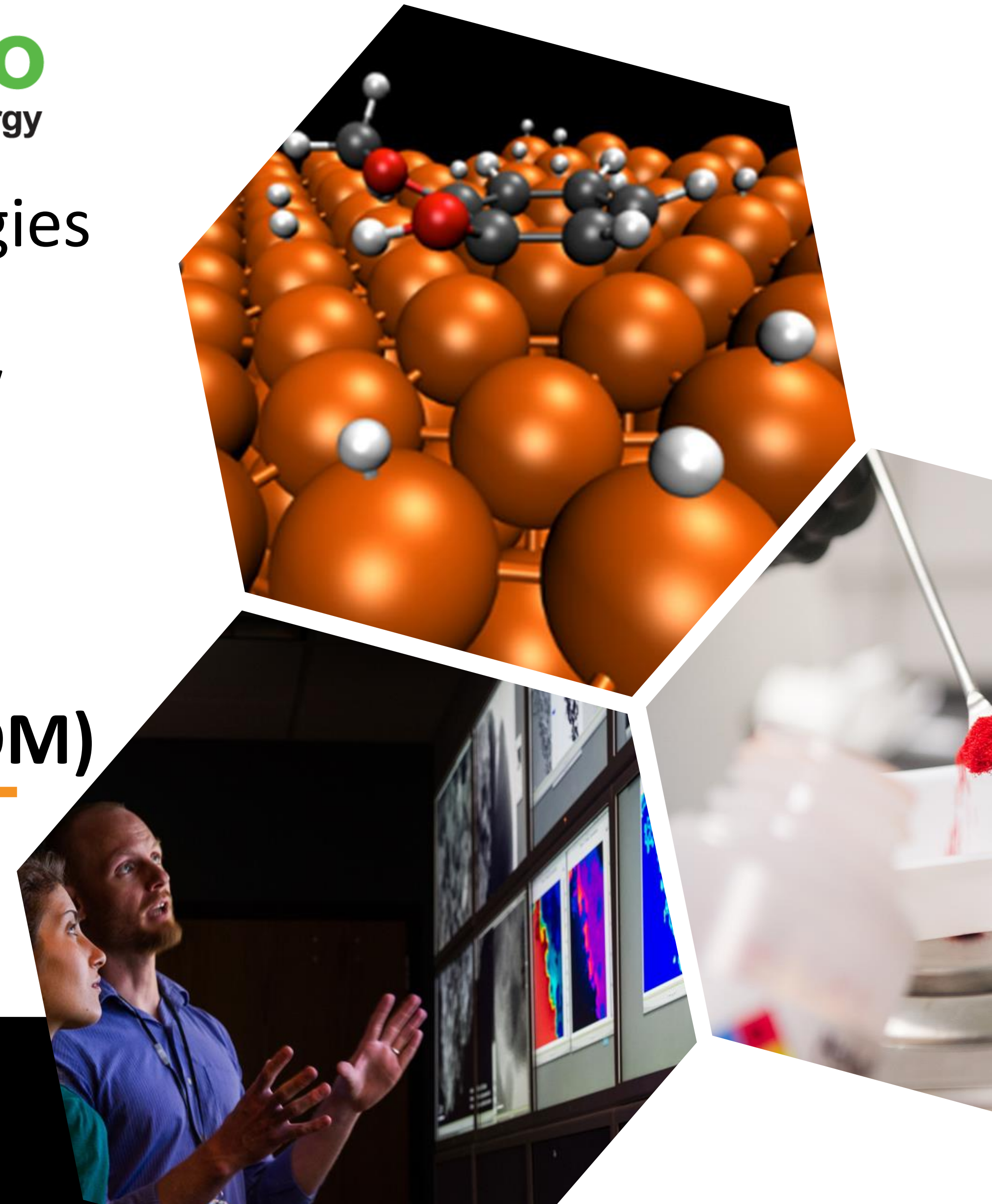
ChemCatBio
Chemical Catalysis for Bioenergy

DOE Bioenergy Technologies Office (BETO) 2019 Project Peer Review

2.5.4.501

Catalyst Deactivation Mitigation for Biomass Conversion (CDM)



March 5th, 2019

Catalytic Upgrading

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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)

CDM Goal Statement

Challenges: Biomass derived feedstocks bring new challenges to catalyst longevity for biomass conversion processes

Project Goal: **Improve catalyst stability** (lifetime) for ChemCatBio (CCB) catalysis projects through **understanding catalyst deactivation and developing mitigation** approaches

Outcome: Collaborate with CCB projects to provide

- Strategies to **extend catalyst lifetime** for catalytic process with specific focus on **catalyst regeneration**
- A document to summarize the **established connection** between characteristics of biomass derived feedstocks and corresponding catalyst deactivation

Relevance:

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

Catalysis for Biomass Conversion

Biomass derived feedstock:
Highly functionalized…
Complex… Unstable …
Water… Corrosive…
Contaminates…

Quad Chart Overview

Timeline

- Project start date: 10/1/2018
- Project end date: 9/30/2021
- Percent complete: 8%

	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19-21)
DOE Funded	$0	$0	$900 k

Barriers Addressed

Ct-E. Improving Catalyst Lifetime

- *Understanding causes of catalyst deactivation*
- *Develop improved catalyst regeneration*

Objective: Address catalyst deactivation challenges in catalytic processes to enable catalyst lifetime improvement for cost and risk reduction of biomass conversion technologies

End of Project Goal: Elucidate catalyst deactivation and mitigation aspects in BETO biomass conversion technologies and demonstrate value by assisting at least two or three CCB core catalysis projects to reach their cost target and/or catalyst lifetime target by understanding catalyst deactivation mechanisms and developing catalyst regeneration protocols

1 – Project Overview - Catalyst stability is no less important than activity and selectivity

Catalysis for
Biomass Conversion

Performance windows in fuel and chemical production processes

	Industrial window
Stability	**10^3 to 10^4 kg product /kg catalyst**
Activity	0.1-10 g product/ml h
Selectivity	70-100 wt.%

