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

Cooperative Research and Development Final Report

CRADA Number: CRD-18-00728

NREL Technical Contact: Susan Habas

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Contract No. DE-AC36-08GO28308

Technical Report
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Cooperative Research and Development Final Report

Report Date: January 13, 2021

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Gevo, Inc.

CRADA Number: CRD-18-728

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

Responsible Technical Contact at Alliance/NREL: Susan Habas | Susan.Habas@nrel.gov

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Sponsoring DOE Program Office(s):

U.S. Department of Energy Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies Office (BETO)

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	$125,000.00
TOTALS	$125,000.00

Executive Summary of CRADA Work:

Participant has developed mixed metal oxide (MMO) catalysts to selectively convert biomass-derived C2-C6 oxygenates to olefins and then hydrocarbon fuels to meet DOE 2022 fuel targets. Selective conversion ethanol to isobutylene with MMO catalysts (ZnOZrOx) requires low ethanol feeds to maintain performance. Increasing the feed results in rapid catalyst deactivation. Participant has increased catalyst stability by adding additional metal oxides. However, variations in performance based on the level and type of additive and catalytic conditions have been observed. This project will use advanced catalyst characterization methods through the ChemCatBio Advanced Catalyst Synthesis and Characterization (ACSC) project to gain insight into key catalyst features and deactivation modes with the goal of tailoring catalyst composition to improve performance.

Summary of Research Results:

The purpose of this section is to capture the original or modified scope, completed work and outcomes of this project. DOE requires that this template address all the planned tasks in the Joint Work Statement.

Phase 1 Task 1: Synthesis, evaluation, and preliminary characterization of MMO catalysts

We have successfully completed the FY18 Q3 Quarterly Progress Measure entitled "Provide catalyst samples and determine characterization parameters" by distributing six MMO catalysts in fresh, spent, and regenerated forms from Gevo's ethanol to olefins (ETO) process and mixed alcohols (fusel oil) to ketones (fusel) process to the National Renewable Energy Laboratory (NREL), Argonne National Laboratory (ANL), and Oak Ridge National Laboratory (ORNL) for advanced characterization. The six catalyst samples were used to identify relevant characterization methods and specific operating parameters for these methods (Figure 1). The preliminary characterization results will be used to determine the type and number of catalyst samples that will be investigated along with the specific characterization techniques that will be applied in Q4 of FY18 in order to provide the most impactful outcome.

