Partial electrochemical oxidation of propene on palladium

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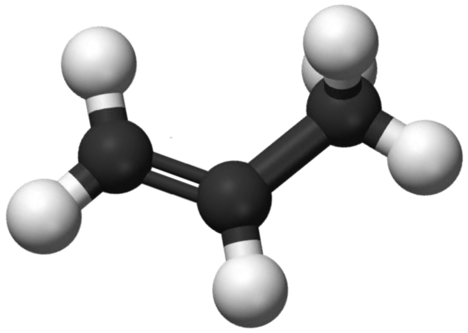
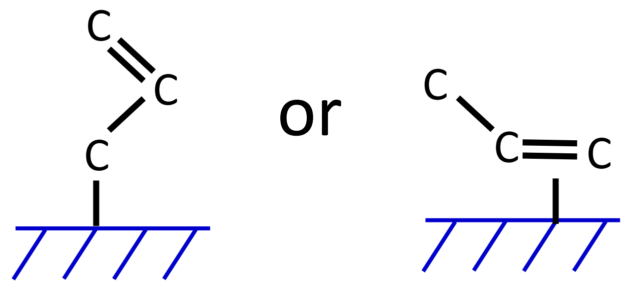


Why propene ?

- Propene allows for adsorption via double-bound carbon or an allyl carbon.

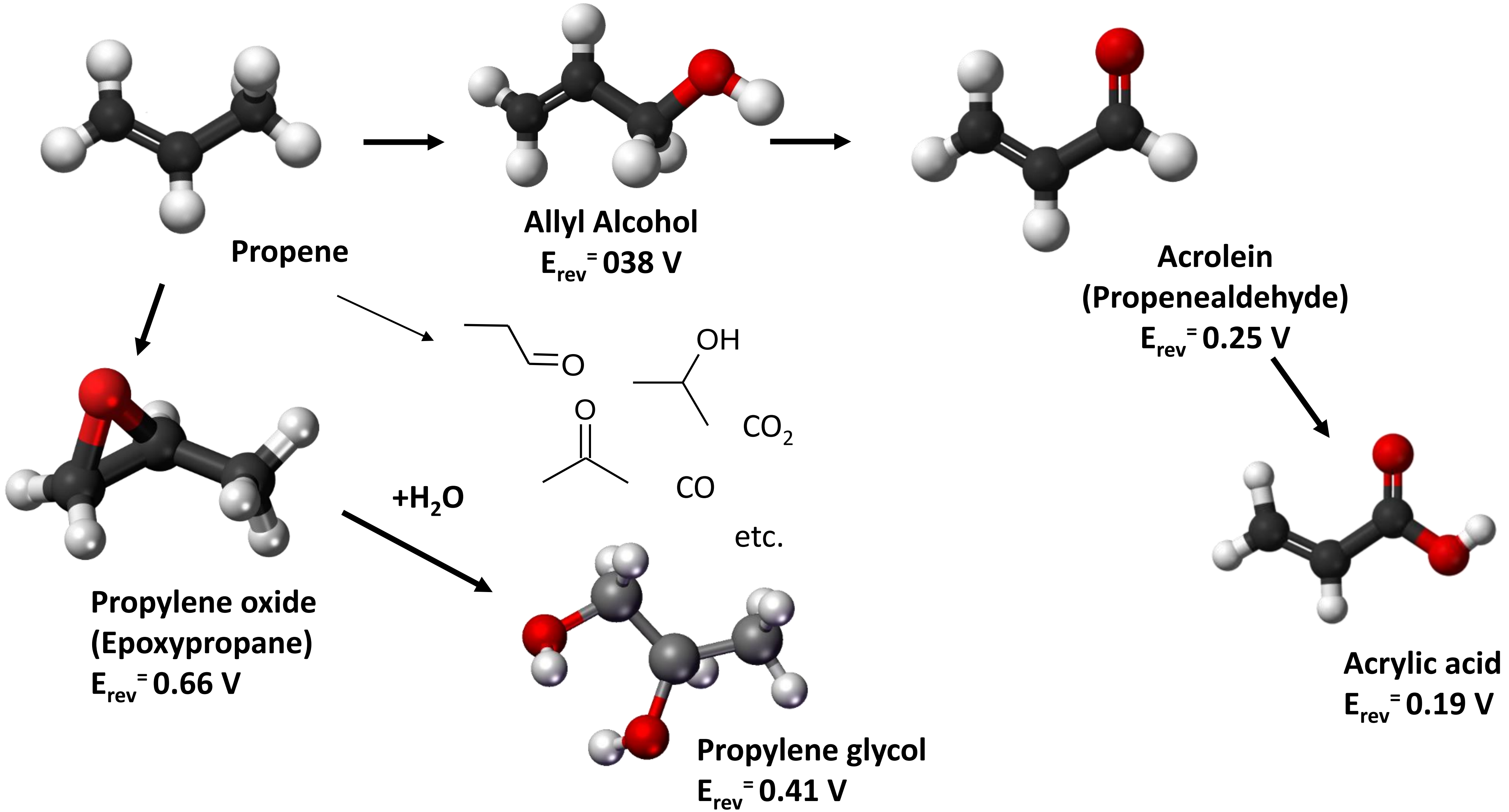


- Partially oxidized propene products have a higher value than propene.

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

- Dream reaction is methane to methanol or formic acid.
- Propene could be a starting point to understand partial hydrocarbon oxidation.