Angew. Chem. Int. Ed. 2015, 54, 13186 – 13197

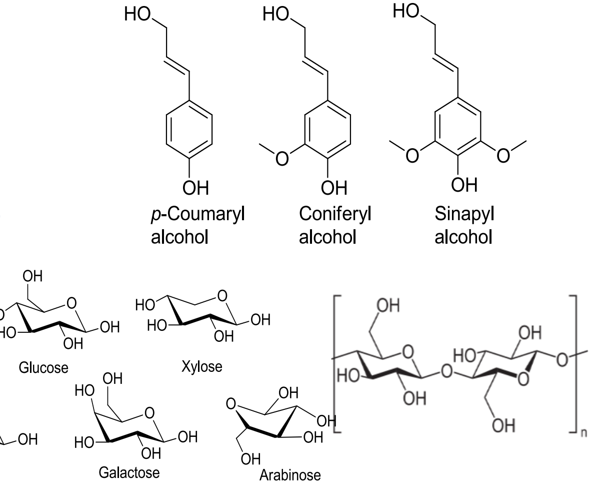
- Mechanistic understanding of catalyst deactivation and developing strategies to extend catalyst lifetime are vital to the success of process development
- Among the three performance metrics, stability is usually the least explored, and the factors that cause catalysts to die are the least understood, at a fundamental level…

ACS Catal. 2018, 8, 8597

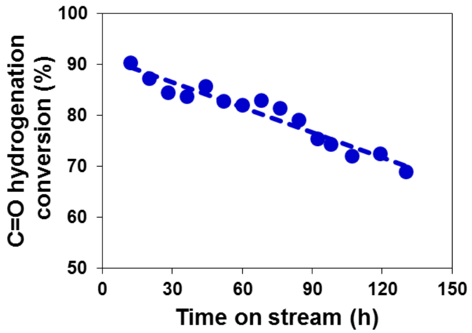
1 – *Project Overview* - Biomass derived feedstocks bring new challenges to catalyst longevity

Compared to fossil, most biomass derived feedstocks are

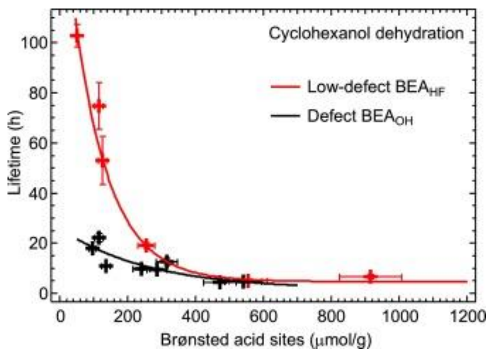
- Complex, highly functionalized, unstable
- Containing contaminates (from biomass or processing unit)
  - S, N containing species
  - Ca, K, Mg, Na, Si, Fe, Cr…
- Requiring polar/aqueous and corrosive conditions



Catalyst deactivation and reactor plugging of pyrolysis oil hydrotreating



Deactivation of Ru catalyst for pyrolysis oil hydrogenation by sulfur and condensation products



Deconstruction of zeolite in hot liquid water for biomass conversion

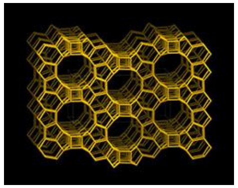
1 – Project Overview - This project is based on PNNL's previous efforts on addressing catalyst deactivation issues

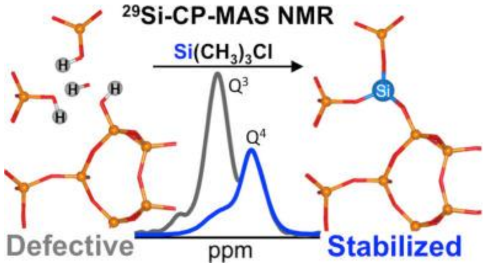
PNNL BETO projects

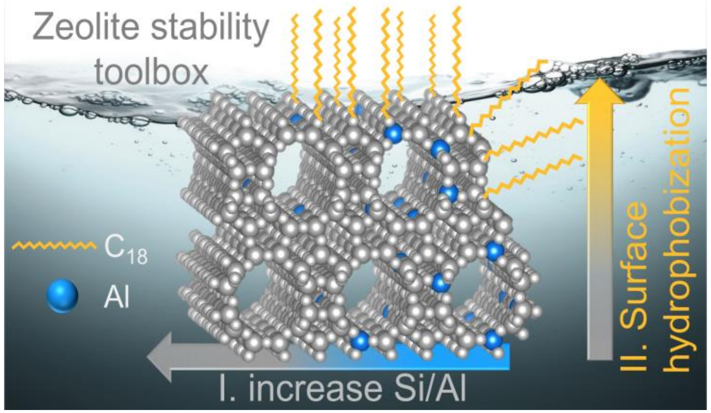
Bio-oil Hydrotreating *Sulfide catalysts*	Prevent plugging and extend operation time from ~90 to >1400 hours
Bio-oil stabilization *Reduced metal catalysts*	Develop regeneration and extend lifetime from ~150 to >800 hours
Aqueous acetic acid conversion *Transition metal oxides*	Demonstrate stable conversion of real feed in condensed phase

PNNL BES and LDRD projects Dehydration in hot condensed water

BEA Zeolite







- **Deactivation**: Silanol defect interaction with water
- **Mitigation**: Lower defect density by new synthesis; Lower water in pore by tuning hydrophobicity
- **Outcome**: >5 times improvement of catalyst lifetime

