2.5.4.501 Catalyst Deactivation Mitigation for Biomass Conversion

Technology Area Session: Catalytic Upgrading

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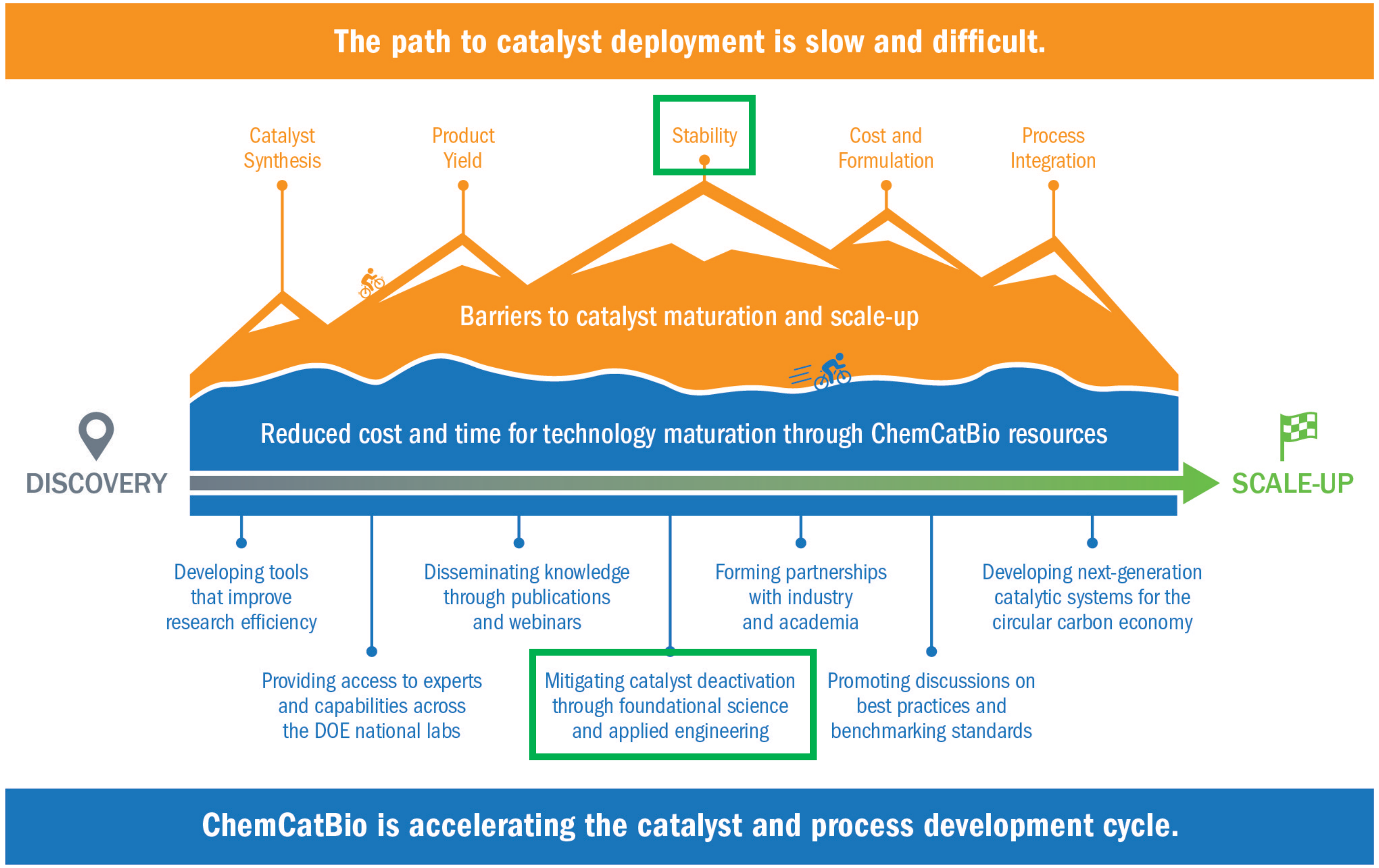
April 07, 2023

Project Overview - Our goal is to address catalyst deactivation challenge

Project Goal: Provide foundational 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:

- ***Understanding** of* overarching catalyst deactivation issues;
- ***Catalysts with extended lifetime;***
- ***Tools/methods*** to understand deactivation and evaluate stability more quickly.

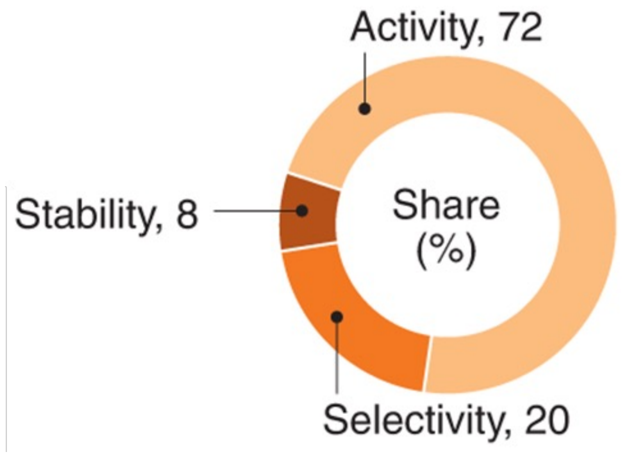


***Relevance*:**

- Enable **cost and risk reductions** of catalytic processes for BETO conversion technologies
- Fulfill gap for catalyst stability in catalysis and biomass conversion R&D (looking beyond activity and selectivity)
- **Avoid pitfalls during technology maturation** by increasing awareness about deactivation challenges in early-stage research

Project Overview - Stability must become a central consideration

- Activity, selectivity, and stability are the three "virtues" of catalyst performance. However, **stability** (or lifetime, directly related to productivity) **is the least explored**.
- Catalyst stability/lifetime plays a critical role in **process economics;** adoption requires confidence/demonstration of stability.
- Biomass-derived feedstocks, especially low-cost feedstocks, bring new and **unique challenges** to catalyst stability and process flexibility.



A small share of catalysis literature address stability

Nature Catalysis, *2022*, 5, 854

Biomass derived feedstocks are likely contaminated, highly functionalized, and contain water

Project Overview - Overarching catalyst deactivation challenges

Interwoven challenges affect catalyst durability in many biomass conversion pathways

How can ChemCatBio address these overarching challenges?

- ***Coke***: determine type, properties, distribution, removal (combustion kinetics)
- ***Contaminants***: determine distribution, interaction with active sites
  - Provide database on catalyst properties and interaction with contaminants
- ***Water***: determine interaction with catalyst, specificity to biomass feedstocks and conversion processes

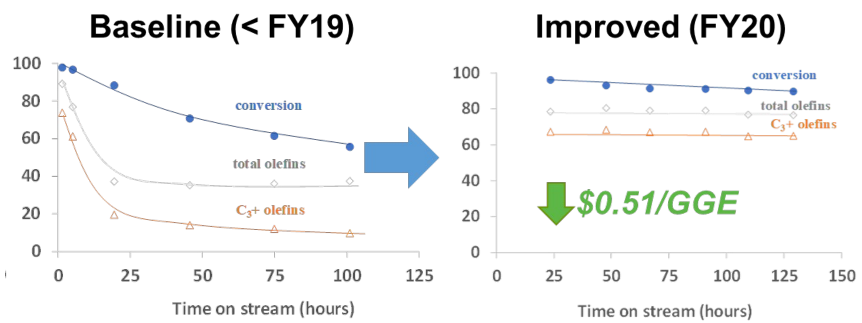
Project Overview - A unique component of *ChemCatBio* since FY19

- 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

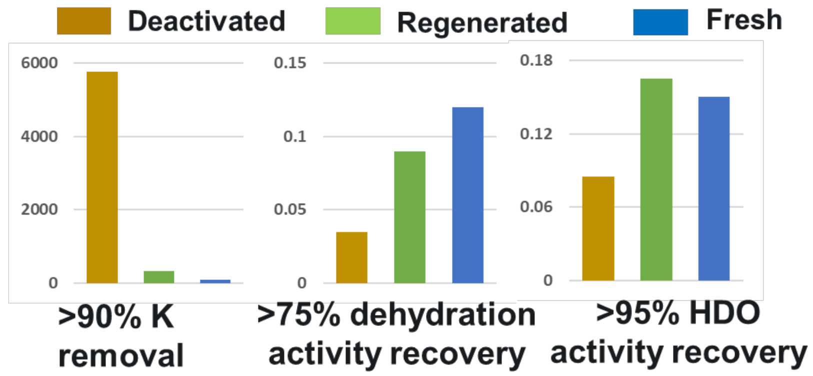
- Increased awareness of catalyst deactivation issues and a focus on catalyst stability within *ChemCatBio*

- FY19-20 work led to impactful outcomes:
  - Tackle overarching catalyst deactivation challenges: addressed the impact of inorganics
  - Support specific *ChemCatBio* catalysis technologies: improved catalyst lifetime for CFP and C2 upgrading projects

FY19-20 highlights



C2 upgrading: *next generation catalyst with much-improved stability and reduced cost*



CFP*: catalyst regeneration for K removal to recover activity*

C2 upgrading: Upgrading of C2 Intermediates; CFP: Catalytic Fast Pyrolysis

1. Approach - An Integrated and collaborative effort

***ChemCatBio* Catalysis Projects**

C2 Upgrading | CFP | CUBI | C1 upgrading | ...

