

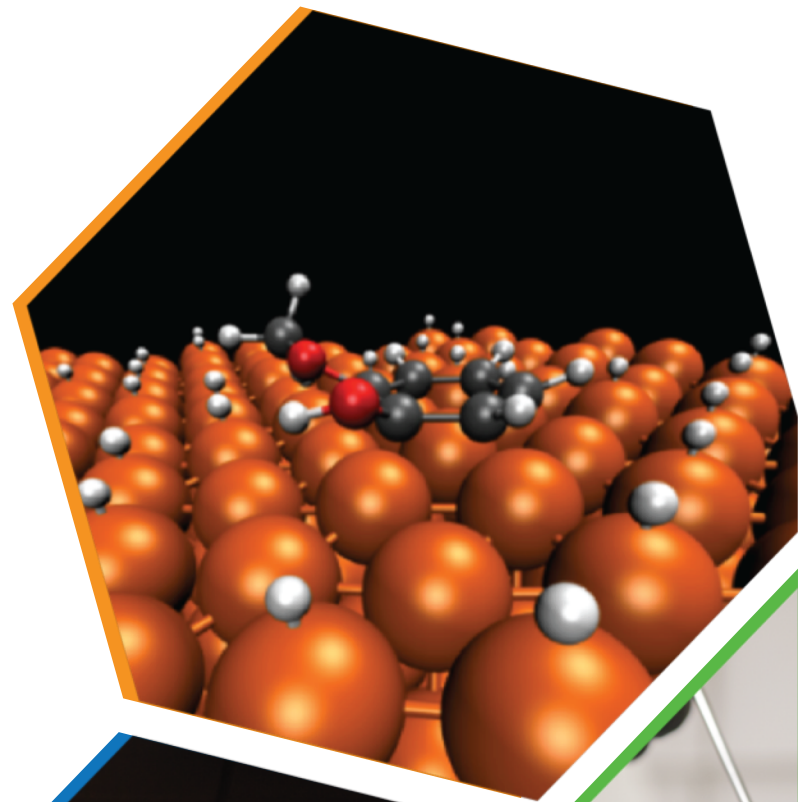


Comprehensive Characterization of Mixed Metal Oxide Catalysts for Enhanced Catalyst Lifetime During Bio-based C₂-C₆ Oxygenates to Olefins Processes

Thermochemical Conversion

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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 CO₂ Utilization

(NREL, ORNL*)

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)

*FY19 Seed Project

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

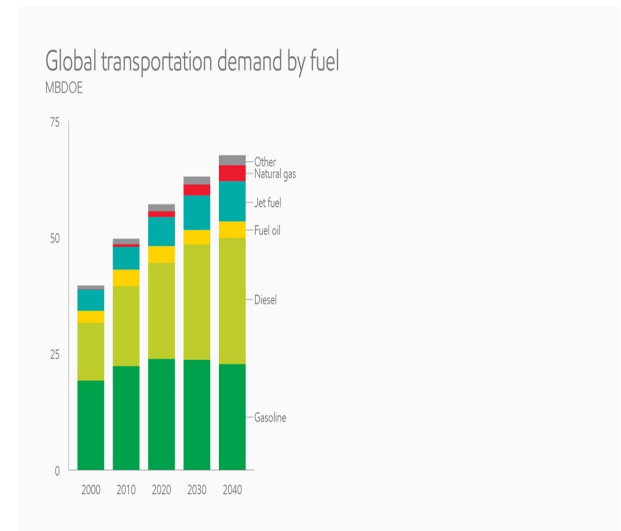
Fusel oil (mixed oxygenates)

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

– IHS Markit report, 2018



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



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

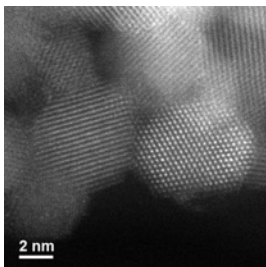
1. Approach and Relevance – Critical Research Challenge

