ChemCatBio
Chemical Catalysis for Bioenergy

ALD Nano/JM DFA: Enhanced Catalyst Durability and Sulfur Tolerance by Atomic Layer Deposition (ALD)

DOE Bioenergy Technologies Office
2019 Peer Review

Derek Vardon, NREL

March 7, 2019

ALD Nano/JM DFA Goal & Outcome

ChemCatBio Goal: Accelerate the development of catalysts and related technologies for the commercialization of biomass-derived fuels and chemicals

- ## ALD Nano/JM DFA Goal

  The goal of this project is to improve our understanding and accelerate the commercialization of atomic layer deposition (ALD) catalyst coatings to improve durability during biomass conversion process.

- ## ALD Nano/JM DFA Outcome

  This project will generate performance data, computational modeling, and techno-economic analysis for ALD coated catalysts during biomass conversion to help reduce barriers to commercialization.

- ## Relevance to Bioenergy Industry

  The development of robust catalysts with ALD has potential to lower the cost of biomass conversion processes if enhanced lifetime productivity can be achieved in harsh environments.

Quad Chart

Timeline

- **Project start date:** Feb 15, 2018
- **Project end date:** March 31, 2020
- **Percent complete:** 50%

	Total Costs Pre FY17*	FY 17 Costs	FY 18 Costs	Total Planned Funding (FY 19- End)
DOE Funded	$0k	$0k	$134k	$402k
Project Cost Share*	$0k	$0k	$58k	$173k

Industrial Partners: ALD NanoSolutions and Johnson Matthey

Barriers Addressed

Ot-B. Cost of Production
Ct-E. Improving Catalyst Lifetime
Ct-G. Decreasing Time and Cost to Develop Novel Industrially Relevant Catalysts

Objectives

Aim 1. Develop sulfur tolerance relationships for dopant-PGM-support interfaces based on first principles

Aim 2. Demonstrate the value of ALD catalyst durability when upgrading biologically derived muconic acid with prolonged time-on-stream

End of Project Goal

The end of project goal is to extend PGM catalyst lifetimes by ≥2x, with key durability targets that include: (i) reduce metal leaching with acidic media to <2 ppm, (ii) reduce sintering after thermal regeneration to retain 85% activity, (iii) reduce the rate of sulfur poisoning by >2x

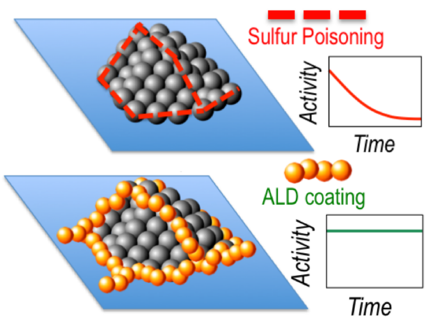
1 - Approach & Relevance

Overall Bio-Economy challenge industry partners want to solve

Atomic Layer Deposition (ALD) for Catalyst Durability

Challenge

Conventional catalysts are challenged by biomass processing conditions & industry lacks access to R&D tools and expertise



Approach

Utilize NREL-industry partnerships to capitalize on unique strengths & capabilities for R&D while addressing scalability

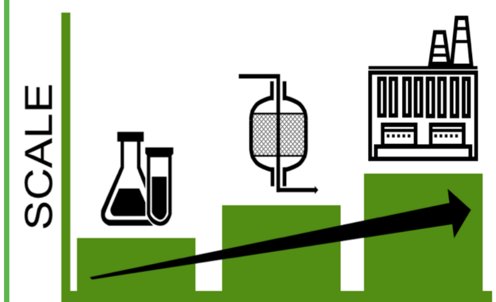
ALD nanosolutions

JM Johnson Matthey
Inspiring science, enhancing life

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Success Outcome

Establish catalyst lifetime productivity enhancement and economic models to accelerate commercialization



