



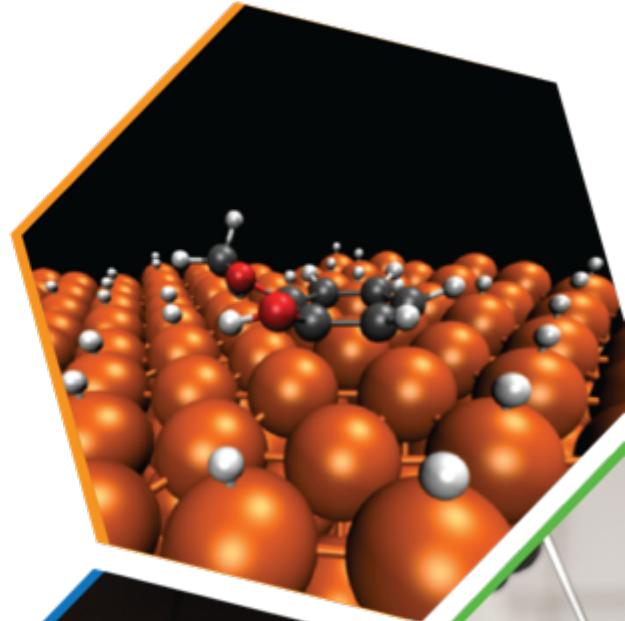
## Advanced Catalyst Synthesis and Characterization (ACSC) Project

WBS 2.5.4.304/303/305

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

March 11, 2021



# 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<sub>2</sub> 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)

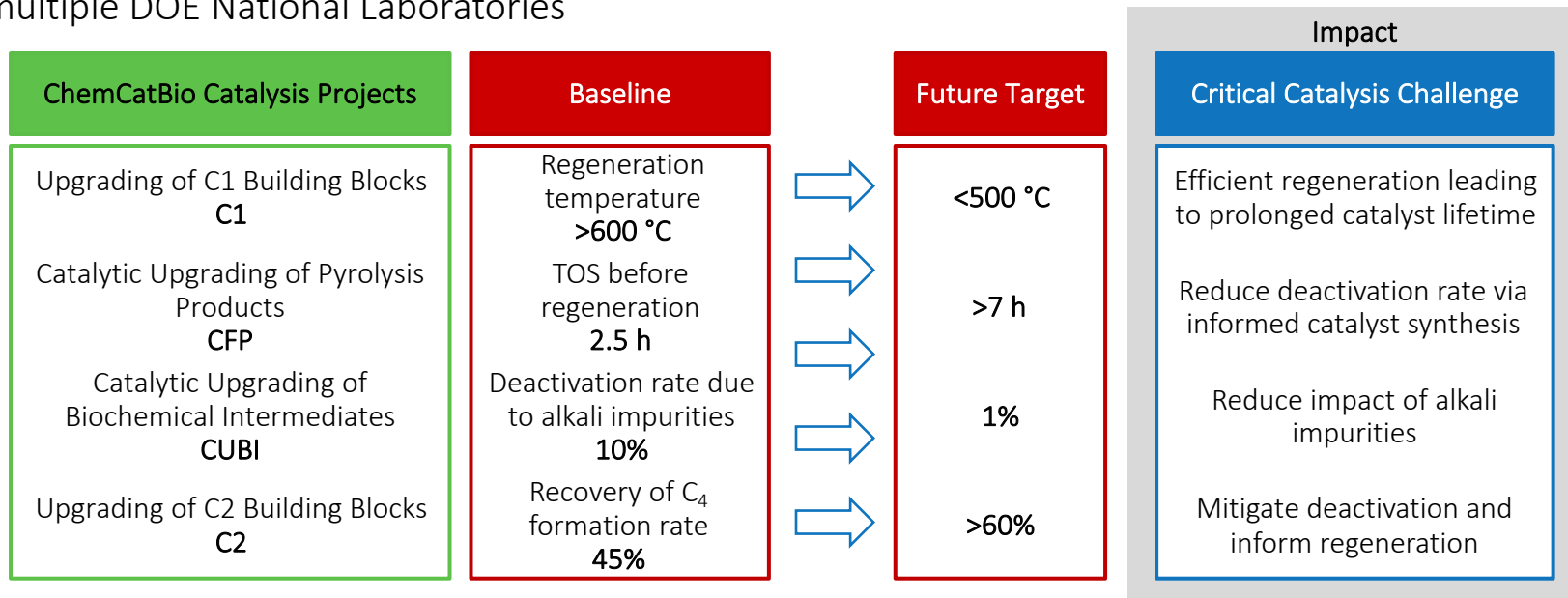
## **Cross-Cutting Support**

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



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

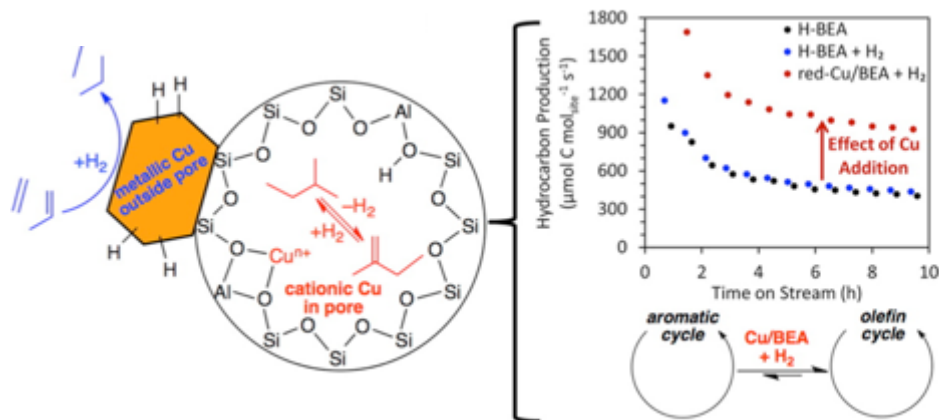
# Project Overview – Based on Successful Collaboration

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

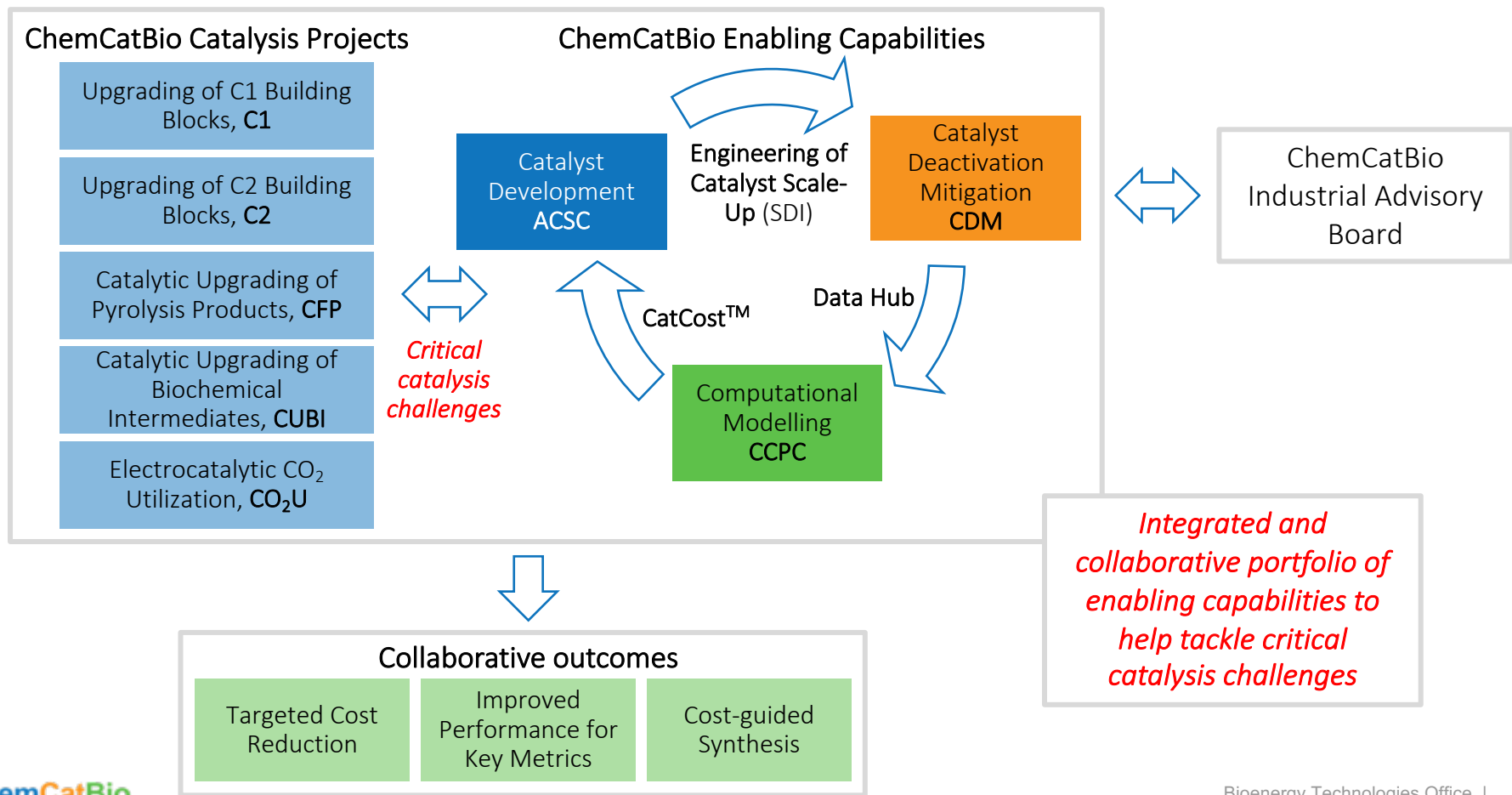


Schaidle et al., *ACS Catal.*, 2015, 5, 1794. <https://doi.org/10.1021/cs501876w>