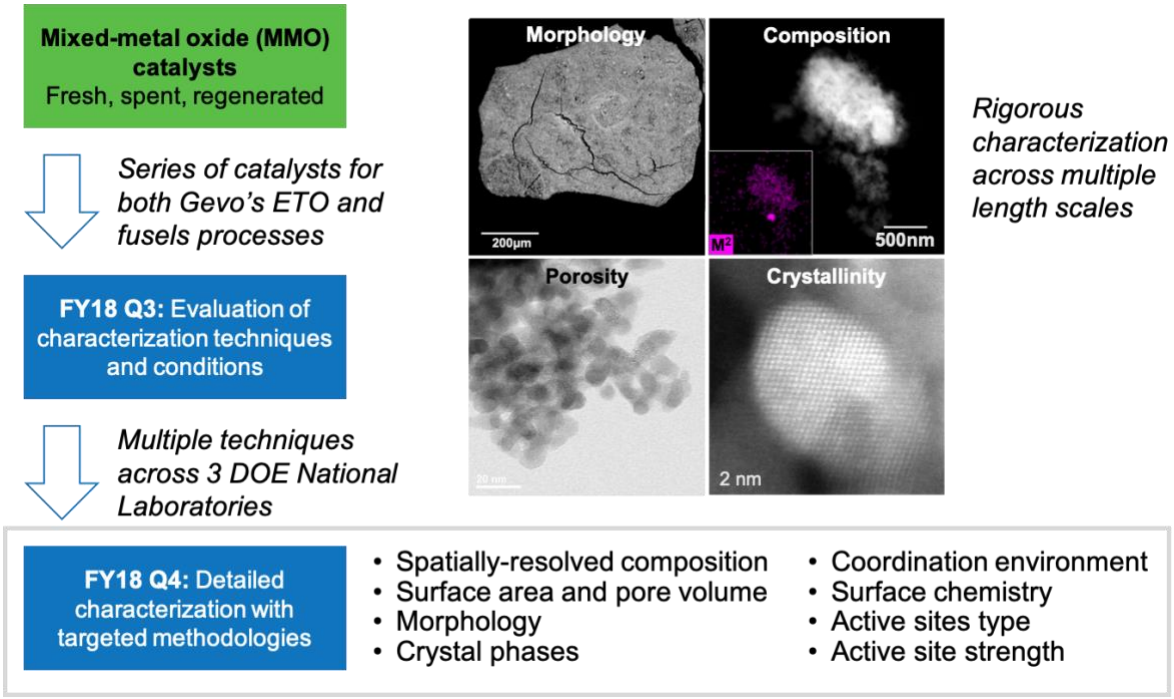


Figure 1. In-depth characterization of MMO catalysts led to the identification of characterization techniques and conditions that provide fundamental insight into MMO catalysts.

At NREL, a series of characterization experiments was initiated on the six catalyst materials. These experiments included N_2 physisorption to quantify surface area and pore volume, thermogravimetric analysis coupled with Fourier transform infrared spectroscopy (TGA-FTIR) to quantify carbon deposition on the spent catalyst and the efficacy of the regeneration procedure, H_2-temperature programmed reduction (TPR) to provide information about the chemical state/environment of the catalyst species, NH_3-temperature programmed desorption

(TPD) to measure catalyst acidity, CO_2-TPD to measure basicity, and pyridine-diffuse reflectance infrared Fourier transform spectroscopy to determine the relative ratio of Brønsted and Lewis acid sites. At ORNL, the 3 fusel catalyst samples (fresh, spent and regenerated) were characterized using light optical microscopy (LOM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) X-ray photoelectron spectroscopy, powder X-ray diffraction (XRD), and scanning transmission electron microscopy (STEM). At ANL, XRD was performed to establish the appropriate conditions for high-energy (HE-XRD) experiments to be conducted in Q4.

Phase 1 Task 2: In-depth characterization of MMO catalysts

We have successfully completed the FY18 Q4 Quarterly Progress Measure entitled "In-depth characterization of MMO catalysts" by performing in-depth characterization of seven mixed metal oxide (MMO) catalysts selected during Q1 and provided by Gevo in at least 1 g quantities. The MMO catalysts included fresh, spent, and regenerated samples from Gevo's ethanol to olefins (ETO) process and mixed alcohols (fusel oil) to ketones (fusel) process. Characterization techniques and methodologies identified and developed during Q3 were applied during Q4 to provide insight into how the structure of the MMO catalysts evolves during pre-treatment, reaction, and regeneration (Figure 2). This information will be correlated with performance data from Gevo in Q1 of FY19 to identify specific catalyst features that are responsible for observed selectivities and changes that occur as the catalyst undergoes deactivation.

