

DOE Bioenergy Technologies Office (BETO) 2021 Project Peer Review

2.5.4.501 Catalyst Deactivation Mitigation for Biomass Conversion

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Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

BIOENERGY TECHNOLOGIES OFFICE



Project Overview - Our Goal is to Address Catalyst Deactivation Challenge

Project Goal: Provide fundamental insight and actionable recommendations for *extending catalyst lifetime* in biomass catalytic conversion by a collective and collaborative effort within ChemCatBio.

Outcome: Accelerated catalyst and process development with:

- *Knowledge on* overarching catalyst deactivation issues;
- Catalyst with extended lifetime;
- Tool/method to understand deactivation and faster evaluate stability.



ChemCatBio is accelerating the catalyst and process development cycle.

Relevance:

- Enable **cost and risk reductions** of catalysis processes for BETO conversion technologies
- Fulfill the need of emphasis on the catalyst stability in catalysis and biomass conversion R&D

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Project Overview - Catalyst Stability is Key to Commercial Viability

- Catalyst stability/lifetime plays a critical role in process economics.
- A systemic need within ChemCatBio to address catalyst deactivation issues.
- Our catalysis R&D communities are • calling for a focus on catalyst stability.



J. Catal. 2019. 369. 518

1. Feedstock 50% Pine & 50% Residues in \$/dry US ton (60 : 70.15 : 80)	-5.6%
2. Fuel Yield % Change from Base Case (+5% : base case : -5%)	-4.8%
3. Online:Regen Reactors Ratio (2:1:2:2:2:4)	-1.8%
4. Coproduct Separation and Recovery (95% : 90% : 75%)	-1.1%
5. Ex Situ Catalyst Lifetime in Years (2 : 2 : 1)	0.
6. Coproduct Value as % of 5-Year Market Average (100% : 90% : 80%)	-1.9%
7. Refinery Co-Hydrotreating Cost (-25% : base case : +25%)	-1.7%
-8	

% Change to MFSP from the *ex situ* CFP base case (\$3.09/GGE) CFP: catalytic fast pyrolysis; MFSP: minimum fuel selling price; GGE: Gasoline gallon equivalent



A Matter of Life(time) and Death

THE CATECHISM

The three "virtues" of catalyst performance are activity, selectivity, and productivity (the last of these being related to catalyst lifetime). In Murzin's textbook "Engineering Catalysis",¹ they are called the "trinity of catalysis". Activity is usually the metric of highest interest to academic researchers (although in practice it is often straightforward to compensate for low activity simply by increasing the amount of catalyst in

supported catalyst may not even be noticed if the molecular fragments also catalyze the desired reaction, and they may reattach to the catalyst when it is isolated at the end of a run. The environment plays a crucial role in catalyst stability. Thus, transformations in an inert atmosphere, in the absence of reactants and/or electrical potential, or without crucial components of the feed such as water, can be very different from those that occur under realistic reaction conditions."

ACS Catal. 2018. 8. 8597

Biomass derived feedstocks bring new challenges to catalyst longevity.

ChemCatBio





pubs.acs.org/acscatalysis



Project Overview - We Leverage our Previous Success



Previously encountered challenges and successful outcomes identified a need for a more collective and collaborative effort within ChemCatBio for a systematic study of catalyst deactivation.

ChemCatBio

1 - Management – ChemCatBio Foundation – FY21

Catalytic Technologies	Enabling Capabilities	In
Catalytic Upgrading of Biochemical	Advanced Catalyst Synthesis and	
Intermediates (CUBI)	Characterization (ACSC)	
(NREL, PNNL, ORNL, LANL)	(NREL, ANL, ORNL)	
Upgrading of C1 Building Blocks	Consortium for Computational	
(NREL)	Physics and Chemistry (CCPC)	
Upgrading of C2 Intermediates	(ORNL, NREL, PNNL, ANL, NETL)	
(PNNL, ORNL)	Catalyst Deactivation Mitigation	
Catalytic Fast Pyrolysis (CFP) (NREL, PNNL)	for Biomass Conversion (CDM) (PNNL)	
Electrocatalytic CO ₂ Utilization		

