ChemCatBio
Chemical Catalysis for Bioenergy

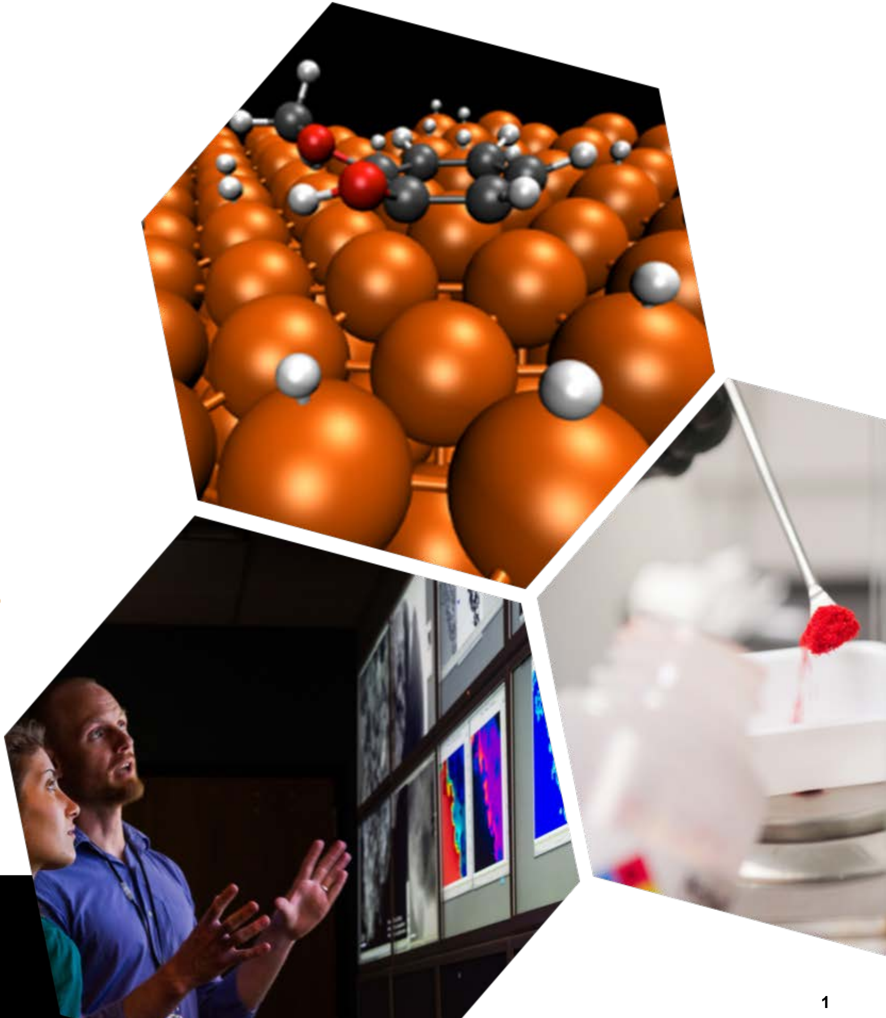
Addressing Unique Catalyst Deactivation Challenges for Converting Biomass-Derived Feedstocks

Huamin Wang

Pacific Northwest National Laboratory

February 19, 2020

Pacific Northwest
NATIONAL LABORATORY

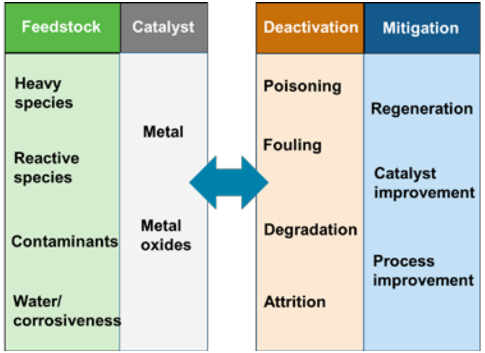


U.S. DEPARTMENT OF ENERGY | Office of ENERGY EFFICIENCY & RENEWABLE ENERGY
BIOENERGY TECHNOLOGIES OFFICE

Catalyst deactivation mitigation for biomass conversion

- **ChemCatBio** is tackling overarching catalysis challenges for biomass conversion, including improving catalyst lifetime
- Biomass derived feedstocks bring new challenges to catalyst longevity
- We present some examples on ChemCatBio’s efforts on understanding and mitigating catalyst deactivation
  - Zeolite and oxide catalysts for aqueous phase reaction
  - Catalysts for pyrolysis vapor/oil upgrading

Catalysis for Biomass Conversion



Feedstock
- Heavy species
- Reactive species
- Contaminants
- Water/ corrosiveness

Catalyst
- Metal
- Metal oxides

Deactivation
- Poisoning
- Fouling
- Degradation
- Attrition

Mitigation
- Regeneration
- Catalyst improvement
- Process improvement

ChemCatBio is a national-lab led R&D consortium dedicated to overcoming catalysis challenges for biomass conversion

- **ChemCatBio** is a node in DOE's Energy Materials Network
- **Our mission** is to accelerate the development of catalysts and related technologies for the commercialization of biomass-derived fuels and chemicals by leveraging unique capabilities of the US DOE national laboratories
- **Our team** comprises over 100 researchers from 7 national labs and has published over 110 peer-reviewed manuscripts in the last 3 years

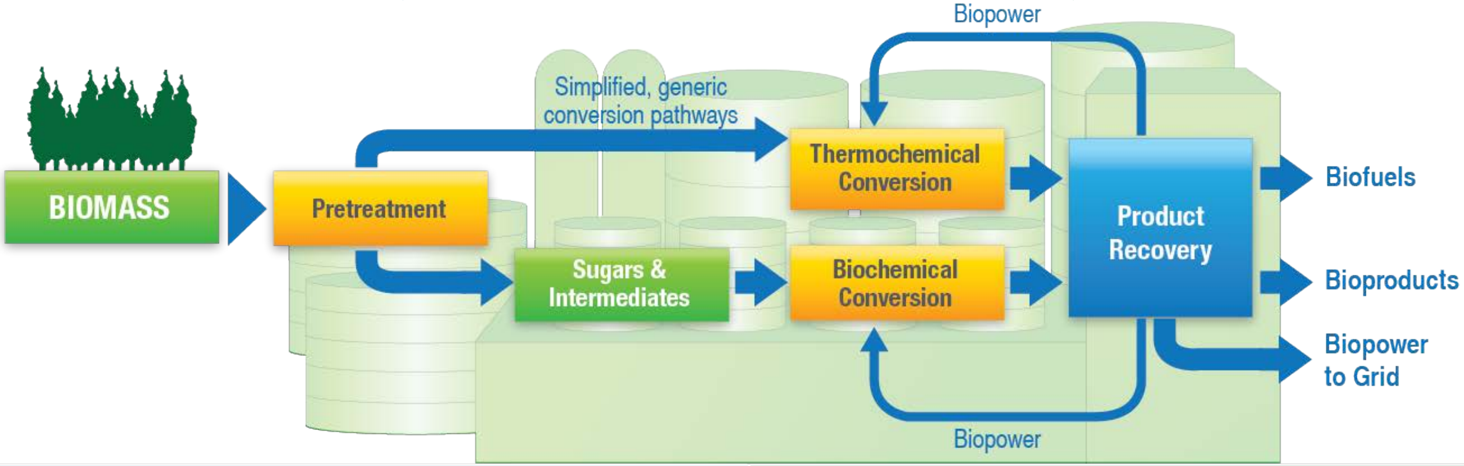
Advanced Synthesis and Characterization

Modeling and Interactive Tools

Multi-Scale Evaluation

Catalysis challenges are pervasive in conversion of biomass and waste feedstocks

Feedstock & Logistics → **Pre-Treatment & Conversion** → **Final Products**



Key Catalytic Bioenergy Processes

- Catalytic Upgrading of Biological Intermediates
- Synthesis Gas Upgrading
- Catalytic Fast Pyrolysis
- Catalytic Upgrading of Aqueous/Gaseous Waste Streams
- Catalytic Hydroprocessing
- Lignin Deconstruction and Upgrading

Challenges due to Biomass Composition

- High oxygen content → Broad reaction space
- Diverse chemical functionalities → Competing reactions
- High water content → Degradation of catalyst supports
- Impurities (S, N, alkali metals, Cl, etc.) → Poisoning
- Multiple states and compositions (solid, liquid, or gas)
- Complex, heterogeneous mixture → Difficult to model

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.%

G. Lange, Angew. Chem. Int. Ed. 2015, 54, 13186

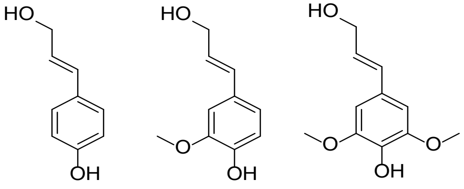
- Among the three performance metrics, stability is usually the least explored, and the factors that cause catalysts to die are the least understood, at a fundamental level…
- Mechanistic understanding of catalyst deactivation and developing strategies to extend catalyst lifetime are vital to the success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

