NREL
Transforming ENERGY

Atomic Layer Deposition for Improved Biomass Conversion Catalysts

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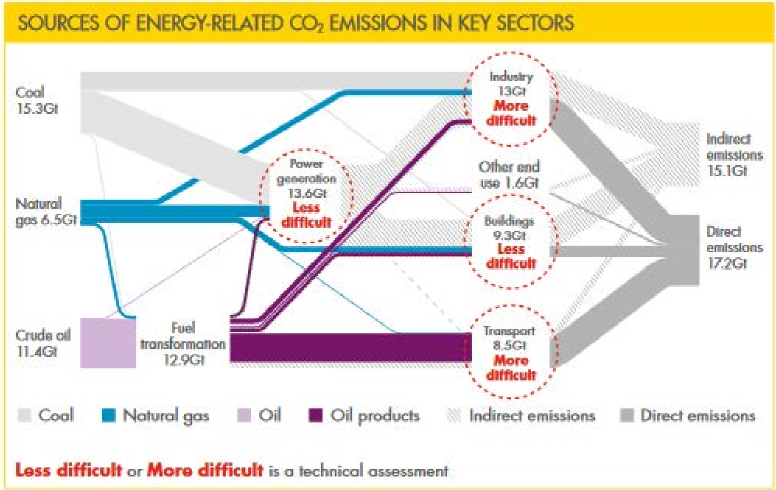
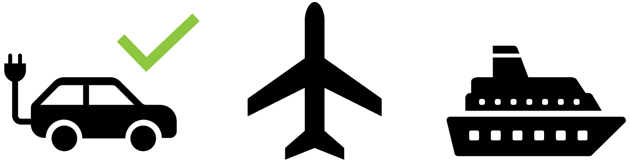
Bioenergy and Decarbonization

"Hard-to-Decarbonize"



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

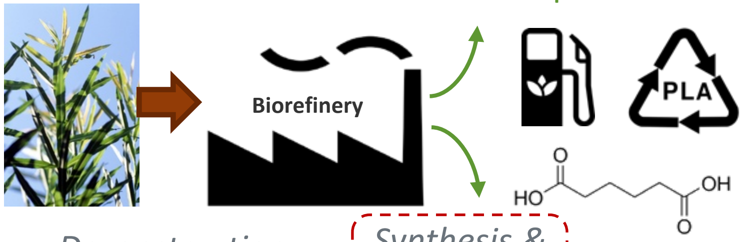


Shift to carbon neutral/negative fuels

Biomass

Chemical Intermediates

Biofuels & Bioproducts



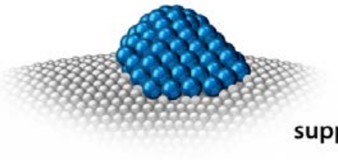
Deconstruction

Synthesis & Upgrading

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

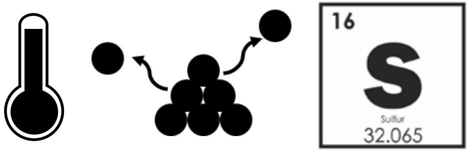
Heterogeneous catalysts

metal active site



support

Stressors



-Sintering
-Support collapse

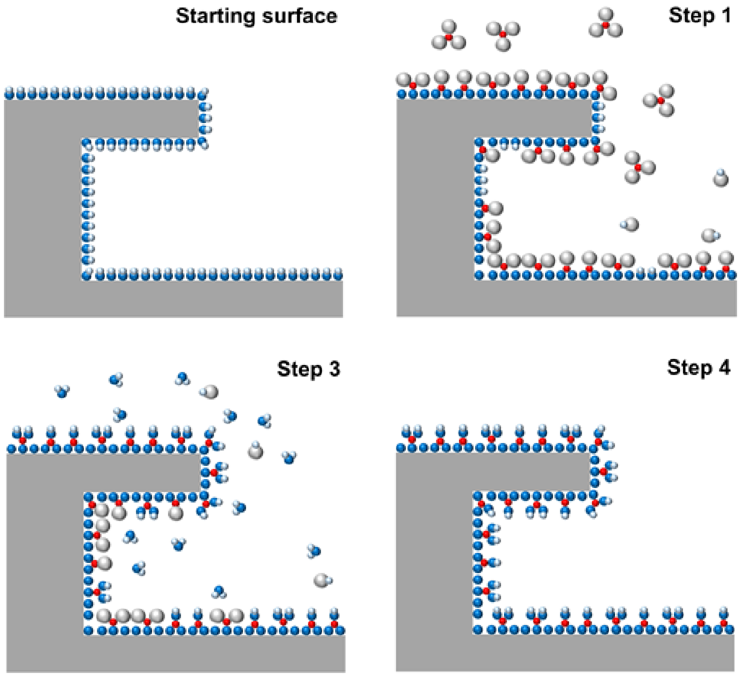
-Leaching

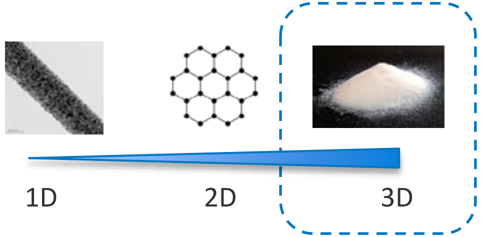
-Deactivation

Tailored catalyst solution to mitigate degradation?

