ChemCatBio
Chemical Catalysis for Bioenergy

CCB DFA: Advanced Characterizations to Accelerate Commercial Catalyst Development w/ Vertimass
2.5.4.703-705

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DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

Thermochemical Conversion

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

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

- **Catalytic Upgrading of Biochemical Intermediates** (NREL, PNNL, ORNL, LANL, NREL*)
- **Catalytic Upgrading of Indirect Liquefaction Intermediates** (NREL, PNNL, ORNL)
- **Catalytic Fast Pyrolysis** (NREL, PNNL)
- **Electrocatalytic and Thermocatalytic CO_2 Utilization** (NREL, ORNL*)

*FY19 Seed Project

Enabling Capabilities

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

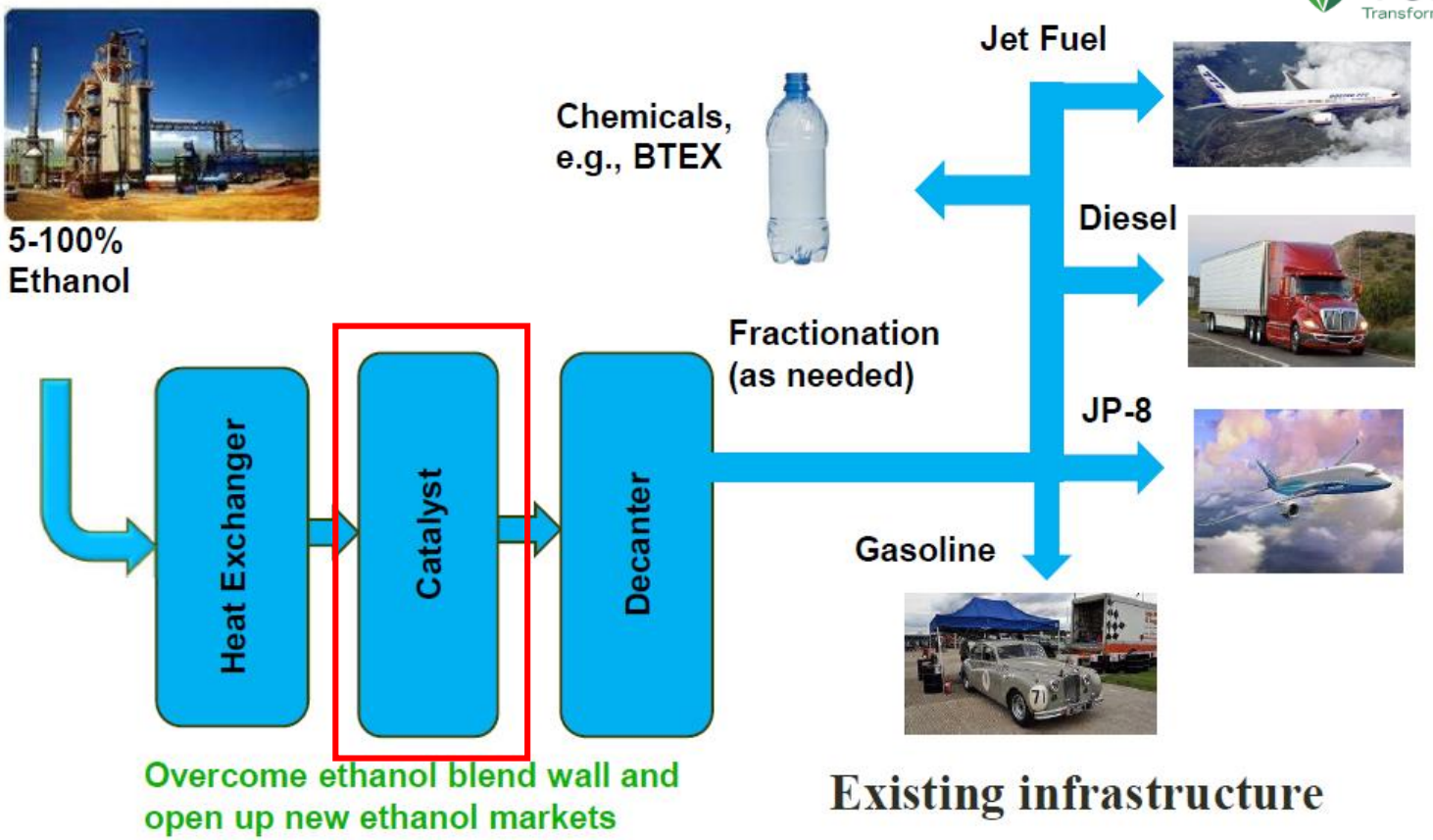
Industry Partnerships (Directed Funding)

