ABSTRACT

We investigated the adsorption of water on a PdO(101) thin film using density functional theory (DFT) calculations, to clarify experimental observations. In the previous study, the water temperature-programmed desorption (TPD) spectrum obtained for PdO(101) from high water coverages exhibits three rate maxima located at the temperatures 149, 197, 350 K. The broad TPD peak between 300 and 350 K is consistent with water desorption from a distribution of adsorbed trimers and other configurations with varying binding energies at coverages of less than 0.75 ML_{cus}. DFT suggests that strong orientation-dependent interactions between trimers create unfavorable environments along rows of coordinatively unsaturated (cus) Pd atoms that hinder adsorption in the first layer when more coverages exceed 0.75 ML_{cus}. The TPD peak at 197 K is of interest to understand how water absorbs on the PdO(101) surface at coverages of more than 0.75 ML_{cus}. The computed binding energy of several different configurations at the 0.875 ML_{cus} are much higher than expected, and unfortunately were not consistent with the believed reason for the 197 K peak. This suggests the peak might be related to the adsorption energies of water on the 4-fold Pd atoms, rather than the 3-fold cus-Pd atoms, or several more configurations need to be explored at coverages of more than 0.75 ML_{cus}. 
**Introduction**

Palladium oxide (PdO) is an exceptional catalyst for the complete oxidation of methane (CH₄) and carbon monoxide (CO) under oxygen-rich conditions[1-4]. It is generally received that PdO formation is responsible for the extraordinary performance of supported Pd catalysts toward the oxidation of CH₄ in lean gas turbines.[2-4] Several studies demonstrate that water can significantly affect the catalytic activity of PdO in oxidation reactions.[1, 5-8] Reports show that water hinders the lean oxidation of CH₄, while water promotes CO oxidation on PdO.[1, 5-8] In previous studies, the adsorption of water on a PdO(101) thin film grown in an ultrahigh vacuum (UHV) was studied to characterize the chemisorbed states of water that develop on the surface. [9, 10]

Water molecules tend to lock strongly to transition-metal (TM) oxides by forming chemical bonds with coordinatively unsaturated (cus) metal cations of the surface. A coordinatively unsaturated complex is a transition metal complex that possesses fewer ligands than exist in the coordinatively saturated complex. Strong water-oxide interaction can also cause water molecules to dissociate, typically through hydrogen transfer to oxygen anions of the surface. [11, 12] Although water molecules dissociate extensively on some TM oxide surfaces, dissociation is limited to defect sites on others, which raises fundamental questions about the conditions and surface properties favoring dissociative versus molecular chemisorptions of water on TM oxides. Both adsorbate-surface and adsorbate-adsorbate interaction in determining the mechanisms for water chemisorptions TM oxide surface and the resulting structure of the chemisorbed water layer are very important.

The stoichiometric PdO(101) surface is a rectangular unit cell and has four types of ions present in equal concentrations; namely, 3-fold and 4-fold Pd and O atoms, where the 3-fold atoms are coordinatively unsaturated (Figure 1).[8, 13] The surface atoms arrange into rows that run parallel to the shorter lattice direction of the unit cell, and each row contains only one type of surface atoms. Thus, this surface structure places the more reactive cus sites in close proximity to one another, which may lead to enhanced bonding with adsorbed molecules. It was recently found that PdO(101) has a high affinity for binding O₂ in molecular form and that the majority of molecule chemisorbed O₂ species experience stronger bonding on PdO(101) than on Pd (111). [5] In the same study, it was observed that CO oxidation is simplistic on PdO(101) under UHV conditions. In early TM oxide studies CO oxidation is inactive due to the strong metal. It is suggested that PdO(101) is likely to interact strongly with other adsorbates as well. Since PdO(101) appears to be uniquely reactive oxide surface, further studies with PdO(101) may help to clarify key factors that influence the surface reactivity of TM oxides. We found that uptake into the first-layer chemisorbed states effectively ceases prior to saturation and resumes only after the second-layer state appreciably populates. The density functional theory (DFT) suggest that strong-orientation-dependent interaction between adsorbed species create unfavorable sites along the cus-Pd rows that hinder adsorption into the first layer when more that 75% of the cus-Pd sites are occupied with adsorbed H₂O.