Critical catalyst stability challenges

ChemCatBio **Industrial Advisory Board**

Enabling Capabilities

Adv. Characterization

ACSC

(Advanced Catalyst Synthesis and Characterization)

Catalyst Deactivation Mitigation

Poisoning species

DataHub

(Catalyst property database)

Theoretical Guidance

CCPC
Consortium for Computational Physics and Chemistry
U.S. DEPARTMENT OF ENERGY
BIOENERGY TECHNOLOGIES OFFICE

BIOPROCESSING SEPARATIONS CONSORTIUM

fcic
FEEDSTOCK-CONVERSION INTERFACE CONSORTIUM
U.S. DEPARTMENT OF ENERGY

PNNL's Basic Energy Sciences Program

Collaborative Outcomes

Catalyst Lifetime Improvement	Cost Reduction and Risk Reduction	Relevant Knowledge for Broader Audiences

Integrated and collaborative portfolio of enabling technologies to help tackle critical catalyst deactivation challenges

CUBI: Catalytic Upgrading of Biochemical Intermediates; CFP: Catalytic Fast Pyrolysis;
C2 upgrading: Upgrading of C2 Intermediates; C1 upgrading: Upgrading of C1 Building Blocks

1. Approach - Close communication with stakeholders

Inputs

BETO quarterly and weekly meetings

BETO Peer review

ChemCatBio Industry Advisor Board

ChemCatBio Steering Committee

***ChemCatBio* Catalysis Project teams**

Literature reviews

Project Structure

Outreach and Communication

Deactivation Mechanism Identification

Deactivation Mitigation Development

Project Management

- Joint milestones
- Go/No-Go decision
- Frequent task meeting with related projects
- Frequent update to *ChemCatBio* Steering Committee
- Annual *ChemCatBio* all hands meeting
- Webinars to public or with Industry Advisory Board

Risk Mitigation and Success Factor:
Ensure being relevant and valuable to catalysis technology developers.

1. Approach - Target most impactful challenges and supporting *ChemCatBio*

- **Identifying** deactivation problems
- **Determine** deactivation mechanism
- **Develop** mitigation approach
- **Verify** performance improvements

Catalyst deactivation mitigation for specific technologies

- $Cu/ZrO_2/SiO_2$ and Y/Beta for ethanol to butenes (with C2 upgrading project)
- Multiple catalysts for BDO conversion (with CUBI)
- Zeolite catalyst for CFP (with CFP)
- Cu/BEA catalyst for C1 conversion (with C1 upgrading project) ***New in FY23-25***

Address overarching catalyst stability challenges

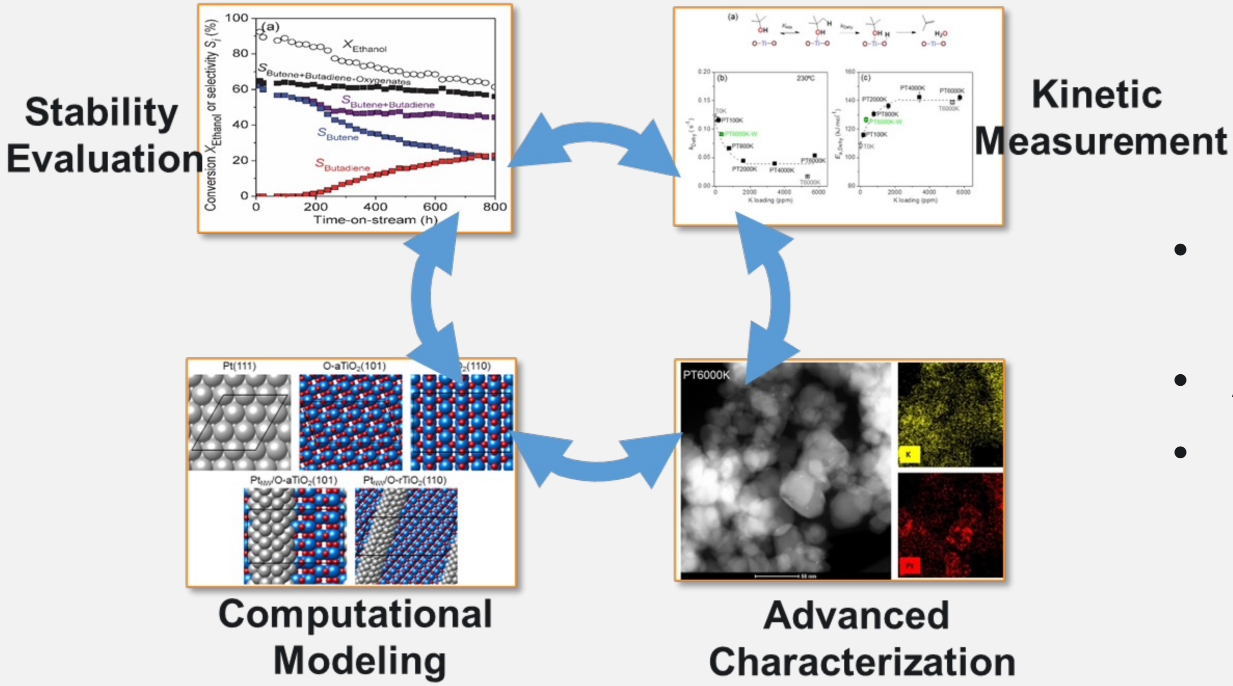
- Three interwoven challenges
  - Contaminants such as inorganics
  - Water (steam and overheated liquid)
  - Fast coke formation
- Stability of engineered catalysts ***New in FY23-25***
  - Change of deactivation mechanism from powder to engineered catalyst

Risk Mitigation and Success Factor:

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

1. Approach - Combine multiple approaches and unique capabilities

- **Identifying** deactivation problems
- **Determine** deactivation mechanism
- **Develop** mitigation approach
- **Verify** performance improvements



- Hypothesis-driven deactivation mechanism identification
- Atomic level description of spent catalyst change
- Structure-performance correlation on catalyst deactivation

Risk Mitigation and Success Factor:

Multiple methodologies to ensure rigorous deactivation mechanism determination.

1. Approach - Provide mitigation strategies

- **Identifying** deactivation problems
- **Determine** deactivation mechanism
- **Develop** mitigation approach
- **Verify** performance improvements

Catalyst Lifetime Improvement Toolbox

✓ Catalyst Regeneration
  - Oxidation/reduction
  - Solvent cleaning

✓ Catalyst Improvement
  - More robust components

✓ Process Improvement
  - Feedstock pretreatment (Coordinate with FCIC (feedstock) and Separation Consortium (separation))
  - Guard bed

- Provide actionable recommendations.
- Performance verified by catalysis projects.
- Guided by economic assessment.

Risk Mitigation and Success Factor:

A coordinated approach to mitigate deactivation with economic assessment guidance.

