A DISPERSION CORRECTED DFT STUDY OF H₂ OXIDATION ON THE PdO(101) SURFACE

By

RAHUL

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To my parents
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td></td>
<td>9</td>
</tr>
</tbody>
</table>

## CHAPTER

1. INTRODUCTION .............................................................................................................. 10

2. COMPUTATIONAL PROCEDURE ............................................................................................................. 14
   2.1 Density Functional Theory (DFT) .................................................................................. 14
   2.2 Dispersion-corrected DFT ............................................................................................ 16
   2.3 Computational Model .................................................................................................. 17
   2.4 Analytical Methods ...................................................................................................... 19
      2.4.1 Normal Mode analysis ......................................................................................... 19
      2.4.2 Nudged Elastic Band Method .............................................................................. 20

3. RESULTS AND DISCUSSION ............................................................................................................. 22
   3.1 H₂ Adsorption and Dissociative Chemisorption on PdO (101) .................................. 22
   3.2 H₂O on PdO(101) Surface ............................................................................................... 24
   3.3 H-atom Diffusion on PdO (101) Thin Film ........................................................................ 27
   3.4 Formation of H₂O on PdO(101) Thin Film Surface at 0.08 ML H₂ Coverage ............ 29
   3.5 Coverage Effect of H₂ in Formation of H₂O ............................................................... 32
      3.5.1 Formation of Water at 0.35 ML H₂ (100% cus) Coverage on PdO (101) Surface ........ 32
      3.5.2 Formation of Water at 0.26 ML H₂ (75% cus) Coverage on PdO (101) Surface ........ 33
   3.6 Effect of Presence of Hydroxyl Moiety and H-atom Diffusion on PdO(101) Surface on water formation .......................................................................................... 35

4. CONCLUSIONS ....................................................................................................................... 45

LIST OF REFERENCES ....................................................................................................................... 48

BIOGRAPHICAL SKETCH .................................................................................................................. 51
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-1</td>
<td>Vibrational frequencies (wave numbers) of various stable and transition state configurations</td>
<td>39</td>
</tr>
<tr>
<td>3-2</td>
<td>Comparison of binding energies of various configurations of H₂ on PdO(101) surface at low coverage on 4x1 and 4x2 PdO(101) slabs</td>
<td>40</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2-1</td>
<td>Hard ball model representation of stoichiometric PdO(101) surface.</td>
<td>21</td>
</tr>
<tr>
<td>3-1</td>
<td>Model representation of adsorption of H₂ on PdO(101) surface followed by dissociative adsorption and subsequent formation of H₂O with adjacent cus-vacancy on PdO(101) surface.</td>
<td>37</td>
</tr>
<tr>
<td>3-2</td>
<td>Potential energy surface profiling of H₂ activity on PdO(101) surface to produce H₂O at low H₂ coverage.</td>
<td>38</td>
</tr>
<tr>
<td>3-3</td>
<td>ZPC potential energy evolution of H₂ for H₂O formation on PdO(101) surface at low H₂ coverage.</td>
<td>41</td>
</tr>
<tr>
<td>3-4</td>
<td>H₂O formation on PdO(101) surface via high energy pathway.</td>
<td>42</td>
</tr>
<tr>
<td>3-5</td>
<td>H₂O formation pathways through disproportionation of 2 adjacent cus-OH at 0.26 ML of H₂ coverage on PdO(101) surface.</td>
<td>43</td>
</tr>
<tr>
<td>3-6</td>
<td>Effect of OH group presence in H₂O formation.</td>
<td>44</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
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<td>Angstrom (unit of length)</td>
<td></td>
</tr>
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<td>BE</td>
<td>Binding energy</td>
<td></td>
</tr>
<tr>
<td>C#</td>
<td>Configuration number, e.g. C1, C2</td>
<td></td>
</tr>
<tr>
<td>cs</td>
<td>Coordinately saturated</td>
<td></td>
</tr>
<tr>
<td>cus</td>
<td>Coordinately unsaturated</td>
<td></td>
</tr>
<tr>
<td>DFT</td>
<td>Density functional theory</td>
<td></td>
</tr>
<tr>
<td>DFT-D3</td>
<td>Dispersion corrected density functional theory</td>
<td></td>
</tr>
<tr>
<td>eV</td>
<td>Electron volt (unit of energy)</td>
<td></td>
</tr>
<tr>
<td>FS</td>
<td>Final structure</td>
<td></td>
</tr>
<tr>
<td>HRCLS</td>
<td>High resolution core level shift</td>
<td></td>
</tr>
<tr>
<td>IS</td>
<td>Initial structure</td>
<td></td>
</tr>
<tr>
<td>LEED</td>
<td>Low energy electron diffraction</td>
<td></td>
</tr>
<tr>
<td>NEB</td>
<td>Nudged elastic band</td>
<td></td>
</tr>
<tr>
<td>NMC</td>
<td>Normal mode calculation</td>
<td></td>
</tr>
<tr>
<td>PAW</td>
<td>Projector-augmented wave</td>
<td></td>
</tr>
<tr>
<td>SCF</td>
<td>Self-consistent field</td>
<td></td>
</tr>
<tr>
<td>TS</td>
<td>Transition structure</td>
<td></td>
</tr>
<tr>
<td>VASP</td>
<td>Vienna ab-initio simulation package</td>
<td></td>
</tr>
<tr>
<td>XC</td>
<td>Exchange-correlation</td>
<td></td>
</tr>
<tr>
<td>ZPC</td>
<td>Zero point corrected</td>
<td></td>
</tr>
</tbody>
</table>
A DISPERSION CORRECTED DFT STUDY OF H₂ OXIDATION ON THE PdO(101) SURFACE

