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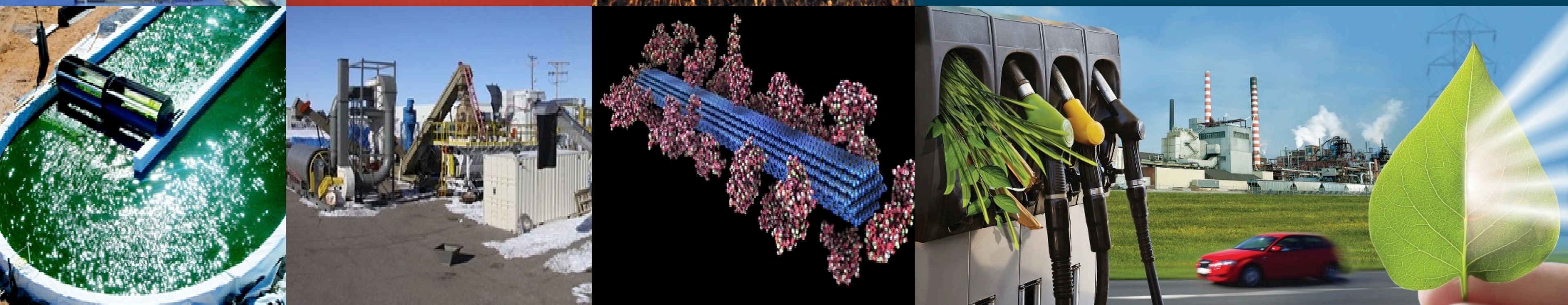


Advanced Catalyst Synthesis and Characterization (ACSC)

WBS: 2.5.4.304/303/305

U.S. Department of Energy (DOE)
Bioenergy Technologies Office (BETO)
2017 Project Peer Review

Thermochemical Conversion

March 7th, 2017

Project Leads:

Susan Habas – NREL

Theodore Krause – ANL

Kinga Unocic – ORNL

ChemCatBio Structure

Core Catalysis Projects

Catalytic Upgrading of Biochemical Intermediates
(NREL, PNNL, ORNL, LANL)

Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates
(NREL, PNNL)

Fast Pyrolysis and Upgrading
(PNNL, ORNL)

Catalytic Fast Pyrolysis
(NREL, PNNL)

Recovering and Upgrading Biogenic Carbon in Aqueous Waste Streams
(PNNL, NREL)

Zeolites and Metal Oxide Catalysts | **Supported Metal Catalysts**

Cross-cutting Discussion Groups

Enabling Projects

Advanced Catalyst Synthesis and Characterization
(NREL, ANL, ORNL)

Catalyst Cost Model Development
(NREL, PNNL)

Consortium for Computational Physics and Chemistry
(ORNL, NREL, PNNL, ANL, NETL)

Consortium Integration

- Core catalysis projects focused on specific *applications*
- *Collaborative* projects leveraging core capabilities across DOE laboratories
- *Cross-fertilization* through discussion groups

ACSC Goal Statement

Project Goal – Deliver high performing, cost-effective catalytic materials that meet the needs of the ChemCatBio (CCB) catalysis projects by leveraging ***advanced characterization*** capabilities and unique ***synthesis expertise*** at multiple DOE National Laboratories

Conversion Technology Area	State of Technology	Future Target	Relevance: Catalyst Development Challenge
Catalytic Upgrading of Biochemical Intermediates	Selectivity **52%**	**60%**	***Improve C–C coupling selectivity***
Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates	Distillate yield **10.3 GGE/ton**	**27.4 GGE/ton**	***Increase olefin production***
Fast Pyrolysis and Upgrading	Catalyst lifetime **154 days**	**278 days**	***Mitigate S deactivation***
Catalytic Fast Pyrolysis	C-efficiency **33%**	**44%**	***Reduce coke formation***
Recovering and Upgrading Biogenic Carbon in Biomass-Derived Aqueous Streams	C lost to aqueous phase **3.4 – 27%**	**50% C recovery**	***Direct waste carbon to valuable chemicals***

Project Outcome and relevance – Reduce conversion costs for biomass processes by ***accelerating the catalyst development*** cycle

Quad chart overview

Timeline

Project start date: 10/1/2016

Project end date: 9/30/2019

Percent complete: 14%

Budget

	FY 15 Costs	FY 16 Costs	Total Planned Funding FY 17*-19
DOE Funded	$0	$0	$2.7 M

*FY17 operating budget reduced to $775 k

Barriers addressed & Actions

Ct-H – Efficient Catalytic Upgrading of Sugars/Aromatics, Gaseous and Bio-Oil Intermediates to Fuels and Chemicals

- *Identify active site structures in working catalysts*
- *Inform computational modeling to predict catalysts with enhanced performance*
- *Develop next-generation catalysts through innovative synthetic routes*

Partners

National Laboratories: NREL (33%); ANL (36%); ORNL (31%)

