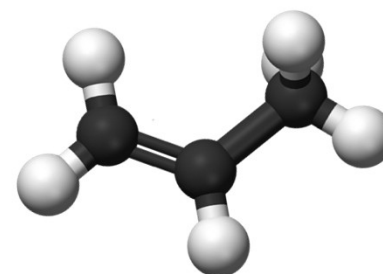


# Partial electrochemical oxidation of propene on palladium

2019 Spring ECS Meeting  
May 26, 2018

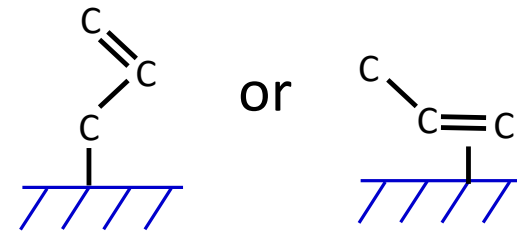
Brian Seger<sup>1</sup>, Anna Winiwarter<sup>1</sup>, Ib Chorkendorff<sup>1</sup>, Luca Sivoli<sup>2</sup>, Jan Rossmeisl<sup>2</sup>

1. *SurfCat Section, Physics Department Technical University of Denmark*
2. *Department of Chemistry, Copenhagen University*



# Why propene ?

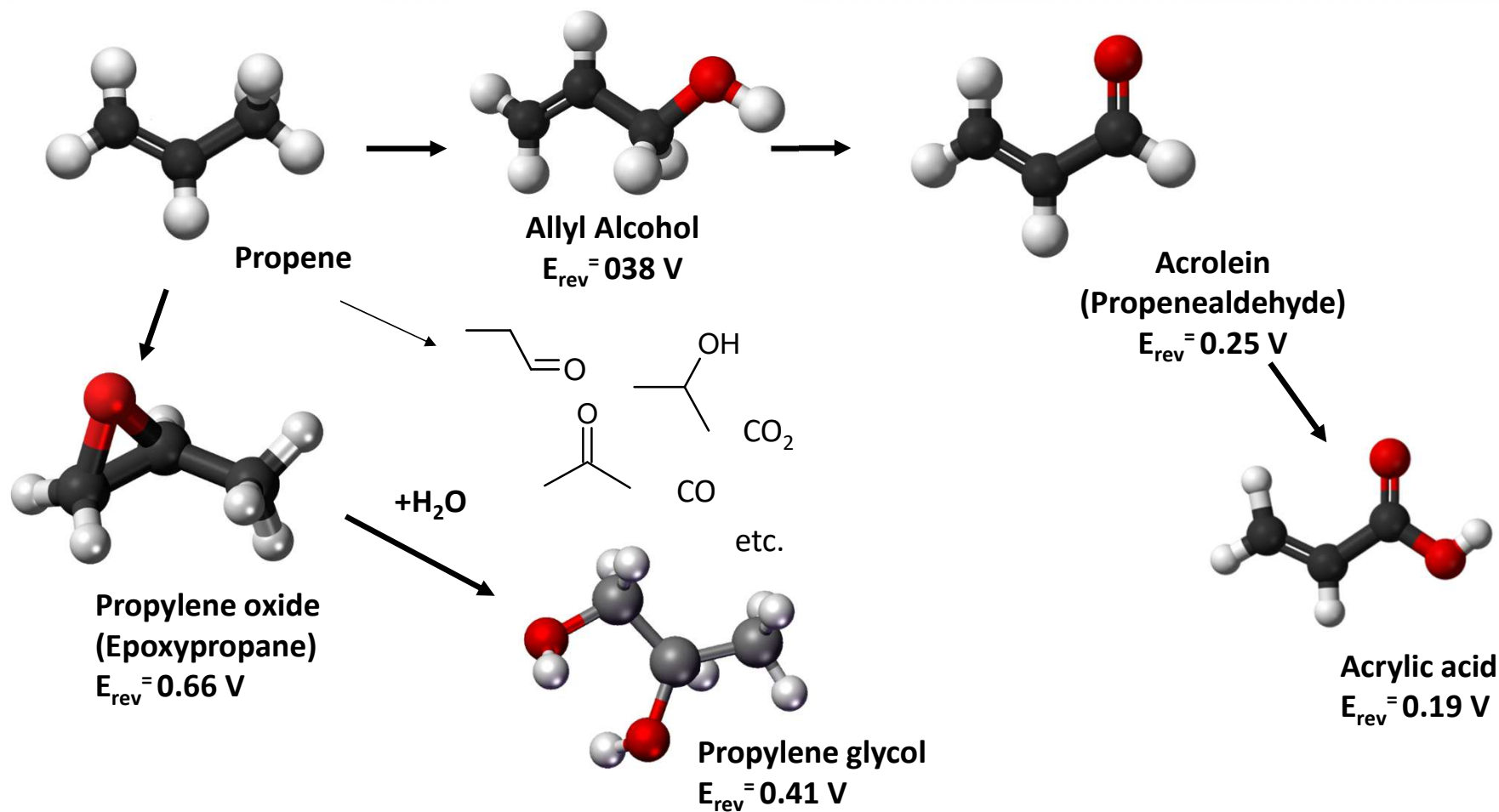
- Propene allows for adsorption via double-bound carbon or an allyl carbon.
- Partially oxidized propene products have a higher value than propene.
- Dream reaction is methane to methanol or formic acid.
- Propene could be a starting point to understand partial hydrocarbon oxidation.