Figure 2 shows H₂O temperature programmed desorption (TPD) spectra obtained from Pd(111) and the PdO(101) film after adsorbing water at 85 K to generate coverage of 1.2 and 1.3 ML, respectively. [9] The water TPD spectrum obtained from PdO(101) exhibits three rate maxima located at temperature of 149, 197, and 350 K. The broad, asymmetric feature between 300 and 350 K is actually composed of two different peaks, labeled as γ₁ and γ₂.

It was suggested that H₂O molecules in the β₁ state are better described as a second monolayer state rather than a second monolayer. A direct comparison of water desorption from PdO(101) and Pd(111) is supportive for clarifying discrete characteristics of water adsorbed on the oxide surface, particularly given that water adsorption of Pd(111) has been studied extensively and is well-understood.[14-16] Since the water monolayer on PdO(101) desorbs in peaks above 165 K, it is clear that H₂O molecules access more strongly bound states on the oxide compared with metal surface. It is particularly interesting that the β₁ peak from PdO(101) appears about 30 K higher than the monolayer from Pd(111), since this observation provides clear evidence that water molecules in the β₁ state experience stronger bonding interactions than water in the physisorbed monolayer on Pd(111). This finding is consistent with the belief that chemisorbed H₂O molecules fasten to the cus-Pd surface sites. [5]

In a previous study we found that DFT predicts that the HO – H₂O – H₂O trimer is preferred over several other trimer configurations at 0.75MLcus coverage (Table 1). As the water coverage increases, H₂O molecules will more frequently encounter sites located between configurationally degenerate dimmers and trimers, where they are
TABLE 1: Adsorption Energies ($E_{\text{ads}}$) of H$_2$O and OH Species on PdO(101) Predicted with DFT Using the GGA-PBE Functional for Coverages of 0.25, 0.50, 0.75 and 1 ML<sub>uc</sub>.

<table>
<thead>
<tr>
<th>Species</th>
<th>$E_{\text{ads}}$ (kJ/mol)</th>
<th>Coverage (ML&lt;sub&gt;uc&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH (O-H)</td>
<td>Monomers</td>
<td>68.2[93.5]</td>
</tr>
<tr>
<td>H$_2$O</td>
<td></td>
<td>79.2[99.6]</td>
</tr>
<tr>
<td>HO-HO</td>
<td>Dimers</td>
<td>66.7[95.5]</td>
</tr>
<tr>
<td>H$_2$O-H$_2$O</td>
<td></td>
<td>82.0[118.1]</td>
</tr>
<tr>
<td>HO-H$_2$O</td>
<td></td>
<td>96.1[118.4]</td>
</tr>
<tr>
<td>H$_2$O-H$_2$O</td>
<td></td>
<td>70.3[92.5]</td>
</tr>
<tr>
<td>3(H$_2$O)</td>
<td></td>
<td>80.8[98.8]</td>
</tr>
<tr>
<td>HO-H$_2$O-H$_2$O</td>
<td></td>
<td>90.3[111.7]</td>
</tr>
<tr>
<td>H$_2$O-H$_2$O-H$_2$O</td>
<td></td>
<td>86.5[107.5]</td>
</tr>
<tr>
<td>HO-H$_2$O-H$_2$O</td>
<td></td>
<td>82.8[108.9]</td>
</tr>
<tr>
<td>4OH</td>
<td></td>
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<tr>
<td>4(H$_2$O)</td>
<td></td>
<td>81.3[99.9]</td>
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<td>2(H$_2$O)-H$_2$O-H$_2$O</td>
<td></td>
<td>85.8[107.2]</td>
</tr>
<tr>
<td>2(HO-H$_2$O)</td>
<td></td>
<td>90.3[115.2]</td>
</tr>
</tbody>
</table>

*The values obtained using the GGA-PBE+U functional is given in brackets. The favored configurations are shown in bold for each coverage.

likely to experience an unfavorable environment due to the strong orientation dependence of the adsorbate – adsorbate interactions[1]. As a result water molecules will likely avoid adsorption into sites between configurationally degenerate complexes. In this study, we continue our investigation on the adsorption of water on PdO(101) with higher concentrations using DFT calculations, by changing the orientation of the HO – H$_2$O – H$_2$O trimer and adding a one water molecule. The DFT calculations predict that dissociation is favorable for the added water molecule.