Universities: Purdue University

Other interactions/collaborations: The ACSC will interface with all CCB enabling technology projects and core catalysis projects

Investment in catalyst development is crucial to improving the economics of fuel and product production, specifically for catalysts offering improved yield, productivity, and product slate

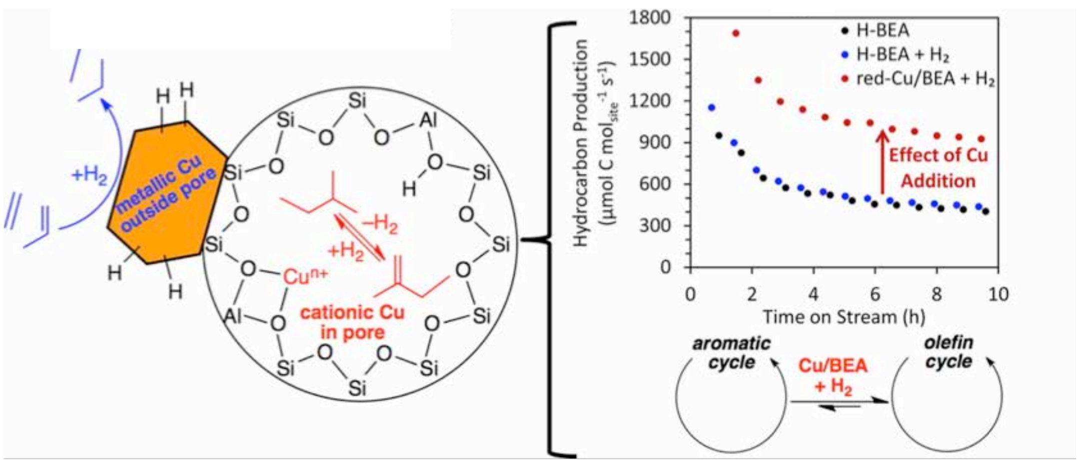
– BETO Multi-Year Program Plan (MYPP)

Project overview – Based on successful collaboration

Cross-cutting enabling technologies supported by BETO

- **Consortium for Computational Physics and Chemistry (CCPC)**
- **Catalyst Cost Model (CCM) project**
- **Project specific access to Advanced Photon Source (APS) at ANL**

X-ray absorption spectroscopy (XAS) at ANL closely coupled with experiment established that both metallic Cu and ionic Cu are responsible for performance



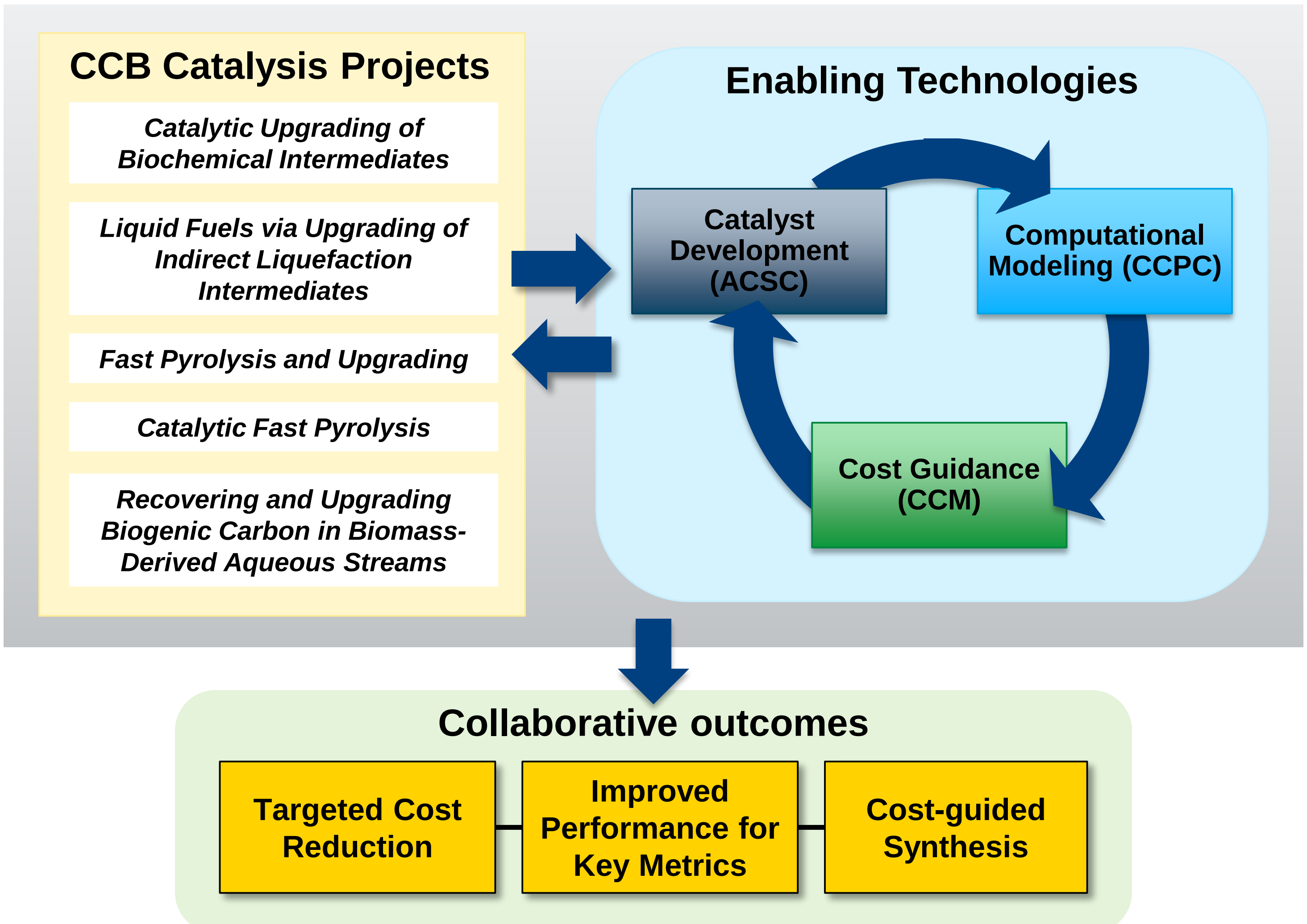
Schaidle et al. *ACS Catal.*, **2015**, *5*, 1794