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*

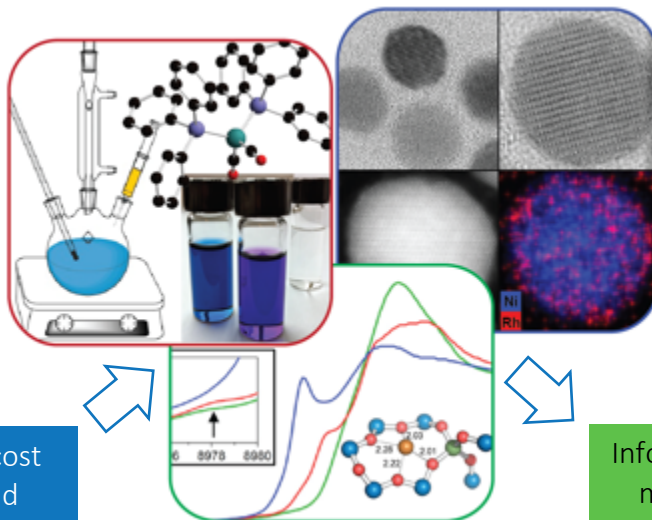
# Project Overview – Enabling Capability Within ChemCatBio



# 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



Advanced spatially resolved imaging and characterization



Identify lower cost precursors and synthesis routes

CatCost™

Inform computational models to predict next-generation catalysts



Advanced spectroscopic techniques for bulk and surface structural and chemical characterization



# 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



## 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



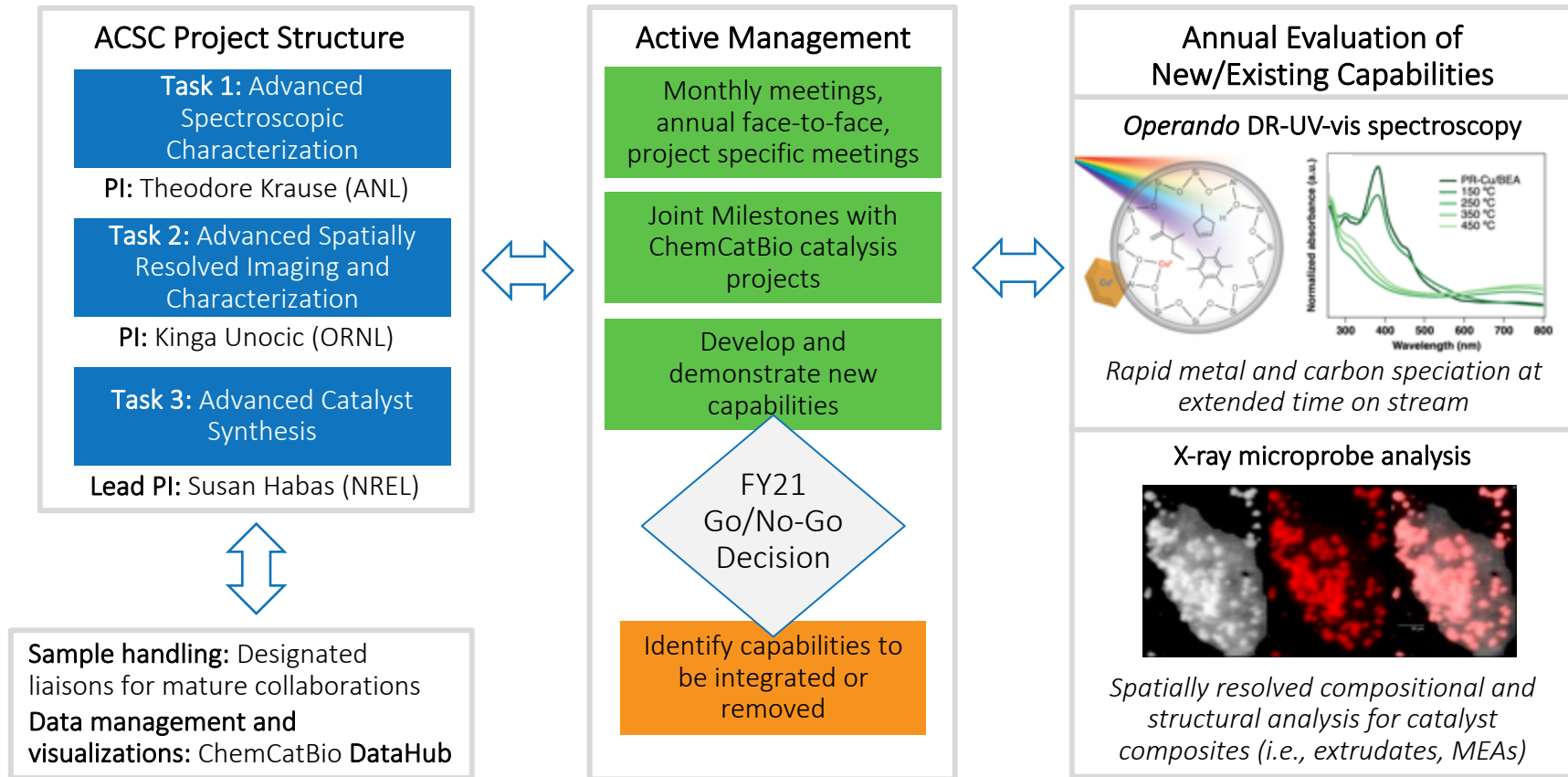
## Advanced Catalyst Synthesis

- 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



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

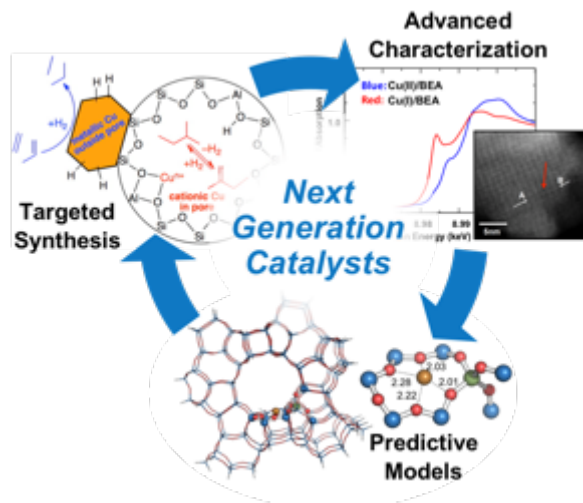
# 1. Management – Evolving to Meet ChemCatBio Needs



*Based on the current and emerging needs of ChemCatBio catalysis projects*

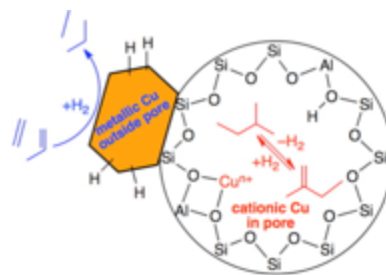


## 2. Approach – Catalyst and Process Development Cycle

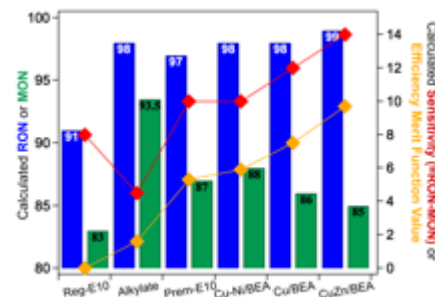


- **Identify** active site structures in *working catalysts* under realistic conditions
- **Inform** computational modeling to *predict active site structures* with enhanced performance
- **Develop** *next-generation catalysts* with predicted structures
- **Verify** *performance improvements* with ChemCatBio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

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



3 years



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<sub>3</sub>–C<sub>6</sub> 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

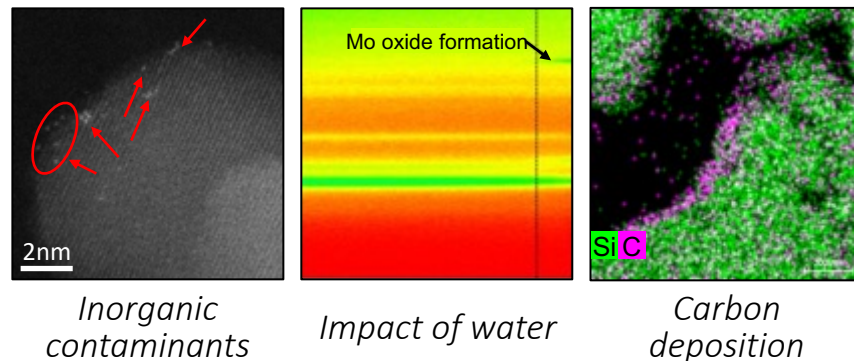
### Direct engagement with *all* of the ChemCatBio catalysis projects