ALD can be used to protect catalysts

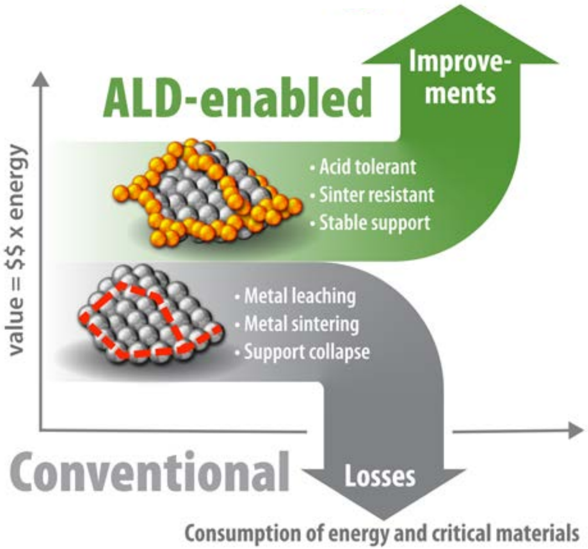
Atomic Layer Deposition = “ALD”





- Self-limiting
- **Conformal**
- Thickness control

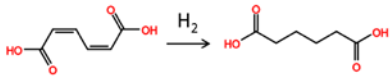
Protective ALD coatings for catalytic nanoparticles

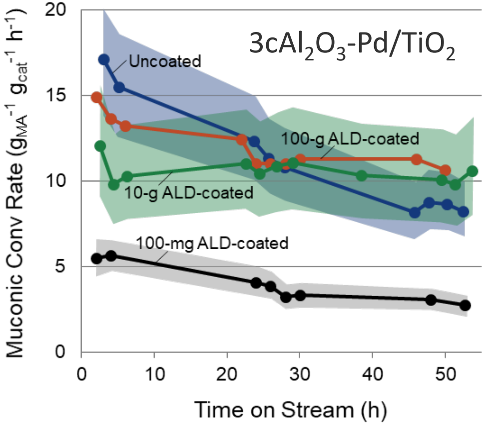


Settle, A. E., et al. *Joule* **3,** 1 (2019).

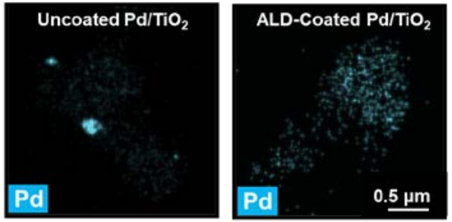
ALD for catalysis in CCT&S Center

Muconic acid HYD



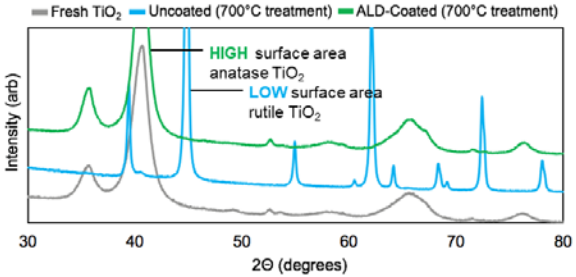


Pd/TiO_2 Catalysts after 700°C Treatment



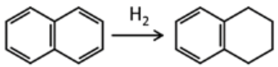
>80% loss of surface area

<25% loss of surface area

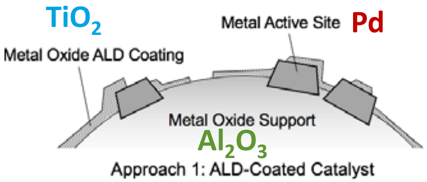


Catalyst	Leaching (Pd ppm)
Uncoated (Pd/TiO_2)	1.4 ±0.7
100-mg ALD-coated	0.3 ±0.1
10-g ALD-coated	0.08 ±0.04
100-g ALD-coated	0.05 ±0.01