- Cu-modified beta zeolite (Cu/BEA) catalyst
- 2-fold increase in hydrocarbon productivity and shifted selectivity towards olefins

Led to reduction in minimum fuel selling price (MFSP) of $1.07/GGE

Project overview – Integrated approach

Establish an integrated and collaborative portfolio of catalytic and enabling technologies

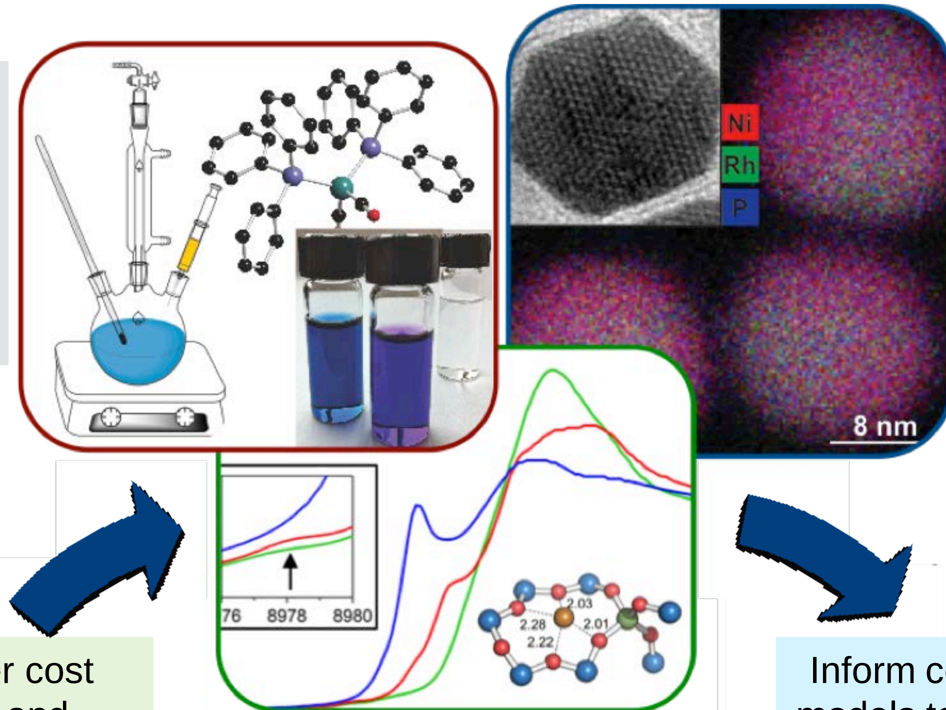


Project overview – Complementary efforts

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



Sub-Ångström resolution scanning transmission electron microscopy (S/TEM) for *local* catalyst structures and chemical compositions

OAK RIDGE
National Laboratory

Identify lower cost precursors and synthesis routes
CCM

X-ray absorption spectroscopy (XAS) for *overall* catalyst coordination environment and oxidation states

Argonne
NATIONAL LABORATORY

Inform computational models to predict next-generation catalysts
CCPC

Management approach

ACSC Project Structure

Task	PI
Task 1: Advanced Catalyst Synthesis	**Lead PI: Susan Habas – NREL**
Task 2: X-ray Absorption Spectroscopy (XAS)	**PI: Theodore Krause – ANL**
Task 3: Advanced Scanning Transmission Electron Microscopy (S/TEM)	**PI: Kinga Unocic – ORNL**