**Computational Methods**

All the DFT calculations in this paper were performed using the Vienna ab initio simulation package or VASP.[17-19] We use the projector augmented wave pseudo potentials provided in the VASP database[17-20]. Calculations have been performed using the Perdew – Burke – Ernzerhof (PBE) exchange-correlation functional[21]. Both the PBE and Perdew Wang PW91 versions of the GGA functional have been shown to be sufficiently accurate to capture adsorption behavior of water on the surface. We have tested several of our most stable minima using the PBE+U functional, just to determine the accuracy of DFT, and the values are reported above (Table 1).

In DFT+U, a Hubbard U term corresponding to the mean-field approximation of the on-site Coulomb interaction is added to the PBE functional. The implementation of the DFT+U method, the underlying functional (GGA), in particular has been found to have some influence in the description of water molecules. Hence, the GGA-PBE+U functional is considered and discussed. The adsorption energies calculated are higher but the differences in adsorption energies from the previous study are the same. So it is accepted that DFT is accurate. This level of accuracy is more than sufficient to conclude that the choice of the exchange-correlation functional will not affect the conclusions discussed in this paper. All of the DFT values discussed in the rest of the paper were obtained using the PBE functional. A plane wave expansion with a cutoff of 400 eV was used, and the total energy calculations are performed using the conjugate gradient method for electronic relaxations, accelerated using Fermi-level smearing with a Gaussian width of 0.1 eV. The positions of the atoms are relaxed until the forces on all unconstrained atoms are < 0.3 eV/Å. Although experimentally the PdO(101) film is grown on the Pd(111) surface, the oxide film is sufficiently thick (13 Å) that we assume the Pd(111) substrate may be ignored in our DFT calculations. Inclusion of the Pd(111) substrate would require large super cells due to the lattice mismatch between the oxide film and the Pd(111) surface. We represent the PdO(101) film with four layers (see figure 1), which corresponds to a thickness of approximately 9 Å. The bottom layer is fixed, while all other atoms in the oxide film and the H$_2$O adsorbates are allowed to relax. We use a vacuum spacing of 20 Å, which is sufficient to minimize any spurious periodic interactions in the surface normal direction.

![H$_2$O TPD spectra obtained from Pd(111) and PdO(101) after generating initial water coverage of 1.2 and 1.3 ML, respectively, at a substrate temperature of 85 K. The TPD spectra were obtained using a constant heating rate of 1 K/s.][9]
Computational Results and Discussion

We used DFT to investigate the adsorption of water into molecular and dissociated states on PdO(101) as a function of the water coverage. The most stable adsorption configurations determined on the (4 x 1) unit cell were then evaluated using a 8 x 1 unit cell. Calculations using a 2 x 2 unit cell predict energies that are within 1 kJ/mol of those determined using the 4 x 1 unit cell, which confirms the expectation that adsorbates have negligible interaction between cus-Pd rows. Adsorbate-adsorbate interactions between cus-Pd rows make only a small contribution to the adsorption energies of water on PdO(101). However, there are several configurations on the actual PdO(101) surface at high H₂O coverages that cannot be adequately captured with the 4 x 1 surface model. In order to study these other configurations we made an 8 x 1 surface model, which allows us to find strongest binding energies, and the 8 x 1 unit cell is a reasonable model for studying water adsorption the PdO(101) surface.

Adsorbate Pair Formation. Since hydrogen bonding is generally important in determining the properties of adsorbed water, we examined the energetic associated with various clusters of H₂O and OH on PdO(101). Table 1 summarizes the energies predicted for the different clusters we considered. First, we predicted a moderate driving force for pairing of H₂O molecules, whereas OH-OH pair formation is slightly unfavorable. OH pairing is slightly less stable than isolated OH groups, whereas H₂O pairing is stabilizing.

The key finding from the calculations is that an HO-H₂O pair, in which the H₂O molecule acts as the proton donor, is highly favored over the other pair configurations. Formation of the HO-H₂O pair from isolated H₂O and OH groups stabilizes these adsorbates. The stabilizations offered by HO-H₂O pair formation greatly ease the dissociation of H₂O. The DFT results indicate that the dissociation of a water molecules on PdO(101) is favorable when the molecules pairs with another H₂O molecule, and produces the stable HO-H₂O complex. The experimental TPD results are consistent with this prediction, since desorption for the γ₁ state can be accurately reproduced with a second-order kinetic model, and a nearly coverage-independent activation energy.