- **Gevo** (NREL)
- **ALD Nano/JM** (NREL)
- **Vertimass** (ORNL)
- **Opus12**(NREL)
- **Visolis** (PNNL)
- **Lanzatech** (PNNL) - Fuel
- **Gevo** (LANL)
- **Lanzatech** (PNNL) - TPA
- **Sironix** (LANL)

Cross-Cutting Support

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

Overview – Vertimass Ethanol Upgrading



- Separate DOE-BETO award $2M in 2014 to demonstrate and scale up technology to convert ethanol into fuel blend stocks (Vertimass Scale-up CRADA, WBS No. 2.3.1.202)
  - "One-Step High-Yield Production of Fungible Gasoline Blend Stocks and high value chemical coproduct (BTEX) from Ethanol without Added Hydrogen"
  - This scale-up project focuses on process and catalyst scale up

Commercialization Challenges: Ethanol Upgrading

- Critical transition from pilot scale to commercial scale
- Challenges to address:
  - Understand catalyst changes after reaction and regeneration
    a) Catalyst changes: mechanism
    b) Examine potential reasons for performance differences
  - Transfer the pilot to commercial scale catalysts
    a) Commercial supports with binders
    b) Particle size, porosity, active site differences
- Scale-up CRADA industrial partners (Vertimass, TechnipFMC, Clariant): process development & engineering, catalyst production
- Critical need in catalyst characterizations to bridge catalyst production and catalyst testing/process engineering
- **Project Goal:** ChemCatBio DFA provides **advanced catalyst characterizations** to **accelerate** Vertimass commercial catalyst development

Quad Chart Overview

Timeline

- Project start date – April 2018
- Project end date – Dec. 2019
- Percent complete – 48%

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs (K $)	Total Planned Funding (FY 19 to Project End Date) (K $)
DOE Funded	0	0	162	338
Project Cost Share*	0	0	65	135

•Partners: ORNL (65%), NREL (15%), ANL (20%)

*Vertimass provides in-kind cost share

Barriers addressed

- Ct-G. Decreasing the Time and Cost to Develop Novel Industrially Relevant Catalysts

Objective:

- Provide valuable characterization information to accelerate Vertimass commercial catalysts development for ethanol upgrading to fungible fuels and valuable chemicals.

End of Project Goal:

- By performing extensive catalyst characterizations and catalyst testing at the pilot scale (existing CRADA, WBS 2.3.1.202), **one commercial formulation will be identified to perform similarly as pilot scale catalyst** with <20% difference in activity, stability and product yield.

1 – Approach (Management)

- **Project Structure**

(DFA project)
Characterization

(Vertimass Scale-up CRADA)
Provide both fresh & used lab (ORNL) and pilot catalysts

Catalyst production
Commercial catalysts

- **Management Approach**

1) Monthly coordination meetings with ORNL, ANL and NREL to discuss results and make plans
2) ORNL coordinates the distribution of samples
3) Interact via email, phone and face-to-face meetings at conferences, workshops, review meetings and on-site visits to discuss project details
4) Communicate project progress and updates with DOE through quarterly reports, success stories and teleconferences

1 – Approach (Technical)

