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)

**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.

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

**Relevance**

- Improve C–C coupling selectivity
- Increase olefin production
- Mitigate S deactivation
- Reduce coke formation
- Direct waste carbon to valuable chemicals
Quad chart overview

Timeline
Project start date: 10/1/2016
Project end date: 9/30/2019
Percent complete: 14%

Budget
<table>
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<tr>
<th>FY 15 Costs</th>
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<th>Total Planned Funding FY 17*-19</th>
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<tbody>
<tr>
<td>DOE Funded</td>
<td>$0</td>
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*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

- 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

Schaidle et al. ACS Catal., 2015, 5, 1794
Establish an integrated and collaborative portfolio of catalytic and enabling technologies

**CCB Catalysis Projects**
- Catalytic Upgrading of Biochemical Intermediates
- Liquid Fuels via Upgrading of Indirect Liquefaction Intermediates
- Fast Pyrolysis and Upgrading
- Catalytic Fast Pyrolysis
- Recovering and Upgrading Biogenic Carbon in Biomass-Derived Aqueous Streams

**Enabling Technologies**
- Catalyst Development (ACSC)
- Computational Modeling (CCPC)
- Cost Guidance (CCM)

**Collaborative outcomes**
- Targeted Cost Reduction
- Improved Performance for Key Metrics
- Cost-guided Synthesis
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
- Identify lower cost precursors and synthesis routes (CCM)
- X-ray absorption spectroscopy (XAS) for overall catalyst coordination environment and oxidation states
- Inform computational models to predict next-generation catalysts (CCPC)
- Sub-Ångström resolution scanning transmission electron microscopy (S/TEM) for local catalyst structures and chemical compositions
Management approach

**ACSC Project Structure**

- **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**

- **Milestones**
- **Go/No-Go Decision**
  - Identify areas for improvement and tasks or capabilities to be integrated or removed

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

**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.

Mesoporous zeolites that reduce coke formation

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

P. Ciesielski
CCPC

C. Farberow
CCPC
Technical Accomplishments – Increase olefin production

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

**Advanced synthesis**

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


**Advanced characterization**

*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

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- **Relevance**
  - **Catalyst Development Challenge**
    - *Improve C–C coupling selectivity*
    - *Increase olefin production*
    - *Mitigate S deactivation*
    - *Reduce coke formation*
    - *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
- Identify active site structures in metal-zeolite catalysts
- Correlate structural characteristics with catalyst deactivation

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

**Advanced characterization**

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


**Advanced Synthesis**

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

Develop mesoporous zeolites based on predictive model.

ORNL

NREL
Future work – Catalyst development targets

**Target:** Increase sulfur tolerance of Ru/TiO₂ stabilization catalyst during fast pyrolysis bio-oil upgrading

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

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

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

1. Synthesize
2. Characterize
3. Model
4. Next Generation Catalysts
Acknowledgements

Daniel Ruddy
Frederick Baddour
Singfoong Cheah
Joshua Schaidle
Theodore Krause
Jeff Miller (Purdue)
Ce Yang
Jennifer Dunn
Cristina Negri
Kinga Unocic
Timothy Theiss

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

This work was supported by DOE BETO under Contract no. DE-AC36-08-GO28308 with NREL, Contract no. DE-AC02-06CH11357 with ANL, and Contract no. DE-AC05-00OR22725 with ORNL
Publications and presentations

Publications


Presentations


## Acronyms and abbreviations

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<td>Advanced Synthesis and Characterization project</td>
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<td>ANL</td>
<td>Argonne National Laboratory</td>
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<td>APS</td>
<td>Advanced Photon Source</td>
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<td>BETO</td>
<td>Bioenergy Technologies Office</td>
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<td>CCB</td>
<td>Chemical Catalysis for Bioenergy Consortium; ChemCatBio consortium</td>
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<td>CFP</td>
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<td>Cu/BEA</td>
<td>Cu-modified beta zeolite</td>
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<td>DME</td>
<td>Dimethyl ether</td>
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<td>DOE</td>
<td>U.S. Department of Energy</td>
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<td>EMN</td>
<td>Energy Materials Network</td>
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### Acronyms and abbreviations (cont.)

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<td>GGE</td>
<td>Gallon gasoline equivalent</td>
</tr>
<tr>
<td>LANL</td>
<td>Los Alamos National Laboratory</td>
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<tr>
<td>MFSP</td>
<td>Minimum fuel selling price</td>
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<td>MYPP</td>
<td>Multi-Year Program Plan</td>
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<td>NETL</td>
<td>National Energy Technology Laboratory</td>
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<td>S/TEM</td>
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<td>Work breakdown structure</td>
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<td>wt%</td>
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<td>XAS</td>
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<td>XRD</td>
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