2. Progress and Outcomes - Support *ChemCatBio* and address overarching challenges

Support *ChemCatBio* projects

	FY 20-22	FY 23-25
CFP	Pt/TiO_2 deactivation and regen.	Zeolite coke combustion
CUBI	BDO catalyst deactivation	Stability in water
C2	Cu(Ag)-Zr/SiO_2 catalyst deactivation	Cu stabilization and coke mitigation
C1		Cu distribution and coke mitigation

Address overarching challenges

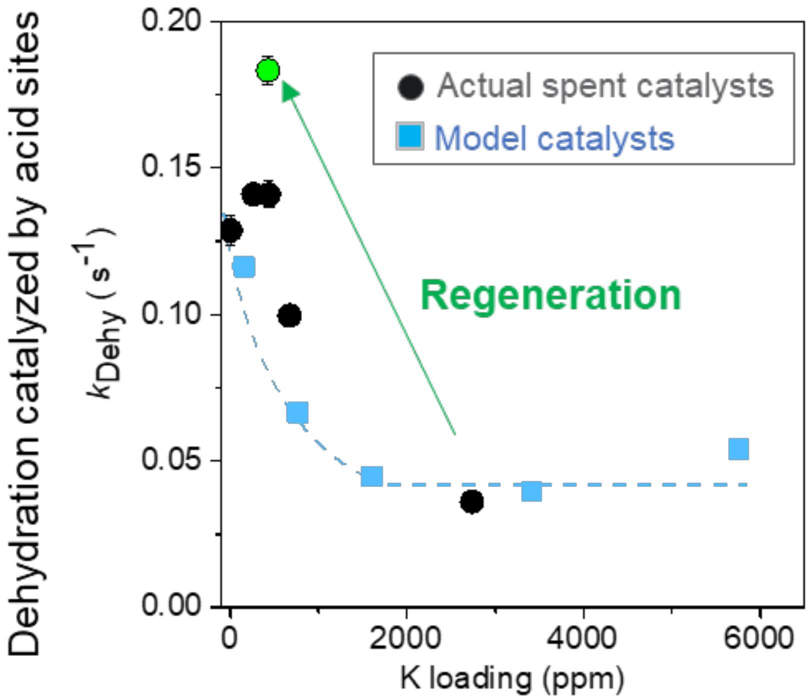
	FY 20-22	FY 23-25
Three interwoven deactivation challenges	Impact of inorganics (K)	
	Impact of water (three case studies)	Impact of water (three case studies)
	Impact of coke (combustion kinetics)	Impact of coke (combustion kinetics)
Stability of engineered catalysts		Deactivation mode change

Objective: Summarize deactivation modes for CFP catalyst and validate inorganic removal method

A comprehensive summary of deactivation modes of CFP catalyst

Mechanism	Timeline	Mitigation strategies	Impact of mitigation on deactivation rate

Inorganic poisoning	Sintering and redistribution of Pt	Carbon deposition	Phase change of TiO_2	Attrition of catalyst particles



A study of the real spent Pt/TiO_2 catalysts validates the impact of K and the regeneration developed based on the model system

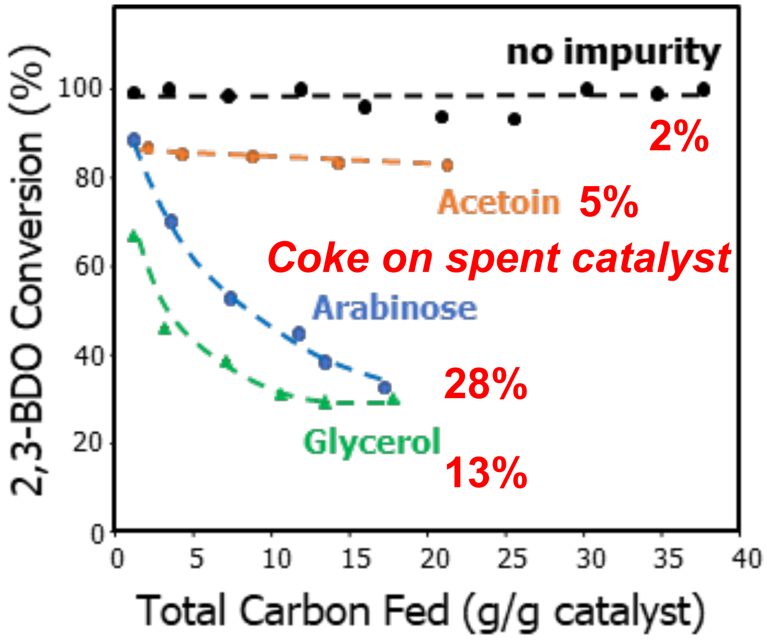
Outcome: Deactivation mechanism identified, and inorganic removal for catalyst regeneration demonstrated

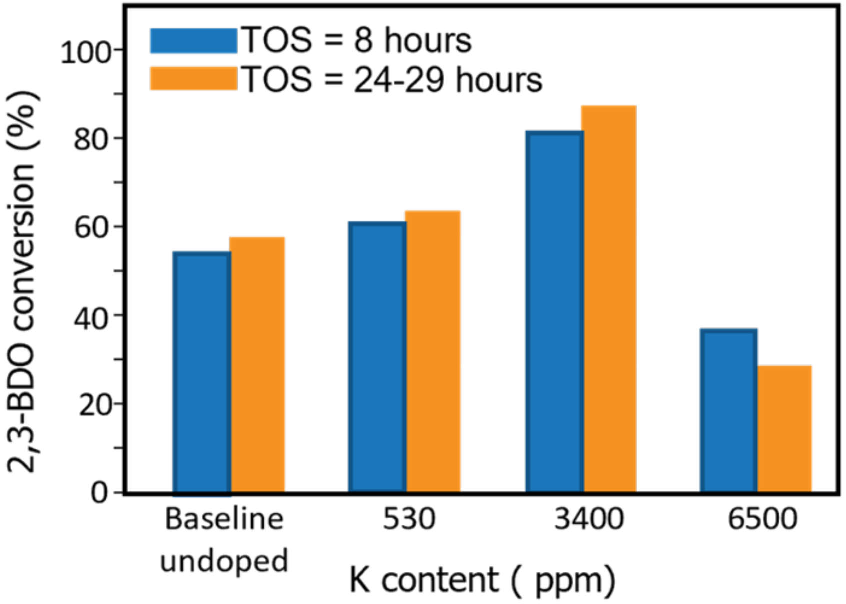
In collaboration with CFP project (2.3.1.314), ACSC (2.5.4.303/304/305), and CCPC (2.5.1.302)

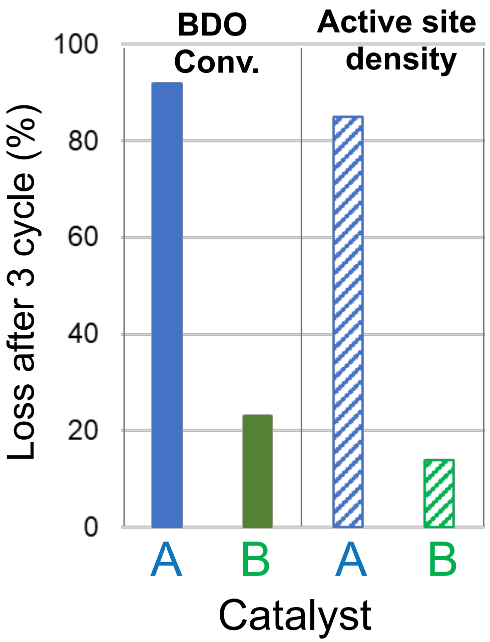
ACS Catalysis, 2022, 12, 465

2. Progress and Outcomes - Support *ChemCatBio* projects, CUBI

Objective: Identify the impact of organic and inorganic contaminants and water in BDO broth on conversion catalysts





