ChemCatBio
Chemical Catalysis for Bioenergy

Comprehensive Characterization of Mixed Metal Oxide Catalysts for Enhanced Catalyst Lifetime During Bio-based C_2-C_6 Oxygenates to Olefins Processes

Thermochemical Conversion

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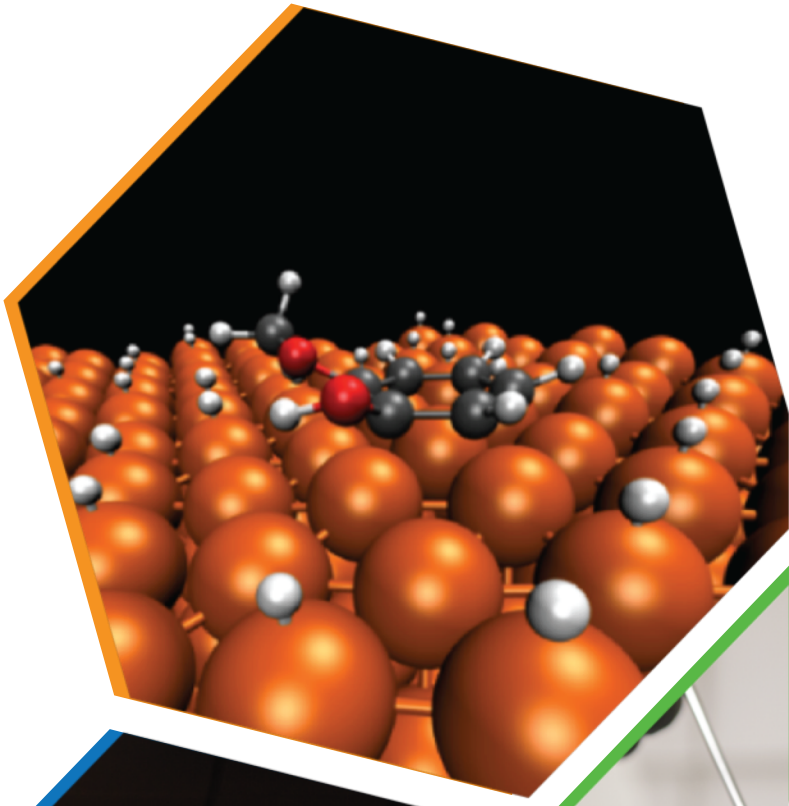


U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

ChemCatBio Foundation

Integrated and collaborative portfolio of catalytic technologies and enabling capabilities

Catalytic Technologies

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

Quad Chart Overview

Timeline

- Project start date: 4/1/2018
- Project end date: 9/30/2019
- Percent complete: 60%

	Total Costs Pre FY17	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	–	–	$120 K	$255 K
Project Cost Share	–	–	$40 K	$85 K

Partners: National Laboratories: NREL (33%); ANL (33%); ORNL (33%)

Barriers addressed

Ct-E. Improving Catalyst Lifetime
Ct-F. Increasing the Yield from Catalytic Processes
Ct-G. Decreasing the Time and Cost to Develop Novel Industrially Relevant Catalysts

Objective

Identify key mixed-metal oxide catalyst features that influence catalyst deactivation by leveraging synthesis and characterization capabilities and expertise across multiple DOE National Laboratories.

End of Project Goal

Next-generation MMO catalysts with tailored compositions that demonstrate enhanced stability during Gevo's ethanol to olefins (ETO) and mixed alcohols (fusel oil) to ketones (fusels) processes.

1. Approach and Relevance – The Opportunity

US capacity for ethanol production

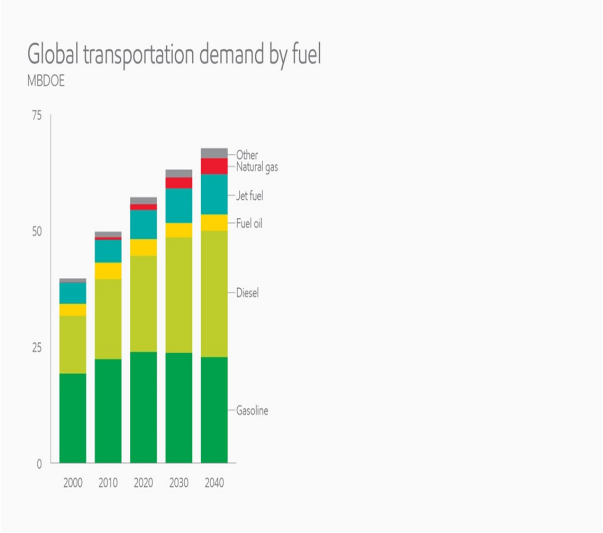
- 15.9 Billion gallons/year

Fusel oil (mixed oxygenates)