S. Scott, ACS Catal. 2018, 8, 8597

Biomass derived feedstocks bring new challenges to catalyst longevity

Compared to fossil, most biomass derived feedstocks are

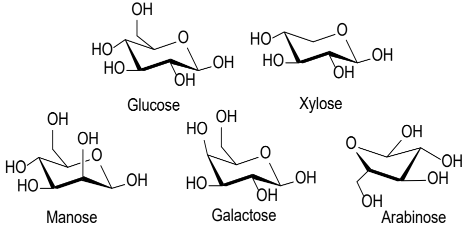
- Complex, highly functionalized, unstable
- Containing contaminates (from biomass or processing unit)
    - S, N containing species
    - Ca, K, Mg, Na, Si, Fe, Cr…
- Requiring polar/aqueous and corrosive conditions



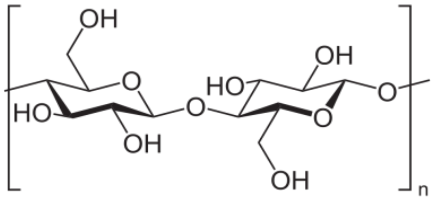
p-Coumaryl alcohol

Coniferyl alcohol

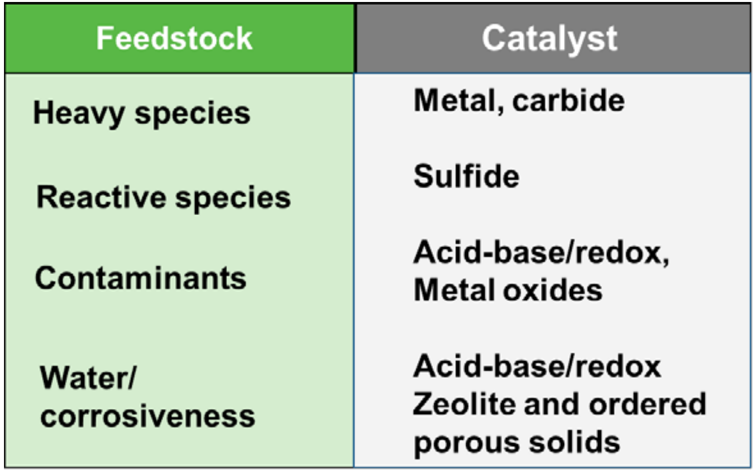
Sinapyl alcohol



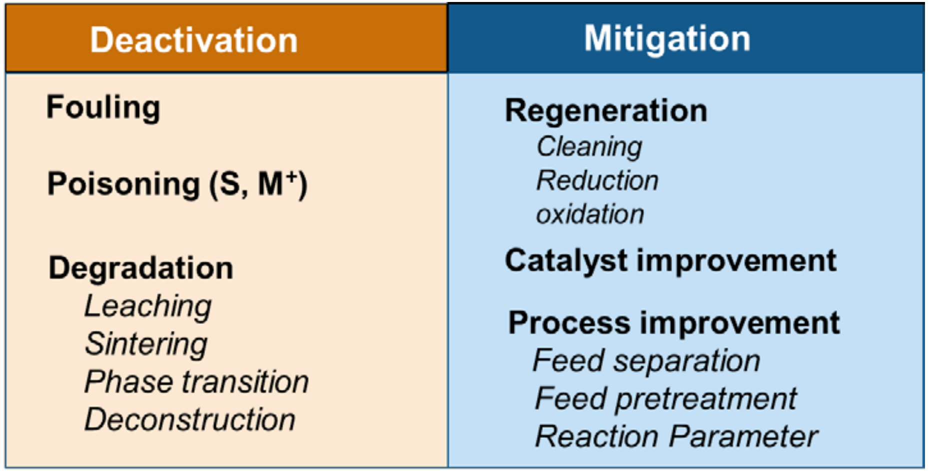
Catalyst deactivation and reactor plugging of pyrolysis oil hydrotreating



Connections between feedstock and catalyst with deactivation and mitigation helps the development of robust catalytic process

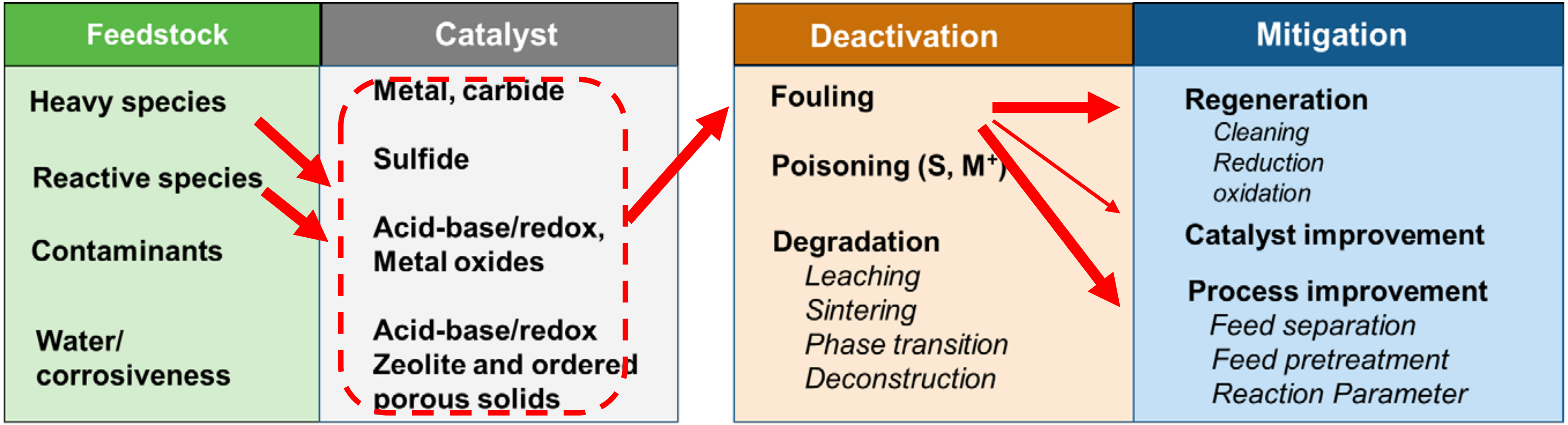


Feedstock	Catalyst
Heavy species	Metal, carbide
Reactive species	Sulfide
Contaminants	Acid-base/redox, Metal oxides
Water/ corrosiveness	Acid-base/redox Zeolite and ordered porous solids



Deactivation	Mitigation
Fouling **Poisoning (S, M^+)** **Degradation** *Leaching* *Sintering* *Phase transition* *Deconstruction*	**Regeneration** *Cleaning* *Reduction* *oxidation* **Catalyst improvement** **Process improvement** *Feed separation* *Feed pretreatment* *Reaction Parameter*

Fouling of catalyst by heavy species and its potential mitigation



Feedstock

Heavy species

Reactive species

Contaminants

Water/ corrosiveness

Catalyst

Metal, carbide

Sulfide

Acid-base/redox, Metal oxides

Acid-base/redox Zeolite and ordered porous solids

Deactivation

Fouling

Poisoning (S, M^+)

Degradation
- *Leaching*
- *Sintering*
- *Phase transition*
- *Deconstruction*

Mitigation

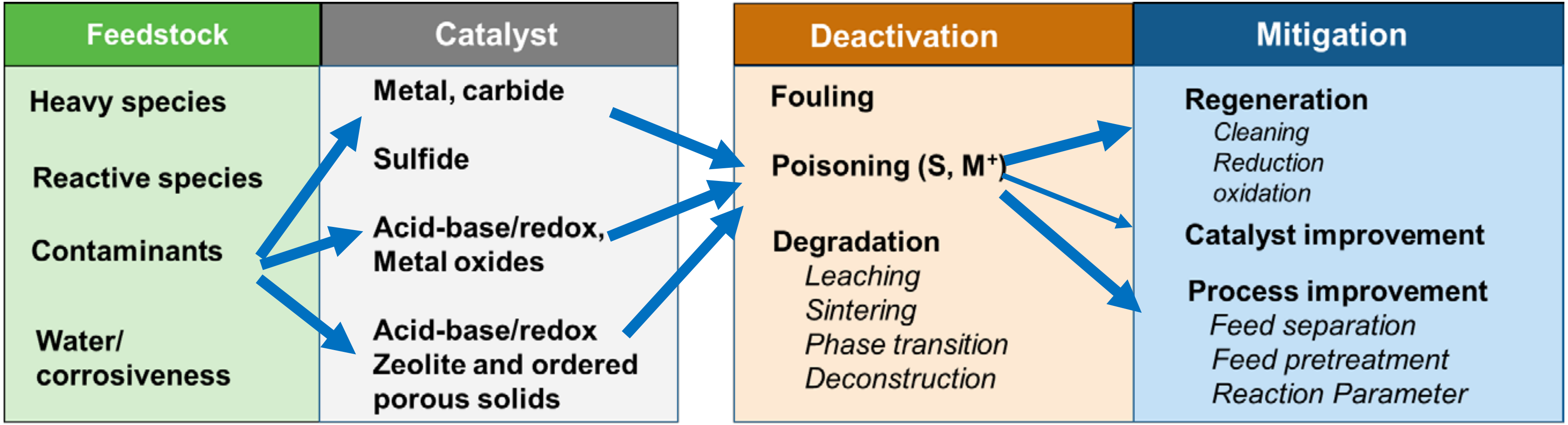
Regeneration
- *Cleaning*
- *Reduction*
- *oxidation*