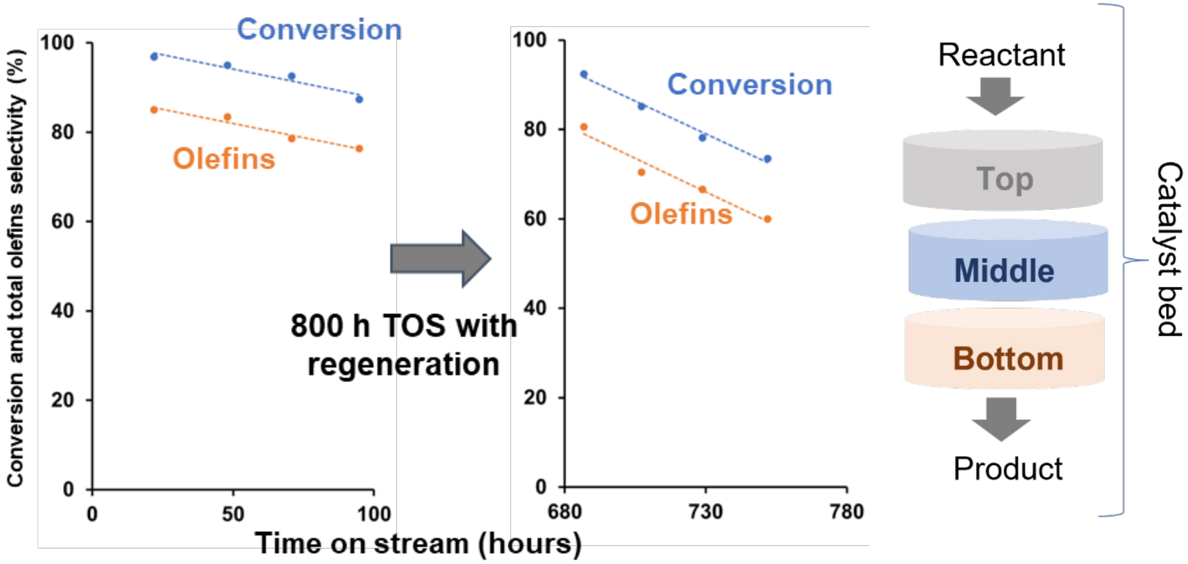


- *Sugar contaminants cause rapid coking*
- *K only impacts at a high content*
- *Water leaching active sites*

Outcome: BDO broth contaminant level requirement suggested and new catalyst formulation with improved hydrothermal stability identified for potential liquid phase conversion

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

Objective: Determine the deactivation mechanism of C2 upgrading catalyst and support the catalyst improvement



- *Spent catalysts from 800 h stability testing*

	Cu size (nm)	Acid site (umol/g)	Coke		
			Content (wt.%)	C=O/C-C (XPS)	Oxidation
Fresh	~ 4	226			
Top	~ 7	55	4.4	1.3	Increase in oxidation temperature and decrease in H/C ratio
Middle	~ 7.5	34	5.2	0.9	
Bottom	~ 8	33	7.0	0.7	

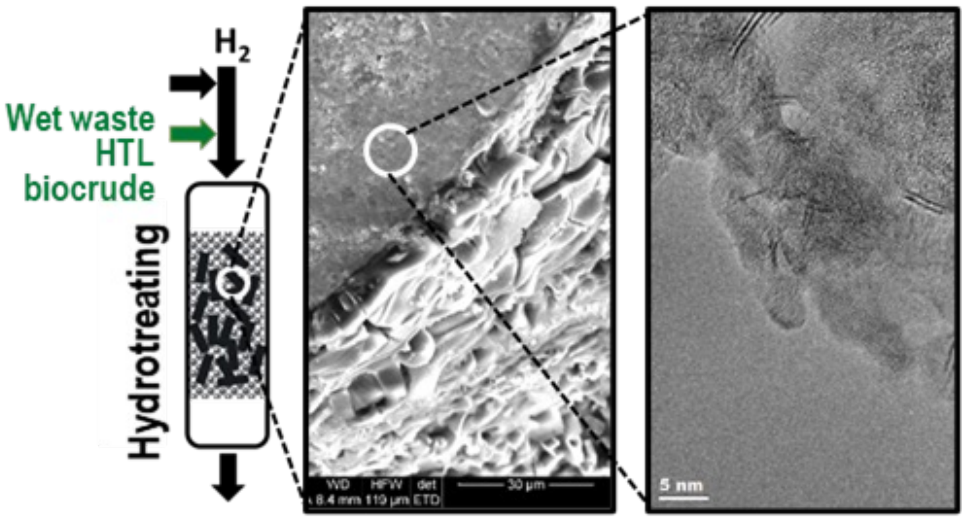
- *Catalyst on the bottom showed greater deactivation by Cu sintering (high H_2O content) and coke formation (additional coking mechanism)*

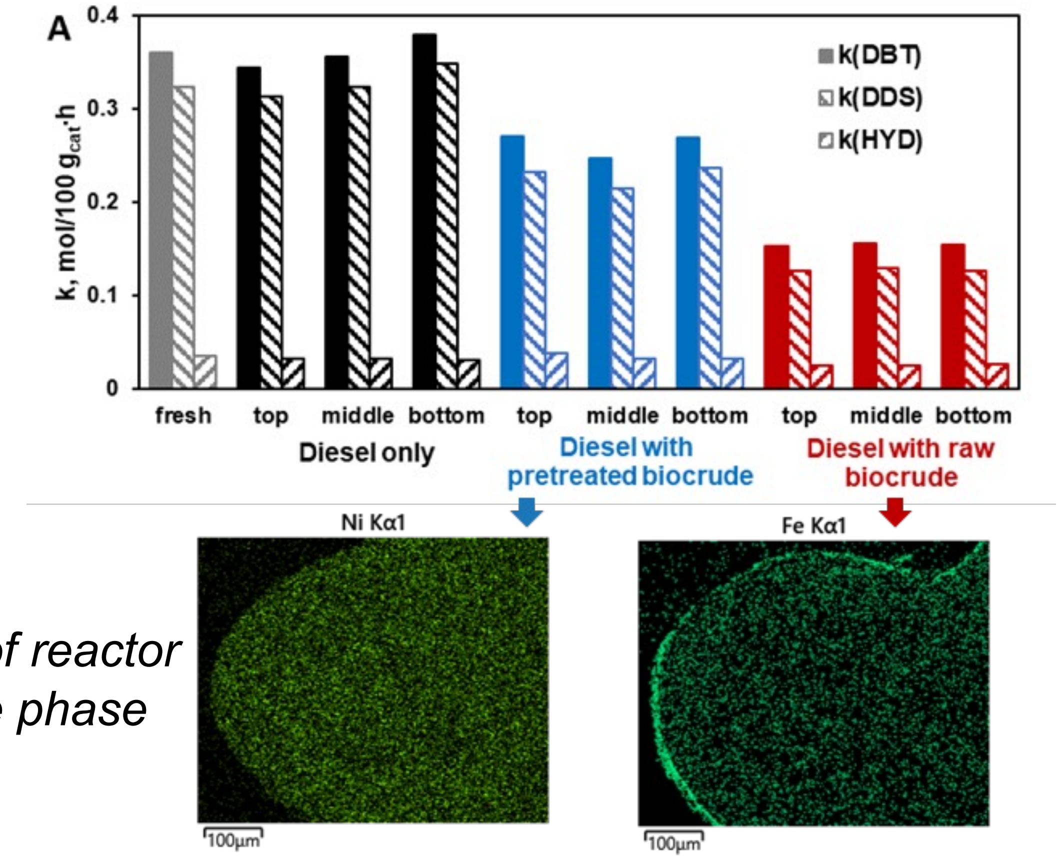
Outcome: Identified deactivation profile, especially coke formation, dependence with catalyst location and possible mechanism difference, suggesting the need of suppressing different side reactions to coke precursors

In collaboration with PNNL C2 upgrading project (2.3.1.314)

2. Progress and Outcomes - Support other BETO project

Objective: How does co-processing HTL bio-crude impact hydrotreating catalyst stability?