- **Understand catalyst changes after ethanol upgrading reactions**
  - Utilize ChemCatBio's unique characterization techniques (e.g., HR-STEM (ORNL), in situ X-ray absorption (ANL), ^{27}Al NMR (NREL))
  - Employ catalysis expertise and experience from the DFA team members
  - Fundamental understanding: reversible or irreversible changes — coking, dealumination, metal sintering, and structure changes
- **Offer solutions to improve catalyst stability/activity & lower catalyst cost**
  - Guided by the structure (characterization) and performance relationship
  - Learn valuable information from the spent samples
  - Provide suggestions on catalyst and process optimization
- **Assist with commercial catalyst development to achieve similar performance as pilot-scale catalyst**
  - Analyze commercial catalysts to understand the metal distribution and acid sites by leveraging DFA advanced characterization tools
- **Technical success is based on:**
  - Successful identification of mechanisms for catalyst changes during ethanol upgrading and regeneration
  - Accelerating commercial catalyst development

Relevance

- ChemCatBio DFA project provide valuable characterizations information to understand the catalyst changes and characterize the commercial catalyst:
  - *Develop more stable and active catalyst with lower cost*
  - *Optimize the process operation*
  - *Accelerate the commercialization of this new technology*

Impact in the words of industry:	*"The ChemCatBio program has provided excellent catalyst characterization insights allowing us to optimize performance and lower conversion costs."* -John Hannon, Chief Operating Officer at Vertimass LLC

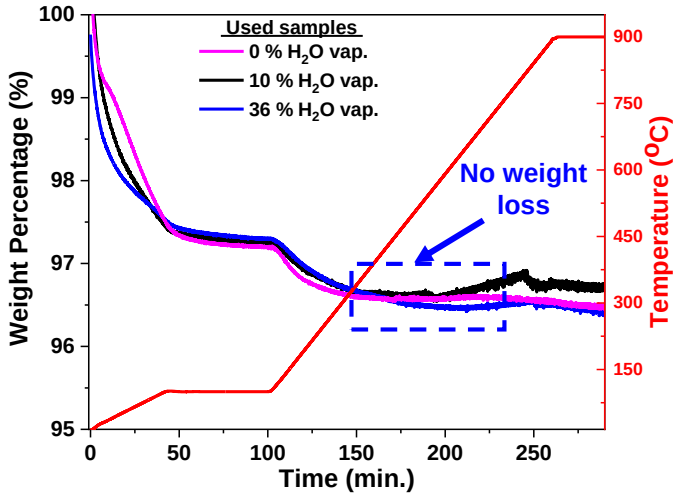
- Approaches developed/lessons learned are valuable to biomass industry:
  - *Approaches to understand catalyst deactivation and commercial catalysts*
  - *Catalyst changes/deactivation in biomass relevant conditions*
- Well ***aligned with the BETO ChemCatBio goal*** "to accelerate the development of catalysts and related technologies for the production of fuels and chemicals derived from biomass and waste feedstocks."

2 – Technical Accomplishments

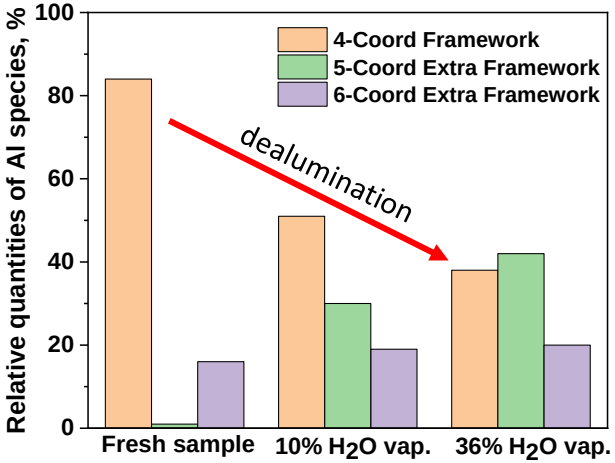
- Milestones:
  - Analysis of **>6 pilot-scale catalysts** (fresh and used) generated from TechnipFMC to provide information on structure, composition and metal distribution changes during ethanol upgrading in the pilot-scale operation. (ORNL, NREL, ANL) (9/30/2018, completed)
  - Analysis of **>4 catalysts (running with aqueous ethanol for 200 h)** to understand changes related to structure, composition and metal distribution in presence of water. (ORNL, NREL, ANL) (12/31/2018, completed)
  - Characterize **4 commercial formulations** to understand the metal distributions. (ORNL, ANL) (03/31/2019, in progress)
- Key Findings:
  - Provided catalyst structural information to correlate with catalyst performance in the pilot-scale operation
  - Developed a correlation between catalyst changes and the water vapor concentration in lab-scale operation
  - Certain level of water vapor concentration changed catalyst structure (low Si/Al) after extended reactions; optimum conditions
  - These characterizations suggest reducing metal loading, which will reduce catalyst cost