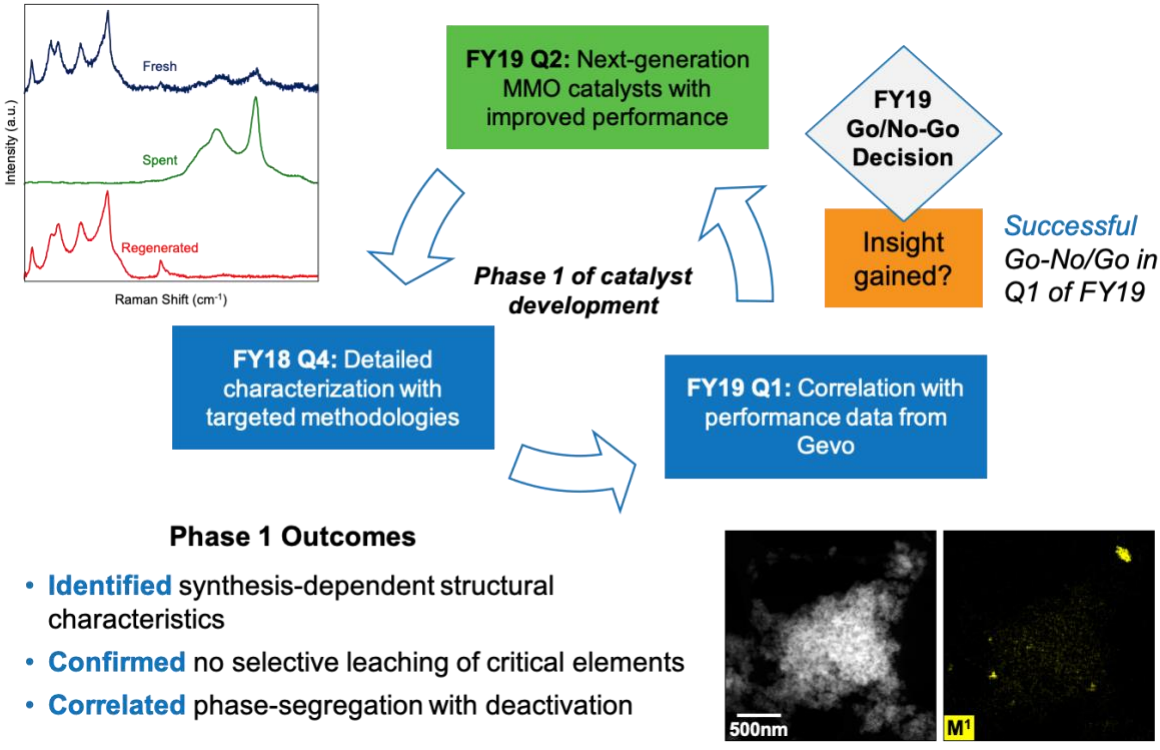


Figure 2. In-depth characterization of MMO catalysts provided detailed understanding of catalyst deactivation modes.

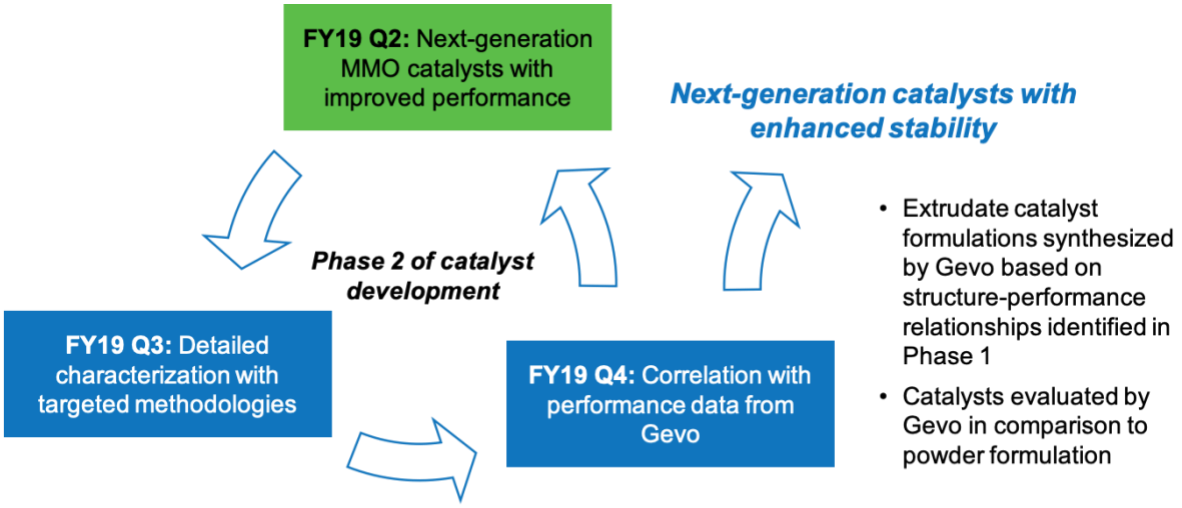
At NREL, the following characterization was performed. Inductively coupled plasma optical emission spectroscopy and combustion analysis to determine the overall elemental composition of the catalysts, thermogravimetric analysis coupled with Fourier transform infrared spectroscopy to quantify carbon deposition on the spent catalyst and the efficacy of the regeneration procedure, N_2 physisorption to quantify surface area and pore volume, H_2-temperature programmed reduction to provide information about the chemical state/environment of the catalyst species, NH_3-temperature programmed desorption (TPD) to measure catalyst acidity, CO_2-TPD to measure basicity, and pyridine-diffuse reflectance infrared Fourier transform spectroscopy to determine the relative ratio of Brønsted and Lewis acid sites. At ORNL, the following characterization was performed. X-ray photoelectron spectroscopy to quantify the elemental composition of the catalysts with spatial resolution, X-ray diffraction to provide insight into crystalline structure and composition, scanning electron microscopy to provide overall catalyst particle morphology, and scanning transmission electron microscopy with high angle annular dark field imaging to provide high resolution structural information and energy dispersive X-ray spectroscopy and electron energy loss spectroscopy to map the elemental composition throughout different regions of the catalyst. At ANL solid-state nuclear magnetic resonance spectroscopy was performed to better understand the coordination environment for key species.

