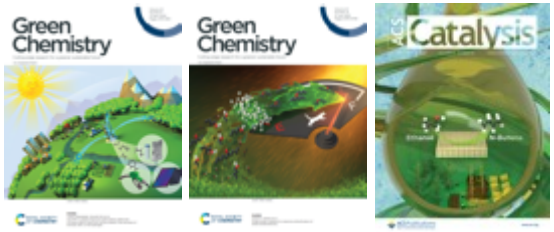


*Extended to regeneration of Cu-Zn-Y/BEA (**C2**)*

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

Externally to the catalysis community

- 13 peer reviewed publications FY20-21
- 5 external presentations FY20-21
- Industry engagement with 5 Directed Funding Opportunities
- Webinar on Accelerating the Catalyst Development Cycle
- Input to ChemCatBio **DataHub**
- New capabilities and expertise available at DOE User Facilities



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

3. Impact – Quantified Benefit to the Catalysis Projects

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

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Catalytic Upgrading of Biochemical Intermediates **CUBI**	Deactivation rate due to alkali impurities **10%**	**1%**	Reduce impact of alkali impurities
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Project Outcome: *Accelerated catalyst and process development cycle* enabling demonstrated performance enhancements in half the time

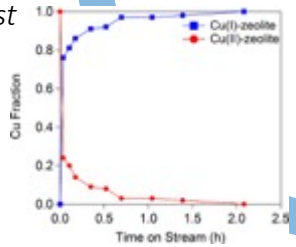
4. Progress and Outcomes – Demonstrated Catalyst Development Cycle (C1)

Challenge: Identify active site for alkane dehydrogenation over Cu/BEA and enable tunable control over P:O ratio from DME

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

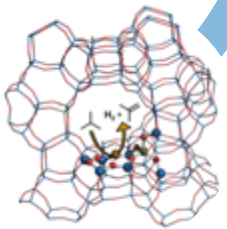
Catalyst	Active site
CuO/SiO_2	CuO particles
Cu/SiO_2	Cu(0) particles
H-BEA	Brønsted acid
ox-IE-Cu/BEA	Ionic Cu(II)-zeolite
red-IE-Cu/BEA	Ionic Cu(I)-zeolite

Synthesized catalysts with active sites in working catalyst

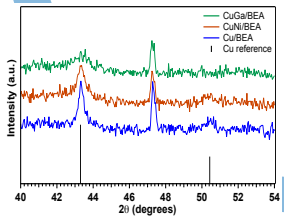


Identified Cu(I) as active site for dehydrogenation

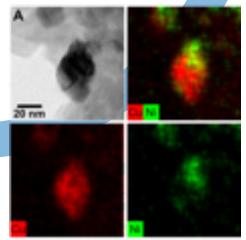
Targets: Ga, Zn, Ni, Co identified as potential next-generation ionic species to maximize dehydrogenation



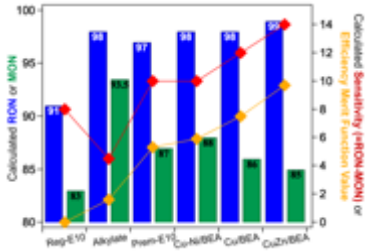
Predictive model for dehydrogenation, CCPC



Synthetic control of speciation in bimetallic catalysts



Determined speciation in working catalysts

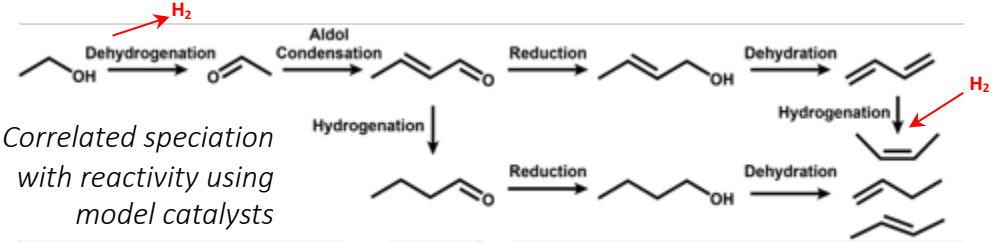


Verified cost-normalized performance improvements, C1, CatCost™

Success in the critical research challenge of improving fuel properties through catalyst design (FY19)

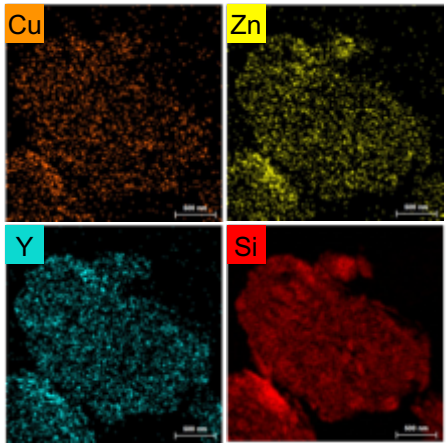
4. Progress and Outcomes – Accelerating the Cycle (C2)

Challenge: Identify active sites for conversion of ethanol to butene-rich C_3–C_6 olefins over Cu-Zn-Y/BEA



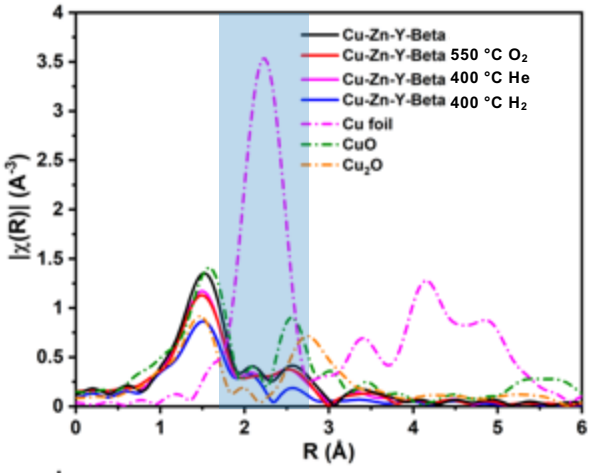
Correlated speciation with reactivity using model catalysts