Propene oxidation – reaction pathways



Chou, T.-C.; Chang, J.-C. Chem. Eng. Sci. 1980, 35, 1581–1590.
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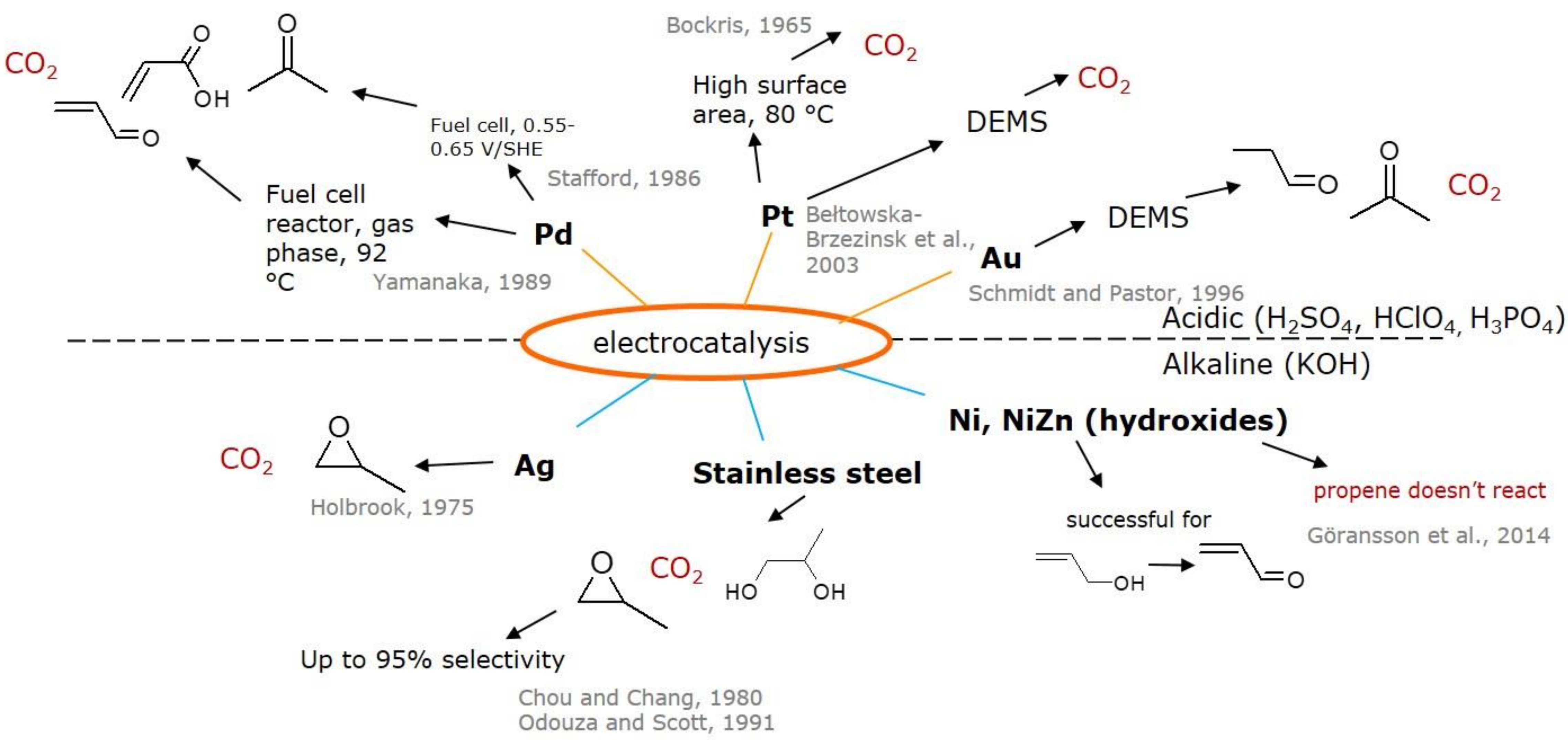
Otsuka, K.; Shimizu, Y.; Yamanaka, I.; Komatsu, T. *Catal. Letters* 1989, *3*, 365–370

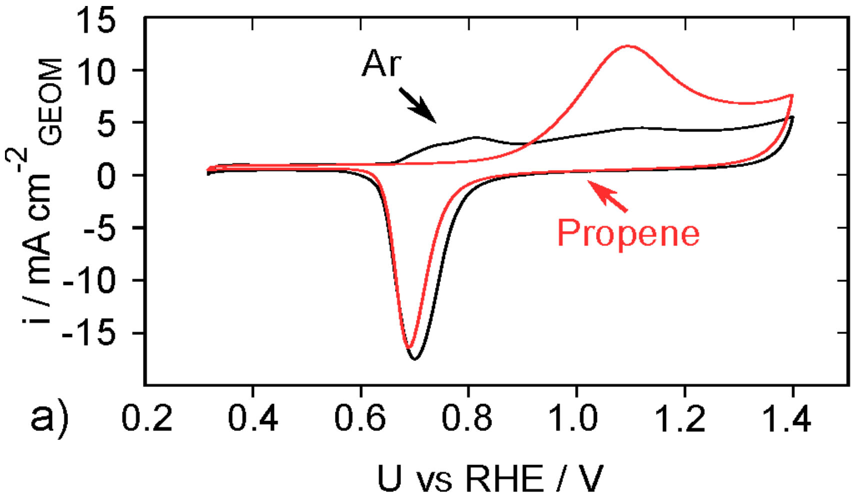
Literature on electrochemical propene oxidation