Catalyst improvement

Process improvement
- *Feed separation*
- *Feed pretreatment*
- *Reaction Parameter*

- Bio-oil hydrogenation – Ru/TiO_2 – fouling by heavy species – Regen. by cleaning
- HMF to FDCA – metal – fouling by FDCA – special solvents or base
- CFP – zeolite – fouling by condensation products / coke – regen. by oxidation
- Bio-oil hydrotreating – sulfides – fouling by condensation products – bio-oil stabilization
- Aqueous ketonization – ZrO_2 – fouling by HMW from sugar – separation or regeneration

Poisoning of catalyst by sulfur or inorganics and its potential mitigation



Feedstock

Heavy species

Reactive species

Contaminants

Water/ corrosiveness

Catalyst

Metal, carbide

Sulfide

Acid-base/redox, Metal oxides

Acid-base/redox Zeolite and ordered porous solids

Deactivation

Fouling

Poisoning (S, M^+)

Degradation
  Leaching
  Sintering
  Phase transition
  Deconstruction

Mitigation

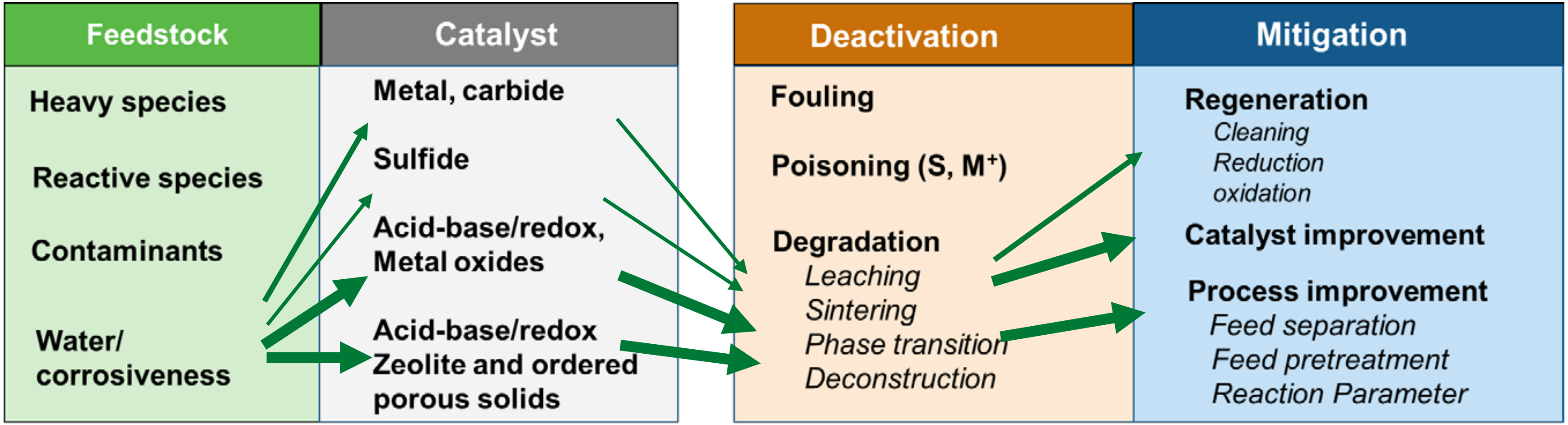
Regeneration
  Cleaning
  Reduction
  oxidation

Catalyst improvement

Process improvement
  Feed separation
  Feed pretreatment
  Reaction Parameter

- Bio-oil hydrogenation – Ru/TiO_2 – poisoning by S – cleaning
- HTL Aqueous product CHG – Ru catalyst – poisoning by S – guard bed for S removal
- Xylose to furfural – zeolite – poisoning by inorganics – feed cleaning and catalyst acid wash
- Catalytic fast pyrolysis – zeolite – poisoning by inorganics –catalyst acid wash

Liquid water causes significant issues of catalyst degradation



Feedstock

Heavy species

Reactive species

Contaminants

Water/ corrosiveness

Catalyst

Metal, carbide

Sulfide

Acid-base/redox, Metal oxides

Acid-base/redox Zeolite and ordered porous solids

Deactivation

Fouling

Poisoning (S, M^+)

Degradation
Leaching
Sintering
Phase transition
Deconstruction

Mitigation

Regeneration
Cleaning
Reduction
oxidation

Catalyst improvement

Process improvement
Feed separation
Feed pretreatment
Reaction Parameter

- Aqueous hydrogenation – Ni/TiO_2 – $Ni(OH)_2$ formation – catalyst surface hydrophobization
- Aqueous hydrogenation – Cu/Al_2O_3 – Cu leaching – overcoat by ALD
- Aqueous ketonization – ZrO_2 – phase transition – La doped ZrO_2
- Aqueous dehydration – zeolite – deconstruction

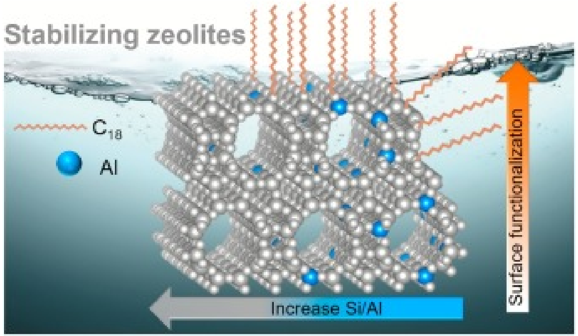
Catalyst stability improvement for aqueous phase reactions

- Stability of zeolite in aqueous phase

  Sebastian Prodinger, Mirek Derewinski, Huamin Wang, Hui Shi, Johannes Lercher

  PNNL MS^3 and CTI LDRD

  S. Prodinger et al., J. Am. Chem. Soc. 2016, 138, 4408
  S. Prodinger, H. Wang, et al., Appl. Catal. B, 2018, 237, 996

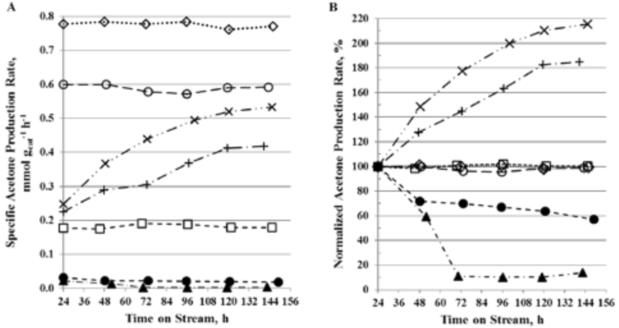


- Enhanced Hydrothermal Stability of ZrO_2 for the Ketonization of Acetic Acid in the Aqueous Condensed Phase

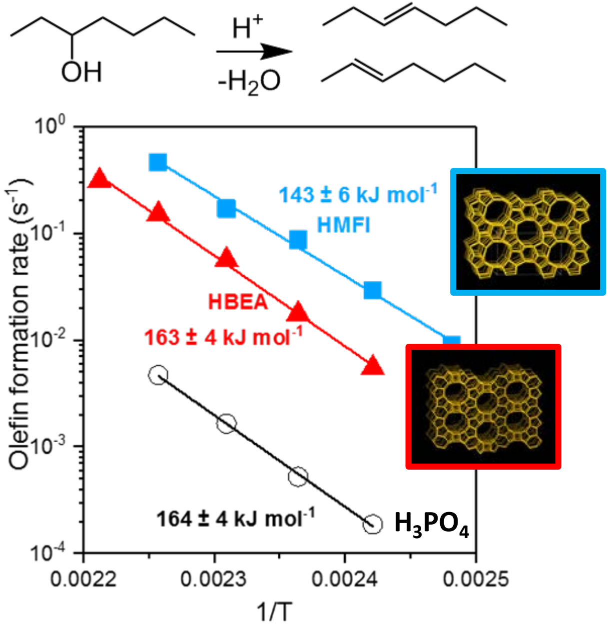
  Juan Lopez-Ruiz, Alan Cooper, and Karl Albrecht

  BETO-*ChemCatBio - Aqueous phase upgrading*

  J. Lopez-Ruiz, et al., ACS Catalysis, 2017, 7, 6400



Zeolites show much improved activity in liquid water by confinement but have stability issue