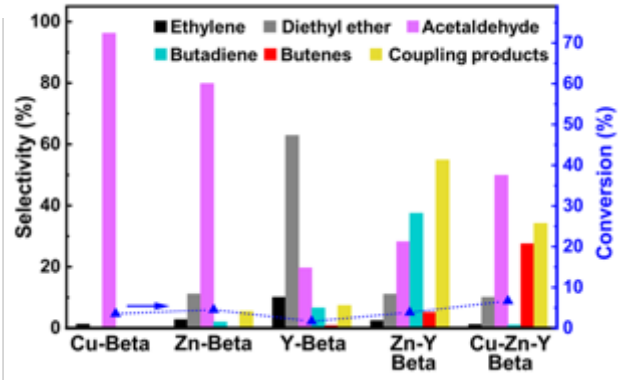
Determined that Cu, Zn, and Y are atomically dispersed



J. Zhang, Z. Li, et al., *In Preparation.*

No metallic Cu clusters or particles present even in a reducing environment





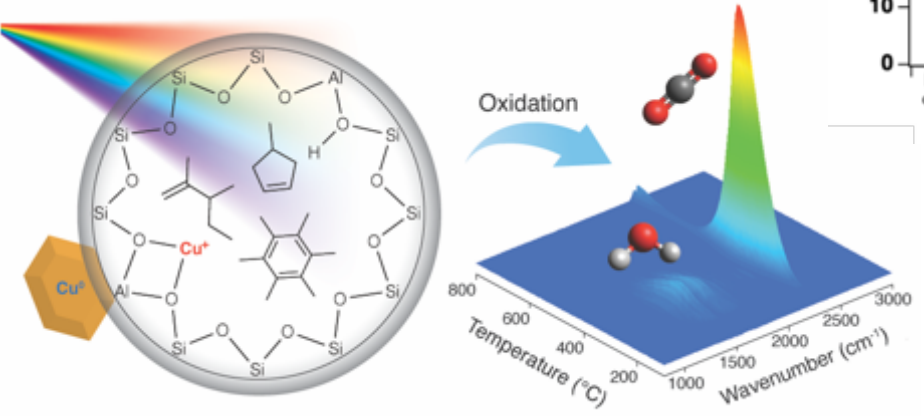
Outcome: Informed next-generation catalyst synthesis for enhanced C_3–C_6 olefin selectivity

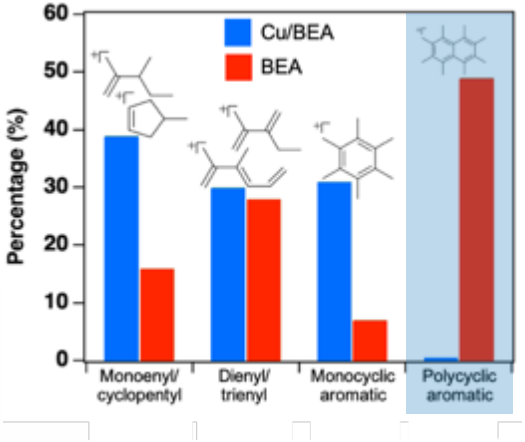
Quantify acceleration of catalyst and process development cycle (FY21 Go/No-go decision)

4. Progress and Outcomes – Regeneration of Metal Zeolite Catalysts (C1)

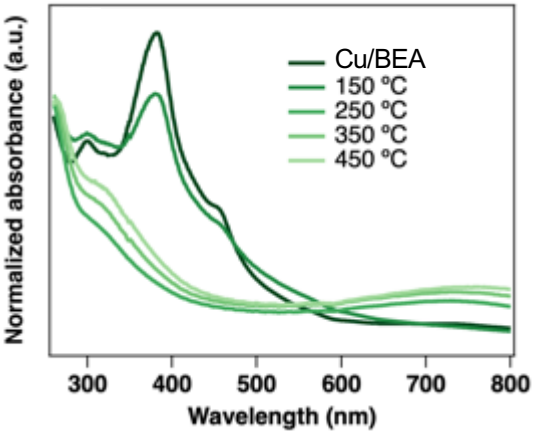
Challenge: Determine speciation of carbon deposited on Cu/BEA during DME to hydrocarbons reaction

Suite of in situ *spectroscopic characterization techniques (DR-UV-Vis, Raman, TGA-FTIR spectroscopy)*





Smaller more defective carbon species on Cu/BEA relative to BEA



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

Outcome: Developed an effective regeneration procedure that enabled full recovery of catalyst activity

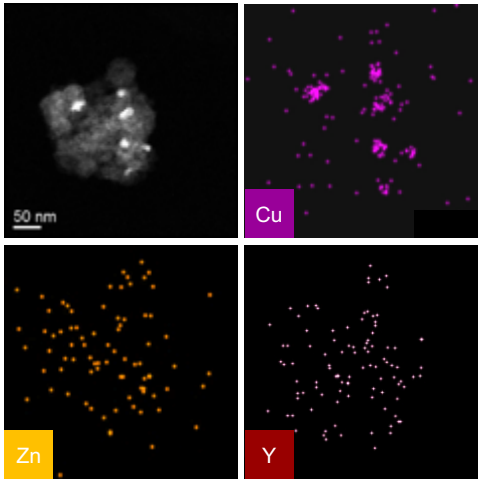
Q. Wu, A. T. To, et al., *Appl. Catal. B,* 2021, 119925.
https://doi.org/10.1016/j.apcatb.2021.119925

Complementary spectroscopic characterization techniques to provide complete insight

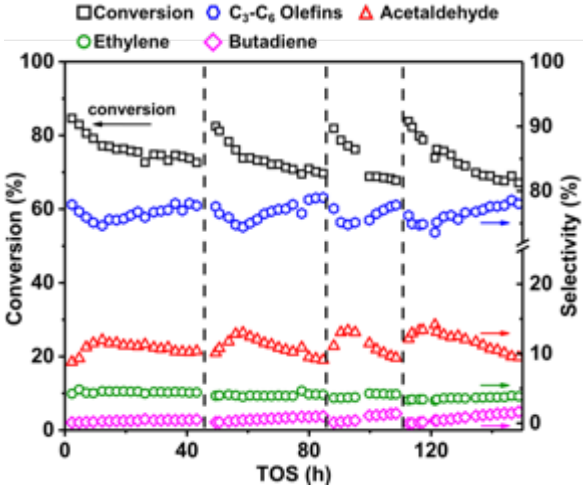
4. Progress and Outcomes – Leveraging Capabilities (C2)

