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

Presented by:
Derek Vardon, PhD
NREL - National Bioenergy Center
North American Catalysis Society Meeting
June 25th, 2019
NREL/PR-5100-75014

Presentation Outline

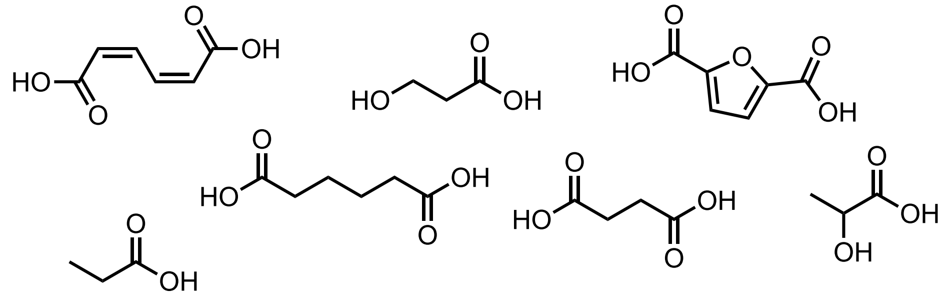
1) Why ALD for catalyst durability

2) Leaching & thermal stability for Pd/TiO_2

3) Techno-economic analysis for ALD

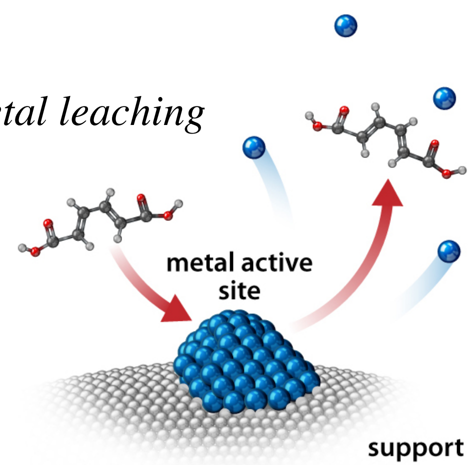
Catalyst stability major challenge for renewables

Microbially produced carboxylic acids

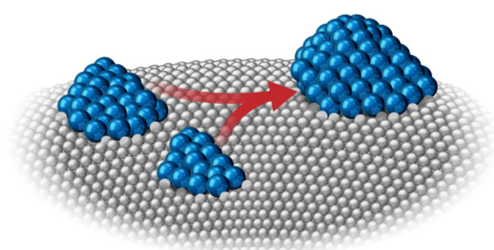


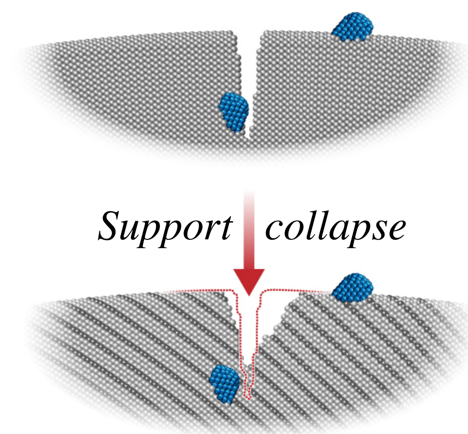
Biobased acids can be catalytically upgraded to myriad chemicals

Metal leaching



Metal sintering



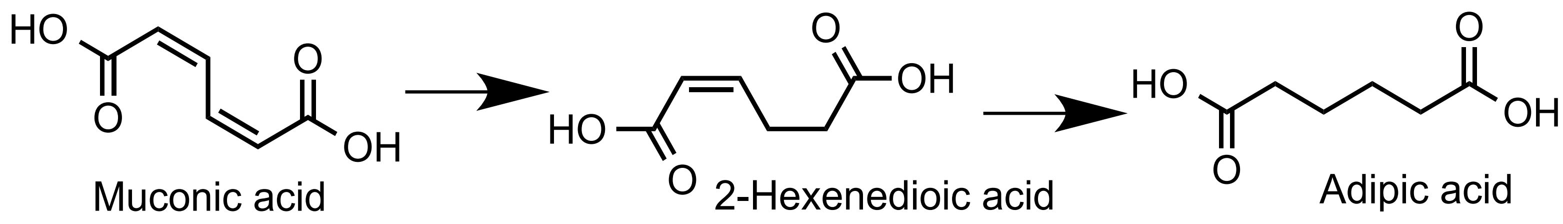


However, acids can readily deactivate conventional catalyst materials

Werpy & Peterson (2004) DOE Value Added Chemicals
Besson & Gallezot (2003) Catalysis Today
Heroguel et al. (2015) Chim Int J Chem

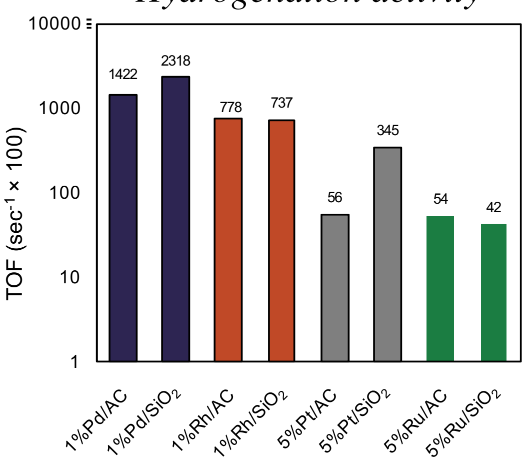
Catalyst stability for biobased adipic acid

Biobased muconic acid hydrogenation pathway

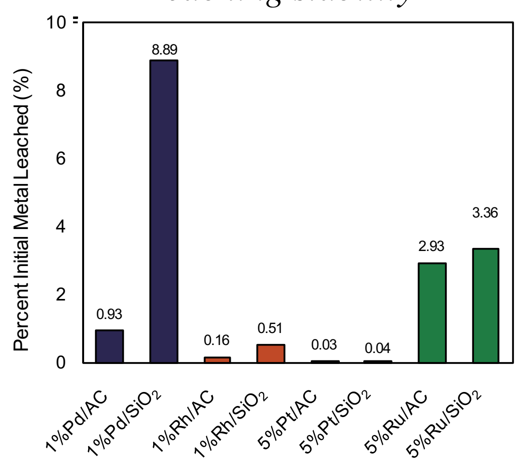


Muconic acid easily hydrogenated to adipic acid chemo-catalytically

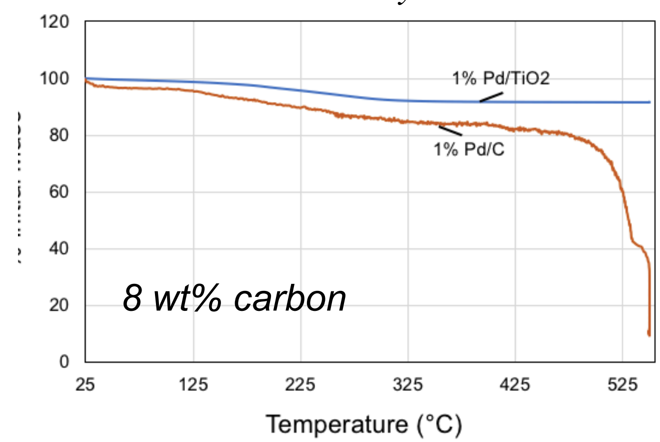
Hydrogenation activity



Leaching stability



Carbon laydown



Pd is the most active metal that readily leaches and fouls

Vardon et al. (2015) Energy & Env. Science *Johnson et al. (2016) Metabolic Eng. Comm.* *Corona et al. (2018) Green Chemistry*

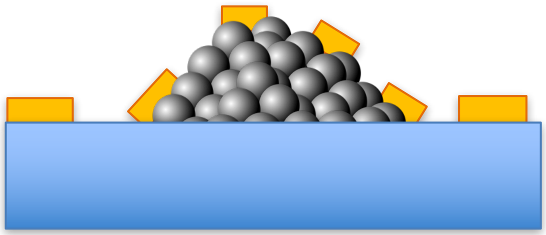
State-of technology & our approach to innovate

LOW CYCLE DOPANT ALD COATING

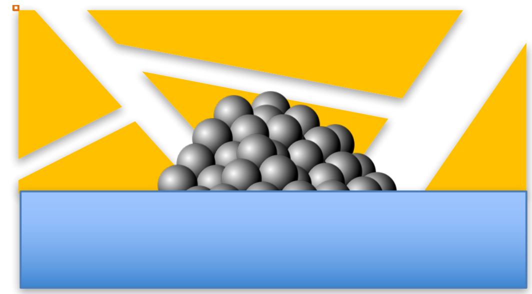
Approach relies on ‘low cycle’ ALD

THICK PROTECTIVE ALD COATING

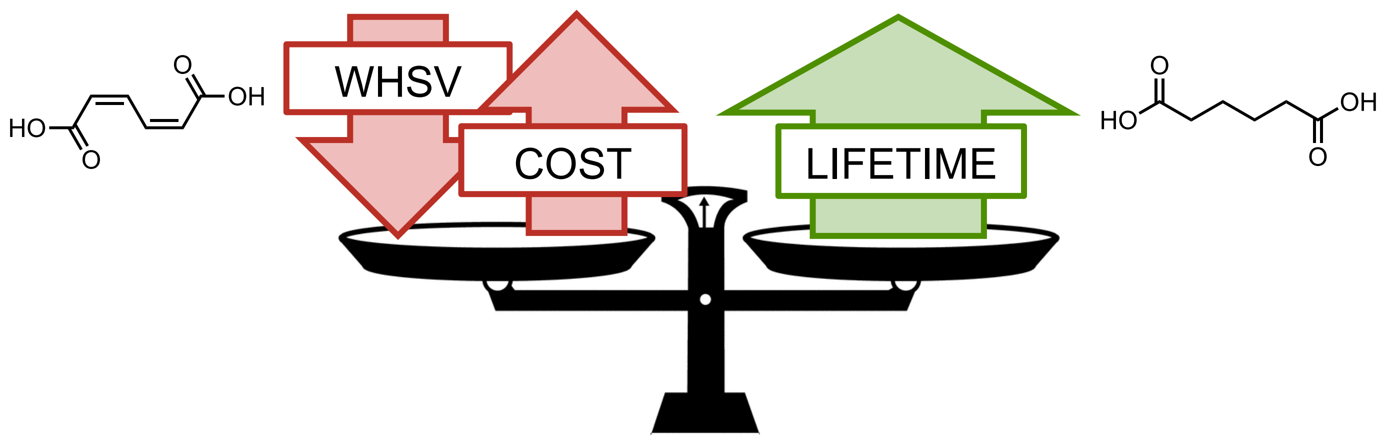
Approach cracks ≥40 cycle ALD coating



Increasing ALD cycle number



ALD COATING & PROCESS ECONOMICS

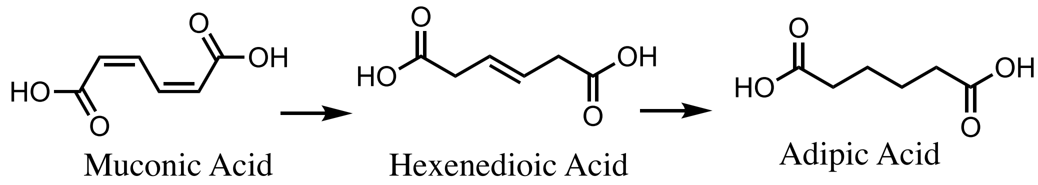


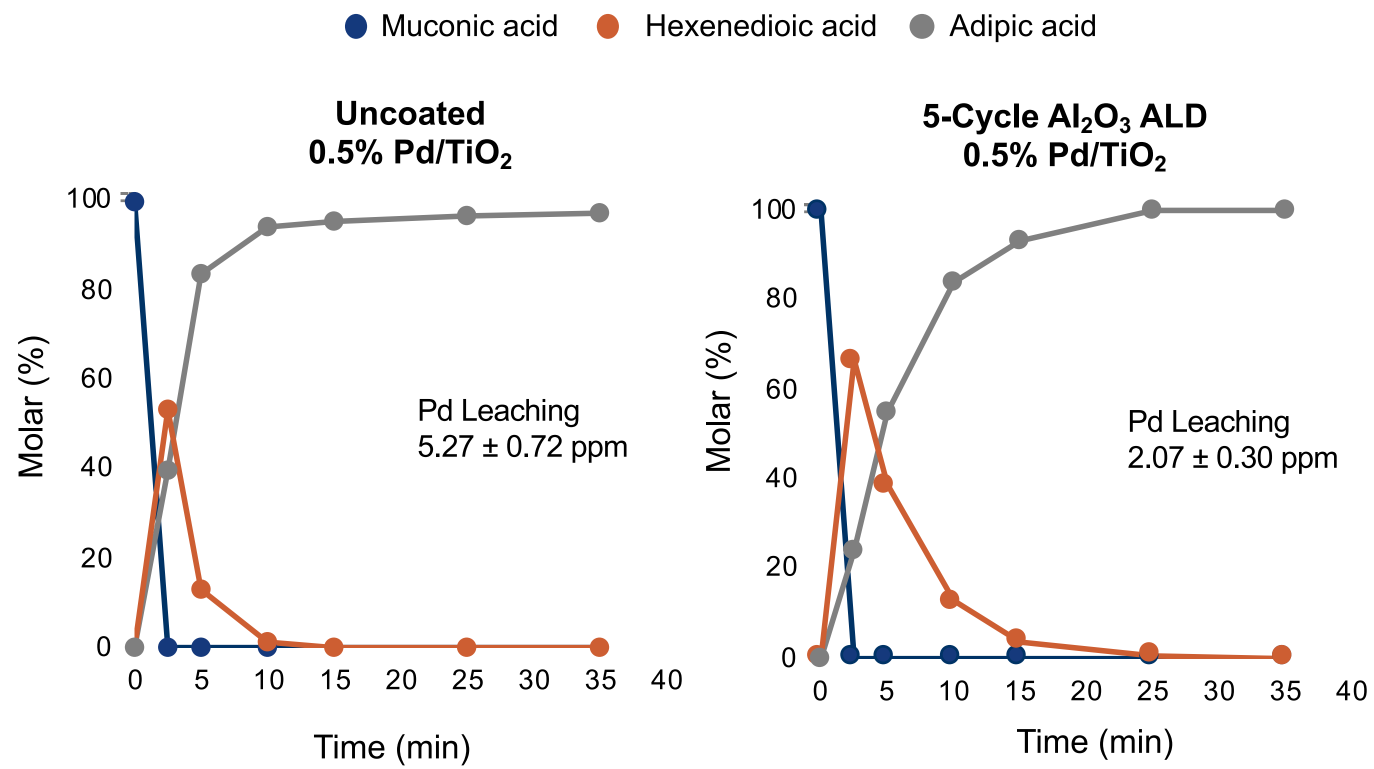
(i) evaluate scaled ALD coatings for Pd/TiO_2 in acidic environments and
(ii) determine the associated techno-economic tradeoffs

Part 2

Leaching & thermal stability for Pd/TiO_2

ALD reduced leaching by 2x, while still active

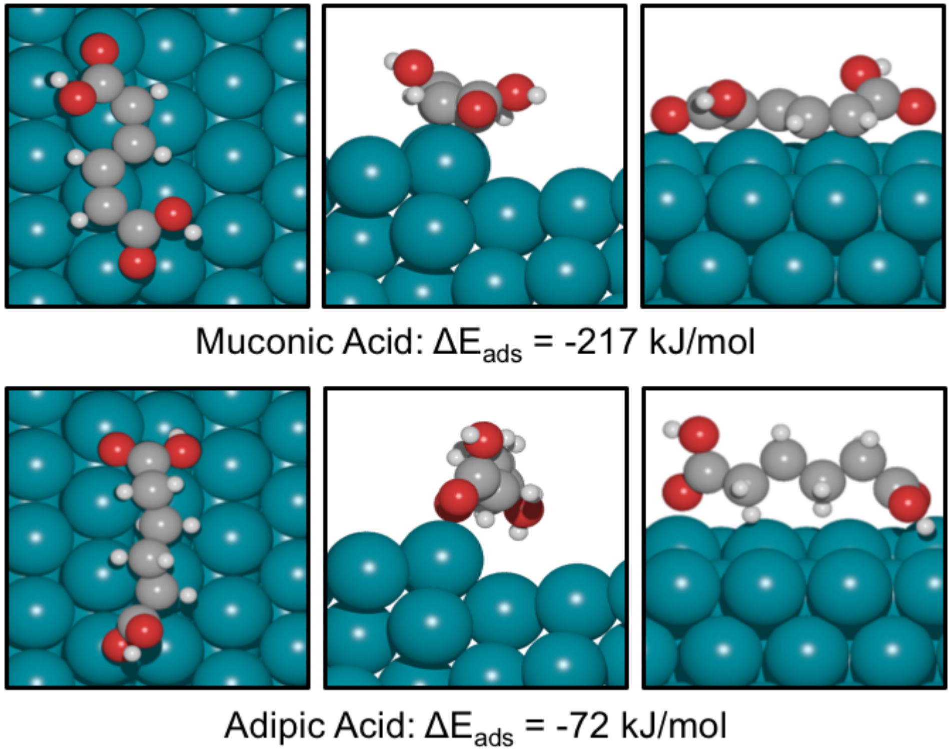




Low-cycle ALD improves catalyst leaching stability with acids, but retains activity

Settle et al. (2019) Joule. In press.

Pd leaching & binding energy of muconic acid

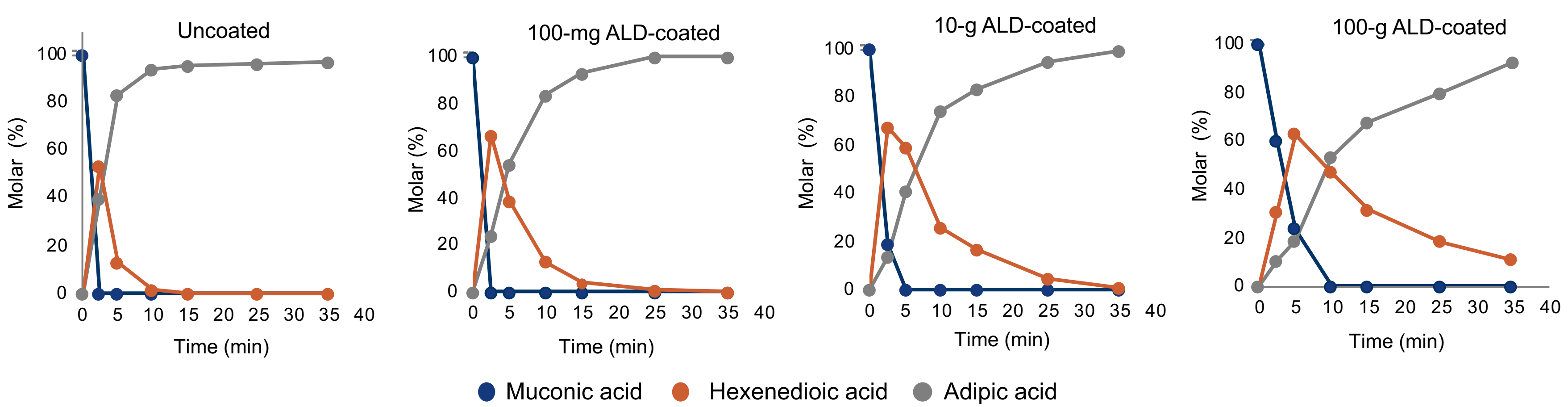


Low-cycle ALD improves catalyst leaching stability with acids, but retains activity

Settle et al. (2019) Joule. In press.

Scaling ALD with stop flow and fluidized bed

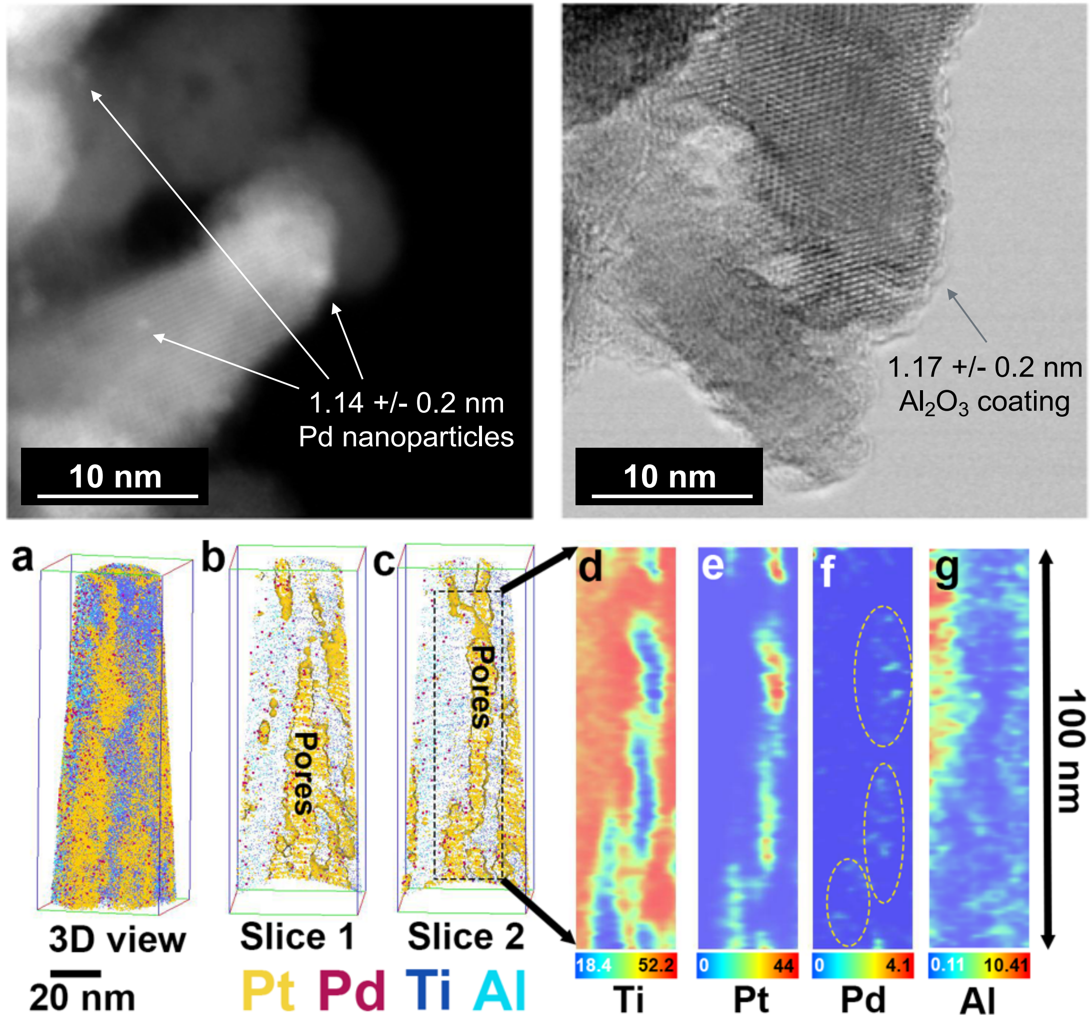
Catalyst Description	Al Content wt%	Surface Area $m^2\ g^{1}$	Pore Diameter nm	Pore Volume mL g^{1}	CO Uptake µmol g^{1}	Productivity (sec ^{1})	Pd Leaching (ppm)
Uncoated Pd/TiO_2	---	140 ± 13	5.8 ± 0.2	0.57 ± 0.05	24 ± 4	10.4 ± 0.3	6.1
Stop Flow ALD 100 mg	3.3 ± 0.04	122	5.6	0.46	14	10.8	2.1
Fluidized Bed ALD 10 g	2.8	121	5.8	0.48	13	6.7	1.2
Fluidized Bed ALD 100 g	4.4	120	4.9	0.50	11	6.1	0.7



Characterization and screening highlight 5-cycles as target coating thickness

Settle et al. (2019) Joule. In press.

Characterization of ALD coated Pd/TiO_2 catalyst

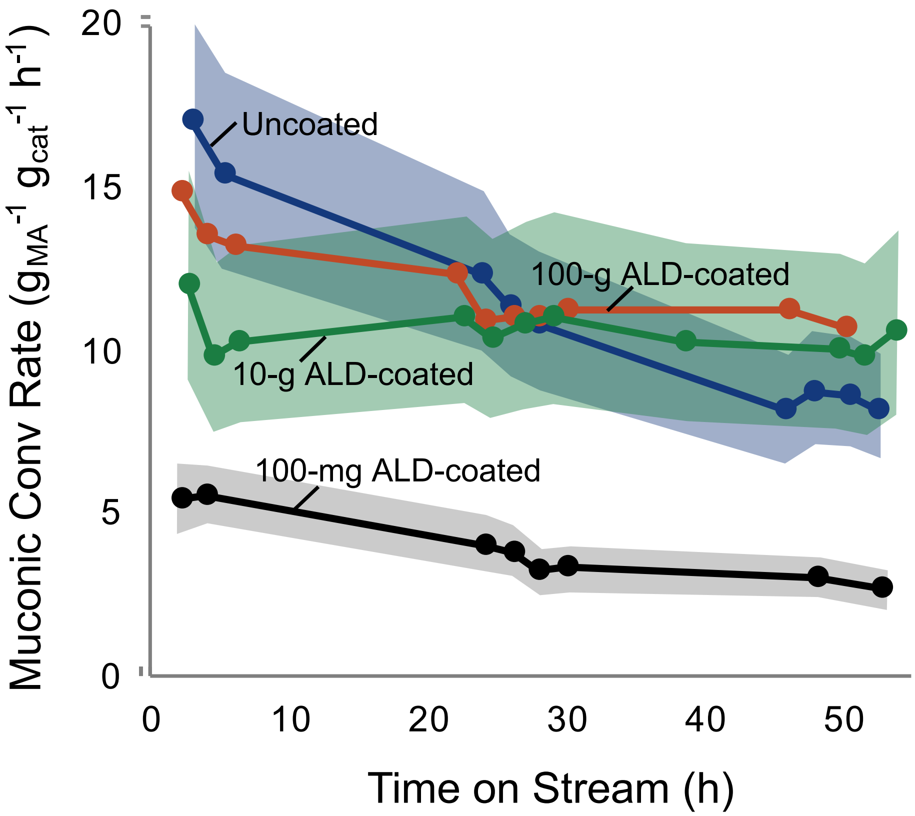


Pt is an artifact of sample preparation using FIB milling

Nanoscale imaging of complex support morphology and ALD coating

Settle et al. (2019) Joule. In press.

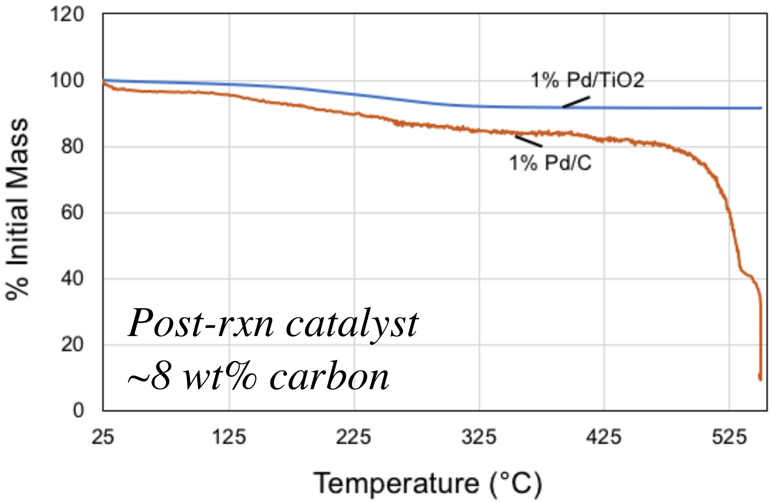
Continuous time-on-stream leaching stability



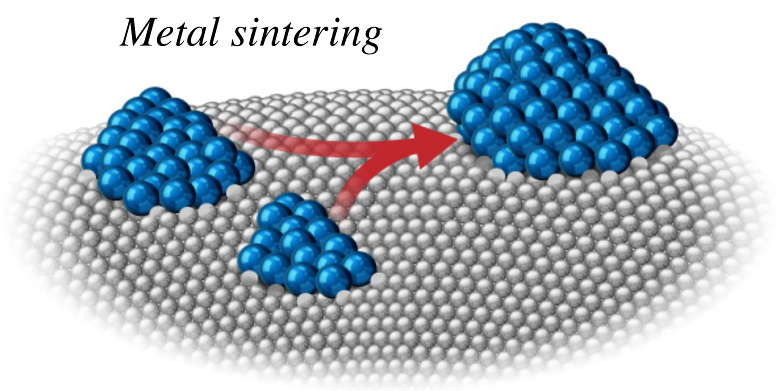
Time-on-stream testing for continuous 4x leaching stability under partial conversion with 50% reduction in activity

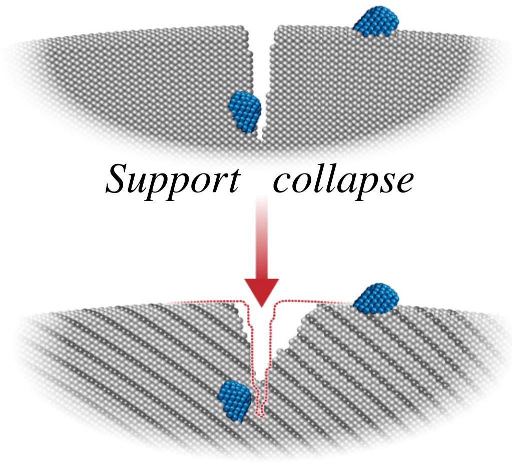
Settle et al. (2019) Joule. In press.

Challenge of uncoated Pd/TiO_2 thermal stability



Muconic acid readily fouls catalyst support and requires thermal regeneration



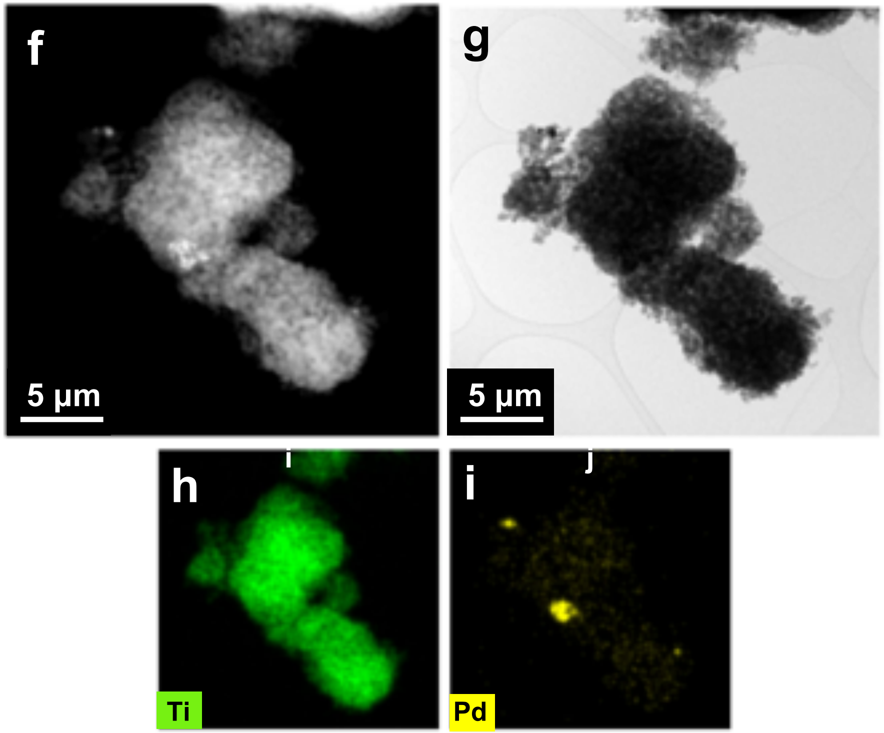


Both Pd and TiO_2 display poor thermal stability at high temperature

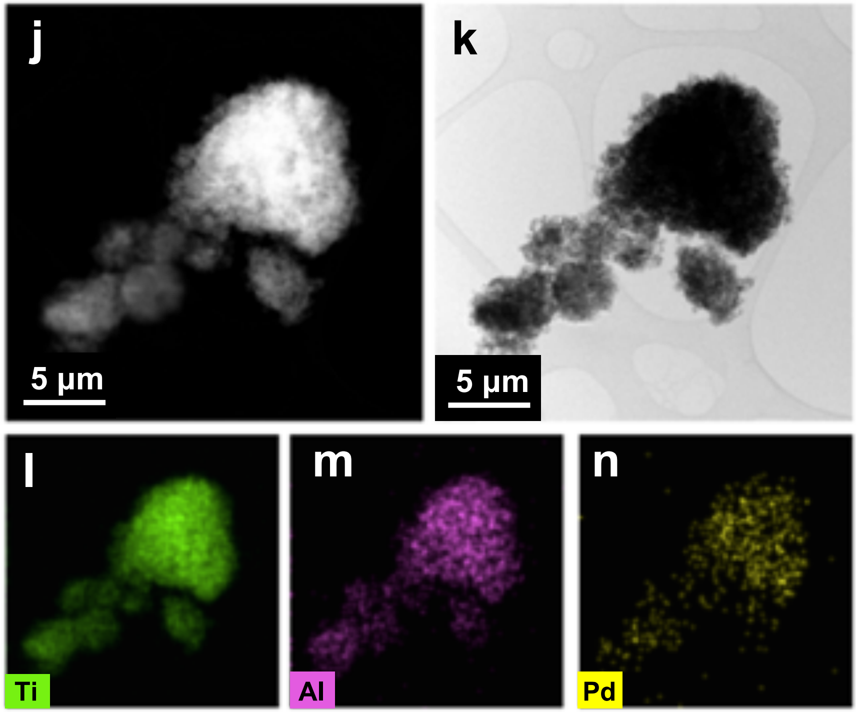
Settle et al. (2019) Joule. In press.

Validating ALD catalyst thermal durability

Uncoated Pd/TiO_2 after 700°C



5-cycle ALD after 700°C

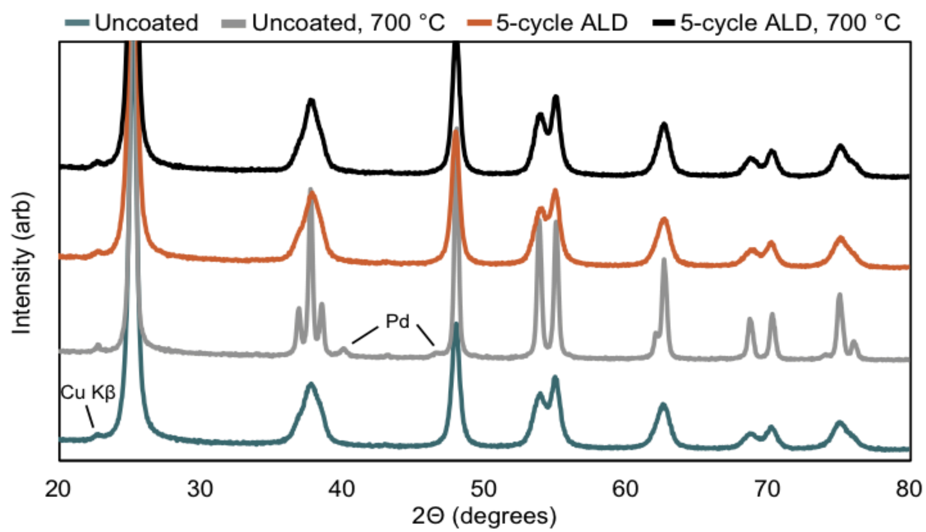


Uncoated catalyst
Pd particles agglomerate by >30x

ALD catalyst
Pd particles retain 2-nm size

Settle et al. (2019) Joule. In press.

Al_2O_3 ALD thermal durability for TiO_2 supports



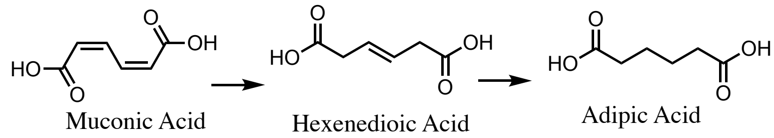
Al_2O_3 ALD retards increasing crystallinity during thermal treatment of TiO_2

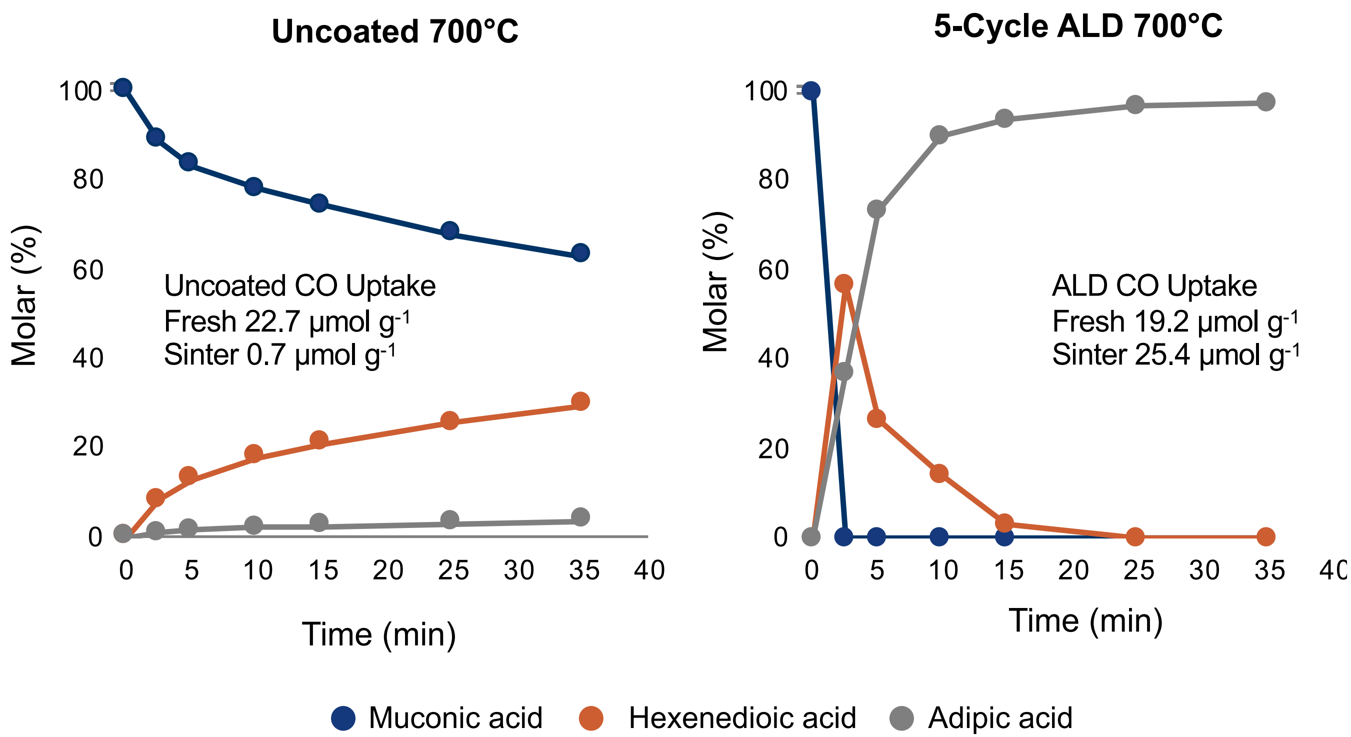
Catalyst Description	Uncoated Fresh		Uncoated 700°C	5 cycle Fresh		5 cycle 700°C
Surface area ($m^2\ g^{-1}$)	130	-80%	22	126	-25%	96
Pore volume ($mL\ g^{-1}$)	0.57	-60		0.50	-6%	0.47
Pore diameter (nm)	5.9	+200%	16.4	5.6	+30%	7.2
CO uptake ($\mu mol\ g^{-1}$)	25	-5		14	+2x	25

Results in improved retention of TiO_2 support morphology

Zhang & Banfield (1999) Jnl Mat. Research *Lin et al. (2017) Inorganics* *Settle et al. (2019) Joule. In press.*

Dramatic activity retention after high temp

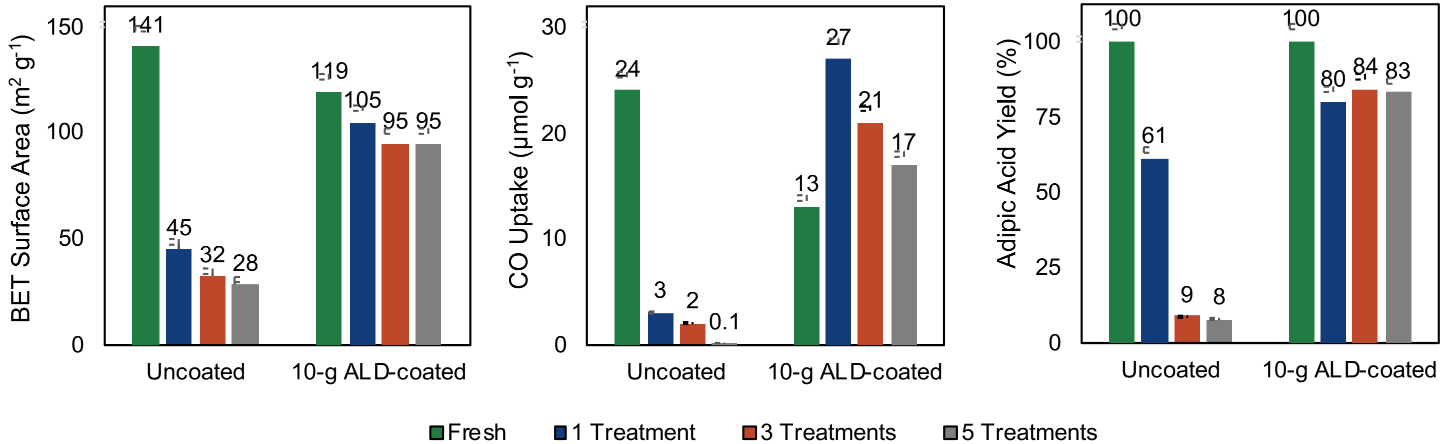


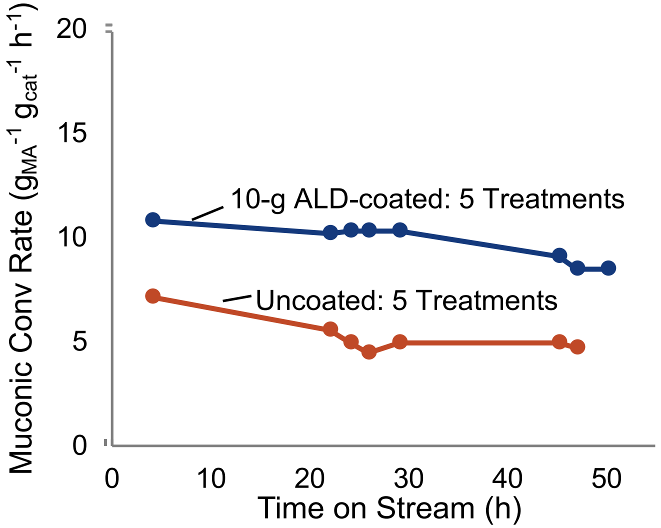


ALD coated catalyst still retains activity & selectivity after treatment at 700°C

Settle et al. (2019) Joule. In press.

Repeated thermal cycling of ALD-coated catalyst





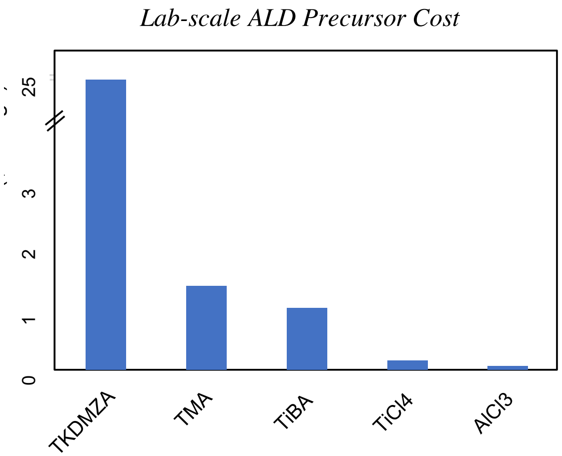
Time-on-stream testing for continuous 4x leaching stability under partial conversion

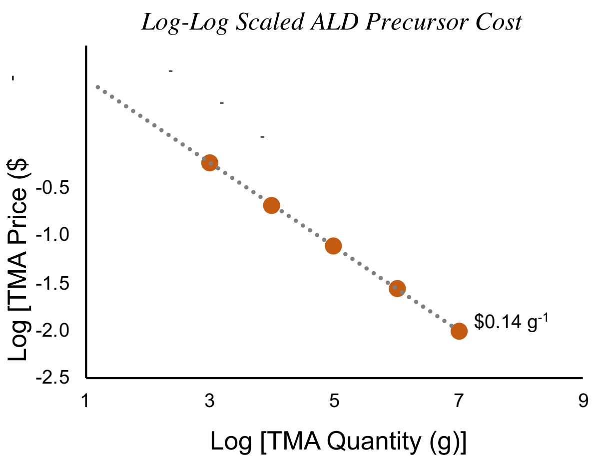
Settle et al. (2019) Joule. In press.

Part 3

Techno-economic analysis for biobased adipic acid

Major cost drivers for ALD coating synthesis





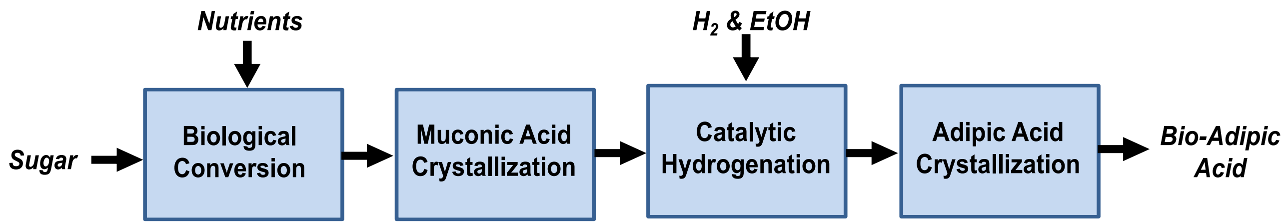
Cost Analysis for ALD Catalyst Coating

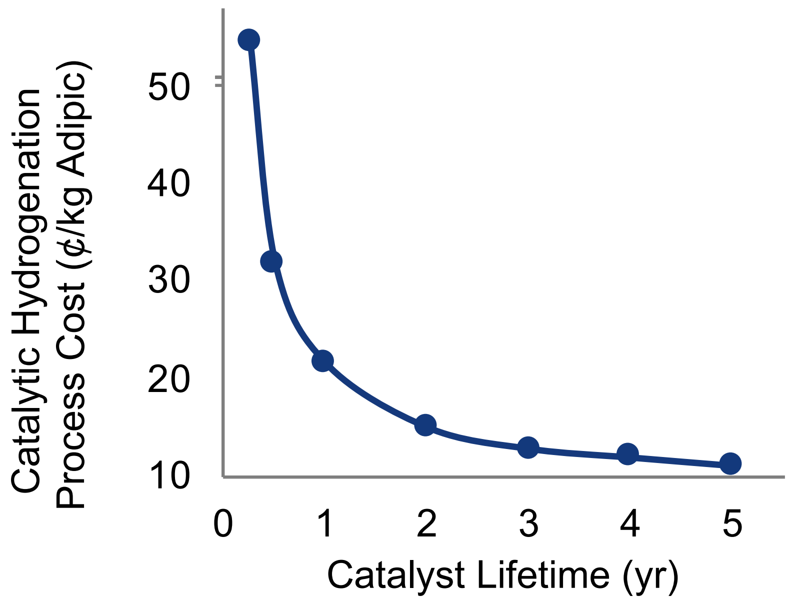
Uncoated catalyst	0.5% Pd/TiO_2
Pd metal 5-year average price	\$23 g^{-1}
TiO_2 support unit price	\$10 kg^{-1}
Uncoated catalyst surface area	130 m^2 g^{-1}
Uncoated catalyst price	**\$130 kg^{-1}**
ALD catalyst coating Al content	3.5 wt%
ALD mass of Al_2O_3 added per kg catalyst	0.066 kg
ALD precursor utilization rate, assumed	50%
ALD manufacturing cost per kg catalyst, assumed	**\$5 kg^{-1}**
TMA precursor unit price, log-log regression	\$0.14 g^{-1}
TMA precursor Al content	37.4%
ALD precursor cost per kg of catalyst	**\$31 kg^{-1}**
ALD coating with 30% margin per kg catalyst	\$41 kg^{-1}
Final ALD coated catalyst cost	**\$160**
ALD coated catalyst price increase	**23%**

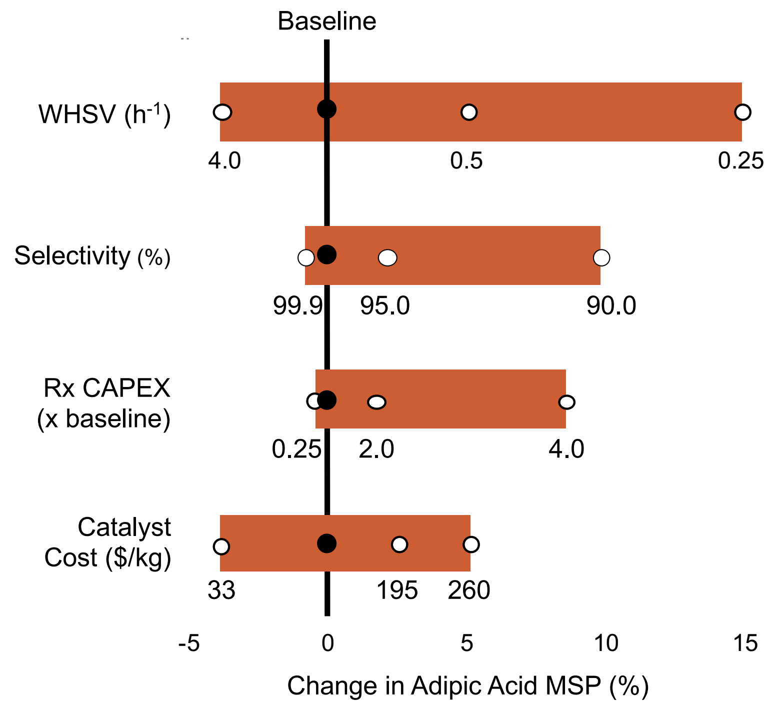
TMA precursor major cost driver for 5-cycle Al_2O_3 ALD on 0.5% Pd/TiO_2

Settle et al. (2019) Joule. In press.

Viable performance-cost-stability tradeoffs







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

Settle et al. (2019) Joule. In press.

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

Acknowledgements and funding support…

Thank you research team…


Steve Christensen
ALD Synthesis


Katherine Hurst
ALD Synthesis


Mike Griffin
Catalyst Characterization


Amy Settle
Microscopy & ICP


Nick Cleveland
Reaction Testing


Eric Tan
TEA & LCA Modeling


Carrie Farberow
Computational Modeling


Allyson York
Physisorption & DRIFTS


Xiangchen Huo
Catalyst Chemisorption

- Davis Conklin (NREL)
- Arun Devaraj (PNNL)
- Elizabeth Kautz (PNNL)
- 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…

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

ChemCatBio
Chemical Catalysis for Bioenergy

C3Bio

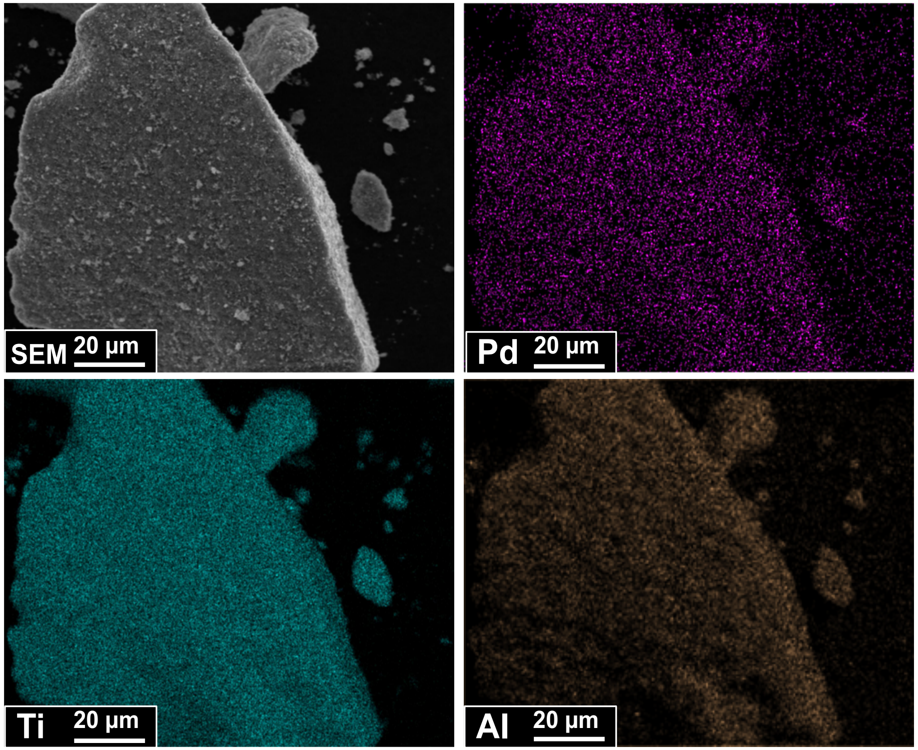
U.S. DEPARTMENT OF ENERGY

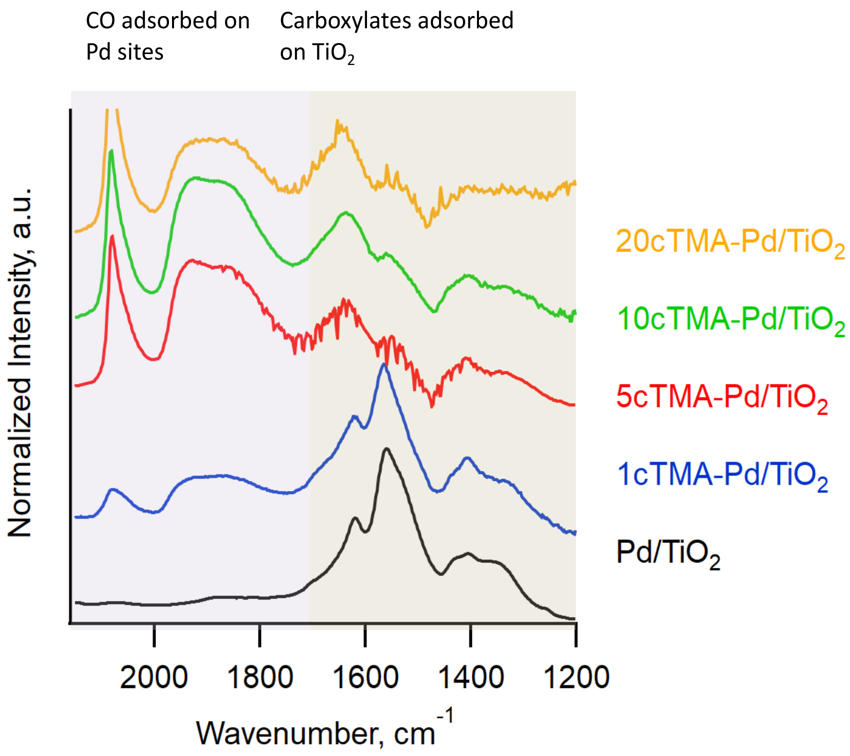
Thank you for your time! Let’s discuss...

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided predominantly by the DOE Office of Energy Efficiency and Renewable Energy's Bioenergy Technologies Office. The views expressed in this presentation do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Validating ALD coating changes bulk properties



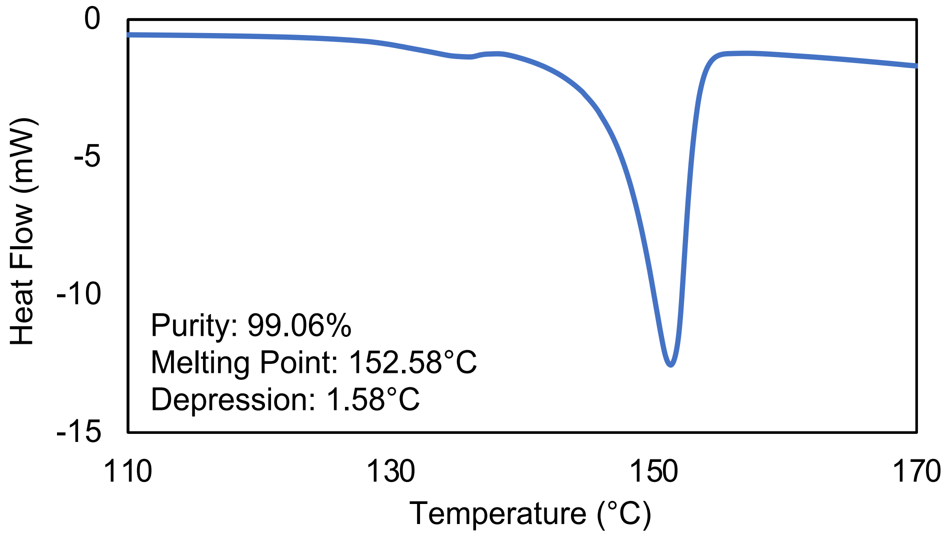


Elemental mapping & DRIFTS support 5-cycle ALD for impacting bulk properties

Settle et al. (2019) Joule. In press.

Complete conversion run with ALD catalyst

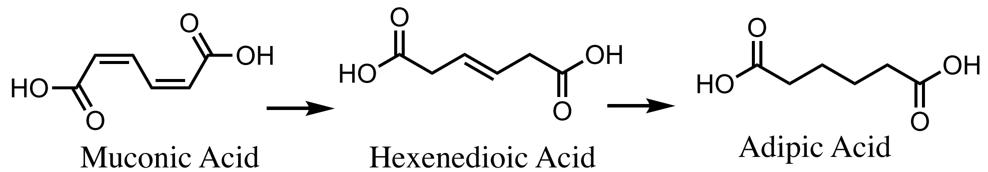
TOS (h)	WHSV (h^{-1})	Adipic yield (%)	Pd leached (ppm)	Al leached (ppm)
15		>99	0.09	14.81
22		>99	0.06	13.06
45	0.52	>99	0.03	3.38
69		>99	0.04	0.17
92		>99	0.03	BDL
110	1.05	>99	0.08	BDL
118		>99	0.10	BDL

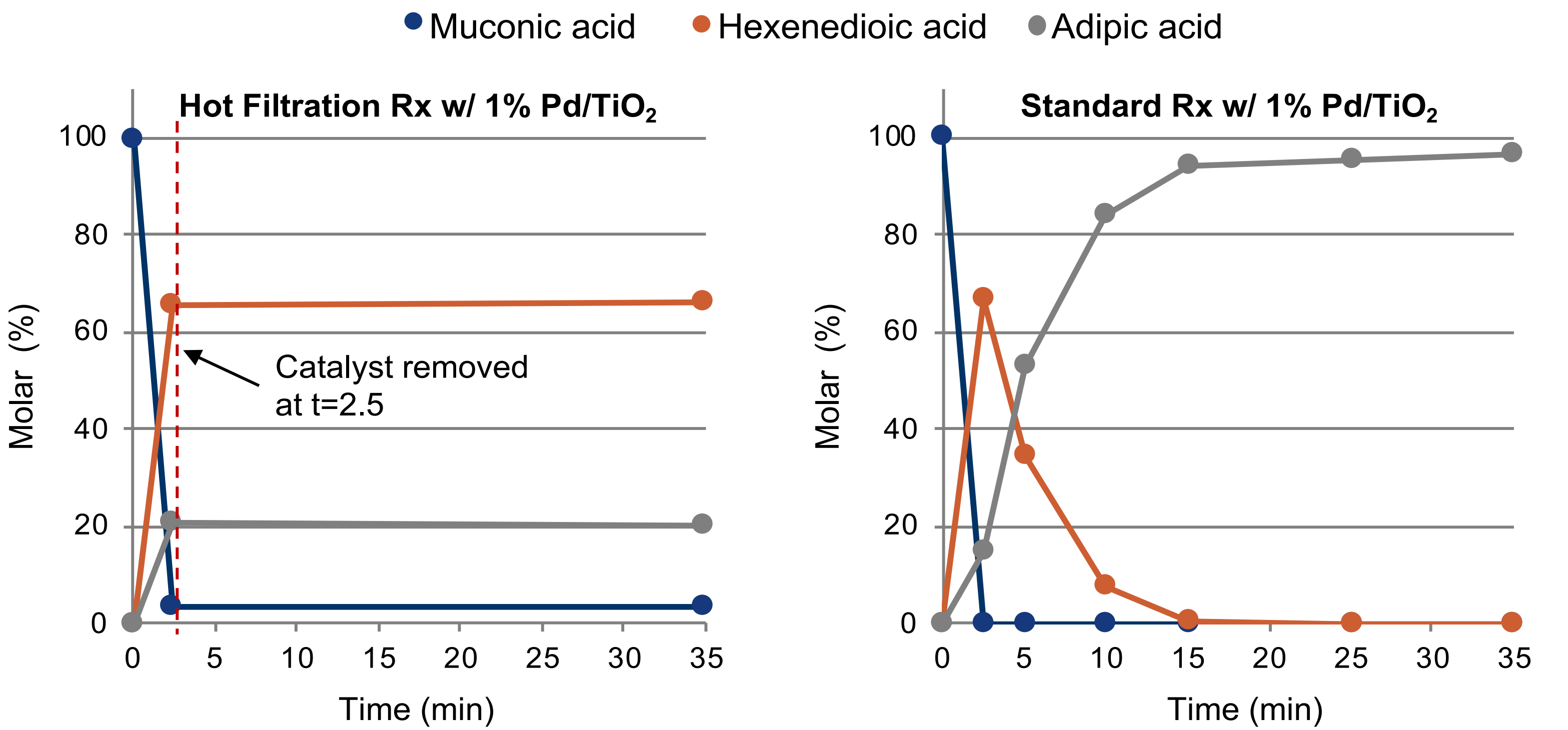


Near quantitative adipic yields at high WHSV with minimum Al leaching

Settle et al. (2018) Under Review

Catalyst leaching control test for activity





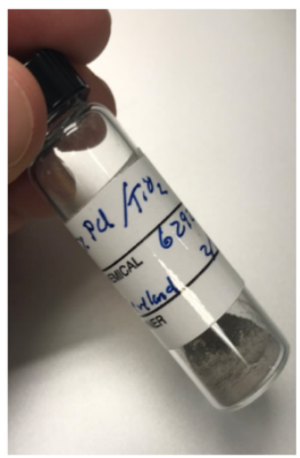
Hot filtration control tests confirm leached Pd not responsible for activity

Settle et al. (2018) Under Review

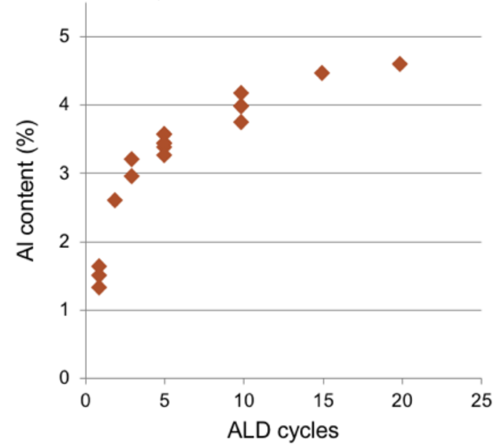
Systematically synthesize suite of ALD catalysts

Commercial TiO_2 pellets Alfa Aesar
↓
Crush & sieve pellets to <140 mesh
↓
Load Pd by strong electrostatic adsorption
↓
Dry in inert at 110°C reduce in H_2 at 150°C
↓
Sieve to <80 mesh pretreat inert 200°C

Uncoated Pd/TiO_2	Catalyst Property
Particle Dia micron	<180
Pack Density g mL^{-1}	0.76
Surface Area m^2 g^{-1}	130
Pore Diameter nm	5.9
Pore Volume mL g^{-1}	0.58
Dispersion % calculated	47



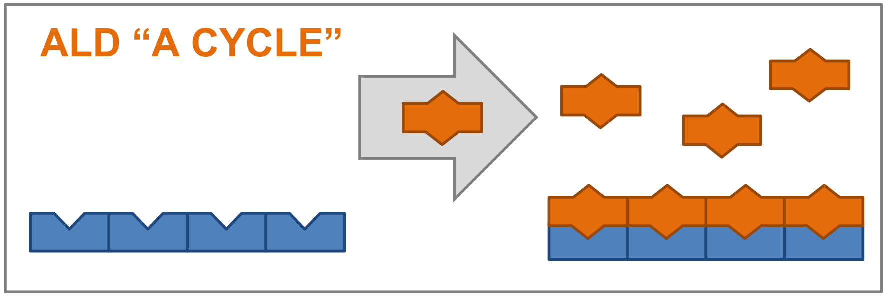
Al_2O_3 ALD on 0.5% Pd/TiO_2

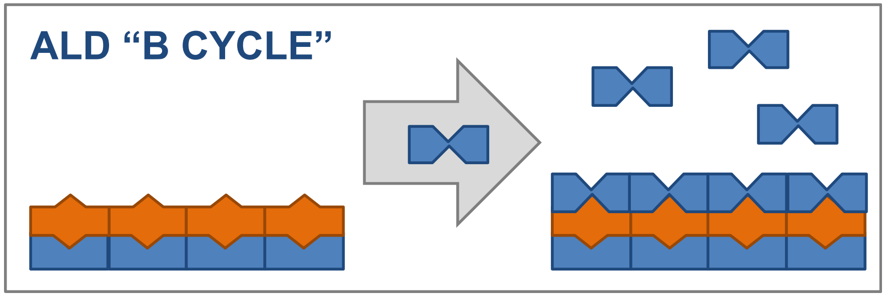


Increasing ALD coating thickness cycle-by-cycle to determine "sweet spot"

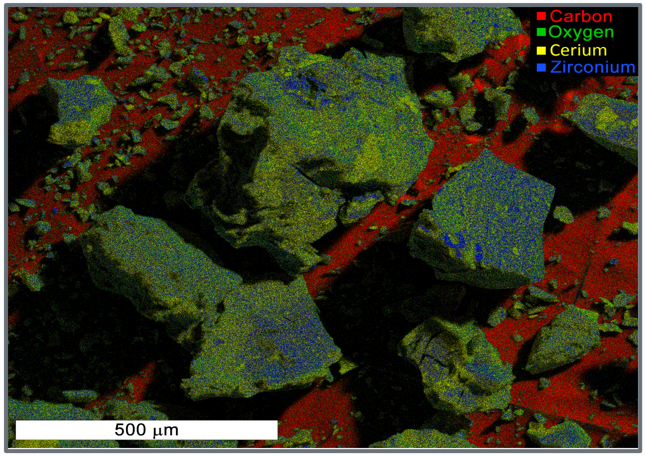
Settle et al. (2019) Joule. In press.

Background on atomic layer deposition (ALD)

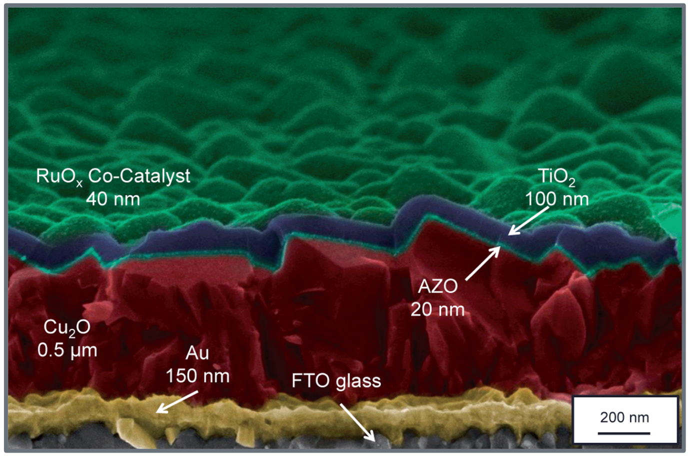




ALD provides self-limiting growth of protective metal oxide layers at atomic scale



Traditional deposition methods



Atomic layer deposition

Offers greater control and uniformity with complex morphologies

Azevedo et al. (2014) Energy Env. Sci. *O'Neill et al. (2015) ACS Catalysis.* *Lu et al. (2016) Surface Sci. Reports.* *Singh et al. (2017) Annual Rev. Chem. Bio. Eng.*