Atomic Layer Deposition for Improved Biomass Conversion Catalysts

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ALD/ALE 2021 | June 28, 2021
Bioenergy and Decarbonization

“Hard-to-Decarbonize”

Shell, A Better Life with a Healthy Planet—Pathways to Net-Zero Emissions

Heterogeneous catalysts

Stressors

Tailored catalyst solution to mitigate degradation?

ALD can be used to protect catalysts

Atomic Layer Deposition = “ALD”

- Self-limiting
- Conformal
- Thickness control

Goulas, Puurunen, van Ommen, 2020. CC BY 4.0 (Creative Commons Attribution 4.0 International)
https://commons.Wikipedia.org/wiki/File:ALD_cartoon_Steps_1-4_Reactant_A_with_three_ligands_no_inert.jpg

ALD for catalysis in CCT&S Center

Muconic acid HYD

\[ \text{H}_2 \]

Catalyst Leaching (Pd ppm)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Leaching (Pd ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated (Pd/TiO_2)</td>
<td>1.4 ±0.7</td>
</tr>
<tr>
<td>100-mg ALD-coated</td>
<td>0.3 ±0.1</td>
</tr>
<tr>
<td>10-g ALD-coated</td>
<td>0.08 ±0.04</td>
</tr>
<tr>
<td>100-g ALD-coated</td>
<td>0.05 ±0.01</td>
</tr>
</tbody>
</table>


Overcoating

Initial catalyst screening

\[ 10\text{cTiO}_2-\text{Pd/Al}_2\text{O}_3 \]

- In-depth characterization
- Reaction testing
- Synthesis scale-up
TiO$_2$ ALD on Pd/Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd/Al$_2$O$_3$</th>
<th>10cTiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd content (wt%)</td>
<td>0.44</td>
<td>0.33</td>
</tr>
<tr>
<td>Ti content (wt%)</td>
<td>--</td>
<td>9.3</td>
</tr>
<tr>
<td>BET (m$^2$ g$^{-1}$)</td>
<td>112</td>
<td>110</td>
</tr>
<tr>
<td>H uptake (µmol g$^{-1}$)</td>
<td>28.2</td>
<td>10.5</td>
</tr>
<tr>
<td>CO uptake (µmol g$^{-1}$)</td>
<td>20.4</td>
<td>4.3</td>
</tr>
</tbody>
</table>

- Conformal layer
- Al$_2$O$_3$ support coated
- H and CO uptakes decreased
- Pd sites covered (extent unclear)

How does Pd coverage by TiO$_2$ impact reactivity?
ALD catalyst performance in aromatic HYD: batch


\[ \text{Tetralin Prod} = \frac{\text{mmol}_{\text{tetralin}}}{g_{\text{cat}}} \times 3h \]

\[ \text{TOF (h}^{-1}\text{)} = \frac{\text{Prod} \left( \frac{\text{mol}_{\text{tet}}}{\text{g}_{\text{cat}}} \right)}{\text{wt frac}_{\text{Pd}}} \times \frac{106 \text{ g mol}}{\text{Disp}_{\text{Pd,CO}}} \]

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pd/Al₂O₃</th>
<th>10cTiO₂-Pd/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene*</td>
<td>40.0%</td>
<td>80.3%</td>
</tr>
<tr>
<td>Styrene*</td>
<td>47.4%</td>
<td>98.3%</td>
</tr>
<tr>
<td>Naphthalene*</td>
<td>55.9%</td>
<td>72.4%</td>
</tr>
</tbody>
</table>

*Conditions: 1wt% substrate, 150°C, 40 bar H₂, 25 mg catalyst, 800 rpm, 30 min. *Conditions above with temp at 200°C and 180 min.
ALD catalyst performance in naphthalene HYD: flow

- Similar trends to batch activity
- 10cTiO$_2$ has ~1.7X Pd-norm activity of base material
- TiO$_2$ ALD overlayer has different behavior than TiO$_2$ support

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Naphthalene Conv (%)</th>
<th>Tetralin Prod (mmol$<em>{tet}$ g$</em>{Pd}^{-1}$ h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/TiO$_2$</td>
<td>9.4</td>
<td>0.45</td>
</tr>
<tr>
<td>Pd/Al$_2$O$_3$</td>
<td>15.9</td>
<td>0.44</td>
</tr>
<tr>
<td>10cTiO$_2$-Pd/Al$_2$O$_3$</td>
<td>19.2</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Why does TiO$_2$ ALD layer boost activity?