Aromatic HYD



Overcoating



Initial catalyst screening

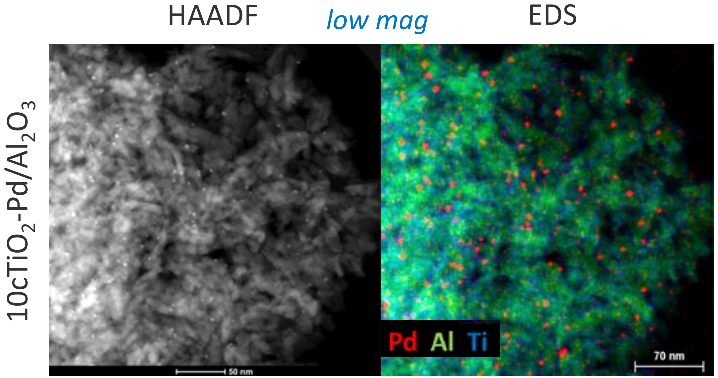
10cTiO_2-Pd/Al_2O_3

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

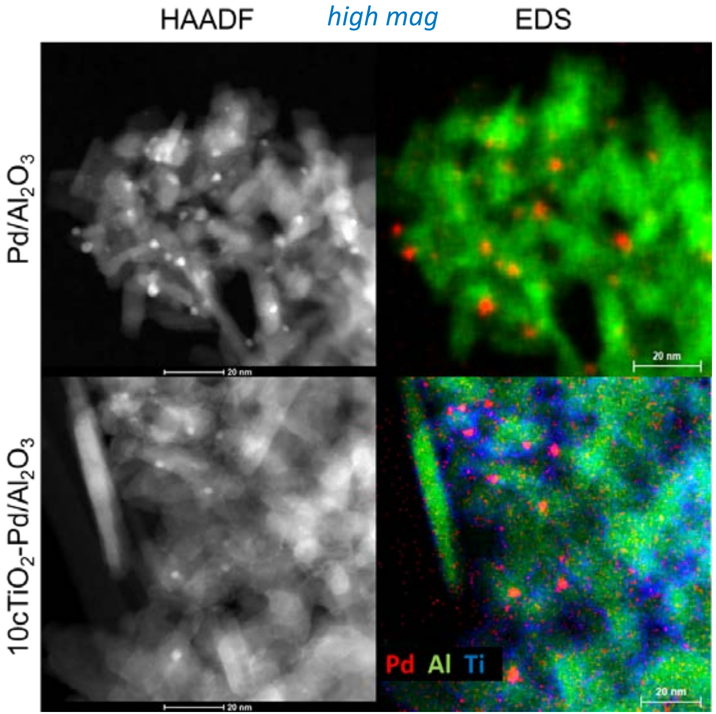
Settle, A. E., et al. *Joule* **3,** 1 (2019).

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 ($\mu mol\ g^{-1}$)	28.2 →	10.5
CO uptake ($\mu mol\ g^{-1}$)	20.4 →	4.3



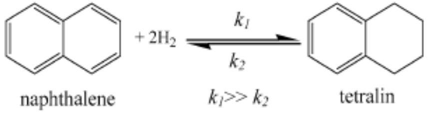
- ✓ Conformal layer
- ✓ Al_2O_3 support coated
- ✓ **H and CO uptakes decreased**
- ✓ Pd sites covered (extent unclear)



How does Pd coverage by TiO_2 impact reactivity?

ALD catalyst performance in aromatic HYD: batch

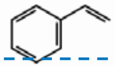
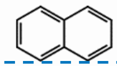
batch reactor



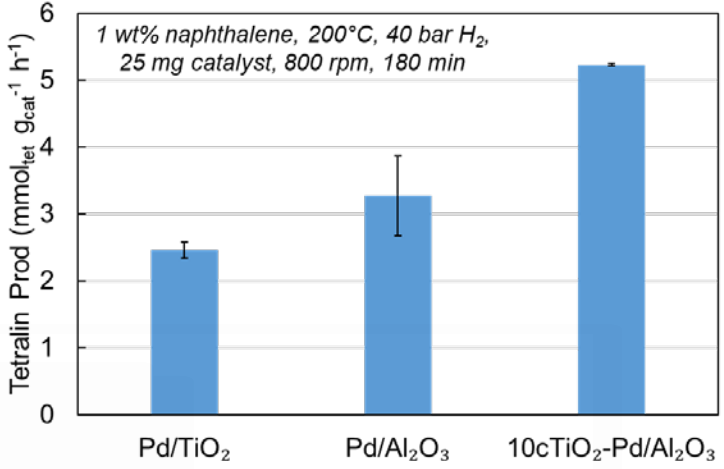
Kirumakki, S., et al. *J Catal* **242**(2), 319 (2006).

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

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

Substrate		Pd/Al_2O_3	$10cTiO_2\text{-}Pd/Al_2O_3$
Benzene[a]		40.0%	80.3%
Styrene[a]		47.4%	98.3%
Naphthalene[b]		55.9%	72.4%

[a]Conditions: 1wt% substrate, 150°C, 40 bar H_2, 25 mg catalyst, 800 rpm, 30 min. [b]Conditions above with temp at 200°C and 180 min.