By

Rahul

August 2013

Chair: Jason F. Weaver
Major: Chemical Engineering

We use dispersion corrected DFT to explore the H₂ chemisorption process on PdO(101) surface leading to PdO(101) surface by H₂O formation. H₂ dissociates on the PdO(101) surface through a precursor mediated mechanism wherein the physisorbed H₂ acts as the precursor to dissociation. We find that the H-atom bound to the cus-Pd site can diffuse freely along the cus-Pd row as the estimated energy barrier for diffusion is less than the barrier for H₂ dissociation on the surface. We also show that there is more than one pathway available for H₂ to reduce the PdO(101) surface by reacting with the lattice cus-O and forming water. Disproportionation of two adjacent OH groups on PdO(101) surface leads H₂O adsorbed on adjacent cus-Pd site leaving a vacancy on the surface. The activation barrier for this reaction is ~82.8 kJ/mol H₂ which is almost independent of the H₂ coverage on PdO(101) surface. However, we also find that at the saturation coverage, hydroxyl disproportionation is theoretically not feasible and H₂O can only form through reaction of the surface OH moiety with the H-atom chemisorbed on cus-Pd atom, which has a high energy barrier of 136 kJ/mol H₂.
CHAPTER 1
INTRODUCTION

In past few decades, chemistry of late transition metal (TM) oxides has drawn much attention from the science community due to its extensive usage in the field of catalysis, gas sensors and electro-chemistry. The primary goal of these studies is to gain atomic scale expertise into their surface structure, composition and the underlying mechanism of reactions involved. Surface science studies under a controlled environment such as ultra-high vacuum (UHV) enable us to understand the underlying chemistry of these surfaces at the fundamental level. Although UHV studies have produced significant results, the knowledge is still limited due to structural complexities of the TM-O surfaces and experimental limitations of UHV set-up. Computational simulations have been proven to be an effective to fill these knowledge gaps to a good extent by providing predictions on structural, vibrational, energetic and electronic properties of adsorbate-adsorbent system. Growing the oxide on the metal surface is a complex process because initial chemisorption of oxygen can give rise to surface reconstruction, and may lead to formation of thin epitaxial surface oxides before the formation of bulk oxide. Characterization of these thin oxide films is a challenging task as the properties of the thin oxide films may differ from that of the corresponding bulk oxides.\textsuperscript{1} The TM oxide surface properties are also found to be a function of oxygen coverage which also affects the surface reactivity.

Pd based catalysts are commonly used in catalytic converters for CH\textsubscript{4} combustion at low temperatures to reduce CH\textsubscript{4} emission from automobiles and in gas turbines for alkane combustion. PdO holds a unique place among late TM oxides due to its ability to completely oxidize low end alkanes.\textsuperscript{2-12} Studies have shown that the
formation of PdO is responsible for the favorable performance of supported Pd
catalysts. The high activity of PdO as a complete oxidizing catalyst has motivated in
depth investigation of the surface chemistry of PdO.

Recent studies have shown that the dissociation of C-H bond in alkanes on PdO
(101) surface at low temperatures occurs by a precursor mediated mechanism\(^7\) in which
adsorbed molecule serves a precursor to dissociation. Small alkanes bind strongly on
PdO(101) surface by forming \(\sigma\)-complexes on \(cus\)-Pd sites.\(^{10}\) These \(\sigma\)-complexes
involve electron donation from and back-donation to the alkane molecule and d-orbitals
of the \(cus\)-Pd atom which on one hand increases alkane adsorption energy on
PdO(101), and weakens the C-H bonds on the other, leading to C-H bond dissociation.

The knowledge of dehydrogenation process of alkanes has motivated the study
of the interactions of \(H_2\) with TM oxide, where adsorption and diffusion of hydrogen as
intermediate steps. The simplest atomic structure of Hydrogen molecule make it
suitable candidate for study of \(\sigma\)-bond formation and subsequent surface reactions. In
addition to this, hydrogen oxidation is prevalent in catalytic oxidation of all alkanes and it
may lead to PdO(101) surface reduction. In this thesis, we examine the behavior of \(H_2\)
on PdO(101) surface computationally and concentrate on searching for low energy
pathway for hydrogen oxidation by the surface oxygen.

Previous studies of \(H_2\) on RuO\(_2\)(110) and PdO(101) have provided us a basic
understanding of \(H_2\) adsorption behavior on TM oxide surfaces.\(^{13-16}\) UHV experiments
as well as DFT studies confirm the formation of \(\sigma\)- complex between molecularly
chemisorbed \(H_2\) molecule and coordinatively unsaturated TM atom on the surface.\(^{14, 17}\)
\(H_2/RuO_2(110)\) studies present strong evidence of precursor mediated dissociation of \(H_2\)
over RuO$_2$(110).$^{16-18}$ This $\sigma$-complex weakens the H-H bond leading to dissociation of H$_2$ on RuO$_2$(110). These workers further report the formation of dihydride species (2H-O$_{br}$) through reaction between molecularly adsorbed H$_2$ and bridging O atom (O$_{br}$) on RuO$_2$(110) surface. These studies present the possibility of H$_2$ oxidation by the coordinatively unsaturated oxygen atom present on the surface.

Molecule binding and surface reactions of PdO(101) has certain resemblance with RuO$_2$(110) surface shares common characteristics. Cus-Pd and cus-O atoms in stoichiometric PdO(101) predominantly define the reactive properties of PdO(101) surface.$^7,^8,^{14,19-22}$ Hakanoglu et al. showed that H$_2$ binds strongly on cus-Pd sites by forming $\sigma$-complexes. TPD experiments have shown that irrespective of the amount of H$_2$ exposed to the PdO(101) surface, most of the H$_2$ reacts with the surface to yield H$_2$O.$^{14}$ The TPD results presented by Hakanoglu et al. show that although most of the water desorbs in a sharp peak around 350 K after exposing PdO(101) to H$_2$, a small amount of water desorbs from the surface at higher temperatures as well.$^{14}$ These results imply a possibility of multiple pathways for water production. Blanco-Rey et al. predicted through DFT calculations that H$_2$ can form H$_2$O by recombining with the cus-O on PdO(101), though a high energy barrier of 1.94 eV was reported.$^{13}$ The group also suggested that the presence of neighboring hydroxyl group that is H-atom adsorbed on the neighboring cus-O atom dramatically lowers the barrier for water formation to 0.69 eV. The experimental results however show that the water formation on PdO(101) surface after H$_2$ exposure is nearly independent of the amount of exposure.$^{14}$