Cross-Cutting Support

ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)

dustry Partnerships (Phase II Directed Funding)

Opus12 (NREL)

Visolis (PNNL)

Sironix (LANL)

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1 - Management - CDM is an Enabling Capability



CUBI: Catalytic Upgrading of Biochemical Intermediates; CFP: Catalytic Fast Pyrolysis;

C2 upgrading: Upgrading of C2 Intermediates; C1 upgrading: Upgrading of C1 Building Blocks **ChemCatBio**

PNNL's Basic Energy

1 - Management - Close Communication with ChemCatBio Catalysis Team



Risk Mitigation and Success Factor:

Ensure being relevant and valuable to catalysis technology developers.

ChemCatBio

- Frequent task meeting with

2 - Approach – Targeting the Most Impactful Challenges and Supporting ChemCatBio

- **Identifying** deactivation problems •
 - catalysis project, CDM
- **Determine** deactivation mechanism
 - CDM, catalysis project, ACSC, CCPC
- **Develop** mitigation approach
 - CDM, catalysis project
- **Verify** performance improvements •
 - catalysis project

Improve catalyst lifetime for specific technologies

- Ag/ZrO₂/SiO₂ for ethanol to butenes (with C2 upgrading project)
- *Pt/TiO*₂ for CFP (with CFP project) •
- Removing barriers and extending catalyst lifetime
- Cost/risk reduction

Address grand catalyst stability challenges

- Impact of inorganics
- Impact of water (steam and overheated liquid)
- Fast coke formation
- Overarching issues with broad impact
- Based on a survey within ChemCatBio on grand catalyst deactivation challenges

Risk Mitigation and Success Factor:

Tackle the most impactful catalyst stability challenges and balance overarching challenges with specific needs of catalysis projects.

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2 - Approach - Combing Multiple Technologies and Unique Capabilities

- **Identifying** deactivation problems •
 - catalysis project, CDM
- **Determine** deactivation mechanism
 - CDM, catalysis project, ACSC, CCPC
- **Develop** mitigation approach ullet
 - CDM, catalysis project
- **Verify** performance improvements
 - catalysis project



- Atomic level description of spent catalyst change
- Structure-performance correlation on catalyst deactivation

Risk Mitigation and Success Factor:

Multiple technologies to ensure rigorous deactivation mechanism determination.

ChemCatBio

Kinetic Measurement

2 - Approach - Providing Mitigation Strategies

- **Identifying** deactivation problems •
 - catalysis project, CDM
- **Determine** deactivation mechanism
 - CDM, catalysis project, ACSC, CCPC
- **Develop** mitigation approach •
 - CDM, catalysis project
- **Verify** performance improvements
 - catalysis project

Catalyst lifetime improvement toolbox

- Catalyst Regeneration
 - Oxidation/reduction
 - Solvent cleaning (e.g. K removal for Pt/TiO₂ for CFP)
- Catalyst Improvement
 - More robust components (e.g. next generation catalyst to replace $Ag/TiO_2/SiO_2$ for ethanol upgrading)
- ✓ Process Improvement
 - Feedstock pretreatment (Coordinate with FCIC (feedstock) and Separation Consortium (separation))
 - Guard bed
- Provide actionable recommendations.
- Performance verified by catalysis projects. \bullet
- Guided by economic assessment.

Risk Mitigation and Success Factor:

A coordinated approach to mitigate deactivation with economic assessment guidance.

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2 - Approach - Major Deliverables Scheduled



Completed Go/No-Go:

Elucidated that this project provided value with two examples, demonstrating:

- Enhanced understanding of catalyst deactivation mechanism and developed mitigation approach, leading to
- Quantitative catalyst stability improvement (>15% reduction of deactivation rate or >80% activity recovery by regeneration). (See more details in slide 27)

All milestones are joint with catalysis and enabling projects.