- 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

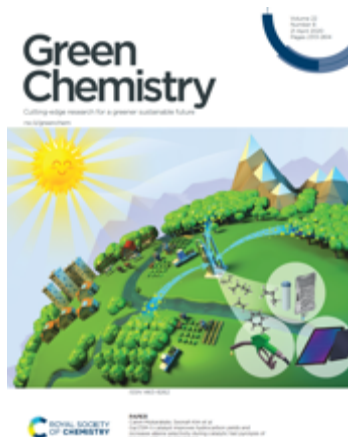


*Balance overarching catalysis challenges with specific needs of catalysis projects*

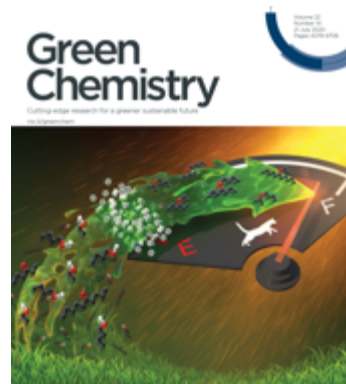
## 2. Approach – Multiple Modes of Interaction

### How to work with the ACSC

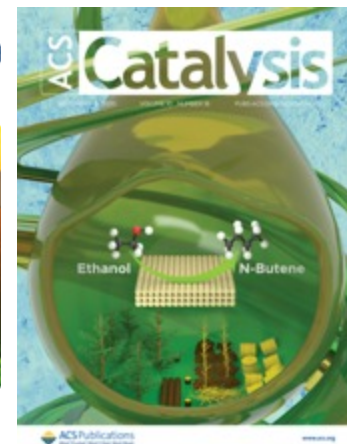
- *Overarching challenges* are collectively tackled with other enabling capabilities yearly
- *Project-specific milestones* with at least one collaboration maintained throughout project cycle
- *Immediate needs* are rapidly responded to via demonstrated capabilities and expertise



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>

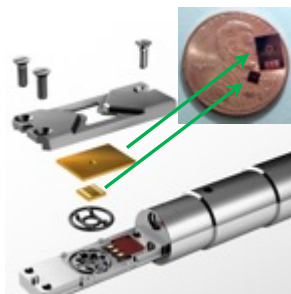
*Enables significant and rapid impact to ChemCatBio Catalysis projects*

## 2. Approach – Responding to New Project Needs

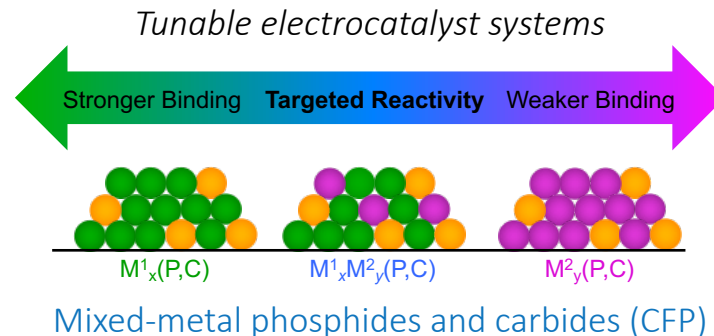
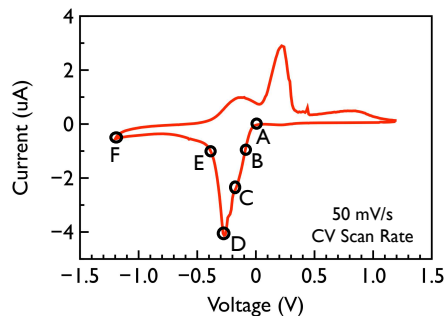
### Electrochemical CO<sub>2</sub> Utilization

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

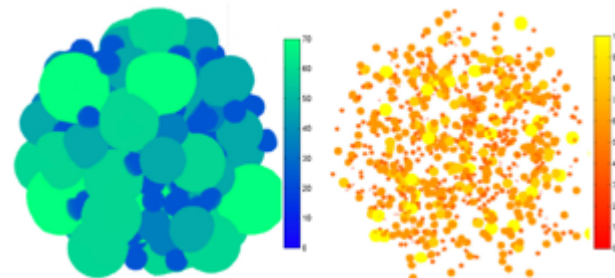
*Structure of working electrocatalyst*



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



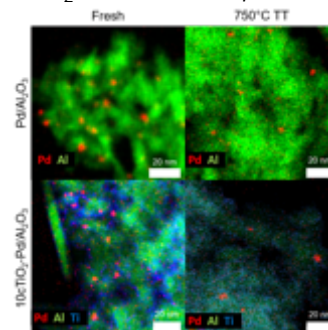
## Feedback from Industrial Advisory Board

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

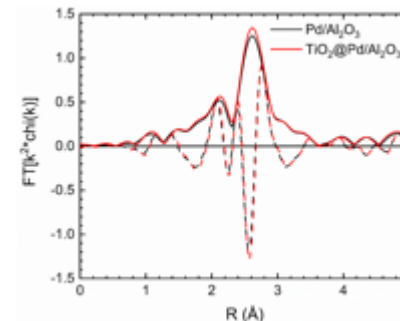
**Challenge:** Identify the origin of enhanced hydrogenation activity for TiO<sub>2</sub>-coated Pd catalyst



*Demonstrated co-location of TiO<sub>2</sub> and Pd nanoparticles*



*Determined Pd electronic structure was not altered by TiO<sub>2</sub>*

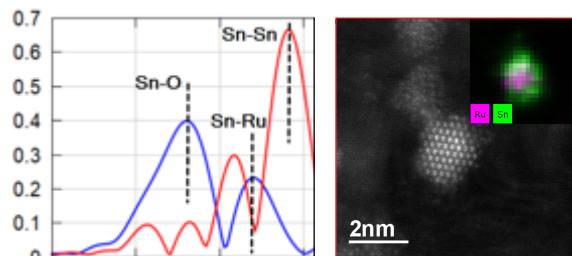


W. W. McNeary, D. R. Vardon, et al., *ACS Catal.* Submitted.

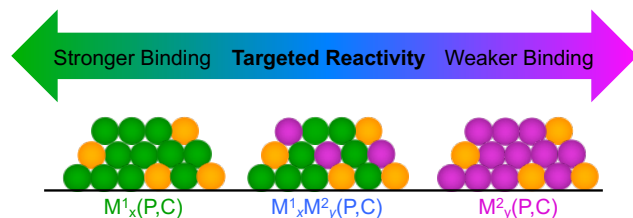
**Outcome:** Determined that enhanced activity was due to ensemble effects from partial TiO<sub>2</sub> coverage of Pd

*Providing capabilities and expertise that are responsive to industry needs*

### 3. Impact – Enabling BETO Goals

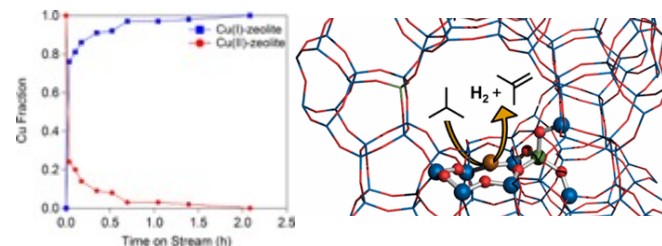


“Developing these processes should be coupled with efforts to obtain a better understanding of the causes of catalyst **poisoning and deactivation**”

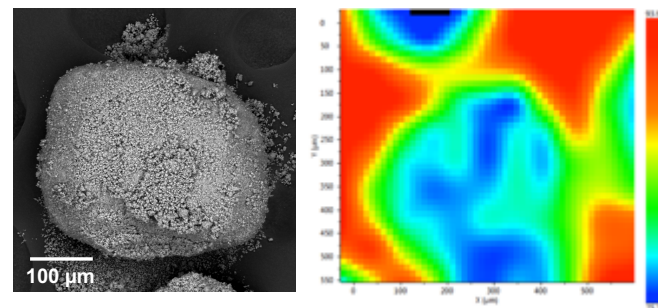


“Emerging technologies and processes may require the design and synthesis of **novel catalysts**.”