Coordination Within CCB

Project organization

- Monthly webinars with PIs
- On-site meetings once per year
- Joint contribution to milestones

Data management

- Dedicated SharePoint site

Sample handling

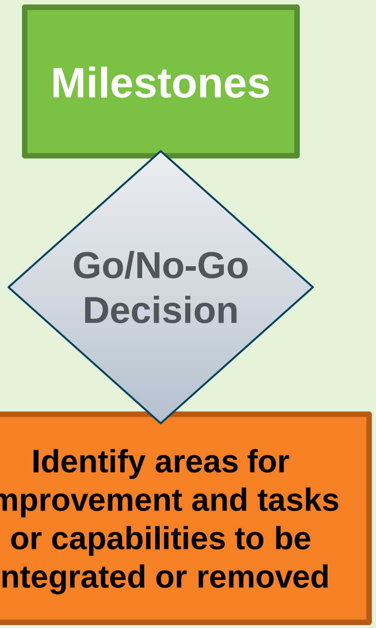
- *Mature collaborations:* Designated liaison
- *Emerging collaborations:* Direct interaction

FY18 Go/No-Go Decision

Prove that the ACSC has provided value to CCB catalysis projects

1. Advanced characterization has informed catalyst development targets
2. Synthesize next-generation catalysts based on targets that demonstrate:
   - Increased stability and enhanced performance
   - Relevance to cost targets from CCM project

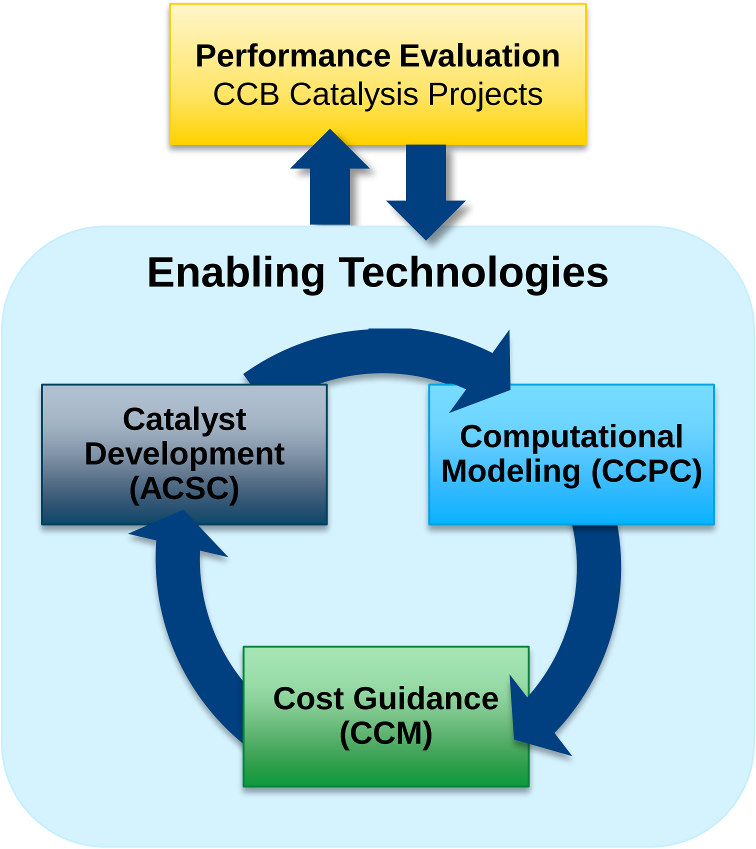
Active Management



Technical approach – Context within CCB

Accelerated catalyst 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
- **Validate** performance improvements with CCB catalysis projects

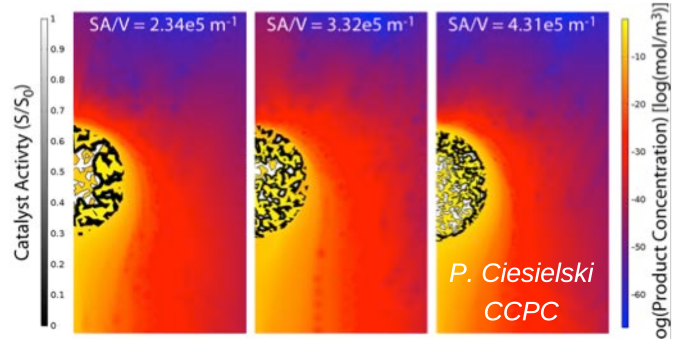


Deliver high performing, cost-effective catalytic materials that meet targets

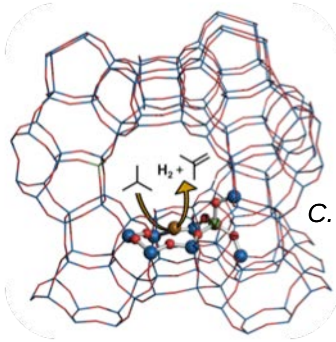
Technical approach – Challenges and success factors