3 - Impact – Significant Catalyst Lifetime Improvement

Enhance the ChemCatBio portfolio

- "Catalyst deactivation is one of the major challenges and its mitigation is one critical component for ChemCatBio" – according to the ChemCatBio Industrial Advisory Board
- De-risking the technology and reducing of cost for the conversion.



- **Leverage** existing applied and fundamental research efforts and industrial supports.
- Support BETO to address barriers and achieve targets (Ct-E. Improving Catalyst Lifetime).

3 - Impact - Provides Demanding Information on Catalysis

- Provide knowledge to industry and catalysis R&D **communities** for rational design of more stable catalysts via:
 - A BETO webinar
 - A review document drafted ullet
 - Publications (three published and two in preparation) and presentations (four presentations)
 - Input to ChemCatBio DataHub ullet
- A focus on catalyst stability within ChemCatBio
 - Most of projects involve catalyst stability milestone(s)
 - Task teams to address grand catalyst stability challenges with extensive collaboration among enabling capabilities

ChemCatChem





"Since such studies (catalyst deactivation) are currently under-presented in the catalysis literature, our science will advance, and our community will benefit from increased emphasis on the productivity (catalyst stability) metric." Susannah L. Scott, Associate Editor, ACS Catalysis ACS Catal. 2018, 8, 8597

4 - Progress and Outcomes -

Addressing Grand Challenges and Supporting ChemCatBio Projects

Progress

Outcomes

Improve Catalyst Lifetime for Specific Technologies

 Enhanced understanding of the deactivation of the Ag-ZrO₂/SiO₂ catalyst for ethanol-to-butene conversion. Characterization along 800 hours' TOS testing Identified three major causes of deactivation Identified the impact of actual feed 	 Based in large part on the dead the C2 Upgrading team succes next-generation catalyst that stability and process econom
 Enhanced understanding of the deactivation of the Pt/TiO₂ catalyst for CFP. Identified three major deactivation modes 	 Further action suggested to stude deactivation modes and explored
Address Gra	and Challenge
Determined the impact of inorganics (K) on different type of active sites and developed regeneration method for K removal.	 The most completed understant to be leveraged by other tech their catalyst/process stability. Regeneration method to remeted

ctivation mechanisms, sfully developed a has much-improved ny.

idy the three e mitigation approach.

iding of the impact K nologies to improve

ove >90% K.

4 - Progress and Outcomes -Supporting ChemCatBio Projects - C2 Upgrading



 Identified additional deactivation with actual fermentation derived feed.

In collaboration with C2 upgrading project (2.3.1.304)

Outcome: Deactivation mechanism identified and the guided catalyst modification leading to stability improvement.

ChemCatChem, 2020, doi.org/10.1002/cctc.202001488

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4 - Progress and Outcomes - Supporting ChemCatBio Projects - CFP

Objective: Determine potential deactivation of CFP catalyst in long-term operation









Uniform distribution of K across catalyst surface with higher content on the leading edge



Outcome: Deactivation mode identified, and further actions suggested to understand the deactivation and improve the catalyst.

In collaboration with CFP project (2.3.1.314) and ACSC (2.5.4.303/304/305)

ChemCatBio

4 - Progress and Outcomes -**Addressing Grand Challenges - Inorganic Contamination**

Objective: How to distinguish impact of K on individual active sites of multifunction catalyst?

K distribution

Actual Model

Model catalysts mimic real spent ones with better controlled uniformity

Dehydration and C-C coupling to probe acid-base sites HDO and CO oxidation to probe metal sites 70 °C, Pco = 1 kPa, Po, = 4 kPa ŬO 2 4000 2000 400 K loading (pp)

Physical and chemical properties



Kinetically distinguish different active sites at increased K coverage

> **Outcome:** Established structureperformance correlation and precise

In collaboration with CFP project (2.3.1.314), ACSC (2.5.4.303/304/305) and CCPC (2.5.1.301-307) **ChemCatBio**





Change of acid-base and metallic sites along increased K coverage

Theory



description of the atomic level interaction of K with each active site of the catalyst.