Challenge: Identify deactivation mechanisms of Cu-Zn-Y/BEA during ethanol to olefins conversion

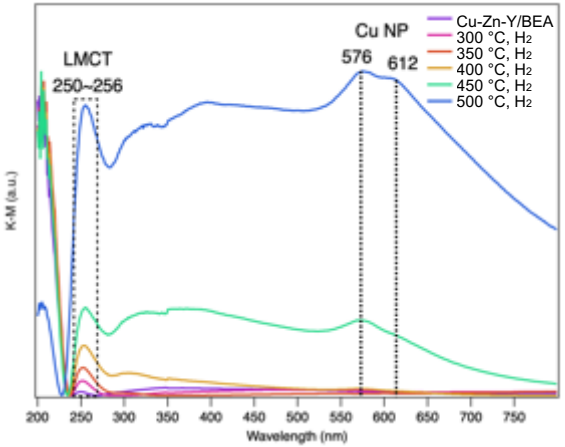
Zn and Y sites maintain atomic dispersion, but Cu begins to cluster at longer time on stream



Cu clustering leads to changes in selectivity and carbon deposition reduces activity



J. Zhang, Z. Li, et al., 2021, *In Preparation.*



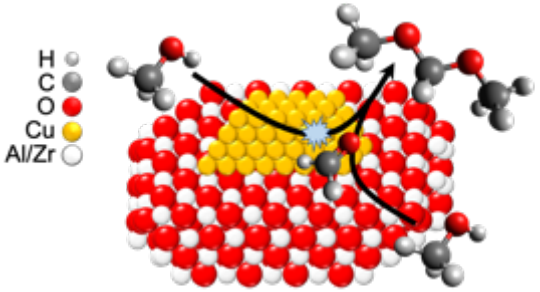
Applying new operando *spectroscopic capabilities to provide rapid insight into Cu and C speciation during reaction/regeneration*

Projected Outcome: A regeneration procedure that enables recovery of >60% of C_4 product formation rate

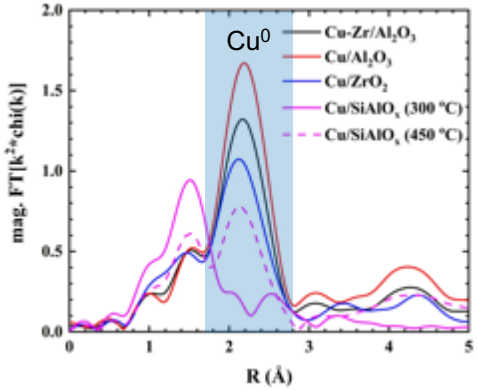
Collaborative effort to provide comprehensive insight (C2, ACSC, CDM, CCPC, Q3 Milestone)

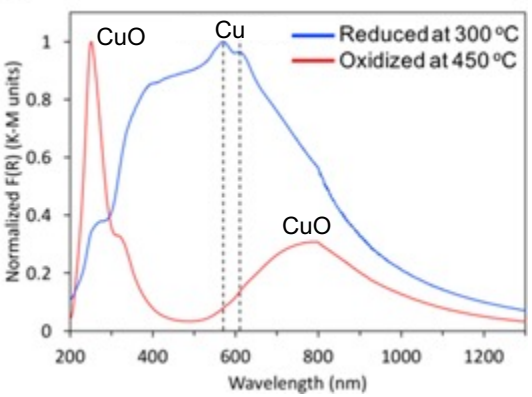
4. Progress and Outcomes – Leveraging Capabilities (Co-Optima)

Challenge: Identify the active sites for direct production of OMEs via dehydrogenative coupling of methanol

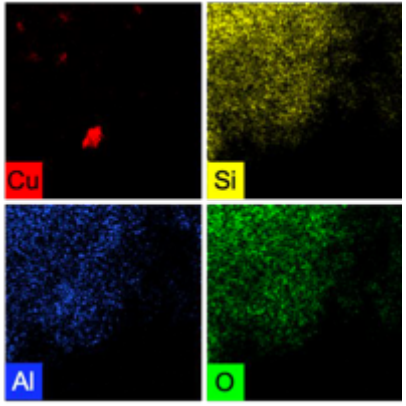


A. T. To, et al., *ACS Sus. Chem. Eng.*, 2020, 8, 12151. https://doi.org/10.1021/acssuschemeng.0c03606





Distribution of acid site strengths on ZrAlO reduces DME selectivity in favor of coupling chemistry



Metallic Cu nanoparticles formed under pre-treatment conditions promote dehydrogenation

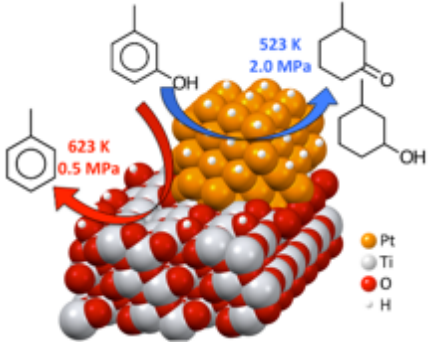
Outcome: Achieved 40% of equilibrium-limited yield under mild conditions by balancing dehydrogenation sites and acid site strengths

Combined insight across all ACSC partners provided actionable insight

4. Progress and Outcomes – Catalyst Deactivation (CFP)

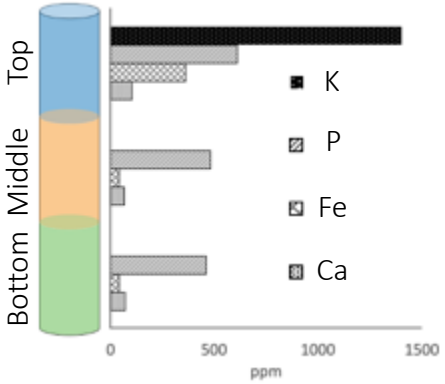
Challenge: Identify causes of catalyst deactivation during *ex situ* CFP over SOT 0.5 wt% Pt/TiO_2 catalyst