These experimental and computation results motivate us to investigate the H$_2$O formation process on PdO(101) after H$_2$ exposure in detail. In this document, we
examine the overall process of H$_2$ adsorption on PdO(101) surface followed by reaction of hydrogen with the coordinatively unsaturated lattice oxygen to form H$_2$O using dispersion corrected DFT (DFT-D3). We explore different possible mechanisms for water formation and compare the obtained results with the already available experimental data. We learn that the H$_2$ dissociates on PdO(101) surface through a precursor mediated mechanism in which the H$_2$ $\sigma$-complex serves as the precursor to dissociation, and the dissociated H-atom can move along the $cus$-Pd row freely. We also find that there is more than one pathway available to H$_2$ to reduce the PdO(101) surface by forming H$_2$O. We present, in this thesis, a potent pathway with an energy barrier that is in a good agreement with the experimental results.
CHAPTER 2
COMPUTATIONAL PROCEDURE

2.1 Density Functional Theory (DFT)

We employ dispersion corrected Density Functional Theory (DFT-D3) to obtain results discussed in this thesis. All DFT-D3 calculations were performed using Vienna Ab-initio Simulation Package (VASP). DFT is nowadays is commonly used computational quantum mechanical modeling approach to predict properties of isolated molecules, fluids, bulk solid surfaces such as metals, semiconductors and insulators and material interfaces. DFT utilizes functionals (functions of another function) of electron density to determine various properties of matter.

DFT computes the electronic structure of matter by solving the time dependent Schrödinger equation which describes the spatial shape and temporal evolvement of a wave function in a given potential and for provided boundary conditions. The Schrödinger equation for a many body system is complex collection of atomic (electronic & nuclei) wave functions. Born-Oppenheimer approximation (mass of nucleus >> mass of electrons) is then applied to order to separate electronic wave function with nucleus wave functions. Electronic wave function is further approximated as Hartee Product which is the product of individual wave function. DFT simplifies the many-body Schrödinger equation by representing it in terms of the spatial coordinate dependent electron density function.

The foundation of DFT is based on two theorems proven by Kohn & Hohenberg and the set of equation derived by Kohn and Sham. Kohn & Hohenberg’s first theorem suggests that ground state energy from Schrödinger’s equation is a unique functional of electron density while the second theorem implies that the electron density
corresponding to the full solution of the Schrödinger equation minimizes the energy of overall functional. The second theorem is also called the variational principle. A functional is written in terms of single-electron wave functions that collectively define the electron density. The energy functionals can describe the kinetic energy of electrons and various intra- and inter-atomic interactions. Kohn & Sham proved that solving a set of equations in which each equation considers interactions of a single electron can yield the correct electron density. DFT applies an iterative algorithm to solve this closed loop problem. The process is usually referred as electronic relaxation or self-consistent field (SCF). The user supplies the structure (number of atoms, atomic arrangement and coordinates) and sets required accuracy parameters for electronic and ionic optimization and an initial trial electron density is defined. Kohn-Sham equation is then solved using the trial electron density to determine the Kohn-Sham electron density. Next, the Kohn-Sham electron density is compared with the trial electron density. If the energies are equal or difference is within the set parameter, the calculation is understood to have attained self-consistency and the energy is considered as the ground-state energy. If the difference is beyond the set parameter, calculation will be continued until the self-consistency is achieved. Once ground state energy is acquired, inter-atomic forces are calculated and tested to satisfy the force criterion. If the force criterion is not fulfilled, atoms are rearranged and SCF calculations are done for the new configuration followed by force optimization calculation. These steps are repeated until the configuration attains the minima based on the specified parameters.

DFT employs exchange-correlational functionals to include quantum mechanical corrections pertaining to treatment of wave functions of electrons and electron densities.
The exchange interaction considers the energy change of the system due to electronic wave function being subjected to exchange symmetry while correlation portion corrects the over-estimation of the energy because of describing electrons as electron densities. Various approximations for XC functionals have been developed such as local density approximation (LDA), generalized gradient approximation (GGA), and meta-GGA and hybrid functionals. GGA is found to be more accurate than LDA in cases of studying systems with sharper variation in electron densities such as solid surfaces. There are distinct GGA functionals available as the gradient in GGA can be treated differently. Calculations performed as part of thesis utilize GGA-PBE exchange correlational functional\textsuperscript{27}.

Electronic wave functions can be further simplified by knowing that core electrons of atoms do not participate in chemical bonds or defining material properties. Using this knowledge, pseudo-potentials are used in DFT to eliminate core electron wave function without excluding their impact on total energy. We use projector-augmented wave (PAW)\textsuperscript{28, 29} provided in VASP database.

2.2 Dispersion-corrected DFT

Accuracy of DFT calculated results is limited in case of insulators and semiconductors because of unaccountability for Van der Waals (dispersion) interactions. However, inclusion of dispersion interactions is critical for the system being studied in this thesis. DFT-D3 is combination of conventional DFT calculations implemented through VASP\textsuperscript{23-26} and dispersion correction technique. In this thesis, we use the method developed by Grimme \textit{et al.} to account for dispersion effects in the system\textsuperscript{30, 31}. The method computes the dispersion effects separately by accounting for non-linear exchange for the long range interactions ignored by conventional DFT.
Calculated dispersion energies and forces are then added to energies and forces determined by conventional DFT relaxation calculations. The total ionic forces are then relaxed using a limited memory Broyden-Fletcher-Goldfrab-Shanno optimization method\textsuperscript{32} until forces are less than the preset parameter. Incorporation of dispersion into DFT is still an active research area as DFT-D3 sometimes overestimates the binding energy of dative bonds which are well characterized by conventional XC functionals.

2.3 Computational Model

As mentioned in previous section, we employed DFT-D3 to obtain the results reported in this thesis. Total ground state energy calculations are performed using projector-augmented wave (PAW) pseudo-potentials provided in VASP database\textsuperscript{28, 29} along with Perdew-Berke-Ernzerhof (PBE) exchange-correlation functionals\textsuperscript{27} and plane wave cut-off of 400 eV and Fermi-level smearing\textsuperscript{33} with a Gaussian width of 0.1 eV. A force relaxation criterion of < 0.03 eV/Å for unconstrained atoms was exercised to obtain all stable structures.