4 - Progress and Outcomes -**Addressing Grand Challenges - Inorganic Contamination**



Objective: Understand the deactivation mechanism by K deposition

- K first titrates strong Lewis acid sites, then weak acid sites and Pt-TiO₂ interfacial sites
- K does not poison metal surface but can induce redispersion to single atom (negligible in Pt/TiO_2 case)
- K could generate (strong) base sites
- K could titrate Bronsted acid site by ion exchange (literature)
- Predict impact of K at a longer time on stream
- Can be expanded to similar catalyst systems

Outcome: A completed understanding of the impact K to be leveraged by other catalyst systems.

4 - Progress and Outcomes -**Addressing Grand Challenges - Inorganic Contamination**

Objective: Mitigate the deactivation from K deposition

- Solvent washing method identified, and impact of solvent studied
- Simple method for straightforward practical implementation



Outcome: Regeneration method to remove >90% K and extend catalyst lifetime.

4 – Progress and Outcomes Lead to Future Works – Continue Addressing Grand Challenges and Supporting ChemCatBio Projects



FY21-22

- Continue addressing the grand challenges

 - and CCPC)
- Continue supporting ChemCatBio projects
- knowledge

Beyond FY21-22

- Develop **accelerated testing** for faster catalyst stability evaluation and more rational catalyst lifetime prediction.
- More rigorously understanding deactivation by **probing deactivation** *in situ* by combing ۲ transient kinetics and operando spectroscopy.

ChemCatBio

– Extend to **other inorganics**

- Impact of water (overheated steam and hot liquid water; in collaboration with C2 upgrading, CUBI, ACSC,

• Develop a **database** on catalyst deactivation as part of central hub of

Summary – **Our Goal is to Address Catalyst Deactivation Challenge**

Management	 Close communication with ChemCatBio catalysis team Targeting the most impactful challenges and supporting ChemCatBio Addressing grand catalyst deactivation challenges (inorganics and water) Improve catalyst lifetime for specific technologies (C2 upgrading and CFP pro-
Approach	 Integrated and collaborative effort within ChemCatBio Combing multiple technologies to understand deactivation mechanism Providing actionable recommendations and developing regeneration method to add
Impact	 Catalyst lifetime improvement - Cost and risk reductions of conversion technolog Provide demanding knowledge for rational design of more stable catalysts
Progress and Outcomes	 Addressing grand catalyst deactivation challenge Determined the impact of inorganics (K) on different type of active sites Developed regeneration method for K removal Improve catalyst lifetime for ChemCatBio projects Understand deactivation of Pt/TiO₂ for Catalytic fast pyrolysis Understand deactivation of Ag/ZrO₂/SiO₂ for ethanol upgrading, leading to in
Future	 Addressing grand catalyst deactivation challenge – water (overheated steam and Improve catalyst lifetime for ChemCatBio projects Knowledge and tools

ojects)

dress deactivation

jies

nproved catalysts

hot liquid water)

Quad Chart Overview

Timeline

- Project start date: 10/1/2019 ٠
- Project end date: 9/30/2022

	FY20	Active Project
DOE Funding	\$300,000	\$900,000 (FY20-22)

Barriers Addressed

Ct-E. Improving Catalyst Lifetime

- Understanding causes of catalyst deactivation
- Develop improved catalyst regeneration

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

Project Goal

Address the catalyst deactivation challenges in catalytic processes for biomass conversion to enable catalyst lifetime improvement for cost and technology uncertainty reduction of biomass conversion technologies and to enable accelerated catalyst and process development.

End of Project Milestone

Assist at least two CCB catalytic process to understand their catalyst deactivation mechanism and develop/propose mitigation approach (such as catalyst regeneration) which leads to reduction of deactivation rate and/or prediction of long-term stability and/or recovery of catalyst activity.