Material	Value	World Prod. (megaton)
	(\$/ton of C)	
Propene	1630	120
Acrylic acid	3200	7.7
Acrolein	1500	0.5
Propylene glycol	3000	2.6



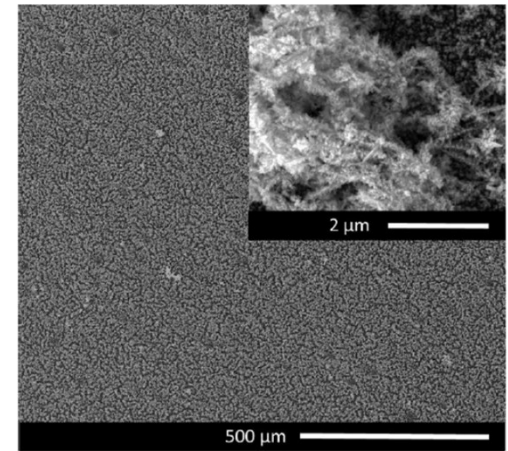
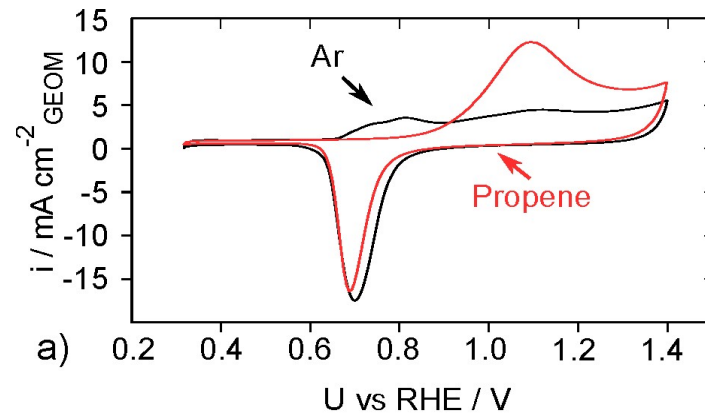
# Propene oxidation – reaction pathways



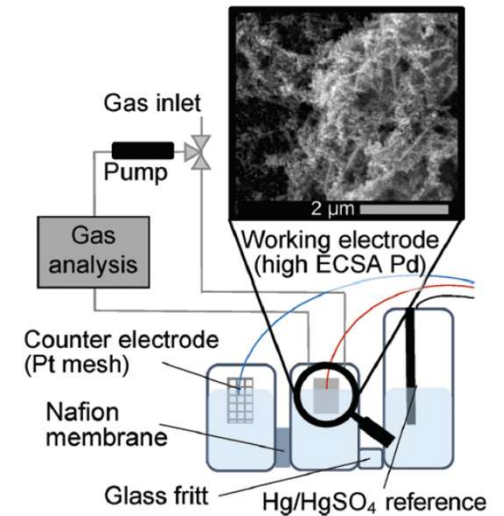
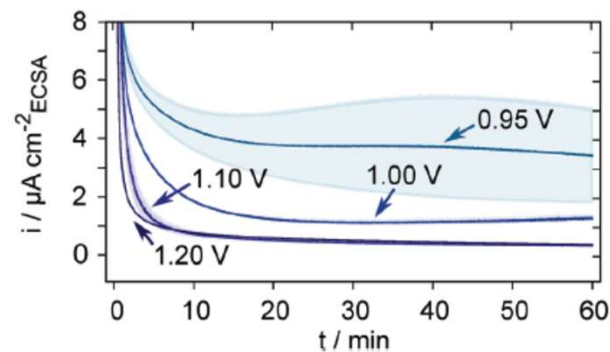
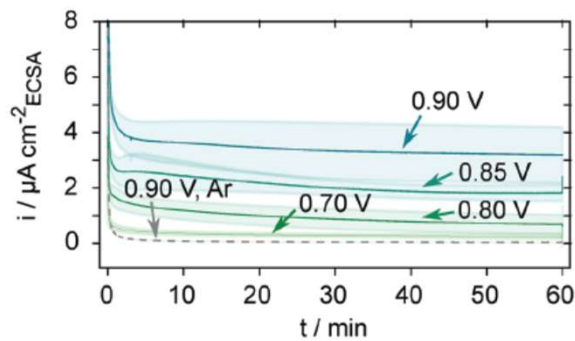


