

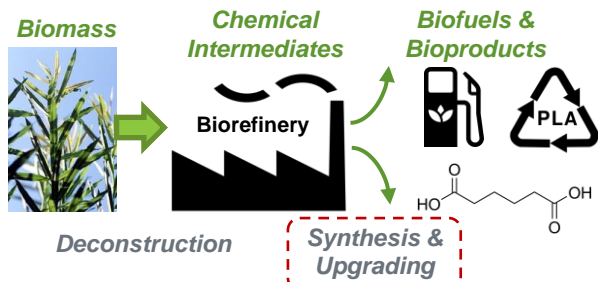
Atomic Layer Deposition for Enhanced Reactivity and Stability of Biomass Conversion Catalysts

W. Wilson McNairy,¹ Gabriella Lahti,¹ Kinga Unocick,² Sean Tacey,¹ Carrie Farberow,¹ Michael Griffin,¹ Kurt Van Allsburg,¹ Chris Gump,³ Arrelaine Dameron,³ Karen Buechler,³ Mike Watson,⁴ Derek Vardon¹ (contact: derek.vardon@nrel.gov)

¹National Renewable Energy Laboratory, Golden, CO; ²Oak Ridge National Laboratory, Oak Ridge, TN; ³Forge Nano, Louisville, CO;

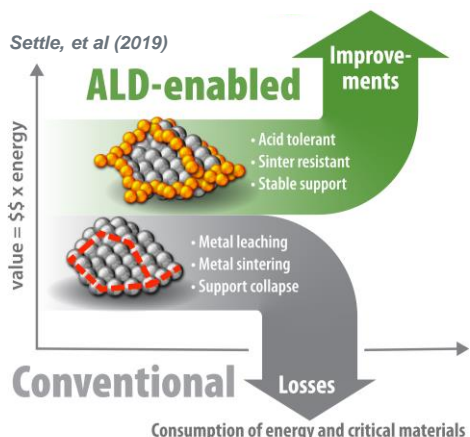
⁴Johnson Matthey, London, UK

Chemistry Challenges of Biomass Conversion



- **Synthesis & Upgrading** requires robust and economical catalytic processes
- Harsh process conditions (temperature, acidity, H₂O₂, high moisture) impose significant barriers
- Thin metal oxide coatings via atomic layer deposition (ALD) developed for next-gen heterogeneous catalysts

Application of ALD Coatings



TiO₂ and Al₂O₃ ALD overcoats applied to supported Pd catalysts for hydrogenation reactions

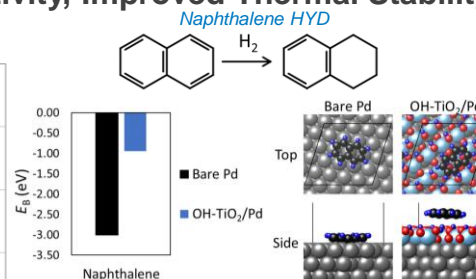
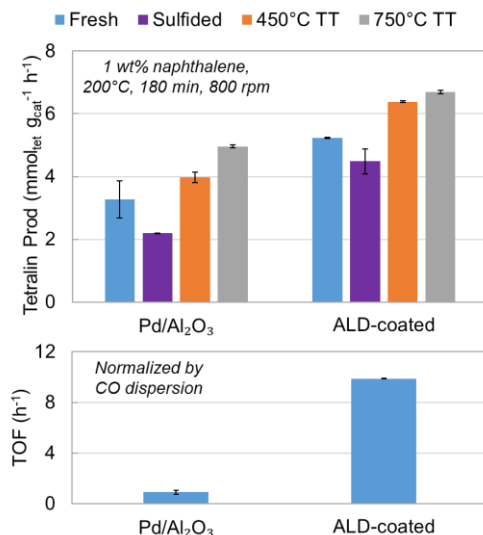
Goal 1