- Changes in Pt particle size
- Alkali metal deposition
- Carbon deposition



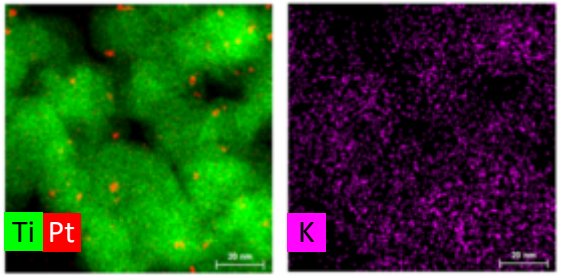
M. Griffin, et al. ACS Catal., 2016, 6, 2715. https://doi.org/10.1021/acscatal.5b02868

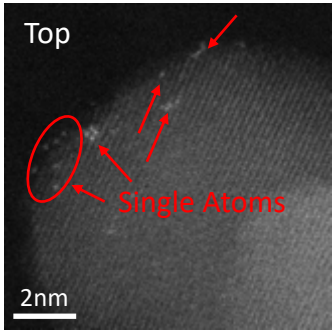
Spent catalyst from multiple bed locations following 4 cycles and 32 hours time on stream

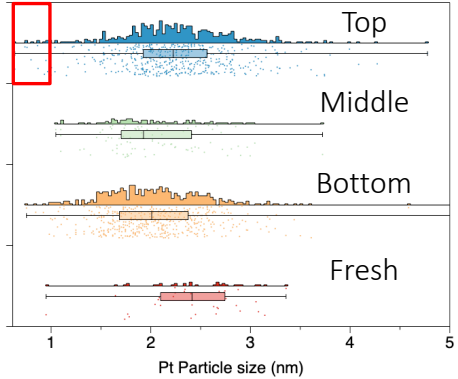


F. Lin, H. Wang, et al., 2021, *In Preparation.*

Spatially resolved distribution of K concentration correlated with single Pt atom concentration







Outcome: Characterization of real catalysts informed model studies by CDM project and computational models by CCPC

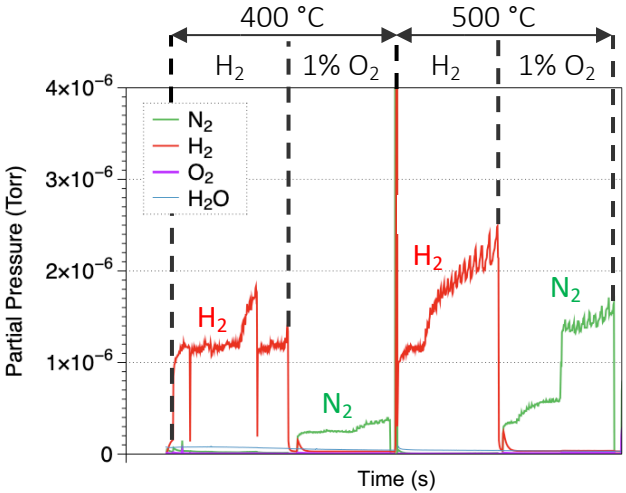
Relationships between real and model systems enable predictive trends (CFP, ACSC, CDM, CCPC, Q4 Milestone)

4. Progress and Outcomes – Catalyst deactivation (CFP)

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

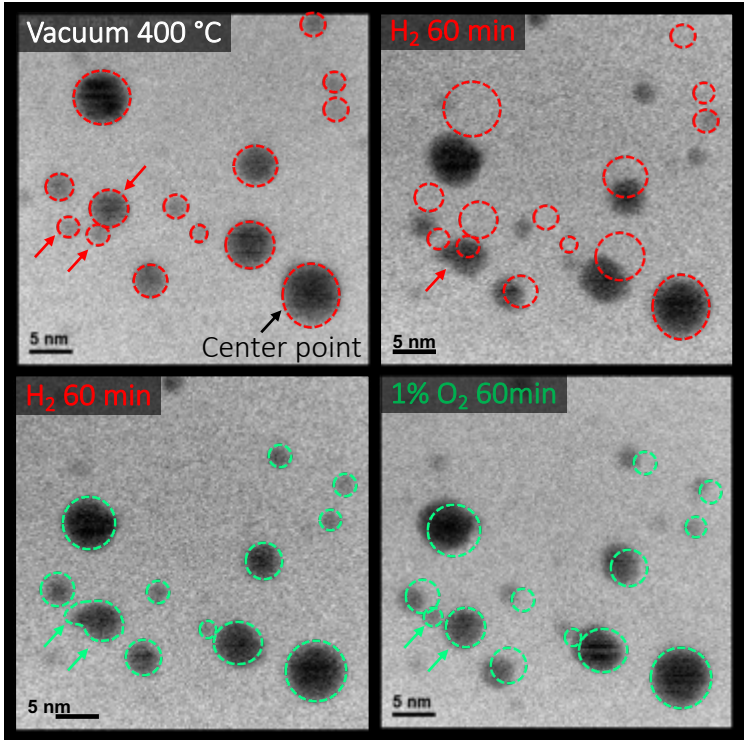
New operando *reactant/product detection capability*

Regeneration by thermal oxidation to remove coke and reduction to regenerate oxygen vacancies



Outcome: Informed pre-treatment and regeneration conditions to minimize changes in Pt particle size and reactivity

K. A. Unocic, et al., *Microsc. Microanal.*, 2020, 1-3. https://doi.org/10.1017/S1431927620019005

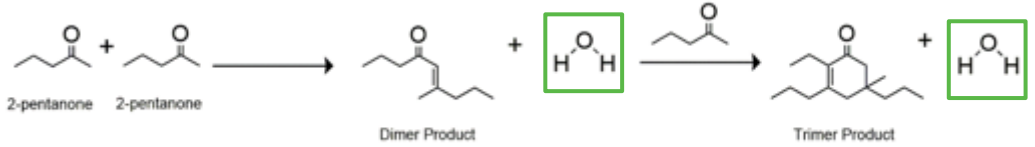


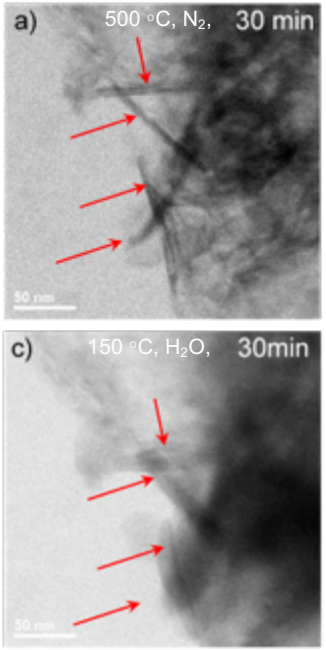
H_2 promotes sintering of Pt particles while O_2 assists with redistribution

Propose mitigation strategies to reduce deactivation rate by 15% (CFP, ACSC, CDM, CCPC Q4 Milestone)

4. Progress and Outcomes – Stability in Water (CUBI)

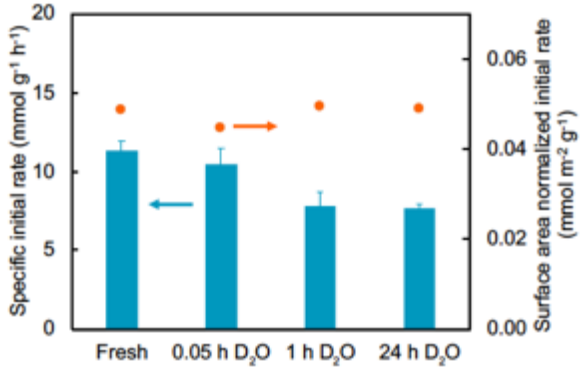
Challenge: Determine the impact of water vapor on activity of MgO catalyst for aldol condensation reactions

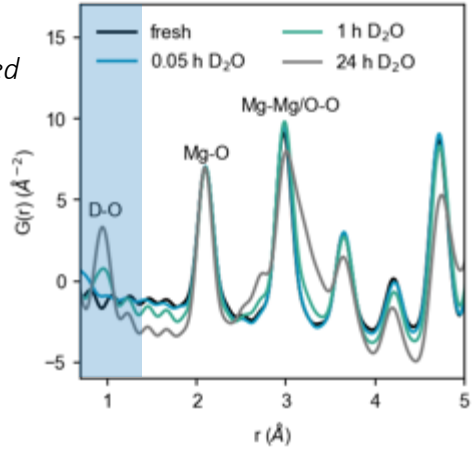




X. Huo, D. R. Vardon, et al., 2021, *Submitted.*

Collaboration with DOE user facility identified surface hydroxyl groups predicted by the CCPC to reduce reaction barrier





Identified textural and structural changes with exposure to water vapor using new operando capability

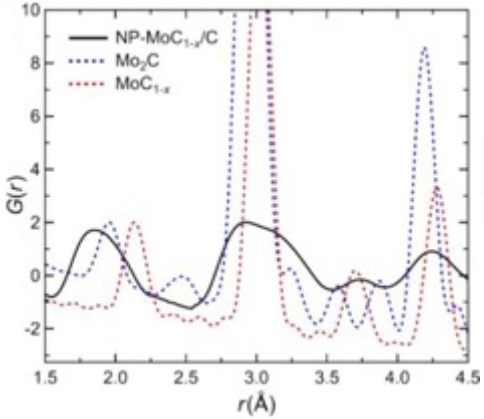
Outcome: Determined that MgO(111)-derived hydroxide is responsible for activity following water exposure and informed thermal regeneration to recover 94% of activity

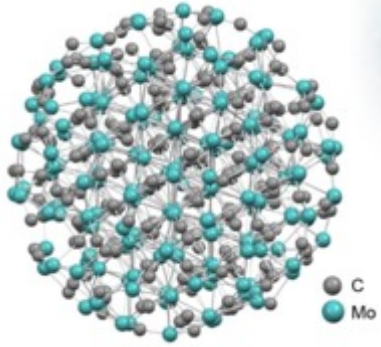
Capability development and demonstration towards project-specific and overarching challenges

4. Progress and Outcomes – Catalyst Design for Emerging Pathways (C1)

Challenge: Leverage non-noble metal multifunctional catalysts from CFP for thermochemical CO_2 reduction

Low-temperature solution synthesis route to high surface area metal carbide nanoparticles

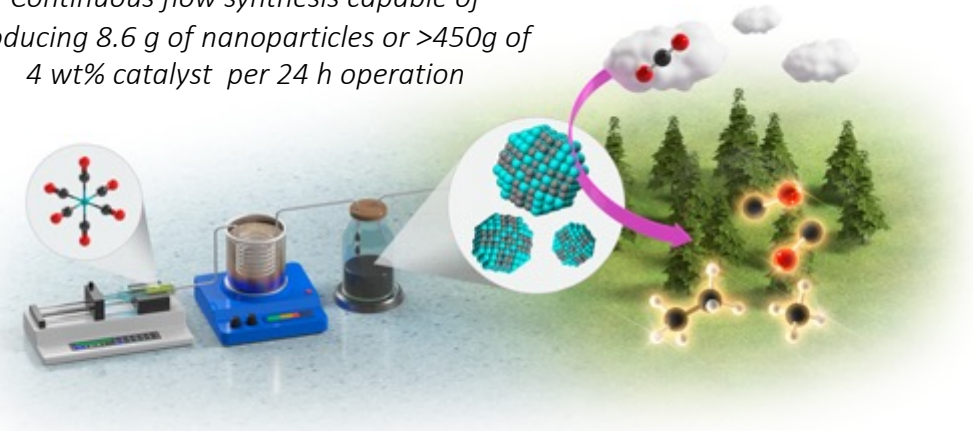




F. G. Baddour, et al., J. Am. Chem. Soc., 2020, 142, 1010.
https://doi.org/10.1021/jacs.9b11238

USC University of Southern California

Continuous flow synthesis capable of producing 8.6 g of nanoparticles or >450g of 4 wt% catalyst per 24 h operation