Experimentally, PdO(101) film is grown on Pd(111) surface at 500 K though oxidation of the metal surface in UHV by plasma generated atomic oxygen. A 13 Å thick PdO(101) film consisting of ~3 ML of oxygen atoms id generated.\textsuperscript{14, 21, 22} We defined 1 ML as equivalent to the Pd(111) surface atom density of $1.53 \times 10^{15}$ cm\textsuperscript{-2}. Figure 2-1 provides a top and isometric view of PdO(101) surface. The surface constitutes alternating rows of coordinatively unsaturated (cus, also known as three-fold or 3f) and coordinatively saturated (cs, also known as four-fold or 4f) Pd and O atoms. The cus sites (both Pd and O) have been shown to be highly active towards many molecular species.\textsuperscript{7, 9-12, 14, 20, 21, 34-36}
The computation model surface of PdO(101) is obtained by cutting the relaxed bulk PdO structure along 101 crystal plane. The structure is then strained to meet the reported experimental lattice parameters \((a = 3.057 \text{ Å} \text{ and } b = 6.352 \text{ Å})\) followed by relaxation using DFT-D3 relaxation criteria stated. The model surface is characterized by a rectangular unit cell where \(\vec{a}\) and \(\vec{b}\) lattice vectors correspond to \([01\overline{1}]\) and \([\overline{1}01]\) direction of PdO(101) crystal, respectively. We use four layered PdO(101) which corresponds to a thickness of 9 Å. All SCF calculations were performed with the bottom PdO layer fixed to provide stability to the structure A 20 Å of vacuum spacing has been provided in the normal direction to the top surface layer to minimize spurious periodic interactions. Our earlier studies have shown that the thickness of 9 Å is sufficient to ignore the effects of the metal substrate Pd(111) as the increasing slab thickness does not impact the results of the calculations.\(^{21}\) A 4 x 8 x 1 Monkhorst-Pack \(k\)-point mesh was used for a 1x1 unit cell and the larger cells were scaled accordingly. A 4 x 2 x 1 and 2 x 2 x 1 \(k\)-point mesh have been used for 4 x 1 and 4 x 2 unit cell sizes, respectively. The 4 x 1 unit cells were used to study the molecular and dissociative adsorption of \(\text{H}_2\) on the surface. \(\text{H}_2\text{O}\) formation on PdO (101) due to reduction creates \(\text{cus-O}\) vacancy on the surface which causes major distortion of the crystal; therefore we switched to the larger unit cell of 4 x 2 sizes to investigate the \(\text{H}_2\text{O}\) formation configurations and pathways.

The adsorption/desorption/binding energies reported in this thesis are calculated by subtracting the ground state energies of the adsorbate system (adsorbed molecule on the surface) from the sum of total ground-state energies for the isolated molecule in gas phase and the bare PdO(101) surface. We define the quantity “dative bond energy”
as binding energy of the DFT-D3 relaxed structure minus the dispersion energy. We calculate the dative energies by performing a single-point conventional DFT calculation on the relaxed structure obtained using DFT-D3. These calculations allow us to quantify contributions due to the dative and dispersion interactions.

2.4 Analytical Methods

2.4.1 Normal Mode analysis

An isolated molecular system comprising of N atoms has total of 3N degrees of freedom – 3 translational DOF, 3 rotational DOF and 3N-6 vibrational DOF. A linear molecule has 3N-5 vibrational DOF. The 3N-5(or 6) uncoupled DOF are periodic motions in the molecule and are referred as vibration modes, the corresponding frequencies are termed as vibrational frequencies. The translational and rotational modes in an isolated molecule are treated redundant. Although when the molecule is adsorbed on a surface, these 6 modes are no longer redundant. Experimentally, these modes can be investigated by infrared spectroscopy or Raman spectroscopy. DFT utilizes numerical finite difference method to determine vibrational states. We use normal mode analyses to confirm whether or not the relaxed configuration is a true minima. The vibrational frequencies are also used to calculate the zero point corrected energies of different configurations. Vibrational modes are usually calculated by fixing the surface atoms while leaving the molecule unconstrained. In our studies, a cus-O atom on the surface is involved in the reaction with two H-atoms to form water. However, we find that fixing the complete system but the 2 H-atoms and a cus-O (involved in H2O formation) does not yield us the imaginary frequencies at the transition state. The imaginary mode was found to be associated with the cus-Pd atom with which H2O is bonded to after formation. Hence, all NMC calculations in this thesis are
performed by setting the adsorbed species (H atoms), \textit{cus}-O and \textit{cus}-Pd atom unconstrained while fixing the rest of the PdO(101) surface.

2.4.2 Nudged Elastic Band Method

Nudged Elastic Band (NEB) is a computational method used to determine the saddle point and minimum energy pathway (MEP) between a pair of stable states.\textsuperscript{37} The method utilizes the fact that any point on MEP is at an energy minimum in all direction perpendicular to the path. We employ the slightly modified version of NEB called climbing image NEB method which can also determine the transition state for a MEP.\textsuperscript{38, 39} In the climbing image NEB method, the image with highest energy (climbing image) is identified after few iterations with conventional NEB method. The energy of the climbing image is the maximized while energy along the rest of the band is tried to be minimized. Climbing image calculations provide the saddle point which is further confirmed to be transition state through normal mode analysis by looking for an imaginary mode of vibration.
Figure 2-1. Hard ball model representation of stoichiometric PdO(101) surface. The surface constitutes 0.35 ML of cus-Pd, cus-O, 4f-Pd and 4f-O each. The $\bar{a}$ and $\bar{b}$ lattice vectors correspond to [010] and [-101] crystallographic directions of PdO. Atomic color code: Blue - Pd, Orange – O.
CHAPTER 3
RESULTS AND DISCUSSION

3.1 H₂ Adsorption and Dissociative Chemisorption on PdO (101)

Molecular chemisorption of H₂ and H₂O has been extensively studied by our group experimentally as well as theoretically. From a previous study done for molecular H₂ adsorption on PdO(101), we gather that most stable configuration of molecular H₂ on PdO(101) is when H₂ molecule sits atop cus-Pd and aligns parallel to a & b lattice vectors (parallel to cus-Pd row and perpendicular to cus-Pd row). DFT-D3 predicts the adsorption energies of 56.9 and 48.7 kJ/mol for parallel and perpendicular H₂ configurations, respectively. Also we observe that the H-H bond in the adsorbed species elongates 0.84 Å compared with the gas phase H2 at 0.75 Å. The Pd-H bond length is 1.74 Å in parallel configuration. Previous studies¹⁰,¹³,¹⁴,¹⁶ have well established the existence of σ-complex formation in adsorption of H₂ on a metal oxide surface. A similar type of dative bonding has been reported in detail for H₂ on RuO₂ (110) surface by Sun, Reuter and Scheffler.¹⁶ The Pd-H bonding contains both charge donation and back donation between Pd and H-atoms. We calculated the dative bond energy of the parallel and perpendicular configurations of adsorbed H₂ by performing single step DFT on DFT-D3 relaxed configurations. The dative bond energies of both configurations are estimated to be 47.2 and 39.2 kJ/mol H₂. The difference between DFT-D3 energy and dative bond energy implies that dispersion forces stabilize the adsorbed species on the surface.