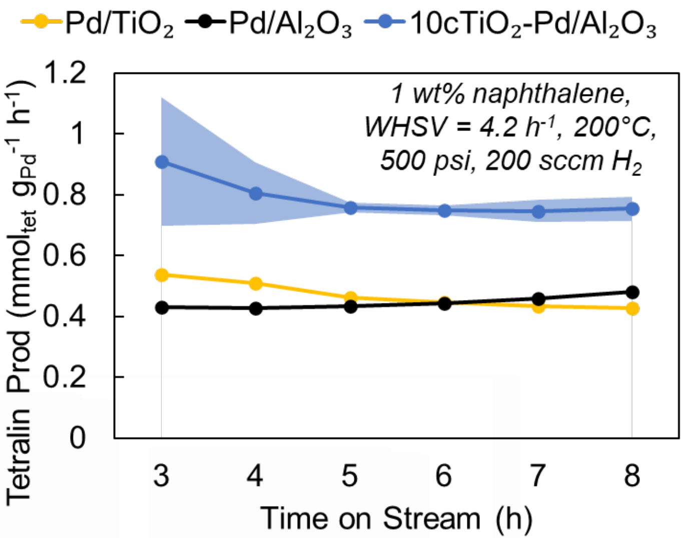


ALD catalyst performance in naphthalene HYD: flow

trickle bed reactor

- ✓ Similar trends to batch activity
- ✓ **10cTiO_2 has ~1.7X Pd-norm activity of base material**
- ✓ TiO_2 ALD overlayer has different behavior than TiO_2 support

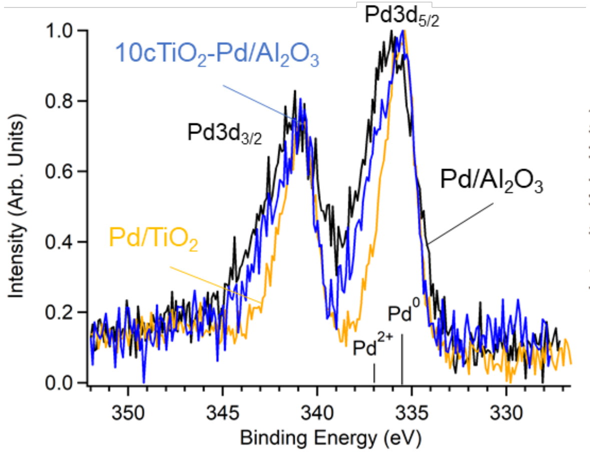
Catalyst	Steady-state (6 h) values	
	Naphthalene Conv (%)	Tetralin Prod ($mmol_{tet}\ g_{Pd}^{-1}\ h^{-1}$)
Pd/TiO_2	9.4	0.45
Pd/Al_2O_3	15.9	0.44
$10cTiO_2$-Pd/Al_2O_3	19.2	0.75



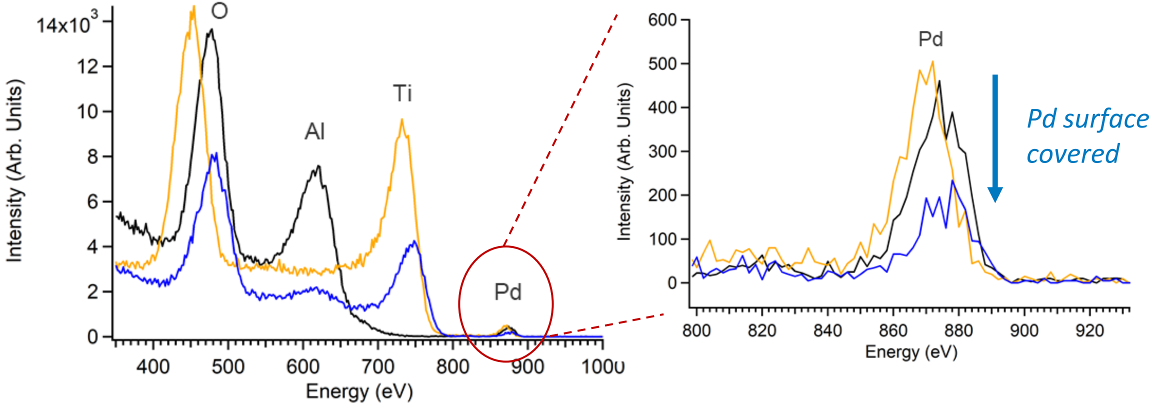
Why does TiO_2 ALD layer boost activity?