Catalyst Development Cycle



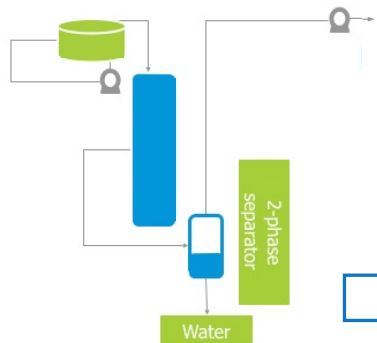
Synthesis

Complex catalysts
($M^1_a M^2_b M^3_c M^4 \dots_d$)O_x



Characterization

Bench-scale evaluation



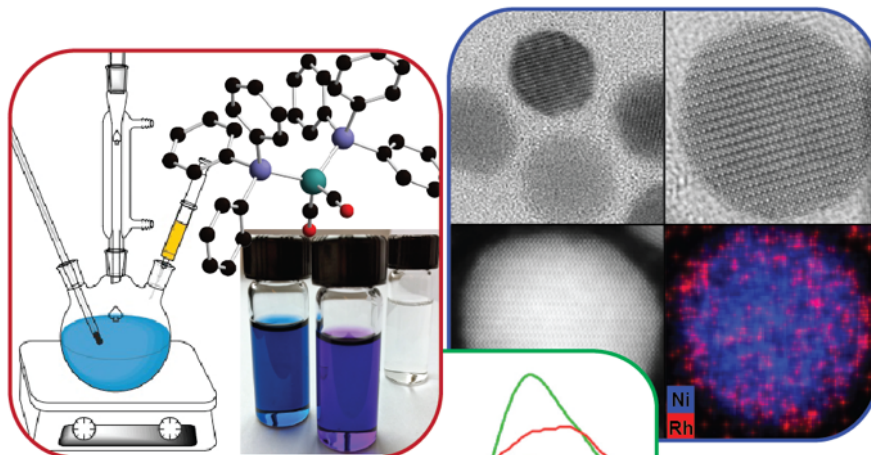
Next-generation catalysts with enhanced stability

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

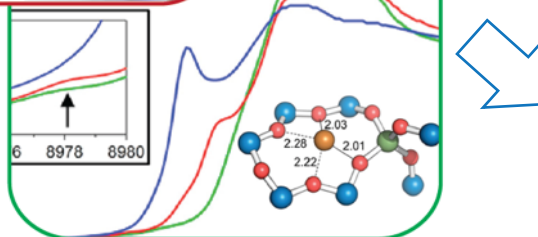


Advanced *spatially resolved* imaging and characterization



Identify lower cost precursors and synthesis routes

CatCost



Inform computational models to predict next-generation catalysts



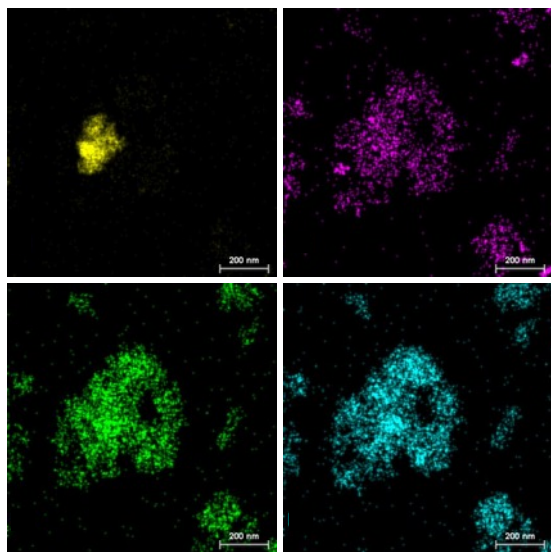
Advanced spectroscopic techniques for *bulk and surface* structural and chemical characterization