Challenge – Demonstrate the accelerated catalyst development cycle

Success factor
Delivering catalytic materials that meet cost and performance targets



Mesoporous zeolites that reduce coke formation

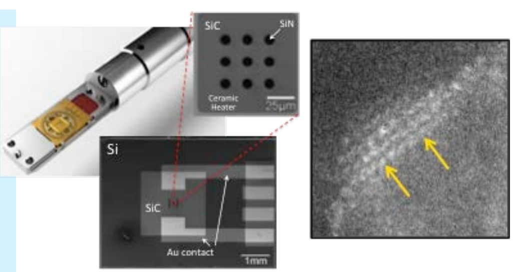


C. Farberow CCPC

Tailored multi-metal zeolites that increase yield of jet fuel from DME (dimethyl ether) by 1.5-fold

Challenge – Deliver relevant information to the CCB projects

Success factor
Developing *in situ* and *operando* characterization capabilities for real working conditions



Success factor
Accessing targeted active site structures through innovative synthetic routes

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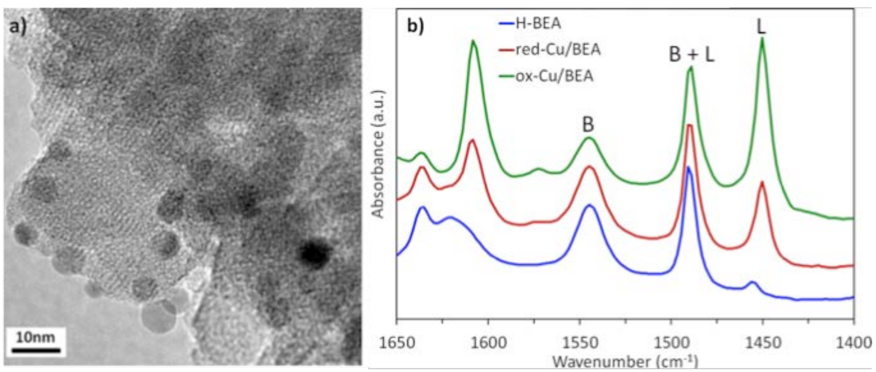
Technical Accomplishments – Increase olefin production

Target: Increase olefin production through alkane reincorporation to enable higher yield of jet fuel

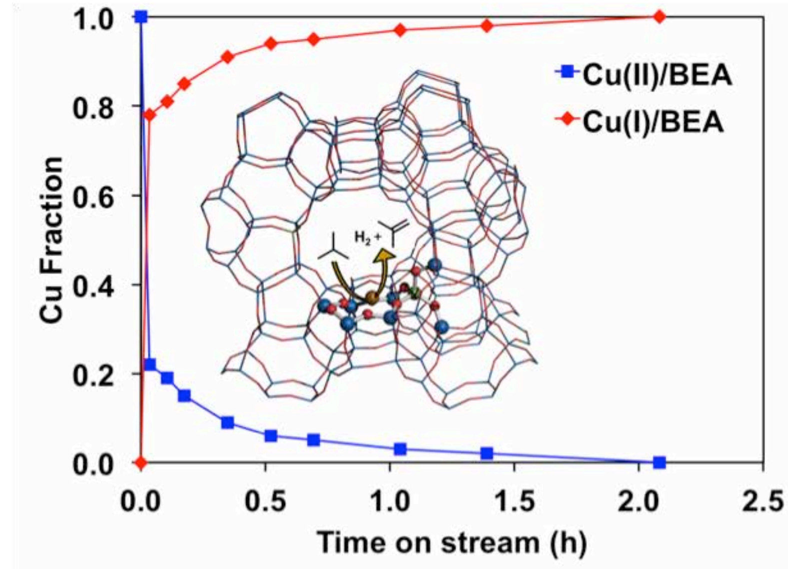
Advanced synthesis



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

Developed materials with discrete types of active sites found in working catalyst

Advanced characterization



Farberow, *et al. ACS Catal.*, **2016**, *Submitted*

In situ and *operando* XAS indicated that Cu(II) is converted to Cu(I) during isobutane dehydrogenation

Ionic Cu(I) was identified as the active site for alkane reincorporation, leading to a computational model and targets for next-generation catalysts

Relevance – CCB catalysis targets

The ACSC will deliver high performing, cost-effective catalytic materials that **meet the needs of the CCB catalysis projects** by leveraging advanced characterization capabilities and unique synthesis expertise at multiple DOE National Laboratories

Outcomes relevant to the CCB catalysis projects

- Catalyst development targets based on characterization of working catalysts
- Next-generation catalysts that meet performance targets

