

Correlations between Electronic Structure, Chemical Properties, and Adsorbate Binding in Size-Selected Model Catalysts

Support:
DOE BES
AFOSR MURI



18.4 m season total
5.2 m settled depth

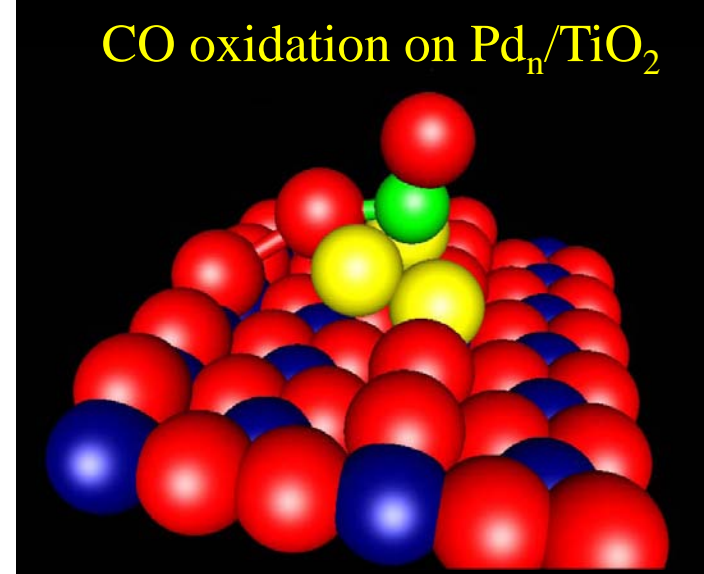
Motivation: What are the active sites in supported cluster catalysts?



Understand how Pd cluster size correlates with:

- Cluster Morphology
- Electronic Structure
- Interactions of the Clusters with the Support
- Catalytic Activity
- Binding of Reactants and Products

Also: How do the initially structures evolve under reaction conditions

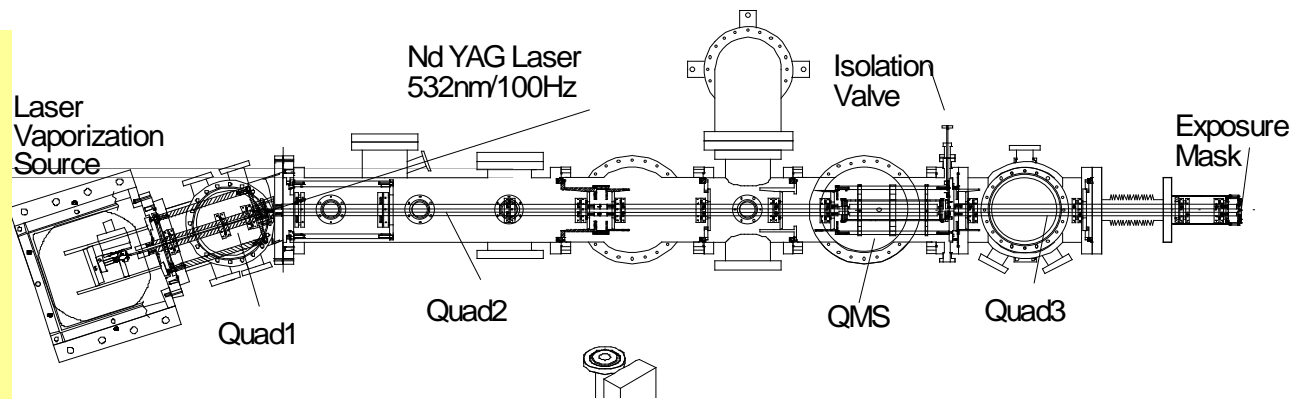


The Instrument:

- Cluster Beamline

- *In situ* analysis:

- XPS
- ISS
- UPS/INS
- AES
- TPD/TPR
- Pulsed reaction
- *In situ* electrochem



Elect Spect

Ion F

oxygen vacancy

bridging oxygen

Protocol:

Clean and anneal $\text{TiO}_2(110)$

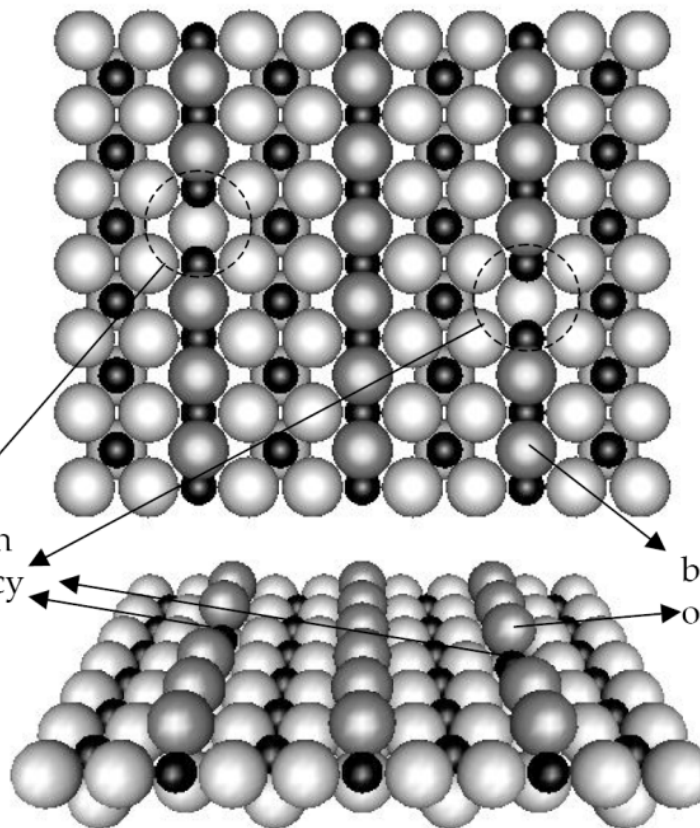
Deposit 0.1 ML of selected Pd_n

Morphology

Electronic structure

Catalytic activity

Reactant binding



Typical Chemistry Experiments

Sample cleaned/prepared in vacuum

Characterized by XPS/ISS

Positioned at mass spectrometer

- 6 pulsed or CW gas dosers

Expose to O₂ for calibrated dose

- vary dose

- T_{oxidation} = 300 or **400 K**

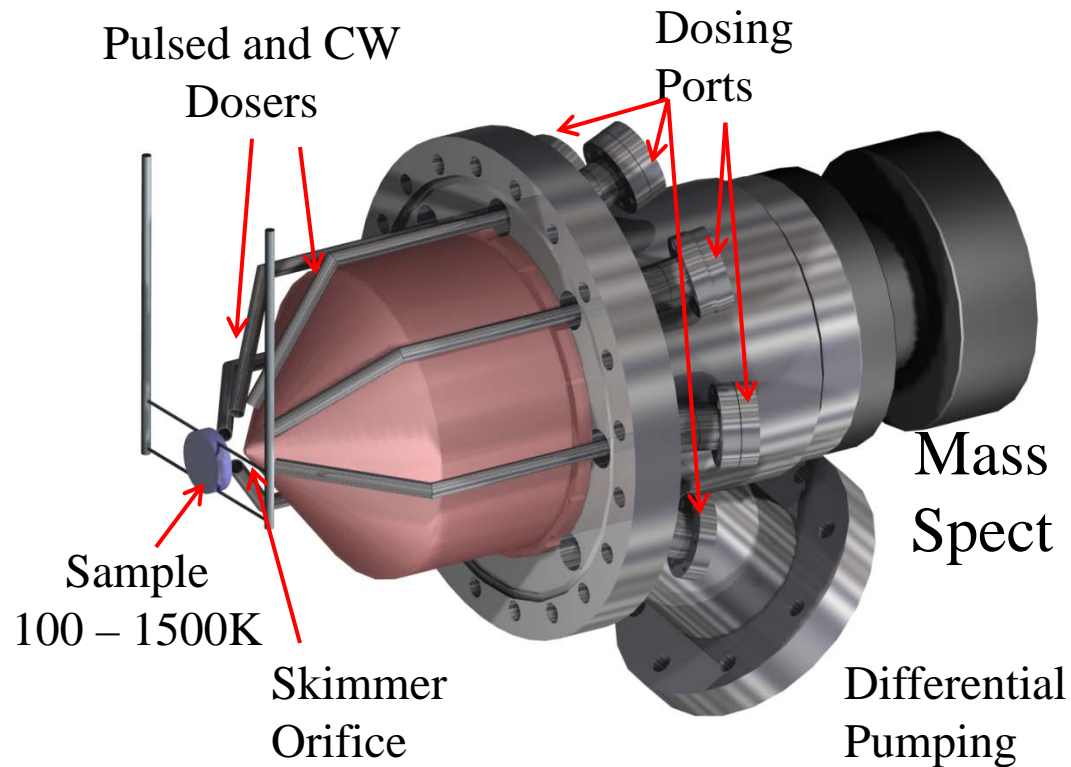
Cool to 180 K, expose to CO

Just above T_{desorption} for TiO₂

Cool to 100 K

Temperature-programmed reaction

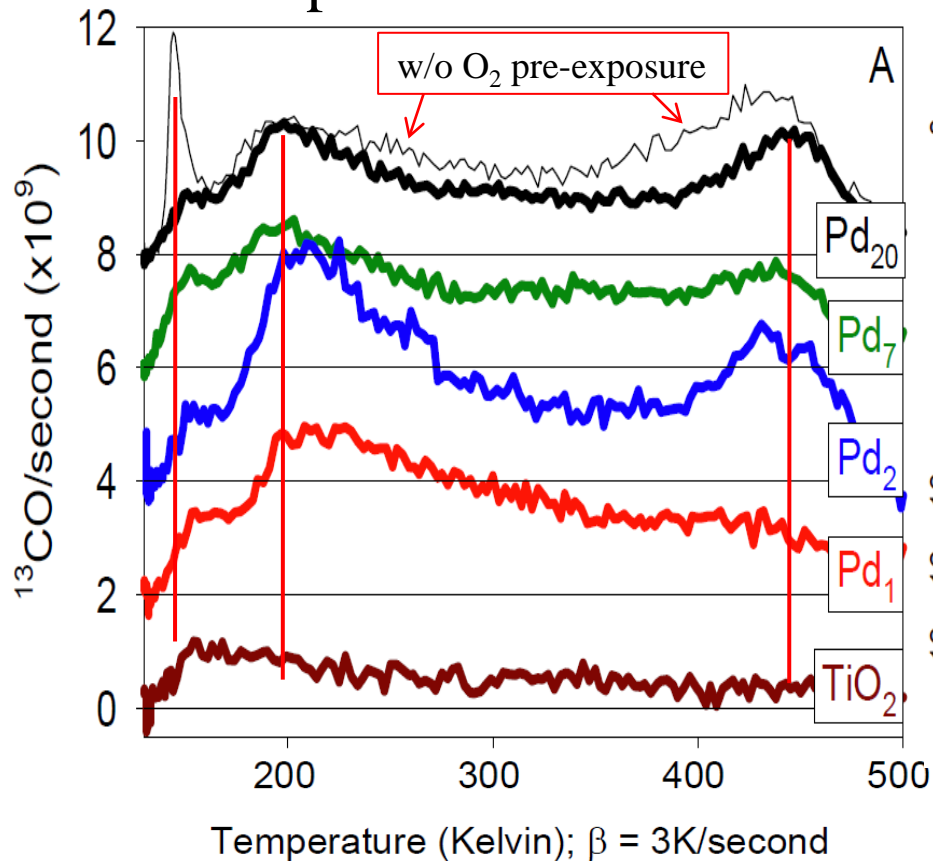
- T_{sample} ramped at 3K/sec
- Desorbing species measured
- Binding energies