Pd partially covered by ALD, no change in e$^-$

XPS (ex-situ)



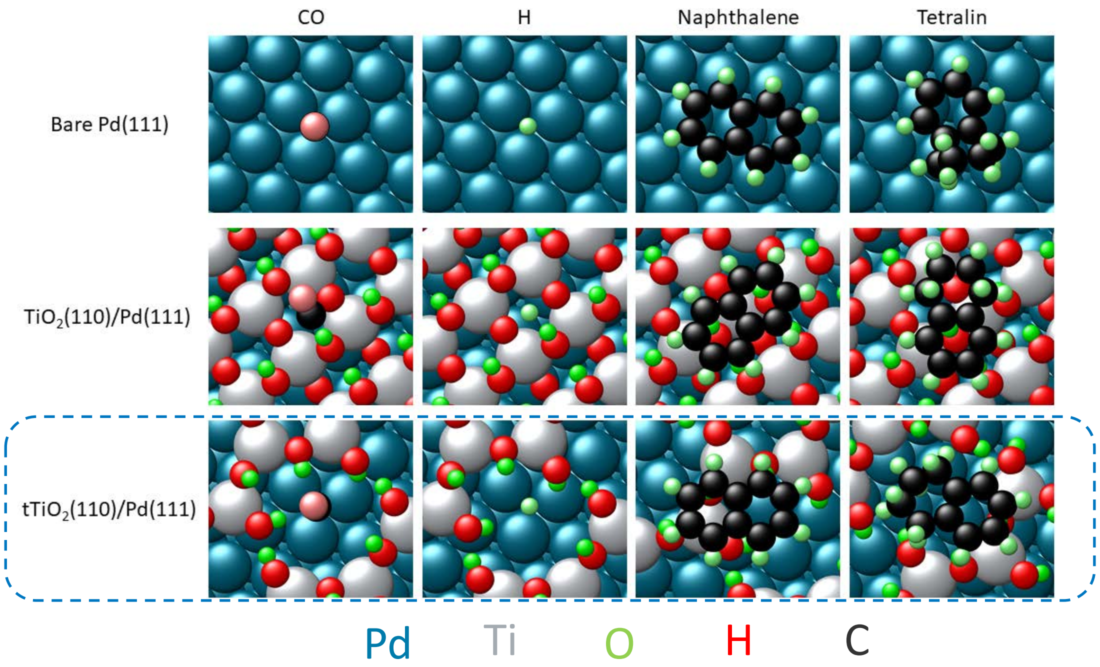
ISS (ex-situ)

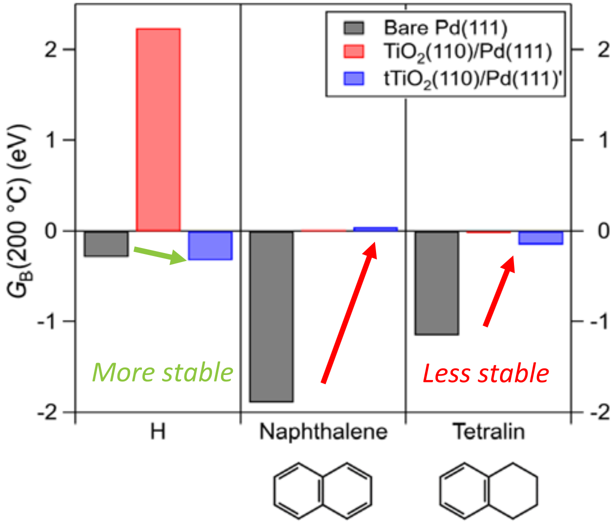


XAS (in-situ H_2 reduction)

Sample	Edge Energy (eV)	Coordination Number	R (Å)	σ^2 ($x10^3$ Å^2)	E_0 (eV)
Pd/Al_2O_3	24351.9	8.6 ± 0.5 (Pd-Pd)	2.80 ± 0.01	10.2 ± 0.5	3.2 ± 0.4
$10cTiO_2$-Pd/Al_2O_3	24351.9	8.6 ± 0.5 (Pd-Pd)	2.80 ± 0.01	9.6 ± 0.5	3.3 ± 0.4