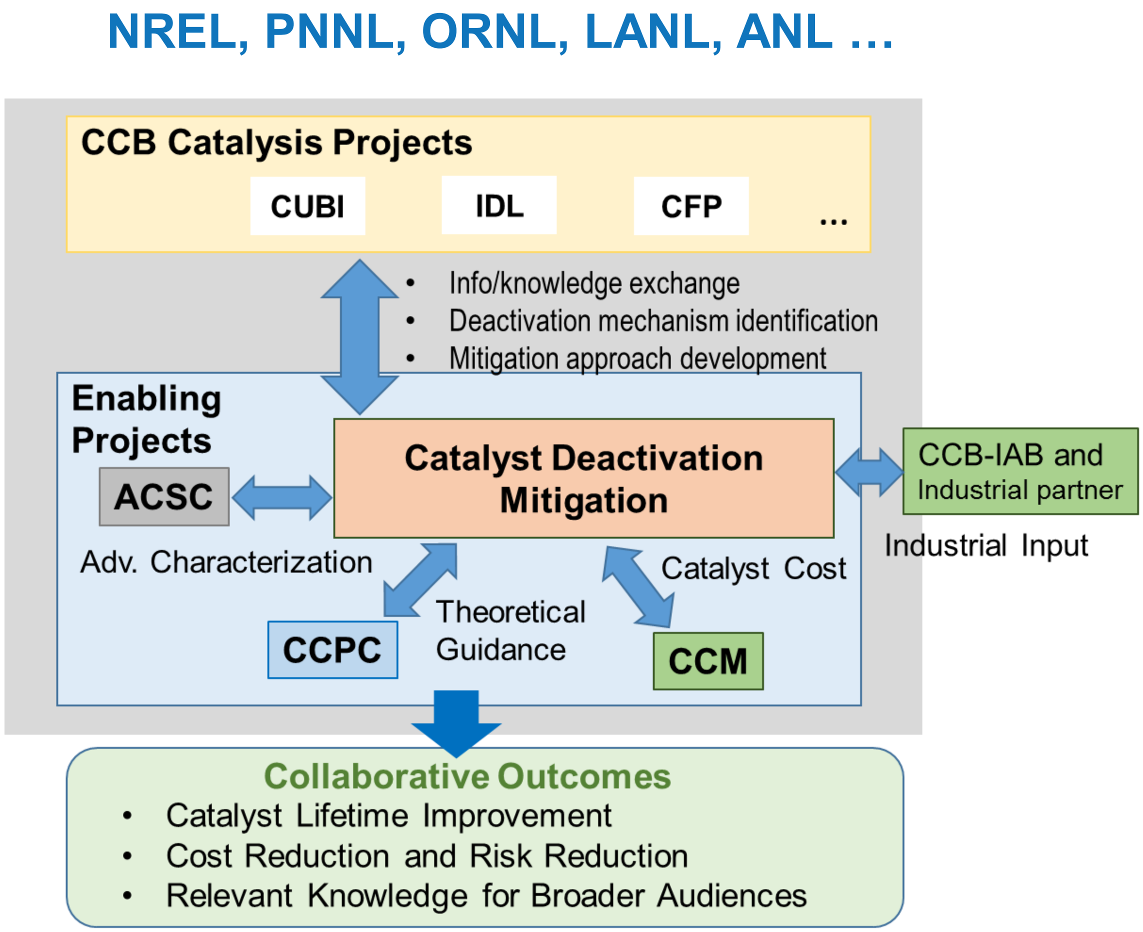
S. Prodinger, et al, J. Am. Chem. Soc. 2016; Chem. Mater. 2017; Appl. Catal. B, 2018

We will leverage our previous efforts to understand and mitigate catalyst deactivation for biomass conversion in both applied and fundamental research projects

1 – Project Overview - Addressing catalyst deactivation issue requires integrated and collaborative efforts within CCB

- Catalyst deactivation is a ***broad*** challenge and shares some ***commonality*** for CCB catalytic projects

- This project will establish an ***integrated and collaborative*** portfolio of catalytic and enabling technologies for addressing overarching ***catalyst deactivation issues*** for biomass conversion

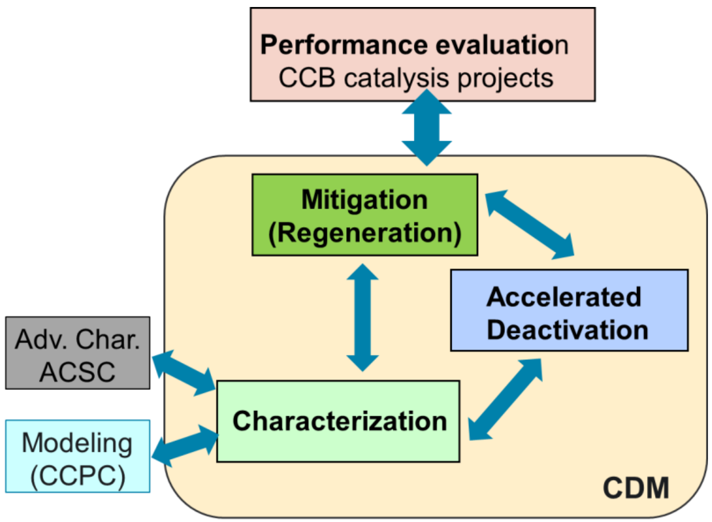


CUBI: Catalytic Upgrading of Biochemical Intermediates
IDL: Catalytic Upgrading of Indirect Liquefaction Intermediates
CFP: Catalytic Fast Pyrolysis

ACSC: Advanced Catalyst Synthesis and Characterization
CCM: Catalyst Cost Model Development
CCPC: Consortium for Computational Physics and Chemistry

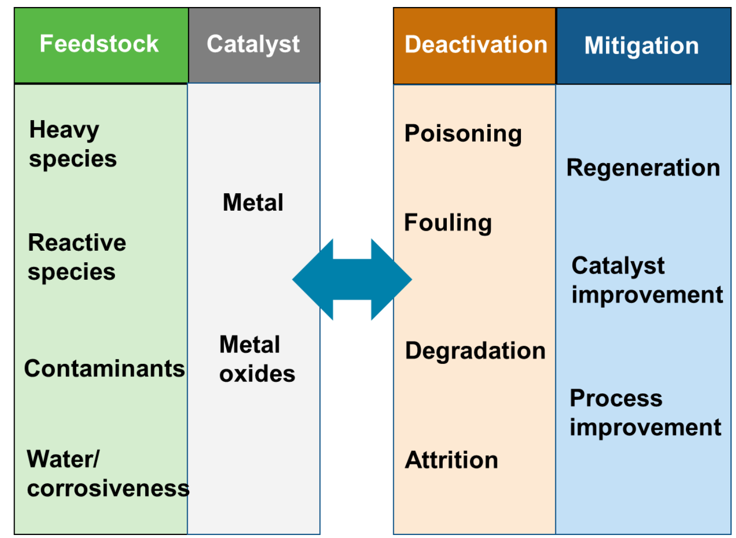
1 – Project Overview - Support CCB projects to mitigate catalyst deactivation and provide a summary document