- *No structural change*
- *Fouling by metal contaminants in raw bio-crude on top of reactor*
- *Fouling by carbonaceous species near the sulfide active phase*
- *Bio-crude pretreatment alleviate catalyst deactivation*

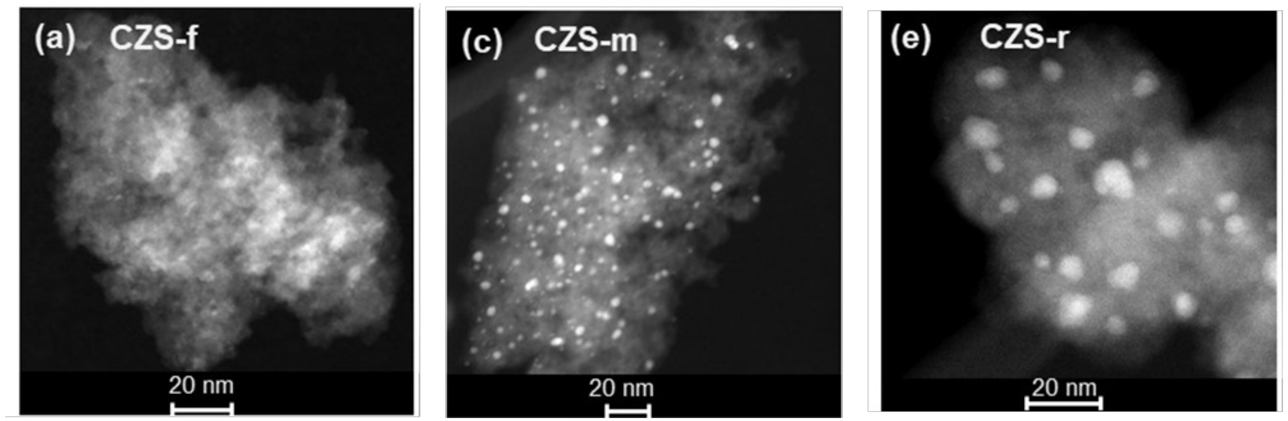
Outcome: The results suggest the need of 1) bio-crude pretreatment; and 2) guard bed improvement to enable minimal impact on hydrotreating catalyst stability when co-processing bio-crude

In collaboration with Bio-oil Co-processing in Refinery project

Energy & Fuels, 2022, 36, 16, 9133

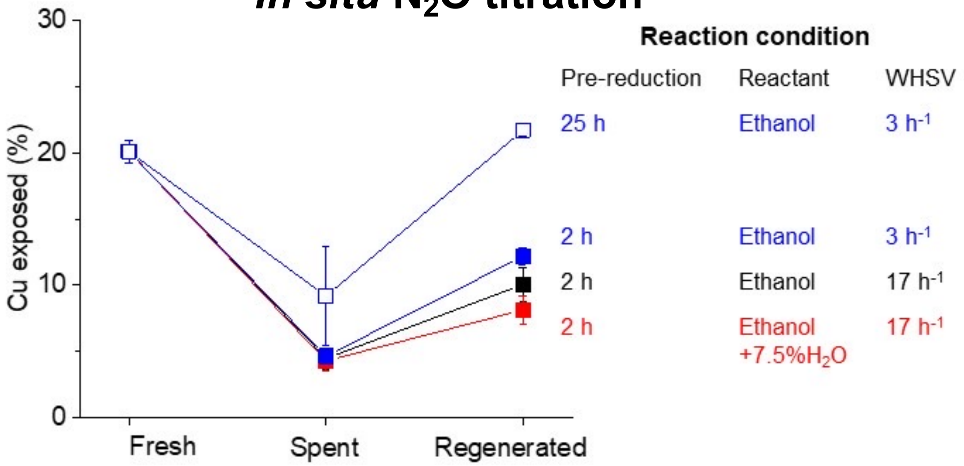
Objective: How does H_2O impact Cu dispersion of $Cu/ZrO_2/SiO_2$ catalyst?

Fresh **Spent- Ethanol only** **Spent- Ethanol + H_2O**



- *Greater sintering of Cu observed for ethanol/water than ethanol only feed*

***In situ* N_2O titration**

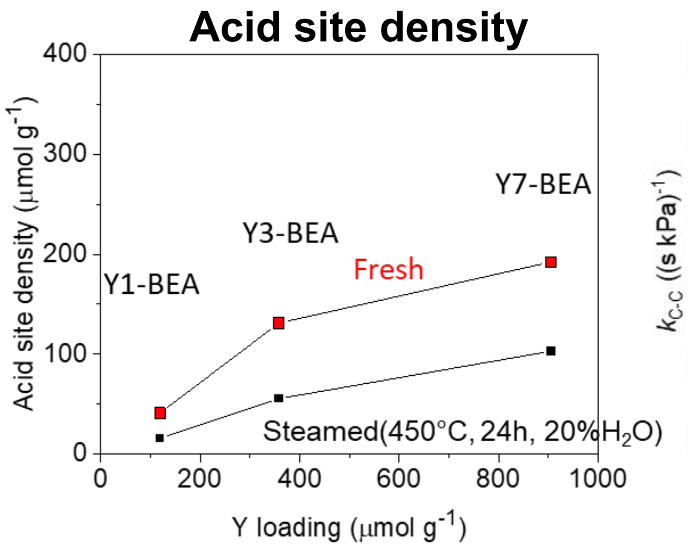


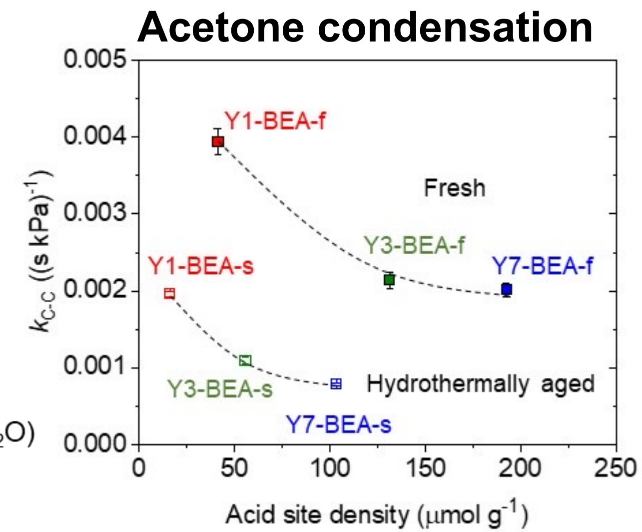
- *In situ titration showed the dependance of Cu particle size on reaction conditions and feed compositions*

Outcome: The extent of H_2O induced Cu sintering depends on several factors. The results led to a development of bimetallic catalyst showing improved Cu stability.

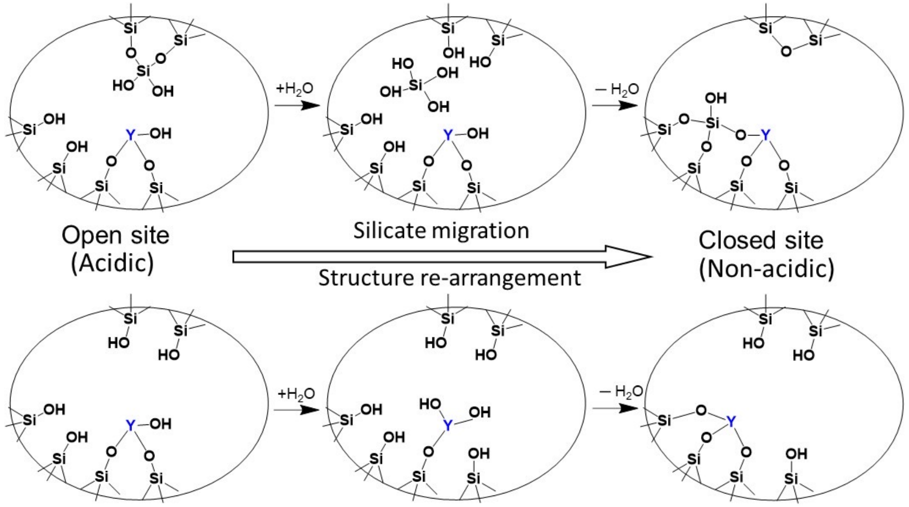
In collaboration with PNNL C2 upgrading project (2.3.1.314)

Objective: How does H_2O impact Y sites on Y/Beta catalyst?