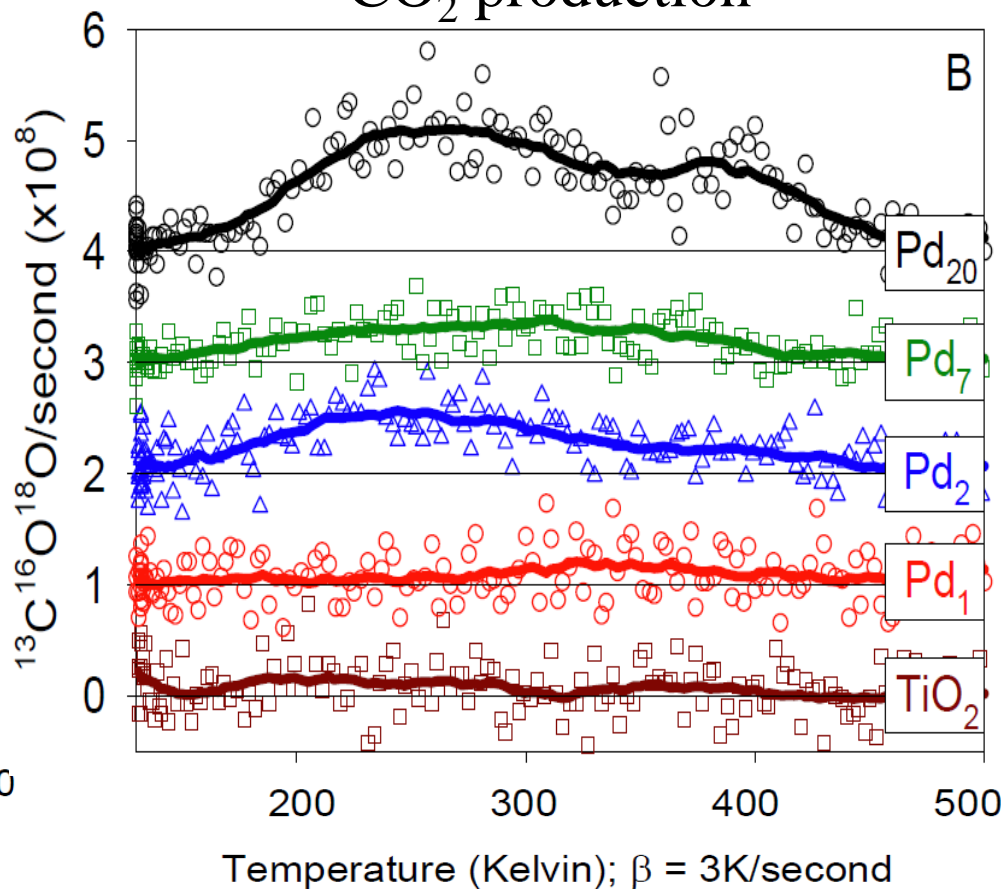
CO oxidation by Pd_n/TiO₂(110)

10L ¹⁸O₂ at 400 K, followed by 5 L of ¹³CO at 180 K
Heat at 3 K/sec, while monitoring desorbing CO and CO₂

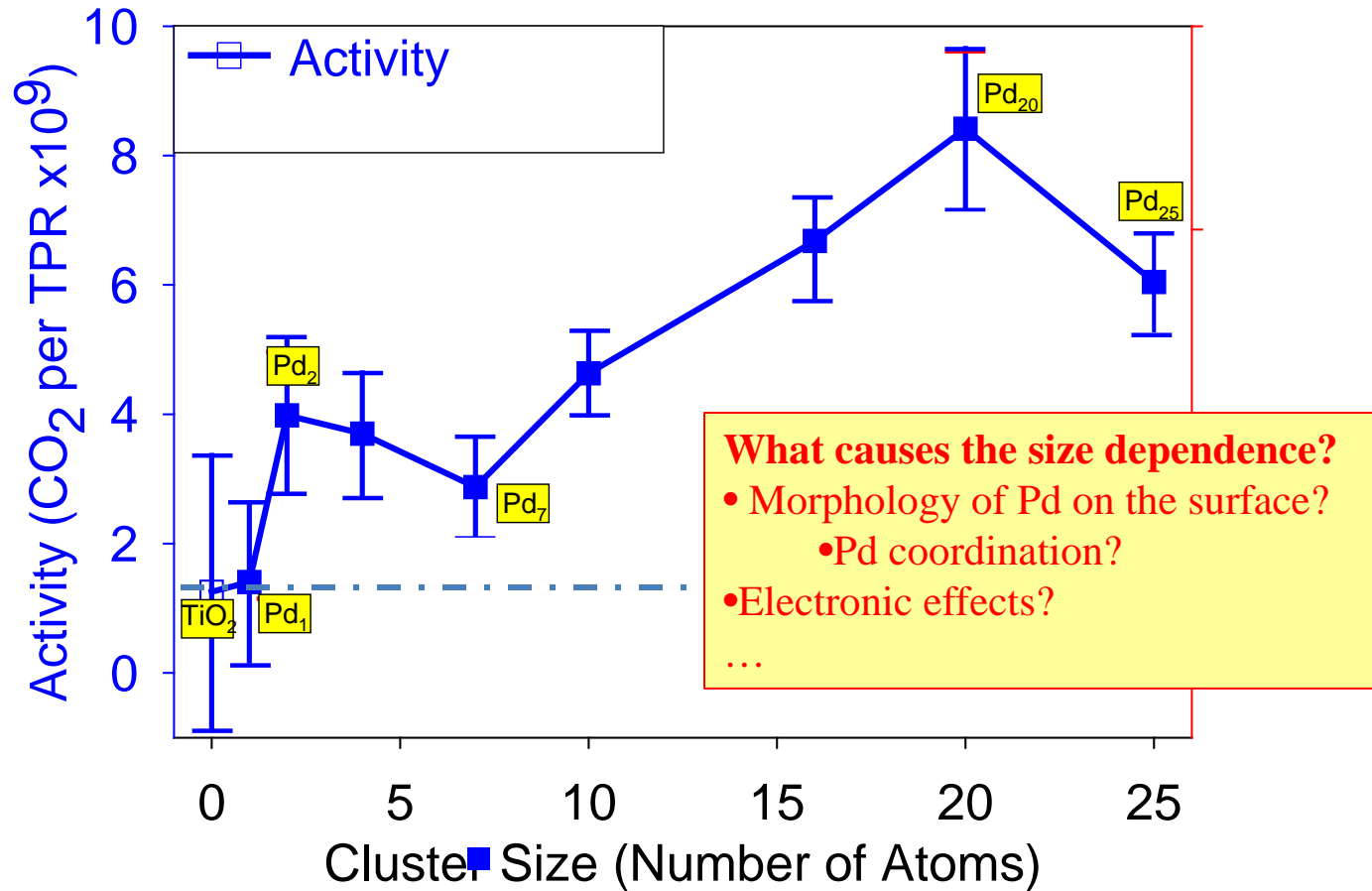
Desorption of residual CO



CO₂ production



CO₂ Production Activity vs. Size



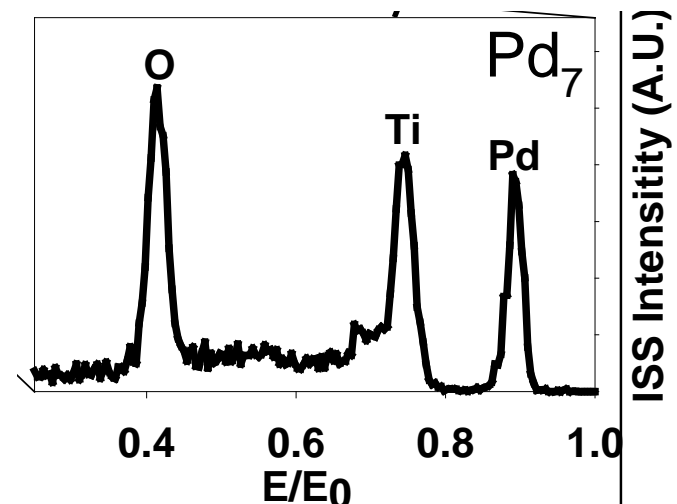
Characterization of As-Deposited Morphology by Ion Scattering

How to probe morphology?

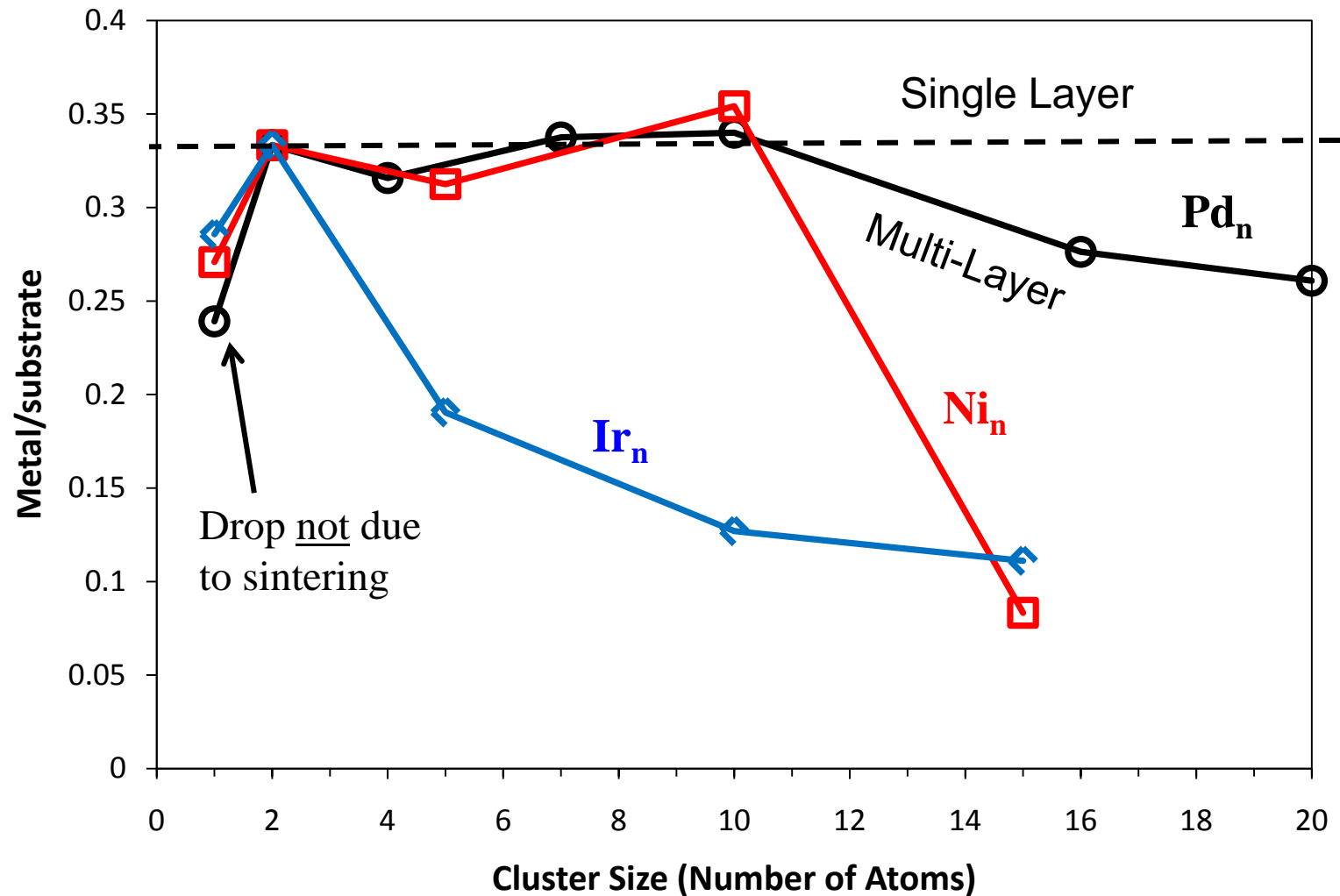
STM is too slow – highly dispersed metal clusters are incredibly efficient at getting contaminated

Use 1 keV He⁺ scattering (ISS)