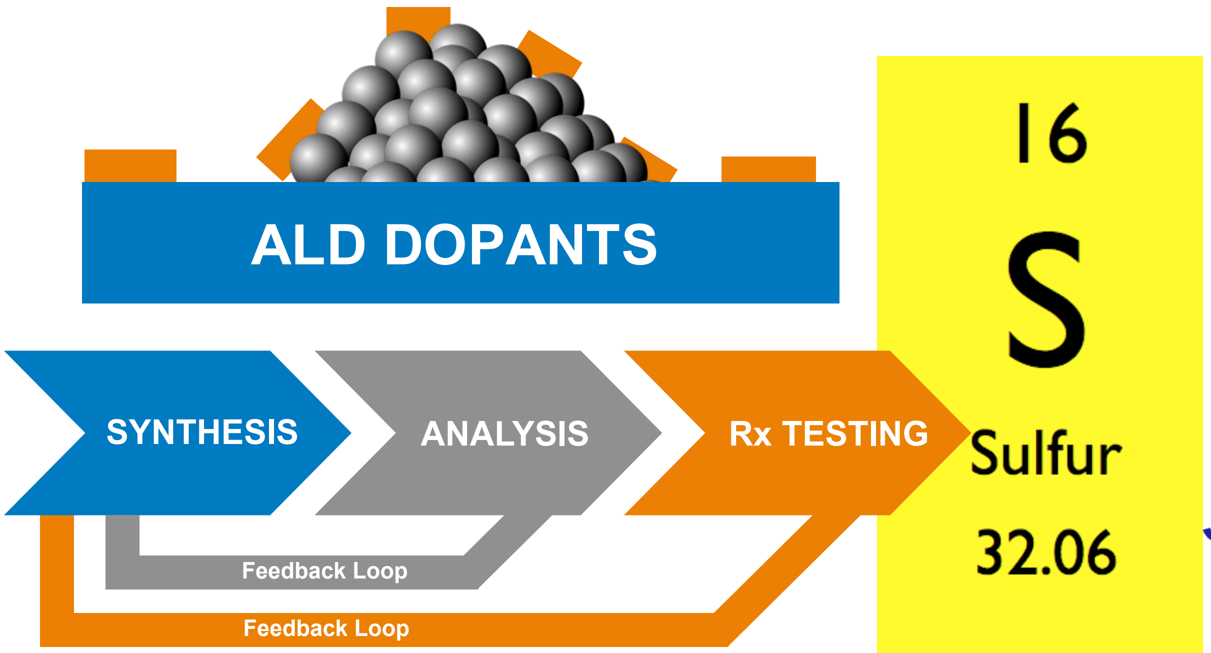
Work with industry partners to achieve goal of commercializing ALD-coated catalysts for harsh biomass conversion applications

1 - Approach & Relevance

Project specific challenge industry partners want to solve

Poor durability and sulfur poisoning detrimental to catalytic processes

- Sulfur present in biomass itself or can arise during biological processes
- Shorten catalyst lifetime can increase process costs and negate viability



NREL NATIONAL RENEWABLE ENERGY LABORATORY

ALD nanosolutions

JM Johnson Matthey Inspiring science, enhancing life

This project seeks to develop tailored ALD catalyst coatings to improve overall durability and enhance biogenic sulfur tolerance

1 - Approach & Relevance

Impact and value of National Labs working with industry

*"The collaboration with NREL provides extremely valuable industrial validation to the emerging applications for advanced catalyst thin film coatings. … **We do not have ready access to such tools and expertise as a company**. … The conversion demonstration and techno-economic modeling generate **key de-risking data to show how improved catalyst durability with ALD can impact the bottom line**."*

- Karen Buechler, CTO

ALD nanosolutions

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*"The combination of catalyst preparation, testing, advanced characterization, computational modelling and techno economic analysis (done by the NREL team) allows both the potential of ALD coated catalysts to be established and also informs the underpinning science behind the technology. **The coordinated application of these tools is not readily available to industry for emerging applications and provides unique value to the biomass community**."*