- *Stream treatment leads to loss of Y acid sites and decrease in activity of the acid sites*



- *Spectroscopy results suggested hydrothermal treatment influences the distribution of open sites and closed sites and the abundance of silanol groups*

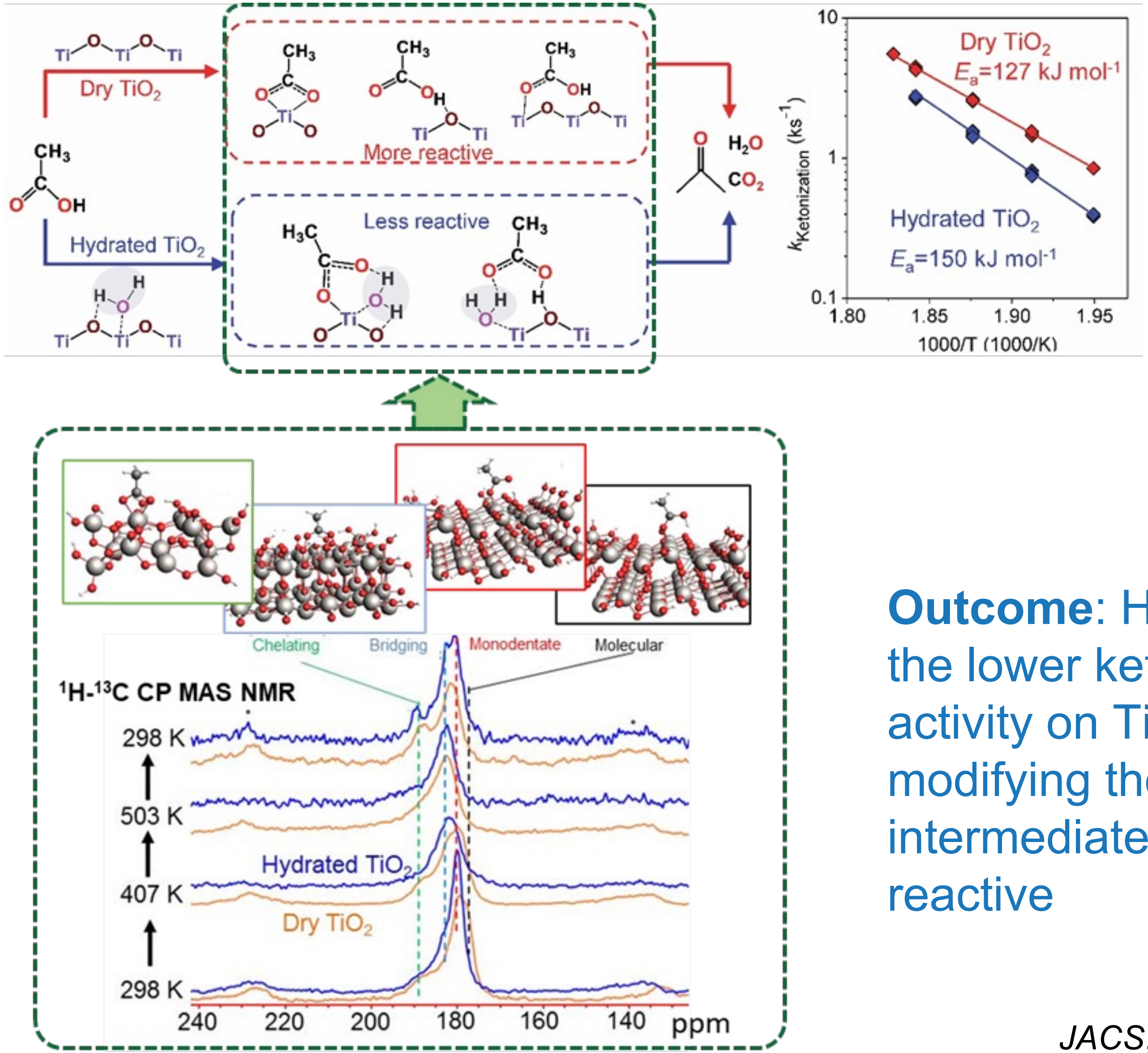
Outcome: H_2O leads to much reduced Y site density and acidic strength of Y/Beta by modifying active site structure

In collaboration with ORNL C2 upgrading project

Manuscript in preparation.

2. Progress and Outcomes - Address overarching challenges, water

Objective: How does H_2O impact carboxylic acid ketonization over TiO_2 Lewis acid-base catalyst?



- *NMR results show the increase of H_2O associated bridging bidentate carboxylates on hydrated TiO_2, which are less reactive for ketonization and responsible for a higher activation barrier*

Outcome: H_2O leads to the lower ketonization activity on TiO_2 by modifying the surface intermediates to be less reactive

In collaboration with PNNL BES project.

JACS, 2023, 145, 99

2. *Progress and Outcomes* - Future R&D

FY 23-25

Support *ChemCatBio* projects

Project	FY 23-25
CFP	Zeolite coke combustion
CUBI	Stability in water
C2	Cu stabilization and coke mitigation
C1	Cu distribution and coke mitigation

Address overarching challenges

Challenge	FY 23-25
Three interwoven deactivation challenges	Impact of coke (combustion kinetics)
Stability of engineered catalysts	Deactivation mode change

- FY23: Determine the impact of **engineered** catalyst formulation on Cu speciation and catalyst deactivation mechanisms (C1, ACSC)
- FY24 Go/No-go: Evaluate the ability of the computational and characterization approach to generate improved **engineered** catalysts (C1, CCPC, ACSC)
- FY24: Establish **coke** characteristics for at least two catalyst systems from different *ChemCatBio* catalytic technologies (CFP, C1, C2, ACSC)
- FY25, End of Project: Develop a predictive model for **engineered** catalysts to reduce risk associated with engineered catalyst formulations when scaling reactor dimensions (C1, CCPC, ACSC)

3. Impact - Enhance the *ChemCatBio* portfolio

- **De-risking *ChemCatBio* catalytic technologies**
  - "Having a program dedicated to understanding and mitigating deactivation is critical" "This is an infrastructure-level project that is not in the spotlight but extremely important for the development of catalysts"– according to the *FY21 peer review comments.*
  - **Enhancing catalyst lifetime**

C2	• H_2O induce Cu sintering • Different coking mechanism	• Control H_2O in feed • Promoters stabilize Cu • Catalyst modification alters reaction pathways
CUBI	• Water, inorganics, and sugar contaminants impacts stability	• New catalysts with improved water resistance • Limit the type of content of organic and inorganic contaminants in BDO broth
CFP	• Impact of contaminants • Coke combustion kinetics	• Improved regeneration method (K removal) • Reactor modeling to de-risk scale up

  - Support **engineered catalyst development**

- **DEI: Supporting UNM – a Minority Serving Institute** – New BETO project applying unique catalysis capabilities toward *ChemCatBio* goals (with C2 upgrading project)

3. Impact - Fill the identified gaps in catalyst stability

- Provide **knowledge to industry and catalysis R&D communities** for the rational design of more stable catalysts via:
  - Five publications and four presentations since last review
  - BETO Bioenergy R&D Blog
  - *ChemCatBio* 2023 Technology Brief
  - Input to *ChemCatBio* Catalyst Property Database (now includes contaminants)

- **A focus on catalyst stability** within *ChemCatBio*
  - Most of the projects involve catalyst stability milestone(s)
  - Address overarching catalyst stability challenges with extensive collaboration among enabling capabilities
  - Focus on deactivation when transitioning from powder to engineered catalyst ***New in FY23-25***

Unlocking the Mystery of Catalyst Poisoning

Date: 8/11/2022

Author: Dr. Asanga Padmaperuma

Description: A research team from Pacific Northwest National Laboratory investigates how potassium in biomass feedstocks poisons a catalyst.