Due to the small size of H₂, we expect a significant impact of zero-point correction (ZPC) which is also a source of strong kinetic isotopic effects observed experimentally.¹⁴ We calculated the vibration frequencies of both adsorption
configurations and it is observed that an imaginary frequency is associated with the H$_2$ perpendicular configuration which indicates that this configuration is not a stable minimum but a transition configuration for dissociation of adsorbed H$_2$ species aligned parallel to *cus*-Pd row. The vibrational frequencies of the parallel configuration are listed in Table 3-1 in column C1. Note that we set 4 atoms (2 H-atoms, *cus*-Pd and *cus*-O) unconstrained while fixing the rest of PdO(101) surface to ensure that we maintain one reference, that is, isolated H$_2$ and bare PdO(101) surface, for all calculation performed at low coverage.

We then studied the H$_2$ dissociation pathway described by Hakanoglu et al by using DFT-D3. The adsorbed H$_2$ dissociates to yield the chemisorbed configuration wherein one H-atom remains adsorbed on the *cus*-Pd and the other H-atom adsorbs on adjacent *cus*-O site (see configuration C2 in Figure 3-1). The binding energy for this chemisorbed H$_2$ configuration is 132.8 kJ/mol with Pd-H and Pd-O bond lengths 1.55 Å and 0.98 Å, respectively. We estimate the dative bond energy for this structure using the method explained above to be 110.4 kJ/mol. The ZPC corrected binding energy for the chemisorbed H$_2$ is estimated to be 108.5 kJ/mol. To probe the H$_2$ dissociation pathway, we used 3 images in the climbing NEB calculation with accuracy limit of 0.03 eV/ Å. The H$_2$ molecule rotates on the *cus*-Pd atom and instead of attaining a more symmetrical TS (perpendicular H$_2$ configuration), the H-H bond begins to stretches at the same time from an initial value of 0.84 Å to 1 Å at the transition state TS1. The dissociation barrier for this pathway is 39.7 kJ/mol. This low energy barrier assures the stability of the dissociated hydrogen configuration and that the dissociated H$_2$ will not recombine to yield molecular hydrogen. This result also suggests the possibility of H$_2$O
formation in the due process. We find that the ZPC dissociation barrier is 33.5 kJ/mol for H₂ using the vibrational frequencies of initial state and transition states. Again, we observe that the DFT-D3 predicted dissociation barrier for H₂ is a lot lower than the desorption barrier (~42.8 kJ/mol). The vibrational frequencies for initial state (C₁), transition state (TS₁) and final state (C₂) are listed in Table 3-1.

**3.2 H₂O on PdO(101) Surface**

Blanco-Rey and coworkers have proposed a mechanism for H₂O formation on PdO(101) which suggests that a water like dihydride structure can form on the PdO(101) surface that will be weakly bound to the *cus*-Pd site and an adjacent vacancy at *cus*-O site. The formation of water occurs from the initial state (C₂) in which the one H-atom is adsorbed on *cus*-Pd site and the other is bonded to the adjacent *cus*-O site. The *cus*-OH group starts to leave the surface and move towards the Pd-H group at the transition state giving birth to H₂O adsorbed *cus*-Pd atom creating a vacancy at *cus*-O site on the PdO(101) surface. However, the barrier for formation of this moiety is reported to be quite large (1.94 eV) which makes it an unlikely pathway for water formation. TPD spectra after exposing the PdO(101) thin film surface to various quantities of H₂ in Ultra high vacuum shows possibility of multiple pathways for water formation - desorption limited water will be formed through low energy pathways whereas the water peak at high temperatures will be resulted from high energy pathways. Another suggested outlook was that water formed at low temperatures is desorbed at high temperature. Therefore, it becomes essential for us to understand the behavior of water on PdO(101) thin film surface.

DFT calculations performed by Kan et al. predict that the H₂O molecule sits atop *cus*-Pd site in the most preferred configuration with its O atom on top of *cus*-Pd
atom forming H₂O-Pd bond and H-O-H plane aligned almost parallel to the PdO(101) surface. One of the H-atoms in H₂O points directly towards cus-O whereas the other interacts with the 4-fold oxygen atom on the surface providing stability to the configuration. The configuration has an estimated adsorption energy of 75.2 kJ/mol with reference to the bare PdO(101) surface and a gas phase ‘isolated’ H₂O molecule. It is suggested that adsorption of water on cus-Pd sites is favored over other sites by at least 40 kJ/mol. These DFT results give us an initial understanding of how the water could form on the PdO(101) surface after H₂ adsorption. We now understand that in every possible pathway for H₂ oxidation, H₂O will be most likely to be bonded to cus-Pd atom before desorption.