# Electrochemical behavior

- The delayed Pd oxidation in propene is due to propene adsorption

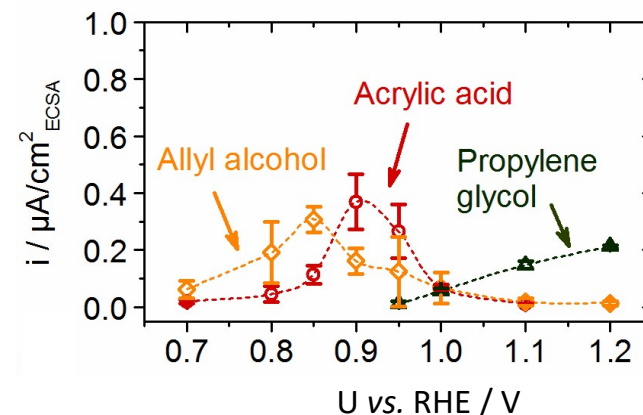
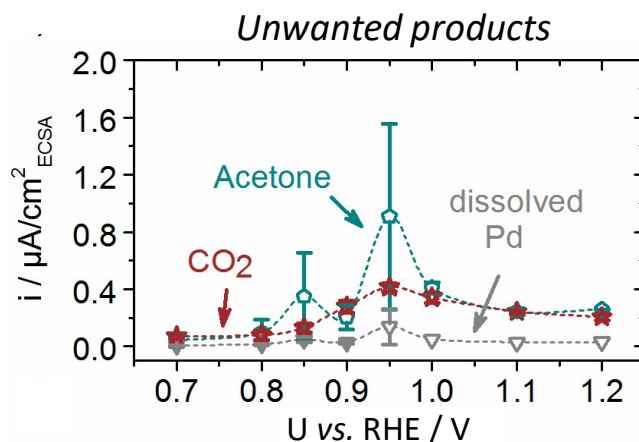
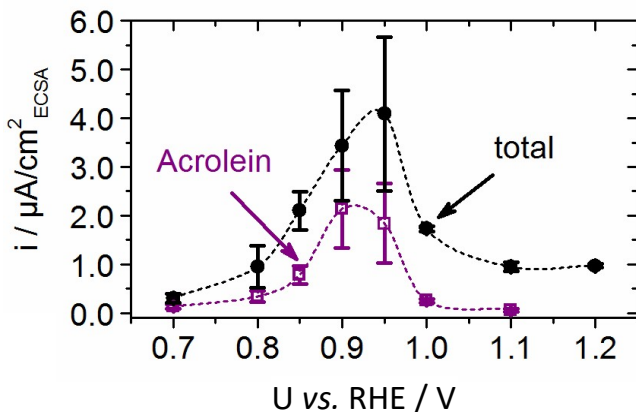
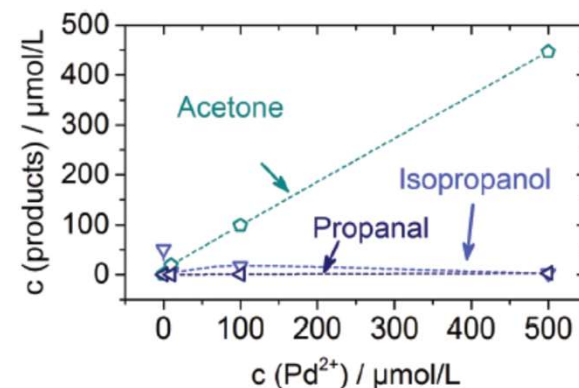


- Low currents meant high surface area was needed for product detection.