High Coverage Configurations: Trimers. The experimental TPD results provide evidence the water begins to populate a new chemisorbed state(s) above 0.50 MLₐₘσ and that uptake into this state slows down above about 0.75 MLₐₘσ. Previously stated, DFT predicts that the HO-H₂O-H₂O trimer is preferred over several other trimer configurations at 0.75 MLₐₘσ.

The directionality of the H₂O-OH interaction appears to be the key factor leading the preferred trimer arrangements. For example, the HO-H₂O-H₂O trimer avoids the destabilizing H₂O-HO configuration while also maintaining the favorable HO-H₂O linkage. H₂O attachment to the HO-H₂O complex appears to produce a weaker H₂O-H₂O interaction than in the corresponding pair and/or destabilizes the HO-H₂O interaction. The net result is that HO-H₂O-H₂O trimer formation is slightly endothermic, in contrast to expectations based only on the pair interactions.

As the water coverage increases, water molecules will more frequently encounter sites located between configurationally degenerate dimers and trimers, where they are likely to experience an unfavorable environment due to the strong orientation dependence of the adsorbate-adsorbate interactions. As a result, H₂O molecules will likely avoid adsorptions into sites between configurationally degenerate complexes. The measured uptake of water into various states on PdO(101) is consistent with this interpretation. The rate of uptake into the high-temperature chemisorbed states abruptly decreases at a total coverage of about 0.75 MLₐₘσ, and water molecules begin to populate the more weakly bound β₁ state instead. In fact, the water concentration in the γ₁ and γ₂ states remains essentially constant until the β₁ state is near saturation, and then only gradually increases to about 0.91 MLₐₘσ as the multilayer starts to develop. We therefore conclude that continued adsorption on cus-Pd sites becomes unfavorable at coverage near 0.75 MLₐₘσ due to destabilizing interaction at sites located between configurationally degenerate adsorbate complexes.

Trimer Orientations. The directionality of the interactions suggests that unfavorable binding environments are prevalent between adsorbate complexes at higher coverages (more than 0.75 MLₐₘσ) and that water molecules tend to avoid these configurations. Additional computational studies were required to clarify the bonding environments present between degenerate dimers and trimers and the nature of the β₁ state. As seen in Figure 3, the DFT calculations illustrate that changing orientations of the trimers do not affect the adsorption energies, which provide evidence that there is no interaction between the HO-H₂O-H₂O trimers at the 0.75 MLₐₘσ coverage, as expected. Now the question is, what affect will an extra water molecule have on these trimer configurations?
Trimmers with Added H$_2$O. In Figure 3, a molecular H$_2$O is added to the preferred HO-H$_2$O-H$_2$O trimer configuration at the 0.75 ML$_{\text{cus}}$ coverage. The adsorption energy for the tetramer and trimer facing the same direction (Figure 3a), 88.4 kJ/mol. This tetramer and trimer formation is slightly destabilizing by 2.6 kJ/mol. The adsorption energies for the tetramer and trimer facing the opposite directions Figures 3b and 3c are 88.4 kJ/mol and 88.8 kJ/mol, respectively. The configurations where they are in opposite directions are destabilizing by ~2.5 kJ/mol. Thus, the H$_2$O attachment to the trimer appears to produce an even weaker H$_2$O-H$_2$O interaction. The net result is that the tetramer and trimer formation is slightly endothermic, in contrast to expectations based on pair and trimer interactions.

The adsorption energies are similar, but we deduce that the energies are not degenerate; due to the fairly significant differences in the added water’s adsorption energies. The added water’s energies for the configurations in Figure 3 are as follows: (a) 72.8, (b) 74.4, and (c) 77.2 kJ/mol. The added water adsorption energy is important to our conclusion for the reason that it allows us to see how the extra water affects the stability of these trimer configurations. Since the added water’s adsorption energy is lower than the adsorption energy of the total configuration, which is an average of all the water molecules, it is concluded that the extra water destabilizes each of these three trimer configurations. Of these three tetramer and trimer configurations, the H$_2$O-HO-H$_2$O-H$_2$O tetramer formation is preferred.