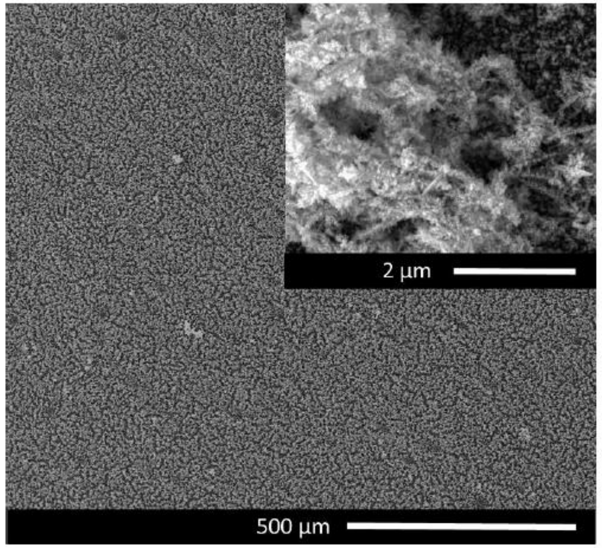


Limited number of studies, different systems, no clear trends

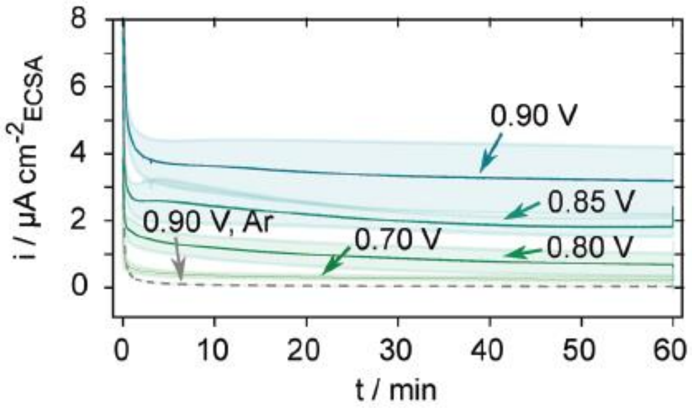
Electrochemical behavior

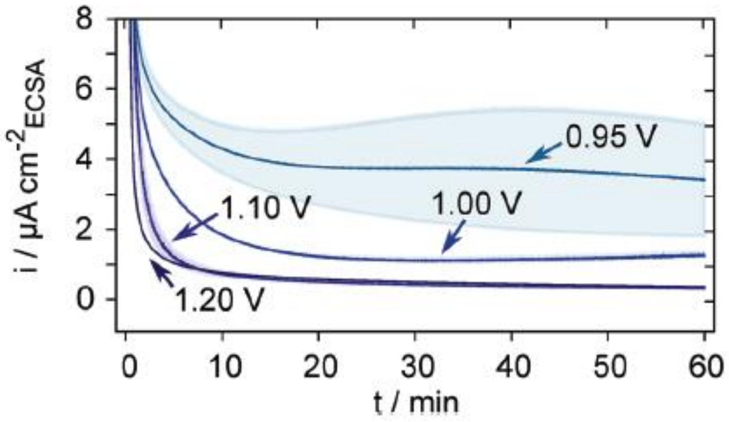
- The delayed Pd oxidation in propene is due to propene adsorption

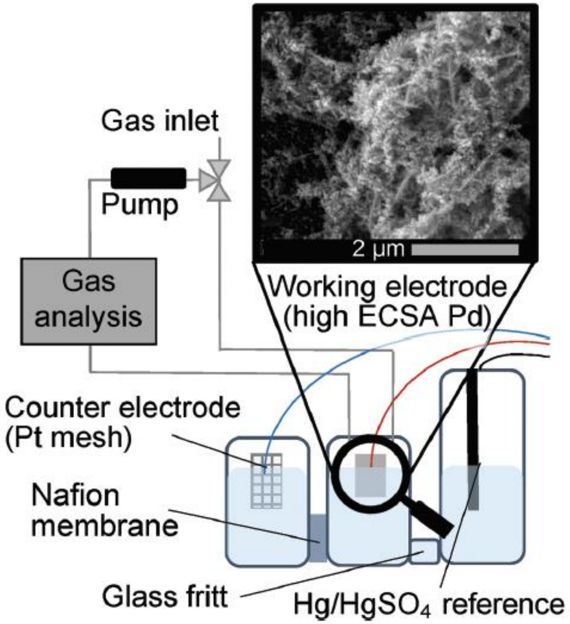




- Low currents meant high surface area was needed for product detection.