To get the H₂O configuration on PdO(101) surface with an adjacent cus-O vacancy, we first relaxed structure using a 4x1 slab. We find that the surface distortion was significant due to coverage effect of the cus-vacancy and we could not obtain a configuration with H₂O adsorbed on PdO(101) surface. We then relaxed the same configuration on a 4x2 a relaxed configuration with H₂O formed on the PdO(101) thin film surface with an adjacent vacancy at cus-O site (refer C5 in Figure 3-1). Unlike H₂O on bare PdO(101) surface where O atom lies directly atop cus-Pd, the O atom in reaction limited H₂O molecule bonds with cus-Pd atom at a bond angle of ~82.5° from PdO(101) surface plane and the H-O-H plane rests away from the PdO(101) surface at a very small angle from surface plane. We also observe from DFT-D3 produced relaxed configuration that due to the nearby vacant cus-O site, cus-Pd atom shifts towards the vacant site distorting the original atomic arrangement of the surface. The H₂O-Pd bond length is 2.15 Å. Both H-O bond lengths are 0.98 Å each and the H-O-H angle is
approximately 105.92°. These values are very close to isolated gas phase H₂O molecule. So, if we get a viable pathway linking configuration C4 to C5, we can confirm the formation of reaction limited H₂O on PdO (101) surface. We calculated the vibrational frequencies of the relaxed C5 configuration using NM calculation. The frequencies are listed in Table 3-1 in column C5. Note that the configuration C5 has an imaginary mode with a very low frequencies, so we rotated the molecule along the imaginary mode and relaxed the structure to obtain a stable structure but a configuration without imaginary frequency could not be obtained. We reckon that this small imaginary frequency indicates soft bonding between the H₂O moiety and cus-Pd (bond length 2.15 Å) and the possibility of immediate desorption of the H₂O molecule as soon as it is formed.

To begin with, we tested the viability of high energy Blanco-Rey’s pathway using DFT-D3 which links configuration C2 to C5 with a 5 image climbing NEB calculation. Since the configuration C5 was obtained on a 4x2 slab, we relaxed configuration C2 on a 4x2 slab as well which almost has same adsorption energy as 4x1 surface (Table 3-2 provides a comparison of energies between 4x1 and 4x2 surface). The NEB calculation does not converge with an accuracy 0.03 eV/Å directly, therefore, we started the calculations at a low accuracy of 0.5 eV/Å and used the results obtained from it in a high accuracy calculation until the required accuracy of 0.03 eV/Å was reached. In this mechanism, the cus-O on surface begins to leave the surface with H-atom still attached to it and move towards the cus-Pd atom creating a vacancy. The H-atom on cus-Pd site starts moving towards the cus-OH group at the transition state as demonstrated in Figure 3-4A. DFT-D3 estimated activation barrier for this pathway is 168.8 kJ/mol H₂
(1.75 eV) which even though lesser than that predicted by Blanco-Rey et al, is still too high to be practically possible. Another noticeable fact is that the apparent barrier for the reaction is positive which makes the transition state unlikely to occur. Above results forced us to look for other possible pathways for water formation on PdO(101) surface due to surface reduction.

**3.3 H-atom Diffusion on PdO (101) Thin Film**

Pathway described by Blanco-Rey & coworkers requires very high temperatures to form H$_2$O from H$_2$ induced PdO(101) surface reduction whereas TPD experiments of H$_2$ chemisorption and dissociation over PdO(101) thin film have shown evidences of H$_2$O formation and desorption near 350 K.$^{14}$ To probe alternative water formation pathways, we examined several other possibilities including the pathway reported by Blanco-Rey and coworkers.$^{13}$ In our attempts, we tested many distinct possible hopping paths - H-atom hopping(diffusion) along cus-Pd row, along cus-O row and hopping from cus-Pd to adjacent cus-O site. We found that H-atom could move along the cus-Pd row with considerably lower energy barrier as compared to that required to dissociative adsorption of H$_2$ molecule on PdO(101) while hopping from cus-Pd to cus-O site could be achieved within a reasonable energy barrier. Probing the next stable configuration which can be attained by two H-atoms in close proximity led us to configurations with one H-atom atop cus-O and the bonded to neighboring cus-Pd (see configuration C3 in Figure 3-1). The binding energy of this configuration is 115.0 kJ/mol with dative bonding contribution of 93.3 kJ/mol. We notice that binding energy of this configuration is lower than the C2 configuration (~132.0) however the bond lengths of cus-PdH and cus-OH bond in C3 are 1.54 Å and 0.98 Å which are as same as that in configuration C2. Figure 3-1 shows a model representation of both C2 and C3 configurations.
It is apparent that transition from C2 to C3 can occur by two possible pathways – H-atom hopping along cus-Pd row and H-atom hopping along cus-O row. We investigated both these pathways. Transition structures for evolution from C2 to C3 are labeled as TS2.1 and TS2.2 in the Figure 3-1. Note in TS2.1 that the H-atom atop cus-Pd begins to move towards the neighboring cus-Pd, the Pd-H bond length elongates from 1.55 Å to 1.72 Å. In TS2.2, the H-atom bonded to cus-O starts to shift toward neighboring cus-O atom stretching the Pd-O bond from 0.98 Å to 1.26 Å. DFT-D3 predicts activation barriers for H-atom hopping along cus-Pd and hopping along cus-O row are 26.0 and 132.4 kJ/mol, respectively. The reason behind the high hopping barrier along cus-O row is strong electronic attraction between H-atom and surface O atom which makes leaping along the cus-O row impractical at lower temperatures. So, we can omit the possibility of H-atom hopping along cus-O row to progress along C2 to C3. Using the vibrational frequencies from Table 3-1 for the initial state (C2) and transition states (TS2.1 and TS2.2), we obtain the ZPC activation barriers of 20.5 and 117.5 kJ/mol H₂, respectively. We also note from the overall energy diagram shown in Figure 3-2 that the apparent barrier for H-atom hopping along cus-O row (TS2.2) is positive which makes the transition state unstable and practically unattainable. Thus, we conclude that H-atom can move along the cus-Pd row freely on the PdO(101) thin film surface due to its activation barrier lower than that for dissociation on adsorbed H₂ on PdO(101) surface.

We examined the possibility of H-atom hopping from cus-Pd to cus-O site and vice-versa. However, since OH bond is stronger than Pd-H bond, breaking the OH bond will require higher energy than breaking the Pd-H bind. With this understanding, we
probed only the pathway for H-atom hopping from \textit{cus}-Pd to \textit{cus}-O site. The final state (labeled as C4) in the transition from C3 is shown in Figure 3-1. In this configuration, both H-atoms bond to adjacent \textit{cus}-O sites, and the O-H bond length is 0.98 Å. The configuration is estimated to be exothermic by 143.9 kJ/mol H$_2$ on a 4x1 PdO(101) surface. DFT-D3 estimates a slightly higher adsorption energy (147.6 kJ/mol H$_2$) for the same atomic arrangement on a 4x2 surface. This stability is attributed to surface coverage effects. Using one image climbing NEB calculation, we linked the C3 and C4 configurations. The Pd-H bond elongates from 1.54 Å to 1.61 Å at the transition state (labeled as TS3 in Figure 3-1 and in subsequent figures) as the H-atom shifts toward neighboring \textit{cus}-O site. The energy barrier for this pathway is estimated to be 88.5 kJ/mol H$_2$. After applying the zero point correction based upon vibrational frequencies of initial state (C3) and transition state (TS3) which are listed in Table 3-1 in corresponding columns, we calculated the ZPC activation barrier for this pathway to be equal to 82.4 kJ/mol H$_2$. Later in this chapter, we shall show that the energy required for H-atom to hop from \textit{cus}-Pd site to \textit{cus}-O site is less than that to form water due to PdO(101) surface reduction.