“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**”

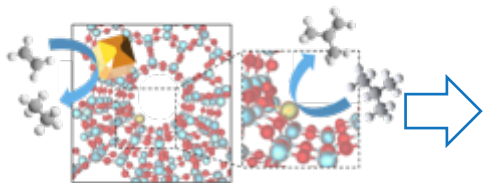


*Derisking bioenergy processes through catalyst development and characterization*

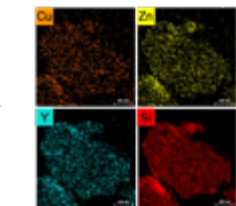
# 3. Impact – Providing Capabilities and Expertise

## Within ChemCatBio and BETO

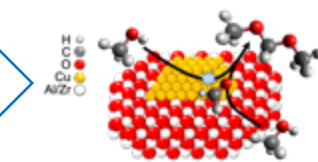
Developing capabilities and expertise that span multiple projects



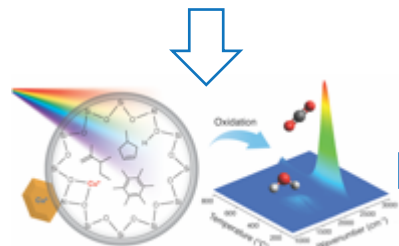
*Precise understanding of active sites in Cu/BEA (C1)*



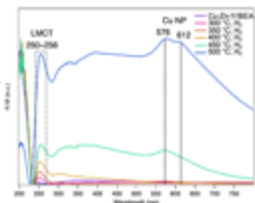
*Extended to Cu-Zn-Y/BEA (C2)*



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



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

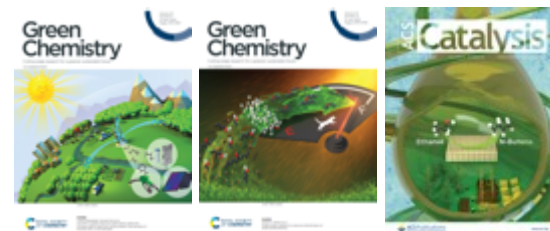


*Extended to regeneration of Cu-Zn-Y/BEA (C2)*

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

## Externally to the catalysis community

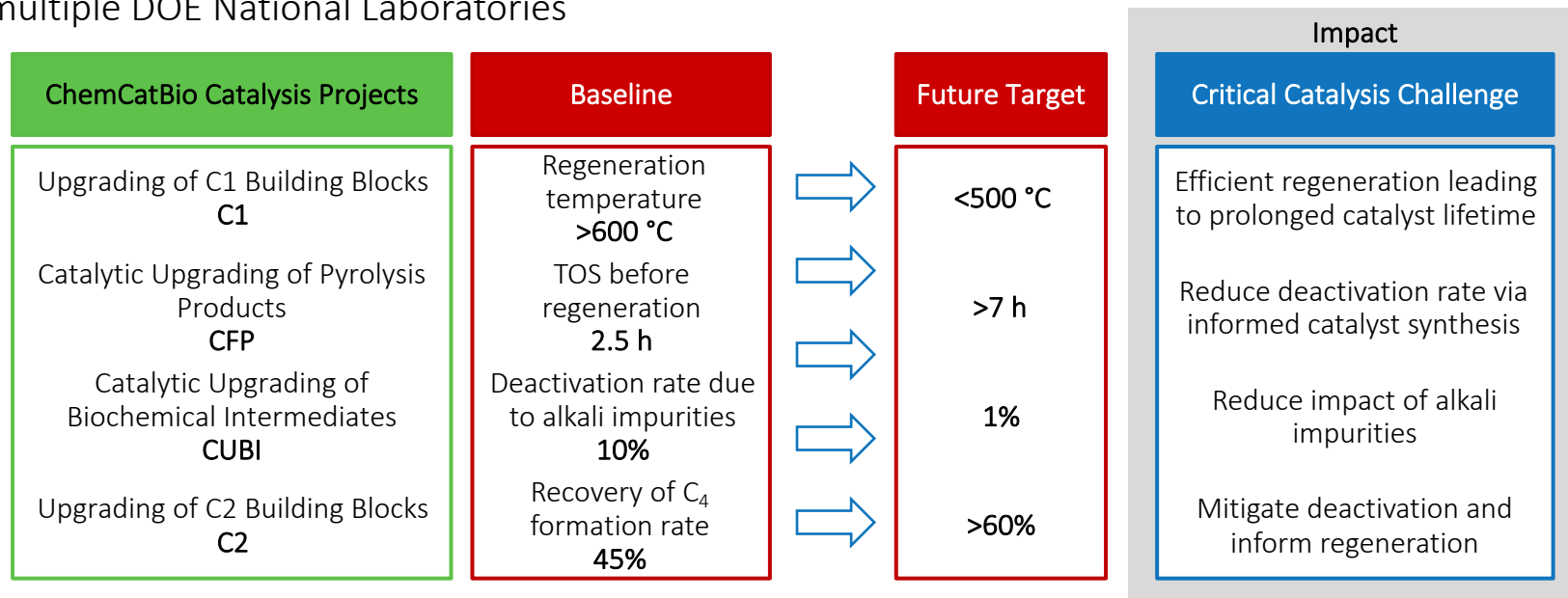
- 13 peer reviewed publications FY20-21
- 5 external presentations FY20-21
- Industry engagement with 5 Directed Funding Opportunities
- Webinar on Accelerating the Catalyst Development Cycle
- Input to ChemCatBio **DataHub**
- New capabilities and expertise available at DOE User Facilities



**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



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



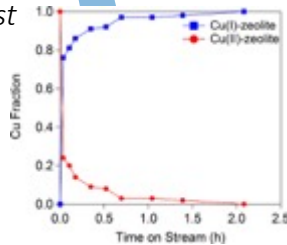
# 4. Progress and Outcomes – Demonstrated Catalyst Development Cycle (C1)

**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

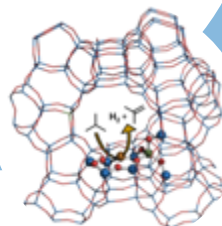
Catalyst	Active site
CuO/SiO <sub>2</sub>	CuO particles
Cu/SiO <sub>2</sub>	Cu(0) particles
H-BEA	Bronsted acid
ox-IE-Cu/BEA	Ionic Cu(II)-zeolite
red-IE-Cu/BEA	Ionic Cu(I)-zeolite

Synthesized catalysts with active sites in working catalyst

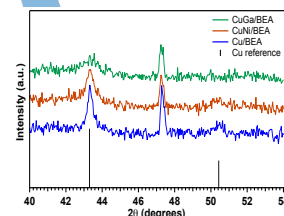


Identified Cu(I) as active site for dehydrogenation

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

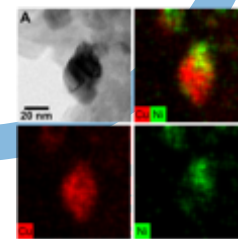
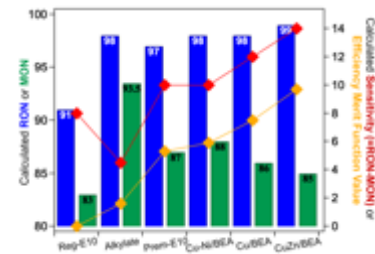


Predictive model for dehydrogenation, CCPC



Synthetic control of speciation in bimetallic catalysts

Verified cost-normalized performance improvements, C1, CatCost™

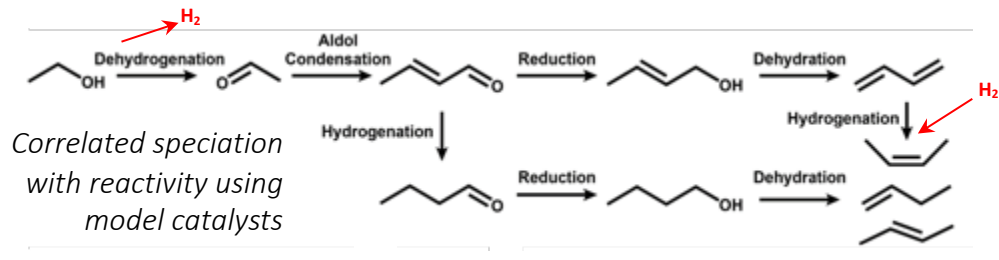


Determined speciation in working catalysts

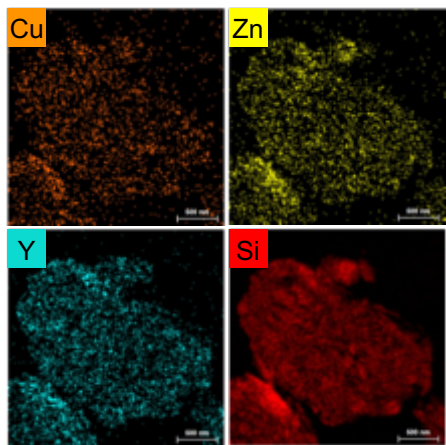
Success in the critical research challenge of improving fuel properties through catalyst design (FY19)

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

**Challenge:** Identify active sites for conversion of ethanol to butene-rich C<sub>3</sub>–C<sub>6</sub> olefins over Cu-Zn-Y/BEA