1. Approach and Relevance – Correlate with Performance

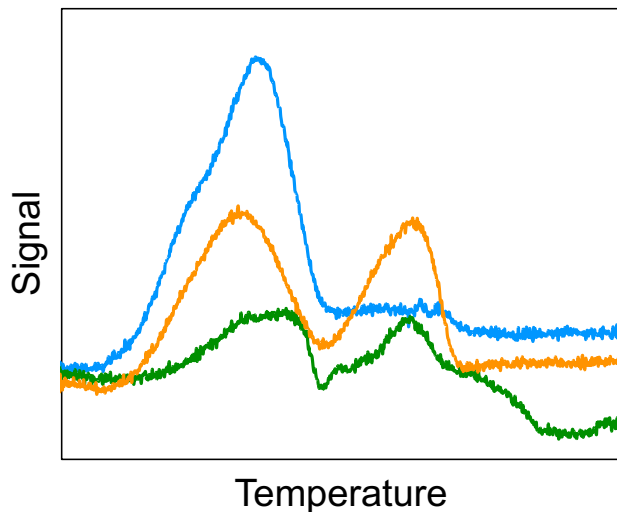
- Coupling **multiple characterization techniques** provides insight into structure and function that can be correlated with performance
- Provides opportunity to **rationally design next-generation catalysts**

Structural differences



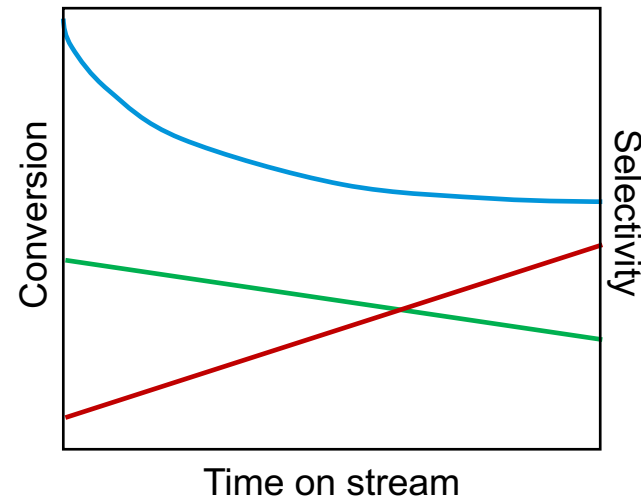
Elemental segregation

Functional differences



Type/strength of active sites

Performance correlation

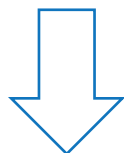


Catalyst deactivation

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

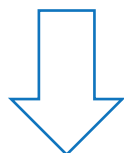
1. Approach and Relevance – Next-generation Catalysts

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

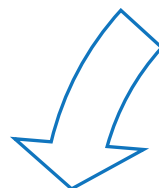


FY18 Q3: Evaluation of
characterization techniques
and conditions

*Challenges: Oxide materials,
low elemental concentrations*



FY18 Q4: Detailed
characterization with
targeted methodologies

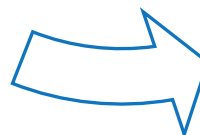


FY19 Q2: Next-generation
MMO catalysts with
improved performance

**2 Cycles of catalyst
development**



FY19 Q1: Correlation with
performance data from
Gevo



FY19
Go/No-Go
Decision

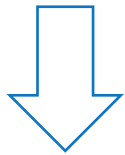
Insight
gained?