ACS Catalysis

pubs.acs.org/acscatalysis — Research Article

Deactivation by Potassium Accumulation on a Pt/TiO_2 Bifunctional Catalyst for Biomass Catalytic Fast Pyrolysis

Fan Lin, Yubing Lu, Kinga A. Unocic, Susan E. Habas, Michael B. Griffin, Joshua A. Schaidle, Harry M. Meyer, III, Yong Wang, and Huamin Wang*

Cite This: *ACS Catal.* 2022, 12, 465–480 — Read Online

JACS — Journal of the American Chemical Society

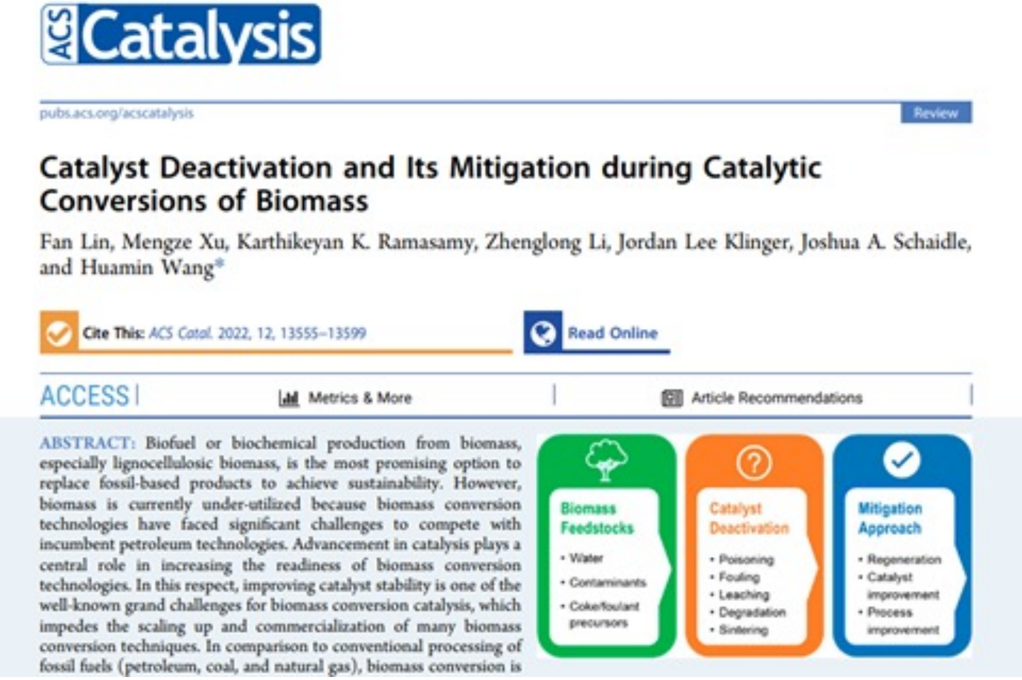
pubs.acs.org/JACS — Article

Elucidation of the Roles of Water on the Reactivity of Surface Intermediates in Carboxylic Acid Ketonization on TiO_2

Fan Lin, Wenda Hu, Nicholas R. Jaegers, Feng Gao, Jian Zhi Hu,* Huamin Wang,* and Yong Wang*

Cite This: *J. Am. Chem. Soc.* 2023, 145, 99–109 — Read Online

3. *Impact* - Review paper on catalyst deactivation in biomass conversion


ACS Catalysis

pubs.acs.org/acscatalysis Review

Catalyst Deactivation and Its Mitigation during Catalytic Conversions of Biomass

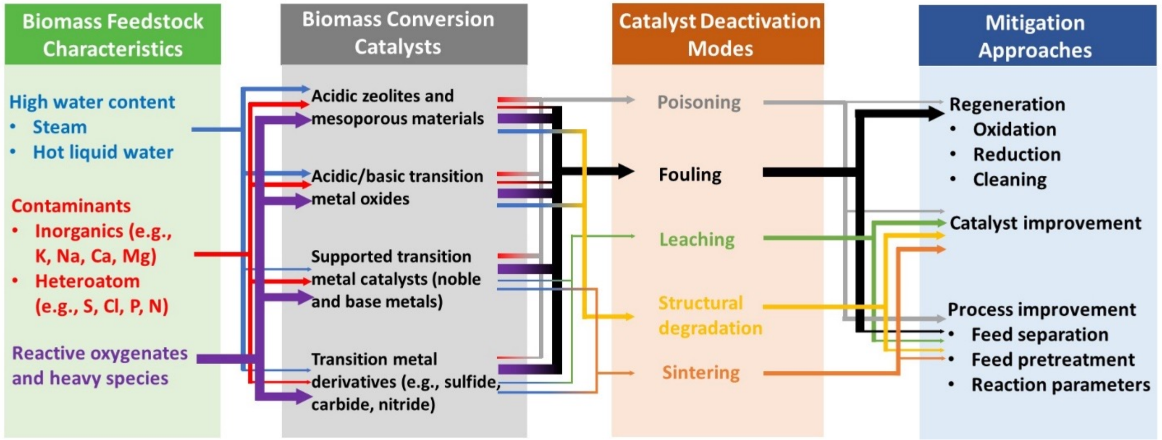
Fan Lin, Mengze Xu, Karthikeyan K. Ramasamy, Zhenglong Li, Jordan Lee Klinger, Joshua A. Schaidle, and Huamin Wang*

Cite This: ACS Catal. 2022, 12, 13555−13599 Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: Biofuel or biochemical production from biomass, especially lignocellulosic biomass, is the most promising option to replace fossil-based products to achieve sustainability. However, biomass is currently under-utilized because biomass conversion technologies have faced significant challenges to compete with incumbent petroleum technologies. Advancement in catalysis plays a central role in increasing the readiness of biomass conversion technologies. In this respect, improving catalyst stability is one of the well-known grand challenges for biomass conversion catalysis, which impedes the scaling up and commercialization of many biomass conversion techniques. In comparison to conventional processing of fossil fuels (petroleum, coal, and natural gas), biomass conversion is

Connection between biomass feedstocks and catalysts with potential catalyst deactivation and mitigation



- A comprehensive review specifically focusing on catalyst deactivation in biomass conversion
- Authors from 4 national labs; **~380 references reviewed**; covered almost every aspect of the biomass conversion reactions
- Perspectives provided

Catalyst deactivation during the catalytic bio-refinery process is the key problem for the industrialization of the biomass conversion process, so it is crucial to carry out fundamental research during the stage of laboratory research.

- Reviewer

Also available in *ChemCatBio* 2023 Technology Brief

ACS Catalysis, 2022, 12, 13555

Summary - Our Goal is to Address Catalyst Deactivation Challenges

Goal	• Provide foundational insight and actionable recommendations for extending catalyst lifetime in biomass catalytic conversion and targeting the most impactful challenges (water, inorganics, and coke) and supporting *ChemCatBio* (C1, C2, CUBI, and CFP)
Approach	• Integrated and collaborative effort within *ChemCatBio* • **Combining multiple approaches** to understand deactivation mechanism • Providing actionable recommendations and developing regeneration method to **address deactivation**
Progress and Outcomes	• Addressing **overarching catalyst deactivation challenges** – Determined the **impact of water** on multiple catalysts – Investigating regeneration method for **Coke removal** – **Impact of catalyst scale up** on stability • **Improve catalyst lifetime** for *ChemCatBio* projects – C1 upgrading, C2 upgrading, CUBI, and CFP
Impact	• **Catalyst lifetime improvement -** Cost and risk reductions of conversion technologies • **Fill gaps and provide knowledge base** for rational design of more stable catalysts
Future	• Addressing overarching catalyst deactivation challenge – **coke and water** • Support development of **engineered catalysts** • Improve catalyst lifetime for *ChemCatBio* projects to accelerate their adoption

Quad Chart Overview

Timeline
- Project start date: 10/1/2022
- Project end date: 9/30/2025

	FY22 Costed	Total Award
DOE Funding	$300 K	$900K (FY23-25)

TRL at Project Start: 1-3
TRL at Project End: 1-3

Project Partners
- Within ChemCatBio Consortium
  - C2
  - C1
  - CFP
  - CUBI
  - ACSC
  - CCPC

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
Develop a predictive model for engineered catalyst properties. A predictive model will be developed for engineered catalysts that correlate CO_2-rich syngas to hydrocarbons (STH) performance with critical properties of engineered catalysts. The model will be informed by the characterization of engineered catalyst properties and deactivation characteristics, as well as kinetic data. This milestone is a joint between the C1, CCPC, CDM, and ACSC projects.

Funding Mechanism
2023 BETO National Laboratory Call

Thank you!