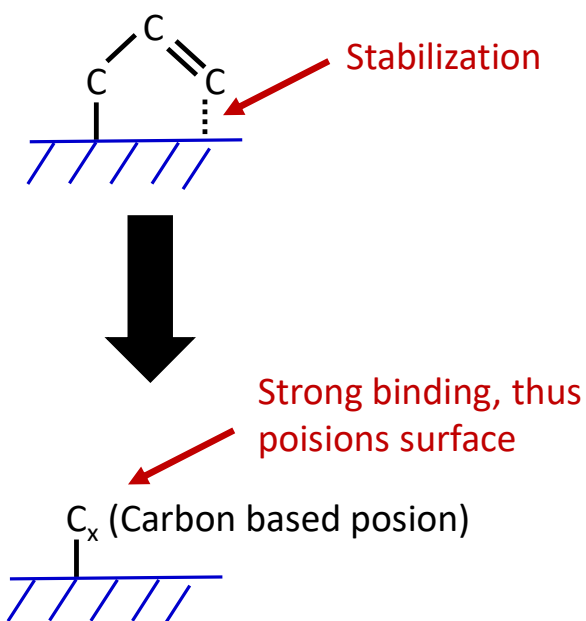


# Electrochemical behavior and product distribution

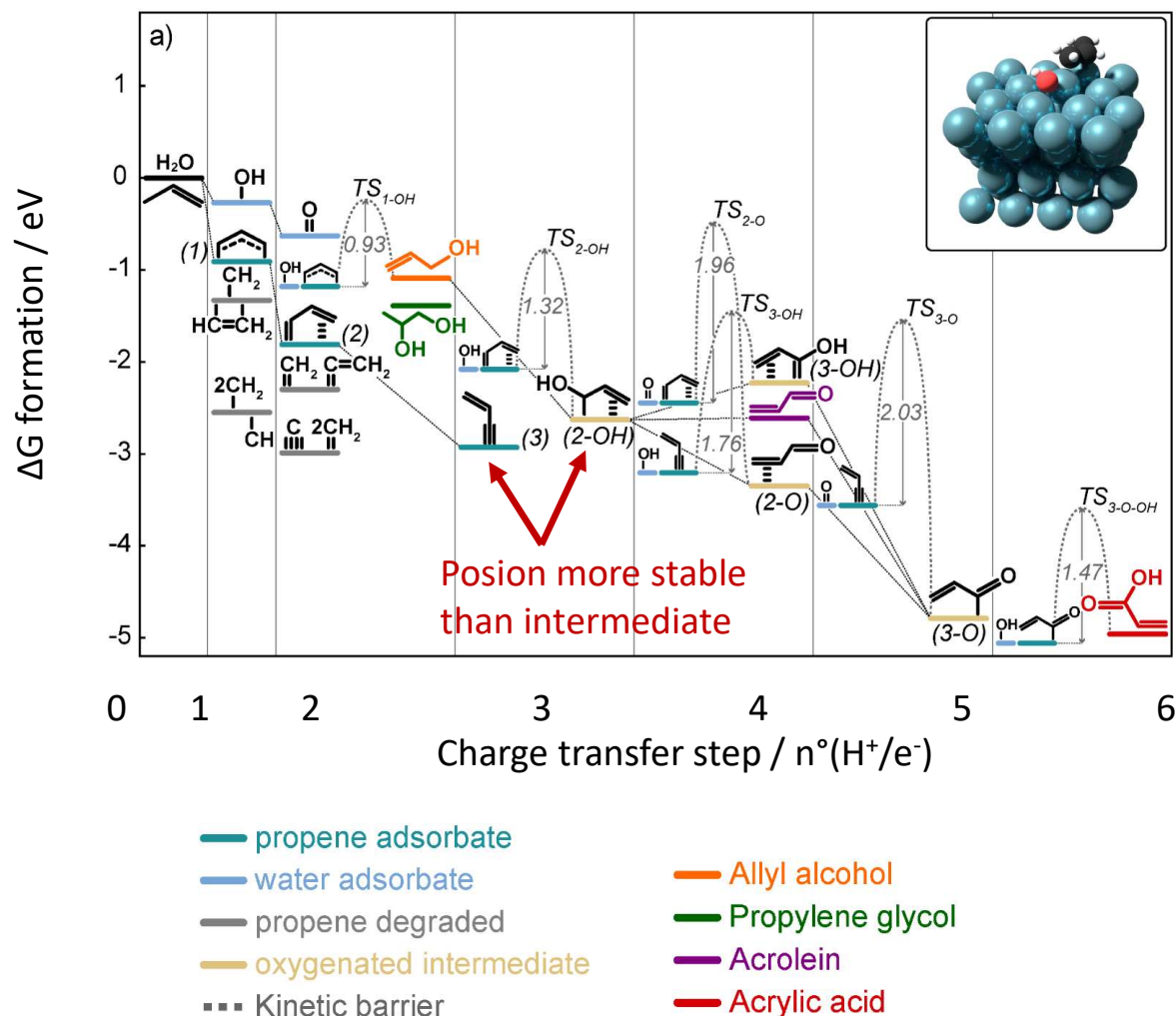
- We achieved a diverse set of products, with minimal complete oxidation to  $\text{CO}_2$ .
- The Pd/PdO redox potential is 0.9 V vs. NHE.
- Dissolved  $\text{Pd}^{2+}$  can act as a homogenous catalyst to reduce propene to acetone.