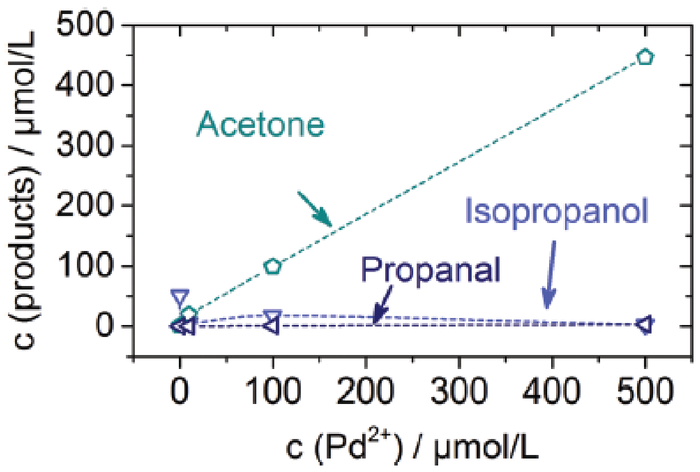


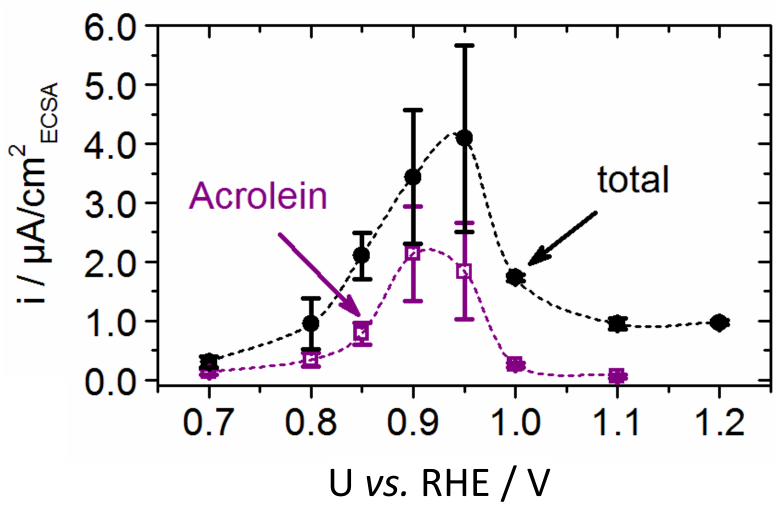


Winiwarter et al., Energy Environ. Sci., 2019, 12, 1055-1067

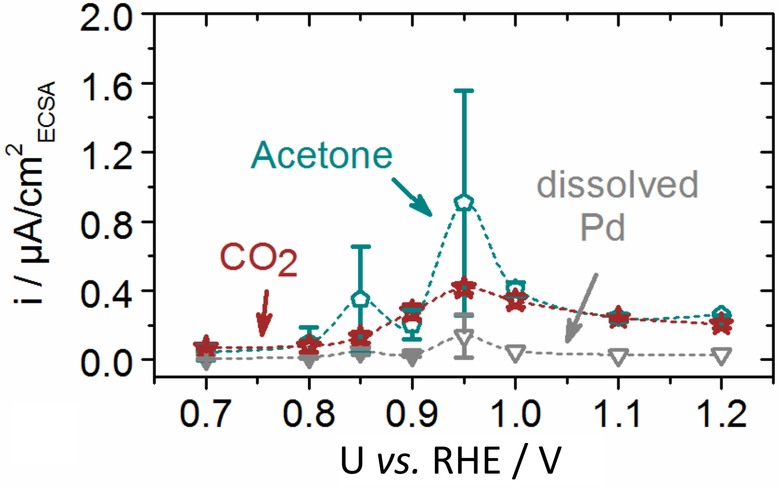
Electrochemical behavior and product distribution

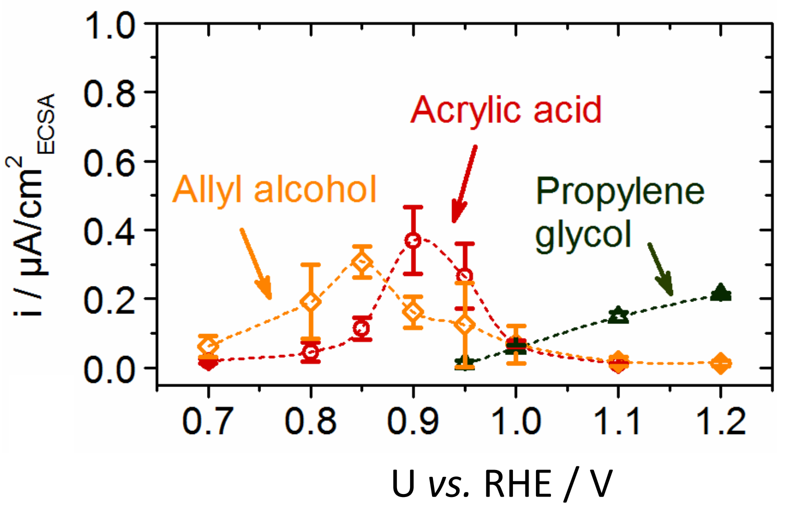
- We achieved a diverse set of products, with minimal complete oxidation to CO_2.
- The Pd/PdO redox potential is 0.9 V vs. NHE.
- Dissolved Pd^{2+} can act as a homogenous catalyst to reduce propene to acetone.





Unwanted products





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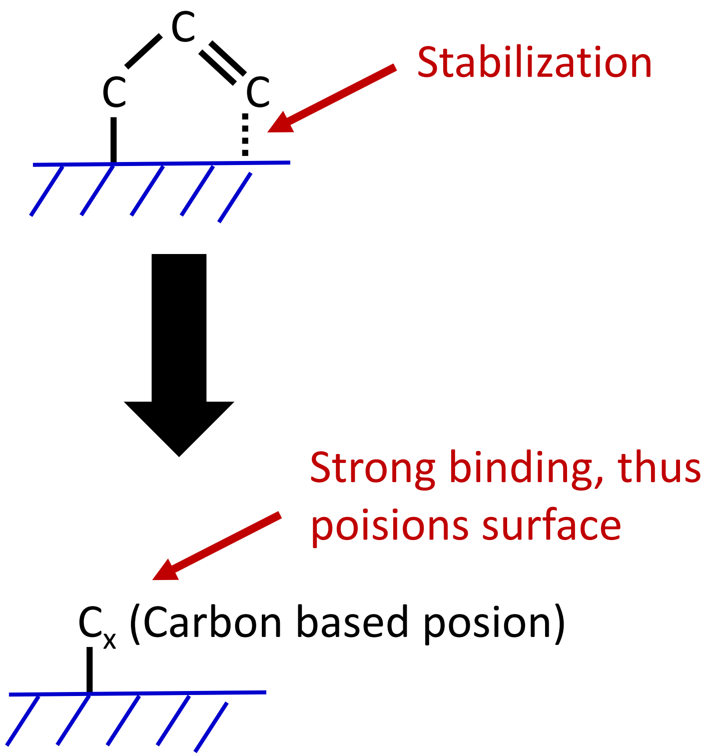
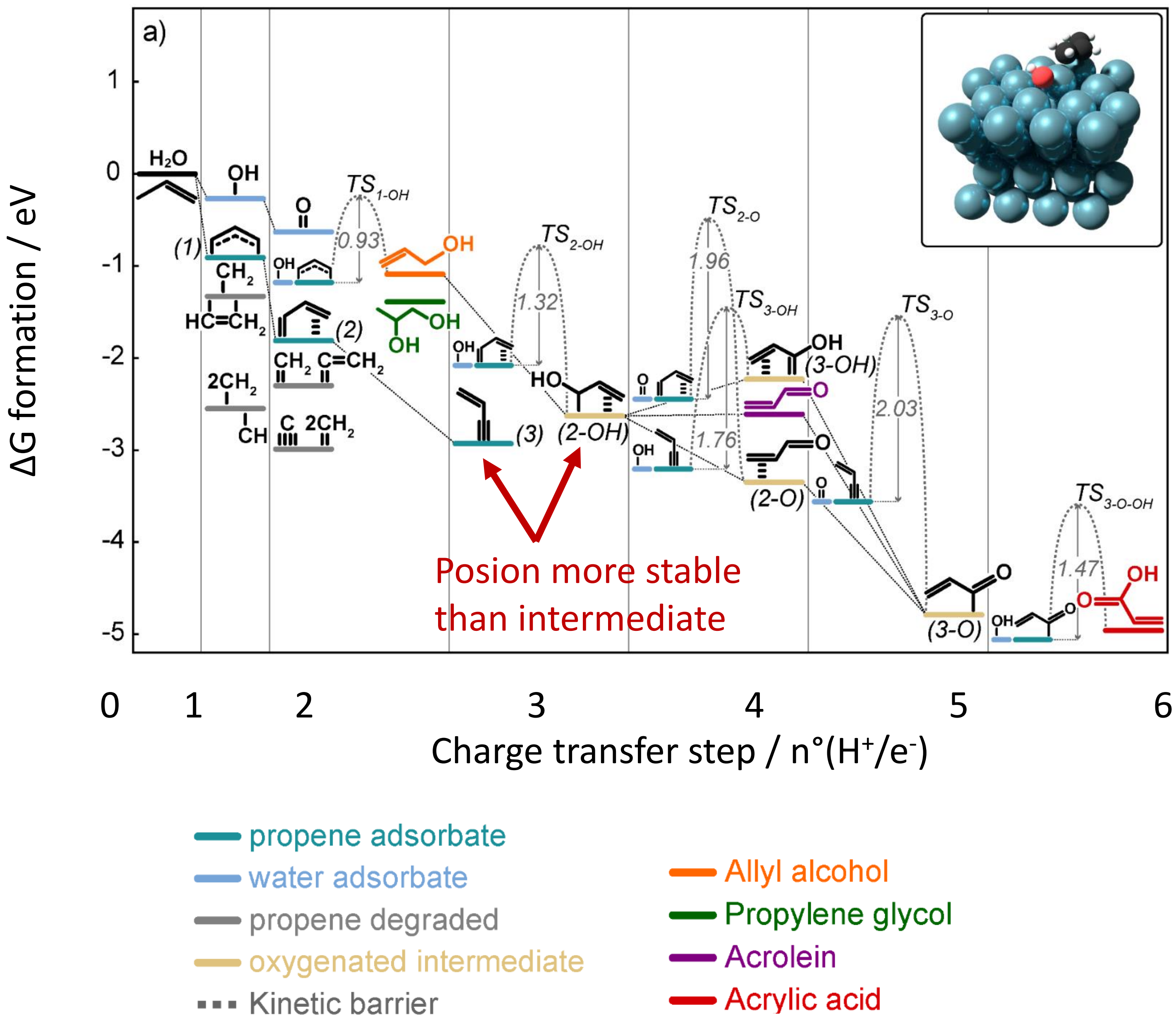
DFT Explaining why this will not work