Outcome: Exhibited 2x increase in CO_2 hydrogenation activity per site and selectivity to C_{2+} products compared to bulk analogue

Developing scalable low-cost methodologies for technical formulations of metal carbide catalysts with Engineering of Scale-up project (SDI)

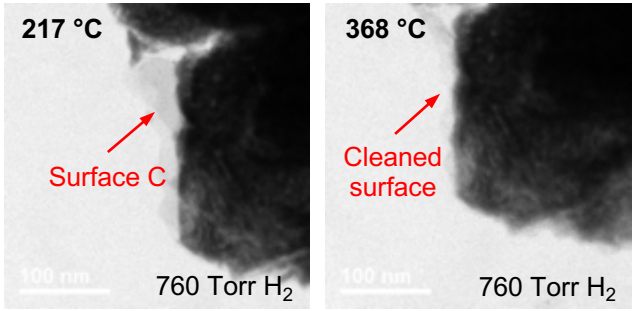
F. G. Baddour, et al., 2020, U.S. Provisional Patent Application No. 62/993,487.

Tunable multifunctional materials for complex transformations (C1, CFP, End of cycle Milestone)

4. Progress and Outcomes – Regeneration of Metal Carbides (CFP, C1)

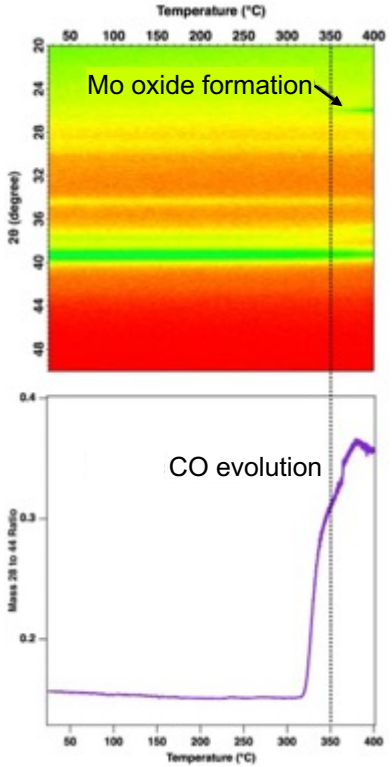
Challenge: Determine speciation of carbon deposited on metal carbides during CFP and CO_2 reduction

Currently, regeneration of metal carbide catalysts relies on costly high-temperature recarburization



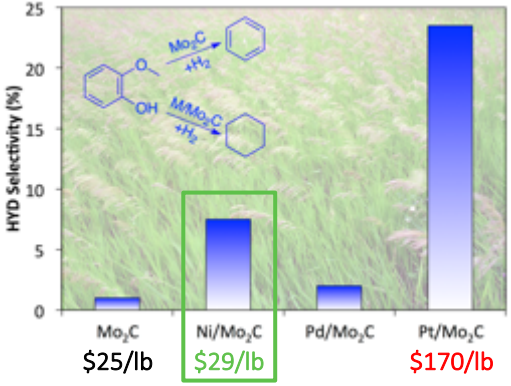
Demonstrated operando *characterization during regeneration to evaluate surface carbon removal as CO/CO_2*

K. A. Unocic, et al., *Microsc. Microanal.,* 2018, 24, 322. https://doi.org/10.1017/S1431927618002106



Evaluating mild oxidants using in situ *characterization*

Synthetic methodologies for metal modification to increase hydrogenation of deactivating carbon species



F. G. Baddour, et al., *ACS Sustainable Chem. Eng.,* 2017, 5, 11433. https://doi.org/10.1021/acssuschemeng.7b02544

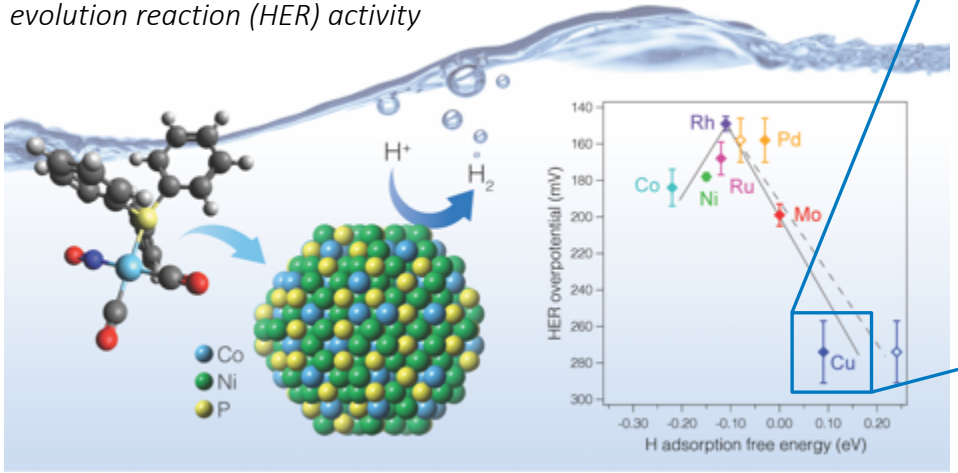
Projected Outcome: A cost-effective regeneration strategy for non-metal/oxide catalysts to recover full activity

Enables application of tunable multifunctional metal carbide catalysts (C1, CFP, End of cycle Milestone)

4. Progress and Outcomes – Catalyst Design for Emerging Pathways (CO_2U)

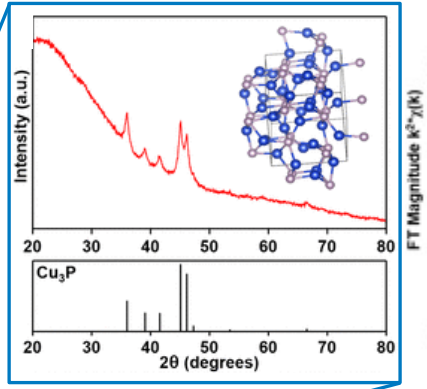
Challenge: Leverage multifunctional catalysts from CFP for electrocatalytic CO_2 reduction