Support CCB projects for catalyst lifetime improvement



- Provide better understanding of catalyst deactivation causes
- Develop mitigation approach with a specific focus on regeneration
- Demonstrate impact on lifetime improvement and cost reduction

A document to summarize the connection



- Summarize the connection between biomass derived feedstock and catalyst with consequent deactivation and mitigation
- Share with CCB and broader audiences

2 – Management Approach - This project will be evaluated by its value to CCB catalysis projects

Coordination Within CCB

- *Information exchange*
  - CCB biweekly steering committee meeting
  - CCB onsite meeting
  - CCB industrial advisory board (IAB) meeting
  - Direct interaction with CCB project PIs
- *Collaboration*
  - Joint efforts to address deactivation challenges (joint milestones)
  - Direct interaction with CCB project PIs for identifying targets and for sample and data handling

Structure

Outreach and Communication	Deactivation Mechanism Identification	Deactivation Mitigation Development

Project Management

- Milestones
- Go/No-Go decision
- Quarterly report
- Regular interaction with CCB and catalysis teams
- Regular interaction with CCB IAB and industrial experts

FY20 Go/No-Go

Prove that the CDM has provided value to CCB catalysis projects

- Enhance understanding deactivation; develop mitigation; extend catalyst lifetime
- Identify catalytic processes for further collaboration

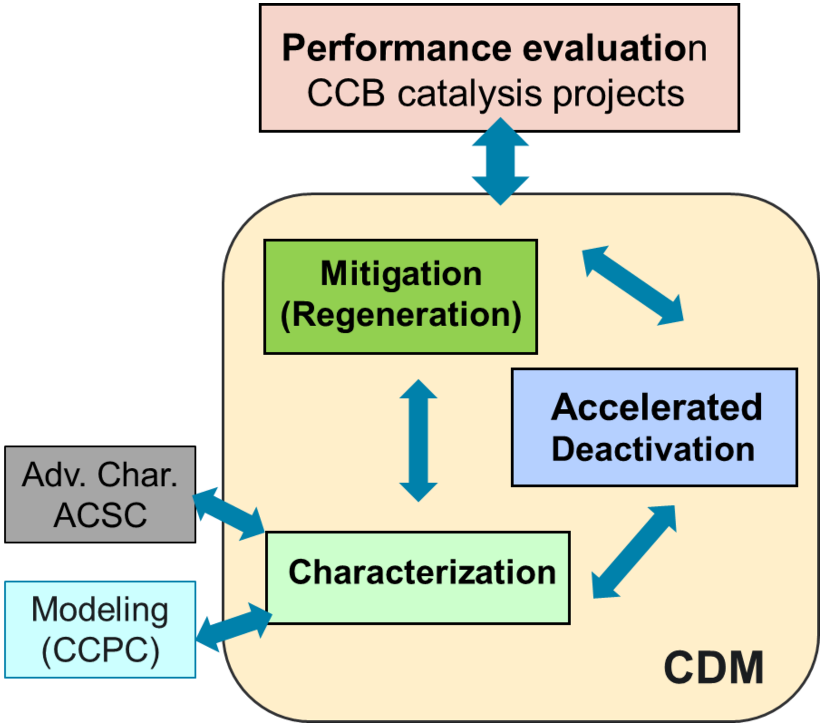
2 – Technical Approach - Understand catalyst deactivation and develop mitigation for CCB projects

- Hypothesis-driven catalyst ***deactivation mechanism identification***
  - Detailed catalyst ***characterization*** (with ACSC)
  - Potential modeling (with CCPC)
  - Catalytic reaction testing

- ***Accelerated deactivation*** method
  - Validate deactivation mechanism
  - Fast stability evaluation

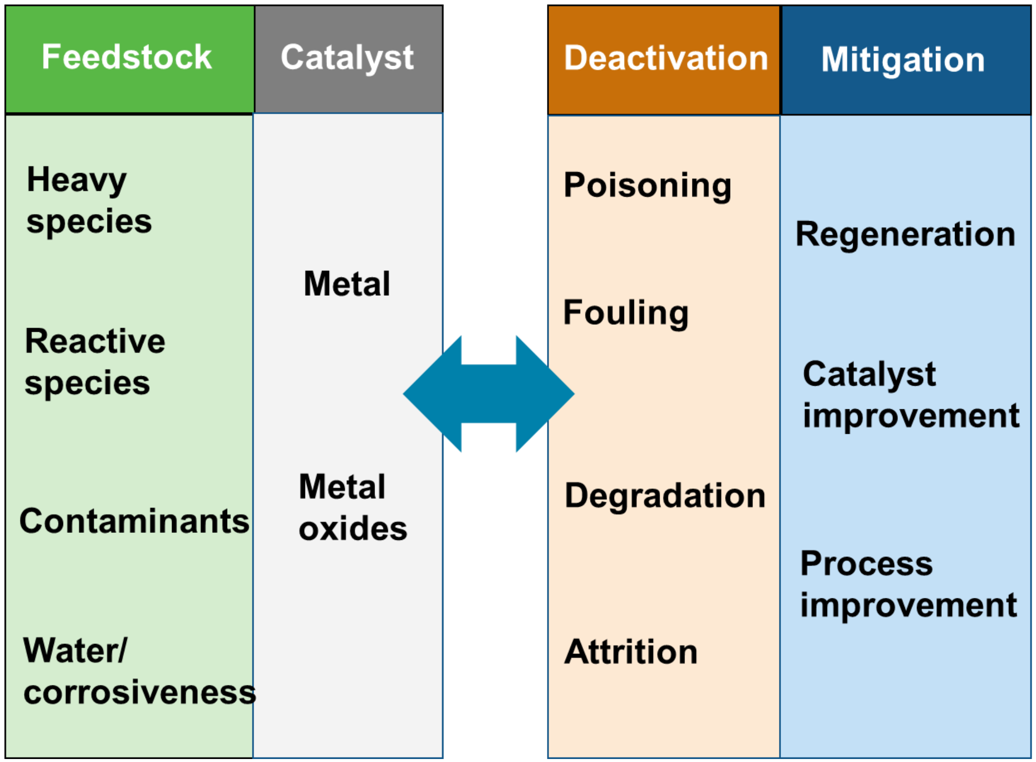
- ***Mitigation*** approach development
  - **Catalyst regeneration,** effective and less energy, and material demand
  - Suggestion on catalyst and process improvement