2 – Technical Accomplishments (Cont'd)

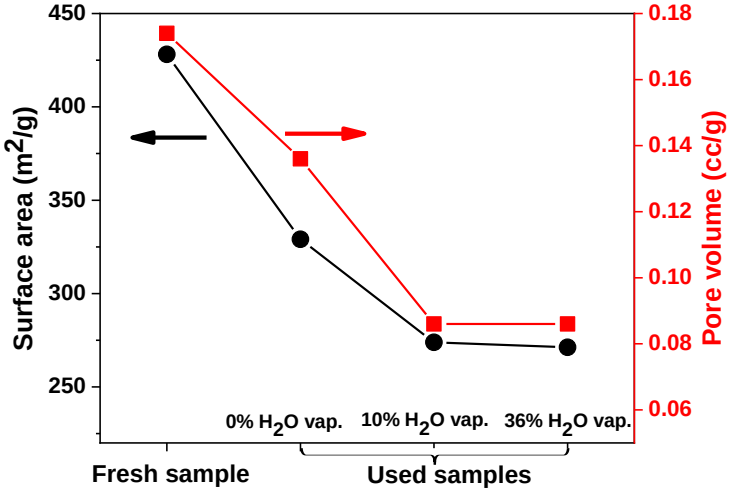
- *Product selectivity changed over extended runs with more water (Scale-up project)*
- *Understand catalyst changes in the presence of water vapor (DFA)*



Thermogravimetric analysis (**ORNL**)



Solid State ^{27}Al NMR (**NREL**)



N_2 physisorption analysis (**ORNL**)

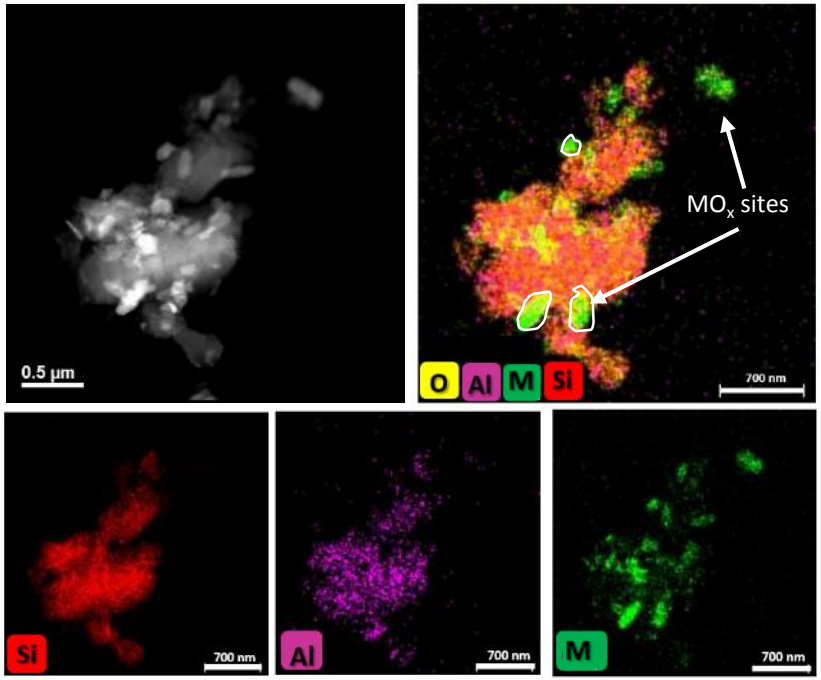
DFA project findings:

- No hard coke formation
- Dealumination exists — increases with water content
- Structure changes