- 159 million gallons/year of *low cost feedstock*

– IHS Markit report, 2018

Catalyst development



– ExxonMobil, The Outlook for Energy: A View to 2040, 2016

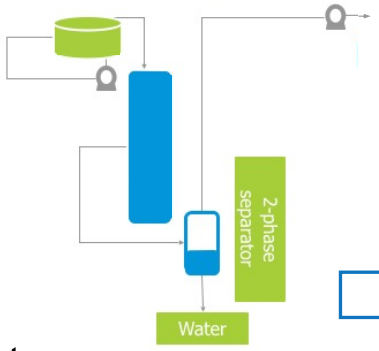
Fusel oil co-process represents un-tapped revenue stream that requires catalyst development

1. Approach and Relevance – Critical Research Challenge

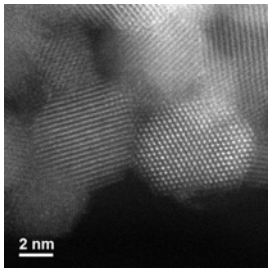
Catalyst Development Cycle

Synthesis

Bench-scale evaluation



Complex catalysts
$(M^1_aM^2_bM^3_cM^{4\cdots}_d)O_x$



Characterization

gevo

Next-generation catalysts with enhanced stability

Understand key mixed-metal oxide catalyst features that can be manipulated to improve catalyst stability

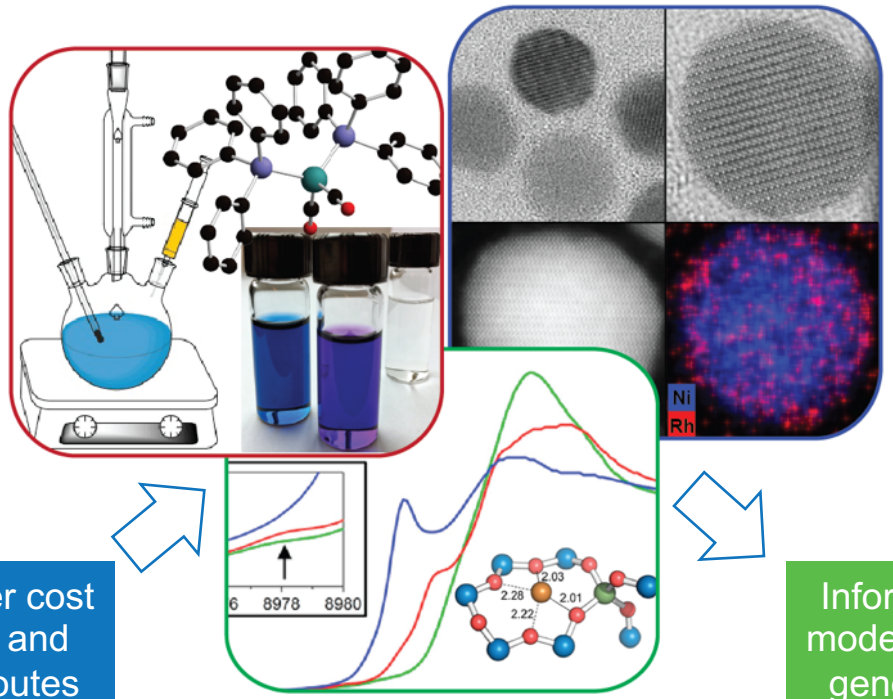
1. Approach and Relevance – Leverage ChemCatBio Capabilities

World class capabilities and expertise directed to answer industrial catalyst development questions

Dedicated synthetic effort for next-generation catalysts through innovative syntheses

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Sandia National Laboratories



Advanced *spatially resolved* imaging and characterization

OAK RIDGE National Laboratory

Identify lower cost precursors and synthesis routes

CatCost

Advanced spectroscopic techniques for *bulk and surface* structural and chemical characterization

