Atomic layer deposition (ALD) to extend catalyst lifetime for biobased adipic acid production

Presented by:
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NREL - National Bioenergy Center
North American Catalysis Society Meeting
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Presentation Outline

1) Why ALD for catalyst durability

2) Leaching & thermal stability for Pd/TiO₂

3) Techno-economic analysis analysis for ALD
Catalyst stability major challenge for renewables

Microbially produced carboxylic acids

Biobased acids can be catalytically upgraded to myriad chemicals

However, acids can readily deactivate conventional catalyst materials

Metal leaching

Metal sintering

Support collapse

Werpy & Peterson (2004) DOE Value Added Chemicals  
Besson & Gallezot (2003) Catalysis Today  
Catalyst stability for biobased adipic acid

Biobased muconic acid hydrogenation pathway

Muconic acid easily hydrogenated to adipic acid chemo-catalytically

Hydrogenation activity

Leaching stability

Carbon laydown

Pd is the most active metal that readily leaches and fouls
LOW CYCLE DOPANT ALD COATING
Approach relies on ‘low cycle’ ALD

THICK PROTECTIVE ALD COATING
Approach cracks ≥40 cycle ALD coating

ALD COATING & PROCESS ECONOMICS

(i) evaluate scaled ALD coatings for Pd/TiO$_2$ in acidic environments and
(ii) determine the associated techno-economic tradeoffs
Part 2
Leaching & thermal stability for Pd/TiO$_2$
ALD reduced leaching by 2x, while still active

Low-cycle ALD improves catalyst leaching stability with acids, but retains activity
<table>
<thead>
<tr>
<th></th>
<th>Pd Leaching (ppm)</th>
<th>Binding Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>0.31 ± 0.01</td>
<td>---</td>
</tr>
<tr>
<td>Hexanoic Acid</td>
<td>1.20 ± 0.70</td>
<td>-58</td>
</tr>
<tr>
<td>Adipic Acid</td>
<td>3.39 ± 1.05</td>
<td>-72</td>
</tr>
<tr>
<td>Muconic Acid</td>
<td>6.09 ± 0.10</td>
<td>-217</td>
</tr>
</tbody>
</table>

Low-cycle ALD improves catalyst leaching stability with acids, but retains activity

Scaling ALD with stop flow and fluidized bed

<table>
<thead>
<tr>
<th>Catalyst Description</th>
<th>Al Content wt%</th>
<th>Surface Area m² g⁻¹</th>
<th>Pore Diameter nm</th>
<th>Pore Volume mL g⁻¹</th>
<th>CO Uptake µmol g⁻¹</th>
<th>Productivity (sec⁻¹)</th>
<th>Pd Leaching (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated Pd/TiO₂</td>
<td>---</td>
<td>140 ± 13</td>
<td>5.8 ± 0.2</td>
<td>0.57 ± 0.05</td>
<td>24 ± 4</td>
<td>10.4 ± 0.3</td>
<td>6.1</td>
</tr>
<tr>
<td>Stop Flow ALD 100 mg</td>
<td>3.3 ± 0.04</td>
<td>122</td>
<td>5.6</td>
<td>0.46</td>
<td>14</td>
<td>10.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Fluidized Bed ALD 10 g</td>
<td>2.8</td>
<td>121</td>
<td>5.8</td>
<td>0.48</td>
<td>13</td>
<td>6.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Fluidized Bed ALD 100 g</td>
<td>4.4</td>
<td>120</td>
<td>4.9</td>
<td>0.50</td>
<td>11</td>
<td>6.1</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Characterization and screening highlight 5-cycles as target coating thickness.
Characterization of ALD coated Pd/TiO$_2$ catalyst

Pt is an artifact of sample preparation using FIB milling

Nanoscale imaging of complex support morphology and ALD coating

Continuous time-on-stream leaching stability

Time-on-stream testing for continuous 4x leaching stability under partial conversion with 50% reduction in activity

Challenge of uncoated Pd/TiO$_2$ thermal stability

Muconic acid readily fouls catalyst support and requires thermal regeneration

Both Pd and TiO$_2$ display poor thermal stability at high temperature

Validating ALD catalyst thermal durability

Uncoated Pd/TiO₂ after 700°C

Uncoated catalyst
Pd particles agglomerate by >30x

5-cycle ALD after 700°C

ALD catalyst
Pd particles retain 2-nm size

Al₂O₃ ALD thermal durability for TiO₂ supports

Al₂O₃ ALD retards increasing crystallinity during thermal treatment of TiO₂

<table>
<thead>
<tr>
<th>Catalyst Description</th>
<th>Uncoated Fresh</th>
<th>Uncoated 700°C</th>
<th>5 cycle Fresh</th>
<th>5 cycle 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m² g⁻¹)</td>
<td>130 -80%</td>
<td>22</td>
<td>126 -25%</td>
<td>96</td>
</tr>
<tr>
<td>Pore volume (mL g⁻¹)</td>
<td>0.57 -60</td>
<td>0.50 -6%</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td>5.9 +200%</td>
<td>16.4</td>
<td>5.6 +30%</td>
<td>7.2</td>
</tr>
<tr>
<td>CO uptake (μmol g⁻¹)</td>
<td>25 -5</td>
<td>14 +2x</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

Results in improved retention of TiO₂ support morphology
Dramatic activity retention after high temp

ALD coated catalyst still retains activity & selectivity after treatment at 700°C
Repeated thermal cycling of ALD-coated catalyst