TiO_2 ALD significantly alters surface binding





Flat-lying aromatic molecules cannot adsorb as readily

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

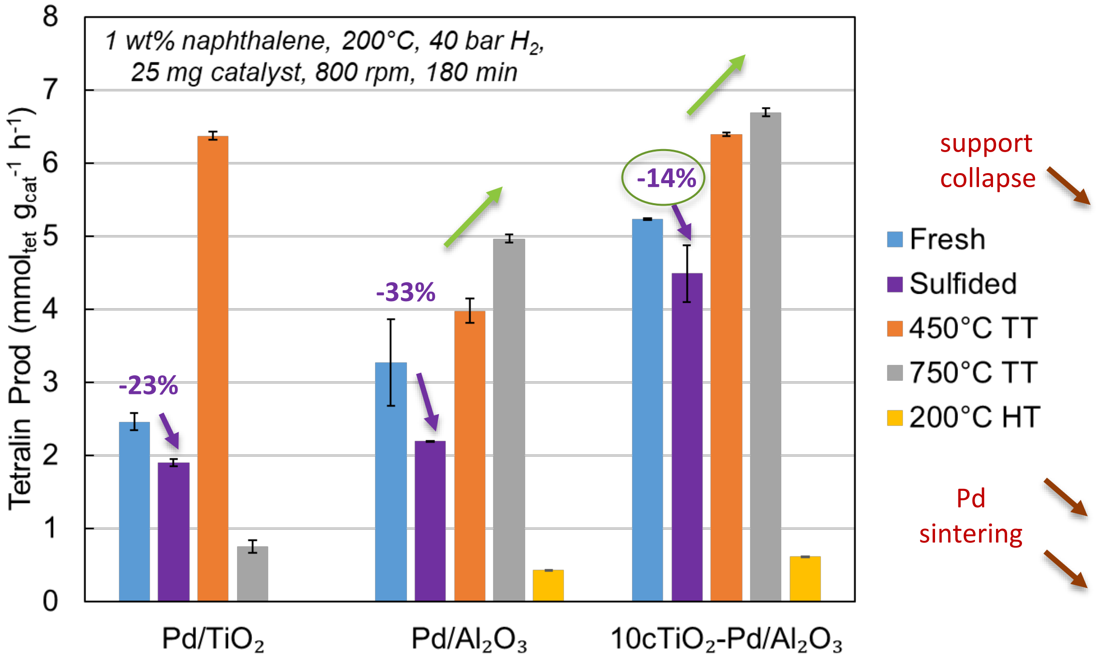
**note: simulated overlayers are rutile TiO_2, while actual ALD layers are amorphous*

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



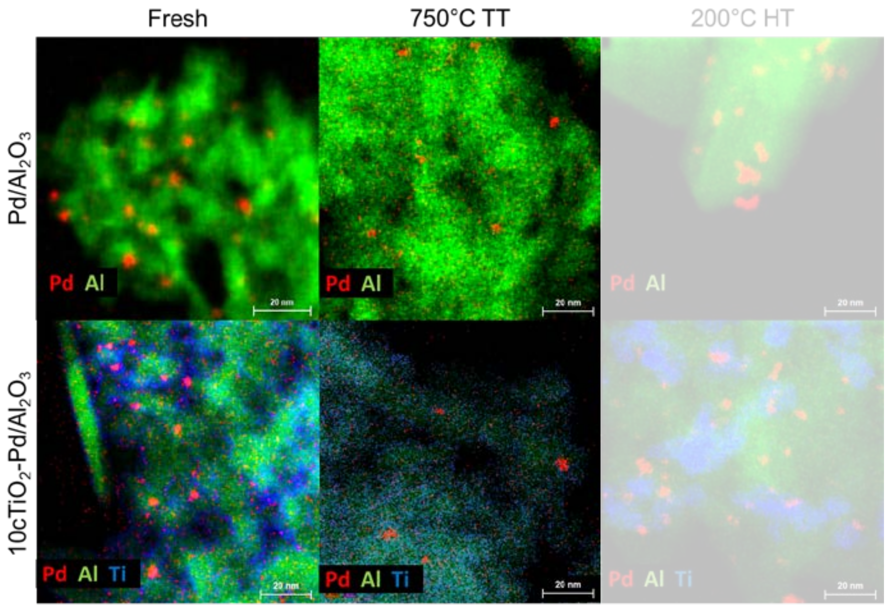
Change in BET surface area ($m^2\ g^{-1}$)

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})

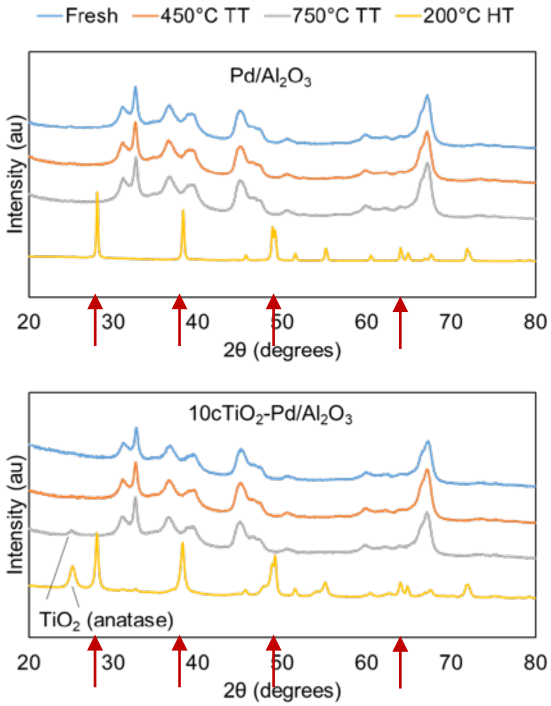
Treatment	Pd/TiO_2	Pd/Al_2O_3	$10cTiO_2$
450°C TT % change	+45%	-18%	+47%
750°C TT % change	-83%	-47%	+120%
200°C HT % change	-95%	-82%	+22%