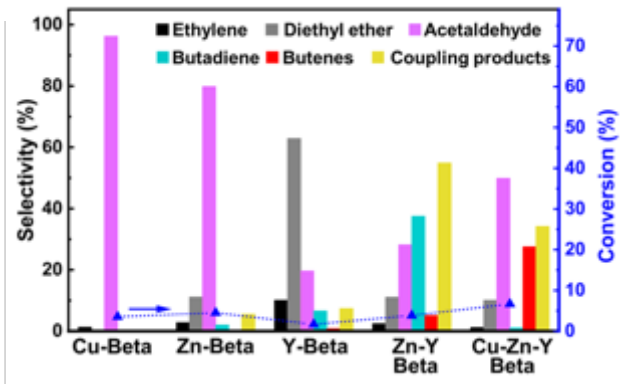
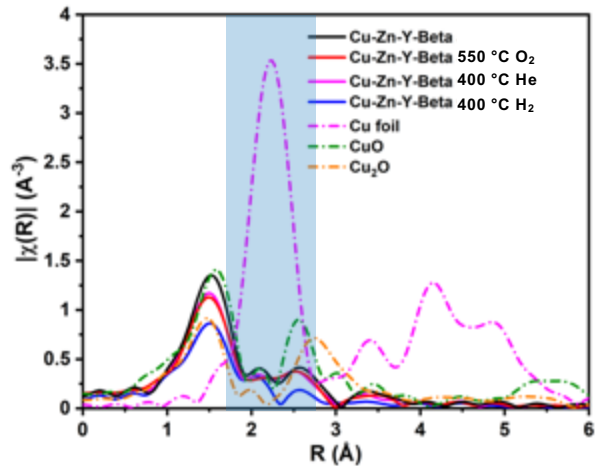


Determined that Cu, Zn, and Y are atomically dispersed



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

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



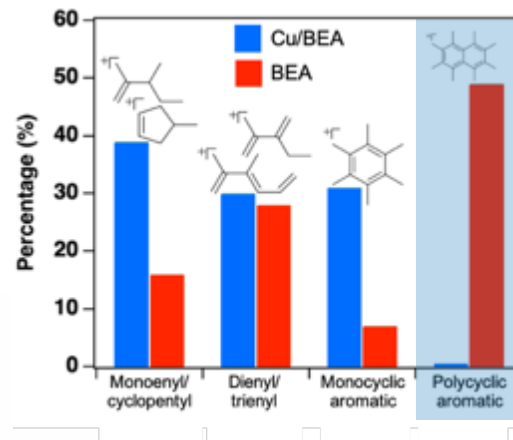
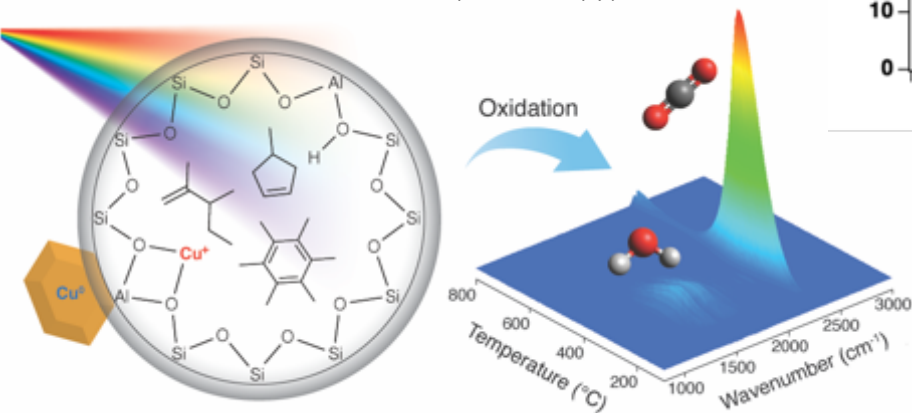
**Outcome:** Informed next-generation catalyst synthesis for enhanced C<sub>3</sub>–C<sub>6</sub> olefin selectivity

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

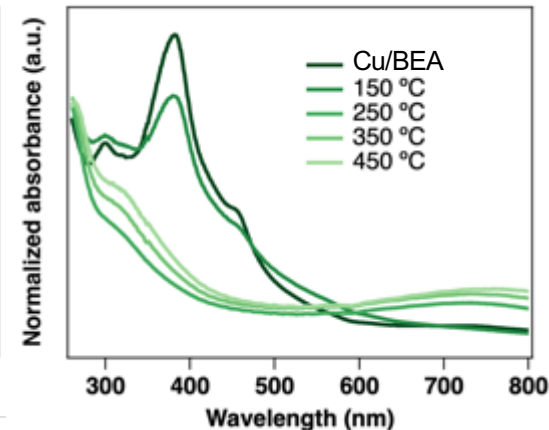
## 4. Progress and Outcomes – Regeneration of Metal Zeolite Catalysts (C1)

**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<sub>2</sub> leading to carbon removal at significantly lower temperature*

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

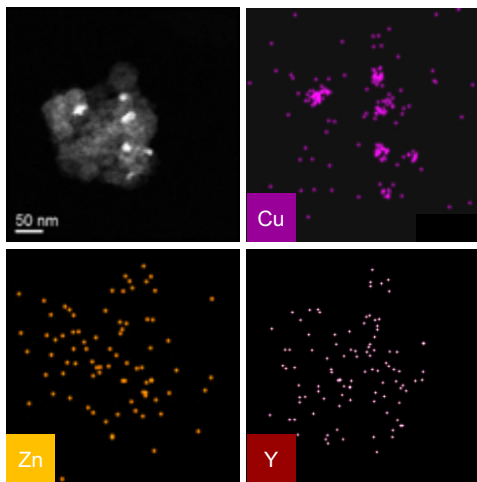
**Outcome:** Developed an effective regeneration procedure that enabled full recovery of catalyst activity

*Complementary spectroscopic characterization techniques to provide complete insight*

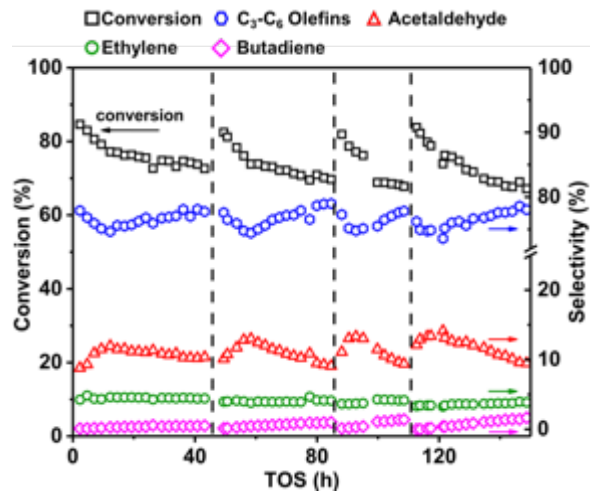
# 4. Progress and Outcomes – Leveraging Capabilities (C2)

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

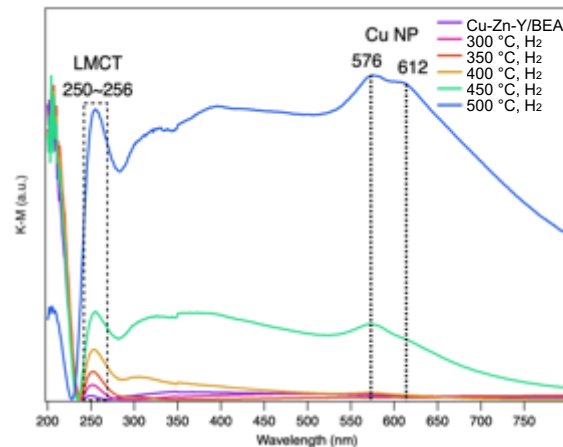
Zn and Y sites maintain atomic dispersion, but Cu begins to cluster at longer time on stream



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



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



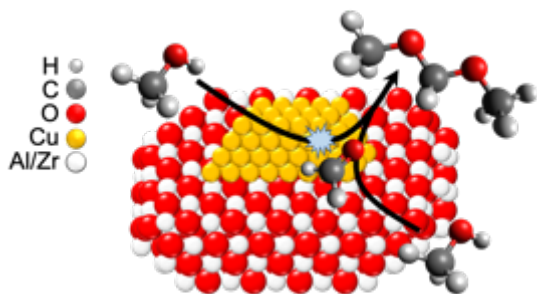
Applying new operando spectroscopic capabilities to provide rapid insight into Cu and C speciation during reaction/regeneration

**Projected Outcome:** A regeneration procedure that enables recovery of >60% of C<sub>4</sub> product formation rate

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

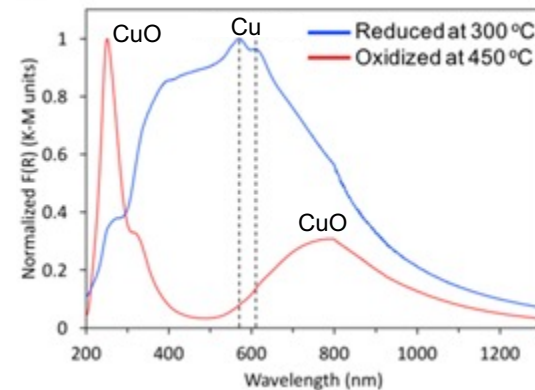
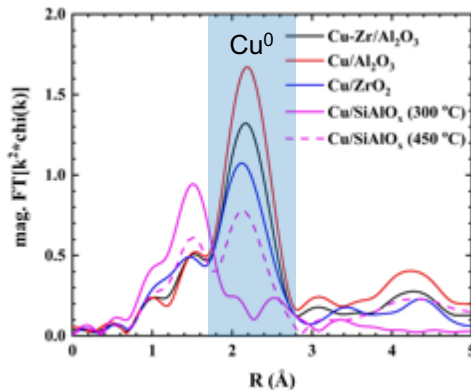
# 4. Progress and Outcomes – Leveraging Capabilities (Co-Optima)