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

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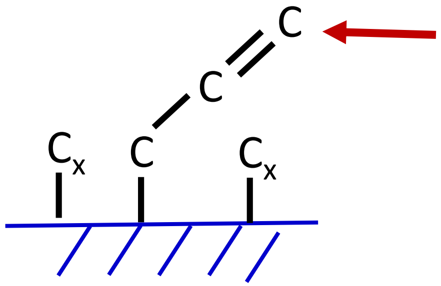
DFT Explaining why this could work

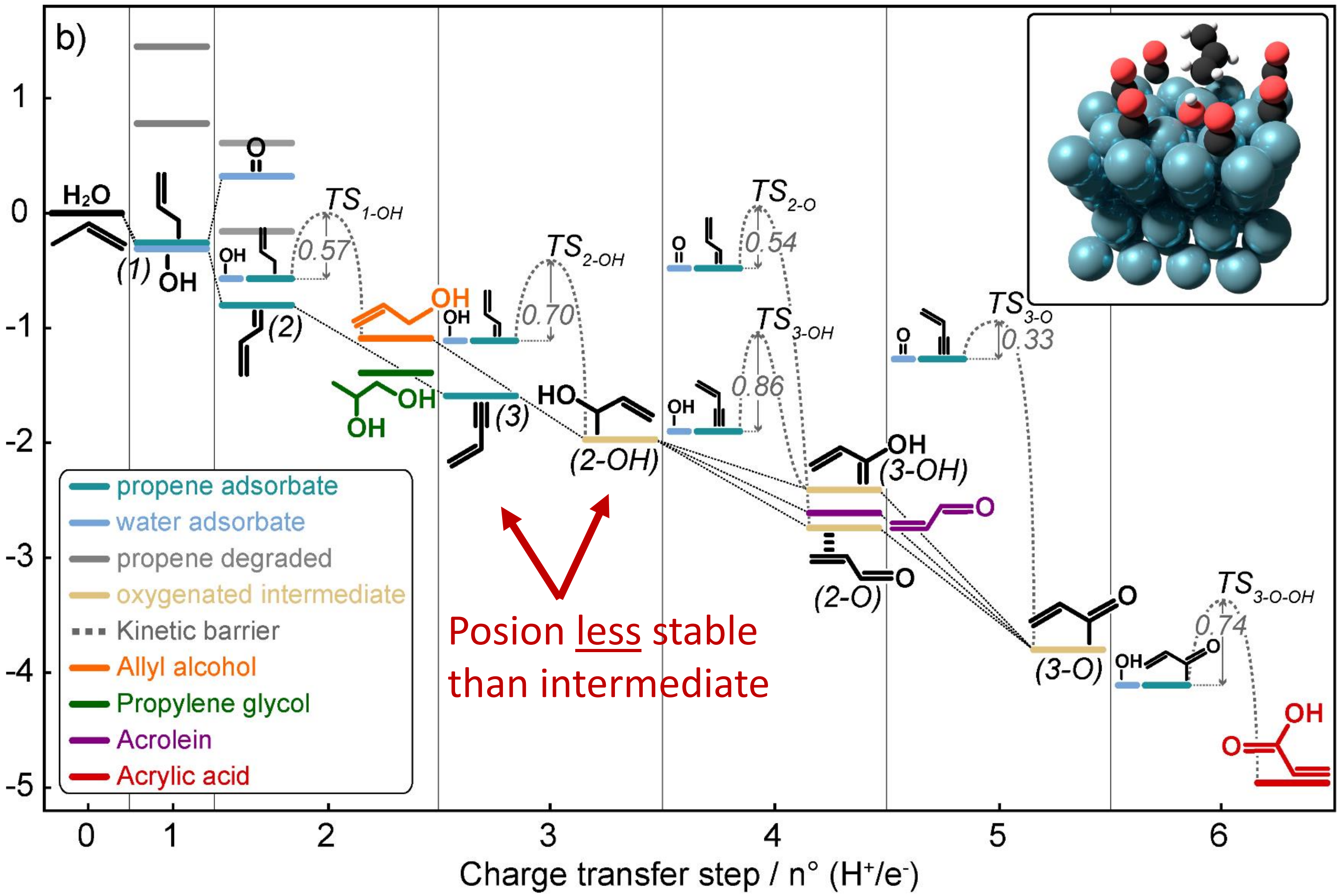
- We looked at the case where we had a high percentage (6/7) of the surface contaminated.