- ***Verify*** lifetime enhancement with CCB catalysis projects



ACSC: Advanced Catalyst Synthesis and Characterization
CCPC: Consortium for Computational Physics and Chemistry

2 – Technical Approach - Provide knowledge on catalyst deactivation issues in biomass conversion



- ***Identify*** previous or ongoing efforts on catalyst deactivation and mitigation in biomass conversion
- ***Establish*** connections between properties of feedstocks and catalyst with consequent deactivation and mitigation
- ***Share*** information with CCB teams and broader biomass catalytic conversion developers (reports and publication)

Provide guideline for rational design of process and catalyst for biomass conversion with enhanced process robustness and catalyst lifetime

2 – Technical Approach - One example includes bio-oil hydrogenation

Feedstock	Catalyst	Deactivation	Mitigation
Heavy species **Reactive species** **Contaminants** **Water/ corrosiveness**	**Supported reduced metal catalysts** **Ru/TiO_2** **Ru/C** **Ni/Al_2O_3**	**Poisoning** *S to Metal* **Fouling** **Degradation** *Leaching of Ni* *Phase transition of Al_2O_3*	**Regeneration** *Cleaning* *Reduction* **Catalyst improvement** *Ru over TiO_2* **Process improvement** *Feed separation* *T, P, LHSV*

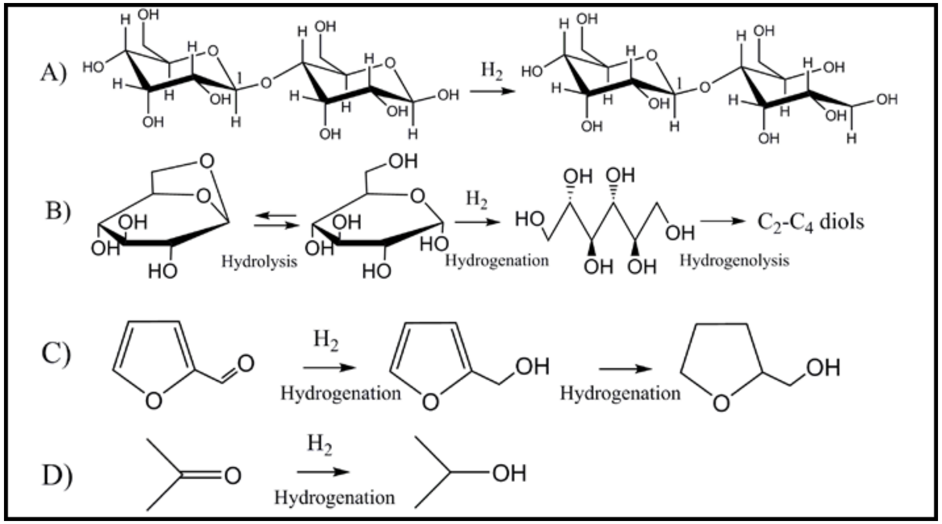
Fast pyrolysis bio-oil

Ru/TiO_2
140 °C, 1800 psig H_2

Stabilized bio-oil

Hydrotreating

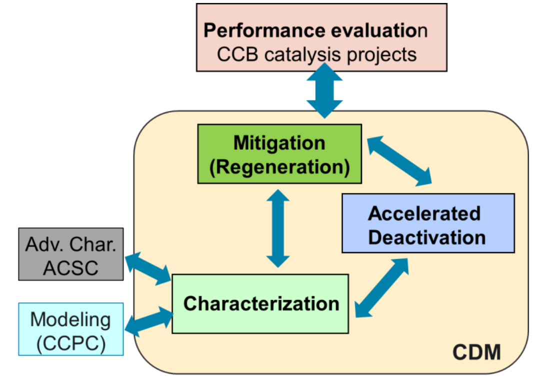
Hydrocarbons



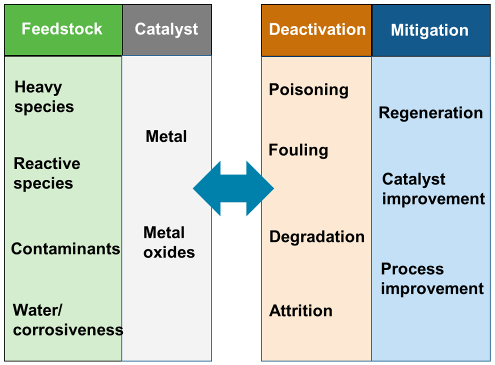
2 – Technical Approach - Challenges and Success Factors

Challenges	Success Factors
Develop rigorous understanding of deactivation mechanism	• Hypothesis-driven research • Advanced characterization (ACSC) • Guidance by theory (CCPC)
Relevant and impactful mitigation approach	• Work closely with CCB catalysis team and their techno-economic analysis partners to ensure economic benefit • Get input from industrial advisors (CCB IAB and subcontract)
Adequate involvement of CCB projects	• Engage CCB projects and steering committee early and frequently • Information exchange by meetings and reports