**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>

*Metallic Cu nanoparticles formed under pre-treatment conditions promote dehydrogenation*



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

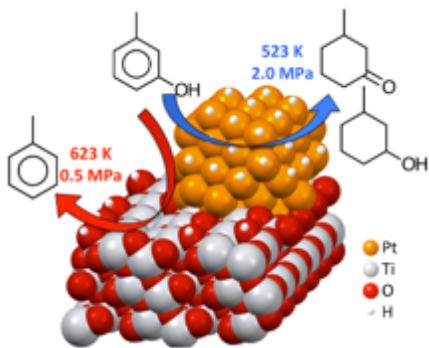
**Outcome:** Achieved 40% of equilibrium-limited yield under mild conditions by balancing dehydrogenation sites and acid site strengths

**Combined insight across all ACSC partners provided actionable insight**

# 4. Progress and Outcomes – Catalyst Deactivation (CFP)

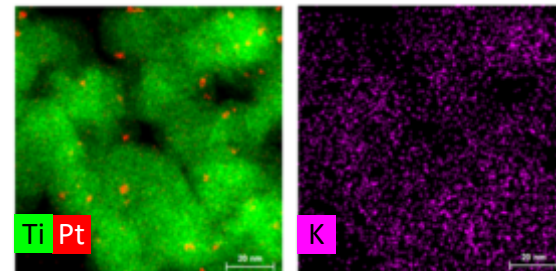
**Challenge:** Identify causes of catalyst deactivation during *ex situ* CFP over SOT 0.5 wt% Pt/TiO<sub>2</sub> catalyst

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

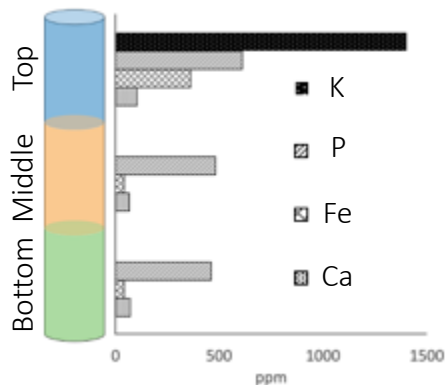


M. Griffin, et al. ACS Catal., 2016, 6, 2715.  
<https://doi.org/10.1021/acscatal.5b02868>

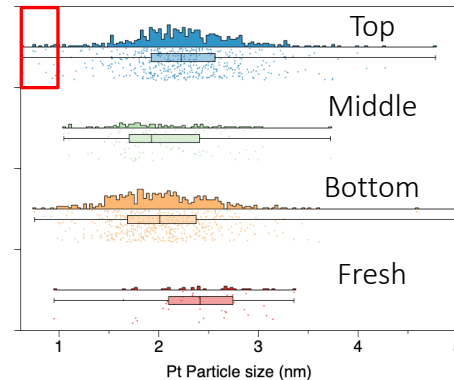
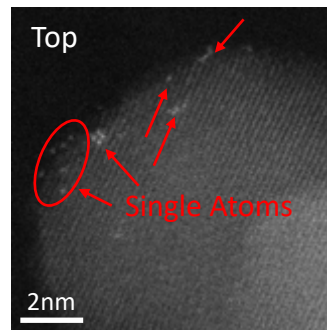
*Spatially resolved distribution of K concentration correlated with single Pt atom concentration*



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



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



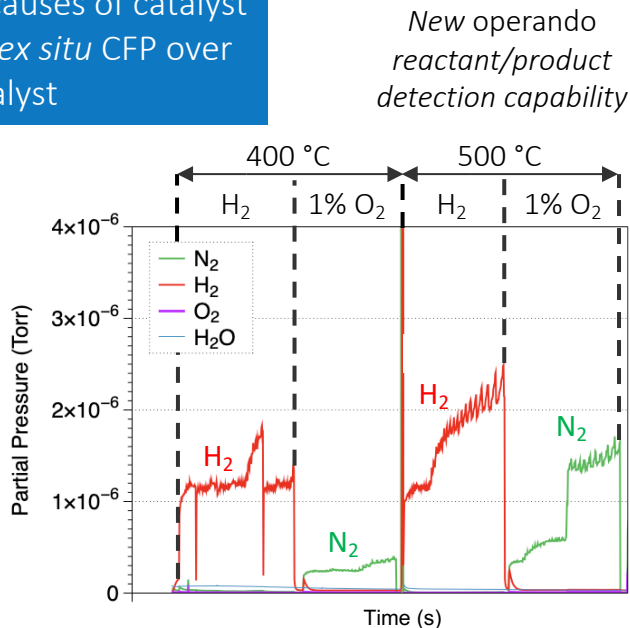
**Outcome:** Characterization of real catalysts informed model studies by CDM project and computational models by CCPC

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

# 4. Progress and Outcomes – Catalyst deactivation (CFP)

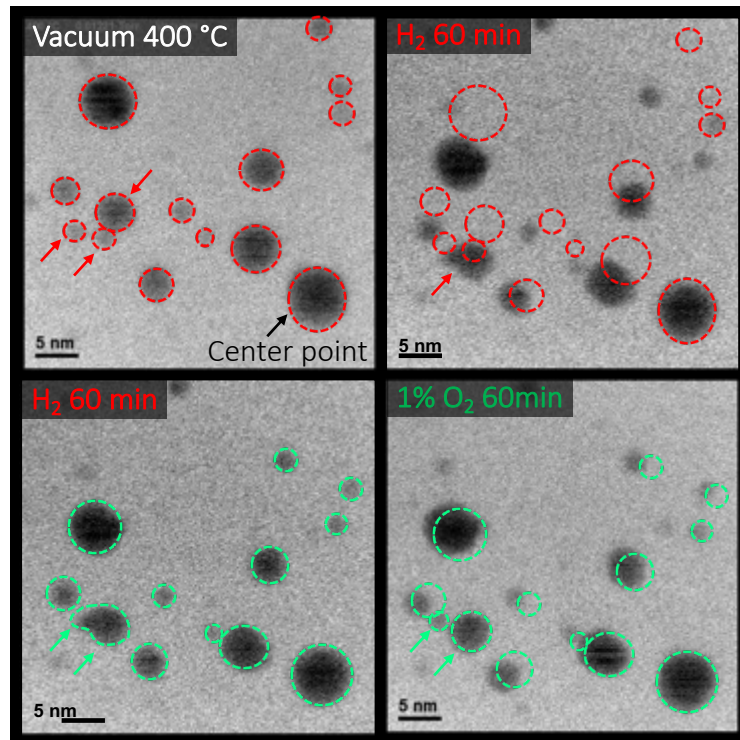
**Challenge:** Identify causes of catalyst deactivation during *ex situ* CFP over 0.5 wt% Pt/TiO<sub>2</sub> catalyst

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>

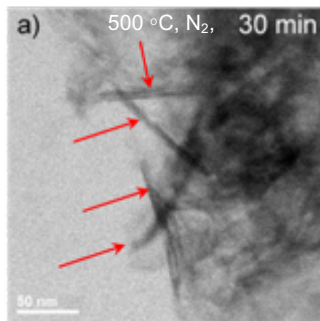
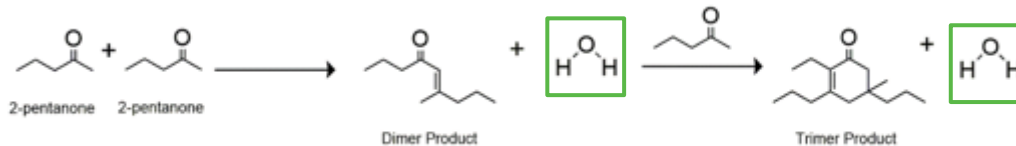


H<sub>2</sub> promotes sintering of Pt particles while O<sub>2</sub> assists with redistribution

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

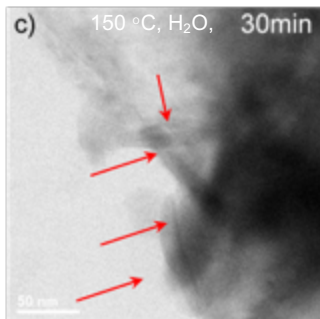
# 4. Progress and Outcomes – Stability in Water (CUBI)