- Steady-state (6 h) values

1 wt% naphthalene, WHSV = 4.2 h$^{-1}$, 200°C,
500 psi, 200 sccm H$_2$
Pd partially covered by ALD, no change in e⁻

### XPS (ex-situ)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Edge Energy (eV)</th>
<th>Coordination Number</th>
<th>R (Å)</th>
<th>σ² (x10³ Å²)</th>
<th>E₀ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/Al₂O₃</td>
<td>24351.9</td>
<td>8.6 ± 0.5 (Pd-Pd)</td>
<td>2.80 ± 0.01</td>
<td>10.2 ± 0.5</td>
<td>3.2 ± 0.4</td>
</tr>
<tr>
<td>10cTiO₂-Pd/Al₂O₃</td>
<td>24351.9</td>
<td>8.6 ± 0.5 (Pd-Pd)</td>
<td>2.80 ± 0.01</td>
<td>9.6 ± 0.5</td>
<td>3.3 ± 0.4</td>
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### ISS (ex-situ)

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### XAS (in-situ H₂ reduction)

- Pd surface covered
TiO$_2$ ALD significantly alters surface binding

*Bnote: simulated overlayers are rutile TiO$_2$, while actual ALD layers are amorphous*
**ALD catalyst stability**

Sulfided = DMDS added at S:Pd = 0.2

XX°C TT = 4 h at XX°C, 200 sccm dry air  → 2 h at 200°C, 200 sccm H₂

XX°C HT = 15 h at XX°C, liquid water, 200 rpm  → 2 h at 200°C, 200 sccm H₂

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Pd/TiO₂</th>
<th>Pd/Al₂O₃</th>
<th>10cTiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>450°C TT % change</td>
<td>+1%</td>
<td>+0.9%</td>
<td>+5%</td>
</tr>
<tr>
<td>750°C TT % change</td>
<td>-74%</td>
<td>-0.9%</td>
<td>-4%</td>
</tr>
<tr>
<td>200°C HT % change</td>
<td>-44%</td>
<td>-83%</td>
<td>-26%</td>
</tr>
</tbody>
</table>

**Change in BET surface area (m² g⁻¹)**

**Change in CO uptake (µmol g⁻¹)**

1 wt% naphthalene, 200°C, 40 bar H₂, 25 mg catalyst, 800 rpm, 180 min

XXX°C TT = 4 h at XXX°C, 200 sccm dry air  → 2 h at 200°C, 200 sccm H₂

XXX°C HT = 15 h at XXX°C, liquid water, 200 rpm  → 2 h at 200°C, 200 sccm H₂
ALD catalyst stability

- **Treatment**: Pd/Al₂O₃ 10cTiO₂
- **Temperature**:
  - 750°C TT
  - 200°C HT

**Change in CO uptake (µmol g⁻¹)**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Pd/Al₂O₃</th>
<th>10cTiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>750°C TT % change</td>
<td>-47%</td>
<td>+120%</td>
</tr>
</tbody>
</table>

- **Calcination may form pores**
- **Pd sintering**
- **ALD layer unstable**
- **Al₂O₃ boehmite transformation**

Refining the value proposition of ALD catalysts

Is ALD “worth it” for HYD catalysts?

<table>
<thead>
<tr>
<th>TTIP Precursor Price ($/kg)</th>
<th>Equipment Capacity (tonnes/d)</th>
<th>ALD Coating Cost ($/kg catalyst)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>30</td>
<td>$12.08</td>
</tr>
<tr>
<td>5</td>
<td>15</td>
<td>$13.47</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>$20.67</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>$29.64</td>
</tr>
<tr>
<td>25</td>
<td>30</td>
<td>$43.84</td>
</tr>
</tbody>
</table>

Is ALD “worth it” for HYD catalysts?

- ALD cost increase neutralized by 2X improvement in either WHSV or lifetime
- Achievable based on our 1.7X activity increase
- Savings compound with further improvements

Savings due to decreased OPEX, CAPEX

Savings due to decreased catalyst purchase price

- ALD cost increase neutralized by 2X improvement in either WHSV or lifetime
- Achievable based on our 1.7X activity increase
- Savings compound with further improvements

2% Pd/Al₂O₃
350°C, 650 psi H₂
Variable WHSV, catalyst lifetime
Conclusions and future work

Sustainable Aviation Fuel

1) Arrested Methanogenesis
2) VFA ketonization
3) Hydrodeoxygenation (HDO)

Oxidation for Biobased Chemicals

Modification of catalyst surface adsorption energetics

Improved process economics

Decreased harmful emissions

Nanoscale Changes

Macroscale Effects

10^3

<table>
<thead>
<tr>
<th>Ketone</th>
<th>Alcohol</th>
<th>Alkane</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>R−OH</td>
<td>R</td>
<td></td>
</tr>
</tbody>
</table>

Initial Uncoated catalyst ALD coated catalyst

After 15 h leaching test

BIO-GLUCONIC ACID

M concentration (ppm)

5% M/Al₂O₃
3% M/Al₂O₃
ALD coated 3% M/Al₂O₃
ALD coated 5% M/Al₂O₃
Acknowledgements

Staci Moulton
Chris Gump
Jessica Burger
Arrelaine Dameron
Karen Buechler

Mike Watson
Luke Tuxworth
Tugce Eralp Erden

PI: Derek Vardon (derek.vardon@nrel.gov)

Gabriella Lahti
Davis Conklin
Kinga Unocic (ORNL)
Sean Tacey

Michael Griffin
Carrie Farberow
Eric Tan
Kurt van Allsburg

The rest of the DeCO₂ team!