Developed tunable bimetallic phosphide nanoparticle catalysts with composition-dependent hydrogen evolution reaction (HER) activity

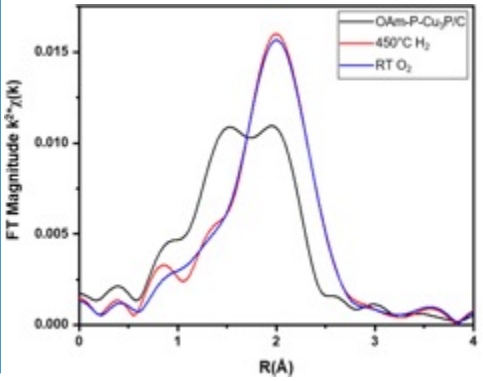


C. A. Downes, K. M. Van Allsburg, J. A. Schaidle, S. E. Habas, et al., *In Preparation.*

Limited HER activity for Cu containing phosphide suggested Cu_3P may be active for CO_2 hydrogenation



Cu–P bond formation during synthesis promotes electrocatalytic stability



C. A. Downes, et al., *ACS Appl. Energy Mater.,* 2020, 3, 10435. https://doi.org/10.1021/acsaem.0c01360

Outcome: Introduction of P to Cu as Cu_3P enabled the production of formate from electrocatalytic reduction of CO_2

Demonstrated synthetic control over electrocatalyst stability and activity

Quad Chart Overview

Timeline
- 10/01/2020
- 9/30/2022

	FY20	Active Project
DOE Funding	$510K (NREL) $530K (ANL) $452.5K (ORNL)	$1.53M (NREL) $1.59M (ANL) $1.37M (ORNL)

Project Partners
- National Renewable Energy Laboratory (NREL)
- Argonne National Laboratory (ANL)
- Oak Ridge National Laboratory (ORNL)

Barriers addressed
- Decreasing the Time and Cost to Develop Novel Industrially Relevant Catalysts
- Improving Catalyst Lifetime

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

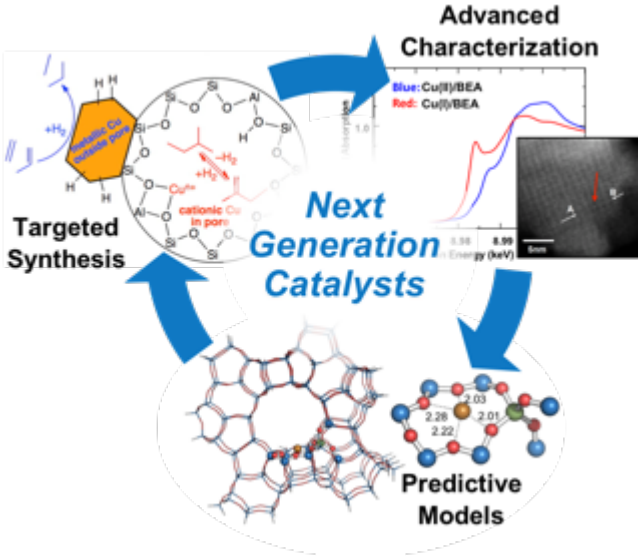
End of Project Milestone
Demonstrate a scalable noble metal-free catalyst for CFP with a corresponding regeneration strategy based on fundamental insight from advanced characterization by the ACSC project and computational modeling by the CCPC.

Funding Mechanism
- Annual operating plan
- Chemical Catalysis for Bioenergy (ChemCatBio) Consortium

Summary

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

- Integrated and collaborative portfolio of enabling capabilities to help address critical catalysis challenges
- Tackling overarching catalysis challenges to enable rapid response to new critical catalysis challenges
- Demonstrated 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

Acknowledgements

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Shawn Reeves
Raymond Unocic
Junyan Zhang

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

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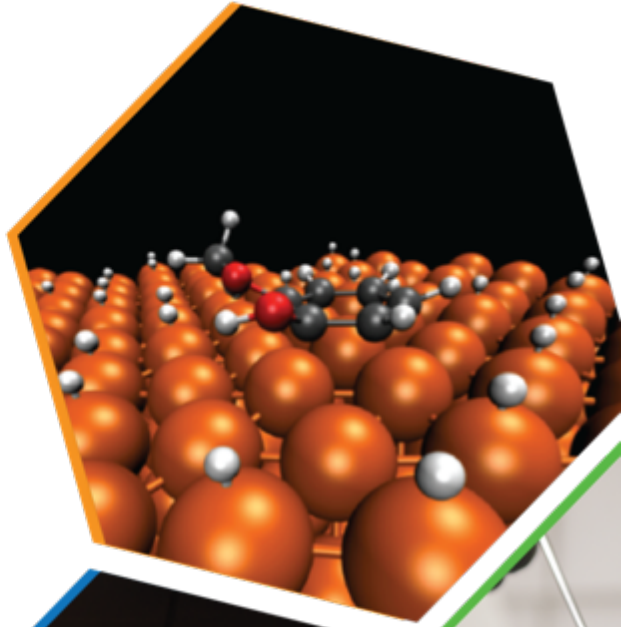
ChemCatBio
Chemical Catalysis for Bioenergy



Thank you!