This work was performed in collaboration with the Chemical Catalysis for Bioenergy Consortium (ChemCatBio, CCB), a member of the Energy Materials Network (EMN)

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

Pacific Northwest NATIONAL LABORATORY

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- **ORNL**: Michael J Cordon, Meijun Li, Kinga A Unocic, Andy Sutton, Zhenglong Li
- **BETO**: Trevor Smith, Sonia Hammache

chemcatbio.org

ChemCatBio
Chemical Catalysis for Bioenergy

Additional Slides

Acronyms and abbreviations

ACSC	Advanced Catalyst Synthesis and Characterization project
BDO	Butanediol
BES	Basic Energy Sciences
BETO	Bioenergy Technologies Office
C2 upgrading	Catalytic Upgrading of C2 Intermediates project
ChemCatBio	Chemical Catalysis for Bioenergy Consortium; ChemCatBio consortium
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
IAB	Industrial Advisory Board
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
UNM	the University of New Mexico

Responses to Previous Reviewers' Comments, 1/2

Overall Comments:

- Since the 2019 Peer Review, this project has matured considerably and grown into a role as a supporting capability for catalytic upgrading programs. Deactivation is ubiquitous in these systems, and it is a major cost driver and risk factor for scale up. Having a program to dedicated to understanding and mitigating deactivation is critical. The team's mitigation toolbox is robust and considers relevant aspects of both prevention of deactivation and restoration of activity losses. This team is helping to improve the lifetimes of catalysts used across the ChemCatBio consortium, which is a significant impact. It is also worth pointing out that the team is addressing a grand challenge in catalysis science (a fundamental understanding of catalyst deactivation), which is often overlooked in the peer reviewed literature.
- This is an "infrastructure-level" project that is not in the spotlight but extremely important for the development of catalysts. Such a project deserves more attention. It is impressive to see the team managed to help the development of quite a few catalysts in the catalytic upgrading technology area and it could be beneficial if they can apply their knowledge and tools to the other projects. Considering the diversity of biomass feedstock, the ability to endure harsh conditions would be important for catalysts.
- Catalyst deactivation is a key problem that needs to be addressed for every process; it is good to see that at least one project is focused on this problem.
- Excellent job managing a key, complex issue for catalysis. Management strategy is solid and maintaining good communication with team and input from IAB board. This is a key to success of the catalytic program cost improvements and viability and program has clear goals and challenges. Good use of all tools and inputs at hand to address the outlined key issues. Large potential to impact multiple programs. Key to success as indicated for multiple programs which is why this is so important. Excellent progress on mitigating deactivation by defining key areas to focus effort by teams.
- The CDM touches every part of the CCB and is highly collaborative. CDM has a very close interaction across CCB with very frequent meetings, interactions with CCB steering committee and IAB. The CCB team brings the advantage of having access to advanced characterization tools to study the material science related to deactivation events. In that regard, the approach here of deactivation mechanistic elucidation for catalysts on the projects bottlenecked by stability issues should advance the SOA every time. The approach of using advanced characterization and computer modeling is a tried-and-true method for understanding deactivation at the fundamental level. The family of next generation catalysts resulting from the experimental synthesis-characterization (structure) - performance (function) cycle will be innovative and generate patents and development opportunities with industry partners across the CCB. The catalysis community will benefit greatly from this work since much of it is done in-house by corporate R&D groups to optimize commercial materials. Now, this information will be available to the public and the CDM understands the impact of their project on the community which is important. Inherently, catalyst deactivation understanding and the generation of new material formulations from this insight has tremendous commercial potential.

Response: We greatly appreciate the support for the project, the thoughtful analysis, and constructive feedback provided by the reviewers. We agree that catalyst deactivation is a key challenge that needs to be addressed for every process in biomass conversion and having a program dedicated to understanding and mitigating deactivation is critical to the success of ChemCatBio. We will continue to build upon the collaborative efforts within ChemCatBio addressing catalyst deactivation challenges and our early-stage technical successes by (1) maintaining a collective and collaborative approach with core catalysis projects and enabling capabilities for this effort; (2) tackling the most impactful and grand catalyst stability challenges and balance overarching challenges with specific needs of catalysis projects; (3) utilizing multiple technologies to ensure rigorous deactivation mechanism determination and robust regeneration method development.

Responses to Previous Reviewers' Comments, 2/2

Some specific comments:

Comments: "It takes a long time (often 1000 hours) to obtain enough data to differentiate these, however. often there are multiple mechanisms of deactivation. The mechanism that is observed can change with time."

Response: We agree with reviewers that understanding long term catalyst stability is critical to obtain enough data and capture the deactivation mechanism change with time. We are working with catalysis projects to evaluate catalyst stability a longer time on stream, for instance 800 hours for the ethanol conversion catalyst, and are targeting to develop accelerated testing for simulating long term stability and faster catalyst stability evaluation.

Comments: "State of the Art (SOA) for providing fundamental insight would be mostly available in the literature or within industrial facilities with plant data." "Although direct industry engagement on the CDM project is not present now, the deliverables will illicit great corporate interest."

Response: We agree with reviewers that direct industry engagement to access existing plant data and attain great corporate interest in our deliverables are important. We are engaging with our industrial advisory board and other industrial partners on this topic and will provide generated knowledge to industry and catalysis R&D communities via publication, workshop, webinar, and ChemCatBio DataHub.

Comments: "Solvent washing is effective; can it be implemented in a commercial system?"

Response: We worked with CFP project to evaluate K removal on actual spent catalysts. As presented in this presentation, the regeneration method works for the actual spent CFP catalysts.

Publications and Presentations (Since FY21 peer review)

Peer Reviewed Journal Article

- Fan Lin, Wenda Hu, Nicholas Jaegers, Feng Gao, Jian Zhi Hu,* Huamin Wang,* Yong Wang*, Elucidation of the roles of water on the reactivity of surface intermediates in carboxylic acid ketonization on TiO_2, *JACS*, 2023, 145, 99.
- Fan Lin, Mengze Xu, Karthi Ramasamy, Zhenglong Li, Jordan L. Klinger, Joshua Schaidle, Huamin Wang*, Catalyst Deactivation and its Mitigation during Catalytic Conversions of Biomass, *ACS Catalysis*, 2022, 12, 13555.
- Fan Lin, Yubing Lu, Kinga A. Unocic, Susan E. Habas, Michael B. Griffin, Joshua A. Schaidle, Harry M. Meyer III, Yong Wang, Huamin Wang*, Deactivation by Potassium Accumulation on a Pt/TiO_2 Bifunctional Catalyst for Biomass Catalytic Fast Pyrolysis, *ACS Catalysis*, 2022, 12, 465.
- Cheng Zhu, Oliver Y. Gutiérrez, Daniel M. Santosa, Igor Kutnyakov, Roland Weindl, Hui Shi, Huamin Wang*, Impact of Co-processing Biocrude with Petroleum Stream on Hydrotreating Catalyst Stability, *Energy & Fuels*, 2022, 36, 16, 9133.
- Michael J Cordon, Junyan Zhang, Stephen C Purdy, Evan C Wegener, Kinga A Unocic, Lawrence F Allard, Mingxia Zhou, Rajeev S Assary, Jeffrey T Miller, Theodore R Krause, Fan Lin, Huamin Wang, A Jeremy Kropf, Ce Yang, Dongxia Liu, Zhenglong Li, Selective Butene Formation in Direct Ethanol-to-C3+-Olefin Valorization over Zn–Y/Beta and Single-Atom Alloy Composite Catalysts Using In Situ-Generated Hydrogen, *ACS Catalysis*, 2021, 11, 7193.

Presentation

- Fan Lin, 2022 ACS Spring meeting, 2022, oral presentation.
- Fan Lin, The 27th North American Catalysis Society Meeting, 2022, oral presentation.
- Huamin Wang, Tcbiomass 2022, 2022, oral presentation.
- Fan Lin, 2021 ACS Spring meeting, 2021, oral presentation.

Report

- Unlocking the Mystery of Catalyst Poisoning, https://www.energy.gov/eere/bioenergy/articles/unlocking-mystery-catalyst-poisoning

Project Overview - An enabling project within ChemCatBio

Catalytic Technologies

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

Upgrading of C1 Building Blocks (NREL)

Upgrading of C2 Intermediates (PNNL, ORNL)

Catalytic Fast Pyrolysis (CFP) (NREL, PNNL)

Electrocatalytic CO_2 Utilization (NREL)

Enabling Capabilities

Advanced Catalyst Synthesis and Characterization (ACSC) (NREL, ANL, ORNL)

Consortium for Computational Physics and Chemistry (CCPC) (ORNL, NREL, PNNL, ANL, NETL)

Catalyst Deactivation Mitigation for Biomass Conversion (CDM) (PNNL)

Industry Partnerships (Phase II Directed Funding)

Opus12 (NREL)

Visolis (PNNL)

Sironix (LANL)

Cross-Cutting Support

ChemCatBio Lead Team Support (NREL)

ChemCatBio DataHUB (NREL)