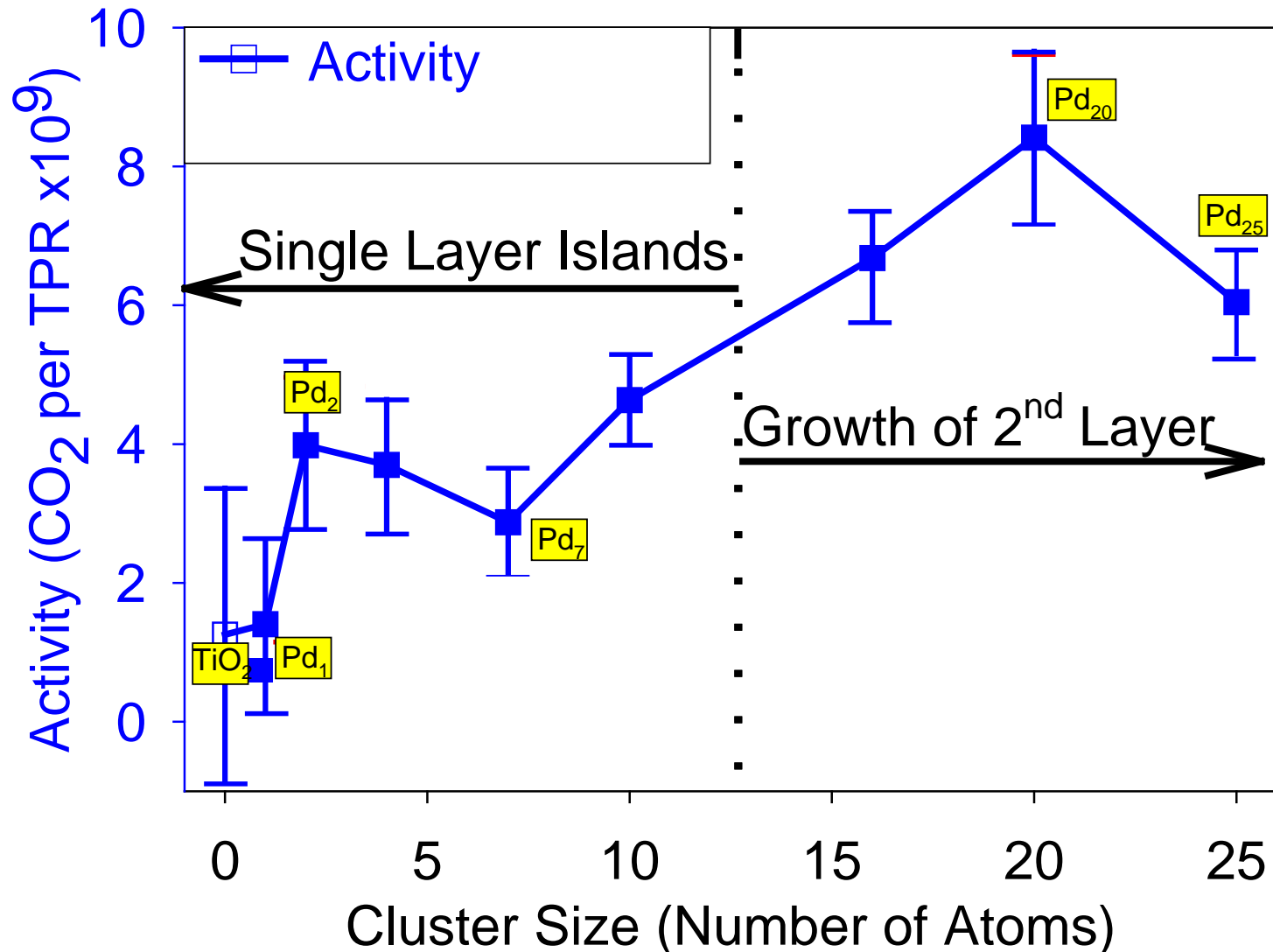
- Probes atomic concentrations in *top most layer*
- Morphology by blocking/shadowing/ion survival
- 30 second expt time
- Have to deal with sputter damage
- Can probe both Pd and adsorbates



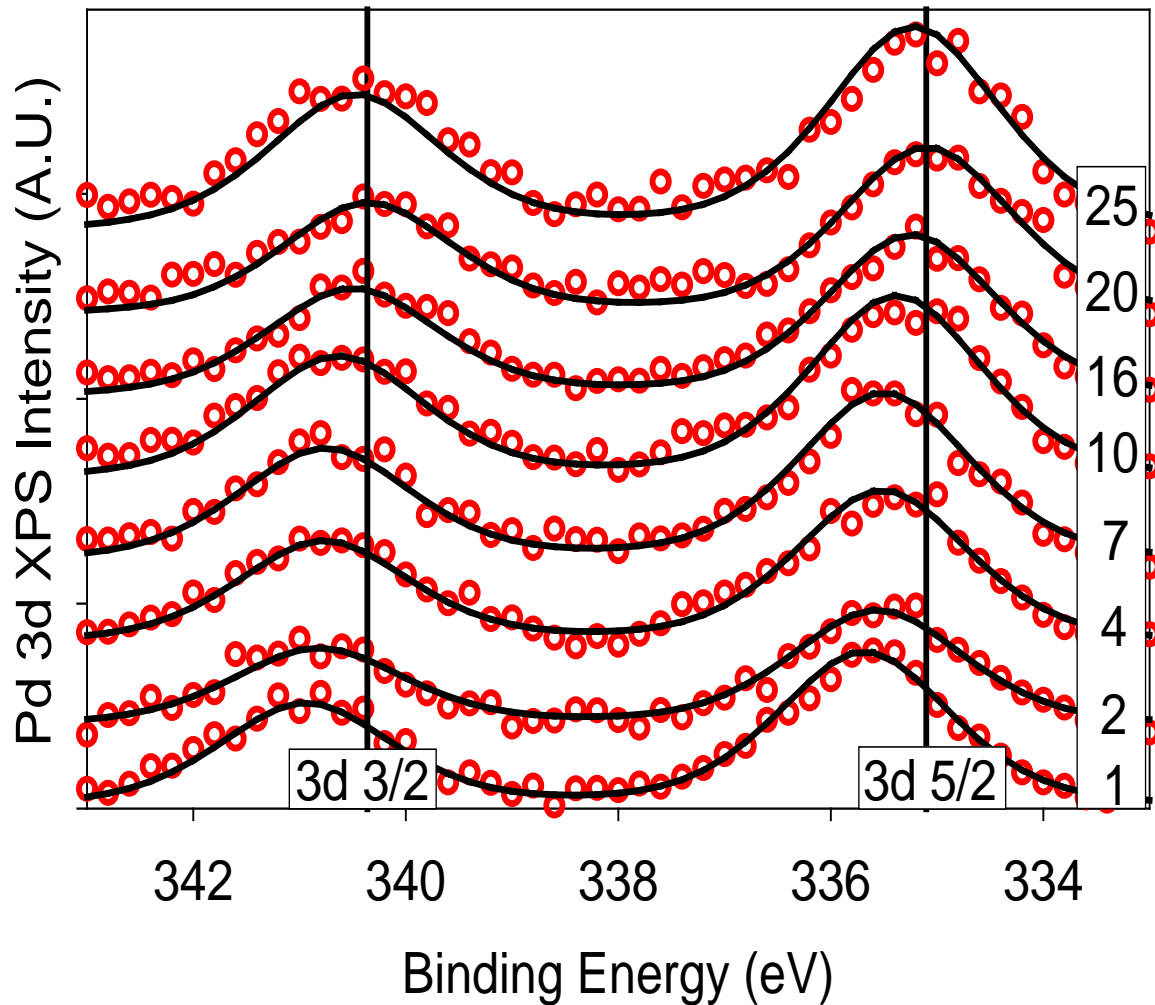
Comparison of different metals



No obvious correlation with the transition to multilayer clusters



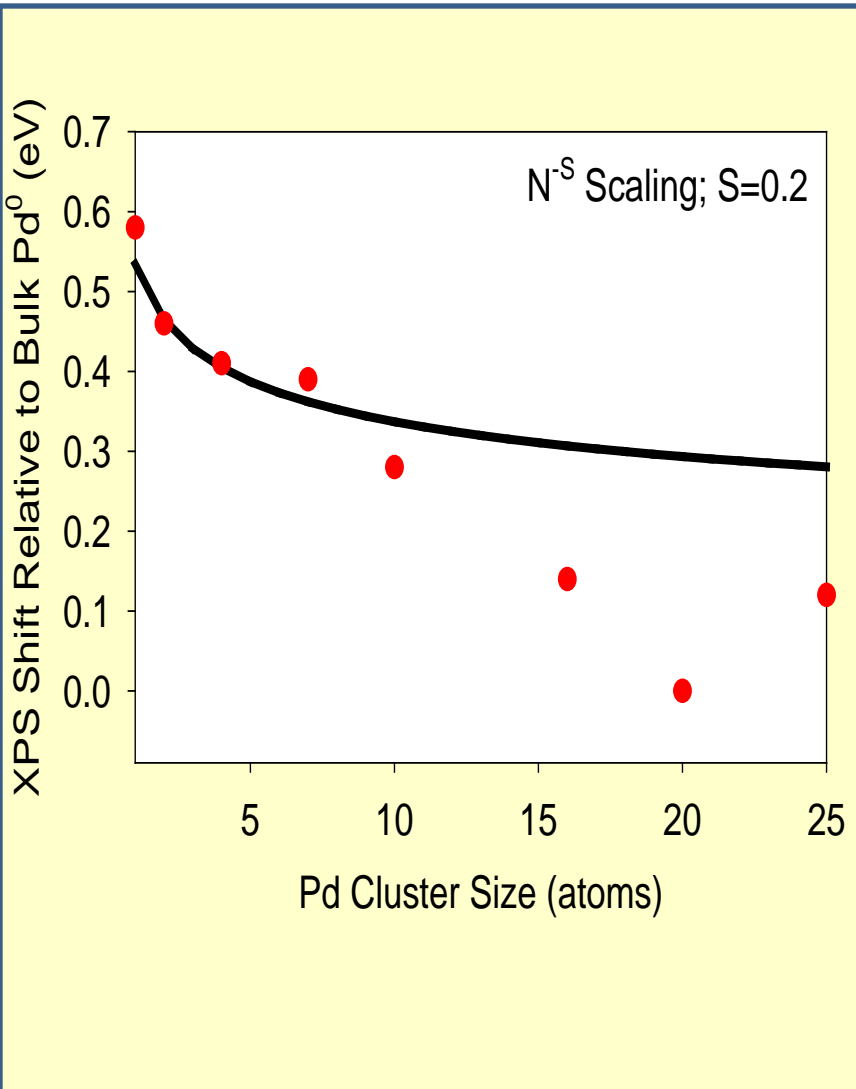
Probe electronic structure with X-ray Photoelectron Spectra (XPS)



Pd core levels are more tightly bound in clusters, than in the bulk.

Why?

Why does BE increase for small clusters



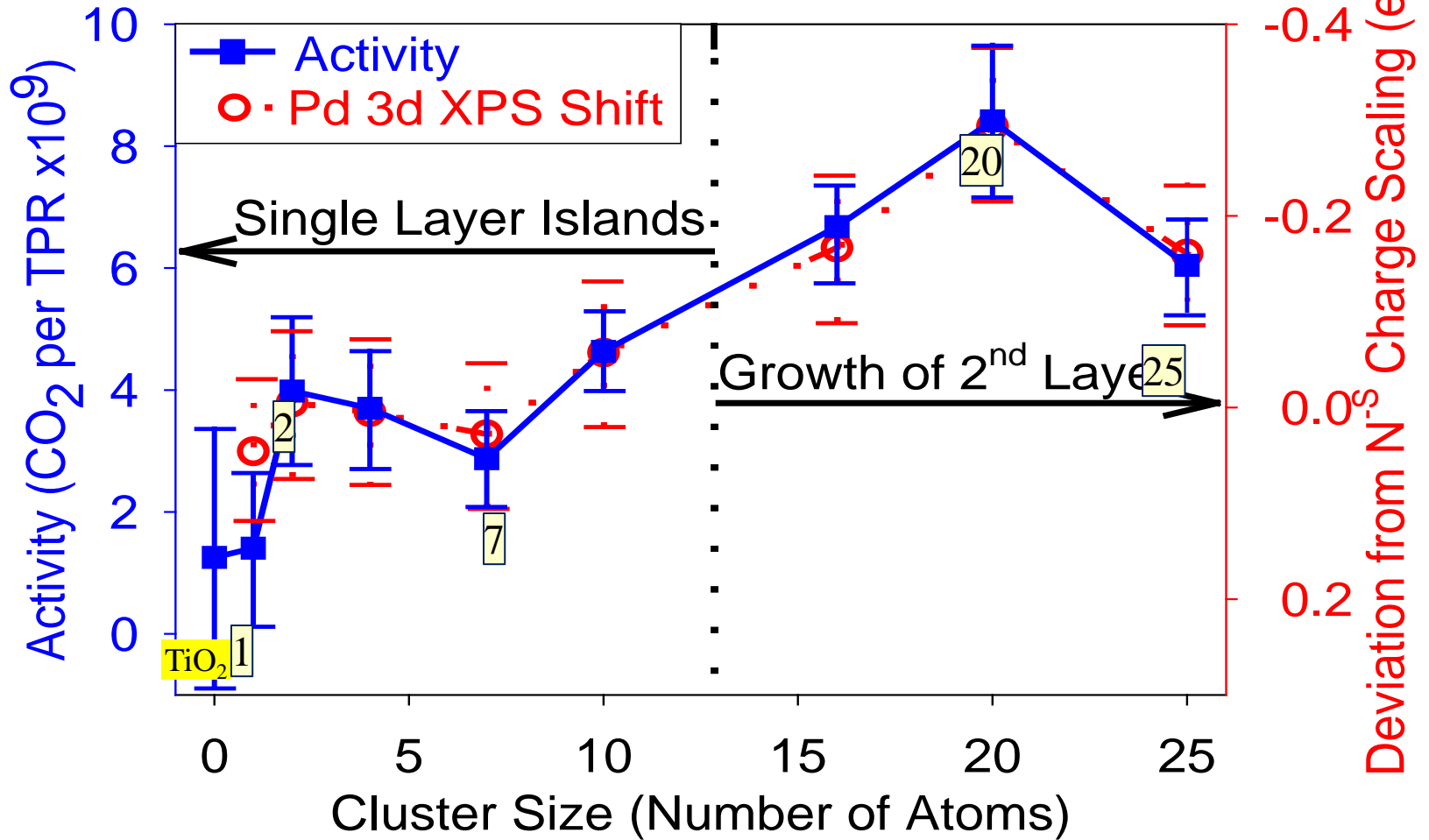
Observation: XPS binding energies shift to higher binding energy with decreasing coverage (cluster size)