Impact/outcome:

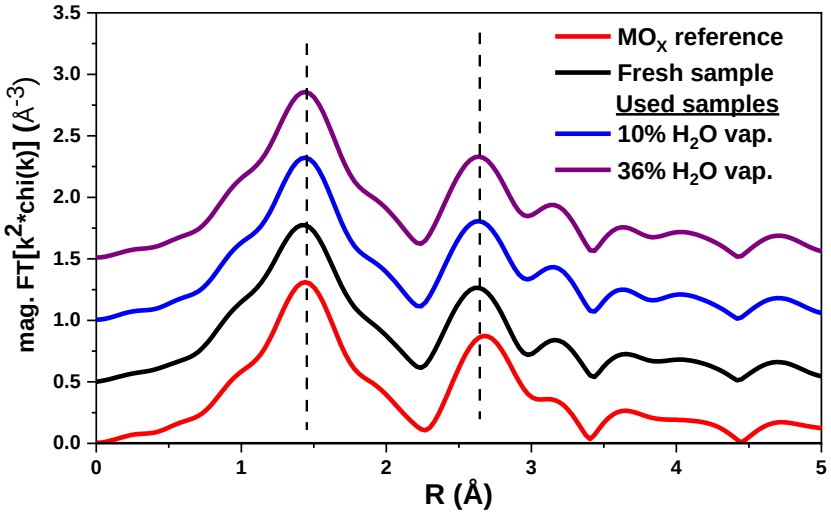
- Optimum condition (water vapor concentration & temperature) for operation
- Develop more stable catalyst

Characterize Active Metal Sites: Reduce Catalyst Cost



STEM/EDS (ORNL)

MO_x particles exist



EXAFS (ANL)

Majority of metal existed as MO_x particles

- Exchanged metal sites are active for ethanol conversion

Impact:

- Potential to reduce metal loading while maintaining the activity
- Further reduce catalyst cost

3 – Future Work

- Plans:
  a) Further characterize the catalyst(s) with new formulation and provide fundamental understanding of the catalyst stability: stable catalyst at more severe operation conditions
  b) Analyze both fresh and used commercial catalysts: understand difference between pilot and commercial catalysts, accelerate the commercial catalyst development

- Key milestones
  a) Analysis of **commercial formulations (fresh)** to understand the metal distributions on commercial supports.
  b) Analyze **used commercial catalysts** after >4 regeneration cycles at pilot scale to understand the catalyst changes after the reaction.
  c) End of project: **identify one commercial formulation** to perform similarly as pilot scale catalyst (<20% difference)

- Well aligned with Vertimass' schedule on commercial catalyst development

Summary

- Provide valuable catalyst characterization information to accelerate Vertimass commercial catalyst development:
  a) Understand catalyst changes
  b) Offer solution to improve catalyst stability/activity, lower catalyst cost
  c) Assist with commercial catalyst development
- **Key findings:**
  - Provided catalyst structural information to correlate with catalyst performance in the pilot-scale operation
  - Developed a correlation between catalyst changes and the water vapor concentration in lab-scale operation
  - These characterizations suggest reducing metal loading, which will reduce catalyst cost
- **Plans:**
  a) Further characterize the catalyst with new formula and provide fundamental understanding of the catalyst stability
  b) Analyze both fresh and used commercial catalysts

Impact in the words of industry:

"The ChemCatBio program has provided excellent catalyst characterization insights allowing us to optimize performance and lower conversion costs."
-John Hannon, Chief Operating Officer at Vertimass LLC

Additional Slides

Presentations

- John Hannon, “Advanced Catalyst Characterization to Accelerate Transforming Ethanol to Hydrocarbon Fuel Blend Stocks” ACS National Meeting, New Orleans, LA, March 20, 2018.
- Zhenglong Li, Kinga Unocic, Frederick Baddour, Theodore R. Krause, Brian Davison. “Advanced Characterizations to Accelerate Commercial Catalyst Development w/ Vertimass”, DOE BETO ChemCatBio Face-to-Face meeting, Denver, CO, August 9, 2018.