Time-on-stream testing for continuous 4x leaching stability under partial conversion

Part 3
Techno-economic analysis for biobased adipic acid
Major cost drivers for ALD coating synthesis

Cost Analysis for ALD Catalyst Coating

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated catalyst</td>
<td>0.5% Pd/TiO₂</td>
</tr>
<tr>
<td>Pd metal 5-year average price</td>
<td>$23 g⁻¹</td>
</tr>
<tr>
<td>TiO₂ support unit price</td>
<td>$10 kg⁻¹</td>
</tr>
<tr>
<td>Uncoated catalyst surface area</td>
<td>130 m² g⁻¹</td>
</tr>
<tr>
<td><strong>Uncoated catalyst price</strong></td>
<td>$130 kg⁻¹</td>
</tr>
<tr>
<td>ALD catalyst coating Al content</td>
<td>3.5 wt%</td>
</tr>
<tr>
<td>ALD mass of Al₂O₃ added per kg catalyst</td>
<td>0.066 kg</td>
</tr>
<tr>
<td>ALD precursor utilization rate, assumed</td>
<td>50%</td>
</tr>
<tr>
<td><strong>ALD manufacturing cost per kg catalyst, assumed</strong></td>
<td>$5 kg⁻¹</td>
</tr>
<tr>
<td>TMA precursor unit price, log-log regression</td>
<td>$0.14 g⁻¹</td>
</tr>
<tr>
<td>TMA precursor Al content</td>
<td>37.4%</td>
</tr>
<tr>
<td><strong>ALD precursor cost per kg of catalyst</strong></td>
<td>$31 kg⁻¹</td>
</tr>
<tr>
<td>ALD coating with 30% margin per kg catalyst</td>
<td>$41 kg⁻¹</td>
</tr>
<tr>
<td><strong>Final ALD coated catalyst cost</strong></td>
<td>$160</td>
</tr>
<tr>
<td>ALD coated catalyst price increase</td>
<td>23%</td>
</tr>
</tbody>
</table>

Log-Log Scaled ALD Precursor Cost

- TMA precursor major cost driver for 5-cycle Al₂O₃ ALD on 0.5% Pd/TiO₂

Techno-economic analysis suggests ALD catalyst cost can increase by 240% if lifetime can be doubled for biobased adipic acid.
Take-Aways

• ALD reduces Pd leaching and retards anatase to rutile transformation for TiO$_2$ support

• Catalyst stability retained when scaling ALD coatings three orders of magnitude

• Techno-economic analysis shows value of extended catalyst lifetime despite ALD cost
Thank you research team...

- Davis Conklin (NREL)
- Arun Devaraj (PNNL)
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- Karthi Ramasamy (PNNL)
- Kinga Unocic (ORNL)
- Ryan Richards (CSM)
- Gregg Beckham (NREL)
- Arrelaine Dameron (FN)
- Ryon Tracy (FN)
- Reuben Sarkar (FN)
- Mike Watson (JM)

And funding support...
Thank you for your time!
Let’s discuss...
Validating ALD coating changes bulk properties

Elemental mapping & DRIFTS support 5-cycle ALD for impacting bulk properties

Complete conversion run with ALD catalyst

Near quantitative adipic yields at high WHSV with minimum Al leaching

<table>
<thead>
<tr>
<th>TOS (h)</th>
<th>WHSV (h⁻¹)</th>
<th>Adipic yield (%)</th>
<th>Pd leached (ppm)</th>
<th>Al leached (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td></td>
<td>&gt;99</td>
<td>0.09</td>
<td>14.81</td>
</tr>
<tr>
<td>22</td>
<td>0.52</td>
<td>&gt;99</td>
<td>0.06</td>
<td>13.06</td>
</tr>
<tr>
<td>45</td>
<td>0.52</td>
<td>&gt;99</td>
<td>0.03</td>
<td>3.38</td>
</tr>
<tr>
<td>69</td>
<td>0.52</td>
<td>&gt;99</td>
<td>0.04</td>
<td>0.17</td>
</tr>
<tr>
<td>92</td>
<td></td>
<td>&gt;99</td>
<td>0.03</td>
<td>BDL</td>
</tr>
<tr>
<td>110</td>
<td>1.05</td>
<td>&gt;99</td>
<td>0.08</td>
<td>BDL</td>
</tr>
<tr>
<td>118</td>
<td>1.05</td>
<td>&gt;99</td>
<td>0.10</td>
<td>BDL</td>
</tr>
</tbody>
</table>

Purity: 99.06%
Melting Point: 152.58°C
Depression: 1.58°C
Catalyst leaching control test for activity

Muconic Acid $\rightarrow$ Hexenedioic Acid $\rightarrow$ Adipic Acid

- **Muconic acid**
- **Hexenedioic acid**
- **Adipic acid**

**Hot Filtration Rx w/ 1% Pd/TiO$_2$**

- Catalyst removed at t=2.5

**Standard Rx w/ 1% Pd/TiO$_2$**

Hot filtration control tests confirm leached Pd not responsible for activity

Settle et al. (2018) Under Review
Systematically synthesize suite of ALD catalysts


Increasing ALD coating thickness cycle-by-cycle to determine “sweet spot”
Background on atomic layer deposition (ALD)

ALD provides self-limiting growth of protective metal oxide layers at atomic scale

Traditional deposition methods

Atomic layer deposition

Offers greater control and uniformity with complex morphologies

Lu et al. (2016) Surface Sci. Reports.  