1. **Initial state** may be more stable: Certain cluster sizes make have more stable electronic shell structures – harder to remove electrons.
2. **Final state charging**: Final state of XPS is a charged cluster on an insulating surface – charge is more localized as size gets smaller – raises BE

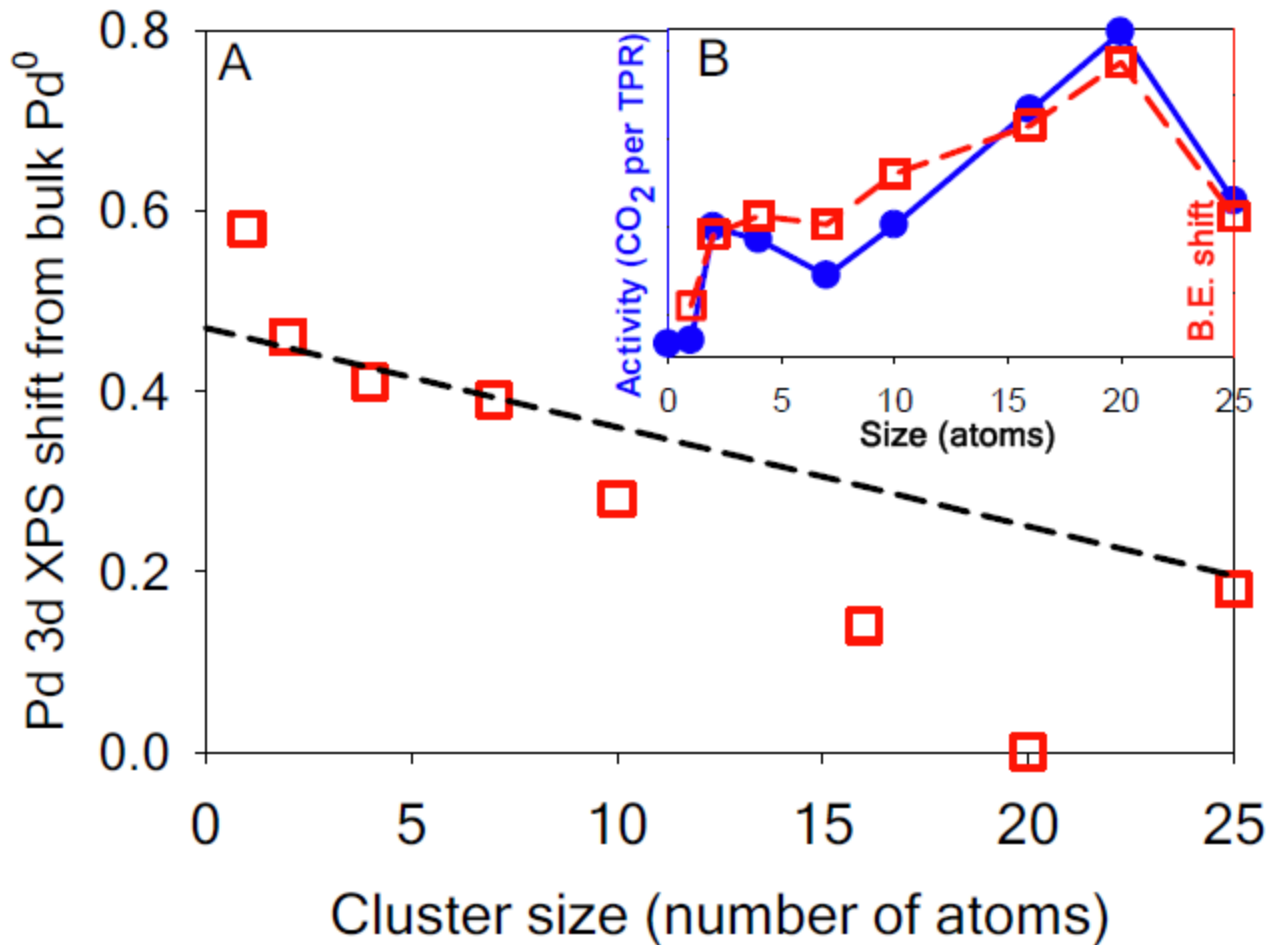
Partially offset by **Screening** of charge by conduction or valence electrons

Electronic Structure → BE → Activity

1st time ever observed (1st time looked for)



Correlation is not an artifact of the $N^{-0.2}$ scaling chosen

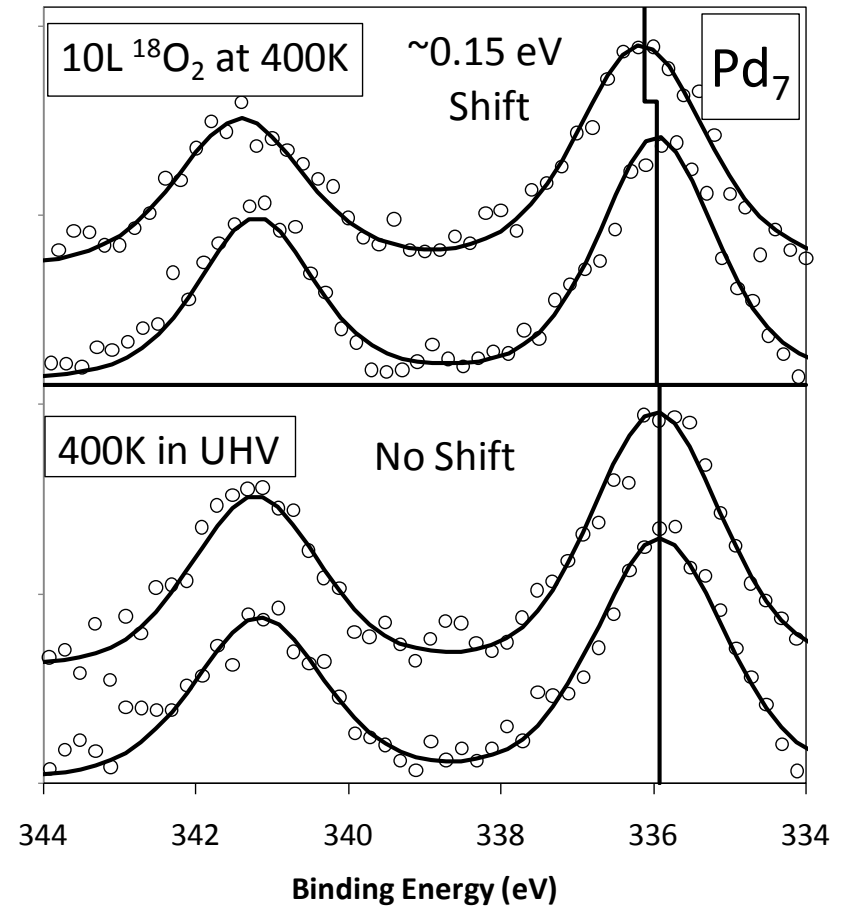


Why does the activity scale with core level energetics?
Screening?

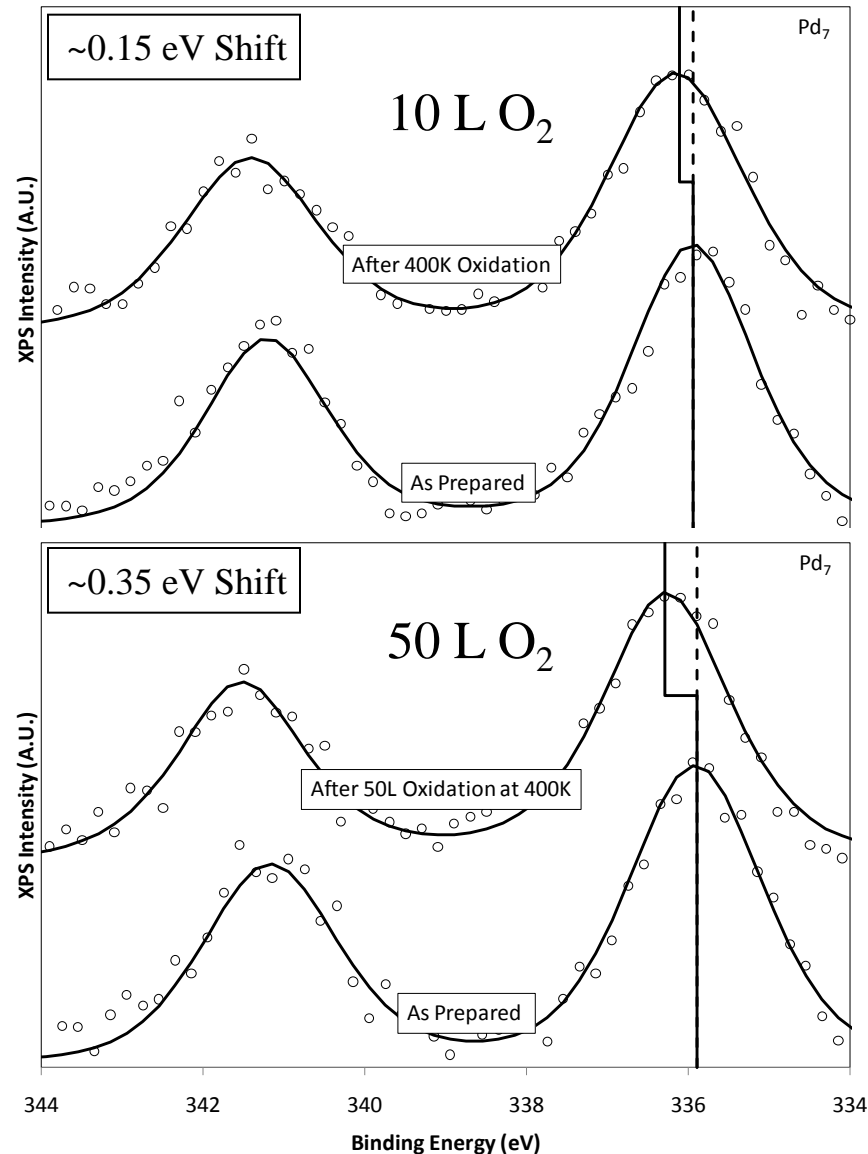
Look at the mechanism in more detail

1. Effects of O₂ exposure

- Deposit Pd_n
- As-deposited XPS
- Expose to O₂ at 400 K
- ISS (separate expt) shows
~50% attenuation of Pd signal
 - O atoms adsorbing on top of Pd clusters
- Post exposure XPS
- Shift to higher binding energy indicates oxidation
- No effect from heating below ~500 K



Effects of changing O_2 exposure or T_{exposure}



Pd₇:

- Additional BE shift (oxidation) w/ larger O₂ dose

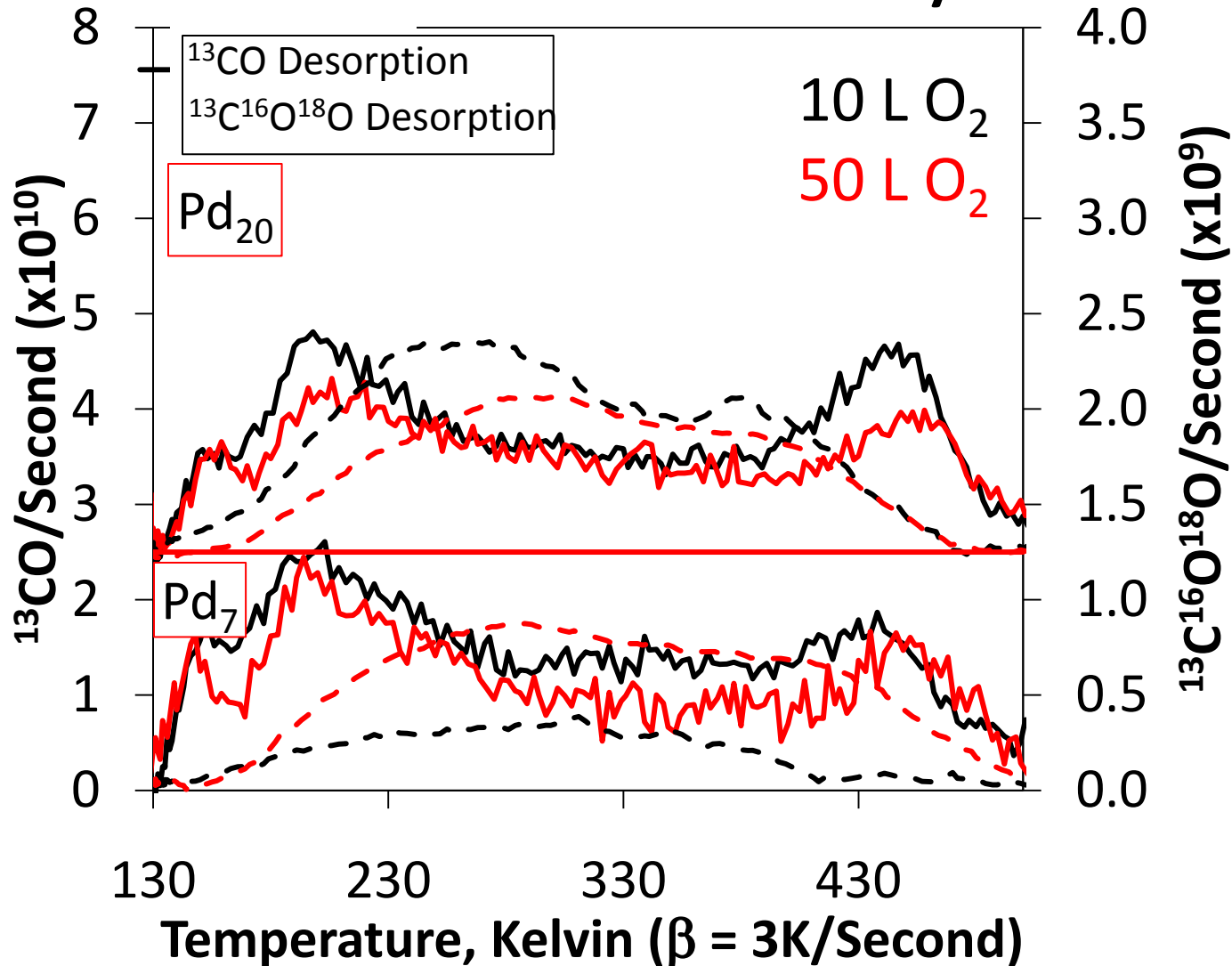
Pd₂₀:

- No additional shift in XPS w/ increasing O₂ exposure

• $T_{\text{oxidation}}$ dependence:

- XPS shifts decrease with $T_{\text{oxidation}}$
- No shifts below 300 K for 10 L O₂ exposures (**activated process?**)
- Not activated on some bulk Pd surfaces

Effect of increasing O₂ exposure on activity



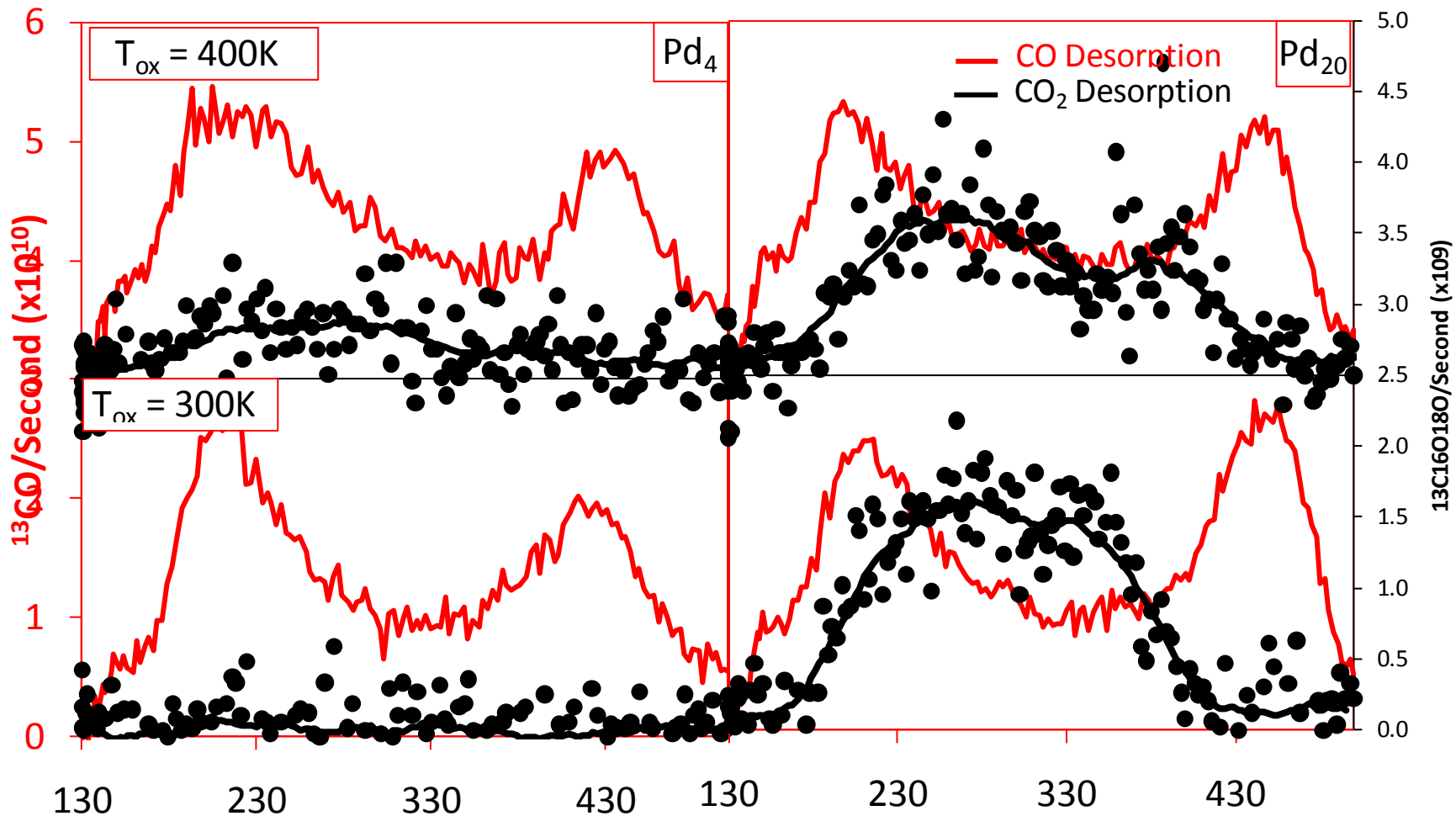
Pd₂₀ now less reactive than Pd₇

Pd₂₀ has less high temperature CO

Higher exposure over-oxidizes Pd₂₀ Blocks sites for CO binding

Less reactive clusters need higher O₂ exposures

$T_{\text{oxidation}}$ Dependence



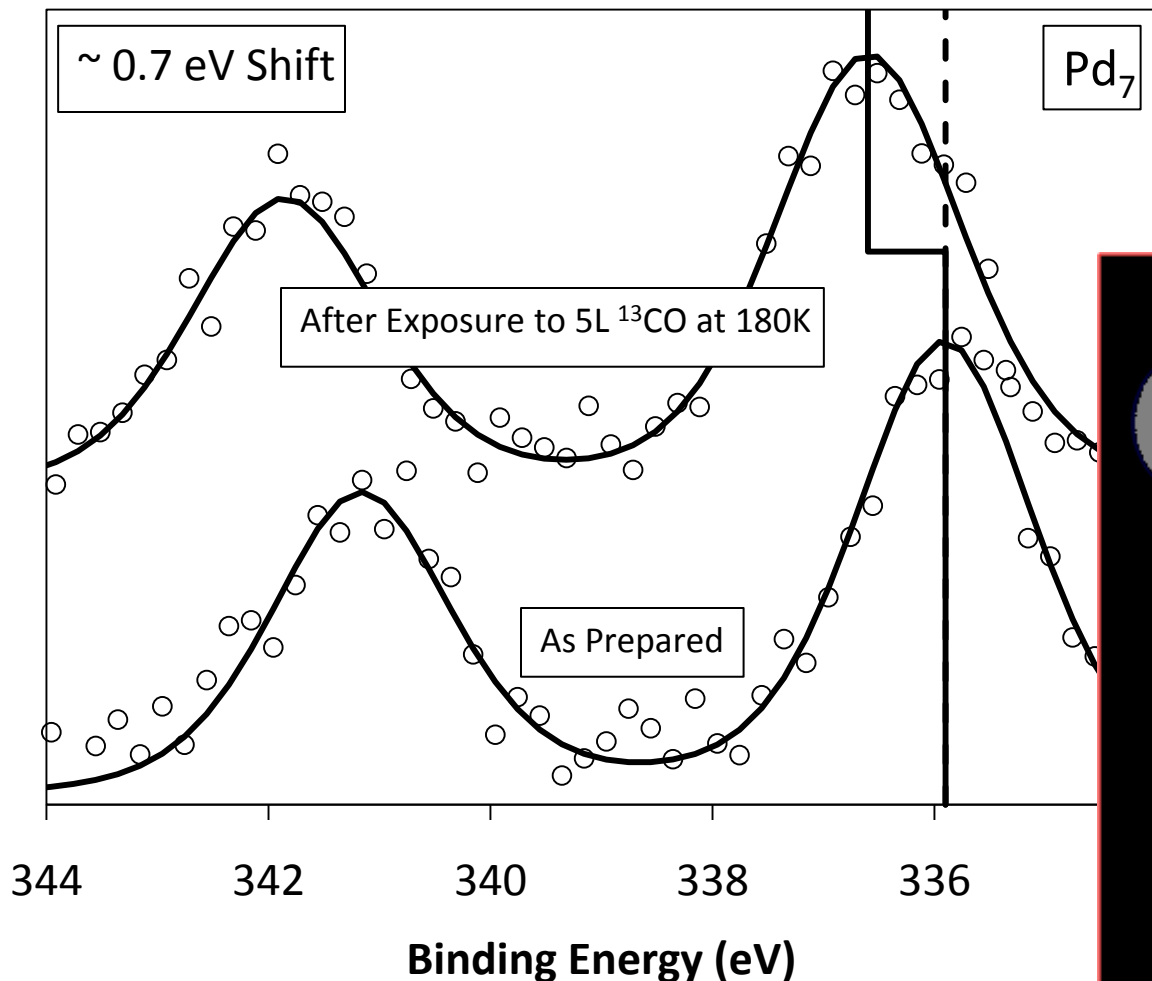
Less reactive clusters do not activate O_2 at 300 K
 Pd_{20} activity increases at 300 K, but *dead* at 200 K

Conclusion about oxygen activation:

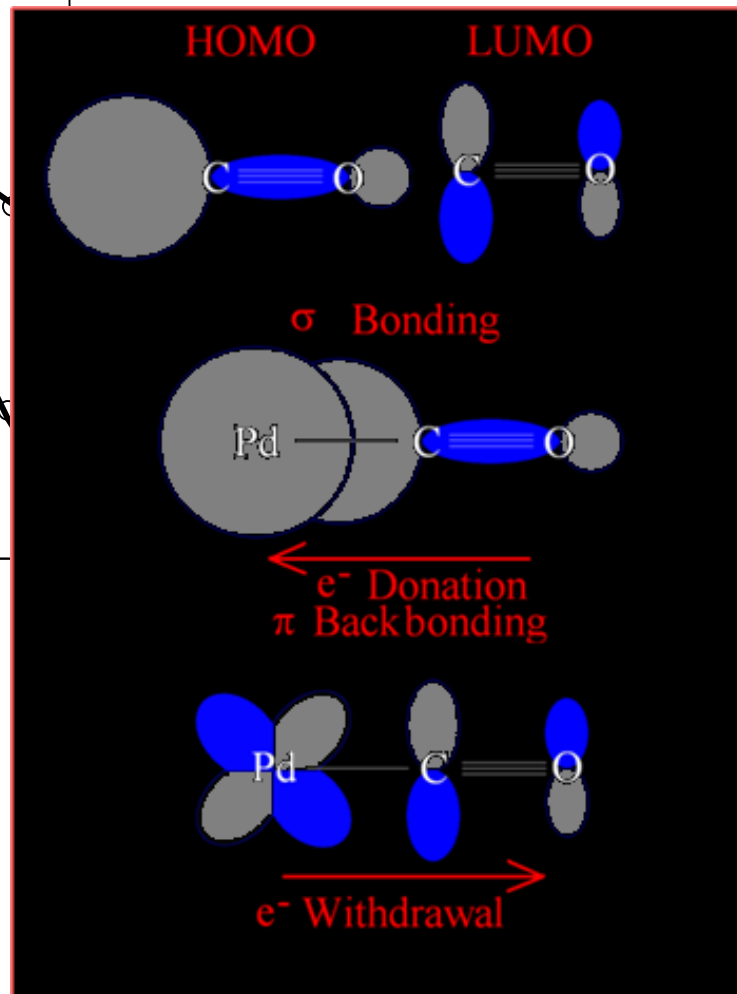
- For *less active* clusters, O_2 activation is rate-limiting for oxygen exposures equivalent to a few ML coverage.
- Increasing $T_{\text{oxidation}}$ or O_2 exposure increases amount of O_{ads} bound on Pd
- Results in increased CO_2 production upon CO exposure

- For most active clusters, O_2 activation is efficient for
 - $T_{\text{oxidation}} \geq 300\text{K}$
- Results in over oxidation, blocking CO sites
- Additional O_2 exposure or $T_{\text{oxidation}}$ results in lower CO oxidation activity

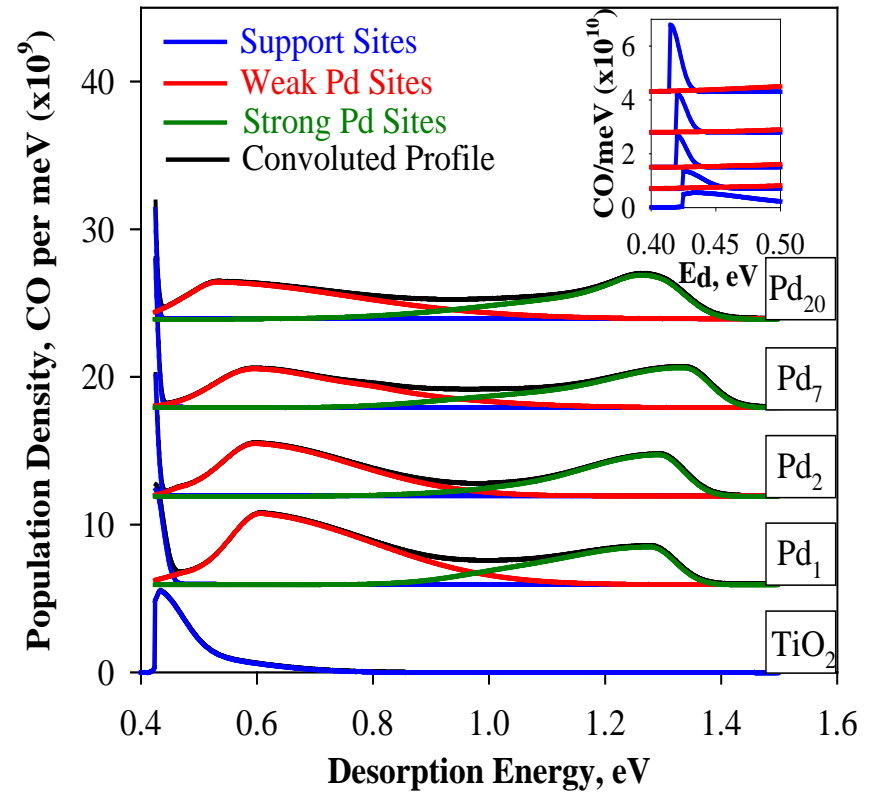
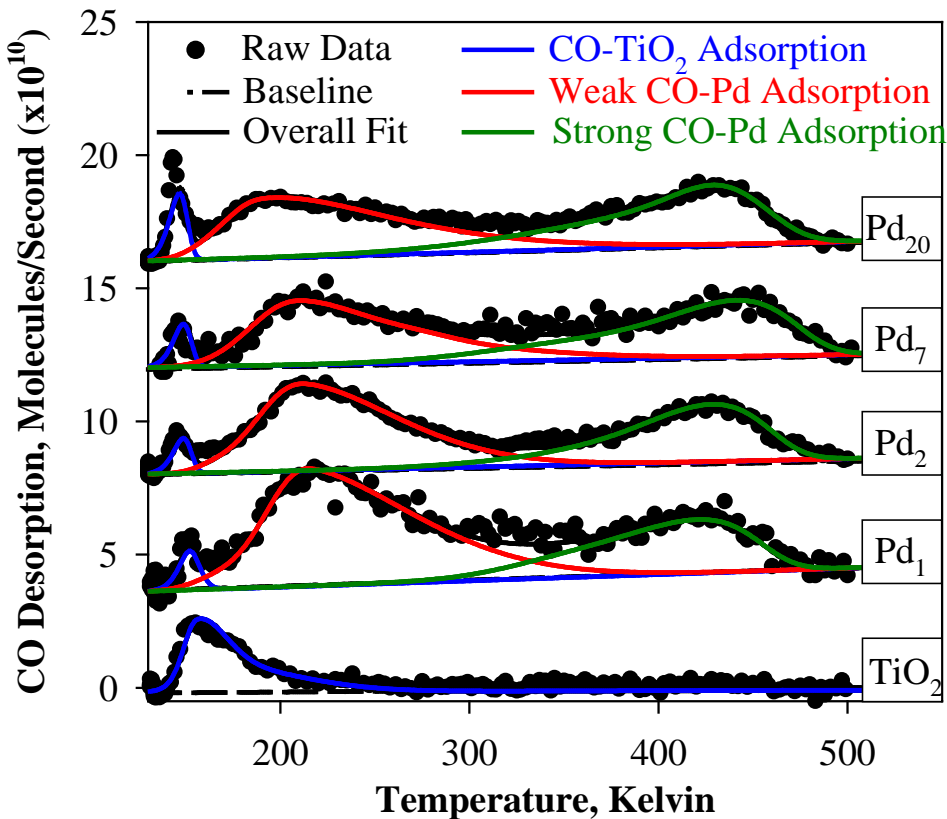
How about the effects of CO binding?



Even larger
"oxidation" shift than
for O₂! – Why?

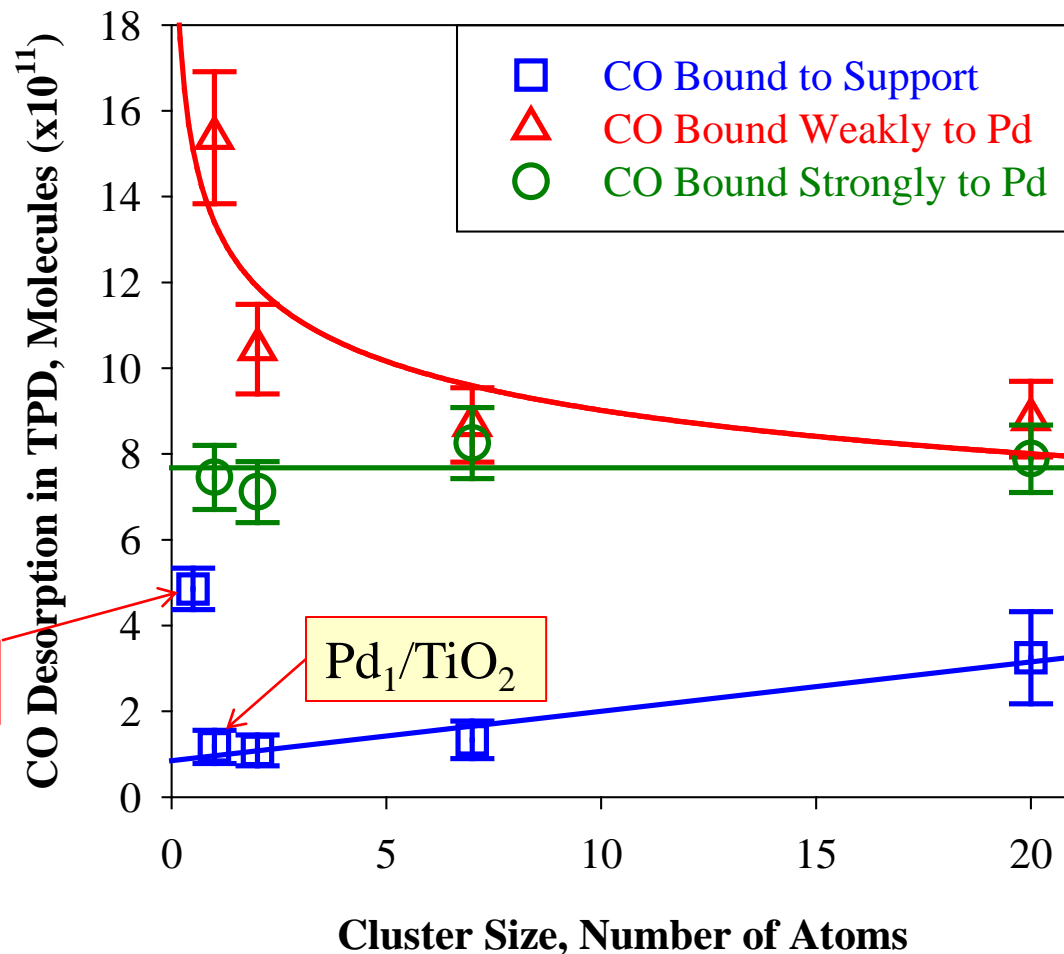


What are the three CO binding sites and how do they contribute to reaction?



Desorption energies shift a little with cluster size, but qualitatively very similar

Population of the three CO sites is strongly dependent on cluster size



“Weak” Pd sites increase with Pd dispersion (decreasing size)