Funding Mechanism ChemCatBio Merit Review AOP for FY20-22

Acknowledgement

- PNNL: Fan Lin, Yilin Wang, Robert Dagle, Vanessa Dagle, Austin Winkelman, Mark Engelhard, Libor Kovarik, Yong Wang, Karthi Ramasamy, Yubing Lu, Asanga Padmaperuma
- NREL: Susan Habas, Mike Griffin, Josh Schaidle, Matt Yung, Carrie Farberow, Sean Tacey
- ANL: Kinga Unocic, Evan Wegener, Theodore Krause
- ORNL: Zhenglong Li, Junyan Zhang
- **BETO**: Andrea Bailey, Trevor Smith, Nichole Fitzgerald, Sonia Hammache

Thank you!







Additional Slides







Acronyms and abbreviations

ACSC	Advanced Catalyst Synthesis and Characterization project
ВЕТО	Bioenergy Technologies Office
C2 upgrading	Catalytic Upgrading of C2 Intermediates project
ChemCatBio	Chemical Catalysis for Bioenergy Consortium; ChemCatBio consortium
ССМ	Catalyst Cost Model project
CCPC	Consortium for Computational Physics and Chemistry project
CDM	Catalyst Deactivation Mitigation for Biomass Conversion project
CFP	Catalytic Fast Pyrolysis project
CUBI	Catalytic Upgrading of Biochemical Intermediates project
FCIC	Feedstock-Conversion Interface Consortium
HDO	Hydrodeoxygenation
IAB	Industrial Advisory Board
PNNL	Pacific Northwest National Laboratory
TOS	Time on stream



Responses to Previous Reviewers' Comments

Comments: This overarching project, along with the theory program, can be a broad but impactful component of ChemCatBio. This project has the potential of becoming an entire center of excellence focused on deactivation of catalysts in bioenergy applications. This is an important project that aims to address catalyst stability in a variety of biomassupgrading technologies. The goal of the project—to improve catalyst stability (lifetime) for ChemCatBio catalysis projects through understanding catalyst deactivation and developing mitigation approaches—is surely relevant for the core work of the consortium

Response: We thank the reviewers for their support of this project. This support enables the overall ChemCatBio program and mission to increase the fundamental understanding of catalyst deactivation mitigation for the scientific community. We agree with the importance of dealing with the deactivation "head on" in a systematic, rigorous, and comprehensive fashion, which is what this project attempts to do.

Comments: It would be helpful to see more specifics about the important modes of deactivation in a specific technology, how they will be investigated, how they will be mitigated, etc. It would be interesting to see more solid and articulated ideas on how to provide stability on the more complicated systems being studied in this consortium, such as the multifunctional systems. It would have benefited from a better discussion of the hypothesis involving catalyst deactivation being studied and the approaches.

Response: We have provided specifics about the hypothesis for modes of deactivation, the approach to investigate and mitigate them, and the clear targets in this presentation. As presented here, we combine various approaches to develop a rigorous deactivation mechanism for the complicated catalyst systems actionable recommendation and regeneration methods to enhance catalyst stability.

Comments: It seemed like more homework could have been done by the authors of the proposed work to identify the needs of the consortium, instead of making one of the tasks to find out what the needs are. Building on and augmenting prior studies is key and something that should be monitored carefully to make sure these deactivation studies do not "reinvent the wheel".

Response: We are working closely with ChemCatBio catalysis teams to make sure we are meeting their target and relevant to their research needs. We identified specific technologies to support and extend their catalyst lifetime. All the technologies are unique and require deactivation mitigation to reduce cost and remove barriers. This project is also tackling overarching challenges to benefit research communities with greater impact.

FY2020 Go/No Go

Go/No-Go Description and Criteria

Elucidate that this project provided value to the core catalysis projects. The outcome of the go/no-go decision will identify areas for improvement and/or tasks that should be integrated with or removed from the project.