Support CCB projects for catalyst stability improvement



Document to summarize connections



ACSC: Advanced Catalyst Synthesis and Characterization
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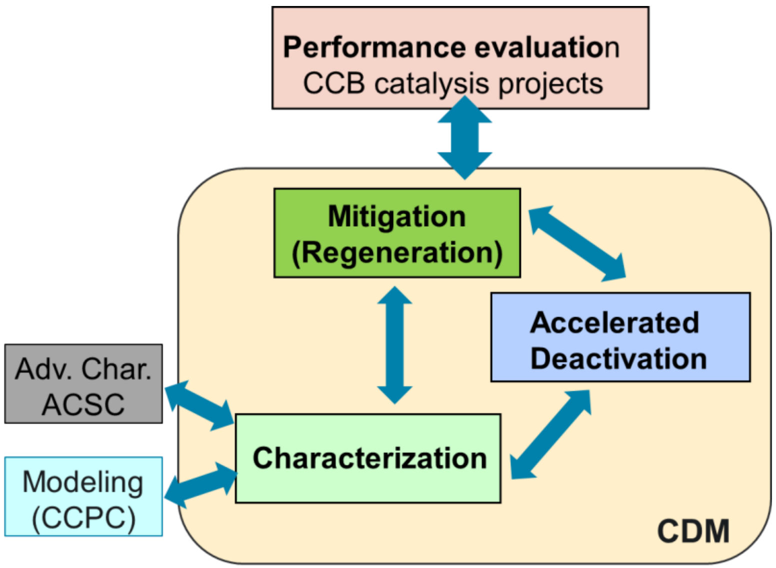
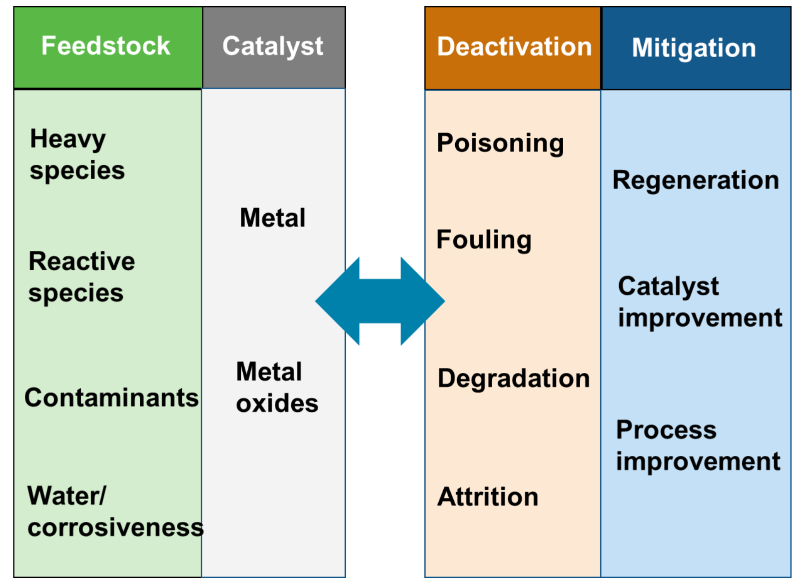
Support CCB projects for catalyst stability improvement



- Pt/TiO_2 catalyst for catalytic fast pyrolysis of woody biomass (NREL, PNNL)
- Ag-ZrO_2/SiO_2 catalyst for ethanol to linear butenes (PNNL)

A document to summarize the connection

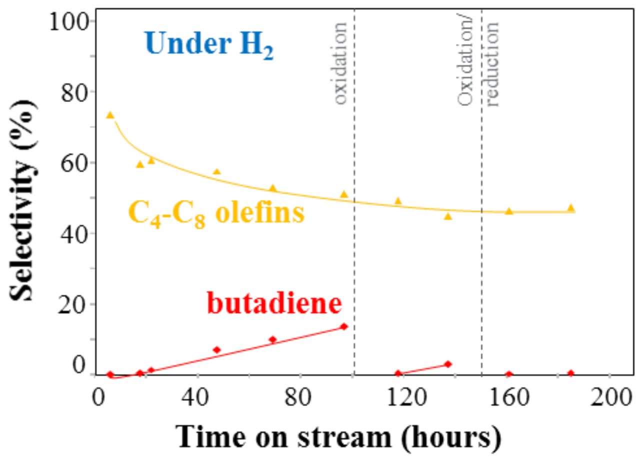


- Bio-oil hydrogenation on Ru catalyst
- Aqueous phase hydration on zeolite
- Oxygenates conversion on zeolite
- Aqueous acid conversion on oxides
- CFP on metal catalysts…

4 – *Relevance* - Addresses catalyst stability issues for BETO CCB catalysis projects

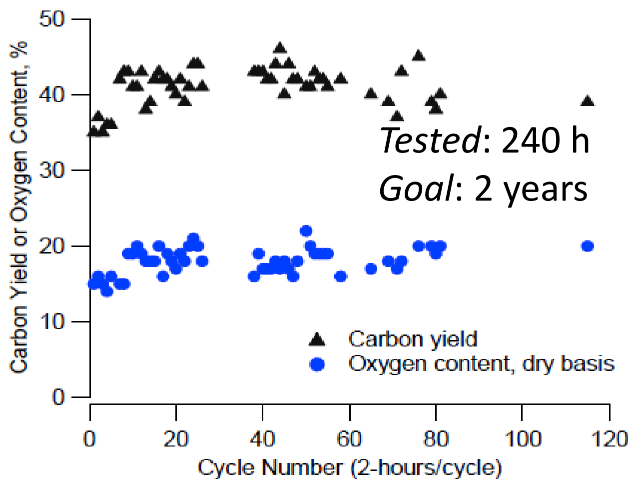
- ***Support BETO*** to address barriers and achieve targets
  - Ct-E. Improving Catalyst Lifetime
- ***Enhance the CCB portfolio***
  - Catalyst deactivation is one of the major challenges and its mitigation is one of critical components for CCB – *CCB Industrial Advisory Board*
  - Achieve cost and risk reduction for the catalytic conversion technologies

Change of product selectivity with TOS of Ag-ZrO_2/SiO_2 catalyst for ethanol to linear butane conversion



IDL

Unclear longer term stability of Pt/TiO_2 catalyst for catalytic fast pyrolysis



CFP

- ***Leverage*** existing applied and fundamental research efforts and industrial supports

4 – Relevance – Provides demanding information on catalyst deactivation and mitigation

- Provide knowledge to ***catalysis R&D communities*** for rational design of robust catalysts
  - "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 Catalysis

