Addressing Unique Catalyst Deactivation Challenges for Converting Biomass-Derived Feedstocks

Huamin Wang
Pacific Northwest National Laboratory
February 19, 2020
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
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

**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

• 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

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

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

Performance windows in fuel and chemical production processes

<table>
<thead>
<tr>
<th></th>
<th>Industrial window</th>
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<tbody>
<tr>
<td>Stability</td>
<td>$10^3$ to $10^4$ kg product /kg catalyst</td>
</tr>
<tr>
<td>Activity</td>
<td>0.1-10 g product/ml h</td>
</tr>
<tr>
<td>Selectivity</td>
<td>70-100 wt.%</td>
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</table>

Catalysis for Biomass Conversion

Activity
Stability
Selectivity
Biomass derived feedstocks bring new challenges to catalyst longevity

Compared to fossil, most biomass derived feedstocks are

- Complex, highly functionalized, unstable
- Containing contaminants (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
Connections between feedstock and catalyst with deactivation and mitigation helps the development of robust catalytic process

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Catalyst</th>
<th>Deactivation</th>
<th>Mitigation</th>
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<td>Heavy species</td>
<td>Metal, carbide</td>
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<td>Reduction oxidation</td>
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<td>Water/corrosiveness</td>
<td>Acid-base/redox Zeolite and ordered porous solids</td>
<td>Deconstruction</td>
<td>Catalyst improvement</td>
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<td>Process improvement</td>
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<td>Feed separation</td>
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## Fouling of catalyst by heavy species and its potential mitigation

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<td>Acid-base/redox, Zeolite and ordered porous solids</td>
<td>Leaching</td>
<td>oxidation</td>
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- Bio-oil hydrogenation – Ru/TiO₂ – 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 – ZrO₂ – fouling by HMW from sugar – separation or regeneration
Bioenergy Technologies Office  
Poisoning of catalyst by sulfur or inorganics and its potential mitigation

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- Bio-oil hydrogenation – Ru/TiO₂ – 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

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<td>Leaching Sintering Phase transition Deconstruction</td>
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- Aqueous hydrogenation – Ni/TiO₂ – Ni(OH)₂ formation – catalyst surface hydrophobization
- Aqueous hydrogenation – Cu/Al₂O₃ – Cu leaching – overcoat by ALD
- Aqueous ketonization – ZrO₂ – phase transition – La doped ZrO₂
- 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 MS³ and CTI LDRD*


- Enhanced Hydrothermal Stability of ZrO₂ for the Ketonization of Acetic Acid in the Aqueous Condensed Phase
  Juan Lopez-Ruiz, Alan Cooper, and Karl Albrecht
  *BETO-ChemCatBio - Aqueous phase upgrading*

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

- $\text{H}_3\text{O}^+$ in confines showed much higher dehydration rate in liquid water

\[ \text{OH} \xrightarrow{\text{H}^+} \text{H}_3\text{O}^+ \xrightarrow{-\text{H}_2\text{O}} \]

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

\[ \text{BEA zeolite before and after treatment in liquid water at 160 } ^\circ\text{C} \]

<table>
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<tr>
<th>Sample</th>
<th>BET, m$^2$/g</th>
<th>$V$ micropore, cm$^3$/g</th>
<th>$V$ mesopore, cm$^3$/g</th>
</tr>
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<tr>
<td>BEA14</td>
<td>585</td>
<td>0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>BEA14 + H$_2$O</td>
<td>235</td>
<td>0.09</td>
<td>0.08</td>
</tr>
</tbody>
</table>

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

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

- 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

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<td>235</td>
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<td>0.08</td>
</tr>
<tr>
<td>BEA14-Si</td>
<td>300</td>
<td>0.12</td>
<td>0.02</td>
</tr>
<tr>
<td>BEA14-Si + H₂O</td>
<td>255</td>
<td>0.10</td>
<td>0.18</td>
</tr>
</tbody>
</table>

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

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

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 ZrO₂ catalysts enable direct catalytic upgrading of aqueous carboxylic acids

Hydrothermal liquefaction (HTL)

Aqueous products

Steam Reforming

Ketonization + Reduction + Dehydration

- Irreversible stabilization of the tetragonal ZrO₂ phase by La enable much improved stability of catalyst for condensed phase ketonization

Catalyst stability improvement for upgrading complex pyrolysis vapor and liquid

- **Fast pyrolysis**

- **Fast pyrolysis oil stabilization catalyst lifetime improvement**
  
  Huamin Wang, Mariefel Olarte, John Frye, Sue-Jane Lee, Miki Santosa, Alan Zacher, Jae-Soon Choi (ORNL)

- **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

- 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

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

- 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

**H₂ consumption vs TOS**

<table>
<thead>
<tr>
<th>S content (ppm)</th>
<th>Carbon content (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>N.D.</td>
</tr>
<tr>
<td>Bio-oil - 39 ppm S</td>
<td>1436</td>
</tr>
<tr>
<td>Bio-oil – 68 ppm S</td>
<td>2169</td>
</tr>
</tbody>
</table>

Carbonyl content, 4.5 mmol/g in feed

<table>
<thead>
<tr>
<th>Time on stream (h)</th>
<th>H₂ addition (mmol/g bio-oil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>15</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>24</td>
<td>0</td>
</tr>
</tbody>
</table>

**Bio-oil A after sulfur removal**
- 39 ppm S
- 0.73
- 0.86

**Bio-oil A, 68 ppm S**
- 1.42
- 2.18

**Bio-oil – 68 ppm S**
- 2169
- 6.3
Lowering sulfur content in bio-oil enables improved catalyst stability for its hydrogenation

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

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

- 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 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/TiO₂ 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/TiO₂ 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

**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

- K is uniformly distributed over catalyst surface
- K influences acid sites rather than metal sites
Consequence of K accumulation on catalytic activity of CFP catalysts was evaluated

Controlled deposition of K with various loading over Pt/TiO₂ for characterization and evaluation.

- 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.

**Tert-butyl-alcohol dehydration**

**Cresol HDO**

- Rate constant
- $E_a$
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.
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Thank you!