# DFT Explaining why this will not work

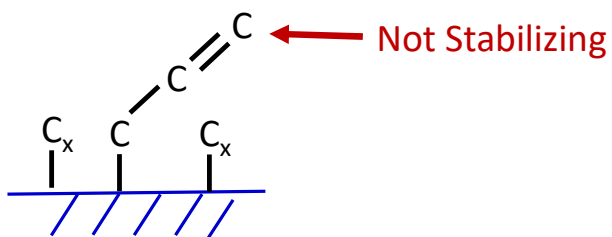


- Theory would expect a poisoned surface.
- This explains low currents, but not why we get any current at all.

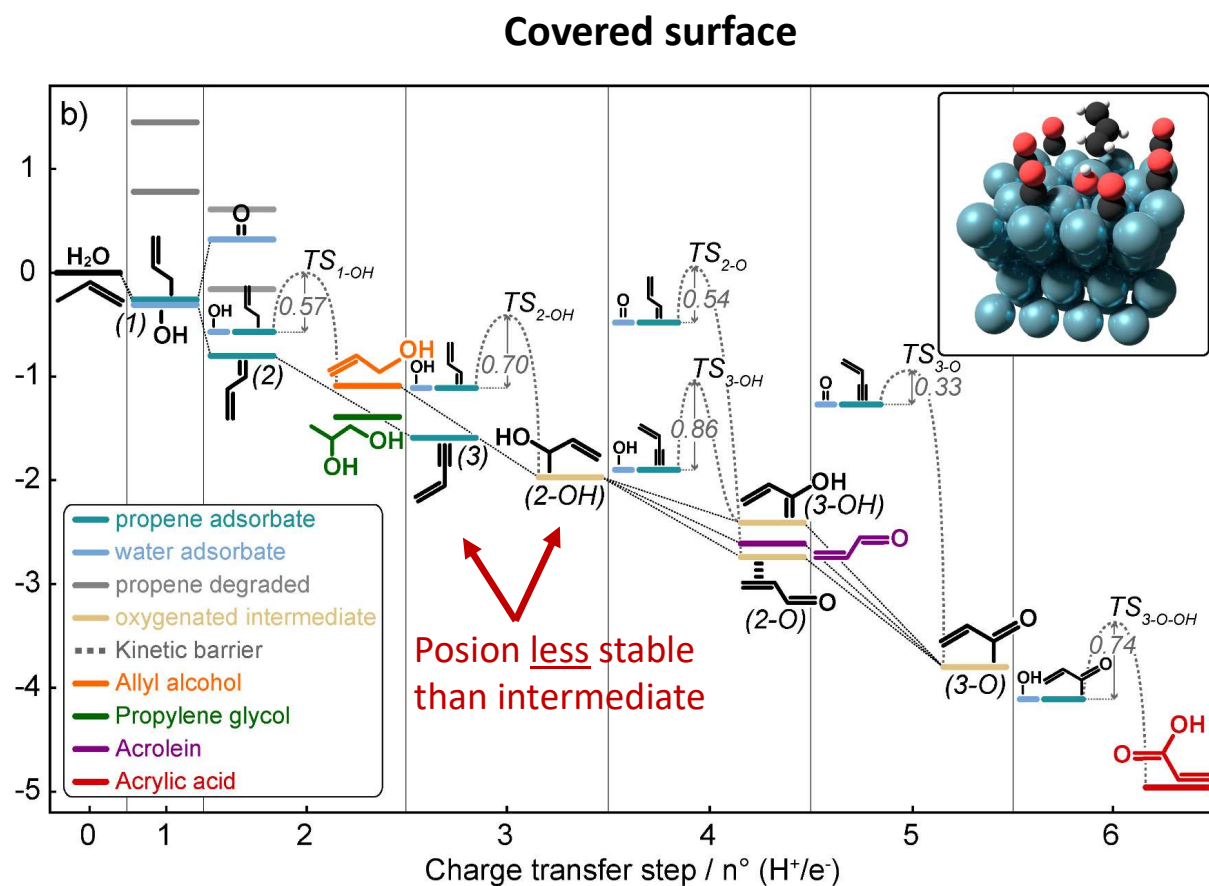


# DFT Explaining why this could work

- We looked at the case where we had a high percentage (6/7) of the surface contaminated.