Johnson Matthey
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- Mike Watson, Technology Manager

Value of private-public partnerships for the Bio-Economy

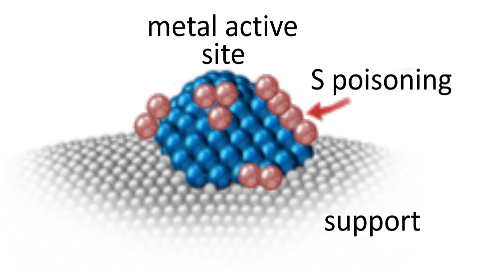
1 - Approach & Relevance

Project targets three modes of catalyst deactivation with ALD

Enhancing Catalyst Durability with ALD

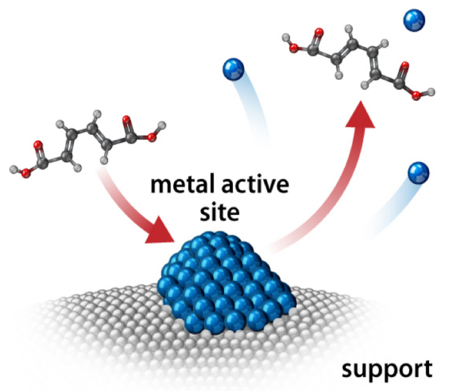
S Tolerance

Muconate hydrogenation doped with cysteine to evaluate impact of biogenic sulfur on catalyst activity



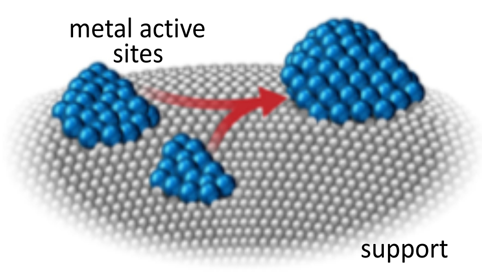
Leaching Resistance

Analysis of reaction products by ICP-MS to determine leached active metal content



Thermal Stability

Thermal treatment and characterization to evaluate extent of metal and support restructuring



Three-fold approach for addressing durability challenges with ALD

1 - Approach & Relevance

How the ALD Nano/JM DFA project fits into and connects with CCB

ALD Nano/JM DFA Project Team

NREL NATIONAL RENEWABLE ENERGY LABORATORY | ALD nanosolutions | JM Johnson Matthey Inspiring science, enhancing life

Fit and Connections within ChemCatBio

Catalytic Technologies	*Enabling Capabilities*	*Industry Partnerships (Directed Funding)*
Catalytic Upgrading of Biochemical Intermediates (NREL, PNNL, ORNL, LANL, NREL*)	**Advanced Catalyst Synthesis and Characterization** (NREL, ANL, ORNL, SNL)	**Gevo** (NREL)
		ALD Nano/JM (NREL)
Catalytic Upgrading of Indirect Liquefaction Intermediates (NREL, PNNL, ORNL)	**Catalyst Cost Model Development** (NREL, PNNL)	**Vertimass** (ORNL)
		Opus12(NREL)
Catalytic Fast Pyrolysis (NREL, PNNL)	**Consortium for Computational Physics and Chemistry** (ORNL, NREL, PNNL, ANL, NETL)	**Visolis** (PNNL)
		Lanzatech (PNNL) - Fuel
Electrocatalytic and Thermocatalytic CO_2 Utilization (NREL, ORNL*)	**Catalyst Deactivation Mitigation for Biomass Conversion** (PNNL)	**Gevo** (LANL)
		Lanzatech (PNNL) - TPA
		Sironix (LANL)
*FY19 Seed Project	*Cross-Cutting Support*	

1 - Approach & Relevance

Project leadership roles clearly defined at each institution

Organizations and Team Leadership

NATIONAL RENEWABLE ENERGY LABORATORY

Derek Vardon, PI
Amy Settle

Karen Buechler, PI

Johnson Matthey
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Mike Watson, PI
Luke Tuxworth