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

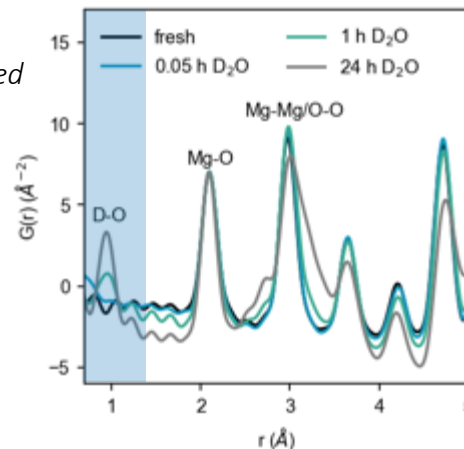
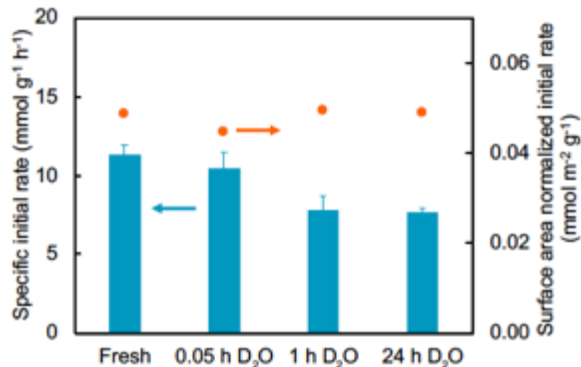


X. Huo, D. R. Vardon, et al., 2021, Submitted.

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

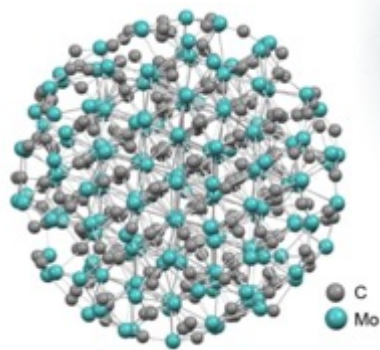
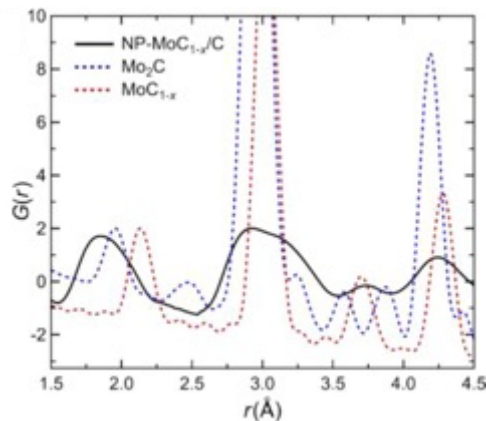
Capability development and demonstration towards project-specific and overarching challenges



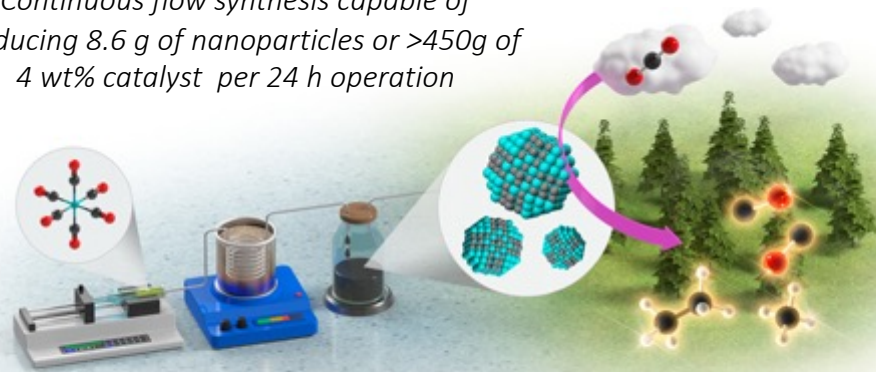
## 4. Progress and Outcomes – Catalyst Design for Emerging Pathways (C1)

**Challenge:** Leverage non-noble metal multifunctional catalysts from CFP for thermochemical CO<sub>2</sub> reduction

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



*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<sub>2</sub> hydrogenation activity per site and selectivity to C<sub>2+</sub> 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.

F. G. Baddour, et al., J. Am. Chem. Soc., 2020, 142, 1010.

<https://doi.org/10.1021/jacs.9b11238>

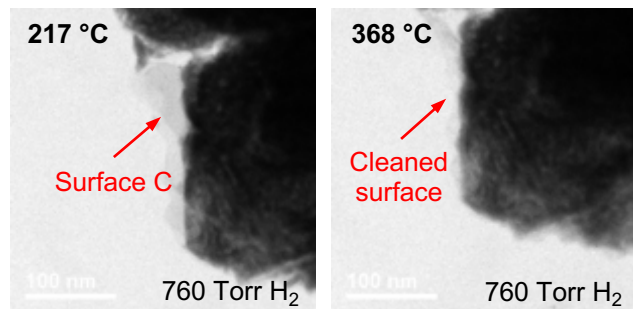


**Tunable multifunctional materials for complex transformations (C1, CFP, End of cycle Milestone)**

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

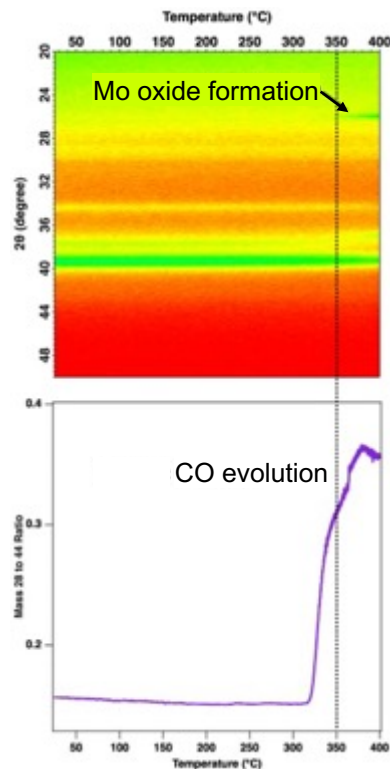
**Challenge:** Determine speciation of carbon deposited on metal carbides during CFP and CO<sub>2</sub> reduction

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



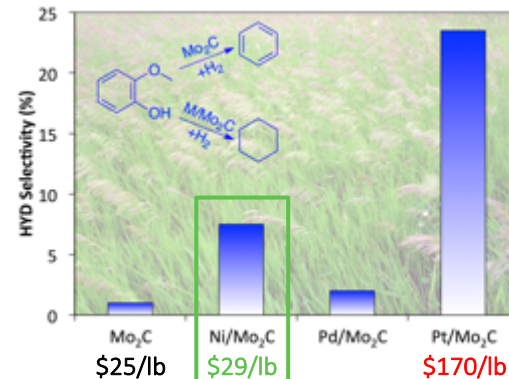
Demonstrated operando characterization during regeneration to evaluate surface carbon removal as CO/CO<sub>2</sub>

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>

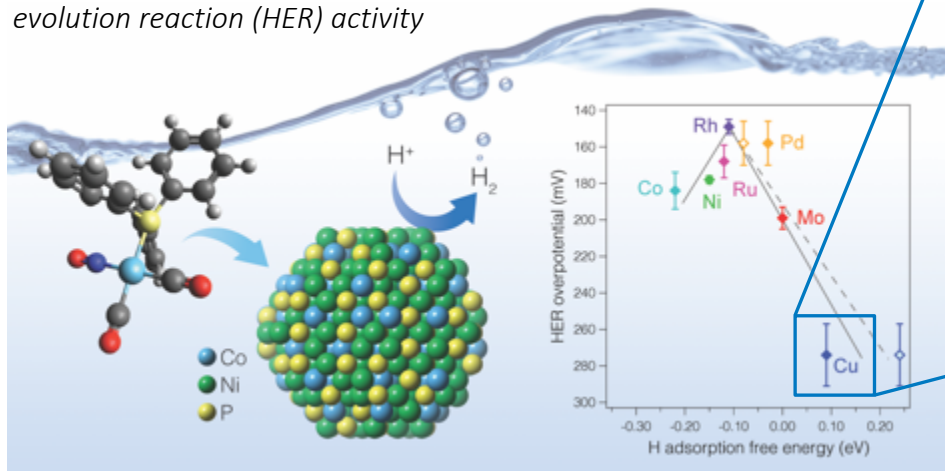
**Projected Outcome:** A cost-effective regeneration strategy for non-metal/oxide catalysts to recover full activity

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

# 4. Progress and Outcomes – Catalyst Design for Emerging Pathways (CO<sub>2</sub>U)

**Challenge:** Leverage multifunctional catalysts from CFP for electrocatalytic CO<sub>2</sub> reduction

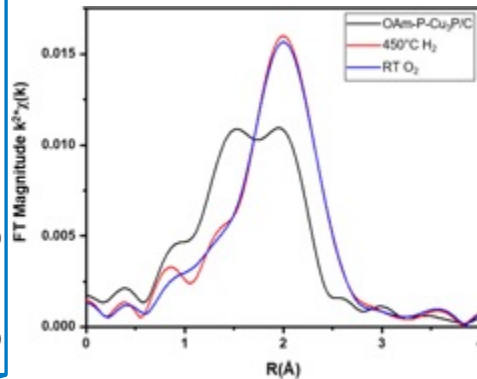
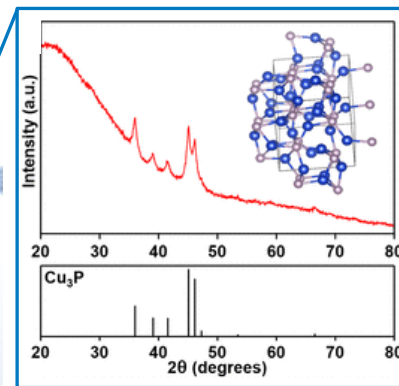
Developed tunable bimetallic phosphide nanoparticle catalysts with composition-dependent hydrogen evolution reaction (HER) activity



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<sub>3</sub>P may be active for CO<sub>2</sub> 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<sub>3</sub>P enabled the production of formate from electrocatalytic reduction of CO<sub>2</sub>

*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.

