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?

\[ \text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 \text{ on Pd}_n/\text{TiO}_2(110) \]

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

Protocol:

Clean and anneal TiO$_2$(110)
Deposit 0.1 ML of selected Pd$_n$
Morphology
Electronic structure
Catalytic activity
Reactant binding

Ion F
Typical Chemistry Experiments

Sample cleaned/prepared in vacuum
Characterized by XPS/ISS
Positioned at mass spectrometer
  • 6 pulsed or CW gas dosers
Expose to O$_2$ for calibrated dose
  • vary dose
  • $T_{\text{oxidation}} = 300$ or 400 K
Cool to 180 K, expose to CO
  Just above $T_{\text{desorption}}$ for TiO$_2$
Cool to 100 K
Temperature-programmed reaction
  • $T_{\text{sample}}$ ramped at 3K/sec
  • Desorbing species measured
  • Binding energies
Desorption of residual CO w/o O₂ pre-exposure

CO oxidation by Pdₙ/TiO₂(110)

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

Desorption of residual CO

CO₂ production

\[13\text{CO}/\text{second} \times 10^9\]

Temperature (Kelvin); \(\beta = 3\text{K/second}\)
CO$_2$ Production Activity vs. Size

What causes the size dependence?
- Morphology of Pd on the surface?
- Pd coordination?
- Electronic effects?

...
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

Cluster Size (Number of Atoms)

Metal/substrate

Drop not due to sintering

Pd\textsubscript{n}

Ni\textsubscript{n}

Ir\textsubscript{n}

Multi-Layer

Single Layer
No obvious correlation with the transition to multilayer clusters
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 $\rightarrow$ BE $\rightarrow$ Activity

$1^{\text{st}}$ time ever observed ($1^{\text{st}}$ time looked for)

Cluster Size (Number of Atoms)

<table>
<thead>
<tr>
<th>Cluster Size</th>
<th>Activity (CO$_2$ per TPR x10$^9$)</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
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<tr>
<td>15</td>
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<td>20</td>
<td>8</td>
</tr>
<tr>
<td>25</td>
<td>10</td>
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</table>

Deviation from N-S Charge Scaling (eV)

-0.4

Activity

Pd 3d XPS Shift

Single Layer Islands

Growth of 2$^{\text{nd}}$ Layer

TiO$_2$

Deviation from N-S Charge Scaling (eV)
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 Pdₙ
- 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

![Graph showing binding energy changes](image)

<table>
<thead>
<tr>
<th>10L ¹⁸O₂ at 400K</th>
<th>400K in UHV</th>
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<tbody>
<tr>
<td>~0.15 eV Shift</td>
<td>No Shift</td>
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</table>

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
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<tbody>
<tr>
<td>344</td>
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<tr>
<td>342</td>
</tr>
<tr>
<td>340</td>
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<td>338</td>
</tr>
<tr>
<td>336</td>
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<tr>
<td>334</td>
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</table>
Effects of changing $O_2$ exposure or $T_{\text{exposure}}$

**Pd$_7$:**
- Additional BE shift (oxidation) with larger $O_2$ dose

**Pd$_{20}$:**
- No additional shift in XPS with increasing $O_2$ exposure

**$T_{\text{oxidation}}$ dependence:**
- XPS shifts decrease with $T_{\text{oxidation}}$
- No shifts below 300 K for 10 L $O_2$ exposures (activated process?)
- Not activated on some bulk Pd surfaces
Effect of increasing $O_2$ exposure on activity

$^{13}$CO Desorption
$^{13}$C$^{16}$O$^{18}$O Desorption

$^{13}$CO/Second (x10$^{10}$)

Pd$_{20}$ now less reactive than Pd$_{7}$

Pd$_{20}$ has less high temperature CO

Higher exposure over-oxidizes Pd$_{20}$
Blocks sites for CO binding
Less reactive clusters need higher $O_2$ exposures

Temperature, Kelvin ($\beta = 3$K/Second)
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 $O_{\text{ads}}$ bound on Pd.
- Results in increased $CO_2$ production upon CO exposure.

- For most active clusters, $O_2$ activation is efficient for $T_{\text{oxidation}} \geq 300K$.
- 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?

After Exposure to 5L $^{13}$CO at 180K

$\sim 0.7$ eV Shift

As Prepared

Pd₇
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.

- **CO Bound to Support**
- **CO Bound Weakly to Pd**
- **CO Bound Strongly to Pd**

“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.
Identifying the CO sites - TDISS

Almost complete recovery above 300K
→ CO removed,
→ minimal sintering

No recovery as the first half of the CO is desorbed
Same for pre-oxidized samples

He\(^{+}\) sputtering exposes Pd ~4 times faster than Pd is sputtered. Actually CO sputter rate is ~10 times faster.

Conclusion:
CO desorbing ~140 K is bound at TiO\(_2\) 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.
- $O_2$ 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
Pd$_7$ – a low activity cluster

- 1st TPR
- 2nd TPR
- 3rd TPR
Deactivation in multiple reaction cycles

$\text{Pd}_{20}$ – a highly active cluster

Note decrease in strongly bound CO – correlated with activity
Decrease in strongly bound CO site is dramatic if sample is not oxidized after CO TPD - Pd$_{20}$

High temperature CO sites recover if the sample is reoxidized
Deactivation ↔ 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

Heating = no change in Pd

Loss of Pd in surface layer much larger than reasonable for sintering

Conclusion: SMSI
Summary:
• Clusters are depositing as flat islands
• Electronic structure fluctuates with Pd$_n$ size and controls activity through influence on O$_2$ 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