NREL Team Members:

ALD Coatings – *Steve Christensen, Katherine Hurst*
DFT Modeling – *Carrie Farberow*
Reaction Eng. – *Mike Griffin*
TEA – *Eric Tan*

External Collaborators:

Atom Probe Tomography - *Elizabeth Kautz, Arun Devaraj, Karthi Ramasamy (PNNL)*
Electron Microscopy – *Kinga Unocic (ORNL)*

Experienced team knowledgeable in biomass catalysis & ALD

1 - Approach & Relevance

Activities aligned to facilitate partner exchange with feedback loops

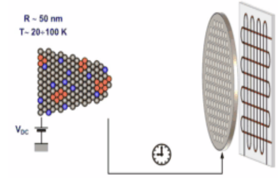
ALD Nano and JM: *provide uncoated and ALD coated catalyst materials; support characterization; inform testing and cost modeling activities*

1. Test & characterize first suite of ALD catalysts (NREL/JM)

Inform next round of ALD coating formulations

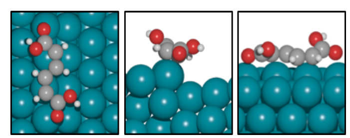
2. Develop preliminary ALD + process TEA (ALD NS/NREL/JM)

3. Test & characterize 2nd suite of ALD catalysts (NREL/JM)



Inform final ALD coating formulation for scale-up

4. Calculate biogenic sulfur adsorption energetics (NREL)



5. Test downselected catalyst ALD coated at scale (NREL)

6. Update final ALD + process TEA (ALD NS/NREL/JM)

NREL: *conduct basic and advanced catalyst characterization; evaluate catalyst performance and stability; carry out computational modeling and TEA*

2 - Progress on DFA Milestones

Milestone status and progress towards the project goal to date

Synthesis and Testing

FY19 Q1 MS. Synthesize an initial suite of ALD-coated catalysts by ALD Nano. Report characterization and batch screening results including S-tolerance, thermal stability, and leaching durability.

Status of Key Milestones

Q1. Synthesize & screen initial ALD-coated catalysts

~ *Q2. Synthesize and screen refined ALD-coated catalysts*

Q3. *Synthesize final catalysts at scale, incorporate computation*

Q4. *Report TOS activity of ALD catalyst & deliver cost models*

FY19

FY19 Q1 MS completed with ongoing progress on Q2 MS

2 - Progress for Leaching Tolerance

ALD coatings strategies being developed for chemical deactivation

Bench-scale ALD (g-scale)