ALD catalyst stability



Pd sintering

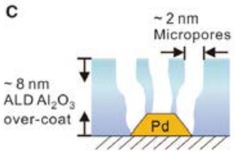
ALD layer unstable



Change in CO uptake (µmol g^{-1})

Treatment	Pd/Al_2O_3	$10cTiO_2$
750°C TT % change	-47%	+120%

Calcination may form pores



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

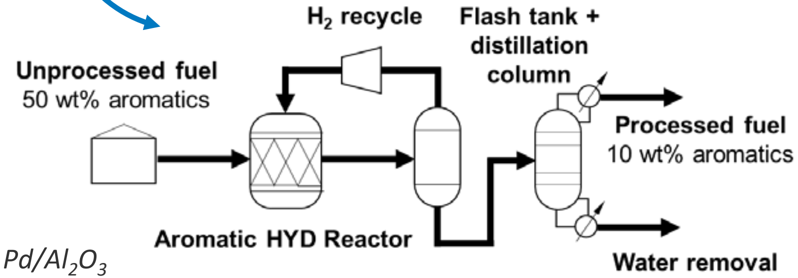
Al_2O_3 boehmite transformation

Refining the value proposition of ALD catalysts

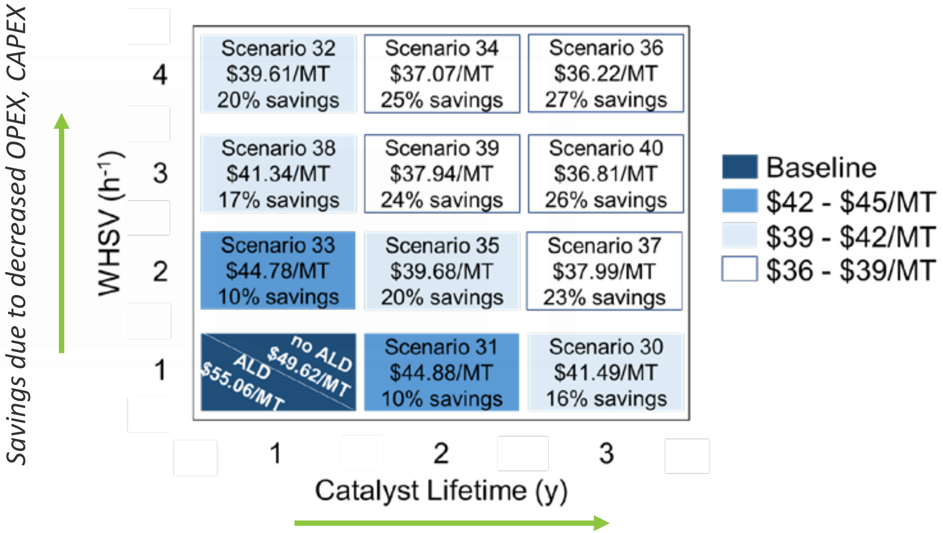
Is ALD "worth it" for HYD catalysts?

TTIP Precursor Price ($/kg)	Equipment Capacity (tonnes/d)	ALD Coating Cost ($/kg catalyst)
5	30	$12.08
5	15	$13.47
10	15	$20.67
10	3	$29.64
25	30	$43.84

CatCost



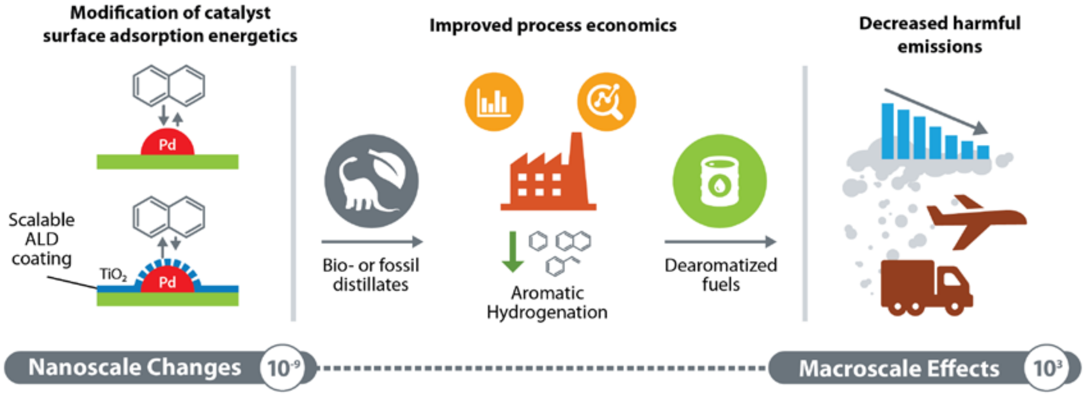
2% Pd/Al_2O_3
350°C, 650 psi H_2
Variable WHSV, catalyst lifetime