Conversion Technology Area	State of Technology		Future Target	Relevance: Catalyst Development Challenge
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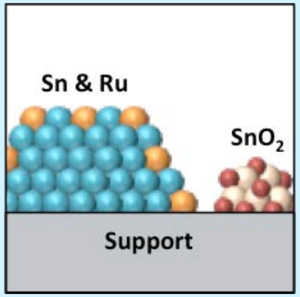
Recovering and Upgrading Biogenic Carbon in Biomass-Derived Aqueous Streams	C lost to aqueous phase **3.4 – 27%**	→	**50% C recovery**	***Direct waste carbon to valuable chemicals***

Relevance – CCB portfolio

Collaborative outcomes that enhance the CCB portfolio

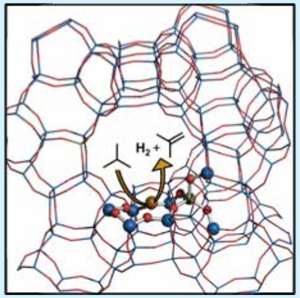
- New ***in situ* and *operando* characterization** capabilities under working conditions
- **Innovative synthetic routes** to lower cost advanced materials with the CCM
- **Predictive models** for catalyst design and process optimization with the CCPC
- Understanding of **overarching catalysis challenges** that can be applied to future catalyst development targets

Overarching catalysis challenges



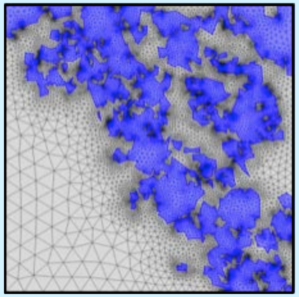
Investigate evolution of metal-support and atomic interfaces

D. Vardon



Identify active site structures in metal-zeolite catalysts

C. Farberow



Correlate structural characteristics with catalyst deactivation

P. Ciesielski

These foundational capabilities will help attract industry partners seeking to understand and develop new catalysts and processes

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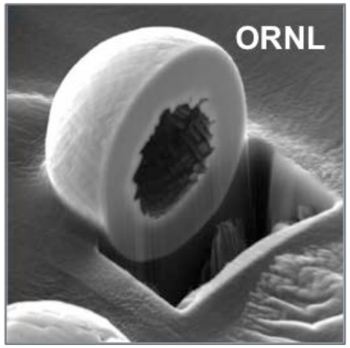
Future work – Reduce coke formation

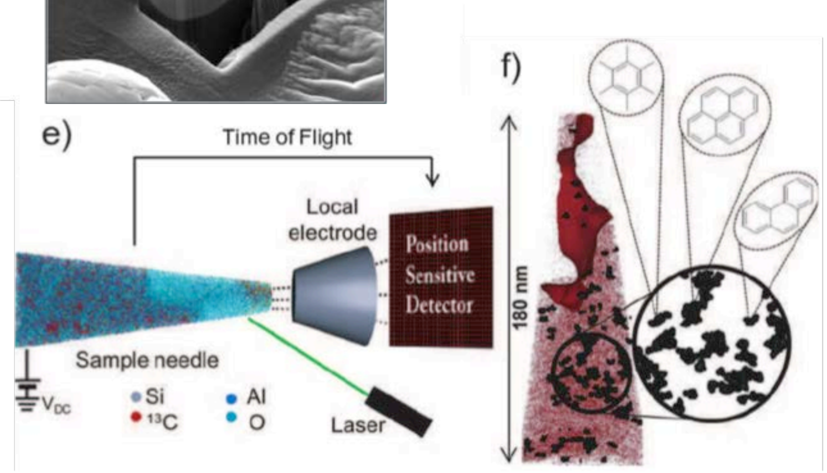
Target: Minimize carbon losses to coke (8.3 wt% of dry biomass) during *ex situ* CFP by understanding coke formation

Inform zeolite deactivation model predicting optimal residence time, temperature, and catalyst mesoporosity

Advanced characterization

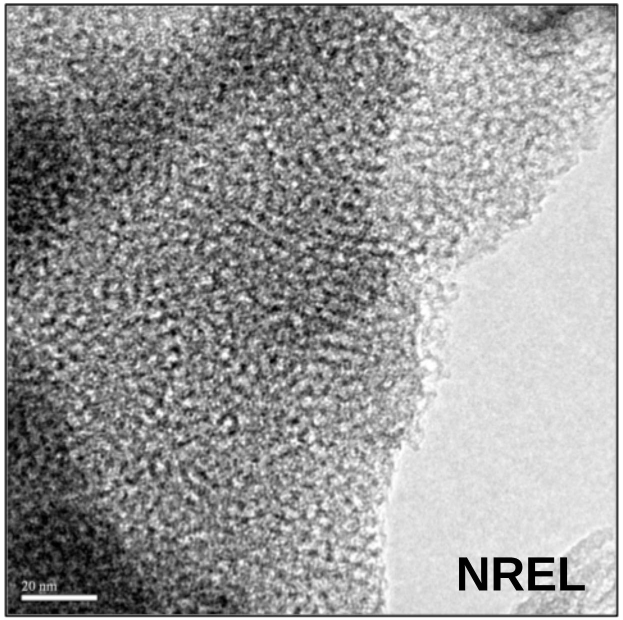


Quantify coke formation, dealumination and changes in pore structure over multiple length scales