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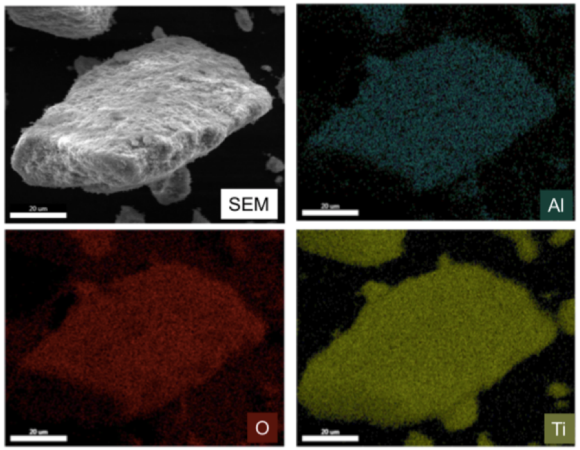
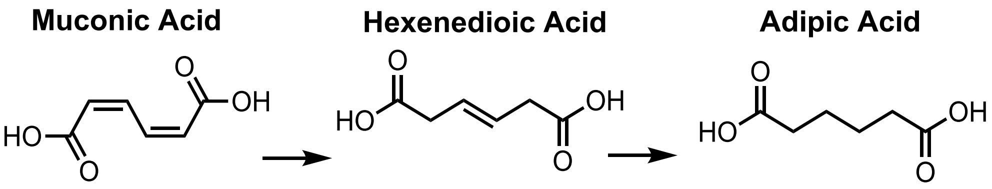
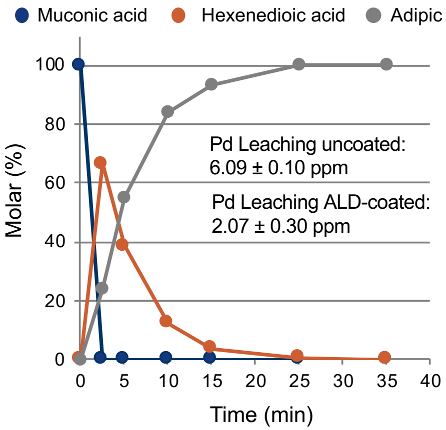
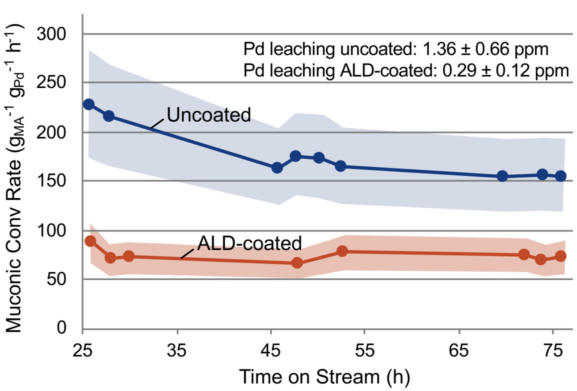




>3x Pd leaching reduction
>38% increase in retained activity



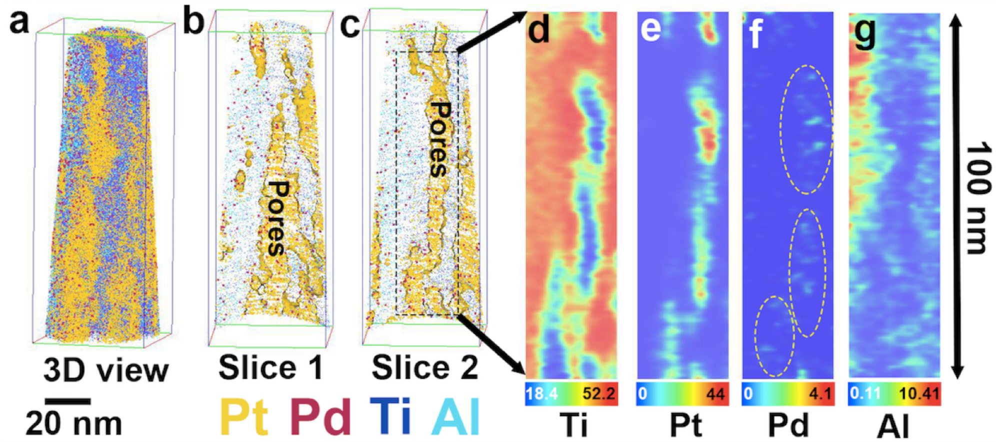


Demonstrated stability improvements with ALD coating strategies

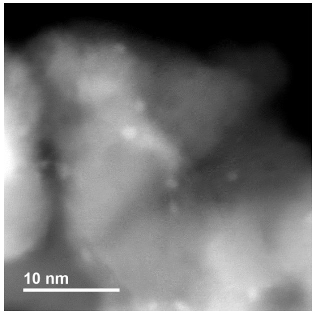
2 - Progress for Advanced Characterization

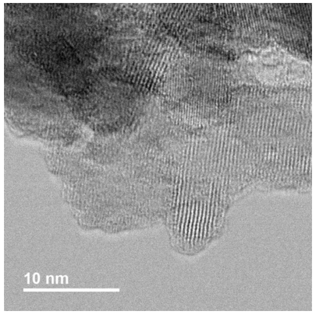
Assess ALD coatings within complex catalyst support morphologies