Argonne NATIONAL LABORATORY

OAK RIDGE National Laboratory

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

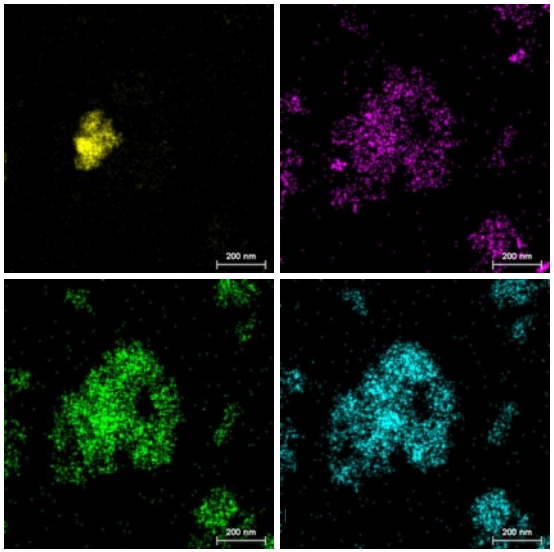
Inform computational models to predict next-generation catalysts

CCPC

1. Approach and Relevance – Correlate with Performance

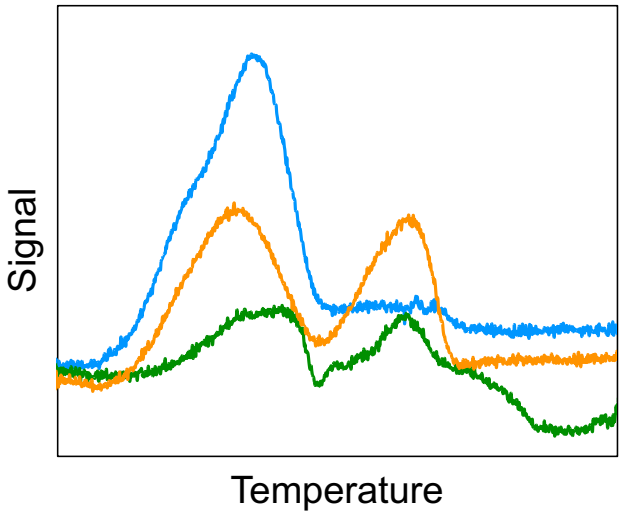
- Coupling **multiple characterization techniques** provides insight into structure and function that can be correlated with performance
- Provides opportunity to **rationally design next-generation catalysts**

Structural differences



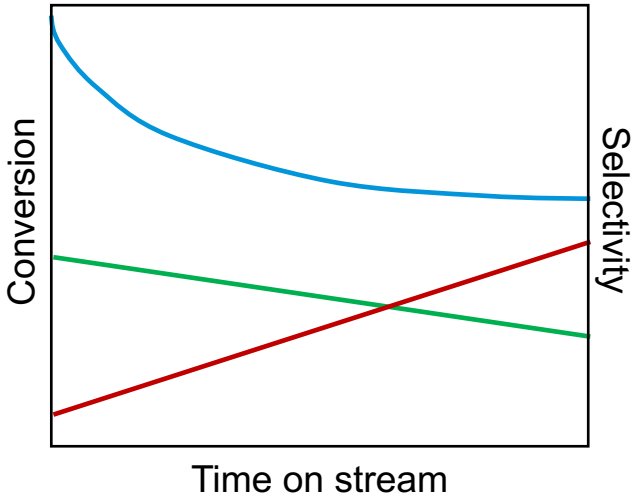
Elemental segregation

Functional differences



Type/strength of active sites

Performance correlation



Catalyst deactivation

Correlate catalyst features with performance to guide next-generation catalyst synthesis

1. Approach and Relevance – Next-generation Catalysts

Mixed-metal oxide (MMO) catalysts
Fresh, spent, regenerated

FY18 Q3: Evaluation of characterization techniques and conditions

Challenges: Oxide materials, low elemental concentrations

FY18 Q4: Detailed characterization with targeted methodologies

FY19 Q1: Correlation with performance data from Gevo

FY19 Q2: Next-generation MMO catalysts with improved performance

FY19 Go/No-Go Decision

Insight gained?