Editorial

Cite This: *ACS Catal.* 2018, 8, 8597−8599

pubs.acs.org/acscatalysis

ACS Catal. 2018, 8, 8597

A Matter of Life(time) and Death

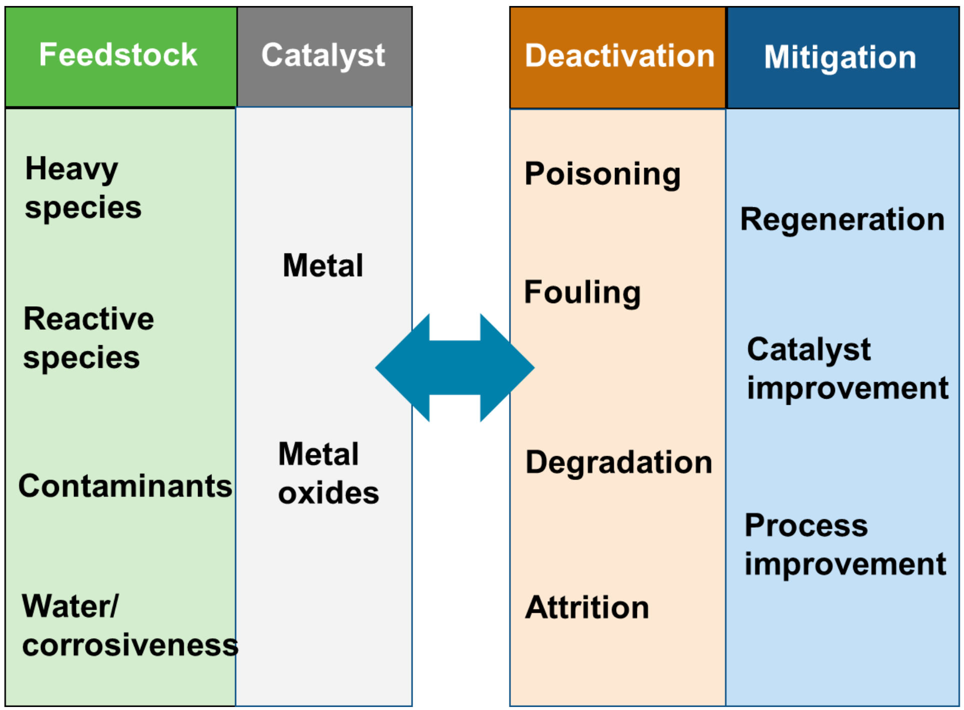
THE CATECHISM

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.[4]

5 – Future Work - We will complete a document summarizing connections



FY19

Q1: Outline and inputs from CCB teams and IAB **(accomplished)**

Q3: Initial draft on at least four catalytic processes

FY20

Additional catalytic processes included

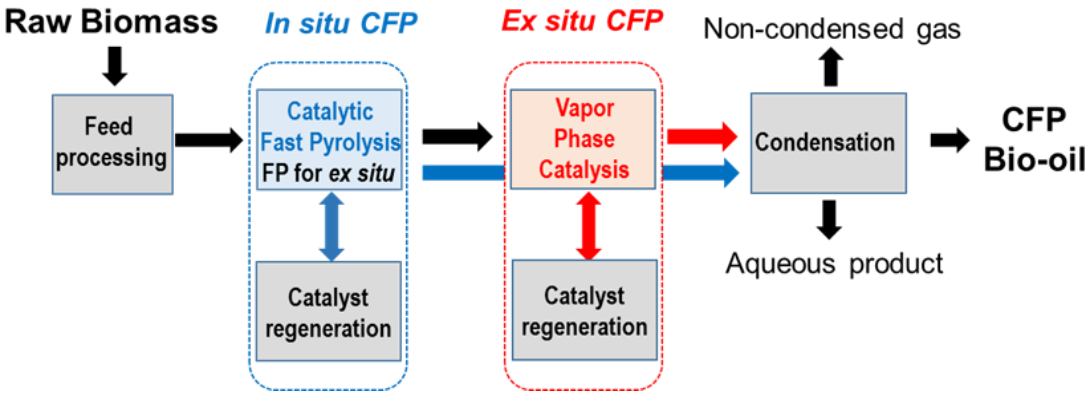
FY21

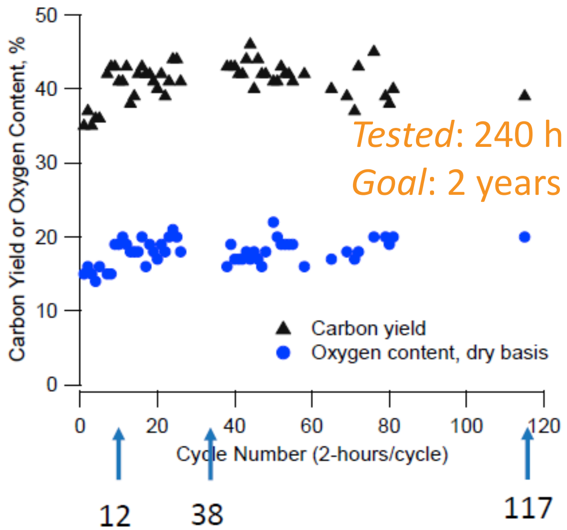
Comprehensive review of current state of knowledge on catalyst deactivation and mitigation in biomass conversion (to be published as a review paper) finished

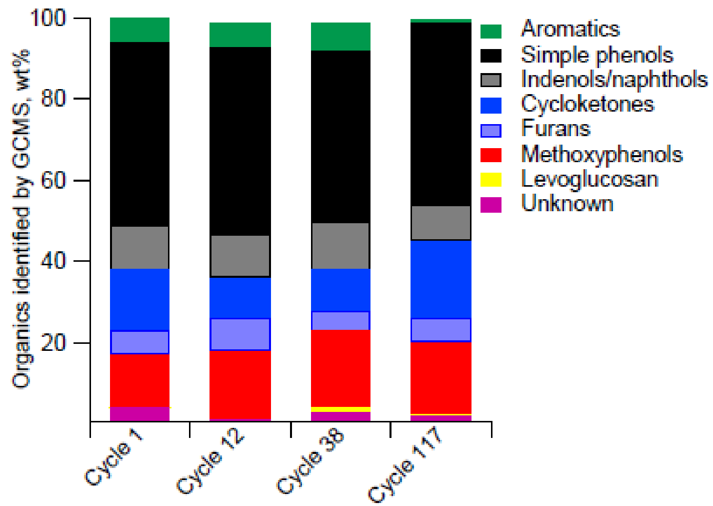
We will share the extracted underlying factors and connections as guidance for more rational catalyst and process design

5 – Future Work - Understanding CFP catalyst deactivation

Target:
Identify the major deactivation mechanism of Pt/TiO_2 catalyst for *ex situ* CFP along the 500 hours TOS testing