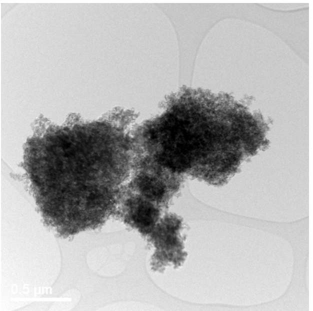
Characterization to gauge coating distribution within relevant supports

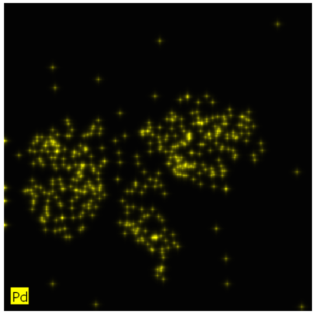


APT by Karthi Ramasamy, Elizabeth Kautz, and Arun Devaraj, PNNL









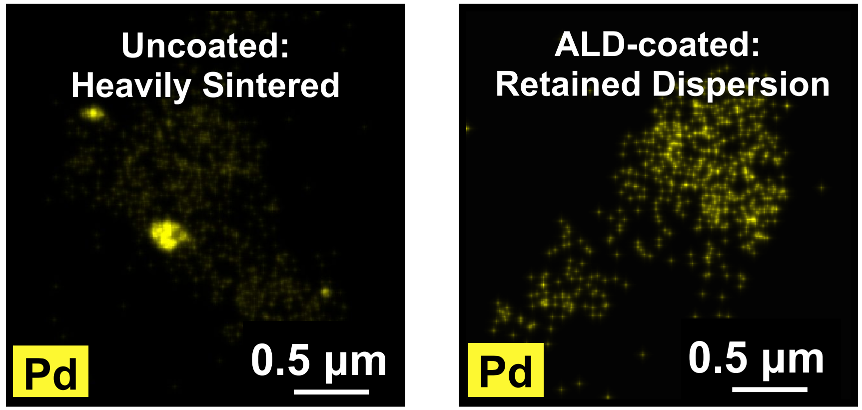
HR-STEM/EDS by Kinga Unocic, ORNL

Materials insight to inform continued ALD process refinement

2 - Progress for Thermal Regenerability

Address deactivation during high temperature regeneration

Impact of thermal treatment on uncoated and ALD-coated catalysts



HR-STEM/EDS by Kinga Unocic, ORNL

Parameter	Uncoated			ALD-coated		
	Fresh		Therm. Treated	Fresh		Therm. Treated
Surface area ($m^2\ g^{-1}$)	130	-80%	22	126	-25%	96
Pore volume ($mL\ g^{-1}$)	0.57	-60%	0.24	0.50	-6%	0.47
Pore diameter (nm)	5.9	+200%	16.4	5.6	+30%	7.2
CO uptake ($\mu mol\ g^{-1}$)	25	-5x	5	14	+2x	25

ALD coatings show dramatic improvement in thermal stability

1. A.E. Settle, et al. Atomic layer deposition for improved catalyst durability during the production of biobased adipic acid. Under Review.
2. Catalysts, catalyst supports and methods of making the same. Provisional patent application US PTO 62/720,444 filed on August 21, 2018.

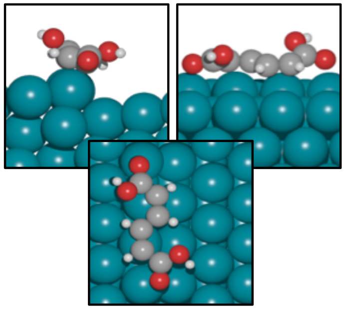
3 - Future Work

Plans, lessons learned, and key technology handoffs

FY19 **FY20**

Planned Activities Moving Forward

Experimental & computational efforts to inform relationship between ALD and S-tolerance



Scaled-up catalyst synthesis by to validate small-scale testing and durability results