2 Cycles of catalyst development

*"The **insight provided by ChemCatBio through advanced characterization techniques that are not readily available to industry** has helped us to develop a better understanding of catalyst deactivation for important Gevo biofuels processes." – Gevo*

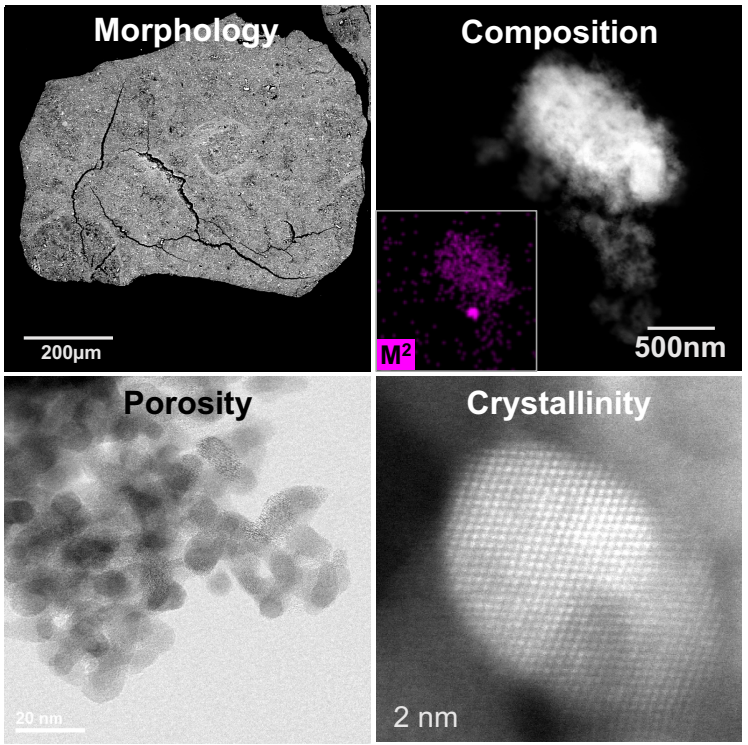
2. Technical Accomplishments – Detailed Characterization

Mixed-metal oxide (MMO) catalysts
Fresh, spent, regenerated

Series of catalysts for both Gevo's ETO and fusels processes

FY18 Q3: Evaluation of characterization techniques and conditions

Multiple techniques across 3 DOE National Laboratories



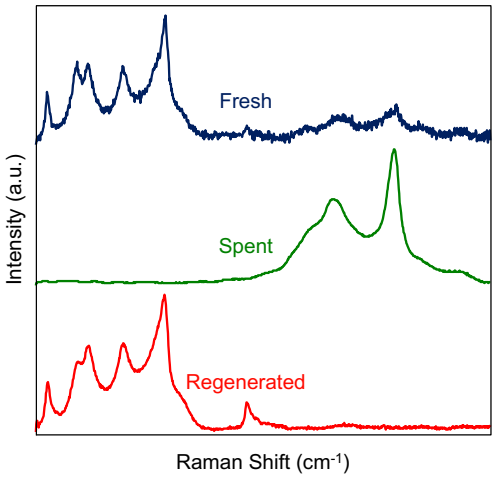
Rigorous characterization across multiple length scales

FY18 Q4: Detailed characterization with targeted methodologies

- Spatially-resolved composition
- Surface area and pore volume
- Morphology
- Crystal phases
- Coordination environment
- Surface chemistry
- Active sites type
- Active site strength

Identified characterization techniques and conditions that provide fundamental insight into MMO catalysts

2. Technical Accomplishments – Correlation with Performance



FY19 Q2: Next-generation MMO catalysts with improved performance

FY19 Go/No-Go Decision

Insight gained?

Successful Go-No/Go in Q1 of FY19

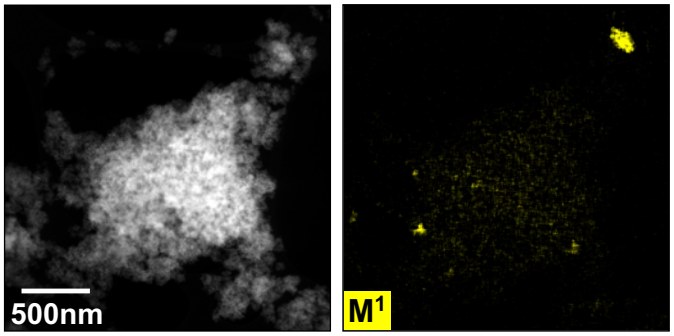
Cycle 1 of catalyst development

FY18 Q4: Detailed characterization with targeted methodologies

FY19 Q1: Correlation with performance data from Gevo

Cycle 1 Outcomes

- **Identified** synthesis-dependent structural characteristics
- **Confirmed** no selective leaching of critical elements
- **Correlated** phase-segregation with deactivation