- H_3O^+ in confines showed much higher dehydration rate in liquid water

H. Shi, Nature Comm., 2017, 8, 15442
M. Shtty, H. Wang, in preparation

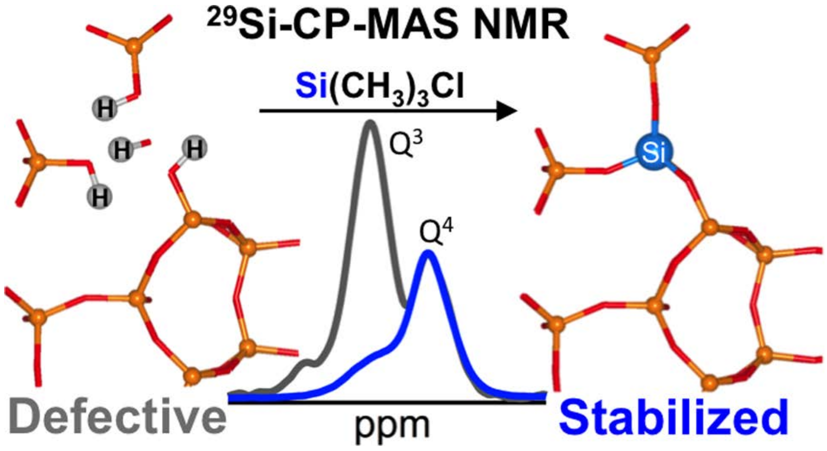
BEA zeolite before and after treatment in liquid water at 160 °C

Sample	BET, m^2/g	V micropore, cm^3/g	V mesopore, cm^3/g
BEA14	585	0.23	0.05
BEA14 + H_2O	235	0.09	0.08

- Hydrolysis of zeolite framework and partial dissolution of the crystal in liquid water causes deconstruction

S. Prodinger et al., J. Am. Chem. Soc. 2016, 138, 4408

Silanol defect is the cause for structural instability of zeolites in hot liquid water



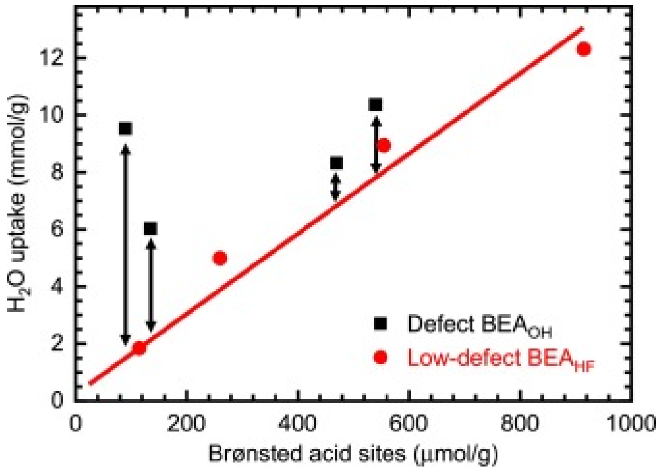
BEA zeolite before and after treatment in liquid water at 160 °C

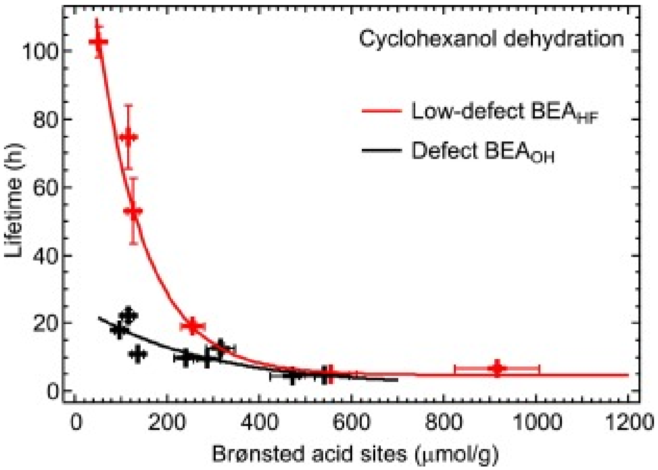
Sample	BET, m^2/g	V micropore, cm^3/g	V mesopore, cm^3/g
BEA14	585	0.23	0.05
BEA14 + H_2O	235	0.09	0.08
BEA14-Si	300	0.12	0.02
BEA14-Si + H_2O	255	0.10	0.18

- Internal silanol defects are known to be the primary active sites for framework hydrolysis.
- The silylation treatment improve material stability in hot liquid water and retain of crystallinity and micro-porosity

S. Prodinger et al., J. Am. Chem. Soc. 2016, 138, 4408

The concentration of intraporous water is directly related to the rate of hydrolysis of zeolite framework

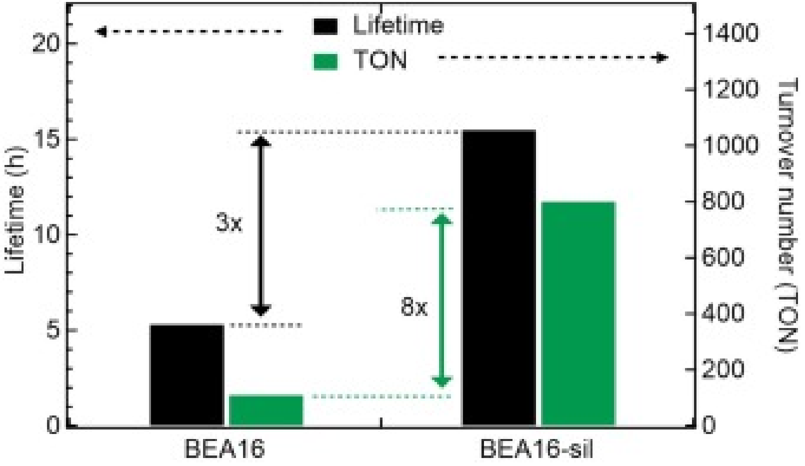


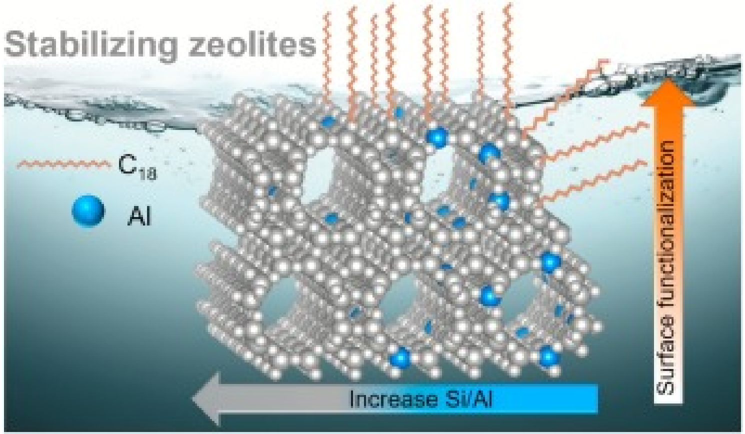


- Reduction of the pore concentration of water is also the key to stabilizing a zeolite for aqueous phase catalysis
- The concentration of Bronsted acid sites (therefore hydrated hydronium ions) is the most important parameter determining the concentration of water in the zeolite pores
- The concentration of defect is only important at low concentrations of hydronium ions

S. Prodinger, H. Wang, et al,. Appl. Catal. B, 2018, 237, 996

External hydrophobization can further improve zeolite stability in liquid water





- External hydrophobization led to an improved lifetime and activity, presumably by retarding the diffusion of liquid water into the pores

S. Prodinger, H. Wang, et al,. Appl. Catal. B, 2018, 237, 996

The tool box:

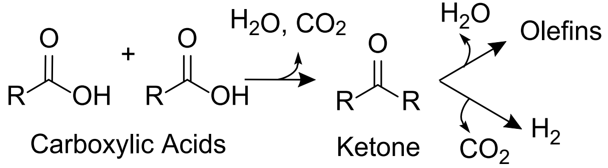
- Lower defect density by synthesizing in F^-
- Lower water in pore by tuning Si/Al ratio and external hydrophobicity

ChemCatBio will leverage this knowledge for developing stable catalyst for upgrading biologically derived intermediates in liquid phase

Stable ZrO_2 catalysts enable direct catalytic upgrading of aqueous carboxylic acids

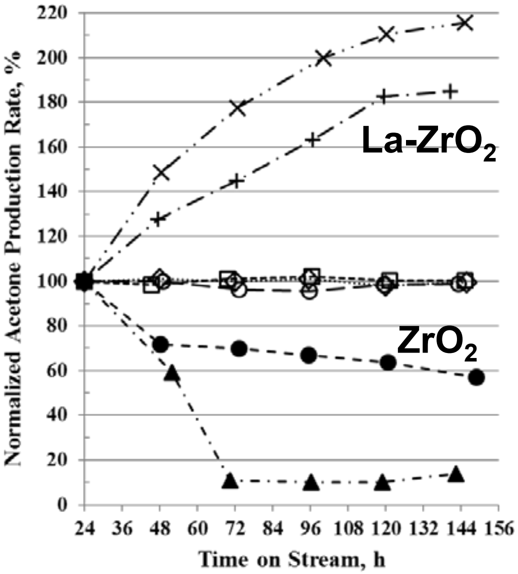
Hydrothermal liquefaction (HTL)