Improve catalyst stability

Goal 2

Scalable ALD synthesis

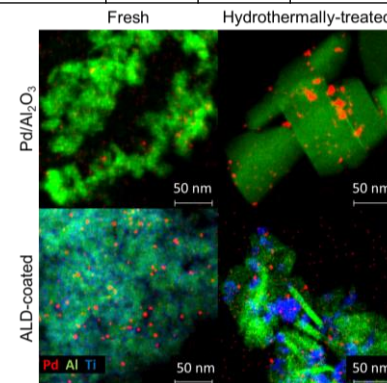
TiO₂ ALD: Increased Activity, Improved Thermal Stability and Sulfur Tolerance



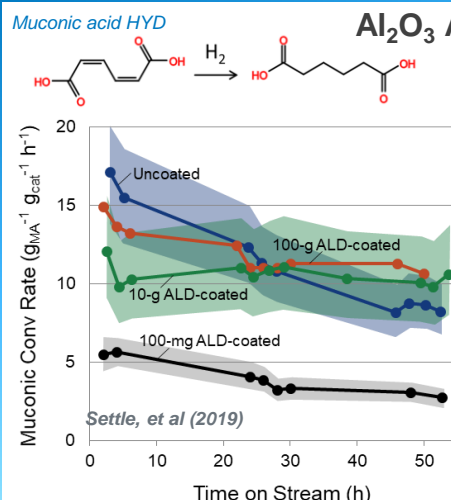
- Activity substantially increased by addition of ALD overcoat; TiO₂ surface affects reactant binding to Pd
- ALD-coated catalyst retained 86% of initial activity after exposure to sulfur
- Activity increased following oxidative thermal treatments
- ALD overcoat improves hydrothermal stability

Effects of 15 h 200°C hydrothermal treatment

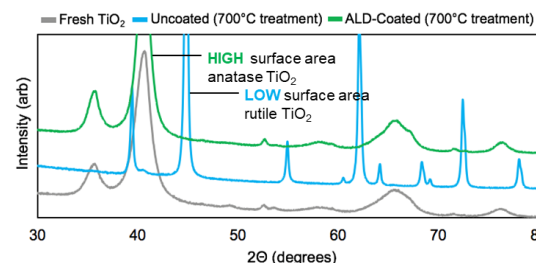
Catalyst	BET _{init} (m ² g ⁻¹)	BET _{final} (m ² g ⁻¹)	% change BET
Uncoated (Pd/Al ₂ O ₃)	112	19	-83%
ALD-coated	110	81	-26%



Al₂O₃ ALD: Improved Leaching and Thermal Stability



- Al₂O₃ ALD overcoat improves stability in muonic acid conversion to adipic acid, an important bioproduct
- Improvements demonstrated with ALD fabrication at multiple scales

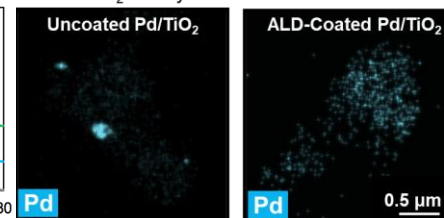


>9x greater surface area retention than uncoated TiO₂ powder

Pd leaching during Muonic Acid HYD

Catalyst	Leaching (Pd ppm)	Leaching Rate (μg _{Pd} h ⁻¹)
Uncoated (Pd/TiO ₂)	1.4 ± 0.7	0.32
100-mg ALD-coated	0.3 ± 0.1	0.07
10-g ALD-coated	0.08 ± 0.04	0.02
100-g ALD-coated	0.05 ± 0.01	0.01

Pd/TiO₂ Catalysts after 700°C Treatment



>80% loss of surface area <25% loss of surface area

Conclusions and Future Outlook

- ALD-enabled catalysts show superior performance vs. conventional catalysts in hydrogenation reactions
- Observed leaching and stability benefits maintained upon ALD synthesis scale-up
- Ongoing work focused on improving leaching resistance in oxidative environments