Phase 1 Task 3: Identification of deactivation modes

We have successfully completed the FY19 Q1 Quarterly Progress Measure entitled "Identification of deactivation modes" by correlating the results of advanced characterization performed during Q3 and Q4 of FY18 with performance data from Gevo in order to identify specific catalyst features that are responsible for observed selectivities and changes that occur as the catalyst undergoes deactivation (Figure 2). The mixed-metal oxide (MMO) catalysts investigated included fresh, spent, and regenerated samples from Gevo's ethanol to olefins (ETO) process and mixed alcohols (fusel oil) to ketones (fusel) process. The primary differences found between the fresh, spent, and regenerated ETO and fusels catalysts included synthesis-dependent structural characteristics, no selective leaching of critical elements, and phase-segregation that was correlated with deactivation.

Phase 2 Task 1: Synthesis, evaluation, and preliminary characterization of MMO catalysts

The FY19 Q2 Quarterly Progress Measure *Synthesis and evaluation of technical catalyst formulations* was successfully met by synthesizing two technical (extrudate) catalyst formulations selected on the basis of structure-performance relationships identified in Q1 of FY19 for research (powder) catalyst formulations. The new catalysts were evaluated by Gevo to understand the impact of translating research catalysts to technical catalysts on performance, and catalytic activities within 20% of each other were achieved for the research and technical catalysts (Figure 3). Preliminary characterization included determination of the catalyst compositions.



Nominal catalyst composition and performance

Catalyst	Metal 1 (wt%)	Metal 2 (wt%)	Conversion (mol%)	Selectivity (mol%)	Yield (mol%)
Powder	2.7	3.5	40	70	28
Extrudate_1	2.7	3.5	30	80	24
Extrudate_1	2.2	3.0	30	75	23

Figure 3: Next generation catalysts developed by Gevo based on insight from advanced characterization demonstrated catalytic activities of powder and extrudate for fusels process within 20% of one another.

Phase 2 Task 2: In-depth characterization of MMO catalysts

The FY19 Q3 Quarterly Progress Measure *In-depth characterization of next-generation MMO catalysts* was successfully met by utilizing techniques and methodologies identified during FY18 Q1 to characterize next-generation catalyst formulations synthesized by Gevo during FY19 Q1 to determine the impact of catalyst modifications on stability (Figure 4). The catalysts were characterized by the following techniques. Inductively coupled plasma optical emission spectroscopy (ICP-OES) at NREL to determine the overall elemental composition of the catalysts, NH_3-temperature programmed desorption (TPD) at NREL to measure changes in acidic active sites, scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) at ORNL to map the elemental composition throughout different regions of the catalyst, X-ray photoelectron spectroscopy (XPS) at ORNL to quantify the elemental composition of the catalysts with spatial resolution, high-resolution X-ray diffraction (XRD) at ANL to provide more detailed insight into the crystalline structure and composition of the catalysts, solid-state magic angle spinning-nuclear magnetic resonance (MAS-NMR) spectroscopy at ANL to better understand the coordination environment, and Raman spectroscopy at ANL to identify subtle differences in crystalline structure as well as the presence and removal of carbonaceous species.