3. Future Work

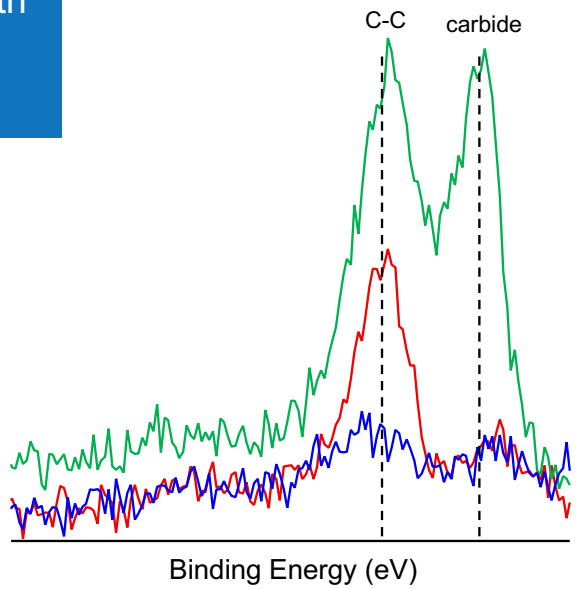
FY19 Q2: Next-generation MMO catalysts with improved performance

Next-generation catalysts with enhanced stability

Cycle 2 of catalyst development

FY19 Q3: Detailed characterization with targeted methodologies

FY19 Q4: Correlation with performance data from Gevo



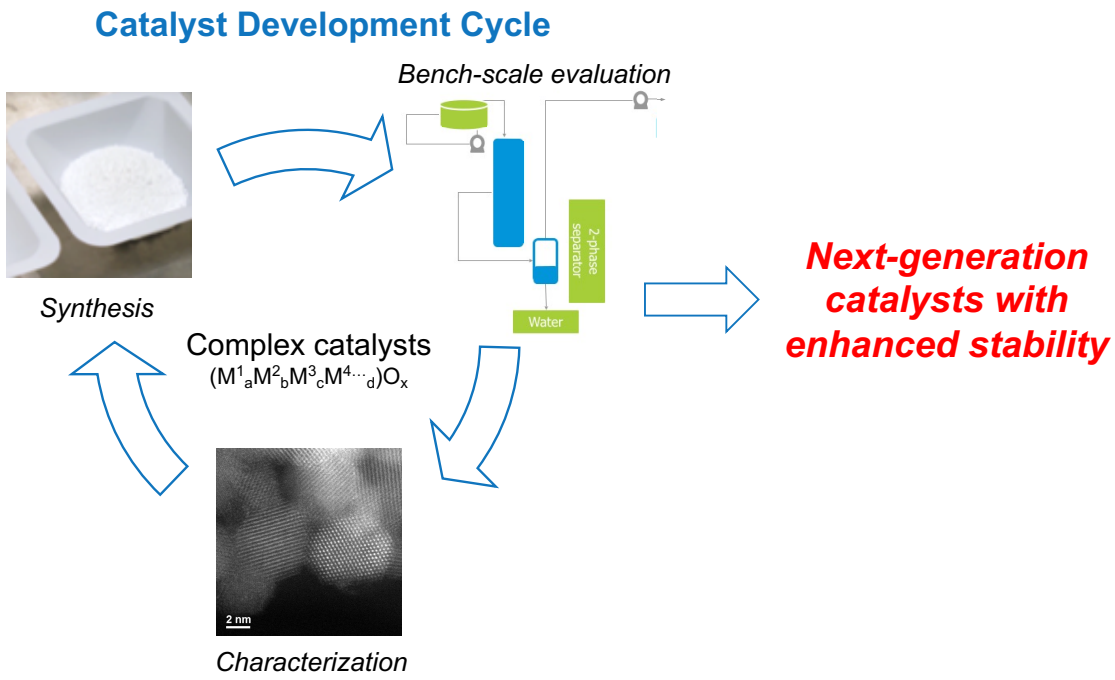
Cycle 2 Objectives

- **Guide** ETO catalyst development to minimize phase segregation and deactivation
- **Achieve** 20% reduction in rate of catalyst activity loss (percent change in C_3 yield/hour)

Summary

Goal: Understand key mixed-metal oxide catalyst features that can be manipulated to improve catalyst stability

- *Leveraged* characterization capabilities and expertise across ChemCatBio Consortium
- *Identified* characterization techniques and conditions to provide fundamental insight into catalysts
- *Correlated* catalyst features with performance to guide next-generation catalyst synthesis



Impact: Next-generation catalysts with tailored compositions that demonstrate enhanced stability for Gevo's ETO and fusels processes

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