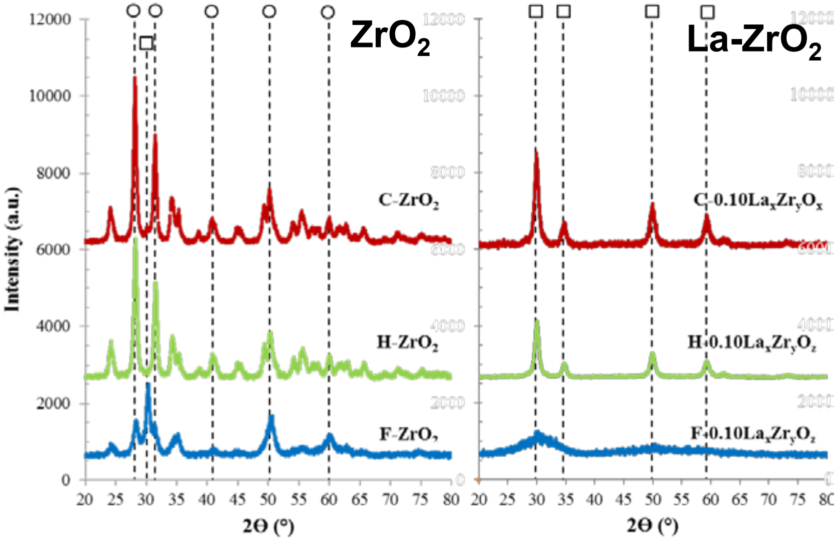
Aqueous products



Ketonization + Reduction + Dehydration

Steam Reforming

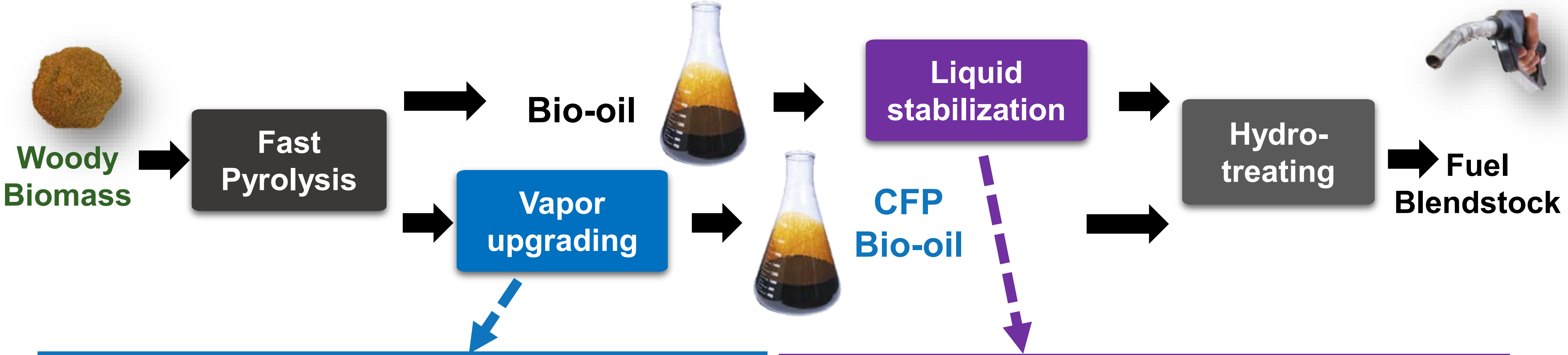




- Irreversible stabilization of the tetragonal ZrO_2 phase by La enable much improved stability of catalyst for condensed phase ketonization

J. Lopez-Ruiz, et al., ACS Catalysis, 2017, 7, 6400

Catalyst stability improvement for upgrading complex pyrolysis vapor and liquid



- Catalytic fast pyrolysis (CFP) catalyst deactivation mechanism determination

  Huamin Wang, Fan Lin, Mike Griffin (NREL), Susan Habas (NREL), Josh Schaidle (NREL), Kinga Unocic (ORNL)

  BETO- ChemCatBio – CDM&CFP&ACSC

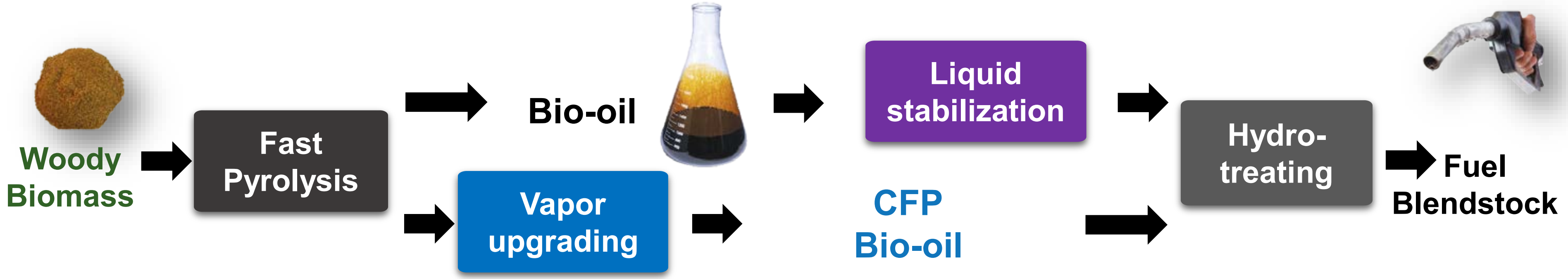
- Fast pyrolysis oil stabilization catalyst lifetime improvement

  Huamin Wang, Mariefel Olarte, John Frye, Sue-Jane Lee, Miki Santosa, Alan Zacher, Jae-Soon Choi (ORNL)

  BETO – ChemCatBio – Fast pyrolysis

***ACSC:** Advanced Catalyst Synthesis and Characterization*

Bio-oil quality improvement by catalytic processes enable hydrotreating to produce a hydrocarbon fuel blendstock


Woody Biomass

Fast Pyrolysis

Bio-oil

Vapor upgrading

Liquid stabilization

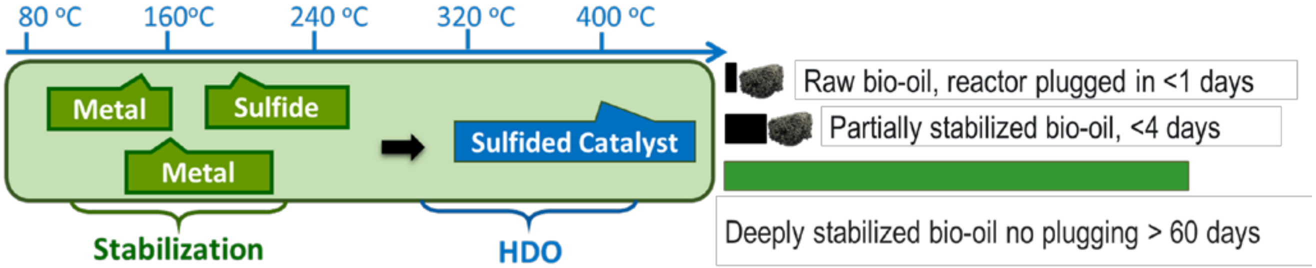
CFP Bio-oil

Hydro-treating

Fuel Blendstock

- Fast pyrolysis with upgrading has great potential for whole biomass conversion to drop-in hydrocarbon fuel at high yields
- Instability of fast pyrolysis bio-oil is the biggest challenge for bio-oil upgrading
- Bio-oil quality improvement enables direct hydrotreating
    - Bio-oil stabilization by low temperature hydrogenation
    - Pyrolysis vapor catalytic upgrading (CFP: catalytic fast pyrolysis)

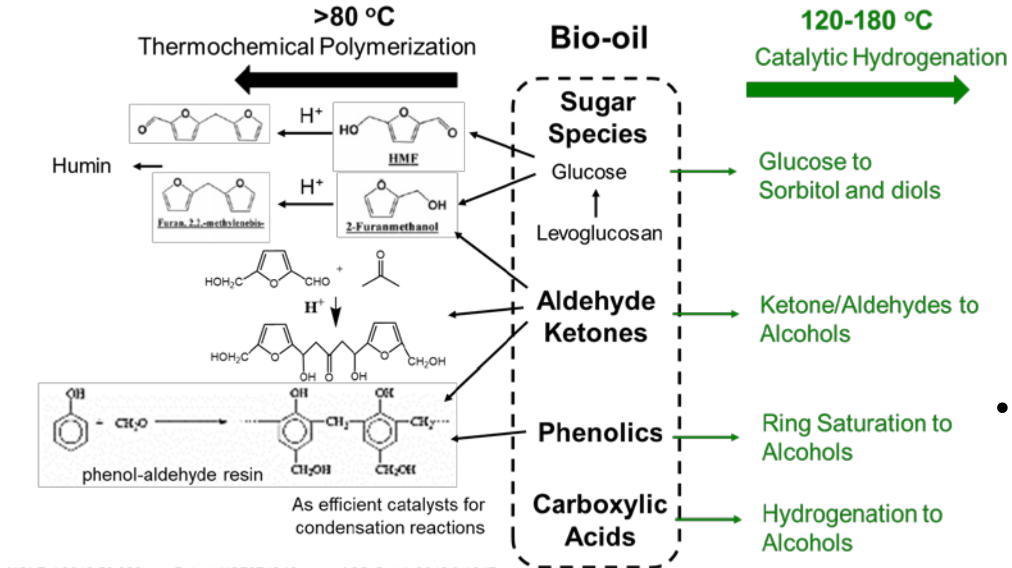
Fast pyrolysis bio-oil stabilization by hydrogenation using Ru catalyst enables its single-step hydrotreating