Not Stabilizing

- Poisioning prevents further poisioning, allowing for products
- How do we test this theory ?

Covered surface



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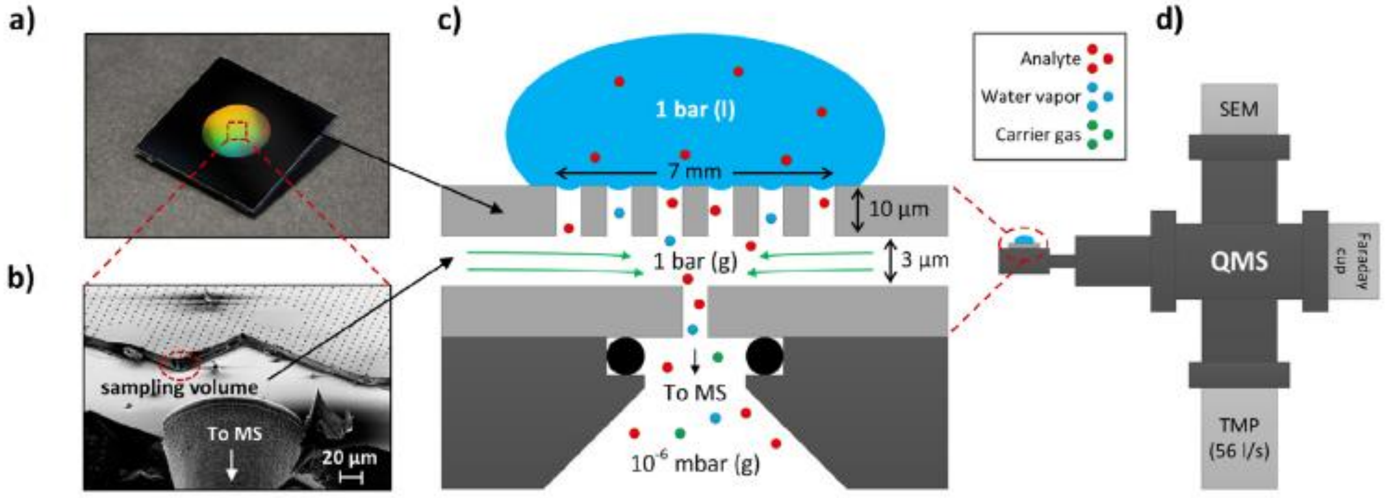
Tool for Product Detection

- We have a 'sniffer chip that basically sucks out the products and sends them to a mass spec.

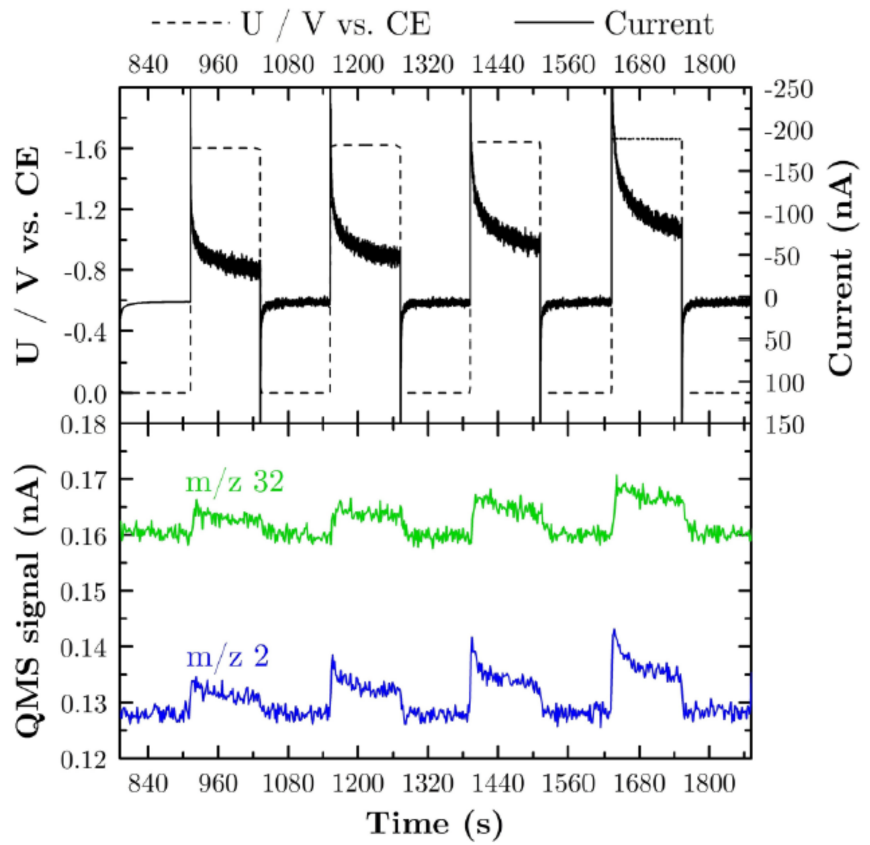
- This gives us submonolayer product detection