3.4 Formation of H$_2$O on PdO(101) Thin Film Surface at 0.08 ML H$_2$ Coverage

To start with, we linked configurations C4 and C5 using 5 image climbing NEB calculation at a low accuracy of 0.5 eV/ Å. The result obtained from the converged calculation was used in NEB calculation at higher accuracy until the required accuracy of 0.03 eV/ Å was achieved. The pathway shows the in presence of neighboring surface hydroxyl group, the \textit{cus}-OH on PdO(101) surface begins to leave the surface. At the transition state, the H-atom on this \textit{cus}-OH rests away from the PdO (101) surface as well as the neighboring surface \textit{cus}-OH group while the H-atom on the surface \textit{cus}-OH
group orients toward the \textit{cus}-OH. As the reaction proceeds, H-atom on surface \textit{cus}-O transfers to the ‘popped’ \textit{cus}-OH to form water. The activation barrier for the reaction pathway is found to be 88.0 kJ/mol H$_2$. An atomic model representation of transition state is shown in Figure 3-1 labeled as TS4. We also notice that the pathway has a local minima after the transition state global maximum. We investigated the possibility of a stable intermediate state by relaxing the local minima structure (labeled as C4i in Figure 3-1 and onwards). The \textit{cus}-OH group relaxes on the \textit{cus}-Pd atom slightly oriented toward the surface \textit{cus}-OH group. The \textit{cus}-Pd atom shifts toward the adjacent vacancy created at \textit{cus}-O site. The binding energy of this configuration is estimated to be 119.4 kJ/mol with reference as isolated H$_2$ and bare PdO(101) surface. We ran two separate 3 image climbing NEB calculations linking C4 and C4i and C4i and C5. The activation barrier for C4-C4i pathway is estimated to be 88.2 kJ/mol H$_2$ with a transition state very similar to configuration TS4 depicted above. The activation barrier for C4i-C5 pathway is found to be almost negligible 8.0 kJ/mol H$_2$. The H-atom bonded to the surface \textit{cus}-O begins to transfer to the \textit{cus}-OH atop \textit{cus}-Pd site at its transition state. We observe that this mechanism for water formation requires only 88.0 kJ/mol as compared with gigantic 168.8 kJ/mol barrier required for Blanco-Rey’s mechanism. The mechanism also points toward a possible effect introduced by the presence neighboring \textit{cus}-OH moiety that lowers the barrier significantly. We shall discuss about the effect of presence of \textit{cus}-OH moiety later in this document.

The vibration frequencies of C4, C4i, TS4, TS4i and TS4ii are listed in Table 3-1 in corresponding columns. Using the vibrational frequencies obtained by NMC calculations on configurations C4, C4i, TS4, TS4i and TS4ii, we estimate the activation
barrier of 82.8-83.0 kJ/mol H$_2$ to evolve from C4 to C5 producing water and a *cus*-vacancy on the PdO(101) surface. ZPC activation barrier for C4i to C5 step is calculated to be negative by 0.5 kJ/mol H$_2$ implying an auto-activated pathway. ZPC calculations for the C4-C5 pathway also provide us a more profound view of the final water formation procedure by disproportionation of *cus*-OH moiety. The pathway can be viewed as a two-step process—cleavage of *cus*-OH moiety from PdO(101) surface in presence of a neighboring *cus*-OH; following by H-atom transfer to ‘popped out’ OH moiety forming H$_2$O. The presence of local minima followed by a very low activation barrier pathway implies the possibility of a flat potential energy surface for the reaction.

Figure 3-3 portrays the overall zero point corrected potential energy variations in evolution of H$_2$ into H$_2$O. Configuration C6 corresponds to the water desorption from the PdO(101) surface leaving a vacancy behind at the *cus*-O site. The activation barrier for C5-C6 evolution is estimated to be 85.1 kJ/mol H$_2$ which the difference between the ZPC energies of C5 and C6 configurations. It must be noted here that the value 85.1 kJ/mol H$_2$ is neither derived through NEB calculation nor it is the desorption energy of water on PdO(101) surface. We have reported this ‘desorption’ process in terms of H$_2$ to keep a constant reference in the whole oxidation cycle depicted in Figure 3-3. Although one must notice that the desorption barrier for water from PdO(101) surface with adjacent *cus*-O vacancy is very close to the energy required to reduce the PdO(101) surface forming water. This result may be significant because it indicates the possibility that experimentally, the water formed on the PdO(101) surface may desorb as soon as it forms. We can also infer from the diagram H$_2$ dissociation and diffusion of H-atom along *cus*-Pd rows can occur at very low temperature owing to low activation barrier,
nevertheless comparatively higher temperature will be required to facilitate water formation. These results do match well with the experimental results obtained by Hakanoglu et al.\textsuperscript{14} and Martin et al.\textsuperscript{40}

3.5 Coverage Effect of H\textsubscript{2} in Formation of H\textsubscript{2}O

3.5.1 Formation of Water at 0.35 ML H\textsubscript{2} (100\% cus) Coverage on PdO (101) Surface

Experimental studies of H\textsubscript{2} over PdO (101) surface have shown that most of the H\textsubscript{2} reacts with the surface to produce H\textsubscript{2}O with an yield of \(~76\%\) of total product yield, and the fractional yield of H\textsubscript{2}O is almost independent of initial H\textsubscript{2} exposure.\textsuperscript{14} So, we studied the water formation mechanism at higher H\textsubscript{2} coverage on PdO(101). We populated 50\% of the adjacent cus sites with H-atom on a 4x2 PdO(101) surface which corresponds to 0.35 ML coverage of H\textsubscript{2}. The relaxed configuration of dissociatively adsorbed H-atom on PdO(101) is shown in Figure 3-4B under the label IS. Since we already know that 4-fold sites on the PdO(101) surface are neutral, and the remaining cus-sites on the surface are too far for H-atom to have any coverage effect, we can safely assume this scenario to be equivalent to 100\% cus site coverage by H\textsubscript{2}. The structure is estimated to have binding energy of 110.1 kJ/mol H\textsubscript{2} with reference to bare PdO(101) surface and isolated H\textsubscript{2} molecule in gas phase. The lower binding energy of the structure compared to the similar low coverage configuration is believed to be due to electronic repulsion among H-atoms. HRCLS experimental results have also confirmed that binding energy of H\textsubscript{2} on PdO(101) surface decreases at the saturation coverage.