Raw bio-oil, reactor plugged in <1 days

Partially stabilized bio-oil, <4 days

Deeply stabilized bio-oil no plugging > 60 days



>80 °C

Thermochemical Polymerization

Humin

phenol-aldehyde resin

As efficient catalysts for condensation reactions

Bio-oil

Sugar Species

Glucose

Levoglucosan

Aldehyde Ketones

Phenolics

Carboxylic Acids

120-180 °C

Catalytic Hydrogenation

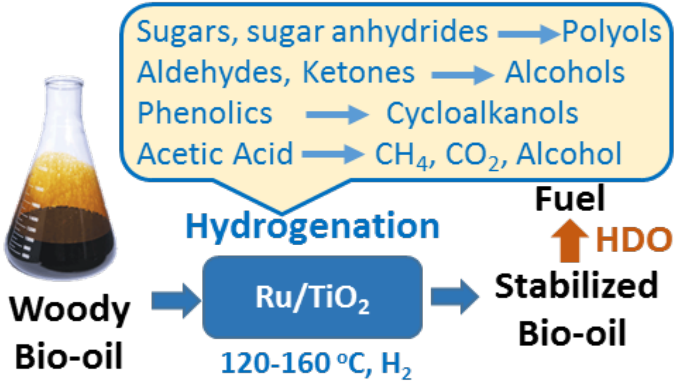
Glucose to Sorbitol and diols

Ketone/Aldehydes to Alcohols

Ring Saturation to Alcohols

Hydrogenation to Alcohols

AIChE J 2013 59 888. Patent US7671246. ACS Catal. 2013 3 1047.



Sugars, sugar anhydrides → Polyols

Aldehydes, Ketones → Alcohols

Phenolics → Cycloalkanols

Acetic Acid → CH_4, CO_2, Alcohol

Hydrogenation

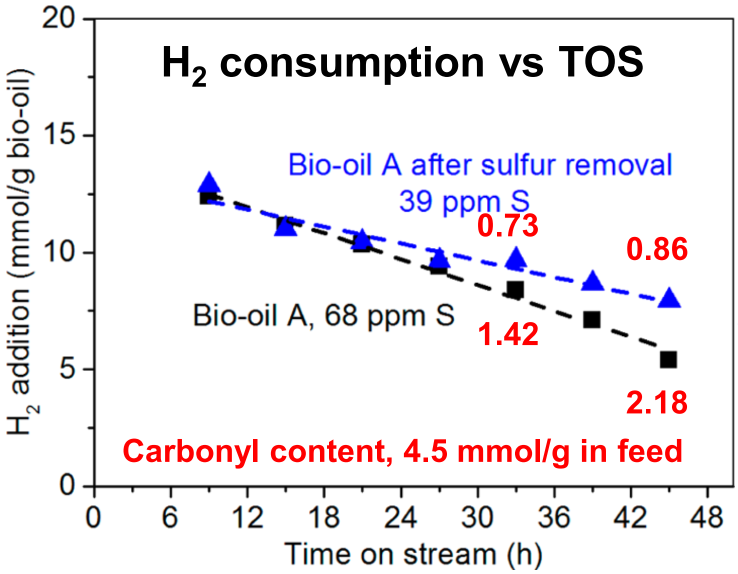
Woody Bio-oil → **Ru/TiO_2** → **Stabilized Bio-oil** → **HDO** → **Fuel**

120-160 °C, H_2

- Hydrogenation of reactive carbonyl species stabilize the bio-oil and Ru catalyst is identified at an efficient catalyst

H. Wang et al., ACS Sus. Chem. Eng., 2016, 4, 5533

Sulfur poisoning and “coke” formation cause deactivation of Ru catalyst for bio-oil hydrogenation



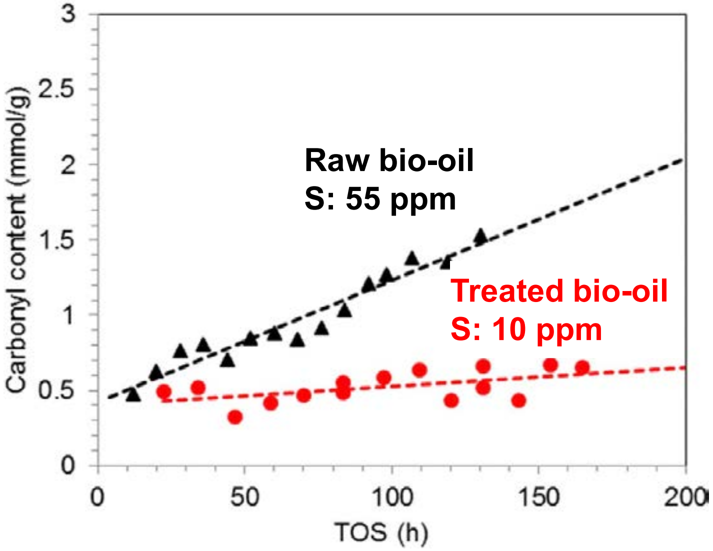
	S content (ppm)	Carbon content (wt.%)
Fresh	N.D.	N.D.
Bio-oil - 39 ppm S	1436	5.5
Bio-oil – 68 ppm S	2169	6.3

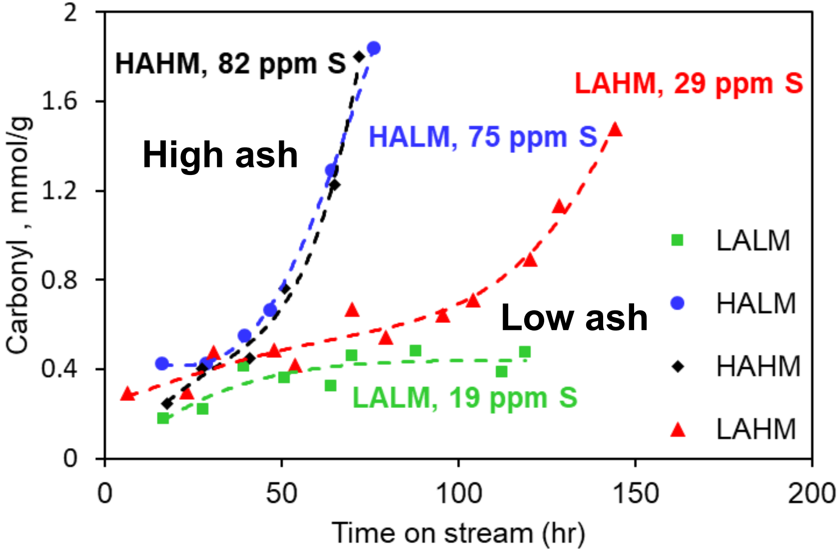
- Sulfur poisoning is the major deactivation mode
- Polymer formation (“coke”) also contributes to catalyst deactivation as a secondary deactivation mode - over a sulfur poisoned catalyst
  - Carbon species formation and surface area decrease on spent catalysts

H. Wang et al., ACS Sus. Chem. Eng., 2016, 4, 5533 *A. Zacher et al., Biomass and Bioenergy, 2019, 125, 151*

Lowering sulfur content in bio-oil enables improved catalyst stability for its hydrogenation

Carbonyl content vs TOS





FCIC

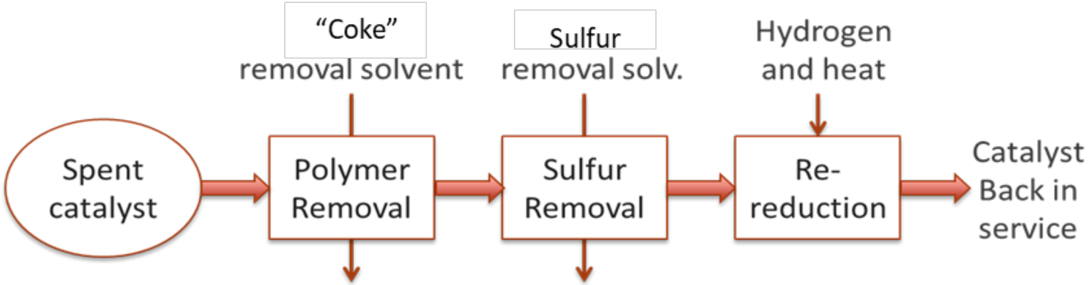
- Lower sulfur content in bio-oil can be achieved by
  - Bio-oil pretreatment over a base metal catalyst
  - Biomass feedstock control

***FCIC:** Feedstock-Conversion Interface Consortium*

A. Zacher et al., Biomass and Bioenergy, 2019, 125, 151

J. Klinger et al., ACS Sus. Chem. Eng., 2020, online

Catalyst regeneration extends lifetime of Ru catalyst for bio-oil hydrogenation



“Coke” removal solvent

Sulfur removal solv.