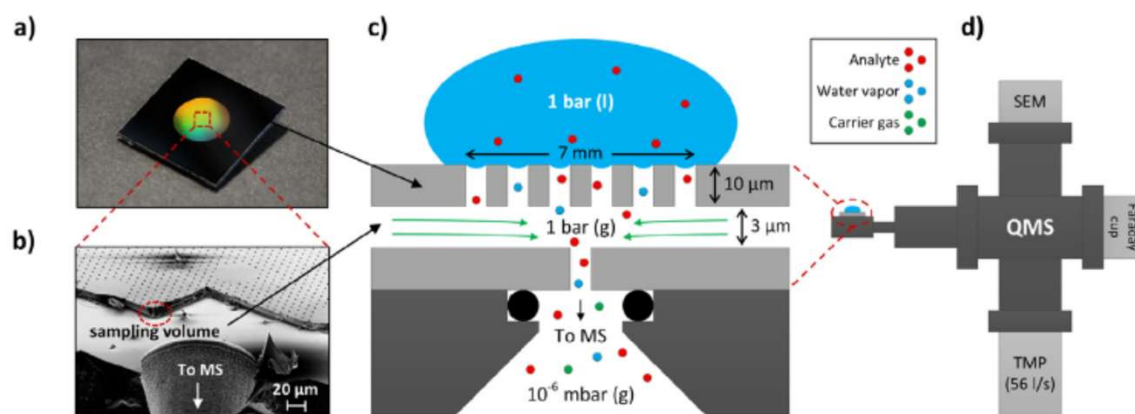


- Poisoning prevents further poisoning, allowing for products
- How do we test this theory ?



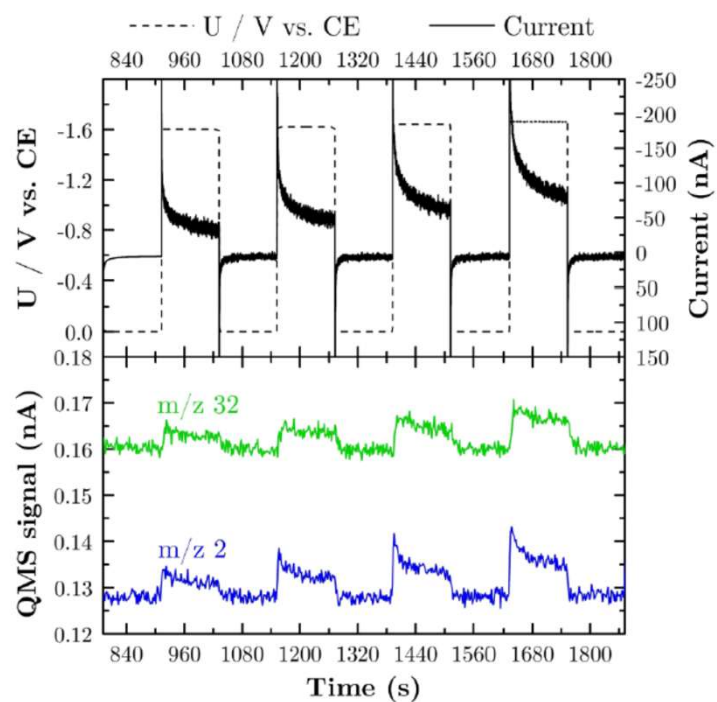
# Tool for Product Detection

- We have a 'sniffer chip' that basically sucks out the products and sends them to a mass spec.
- This gives us submonolayer product detection



