Adsorption of water on a PdO(101) thin film

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Introduction to Catalysis

Heterogeneous catalysis is a key element of many processes

Motivation: Ability to interpret and optimize catalyst behavior enhanced by an atomic-level understanding of changes to the surface

“Real-world” catalysts
Complex materials (polycrystals)
P ~ 1 atm

Experiments in ultrahigh vacuum (UHV)
Single crystal surfaces
P ~ 10^{-10} atm

Combustion exhaust remediation

Fuels from crude oil
Why Study Water/PdO Interactions?

- PdO: excellent catalyst for \( \text{CH}_4 \) and CO oxidation
- Water significantly affects catalytic activity of PdO
  - *Inhibits* \( \text{CH}_4 \) oxidation
  - *Enhances* CO oxidation

What happens to the surface in oxygen rich conditions?
PdO(101)-PdO Surface Grown in UHV

GOAL: Characterize behavior of water on PdO(101)
Temperature Programmed Desorption (TPD)

- Provides indirect information about the binding sites for H$_2$O
- Use DFT energies to develop a model for H$_2$O behavior on PdO(101) as a function of coverage.

$\gamma_1 + \gamma_2$ associated with coverages of $\leq 0.75$ ML

Jason Weaver Group

$\beta_1$ peak – focus of my work $0.75$ ML $\leq 1.0$ ML

$\gamma_1 + \gamma_2$ associated with coverages of $\leq 0.75$ ML

H$_2$O TPD
$T_s = 85$ K
$\beta = 1$ K s$^{-1}$

1.2 ML H$_2$O/Pd(111)
1.3 ML H$_2$O/PdO(101)

0.35 ML = 1 ML$_{\text{cus}}$
**Introduction to the Density Functional Theory (DFT)**

DFT: an accurate *first-principles* method to *solve Schrodinger Equation* – used widely in the catalysis and surface science community

Calculation details:
- Plane wave DFT implemented in VASP
- Calculations performed with GGA-PBE but also spot check with PW-91

<table>
<thead>
<tr>
<th>DFT Results for Bulk Materials</th>
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</thead>
<tbody>
<tr>
<td><strong>Lattice constants (Å)</strong></td>
</tr>
<tr>
<td>PdO 3.02 (DFT) 3.043(expt.)</td>
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We have tested our results using GGA+U where the parameters were fitted to reproduce the experimental band gap of PdO

- Adsorption energies are ~20 kJ/mol higher
- **BUT** differences in adsorption energies are the same
Heterogeneous Adsorbate Pairs

Water coverage = 0.50 ML$_{\text{cus}}$

- Mixed HO-H$_2$O dimer with H$_2$O as proton donor is highly favorable
- Orientational degeneracy: “up” and “down” HO-H$_2$O configurations

Formation of HO-H$_2$O dimer relates to gamma 1 peak

$E_{\text{ad}}$ = 70.3 kJ/mol

HO-H$_2$O

$E_{\text{ad}}$ = 96.1 kJ/mol

($E_{\text{exp}}$ = 99 kJ/mol)
Trimers

Water coverage = 0.75 ML_{cus}

- HO-H_{2}O-H_{2}O trimer formation is preferred
- Molecular adsorption favored at high coverages
- \( \gamma_{2} \) peak relates to HO-H_{2}O-H_{2}O & H_{2}O-HO-H_{2}O trimers
HO-H$_2$O-H$_2$O Trimer

Water coverage = 0.75 ML$_{\text{cus}}$

- As expected, changing orientation of one trimer fails to affect other trimer at 0.75 ML$_{\text{cus}}$ coverage.
HO-H$_2$O-H$_2$O Trimer with H$_2$O

Water coverage = 0.875 ML$_{cus}$

- Added H$_2$O at coverages more than 0.75 ML do not reproduce adsorption energies consistent with $\beta_1$ peak.
New $\text{H}_2\text{O-HO-H}_2\text{O}$ Trimer Configuration

Water coverage = 0.375 $\text{ML}_{\text{cus}}$

$E_{\text{ad}} = 94.4 \text{ kJ/mol}$
$E_{\text{add, H}_2\text{O}} = 88.2 \text{ kJ/mol}$

- Other HO-H$_2$O-H$_2$O trimer configurations
- HO-H$_2$O-H$_2$O with H$_2$O-HO-H$_2$O trimer configurations
- At Coverages of more than 0.75 ML

$E_{\text{add, H}_2\text{O}} = 88.2 \text{ kJ/mol}$
HO-H$_2$O-H$_2$O Trimer with Dissociated H$_2$O

Water coverage = 0.875 ML$_{\text{cus}}$

- As expected, disassociated H$_2$O is not favored over molecular H$_2$O at higher coverages.
HO-H$_2$O-H$_2$O Trimer with 2(HO-H$_2$O)

Water coverage = 0.875 ML$_{cus}$

E$_{ad}$ = 91.2 kJ/mol

E$_{ad}$ = 91.1 kJ/mol

- Preliminary DFT results at coverages more than 0.75 ML suggest need to examine additional configurations
Summary

• DFT studies initiated to understand water behavior at higher coverages on PdO(101)
• Preliminary results suggest need to revisit initial hypothesis
  – $\beta_1$ peak is associated with 4-fold Pd sites
  – What hinders filling off CUS Pd sites at coverages > 0.75 ML?
• Current work: examine adsorption of H$_2$O on 4-fold Pd sites at high coverages