Hydrogen and heat

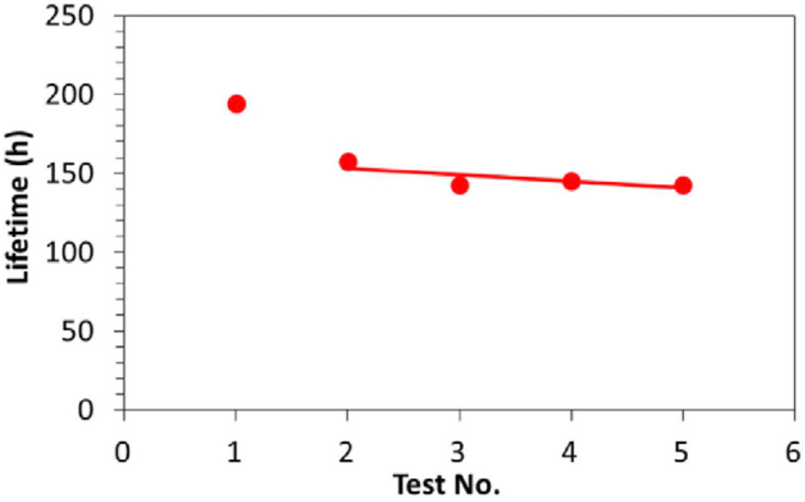
Spent catalyst

Polymer Removal

Sulfur Removal

Re-reduction

Catalyst Back in service

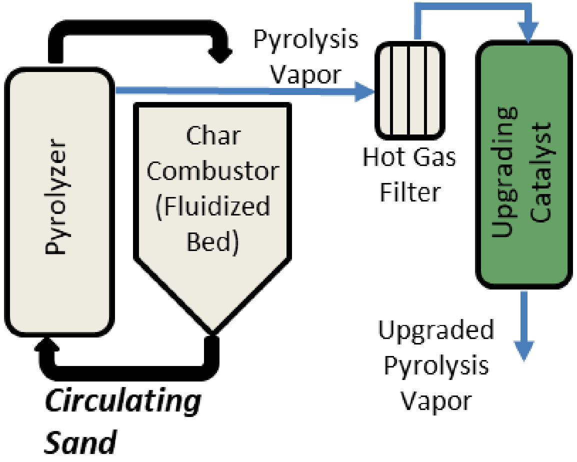


- A regeneration protocol which could remove sulfur and “coke” and therefore regenerate the catalyst was demonstrated over a oak bio-oil
- A multiple reactor system was proposed to enable improved catalyst lifetime
- Further development is required to apply this method for other bio-oils

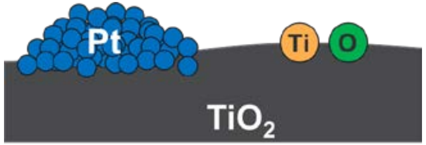
A. Zacher et al., Biomass and Bioenergy, 2019, 125,

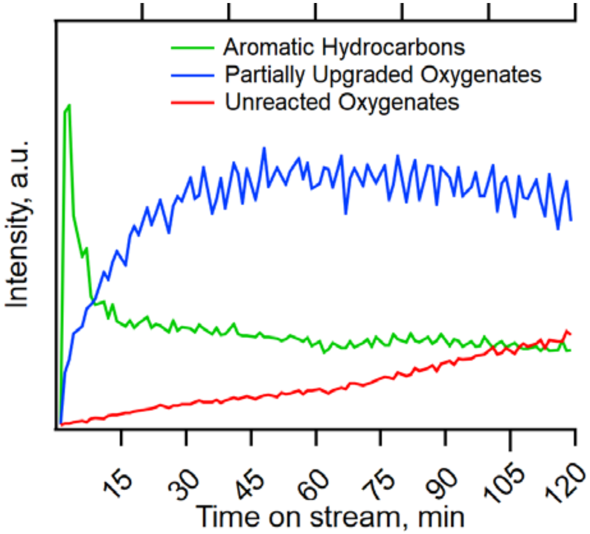
Robust catalyst is the key for *ex situ* fixed bed CFP

Ex-situ Fixed Bed CFP


Pyrolyzer
Pyrolysis Vapor
Char Combustor (Fluidized Bed)
Hot Gas Filter
Upgrading Catalyst
Upgraded Pyrolysis Vapor
Circulating Sand

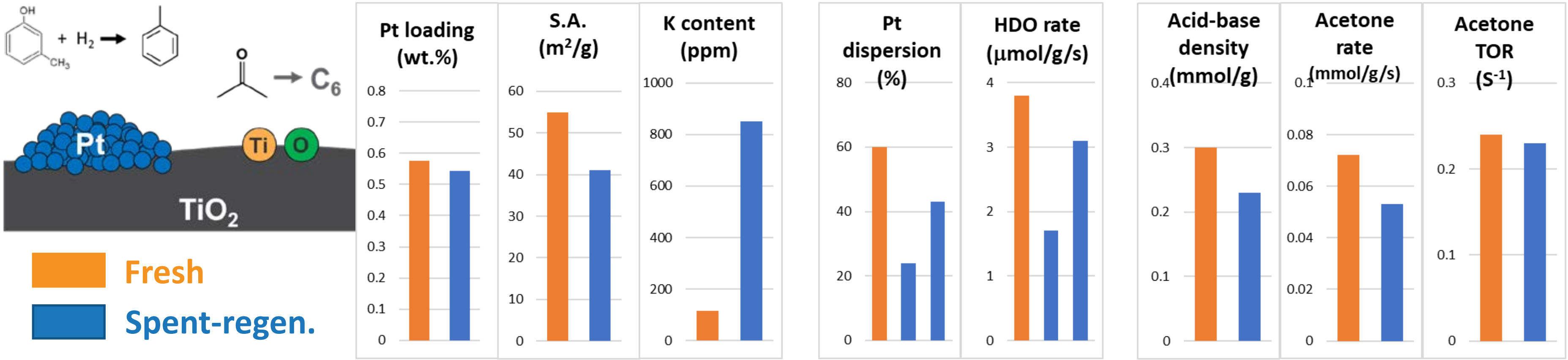
Bifunctional catalyst





- *Ex situ* fixed bed CFP enables more diverse catalysts and chemistry and requires long catalyst lifetime
- Understanding the deactivation mechanism of Pt/TiO_2 catalyst is critical to reach catalyst lifetime target

The change of a Pt/TiO_2 after a 200 h CFP testing was probed by combining detailed characterization with kinetic study



👍 Active sites and activity largely maintained and sulfur not found

? K accumulation

? Dynamic Pt particles

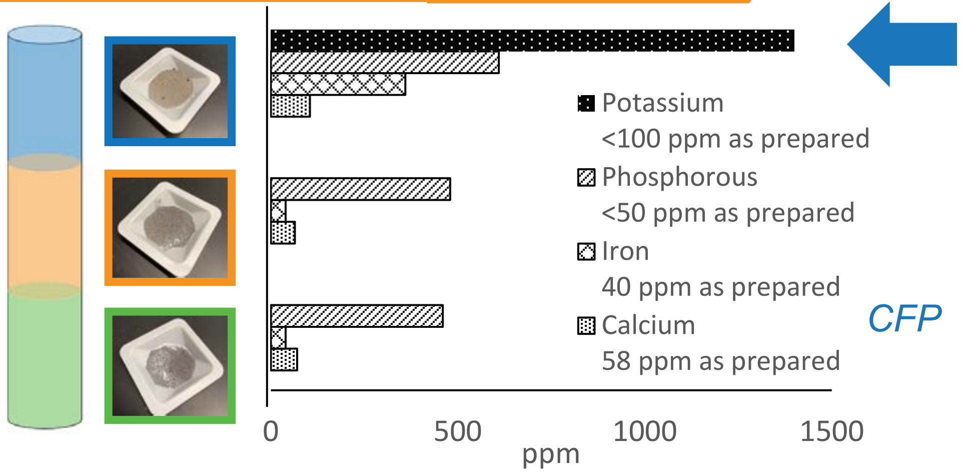
👎 Loss of surface area and acid base sites

- Change of Pt particle size and accumulation of K could potentially impact catalyst long-term stability

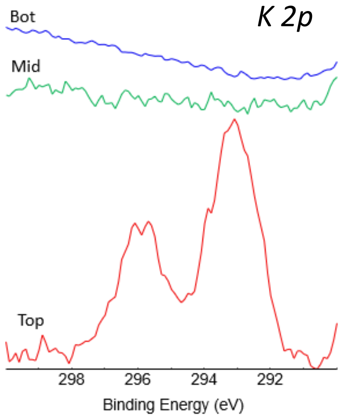
K accumulation on catalysts is widely observed in *in situ* and *ex situ* CFP and hydropyrolysis

Elemental analysis of post-reaction Pt/TiO_2 indicates K deposition on the leading edge of the catalyst bed:

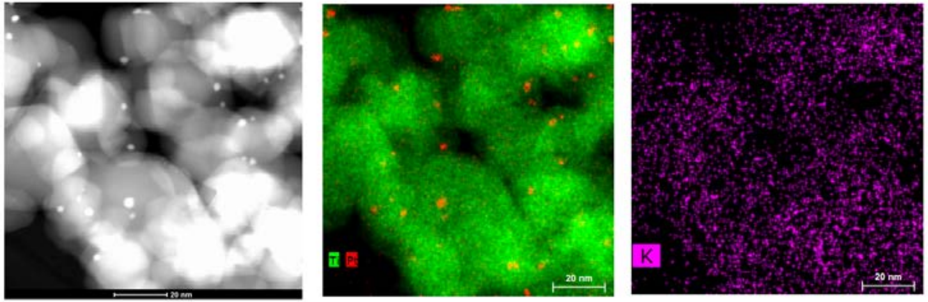
1. How is K distributed at the atomic scale
2. What is the impact on catalyst performance



CFP



XPS data confirms K deposition on the leading edge of the catalyst bed. (ACSC)

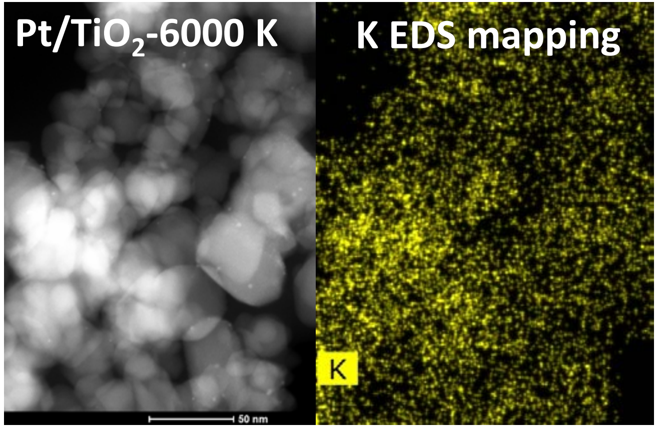


Preliminary EDS-STEM imaging suggests a uniform distribution of K across catalyst surface. (ACSC)

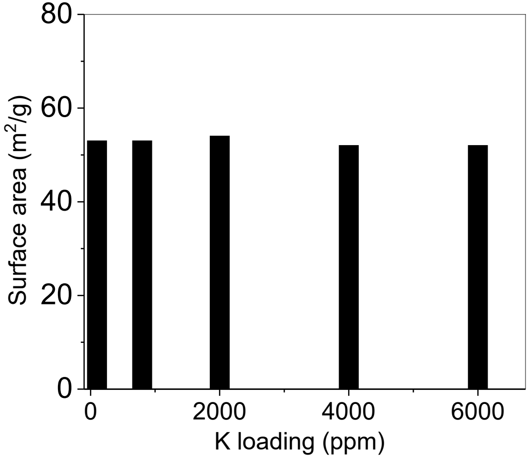
Consequence of K accumulation on catalytic activity of CFP catalysts was evaluated

Controlled deposition of K with various loading over Pt/TiO_2 for characterization and evaluation

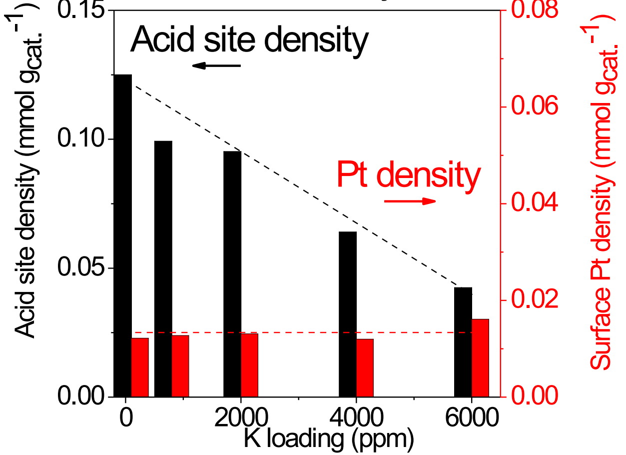
STEM



Surface area



Site density

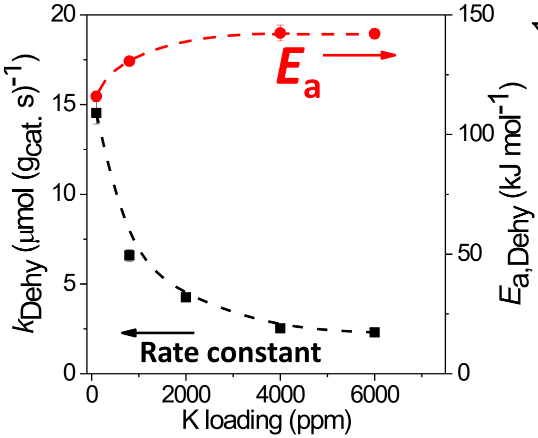


- K is uniformly distributed over catalyst surface
- K influences acid sites rather then metal sites

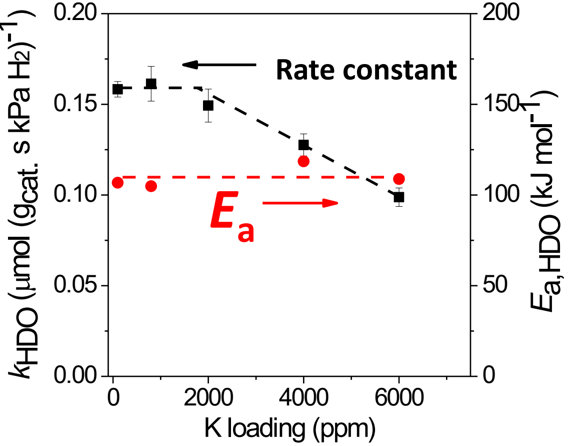
Consequence of K accumulation on catalytic activity of CFP catalysts was evaluated

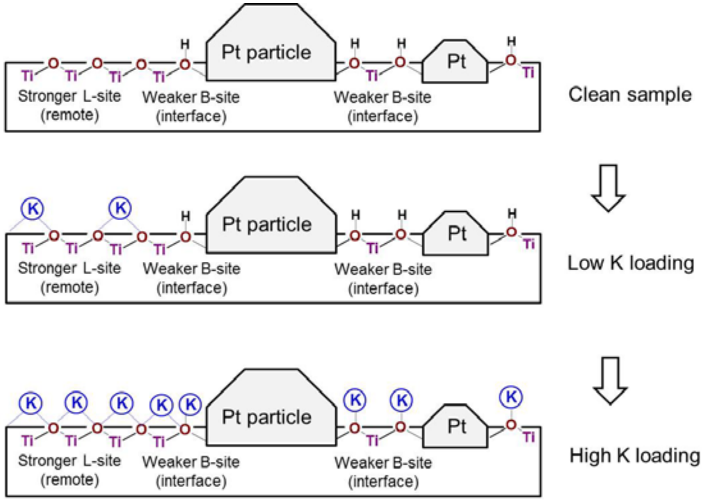
Controlled deposition of K with various loading over Pt/TiO_2 for characterization and evaluation

Tert-butyl-alcohol dehydration



Cresol HDO



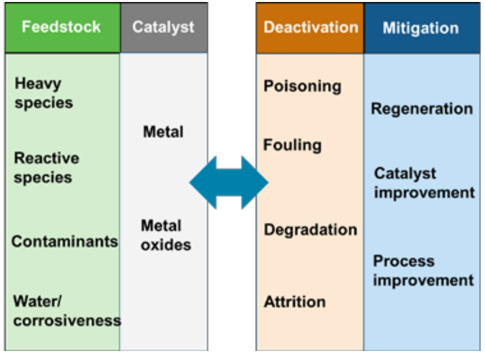


- Interaction of K with active sites depends on K loading and leads to different catalytic consequence
- Enabling catalyst performance prediction with TOS and catalyst regeneration development

Summary

- **ChemCatBio** is tackling overarching catalysis challenges for biomass conversion, including improving catalyst lifetime
- Biomass derived feedstocks bring new challenges to catalyst longevity
- Examples on ChemCatBio's efforts on understanding and mitigating catalyst deactivation
  - Modification of zeolite and oxide catalysts enable improved stability for aqueous phase reaction
  - Sulfur managing and catalyst regeneration extend Ru catalyst lifetime for bio-oil stabilization
  - Foundational understanding of deactivation mechanism, especially impact of inorganics, of Pt/TiO_2 CFP catalyst could lead to process and catalyst lifetime improvement

Catalysis for Biomass Conversion



Feedstock
Heavy species
Reactive species
Contaminants
Water/ corrosiveness

Catalyst
Metal
Metal oxides

Deactivation
Poisoning
Fouling
Degradation
Attrition

Mitigation
Regeneration
Catalyst improvement
Process improvement

Acknowledgements

ChemCatBio
Chemical Catalysis for Bioenergy

Energy Materials Network
U.S. Department of Energy

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Bioenergy Technologies Office

Nichole Fitzgerald Andrea Bailey

PNNL

F. Lin
D. Santosa
J. Frye
S. Lee
Y. Wang
I. Kutnyakov
J. Lopez-Ruiz
A. Cooper
K. Albrecht
M. Olarte

S. Prodinger
M. Derewinski
H. Shi
J. Lercher
A. Zacher
A. Padmaperuma
C. Drennan
D. Elliott
R. Orth

NREL

S. Habas
M. Griffin
J. Schaidle

ORNL

J. Choi
K. Unocic

Thank you!