Trimarco et al., *Electrochimica Acta*, 268 (2018) 520-530

*Example: water splitting*

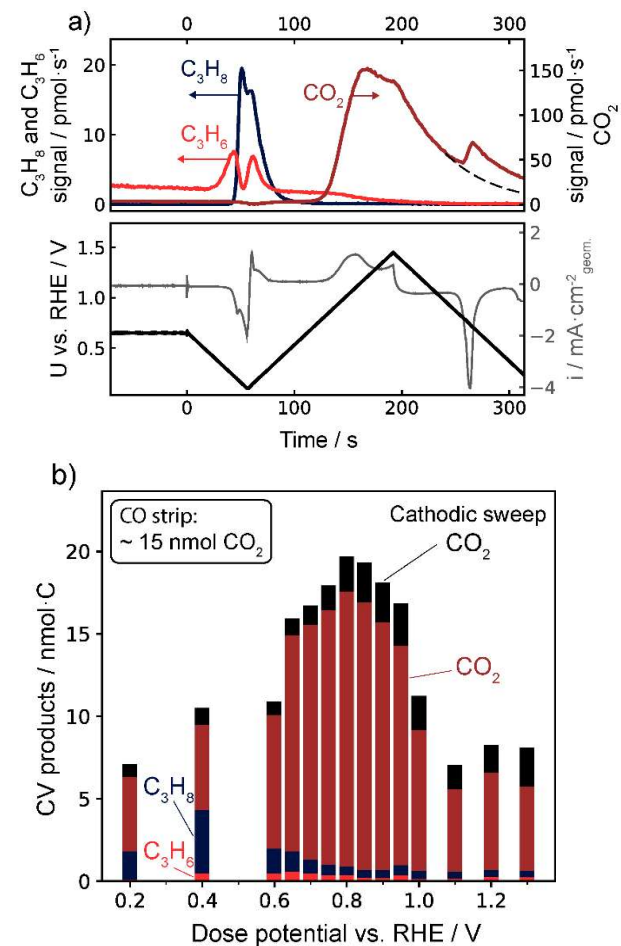
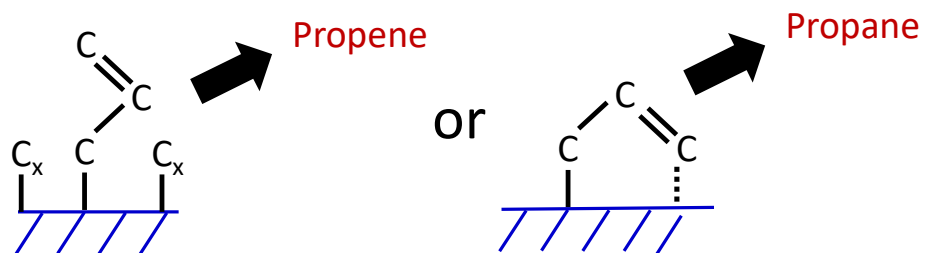


# Propene stripping

- The 'sniffer chip' allowed us to investigate sub-monolayer product formation.

## Process

- 1) Add propene at a potential
- 2) Flush out system with Ar
- 3) Scan cathodically to reduce propene to propane
- 4) Scan anodically to oxidize any 'stuck' propene to  $\text{CO}_2$

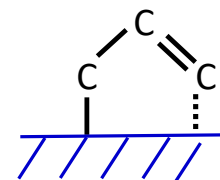


# Analyzing propene to propane results

## Process

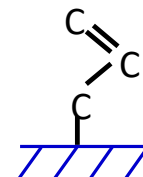
- 1) Added propene at 0.4V vs. RHE.
- 2) We partially cleaned surface (cathodically, then partially anodically).
- 3) We added propene again at 0.4V vs. RHE.
- 4) We scan cathodically again to see the propane/propene ratio.

Very clean  
(Many empty sites)



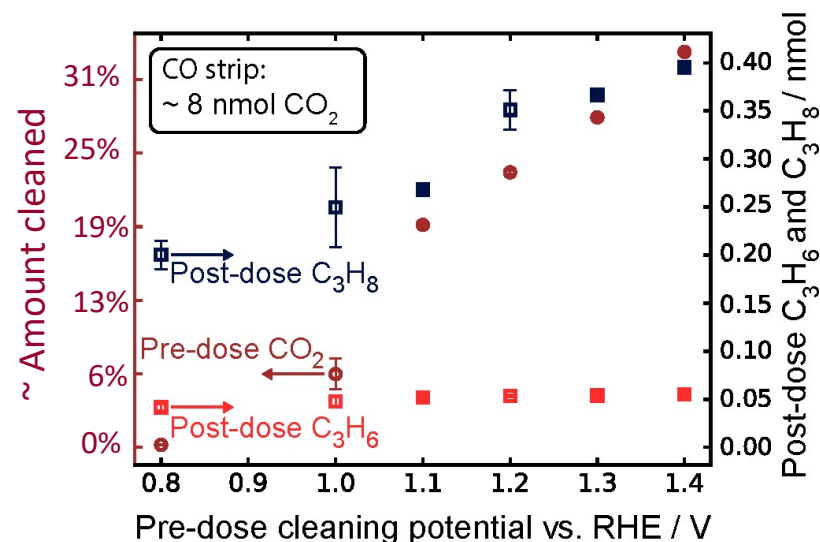
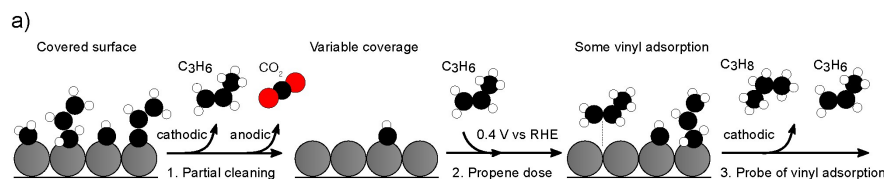
Propane