“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

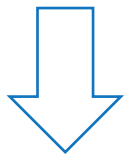
Mixed-metal oxide (MMO) catalysts

Fresh, spent, regenerated

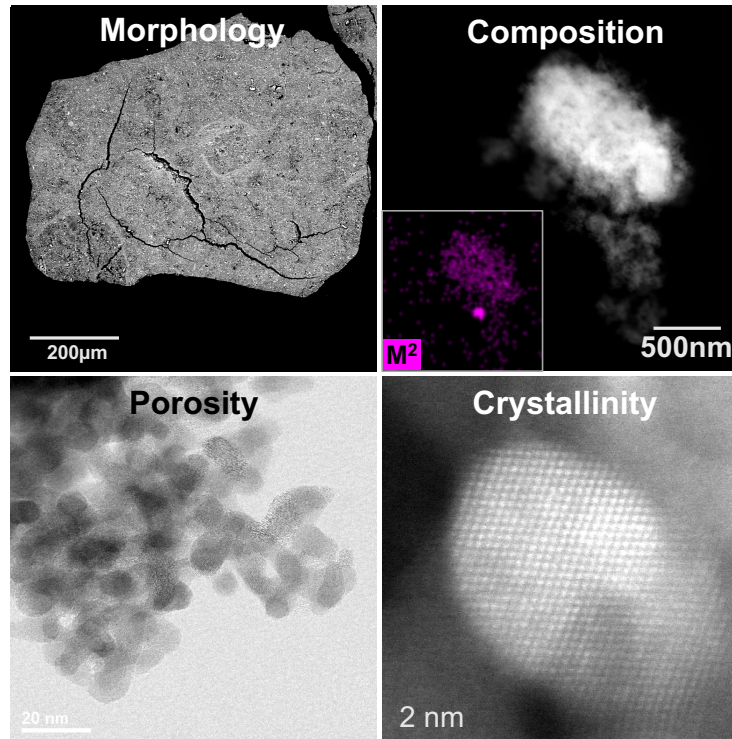


Series of catalysts for both Gevo's ETO and fusels processes

FY18 Q3: Evaluation of characterization techniques and conditions



Multiple techniques across 3 DOE National Laboratories



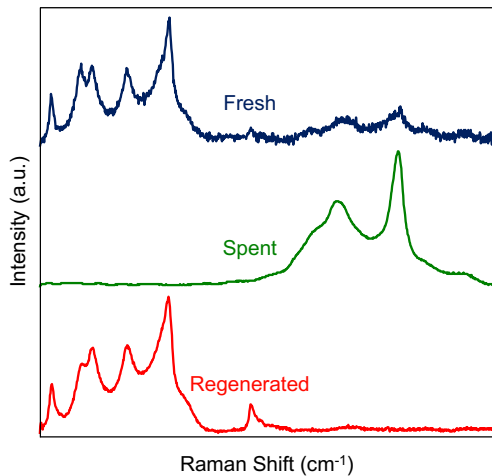
Rigorous characterization across multiple length scales

FY18 Q4: Detailed characterization with targeted methodologies

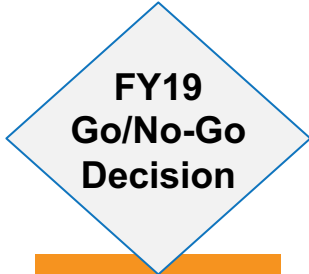
- Spatially-resolved composition
- Surface area and pore volume
- Morphology
- Crystal phases
- Coordination environment
- Surface chemistry
- Active sites type
- Active site strength

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



Insight gained?