The value of this project will be evaluated based on one of the following criteria: 1) demonstrating the **enhanced understanding of** catalyst deactivation for a catalytic process that leads to proposing mitigation strategies that can reduce the deactivation rate by 15% and/or prediction of long-term stability of the catalyst used; or 2) developing a mitigation approach that could recover at least 80% of catalyst activity by regeneration or could increase the catalyst lifetime by at least 20%.

Accomplishment

In working with the C2 Upgrading project, we enhanced understanding of the deactivation of the incumbent catalyst system developed at PNNL for one-step ethanol-to-butene conversion. Based in large part on the deactivation mechanisms identified in this work, the C2 Upgrading experimental team successfully improved the catalyst formulation and developed a next-generation catalyst that has muchimproved stability. The newly developed catalyst showed a much slower deactivation (~6% decrease in ethanol conversion over ~80 hours' time-on-stream) than Ag-ZrO₂/SBA-16 (\sim 25% decrease in ethanol conversion over \sim 80 hours' time-on-stream).

Working with NREL's CFP Project, we provided enhanced understanding of deactivation of the Pt/TiO₂ catalyst, especially related to the impact of potassium (K) accumulation on Pt/TiO₂. We developed a regeneration method to remove K and demonstrate significant active recovery over a model system (>90% K removal, >95% recovery of hydrodeoxygenation activity for its metallic function and >75% recovery of dehydration activity for its acidic function).

Based on the accomplishments listed above, we conclude that this CDM project is providing significant value to the core catalysis project of the ChemCatBio consortium, and our recommendation is to proceed with current tasks and scopes as described in the AOP.

Publications and Presentations

Peer Reviewed Journal Article and Book Chapter

- F Lin, V.L. Dagle, A.D. Winkelman, M. Engelhard, L. Kovarik, Y. Wang, Y. Wang, R. Dagle, H. Wang, Understanding the Deactivation of Ag-ZrO₂/SiO₂ Catalysts for the Single-Step Conversion of Ethanol to Butenes, ChemCatChem, 2020, doi.org/10.1002/cctc.202001488
- F. A. Agblevor, H. Wang, S. Beis, K. Christian, A. Slade, O. Hietsoi, and D. M. Santosa, **Reformulated Red Mud: a Robust Catalyst** for In Situ Catalytic Pyrolysis of Biomass, Energy Fuels, 2020, 34, 3, 3272–3283
- H. Shi, K. Ramasamy, R. Ma, H. Wang, Nanoporous Catalysts for Biomass Conversion, in "Nanoporous Materials for Molecule Separation and Conversion", edited by Jian Liu and Frank Ding, Elsevier, Chapter 12, 2020.
- F. Lin, Y. Lu, K. Unocic, S. Habas, M. Griffin, J. Schaidle, Y. Wang, H. Wang, Deactivation by Potassium Accumulation of Pt/TiO₂ **Bifunctional Catalyst for Biomass Catalytic Fast Pyrolysis**, in preparation for ACS Catalysis.
- F. Lin, M. Xu, K. Ramasamy, Z. Li, J. Schaidle, H. Wang, Catalyst Deactivation and its Mitigation during Catalytic Conversions of **Biomass**, in preparation for Chemical Society Reviews.

Presentation

- H. Wang, Catalyst Deactivation Mitigation in Biomass Conversion: Connections and Zeolite Stability in Water, 2019, ACS Spring Meeting, Orlando, invited oral presentation.
- F. Lin, H. Wang, Deactivation of Pt/TiO₂ Catalyst for Biomass ex situ Catalytic Fast Pyrolysis by Potassium Accumulation, 2020, accepted for presentation at ICC-2020
- F. Lin, H. Wang, Deactivation of Pt/TiO₂ Catalyst for Biomass ex situ Catalytic Fast Pyrolysis by Potassium Accumulation, 2020, Oral presentation at TCS-2020 virtual meeting.
- H. Wang, Addressing Unique Catalyst Deactivation Challenges for Converting Biomass-Derived Feedstocks, 2020, ChemCatBio Webinar