Not that clean  
(Few empty sites)



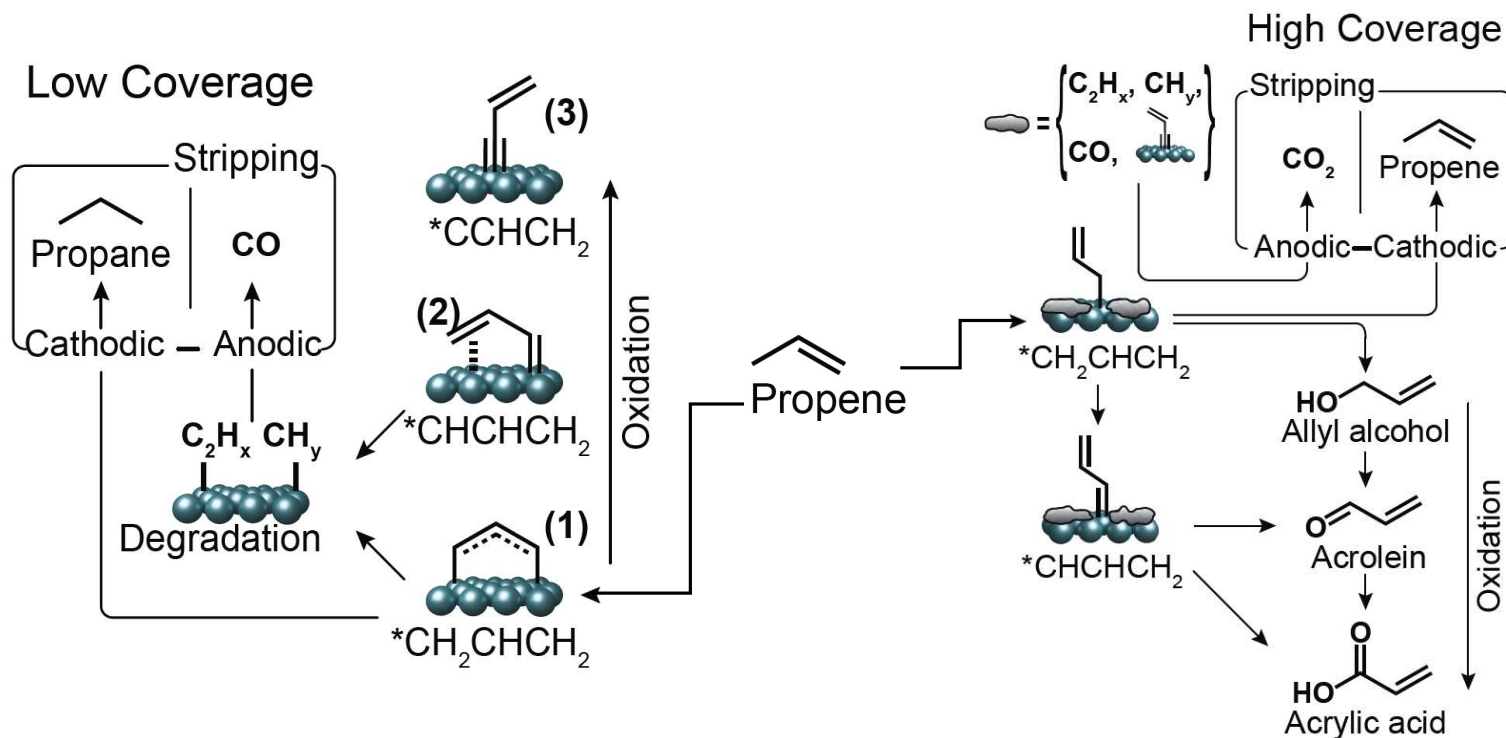
Propene

- The more room for vinyl carbon to absorb, the more propane.



# Conclusion – selectivity through coverage

- The simple conclusion is that partial ‘poisoning’ is needed to allow us to get our desired products.



# Acknowledgements



UNIVERSITY OF  
COPENHAGEN



Presentation based on: Winiwarter, L. Silvioli, S. B. Scott, K. Enemark-Rasmussen, M. Sariç, D. B. Trimarco, P. C. K. Vesborg, P. G. Moses, I. E. L. Stephens, B. Seger and I. Chorkendorff, “Towards an atomistic understanding of electrocatalytic partial hydrocarbon oxidation: propene on palladium.” *Energy Environ. Sci.*, 2019, 12, 1055–1067.