Savings due to decreased catalyst purchase price

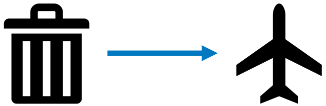
- ✓ **ALD cost increase neutralized by 2X improvement in either WHSV or lifetime**
- ✓ Achievable based on our 1.7X activity increase
- ✓ Savings compound with further improvements

Conclusions and future work

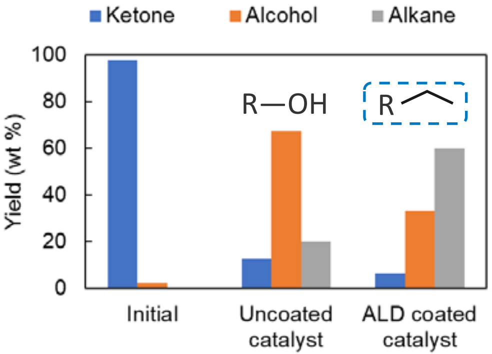


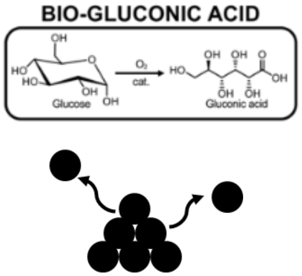
Sustainable Aviation Fuel

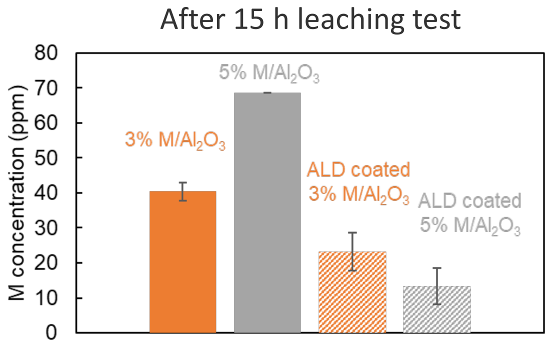
Oxidation for Biobased Chemicals

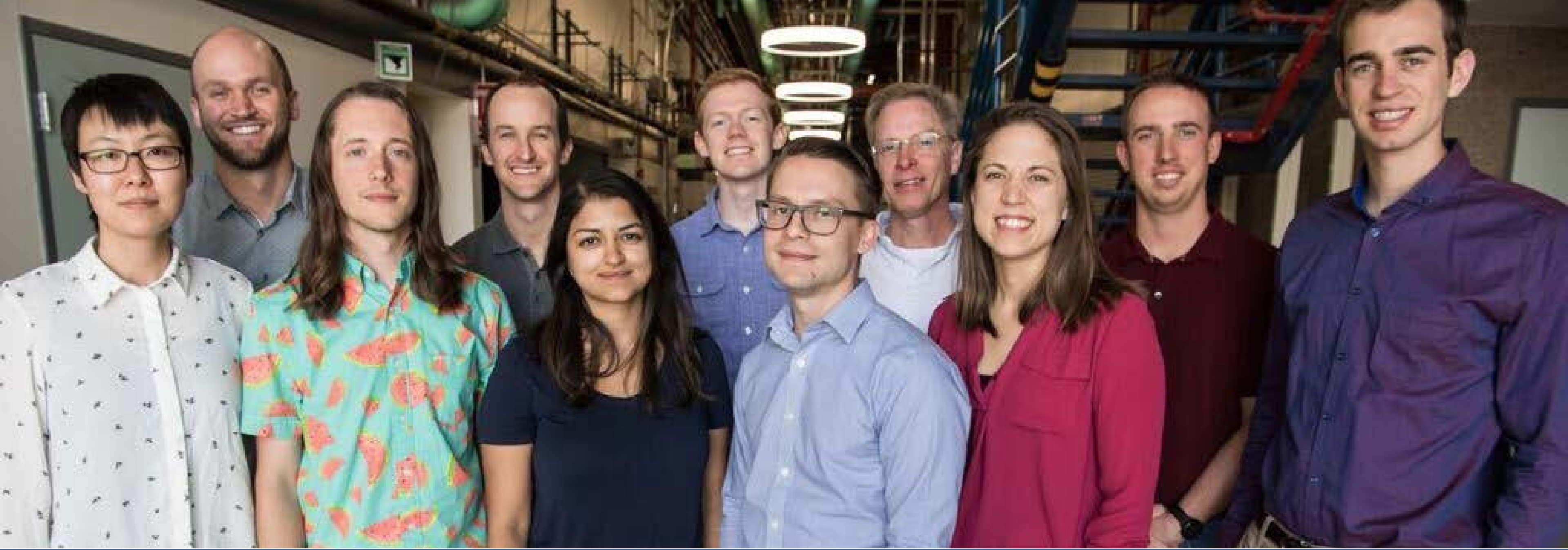


1) Arrested Methanogenesis
2) VFA ketonization
3) Hydrodeoxygenation (HDO)









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Thank you!

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