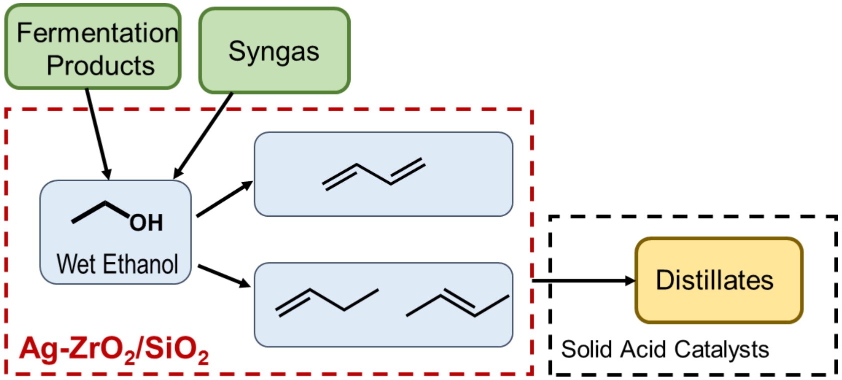


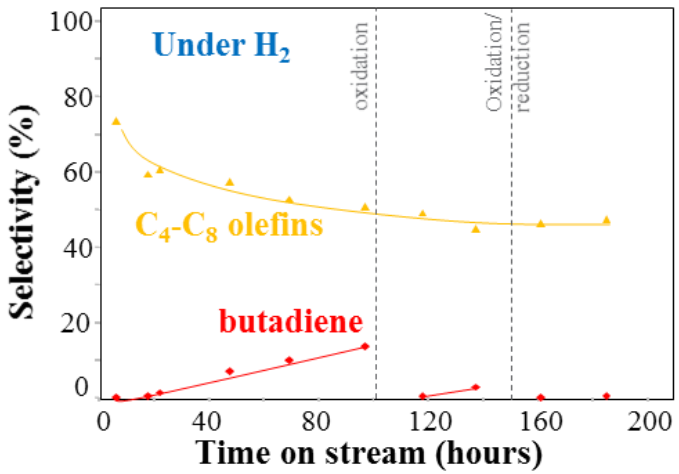
Catalyst deactivation issues: Change of product selectivity with TOS; requirement of frequent regeneration; unclear long-term stability

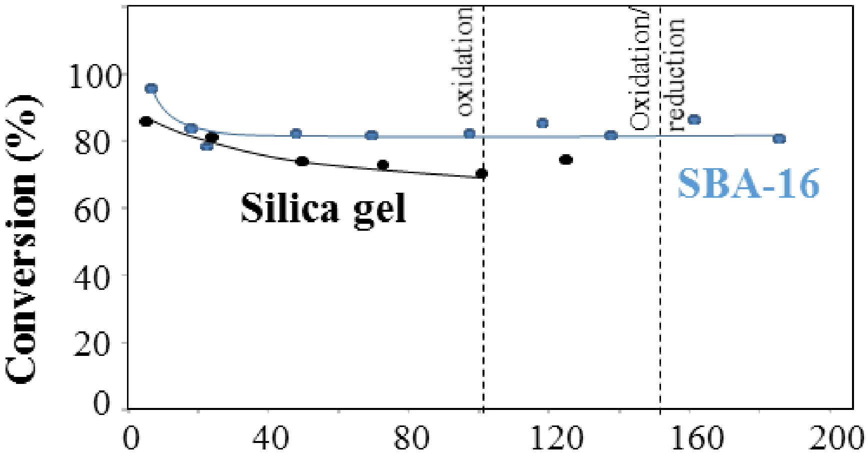
Approach: Identify deactivation mechanism along the 500 hours TOS testing through characterization; develop improved regeneration; develop accelerated deactivation

5 – Future Work - Extending IDL catalyst lifetime

Target:
1. Achieve FY19 IDL milestone on developing a regeneration protocol
2. Demonstrate stability improvement of catalyst: 25% increase of linear butene yield stability







Catalyst deactivation issues: Change of selectivity with TOS; improvement of regeneration required; supports impact stability

Approach: Suggest deactivation mechanism; develop accelerated deactivation; develop improved regeneration

Summary

Overview	Address overarching catalyst deactivation challenges and improve catalyst stability (lifetime) for catalytic conversion of biomass
Approach	• Integrated and collaborative effort within CCB • Share document on understanding catalyst deactivation and mitigation • Improve catalyst lifetime for CCB projects – Hypothesis-driven catalyst deactivation mechanism identification – Accelerated deactivation method development – Catalyst regeneration development
Relevance	• Enable cost and risk reductions of catalysis processes for BETO conversion technologies • Provide demanding knowledge to CCB and catalysis R&D communities for rational design of robust catalysts
Future work	• Complete the document on catalyst deactivation and mitigation – Case studies and established connection between feedstocks, catalyst, deactivation, and mitigation • Improve catalyst lifetime for CCB projects – Extend catalyst lifetime for ethanol to linear butene for IDL – Understand deactivation of Pt/TiO_2 for CFP

Thank you!

- ***BETO:*** Nichole Fitzgerald, Andrea Bailey, Jeremy Leong
- ***PNNL***: Vanessa Dagle, Robert Dagle, Yilin Wang, Michael Thorson, and Asanga Padmaperuma
- ***NREL***: Josh Schaidle
- ***ORNL***: Zhenglong Li

ChemCatBio
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Additional Slides

ChemCatBio
Chemical Catalysis for Bioenergy

Acronyms and abbreviations

ACSC	Advanced Synthesis and Characterization project
ANL	Argonne National Laboratory
BETO	Bioenergy Technologies Office
BES	Basic Energy Science, Office of Science
CCB	Chemical Catalysis for Bioenergy Consortium; ChemCatBio consortium
CCM	Catalyst Cost Model Development project
CCPC	Consortium for Computational Physics and Chemistry
CDM	Catalyst Deactivation Mitigation project
CFP	Catalytic fast pyrolysis
DOE	U.S. Department of Energy
IAB	Industrial Advisory Board
LANL	Los Alamos National Laboratory
LDRD	Laboratory Directed Research and Development
NETL	National Energy Technology Laboratory
NREL	National Renewable Energy Laboratory
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory
WBS	Work breakdown structure

Responses to Previous Reviewers' Comments

- This is a new start for FY19

Publications, Patents, Presentations, Awards, and Commercialization

- This is a new start for FY19