Refine cost-models for techno-economic analysis of ALD coated materials at-scale

Key Handoffs with Industry Partners

- New foundational knowledge for stability
- Tailored ALD formulations with IP potential
- ALD catalyst testing & characterization data
- Harmonized techno-economic models

3 - Future Work

Key planned milestones, decision points, and advancement needs

Technology Advancement

FY19 Milestones will address critical technology advancement needs for commercialization, including:

(i) A minimum 2x increase in catalyst durability by ALD coating

(ii) Demonstration of successful ALD catalyst scalability

DFA Project Milestones

- Q1. *Synthesize & screen initial ALD-coated catalysts*
- *Q2. Synthesize and screen refined ALD-coated catalysts*
- Q3. *Synthesize final catalysts at scale, incorporate computation*
- Q4. *Report TOS activity of ALD catalyst & deliver cost models*

FY19

Future milestones will address success criteria for commercialization

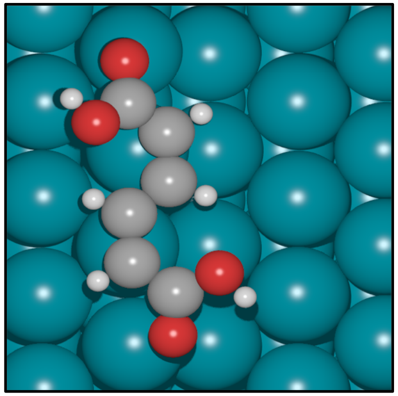
3 - Future Work

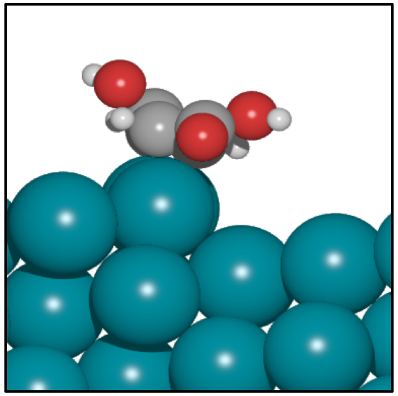
Understanding substrate and sulfur interactions with active metal

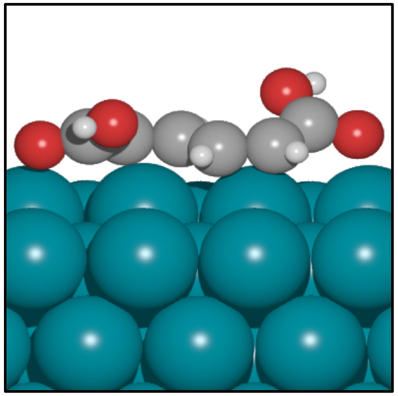
Leveraging computation to support experiment

Experimental Leaching Evaluation	
Acid	**Pd Leaching**
Hexanoic Acid	1.20 ± 0.70 ppm
Adipic Acid	3.39 ± 1.05 ppm
Muconic Acid	6.09 ± 0.10 ppm

Computational Pd Binding Energy	
Acid	**Binding Energy**
Hexanoic Acid	-58 kJ/mol
Adipic Acid	-72 kJ/mol
Muconic Acid	-217 kJ/mol







Computation by Carrie Farberow, NREL

Ongoing work to evaluate mechanisms for leaching stability

3 - Future Work

Synthesize tailored formulation at the kg-scale for testing & TEA

Bench-scale ALD (g-scale)

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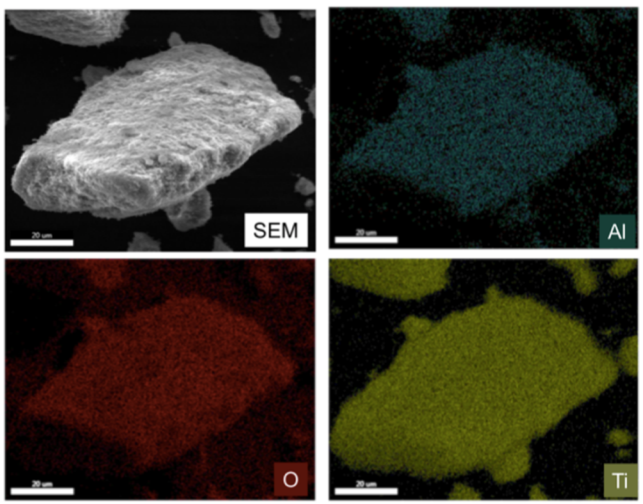

Scaled ALD Synthesis (kg-scale)

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Translating bench-scale ALD for scaling by industry partners

Summary for ALD Nano/JM DFA

Overview	**The goal of this project is to:** **(i) improve understanding of ALD interactions for sulfur tolerance, and** **(ii) demonstrate ≥2x lifetime durability gains and associated value in harsh environments using biobased adipic acid as a exemplary chemistry**
Approach	• Develop relationships between catalyst durability and ALD catalyst formulations • Leverage advanced national lab tools to accelerate development (ACSC, CCPC) • Demonstrate economic value of ALD catalysts and de-risk scaled adoption
Technical Progress	• **ALD catalyst synthesis:** Scaled bench ALD coatings with industry partners • **Enhanced stability:** Shown how ALD can improve chemical and thermal stability • **Advanced tools:** Ongoing computational modeling & advanced characterization • **Economic modeling:** Adapting bio-adipic acid TEA models to assess impact
Relevance	**Robust ALD coatings have potential to lower the cost of biomass conversion if enhanced catalyst lifetime productivity can be achieved in harsh environments**
Future Work	• Continue experimental and computational work to inform relationships between ALD coating formulations and sulfur tolerance • Demonstrate kg-scale synthesis of promising ALD catalyst coating formulations • Refine techno-economic models for ALD coatings at scale

Thank you for listening…
Let’s discuss!

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Chemical Catalysis for Bioenergy

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

Publications, Patents, Presentations, Awards, and Commercialization

Publications

- *A.E. Settle, N.S. Cleveland, X. Huo, A.M. York, E.J. Kautz, A. Devaraj, K.K. Ramasamy, R.M. Richards, K.A. Unocic, G.T. Beckham, M.B. Griffin, K.E. Hurst, E.C.D. Tan, S.T. Christensen, D.R. Vardon. Atomic layer deposition for improved catalyst durability during the production of biobased adipic acid. Under Review.*

Patents

- *Catalysts, catalyst supports and methods of making the same. Provisional patent application US PTO 62/720,444 filed on August 21, 2018.*

Presentations

- *A.E. Settle, N.S. Cleveland, X. Huo, A.M. York, A. Devaraj, E.J. Kautz, K.K. Ramasamy, G. Burton, G.T. Beckham, M.B. Griffin, K.E. Hurst, C.A. Farberow, E.C.D. Tan, S.T. Christensen, D.R. Vardon. Atomic layer deposition with Al2O3 for enhanced Pd/TiO2 stability during biobased adipic acid production. Fall 2018 American Chemical Society Meeting, Boston, MA. August 2018.*
- *D.R. Vardon, A.E. Settle, N.S. Cleveland, X. Huo, A.M. York, E.J. Kautz, A. Devaraj, K.K. Ramasamy, R.M. Richards, K.A. Unocic, G.T. Beckham, M.B. Griffin, K.E. Hurst, E.C.D. Tan, S.T. Christensen. Low-cycle atomic layer deposition for enhanced catalyst stability during biobased adipic acid production. Frontiers in Biorefining, St. Simons Island, GA. November 2018.*

Commercialization

- *ALD NanoSolutions executed option to license: Catalysts, systems, and methods for the conversion of biomass to chemicals. Provisional patent application US PTO 62/423,831 file on November 18, 2016. World patent application No. PCT/US17/62157 filed on November 17, 2017.*