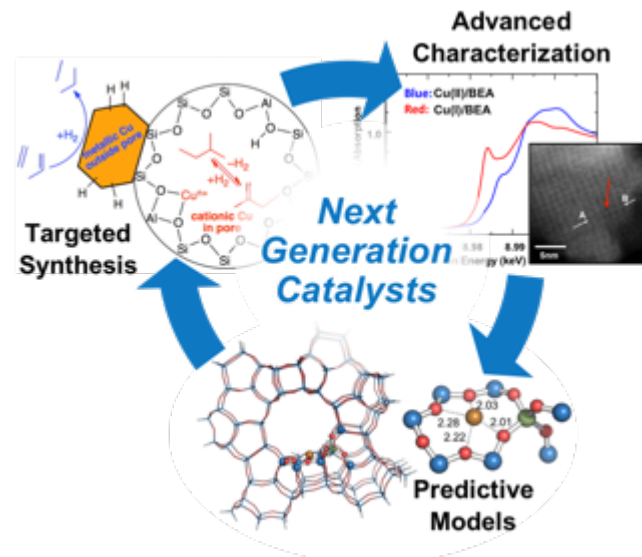
## Funding Mechanism

- 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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Jeremy Kropf  
Evan Wegener



Jeffrey Miller



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Jonathan Poplawsky  
Shawn Reeves  
Raymond Unocic  
Junyan Zhang



**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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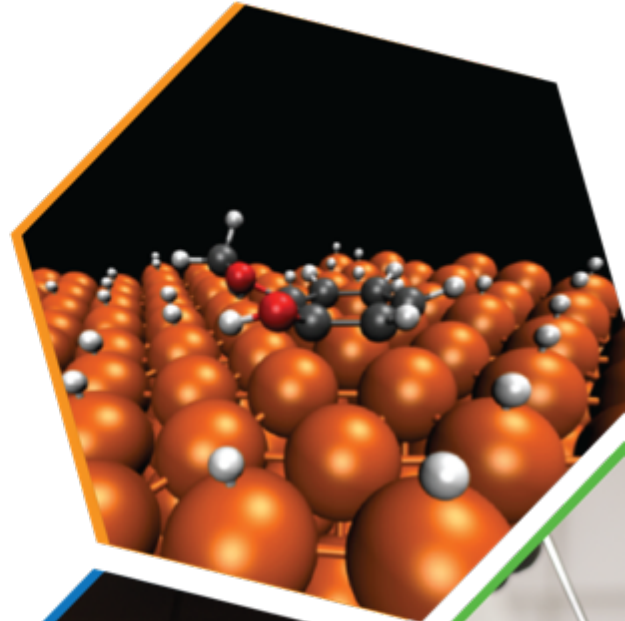
This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, in part by Argonne National Laboratory, operated by The University of Chicago, and in part by Oak Ridge National Laboratory, operated by UT-Battelle, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308, DE-AC02-06CH11357, and DE-AC05-00OR22725, respectively. Funding provided by U.S. DOE Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.



**ChemCatBio**  
Chemical Catalysis for Bioenergy

Thank you!

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# 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>
2. C. A. Downes, N. J. LiBretto, A. E. Harman-Ware, R. M. Happs, D. A. Ruddy, F. G. Baddour, J. R. Ferrell III, S. E. Habas\*, J. A. Schaidle\*, “Electrocatalytic CO<sub>2</sub> reduction over Cu<sub>3</sub>P nanoparticles generated via a molecular precursor route”, *ACS Appl. Energy Mater.*, 2020, 3, 10435. <https://doi.org/10.1021/acsaem.0c01360>
3. A. T. To, J. Wilke, E. Nelson, C. P. Nash, A. Bartling, E. C. Wegener, K. A. Unocic, S. E. Habas, T. D. Foust\*, D. A. Ruddy\*, “Dehydrogenative coupling of methanol for the gas-phase, one-step synthesis of dimethoxymethane over supported copper catalysts”, *ACS Sus. Chem. Eng.*, 2020. <https://doi.org/10.1021/acssuschemeng.0c03606>
4. 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. Habas, “Operando S/TEM Reactions of Pt/TiO<sub>2</sub> Catalysts for Catalytic Fast Pyrolysis”, *Microsc. Microanal.*, 2020, 1-3. <https://doi.org/10.1017/S1431927620019005>
5. Q. Guo, H. Meyer, A. Levlev, A. Starace, C. Mukarakate, S. Habas, K. A. Unocic, “Multi-scale Characterization Study Enabling Deactivation Mechanism in Formed Zeolite Catalyst”, *Microsc. Microanal.*, 2020, 1-3. <https://doi.org/10.1017/S1431927620017535>
6. V. Dagle, A. D. Winkelman, N. R. Jaegers, J. Saavedra-Lopez, J. Z. Hu, M. H. Engelhard, S. E. Habas, S. A. Akhade, L. Kovarik, V.-A. Glezakou, R. Rousseau, Y. Wang, R. A. Dagle, “Single-step conversion of ethanol to *n*-butenes over Ag-ZrO<sub>2</sub>/SiO<sub>2</sub> catalysts”, 2020, *ACS Catal.*, Published online. <https://doi.org/10.1021/acscatal.0c02235>
7. G. R. Hafenstine, N. A. Huq, D. R. Conklin, M. R. Wiatrowski, X. Huo, Q. Guo, K. A. Unocic, D. R. Vardon\*, “Single-phase catalysis for reductive etherification of diesel bioblendstocks”, *Green Chem.*, 2020, 22, 4463. <https://doi.org/10.1039/D0GC00939C>



# Publications and Patents (FY20–21)

8. S. P. Adhikari, J. Zhang, Q. Guo, K. A. Unocic, L. Tao, Z. Li\*, “A Hybrid Pathway to Biojet Fuel via 2,3-Butanediol”, *Sustain. Energy Fuels*, 2020, 4, 3904. <https://doi.org/10.1039/DO5E00480D>
9. K. A. Unocic, F. S. Walden, N. L. Marthe, A. K. Datye, W. C. Bigelow, L. F. Allard, “Introducing and Controlling Water Vapor in Closed-Cell *In Situ* Electron Microscopy Gas Reactions”, *Microsc. Microanal.*, 2020, 26, 229. <https://doi.org/10.1017/S1431927620000185>
10. K. Iisa, Y. Kim, K. A. Orton, D. J. Robichaud, R. Katahira, M. J. Watson, E. C. Wegener, M. R. Nimlos, J. A. Schaidle, C. Mukarakate\*, S. Kim\*, “Ga/ZSM-5 Catalyst Improves Hydrocarbon Yields and Increases Alkene Selectivity During Catalytic Fast Pyrolysis of Biomass with Co-Fed Hydrogen”, *Green Chem.*, 2020, 22, 2403. <https://doi.org/10.1039/C9GC03408>
11. F. G. Baddour\*, E. J. Roberts, A. T. To, L. Wang, S. E. Habas, D. A. Ruddy, N. M. Bedford, J. Wright, C. P. Nash, J. A. Schaidle, R. L. Brutchey\*, N. Malmstadt\*, “An Exceptionally Mild and Scalable Solution-Phase Synthesis of Molybdenum Carbide Nanoparticles for Thermocatalytic CO<sub>2</sub> Hydrogenation”, *J. Am. Chem. Soc.*, 2020, 142, 1010. <https://doi.org/10.1021/jacs.9b11238>
12. K.-Y. Kim\*, S. E. Habas, J. A. Schaidle, B. E. Logan, “Application of phase-pure nickel phosphide nanoparticles as cathode catalysts for hydrogen production in microbial electrolysis cells”, *Bioresour. Technol.*, 2019, 293, 122067. <https://doi.org/10.1016/j.biortech.2019.122067>
13. V. Vorotnikov, T. R. Eaton, A. E. Settle, K. Orton, E. C. Wegener, C. Yang, J. T. Miller, G. T. Beckham\*, D. R. Vardon\*, “Inverse Bimetallic RuSn Catalyst for Selective Carboxylic Acid Reduction”, *ACS Catal.*, 2019, 9, 11350. <https://doi.org/10.1021/acscatal.9b02726>
14. F. G. Baddour, A. Kumar, K. Van Allsburg, D. Ruddy, S. Habas, A. D. Royappa, “Metal Carbides and Methods for Making the Same”, U.S. Provisional Patent Application No. 62/993,487, March 23, 2020.

# Presentations (FY20–21)

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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<sub>2</sub> 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.*