Weckhuysen, et al., *Angew. Chem. Int. Ed.* **2016,** *55,* 11173

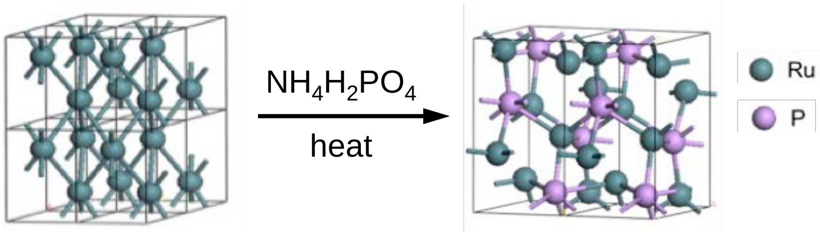
Advanced Synthesis



Develop mesoporous zeolites based on predictive model

Future work – Catalyst development targets

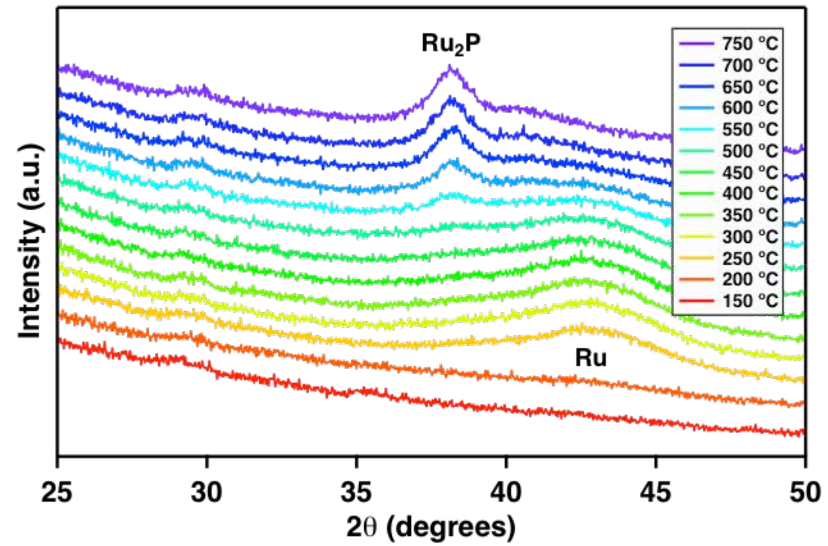
Target: *Increase sulfur tolerance* of Ru/TiO_2 stabilization catalyst during fast pyrolysis bio-oil upgrading



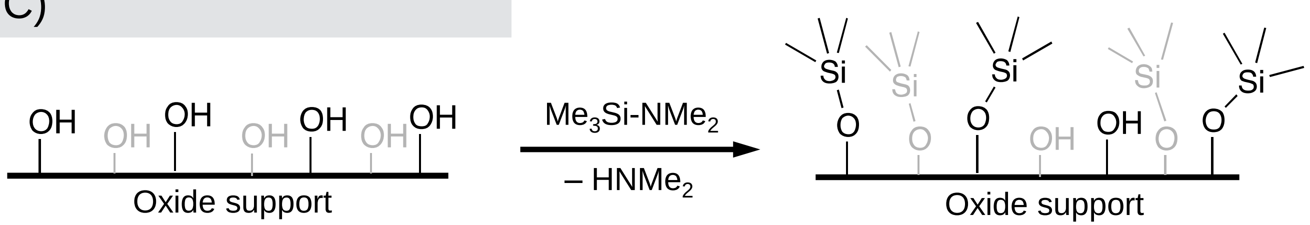
Hexagonal **Ru** → *Orthorhombic* **Ru_2P**

Adapted from Guan et al., *Catal. Commun.*, **2011**, *14*, 114

***In situ* XRD during Ru_2P synthesis**



Target: *Enhance conversion* by controlling catalyst solvophilicity (with CCPC)



Brutchey, et al. *Langmuir* **2005**, *21,* 9576
Baddour, et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 9026