Successful Go-No/Go in Q1 of FY19

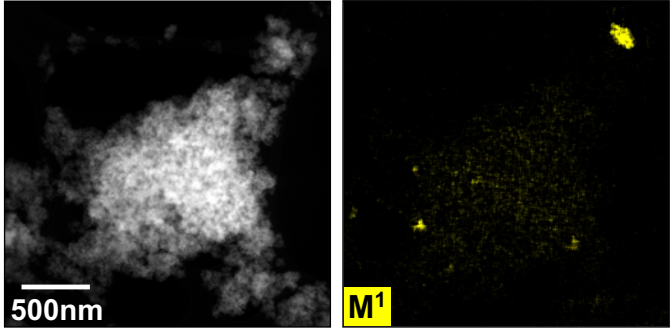


FY18 Q4: Detailed characterization with targeted methodologies

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

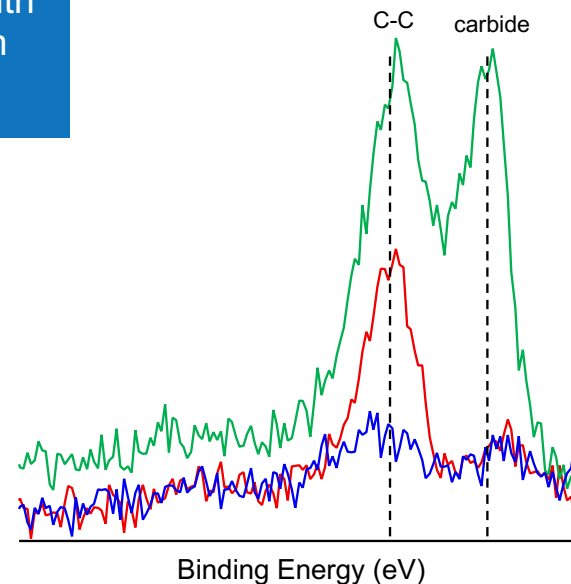
Cycle 2 of catalyst development

FY19 Q3: Detailed characterization with targeted methodologies

FY19 Q4: Correlation with performance data from Gevo

Cycle 2 Objectives

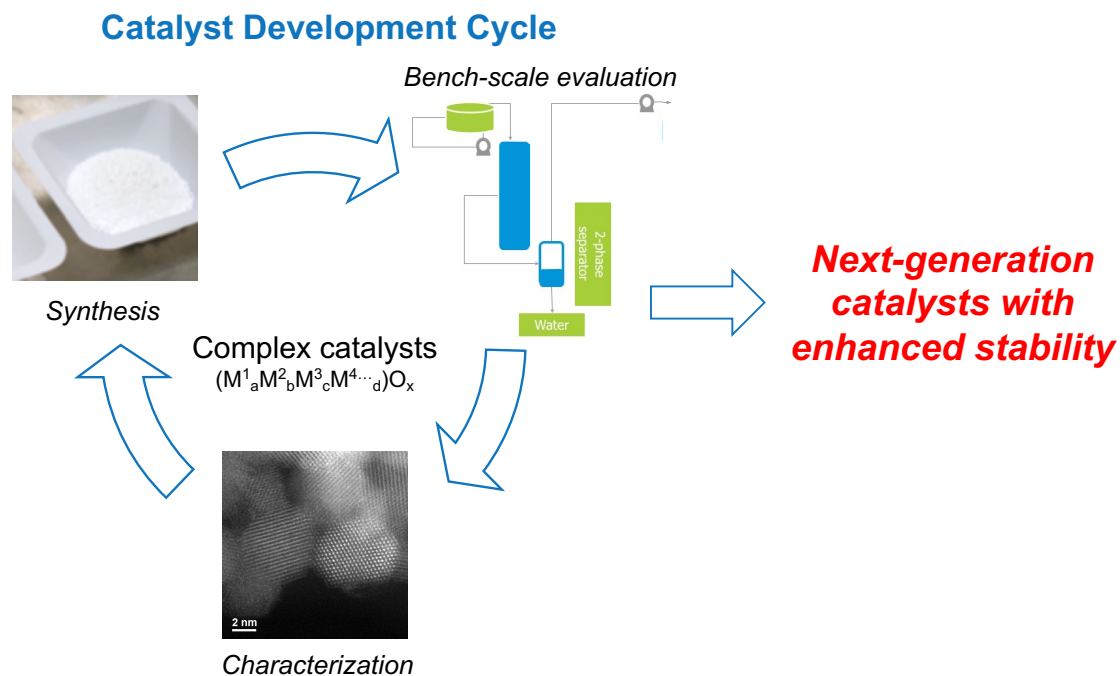
- **Guide** ETO catalyst development to minimize phase segregation and deactivation
- **Achieve** 20% reduction in rate of catalyst activity loss (percent change in C₃ yield/hour)



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

Acknowledgements

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ChemCatBio
Chemical Catalysis for Bioenergy

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BIOENERGY TECHNOLOGIES OFFICE