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

SpectroInlets
Enabling real-time analysis

Example: water splitting

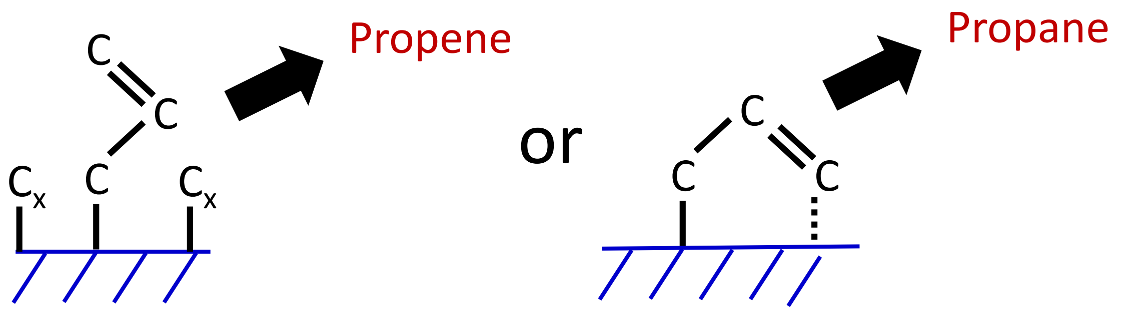


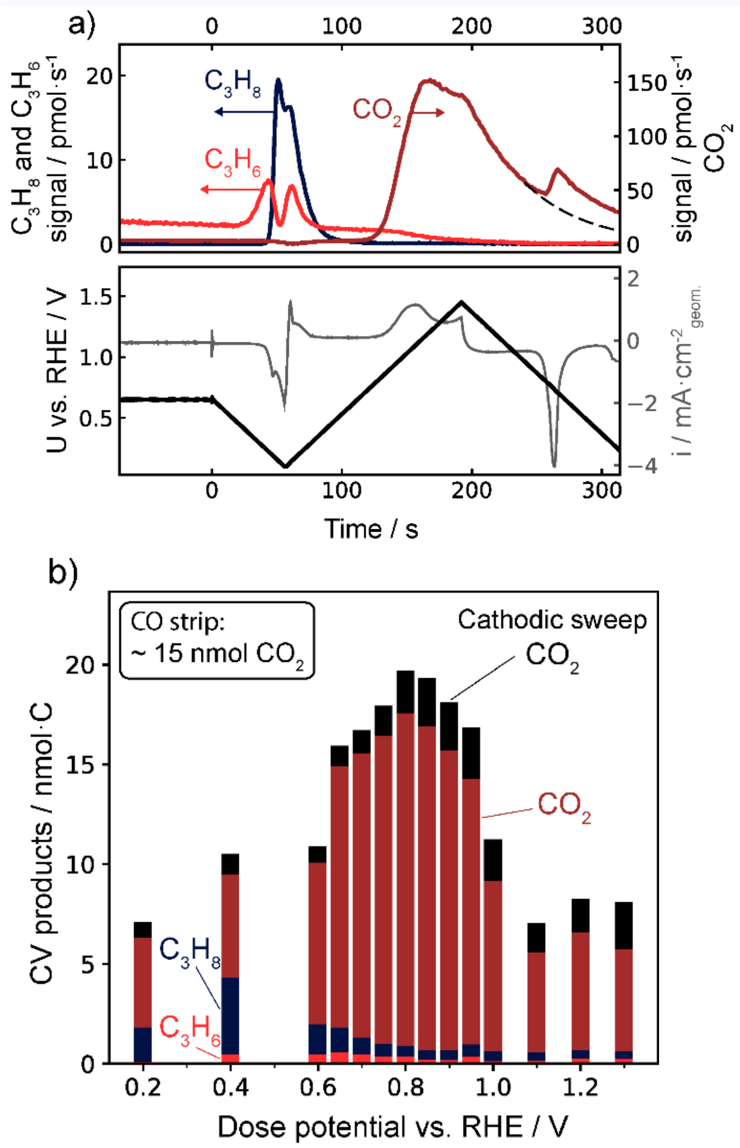
Propene stripping

- 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 CO_2





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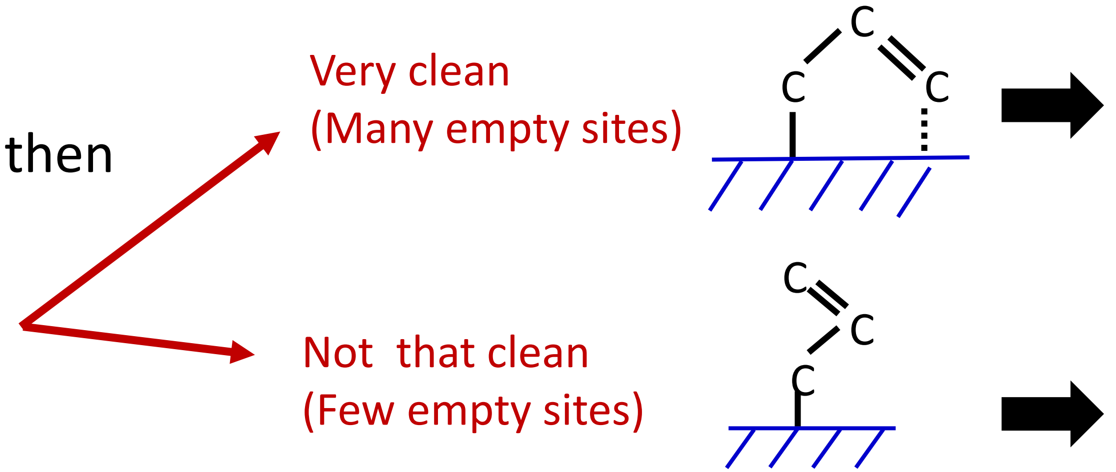
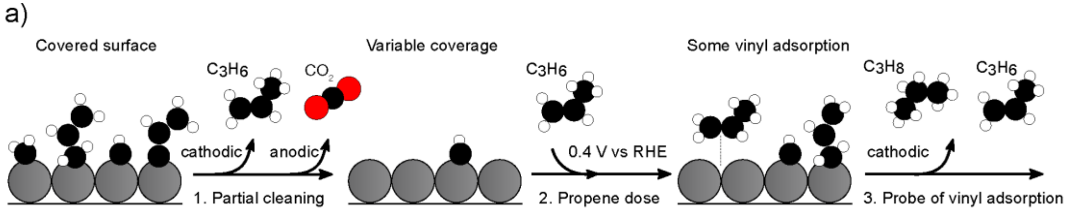
Analyzing propene to propane results