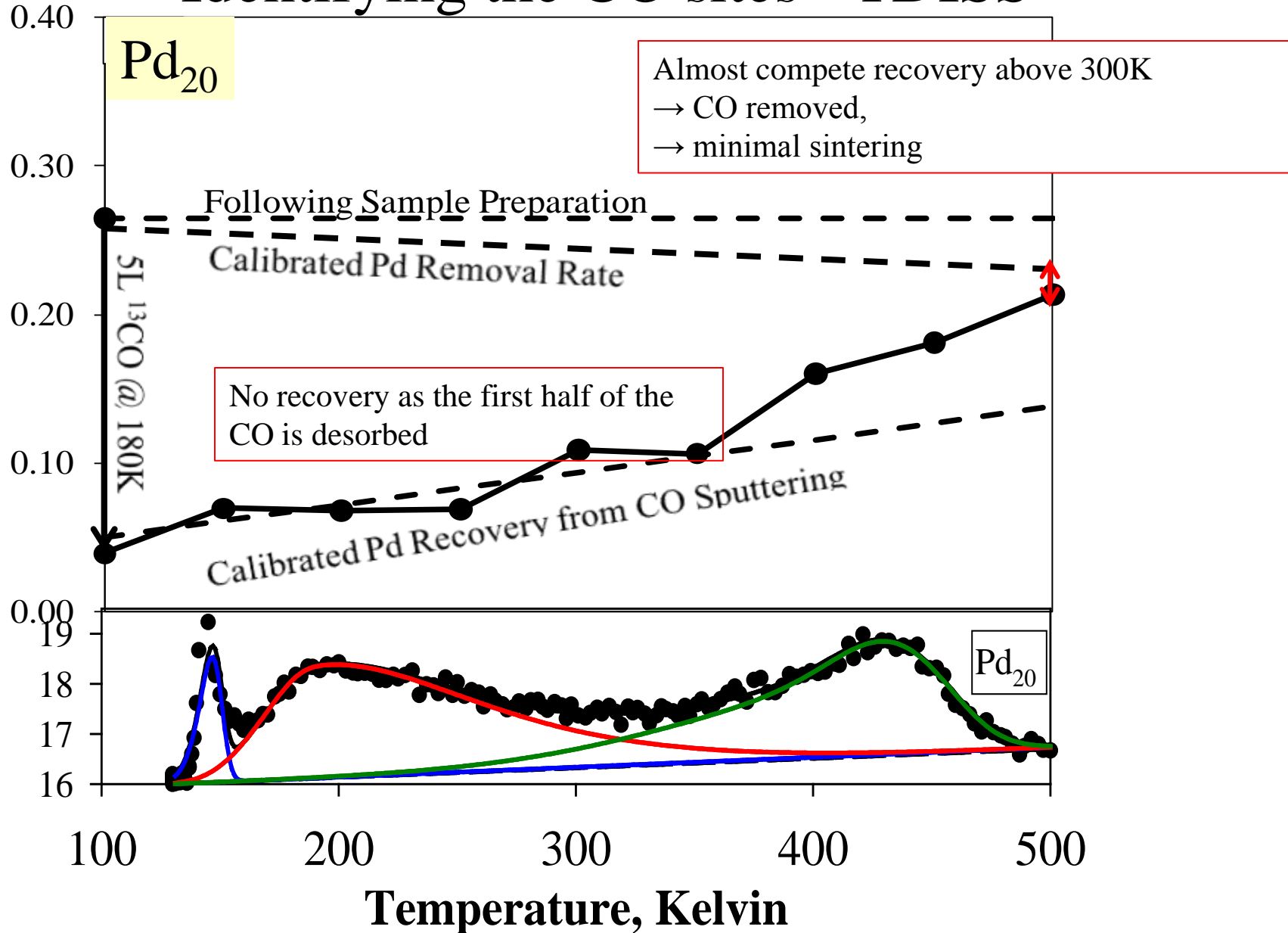
“Strong” Pd sites independent of Pd size/dispersion

Decrease upon Pd adsorption due to preferential binding at more stable Pd sites

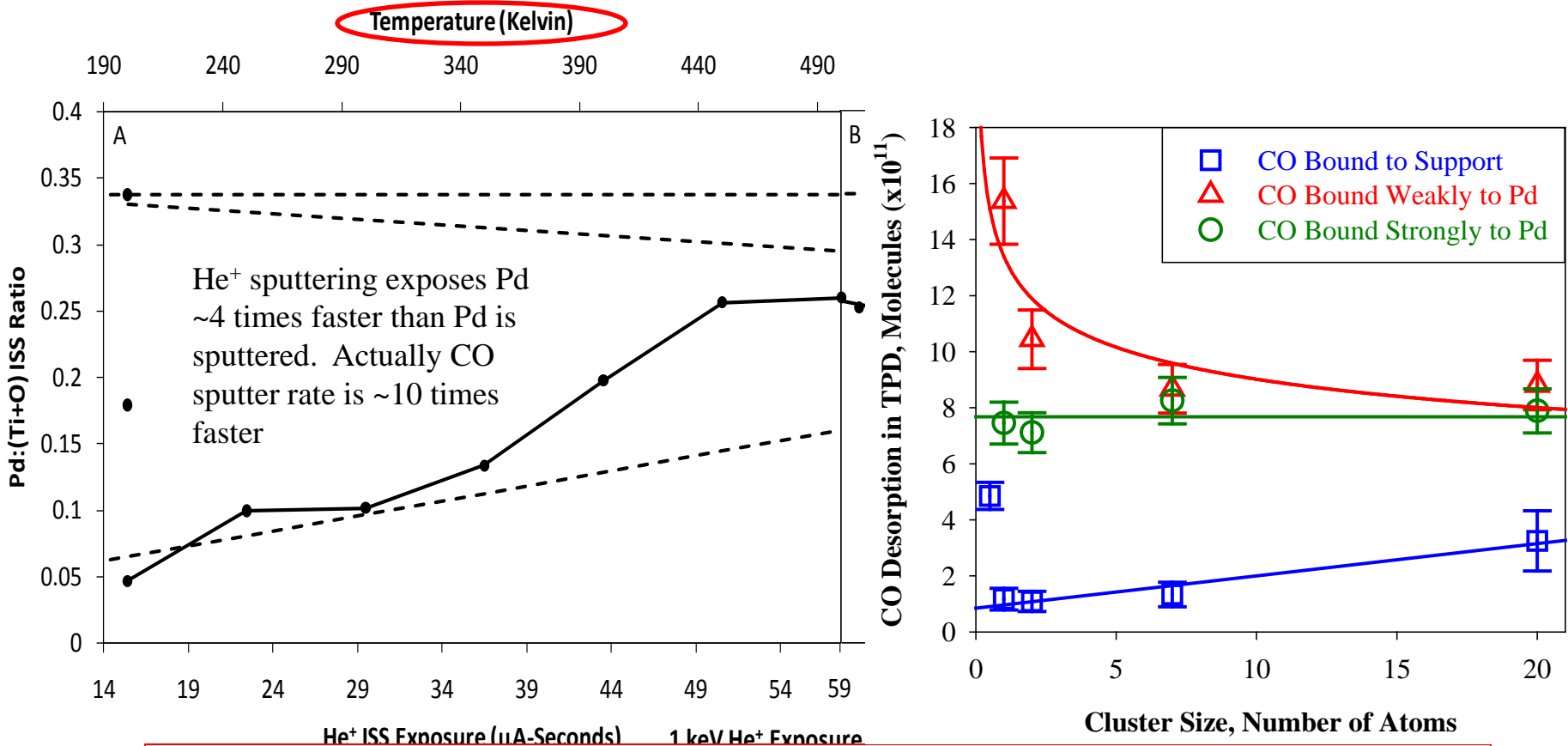
TiO₂

Pd₁/TiO₂

Identifying the CO sites - TDISS



Same for pre-oxidized samples



Conclusion:

CO desorbing ~140 K is bound at TiO₂ defects

CO desorbing <300K is bound peripherally

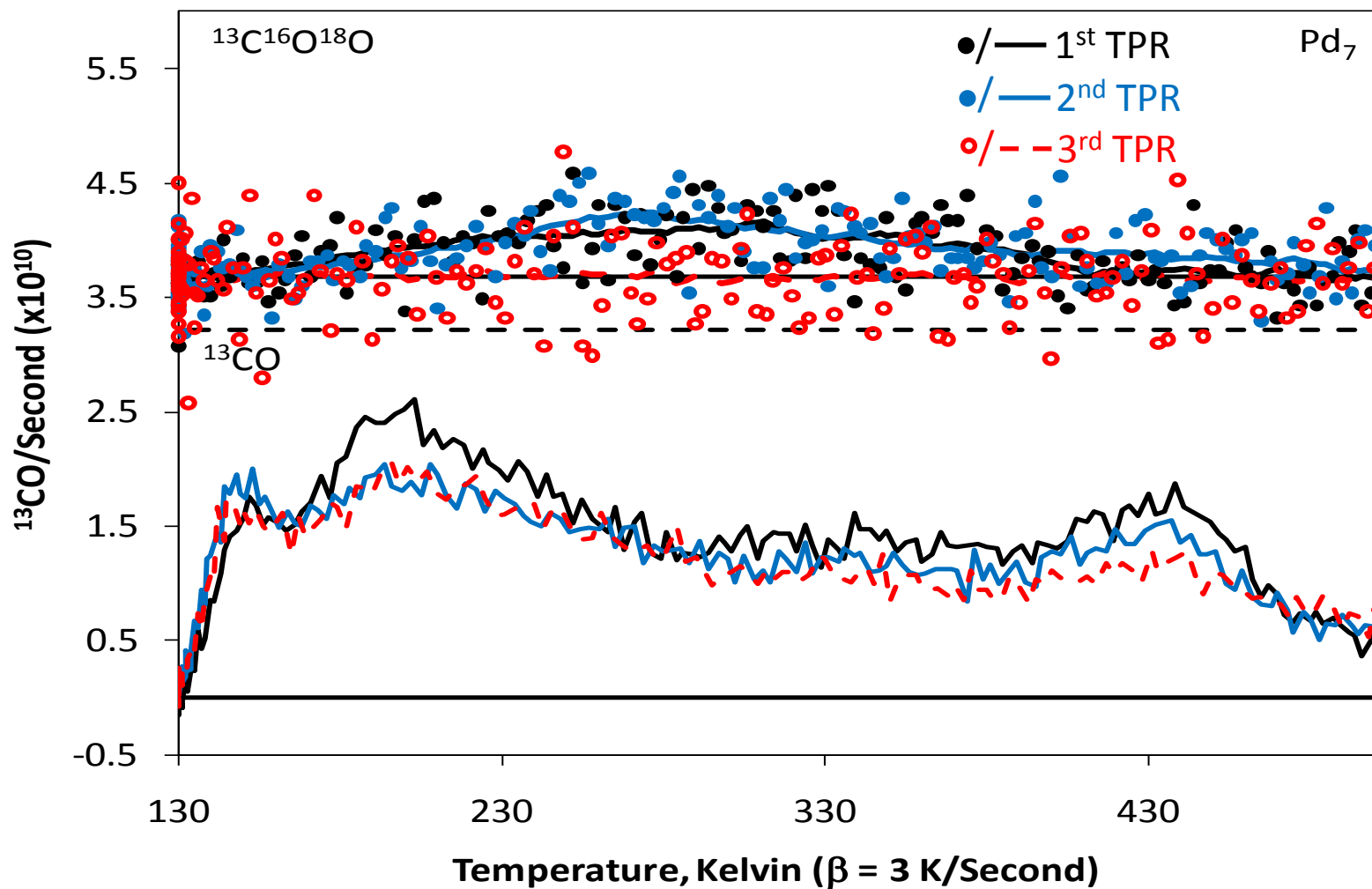
CO desorbing >300K is on top of Pd

Conclusions so far:

- Clusters are depositing as flat islands
- Electronic structure fluctuates with Pd_n size
 - Correlates with reactivity
 - Both core level and activity controlled by valence electronic structure.
- CO on top of Pd is active.
- Peripheral CO is not.
- O₂ activation is rate limiting except for large exposures
- At large exposures, O blocks CO sites
- What effects do reaction/heating have on the catalysts?

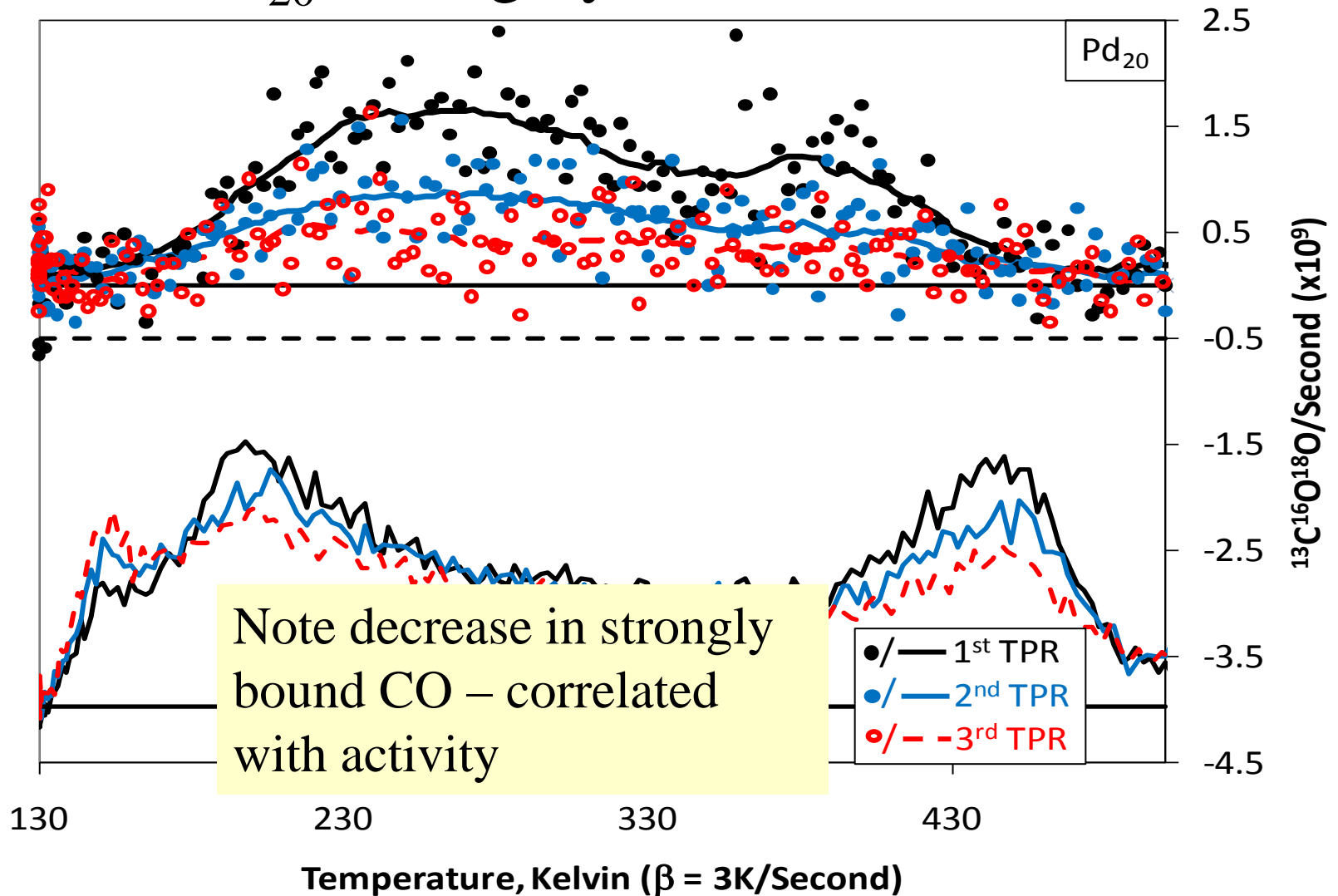
Deactivation in multiple reaction cycles