The H$_2$O-HO-H$_2$O trimer is encompassed in this preferred tetramer but with a different orientation of the disassociated water. This “new” H$_2$O-HO-H$_2$O trimer turns out that it is 2 kJ/mol (94.4 kJ/mol) more stable than having the disassociated H$_2$O on the end of the trimer. There is still a water molecule adjacent to the dimer complex; it is just a little more firmly bound. In reality, as illustrated in the previous study, there is a range of trimer states which yield a range of H$_2$O desorption states that show up in the broadness of the $\gamma_1$ and $\gamma_2$ TPD peaks. As the temperature is increased at a coverage of about 0.75 ML$_{\text{cus}}$ the first molecules to come off will be these molecular H$_2$O but they will come off in a relatively small range of temperatures. This again proves that the H$_2$O-HO-H$_2$O and HO-H$_2$O-H$_2$O trimers will coexist on the PdO(101) surface.

Trimmers with Added Disassociated H$_2$O. In Figure 4, a disassociated H$_2$O is added to the preferred HO-H$_2$O-H$_2$O trimer configuration at the 0.75 ML$_{\text{cus}}$ coverage. The adsorption energy for the tetramer and trimer facing the same direction (Figure 4a), is 86.0 kJ/mol. This tetramer and trimer formation is destabilizing by 5 kJ/mol. The adsorption energy for the tetramer and trimer facing the opposite directions (Figure 4b), is 84.4 kJ/mol. This second tetramer and trimer formation is destabilizing by 6.6 kJ/mol. Thus, the disassociated H$_2$O attachment to the trimer appears to produce an even weaker H$_2$O-H$_2$O interaction, than with a molecular H$_2$O. Again, the net result is that the tetramer and trimer formation is slightly endothermic, in contrast to expectations based on pair and trimer interactions.

The adsorption energies are similar, but we deduce that the energies are not degenerate; due to the fairly significant differences in the added water’s adsorption energies. The added water’s energies for the configurations in Figure 4 are as follows: (a) 57.6 and (b) 46.0 kJ/mol. The added water’s adsorption energy is extensively lower than the adsorption energy of the total configuration. Hence molecular H$_2$O is preferred over disassociated H$_2$O at higher coverages.

Trimer with Two Dimers. Two of the preferred HO-H$_2$O dimer and the preferred HO-H$_2$O-H$_2$O trimer found in the previous study was adsorption on the PdO(101) surface using DFT. One configuration had the dimers and trimer pointing in the same direction and another with the dimers pointed in one direction and the trimer pointed in the other. It is concluded that these configurations are degenerate, which is interesting because it demonstrates that there are no dimer and trimer interactions at the 0.875 ML$_{\text{cus}}$ coverage. It also shows us that this the most preferred water configuration at this coverage so far. Additional computational studies are required to understand the nature of the $\beta_1$ peak and how water bindings to the PdO(101) surface.
Summary

We investigated the adsorption of water onto a PdO(101) thin film using DFT calculations at higher coverages. Our DFT calculations, as expected, predicted disassociated H2O is not favored over molecular H2O at higher coverages. Finally the DFT calculations suggest that strong orientation-dependent interactions create unfavorable binding sites between trimers adsorbed along the 3-fold cus-Pd rows and that water molecule will tend to avoid sites at water coverages above 0.75 ML cus. Overall, the DFT results provide more insight to our previous conclusion in an early study but do not provide significant evidence for selective HO-H2O-H2O trimer formation. From these configurations we are unable to reproduce adsorption energies related to the $\beta_1$ peak. Since the temperature difference between the gamma peaks and beta peak is about 100 K we expected the adsorption energies to be between 50 and 60 kJ/mol instead of about 90 kJ/mol. The results of this study, particularly the evidence for HO-H2O-H2O and H2O-HO-H2O trimers to coexist on the PdO(101) surface, provide new insight for different trimer and dimer configurations to study. Preliminary DFT results suggest the need to revisit our initial hypothesis. We would like to look at whether or not the $\beta_1$ peak is associated with 4-fold Pd sites, and what exactly hinders the filling of the 3-fold cus-Pd sites at coverages more than 0.75 ML. Additional computational studies are considered necessary to examine the adsorption of H2O on 4-fold Pd sites at high coverages, and the nature of the $\beta_1$ state.

Acknowledgment. I gratefully acknowledge, Dr. Aravind Asthagiri and Jeff Hawkins at the University of Florida for their guidance, and the University of Florida High-Performance Computing Center (http://hpc.ufl.edu) for providing computational resources for performing the calculations reported in this paper.

References and Notes