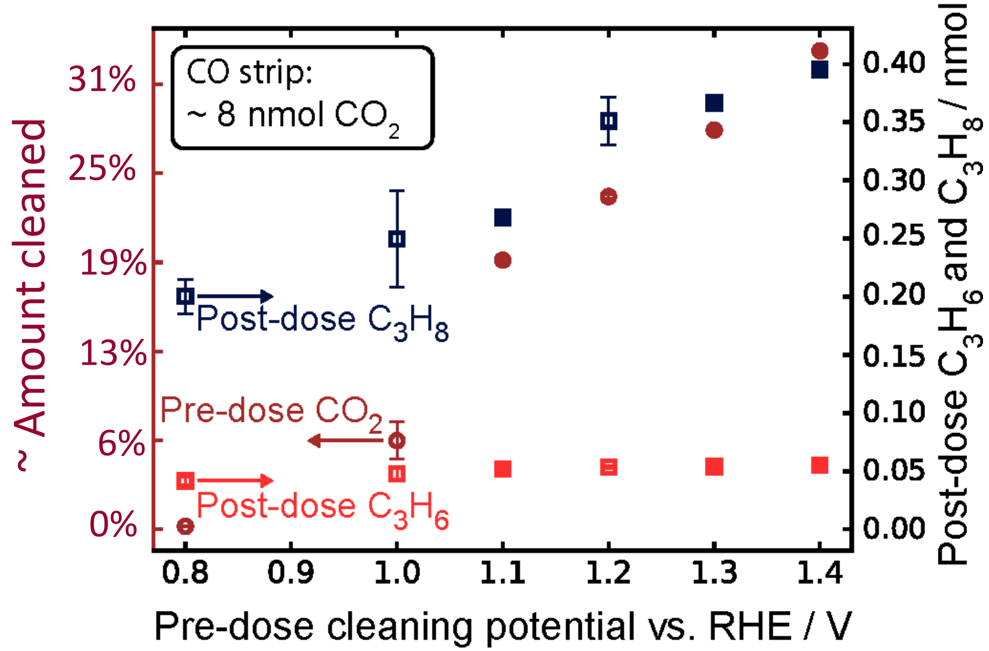
Process

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



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





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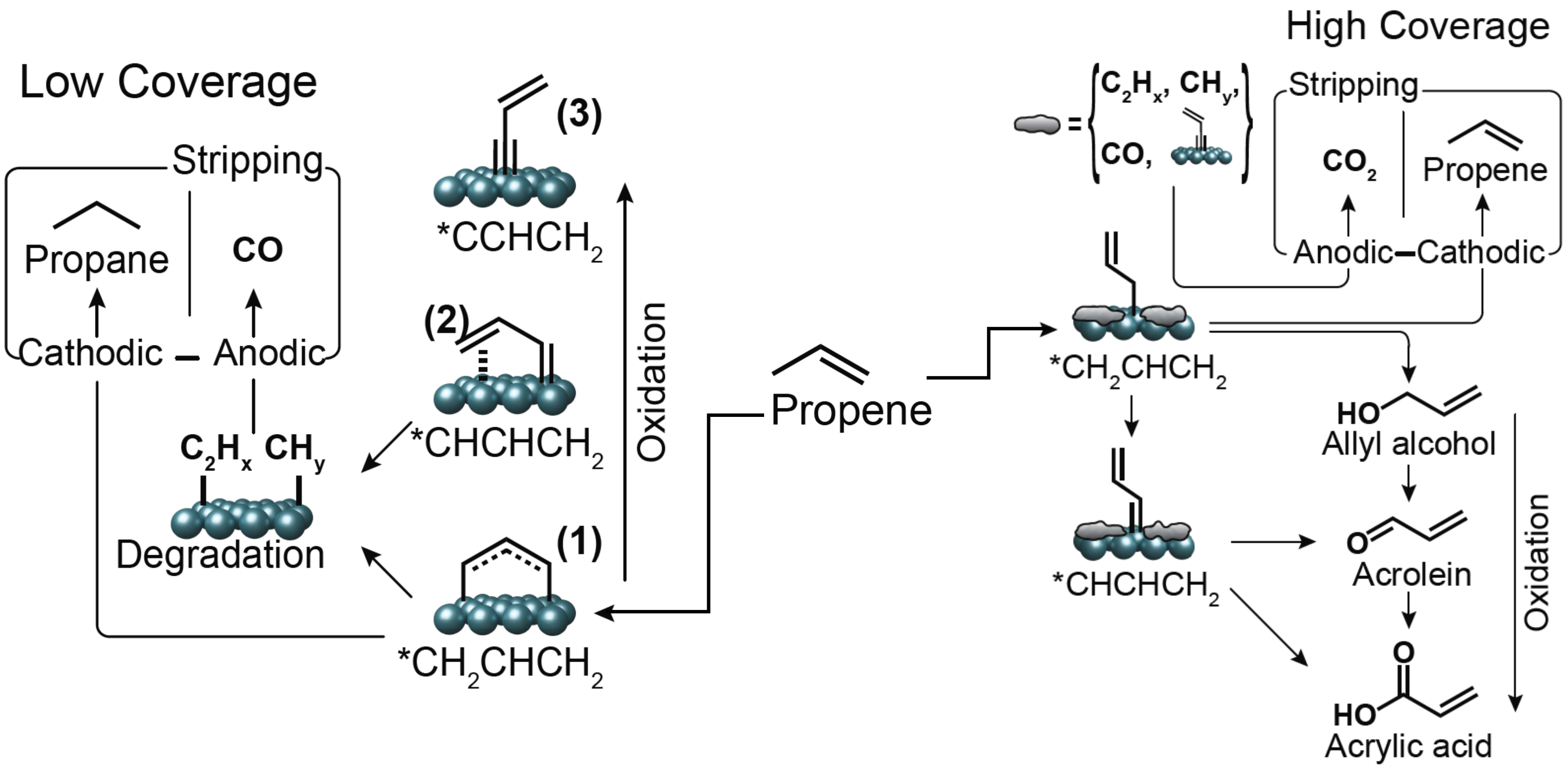
Conclusion – selectivity through coverage

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



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