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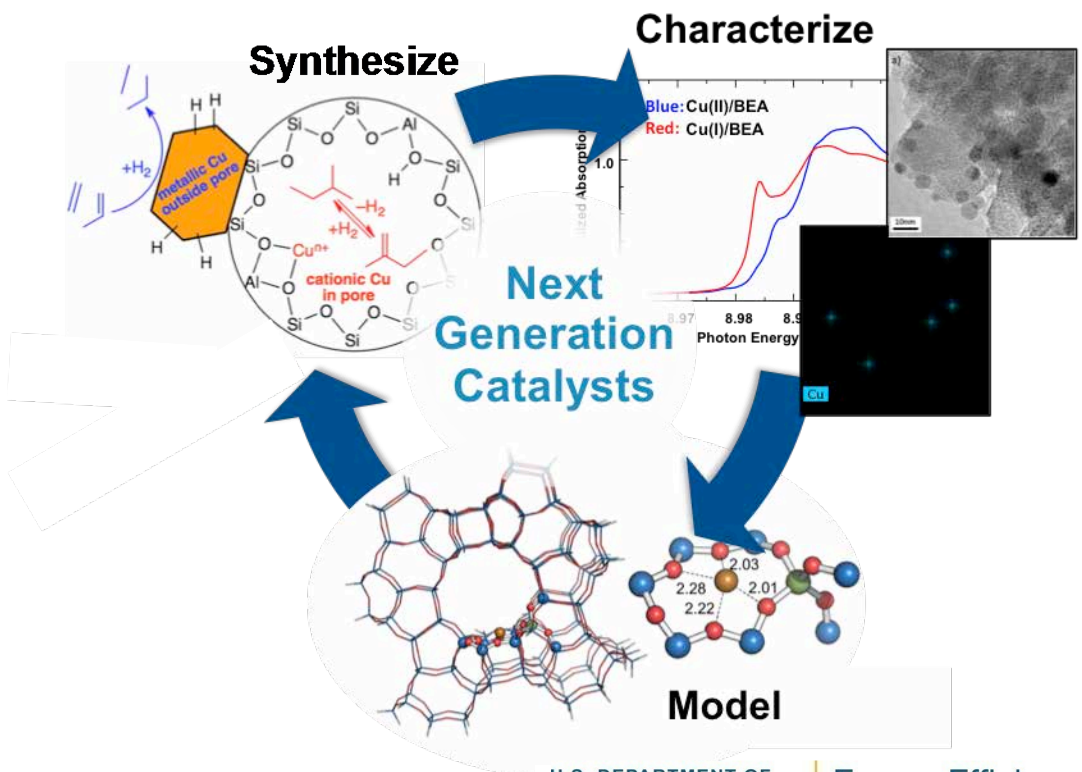
Summary

Project Goal – Deliver high performing, cost-effective catalytic materials that meet the needs of the CCB catalysis projects by leveraging advanced characterization capabilities and unique synthesis expertise at multiple DOE National Laboratories

- Investment in catalyst development is crucial to **improving the economics** of fuel and product production
- Collaboration between advanced characterization, synthesis, and experiment can directly **reduce conversion costs**
- This approach will enable us to **tackle key catalyst development challenges** required to meet cost and performance targets

Accelerated catalyst development cycle



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Oak Ridge National Laboratory

Kinga Unocic
Timothy Theiss

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Publications and presentations

Publications

- J. A. Schaidle*, S. E. Habas, F. G. Baddour, C. A. Farberow, D. A. Ruddy, J. E. Hensley, R. L. Brutchey, N. Malmstadt, and H. Robota, "Transitioning Rationally Designed Catalytic Materials to Real ‘‘Working’’ Catalysts Produced at Commercial Scale: Nanoparticle Materials", *Catalysis*, RSC Publishing, **2017**, *29*, 213, DOI: 10.1039/9781788010634-00213.

Presentations

- S. Habas*, F. Baddour, D. Ruddy, C. Nash, J. Schaidle, "A Facile Route to Nanostructured Metal Phosphide Catalysts for Hydrodeoxygenation of Bio-oil Compounds", Frontiers in Biorefining Meeting, St. Simons Island, GA, November 11, 2016.

- K. Unocic, T. Krause, S. Habas, "Accelerated Catalyst Development for Emerging Biomass Conversion Processes", Physical Sciences Directorate 2017 Advisory Committee Meeting, Oak Ridge, TN, February 9, 2017.

Acronyms and abbreviations

ACSC	Advanced Synthesis and Characterization project
ANL	Argonne National Laboratory
APS	Advanced Photon Source
BETO	Bioenergy Technologies Office
CCB	Chemical Catalysis for Bioenergy Consortium; ChemCatBio consortium
CCM	Catalyst Cost Model Development project
CCPC	Consortium for Computational Physics and Chemistry
CFP	Catalytic fast pyrolysis
Cu/BEA	Cu-modified beta zeolite
DME	Dimethyl ether
DOE	U.S. Department of Energy
EMN	Energy Materials Network

Acronyms and abbreviations (cont.)

GGE	Gallon gasoline equivalent
LANL	Los Alamos National Laboratory
MFSP	Minimum fuel selling price
MYPP	Multi-Year Program Plan
NETL	National Energy Technology Laboratory
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
S/TEM	Scanning transmission electron microscopy
WBS	Work breakdown structure
wt%	Percentage by weight
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction