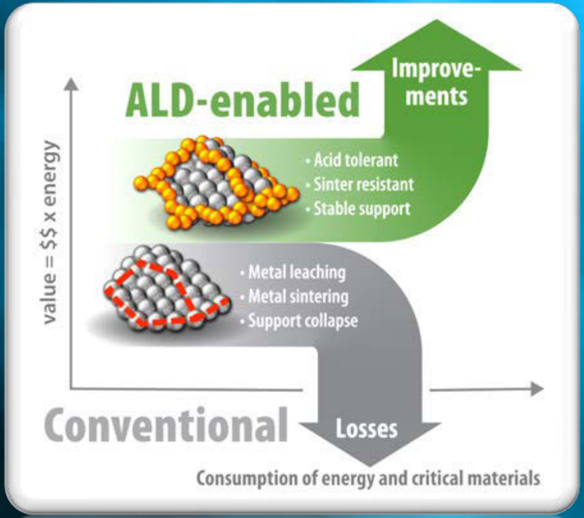
Atomic Layer Deposition for Enhanced Reactivity, Stability, and Sulfur Tolerance of Hydrogenation Catalysts



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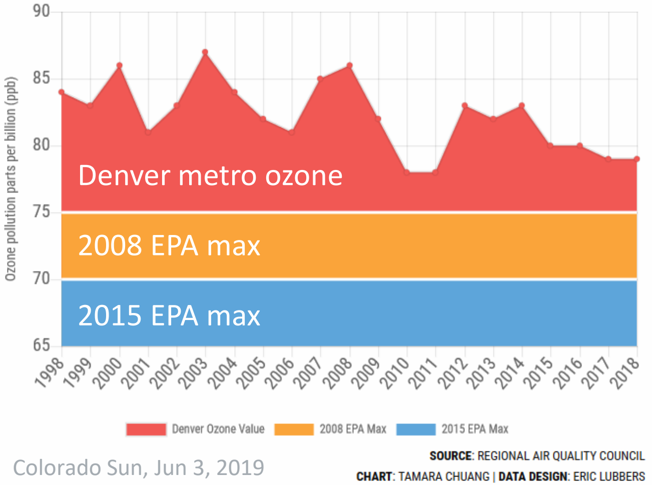
ACS Virtual Postdoc Symposium
November 19, 2020

That fresh mountain air

Colorado's dirty little secret



Colorado Sun, Jun 3, 2019

NEWS › ENVIRONMENT • News

Denver among top 10 worst U.S. cities for hazardous air pollution, 2 new studies say

EPA tallies show Denver residents inhaled elevated pollution on more than 260 days a year for the past two years

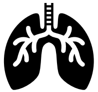
Denver Post, Jan 30, 2020

Dec 2019: EPA nonattainment "moderate" → "serious"

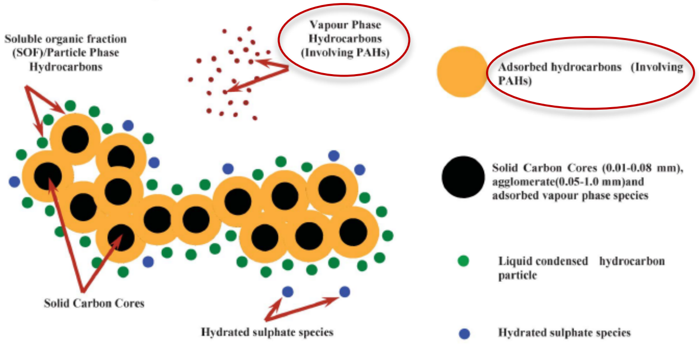
Need for hydrogenation catalysts

Diesel fuel

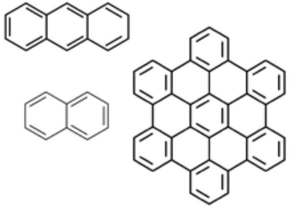
NO_x PAH
SO_x PM
CO_x



- Asthma
- Pulmonary disease
- Lung and skin cancer

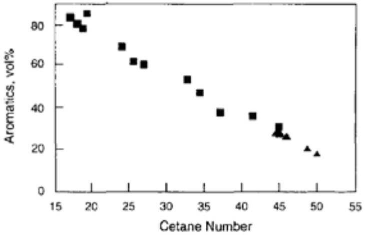


Aromatic content ↑

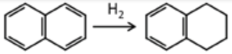


PM/PAH emissions ↑

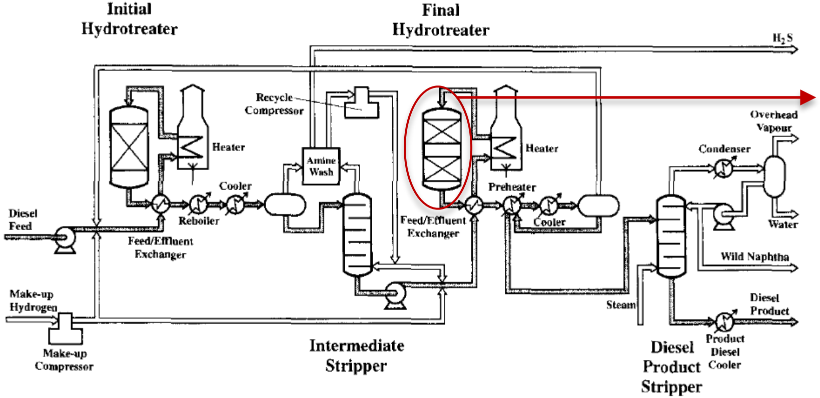
Fuel quality ↓



Catalytic Hydrogenation (HYD)

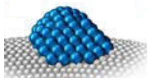


Remove S, N **Aromatic HYD**



+ΔH

PGM



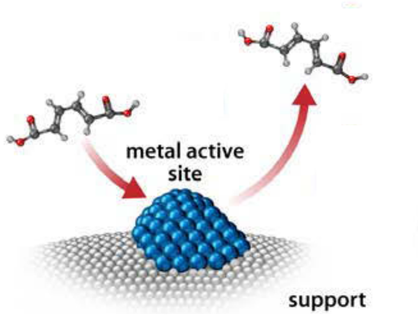
300-400°C
6-10 MPa H_2
↓
~20-30 wt% aromatics

1. Increase HYD activity

Worldwide Fuel Charter (WWFC)	Diesel aromatics limit (wt %)
Category 1	--
Category 2	25
Category 3	20
Category 4	15

Sharma, M., et al. *RSC Advances* **3**(26), 10103 (2013).
Cooper, B. H. and B. B. L. Donnis. *Appl Catal A: General* **137**, 203 (1996).

Catalyst degradation pathways



200-700°C

-Oxidizing/Reducing
-Condensed phase
-Coking
-Impurities (S)

1. Increase HYD activity
2. Improve lifetime durability

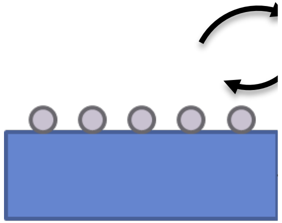
→ Tailored catalyst solution

ALD can be used to protect catalysts

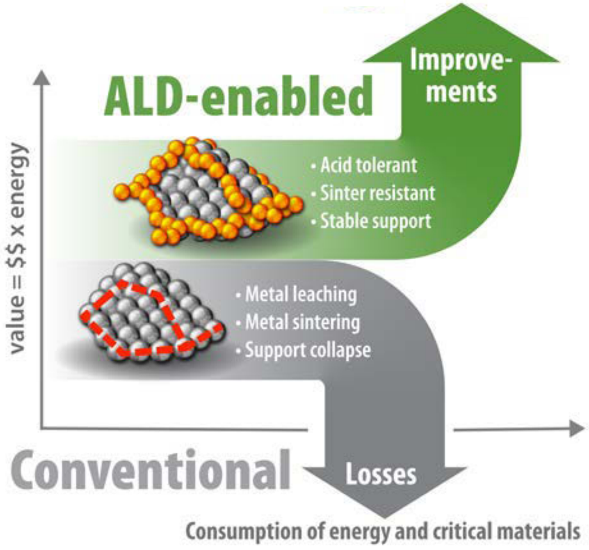
Atomic Layer Deposition (ALD)

Flat surfaces
1D (nanowires)

Ligand exchange reaction



Protective ALD coatings for catalytic nanoparticles



Settle, A. E., et al. *Joule* **3,** 1 (2019).

ALD can be used to protect catalysts

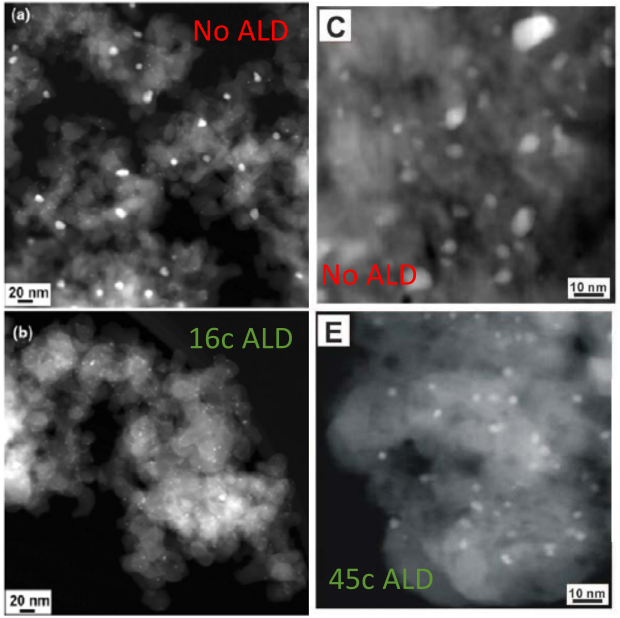
Thermal

Al_2O_3-Pd/SiO_2

6h, 500°C

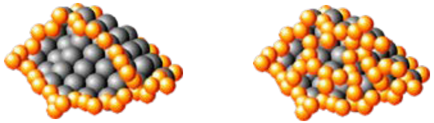
Al_2O_3-Pd/Al_2O_3

675°C



30 min

1700 min

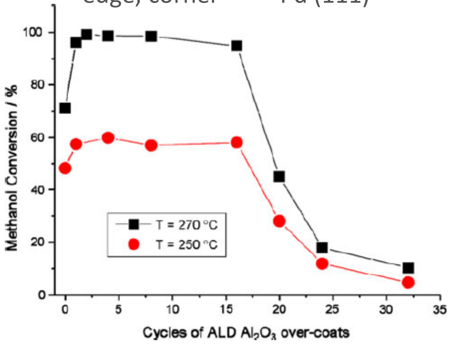


Coating low-coordination sites

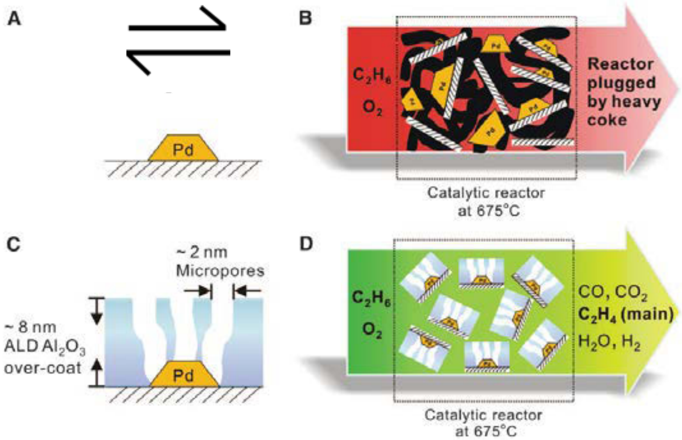
Complete encapsulation

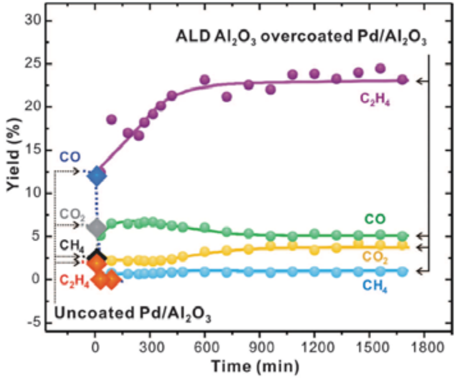
edge, corner

Pd (111)



Reactivity



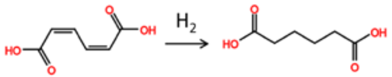


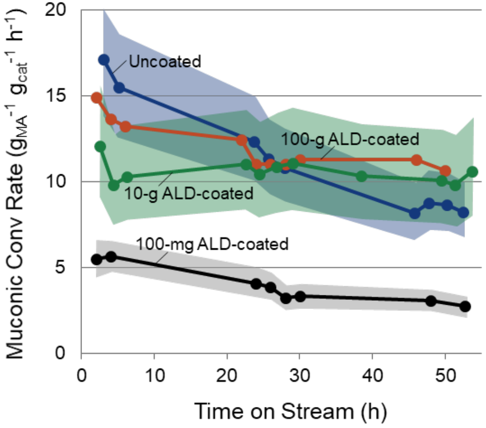
Feng H., et al. *Catal Lett* **141**, 512 (2011).
Lu J., et al. *Science* **335**, 1205 (2012).

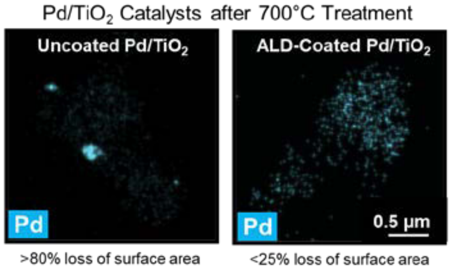
ALD for catalysis in CCT&S Center

Muconic acid HYD

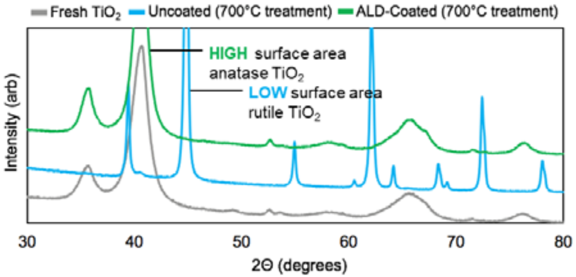
$3cAl_2O_3$-Pd/TiO_2







Catalyst	Leaching (Pd ppm)
Uncoated (Pd/TiO_2)	1.4 ±0.7
100-mg ALD-coated	0.3 ±0.1
10-g ALD-coated	0.08 ±0.04
100-g ALD-coated	0.05 ±0.01

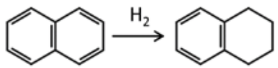


Settle, A. E., et al. *Joule* **3,** 1 (2019).

3 g batches

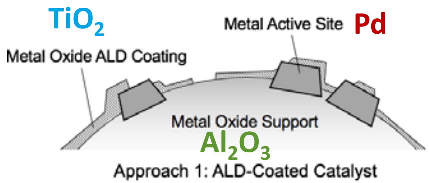
- x cAl_2O_3-Pd/TiO_2
- x $cTiO_2$-Pd/TiO_2
- x cAl_2O_3-Pd/Al_2O_3
- x $cTiO_2$-Pd/Al_2O_3

Naphthalene HYD



-Aromatic HYD
-Probe rxn for S tolerance

Overcoating



Initial catalyst screening

$10cTiO_2$-Pd/Al_2O_3

- In-depth characterization
- Reaction testing
- Synthesis scale-up

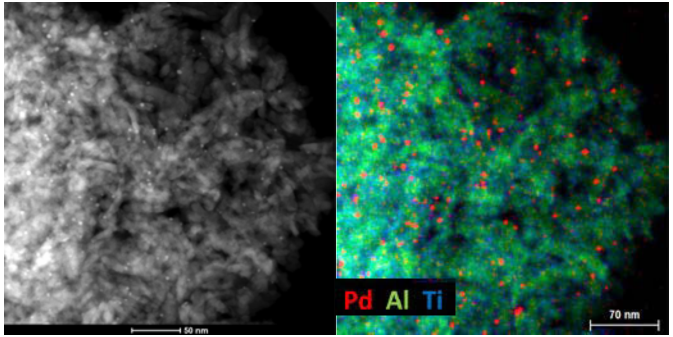
TiO_2 ALD on Pd/Al_2O_3

Catalyst	Pd/Al_2O_3	$10cTiO_2$
Pd content (wt%)	0.44	0.33
Ti content (wt%)	--	9.3
BET (m^2 g^{-1})	112	110
H uptake (μmol g^{-1})	28.2 →	10.5
CO uptake (μmol g^{-1})	20.4 →	4.3

When normalized by Pd wt%:
H uptake: -50%
CO uptake: -74%

HAADF *low mag* EDS

$10cTiO_2$-Pd/Al_2O_3

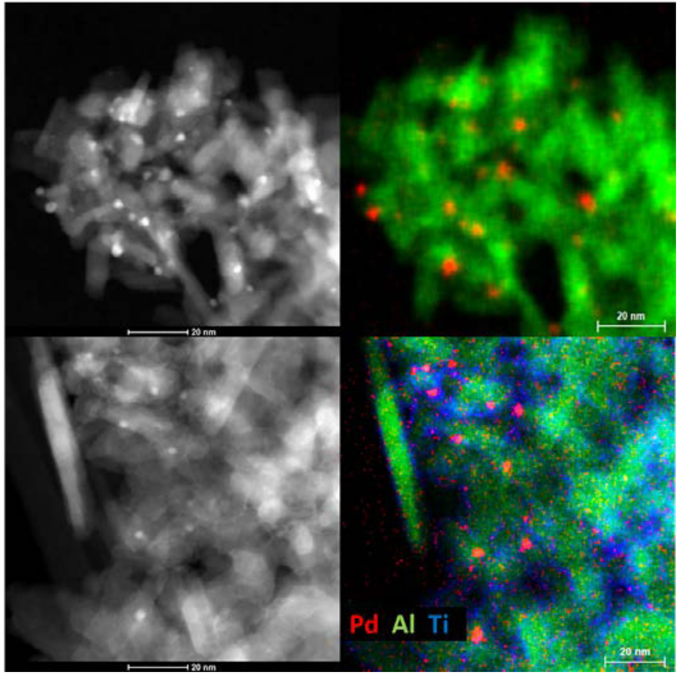


- ✓ Conformal layer
- ✓ Al_2O_3 support coated
- ✓ **H and CO uptakes decreased**
- ✓ Pd sites covered (extent unclear)

HAADF *high mag* EDS

Pd/Al_2O_3

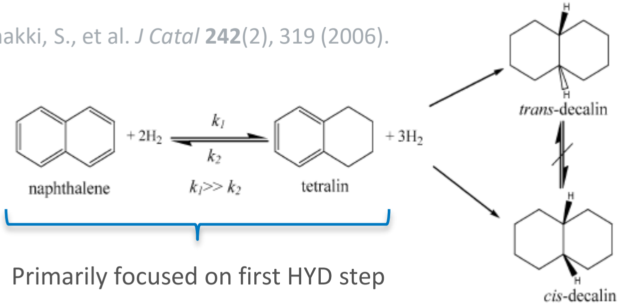
$10cTiO_2$-Pd/Al_2O_3



How does TiO_2 coverage impact reactivity?

ALD catalyst performance in naphthalene HYD: batch

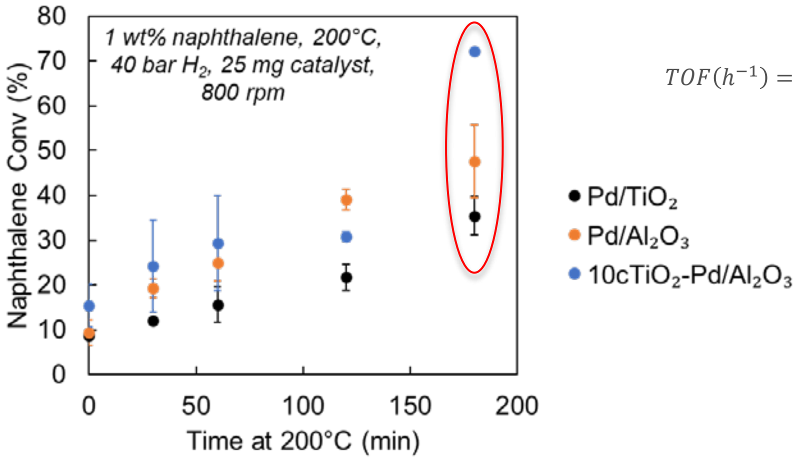
Kirumakki, S., et al. *J Catal* **242**(2), 319 (2006).

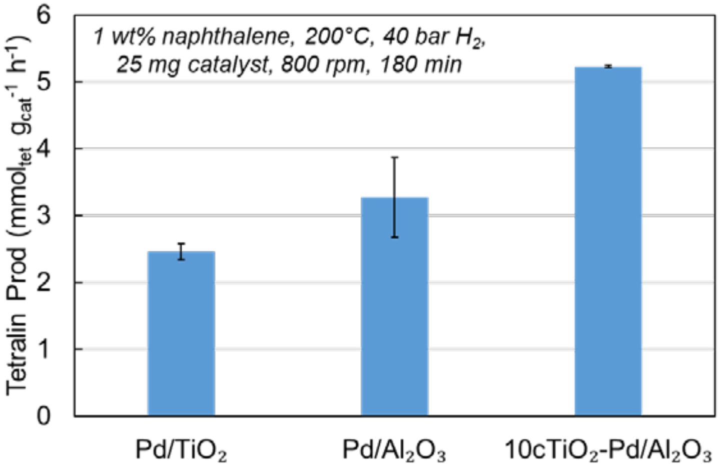


Primarily focused on first HYD step

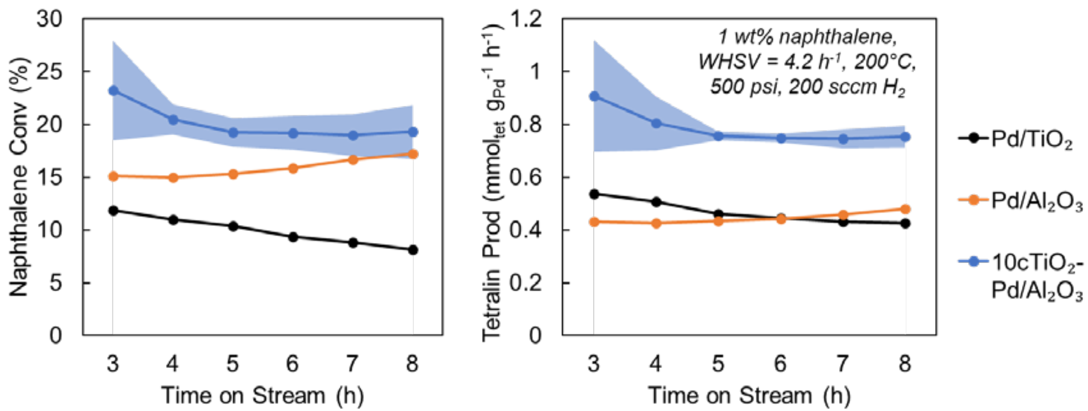
$$Tetralin\ Prod = \frac{mmol_{tetralin}}{g_{cat} * 3h}$$

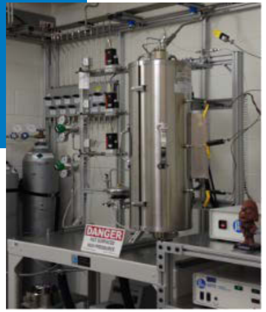
$$TOF(h^{-1}) = \frac{Prod\left(\frac{mol_{tet}}{g_{cat}}\right)}{wt\ frac_{Pd}} * \frac{106\frac{g}{mol}}{Disp_{Pd,CO}}$$



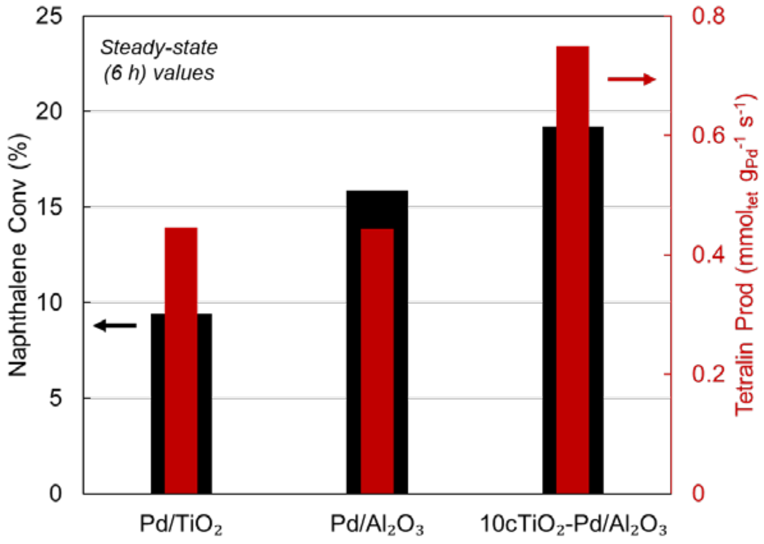


ALD catalyst performance in naphthalene HYD: flow





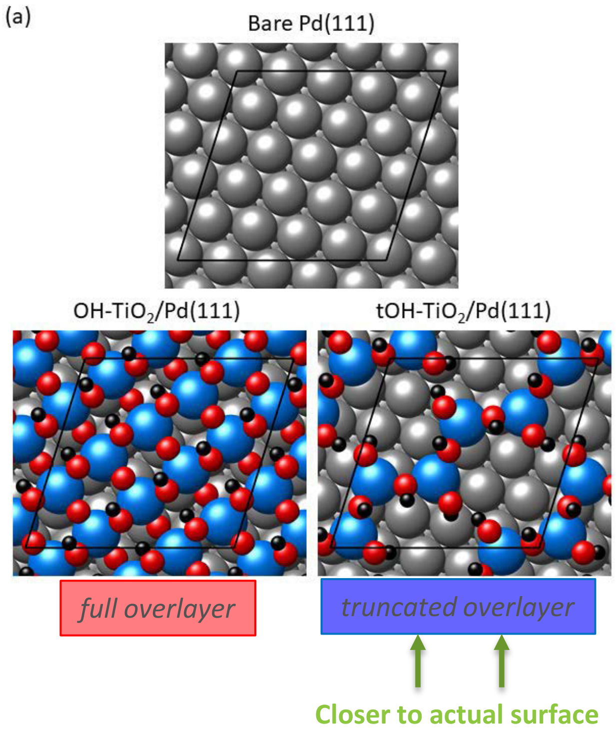
trickle bed reactor

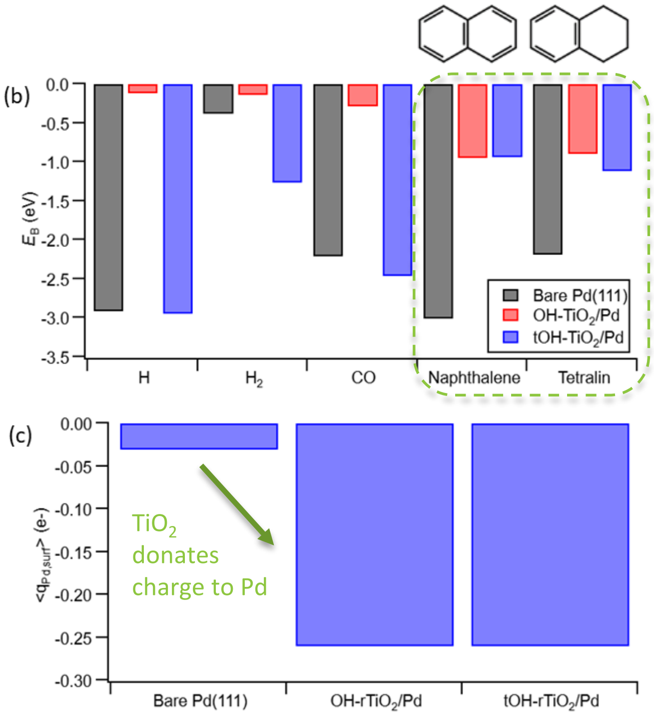


- ✓ Similar trends to batch activity
- ✓ **10cTiO_2 has ~1.7X Pd-norm activity of base material**
- ✓ Alumina-based catalysts stable over 8 h run

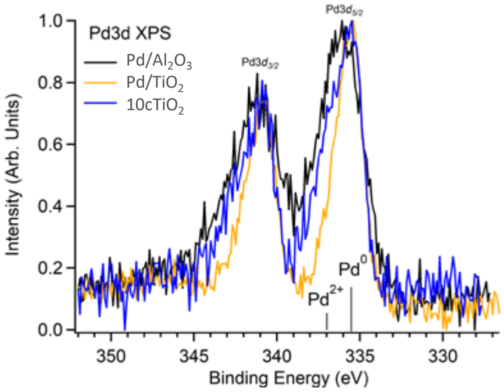
Why does TiO_2 ALD layer boost activity?

Probing the source of catalytic enhancement





- ✓ Naphthalene and tetralin destabilized
- ✓ H and H_2 stabilized (Pd surface charge)



- ✓ No change in Pd electronic structure

↑H_2 binding +
↓strongly-bound product
= Increased HYD rate

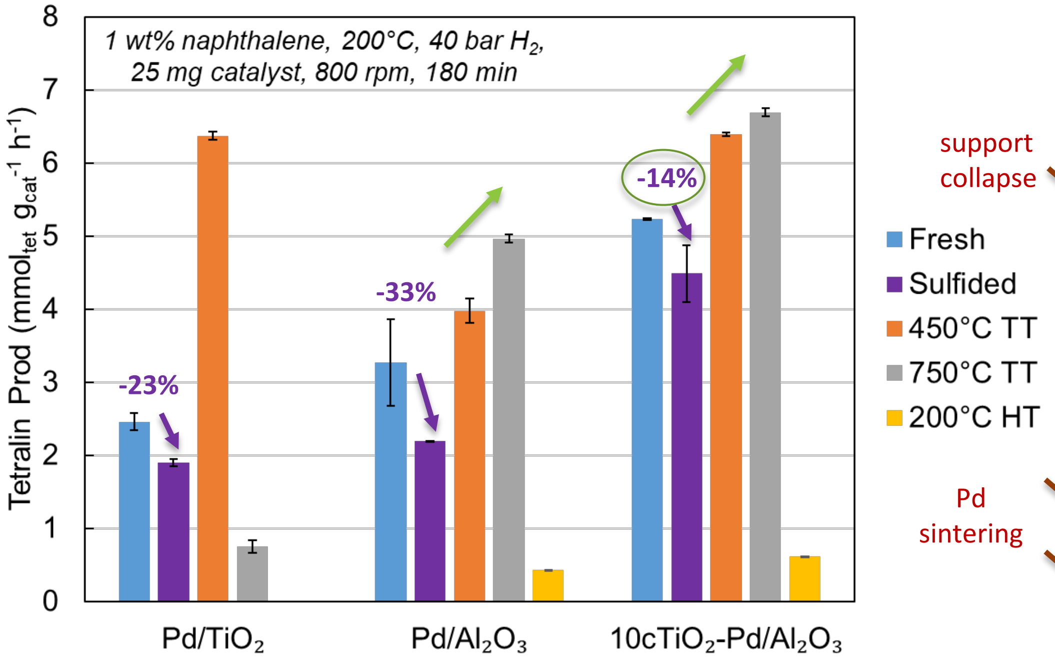
**note: simulated overlayers are rutile TiO_2, while actual ALD layers are amorphous*

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 H_2

XX°C HT = 15 h at XX°C, liquid water, 200 rpm → 2 h at 200°C, 200 sccm H_2



support collapse

Pd sintering

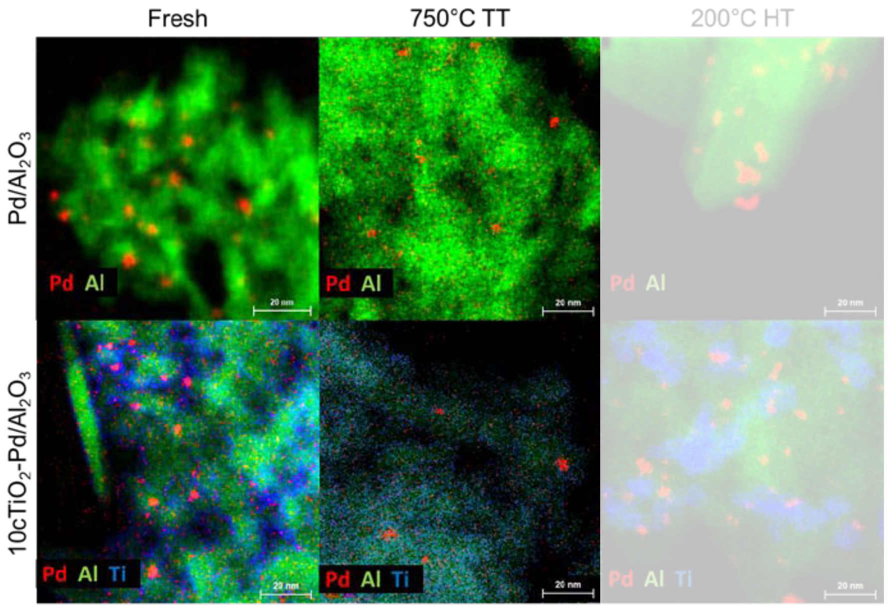
Change in BET surface area ($m^2 g^{-1}$)

Treatment	Pd/TiO_2	Pd/Al_2O_3	$10cTiO_2$
450°C TT % change	+1%	+0.9%	+5%
750°C TT % change	-74%	-0.9%	-4%
200°C HT % change	-44%	-83%	-26%

Change in CO uptake (μmol g^{-1})

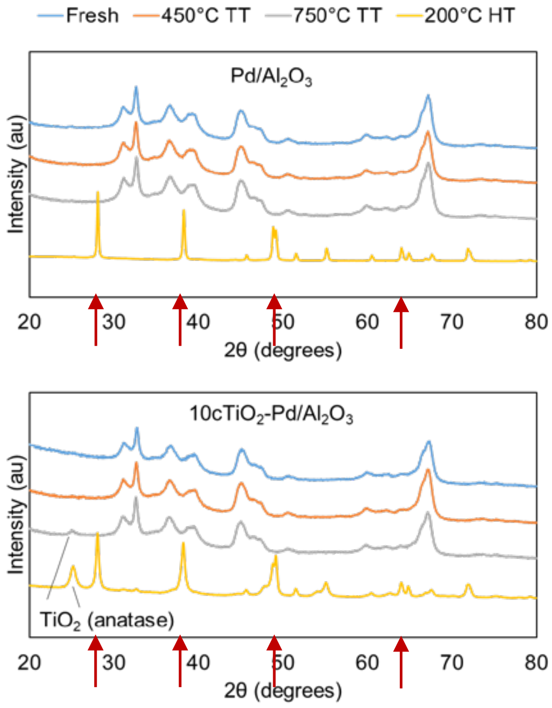
Treatment	Pd/TiO_2	Pd/Al_2O_3	$10cTiO_2$
450°C TT % change	+45%	-18%	+47%
750°C TT % change	-83%	-47%	+120%
200°C HT % change	-95%	-82%	+22%

ALD catalyst stability



Pd sintering

ALD layer unstable

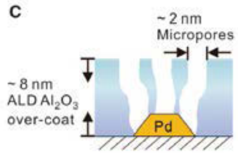


Al_2O_3 boehmite transformation

Change in CO uptake (μmol g^{-1})

Treatment	Pd/Al$_2$O$_3$	10cTiO$_2$
750°C TT % change	-47%	+120%

Calcination may form pores



Lu J., et al. *Science* **335**, 1205 (2012).

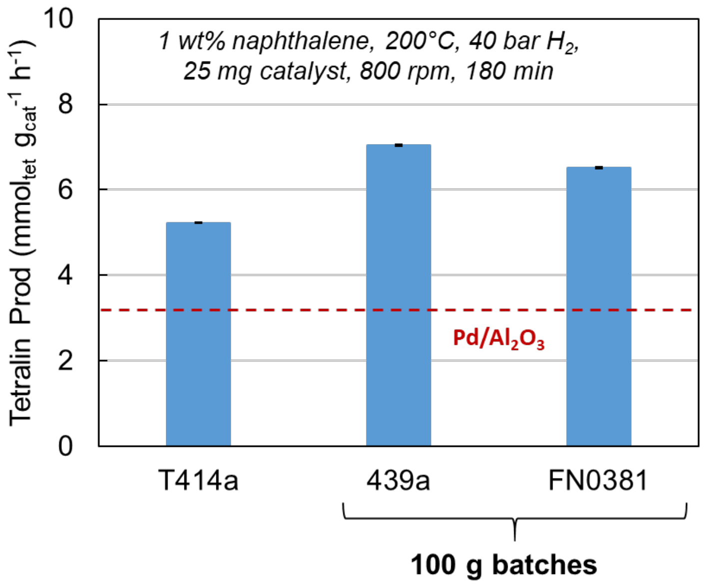
ALD synthesis can be scaled

kg-scale fluidized bed ALD

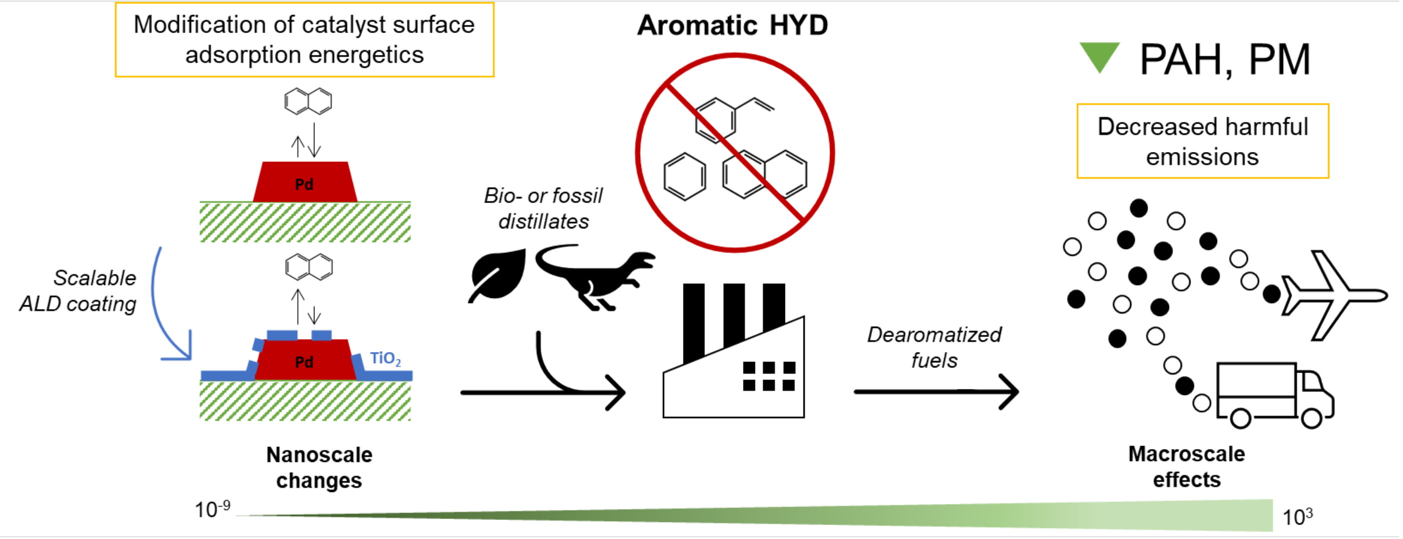
Properties of scaled 10cTiO$_2$

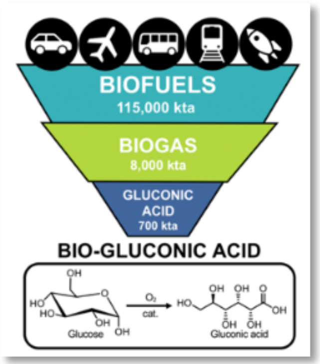
Catalyst	Batch size	BET (m^2 g^{-1})	H uptake (µmol g^{-1})
T414a (original 10cTiO$_2$)	3 g	110	10.5
439a	100 g	122	24.0
FN0381-1-2	100 g	122	18.1

- ✓ **Activity enhancement preserved across 2 orders of magnitude**
- ✓ Some deviation in H uptake upon scale-up
- ✓ Repeatable at 100 g scale

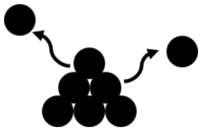


Conclusions and future work

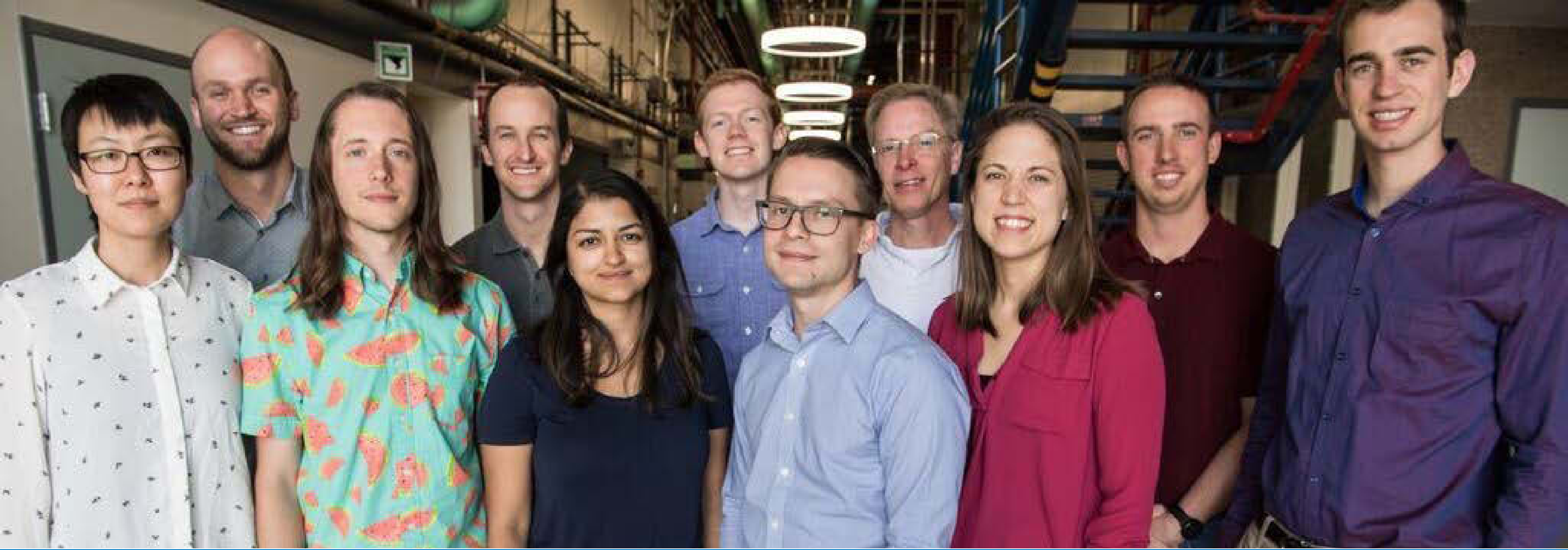




Oxidative chemistry



- Bioproducts
- Leaching resistance
- Scalable synthesis



Acknowledgements

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

FORGE NANO

Arrelaine Dameron
Karen Buechler
Chris Gump

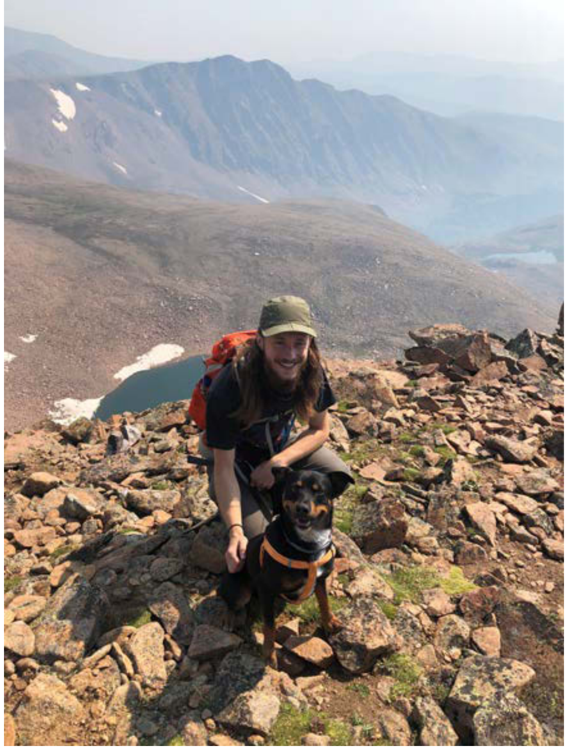
JM

Mike Watson
Luke Tuxworth

Gabriella Lahti
Davis Conklin
Kinga Unocic (ORNL)
Sean Tacey
The rest of the $DeCO_2$ team!

Sean Tacey
Carrie Farberow
Jim Stunkel
Kurt van Allsburg

About me



PhD, Chemical Engineering
PI: Prof. Alan Weimer
2014-2019

Postdoc, CCT&S Center
PI: Derek Vardon
Jul 2019-present

??

Pursuing National Lab or industry opportunities

Thank you!

www.nrel.gov

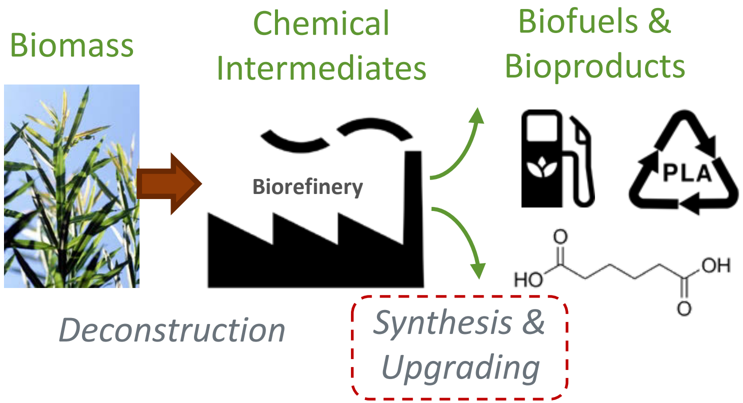
NREL/PR-5100-78357

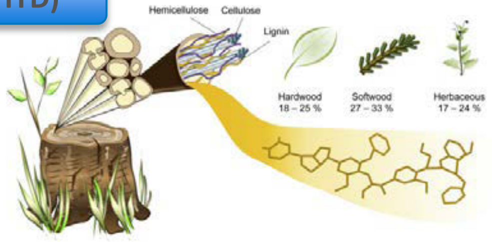
This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Bioenergy Technologies Office. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government.

NREL Transforming ENERGY

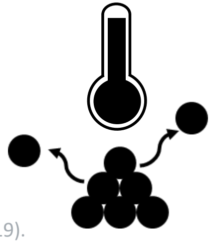
Biomass conversion presents additional challenges

Catalytic Hydrogenation (HYD)

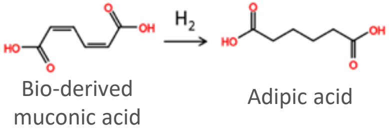


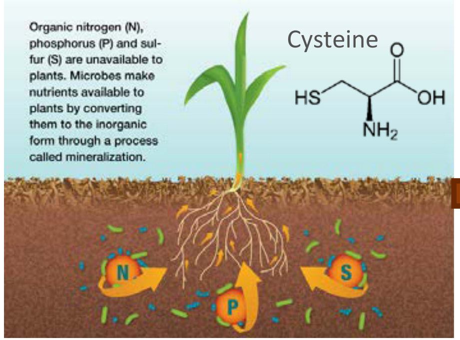


Becker, J. and C. Whitman. *Biotechnol. Adv.* **37**(6), 107360 (2019).



- -Oxidizing/Reducing
- -Condensed phase
- -Coking
- **-Acidic/alkaline**





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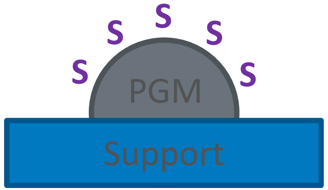

- **Robust and inexpensive catalytic processes**
- Separations
- Waste-stream valorization
- New biochemical processes
- Streamlined biological engineering
- Renewable H_2 generation

1. Increase HYD activity
2. Improve lifetime durability (incl. S tolerance)

Tailored catalyst solution

Adapted from Fitzgerald, N. *Nat. Rev. Chem.* **1**(10), 1 (2017).