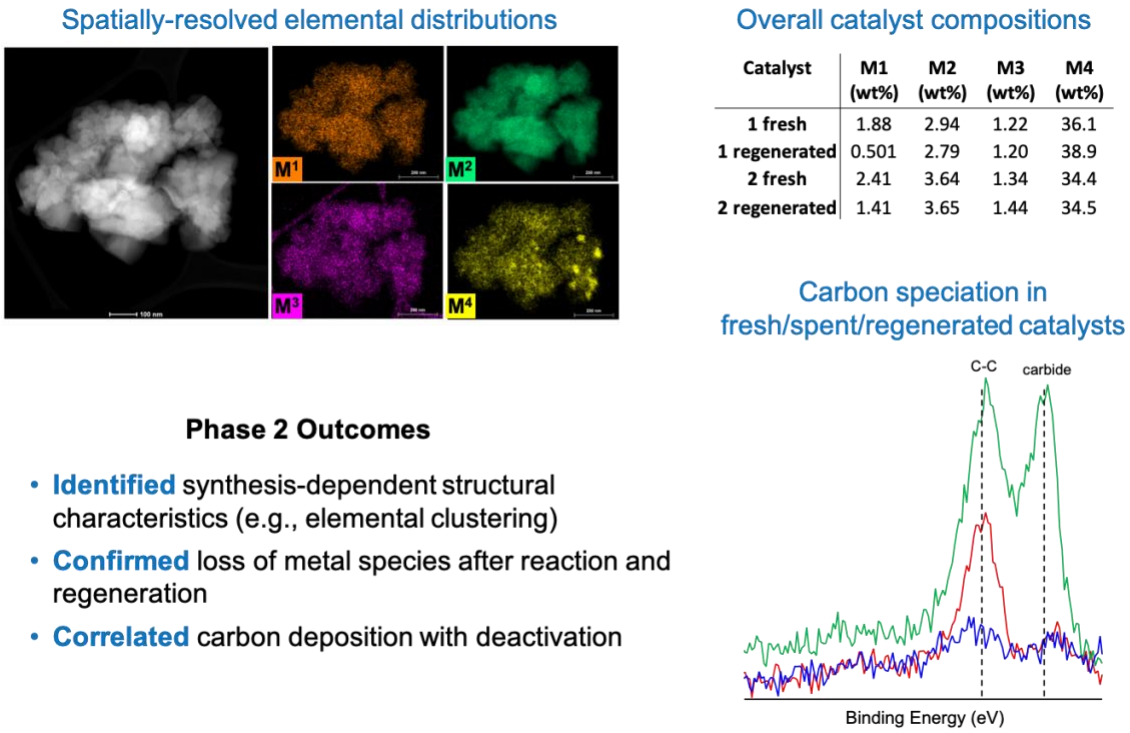


Figure 4. In-depth characterization of next-generation MMO catalysts provided detailed insight into modes of deactivation.

Phase 2 Task 3: Identification of deactivation modes

The FY19 Q4 Quarterly Progress Measure *Feasibility of next-generation catalyst formulations* was successfully met by completing a preliminary technical feasibility assessment of next-generation mixed-metal oxide (MMO) catalyst formulations. To conduct this assessment, we built on the insight gained from in-depth characterization studies performed during Q3 and performed further characterization of the stability of Gevo's MMO catalysts this quarter (Figure 4). It was determined through analysis of the compiled performance and characterization data that Gevo's research (powdered) catalysts could be successfully translated to formed technical catalysts (extrudates) while maintaining targeted performance metrics to within 20%. Further, it is clear that the regeneration protocols that have been developed are suitable for the removal of carbon deposits without damaging the morphological properties of the MMO catalysts. In addition, this feasibility study highlights the potential importance of tracking the restructuring and leaching of critical dopant elements on the large-scale feasibility of the fusel process. This comprehensive technical feasibility data set was supplied to Gevo for incorporation into their technoeconomic analysis. The combination of thorough catalyst characterization with stability information obtained from the analysis of regenerated and end-of-life MMO catalysts can now be used by Gevo to determine the technical and economic feasibility of utilizing their next-generation MMO catalysts for the selective conversion of oxygenates to hydrocarbon fuels.

Subject Inventions Listing:

None

ROI #:

None