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BIOENERGY TECHNOLOGIES OFFICE

Publications and Patents (FY20–21)

1. 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
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1. N. J. LiBretto, C. A. Downes, K. Unocic, F. G. Baddour, D. A. Ruddy, S. E. Habas, “Mild Solution Synthesis Approach to Transition Metal Phosphide Nanoparticles from Molecular Precursors”, *Front Range Inorganic Colloquium (FRIC) 2021*, Virtual Meeting, January 7, 2021.
2. *Invited Keynote* D. A. Ruddy “Molybdenum carbide catalysts for biomass upgrading – from bulk to nanoscale”, Catalysis Club of Chicago 2020 Symposium, Virtual Meeting, Aug 28, 2020.
3. K. A. Unocic, M. Griffin, M. Yung, E. C. Wegener, T. R. Krause, H. Wang, H. M. Meyer III, L. F. Allard, J. Schaidle, S. E. Habbas, “*Operando* S/TEM Reactions of Pt/TiO_2 Catalysts for Catalytic Fast Pyrolysis”, *Microscopy and Microanalysis 2020 Meeting,* Virtual Meeting, August 3-7, 2020.
4. *Invited* S. E. Habas, “Advances in Nanostructured Metal Phosphide Catalysts for Renewable Fuels”, *Inorganic Chemistry Seminar,* University of California, San Diego, November 8, 2019.
5. *Invited Plenary* F. G. Baddour, “Synthesis of Nanostructured Catalysts for the Conversion of Biomass to Renewable Fuels and Chemicals”, *Boston Regional Inorganic Colloquium – 50th anniversary,* Boston University, Boston, October 5, 2019.

Responses to Feedback from 2019 Peer Review

- **Reviewer Comment:** Overall, a well integrated activity that strengthens the entire CCB project portfolio. The expertise of the group compliments the needs of the CCB projects. The value has been demonstrated in past and existing projects. The future projects ask clear questions which the current characterization efforts assist in answering. The attempt to remain responsive to the needs of the CCB portfolio by introducing new techniques is very important but should continue to be evaluated so the right tools are used in the appropriate settings.
- **Reviewer Comment:** The ACSC is another solid, good technical story coming out of the CCB with money well-invested and the scientific discovery return on investment very important. The ACSC is a well managed project knowing where their targets, challenges and milestones lie. They should be applauded by CCB for their ability to work together across labs as a unified organization that will most likely change the trajectory of the biofuels industry. Their work is impressive, and they understand that they must create actionable recommendations that also allow for practical implementation.
- ***Response:*** *We thank the reviewers for the positive feedback regarding the value of the ACSC project to the ChemCatBio catalysis projects and fully agree that it is important to remain responsive to the needs of these projects and to continue to create actionable recommendations to support the catalysis portfolio. We have specifically included an Annual Evaluation of New/Existing Capabilities in our management plan to ensure that ACSC capabilities are continually evolving to meet the existing and emerging needs of the ChemCatBio catalysis projects.*

Responses to Feedback from 2019 Peer Review

- **Reviewer Comment:** The advanced catalyst characterization and synthesis project can impact most of the process development work supported by BETO. The characterization portion of the project has clearly impacted a number of BETO projects and has helped several bio economy start-ups. The synthesis portion is less evolved and has not yet had a major impact. However, it is difficult to show the clear benefits of fundamental research in this area in the short term. It is a high-risk high reward project. Most new catalysts are not successful. The work done by the ACSC team is similar to that conducted as part of R&D at leading commercial and government catalyst and development labs throughout the world. There is wide agreement that this work is worthwhile. What makes the ACSC team unique is the focus of the BETO mission and integration into the BETO project teams. One area in which project is lacking is in the ability to prepare industrial style formed catalysts. The BETO team relies on outside industry groups to provide this expertise and to prepare the volumes of these types of materials required for testing.
- ***Response:*** *We agree that the characterization component of the ACSC has been impactful and was well highlighted during the review, and we will make similar efforts to highlight the synthesis capabilities similarly in the future. The synthesis platform has been critical to advancing the state of technology for a number of catalysis projects. For example, within the C1 project, the synthesis of model catalysts with defined active sites was essential to enabling the identification of the active site for dehydrogenation by operando characterization. Realization of the next generation catalysts, identified by the CCPC, relied on targeted synthesis methods to controllably incorporate dehydrogenation and hydrogenation active sites. We are addressing the absence of technical catalyst synthesis capabilities by engaging with the Engineering of Catalyst Scale Up project that started in FY19.*

Responses to Feedback from 2019 Peer Review

- **Reviewer Comment:** This is a nice foundational effort that really goes toward enabling all other upgrading research within the various DOE-supported consortia. Susan Habas gave an excellent presentation. It is really difficult to make sense of catalyst performance without accompanying effort in controlled synthesis and characterization. I like the nice effort toward characterizing materials under reaction conditions and/or complex media (to the extent that the capabilities will allow). Our conventional approach has been to study the reactor performance of a material under steady state conditions, where the structure of the material is almost certainly different from the as synthesized material. This effort goes toward addressing that discrepancy.
- **Reviewer Comment:** The Synthesis and Characterization project is vital to the entirety of CCB, and meshes especially nicely with CatCost and CCPC. One area which might be added to the portfolio is controlled deposition of metal precursors onto catalyst supports (as opposed to solution synthesis of NPs followed by deposition). This suite of methods did not appear in the presentation.
- ***Response:*** *Within the review we sought to highlight the unique capabilities of the ACSC including advanced synthesis methodologies. However, the controlled deposition of metal precursors and impregnation-based methods are core components of our catalyst synthesis capabilities and have been instrumental in the development of model catalysts and next-generation materials for the C1 and CFP projects.*

Responses to Feedback from 2019 Peer Review

- **Reviewer Comment:** The goal of providing fundamental insight leading to actionable recommendations for critical research challenges by leveraging world-class synthesis and characterization capabilities across multiple DOE National Laboratories is certainly a core need for all the projects within the consortium. Integration with the DataHub seems to be working really well and the researchers are encouraged to continue this effort. The attempt to remain responsive to the needs of the CCB portfolio by introducing new techniques is very important but should continue to be evaluated so the right tools are used in the appropriate settings. For instance, neutron effort should be evaluated to make sure it is suitable for the work being emphasized in this project, as well as have a good justification for inclusion of MOF synthesis work. Also, the synthesis portion of the project was downplayed relative to characterization efforts and should be better highlighted in the future.
- ***Response:*** *We are encouraged by the reviewer's thoughts on introducing new capabilities into the ACSC project and we will continue to evaluate the suitability of the techniques for the catalysis projects. The neutron scattering characterization and MOF synthesis efforts will be subject to a Go/No-go decision point to assess their ability to meet the needs of the Consortium as will all future efforts. As a result of the Go-No-go decision point in FY19, we descoped these efforts to focus on other more critical needs of the ChemCatBio projects.*