Pd₇ – a low activity cluster

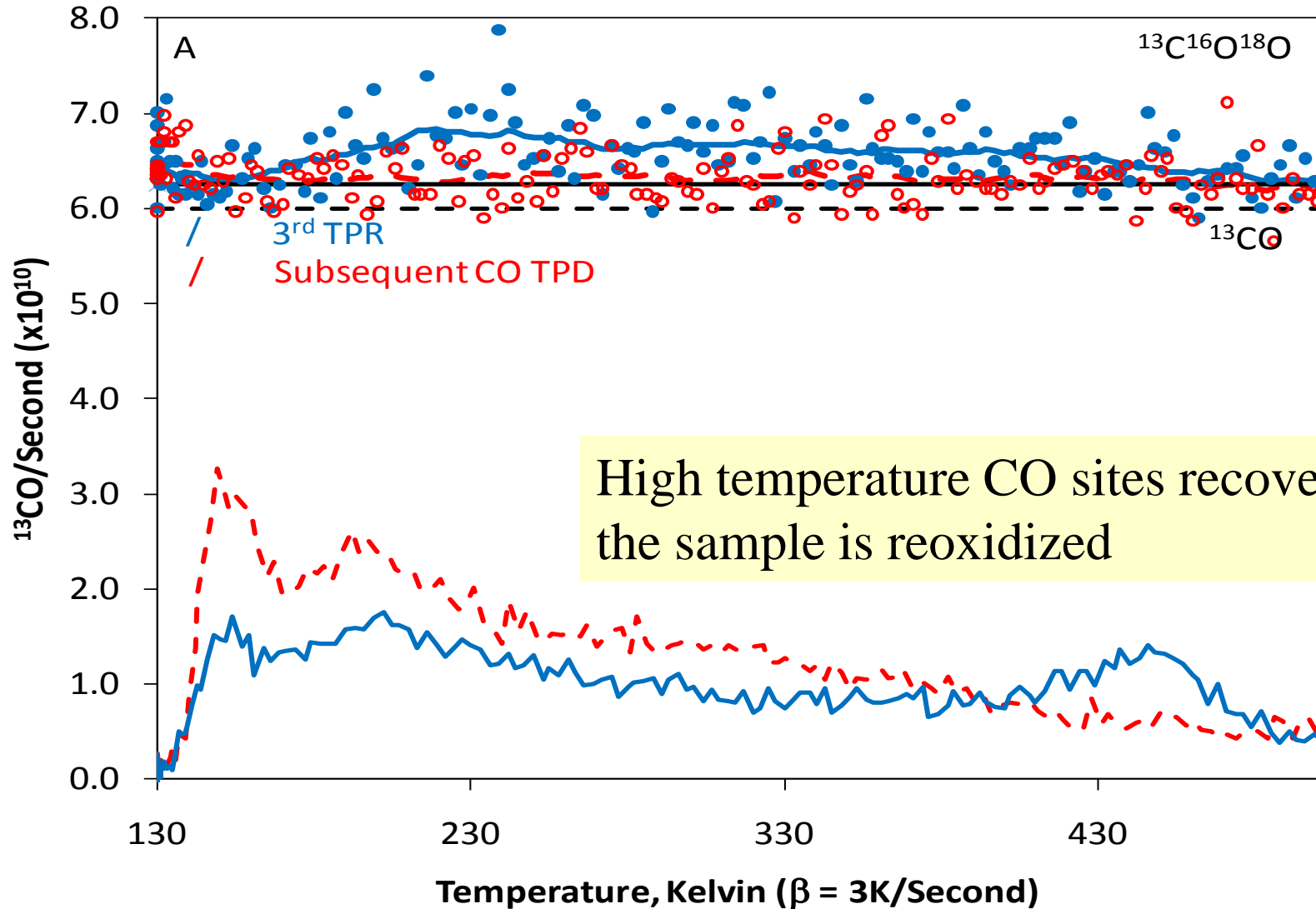


Deactivation in multiple reaction cycles

Pd_{20} – a highly active cluster



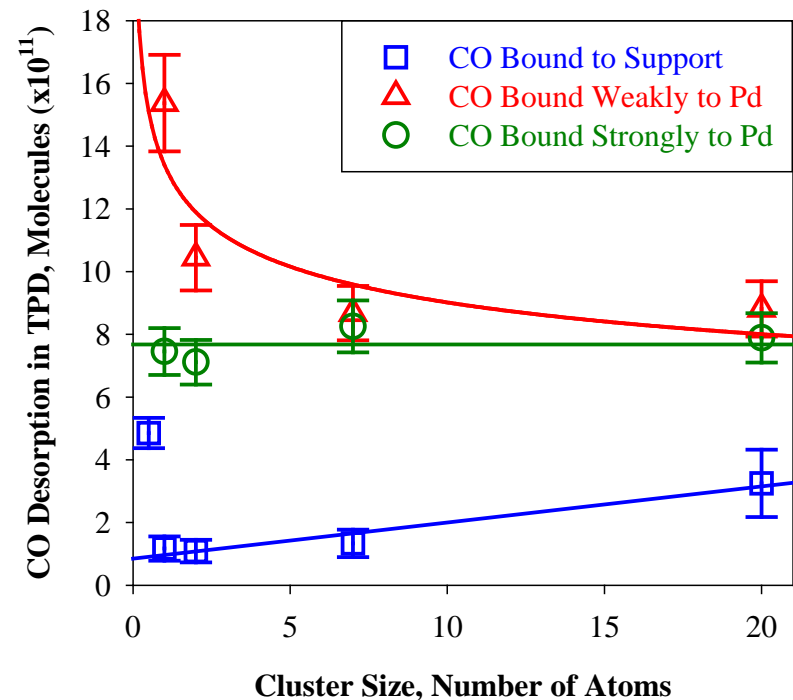
Decrease in strongly bound CO site is dramatic if sample is not oxidized after CO TPD - Pd₂₀



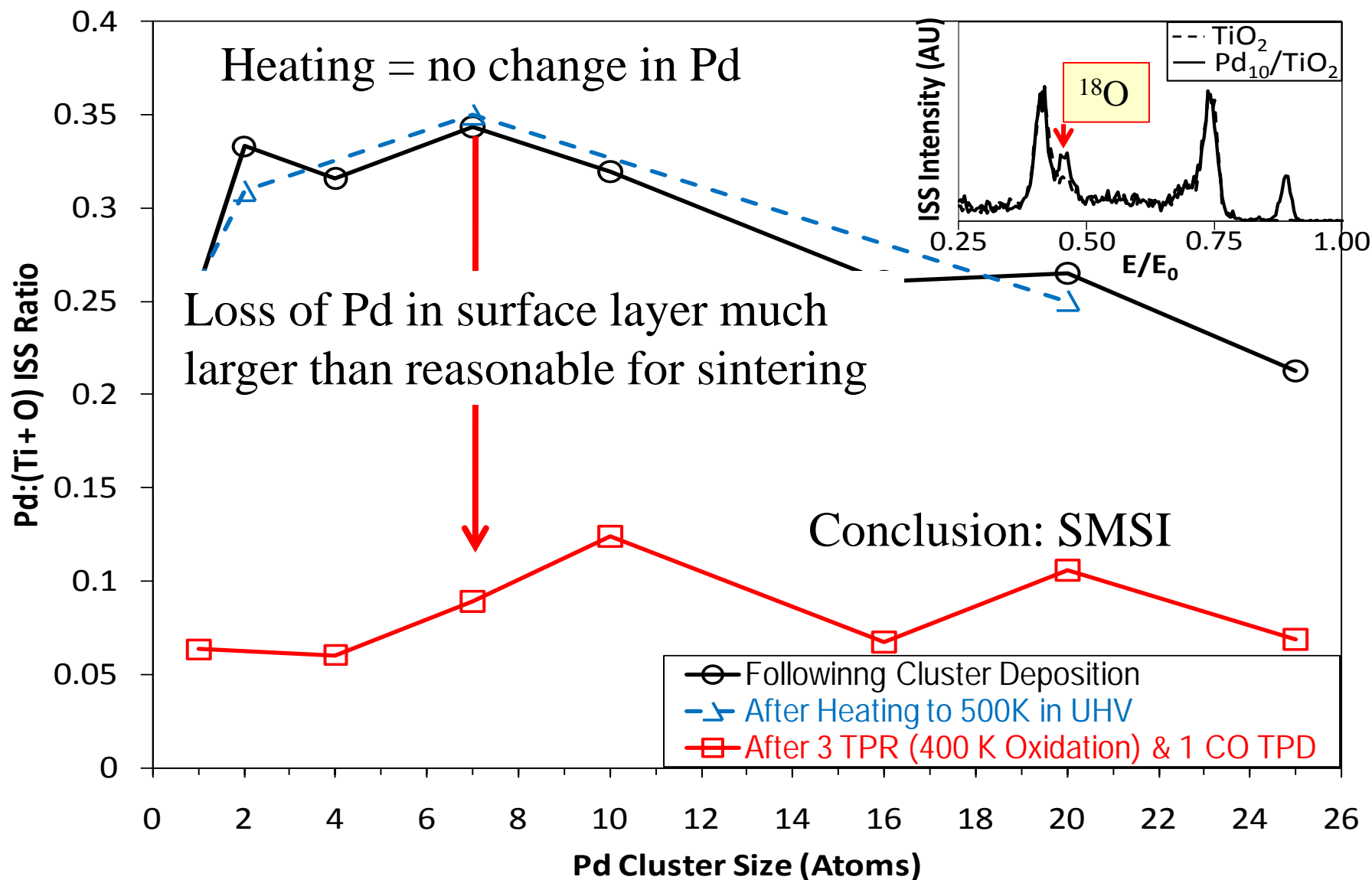
Deactivation \leftrightarrow Loss of “on top” CO binding sites?

Possible mechanisms:

1. Sintering of small clusters to larger 3-D clusters
 - Consistent with decrease in “on top” sites with increasing size.
 - Sintering common when small clusters are heated
 - **Problem: large clusters much more reactive than small ones.**
2. On-top sites poisoned by some adsorbate



ISS after deactivation in multiple TPR cycles



Summary:

- Clusters are depositing as flat islands
- Electronic structure fluctuates with Pd_n size and controls activity through influence on O₂ activation
- CO on top of Pd is active
- Deactivation results from loss of “on top” CO binding sites – Why?

1. Sintering of Pd clusters

- NO – sintering seems minor for T < 500K
- Sintering of small clusters would increase activity

2. Strong Metal Support Interaction

- Encapsulation of Pd in TiO_x under reducing condition
- Partly reversed by reoxidizing