We looked for all possible pathways for water formation and none but the Blanco-Rey’s pathway\textsuperscript{13} converged to yield the MEP. As explained earlier in the document and by Blanco-Rey and coworkers\textsuperscript{13}, the cus-OH moiety on PdO(101) moves out of the surface and move toward the adjacent cus-Pd atom with adsorbed H-atom and the cus-
Pd-H bond stretches as the H-atom begins to move toward OH group at the transition state. The activation barrier for MEP is estimated to be 136.6 kJ/mol H$_2$ at H$_2$ coverage equivalent to 0.35 ML which a lot lower than the 168.8 kJ/mol H$_2$ barrier calculated at a H$_2$ coverage of 0.04 ML on PdO (101) surface (see graphs in Figure 3-4). The presence of adjacent cus-OH moieties promotes the cleavage of cus-OH bonds with the surface hence lowering the energy barrier for the water formation. We reckon that even though interaction between H-atom and cus-O atom weakens bonds between cus-OH moieties and surface leading to low adsorption energy of the initial configuration (shown under label IS in Figure 3-4B) steric hindrance and electronic repulsion among adsorbates at 100% cus site coverage by H-atoms restrict the water formation via low barrier pathway i.e. cus-OH disproportionation pathway.

3.5.2 Formation of Water at 0.26 ML H$_2$ (75% cus) Coverage on PdO (101) Surface

Our calculations show that only high energy pathway facilitates the formation of H$_2$O at the saturation coverage of H$_2$ on PdO(101) surface. Since the energy barrier for water formation at 100% cus site coverage is very high, it is very much possible that molecular H$_2$ can desorb from the PdO(101) surface before the water is form on the surface creating few vacant cus sites. With this understanding, we studied the H$_2$O formation reaction process on a surface with 75 % of cus site covered by H-atom (0.26 ML coverage on a 4x2 PdO(101) surface). The 2 cus-Pd sites are kept vacant as shown in Figure 3-5 (labeled as IS). The adsorption energy of this configuration is calculated to be 119.7 kJ/mol H$_2$. The low binding energy of H$_2$ on PdO(101) surface at high coverage has been confirmed through high resolution core-level shift experiments as well. There can be three possible arrangements by which H$_2$O can form on this surface. These configurations have been labeled as C5-1, C5-2 and C5-3 in Figure 3-5.
Case-1 – The \textit{cus-OH}^1 and \textit{H}^2 atom adsorbed at \textit{cus-O} site react to form \textit{H}_2\textit{O} creating an adjacent vacancy on the surface. (Image C5-1 in Figure 3-5)

Case-2 – The \textit{cus-OH}^1 and \textit{H}^3 atom adsorbed at \textit{cus-O} site react to produce adsorbed \textit{H}_2\textit{O} on the PdO(101). (Image C5-2 in Figure 3-5)

Case-3 – The \textit{cus-OH}^1 and \textit{H}^4 atom adsorbed at \textit{cus-Pd} site react to produce adsorbed \textit{H}_2\textit{O} species on the PdO(101). (Image C5-3 in Figure 3-5)

The energies of these configurations are very close to each other. The most stable configuration is the final state for case-1 with a binding energy of 121.52 kJ/mol \textit{H}_2\textit{O} whereas the case-3 has the least binding energy (119.8 kJ/mol \textit{H}_2\textit{O}). Note that the energy of the initial state (dissociatively adsorbed \textit{H}_2 on PdO(101)) surface) and the final states (\textit{H}_2\textit{O} on PdO(101) surface with adjacent vacancy) have their binding energies in very close proximity. We linked each final state with the initial state using 3 separate climbing NEB calculations. \textit{Cus-OH}^1 moiety on PdO(101) splits from the surface and the \textit{cus-OH}^* (\* = 2,3,4) elongates as the \textit{H} atom begins to move toward the ‘popped out’ \textit{cus-OH}^1 moiety at the transition state. The reaction pathway from dissociatively adsorbed \textit{H}_2 to adsorbed \textit{H}_2\textit{O} on PdO(101) is shown in Figure 3-5 for all three possible pathways at high coverage of \textit{H}_2. DFT-D3 estimates energy barriers for case-1, case-2 and case-3 to be 91.4, 96.4 and 91.2 kJ, respectively. As observed in case-3, the barrier for \textit{H} atom to hop from \textit{cus-Pd} site diagonally and interact with the \textit{OH} atop \textit{cus-Pd} to form \textit{H}_2\textit{O} becomes negligible. Note that the energy barrier for \textit{H}_2\textit{O} formation at high \textit{H}_2 coverage is very close to that at low hydrogen coverage. These results are further strengthened by high resolution core level shift calculations reported by Martin et al.\textsuperscript{40}
3.6 Effect of Presence of Hydroxyl Moiety and H-atom Diffusion on PdO(101) Surface on water formation

To understand whether or not the presence of OH group affects the energy barrier for H2O formation, we carried out few additional tests with H2 over PdO(101) surface. In three separate simulations, we calculated the energy barrier for OH cleavage from PdO(101) surface in presence of H-atom adsorbed on neighboring cus-Pd, the solo OH group pop out barrier and in presence of adjacent hydroxyl group. We find an energy barrier of 101.7 kJ at the accuracy level 0.3 eV/Å for the cus-OH to cleave its bonds from the surface when all neighboring cus sites are vacant. The barrier is estimated to be higher by ~15 kJ when a H-atom is adsorbed on the neighboring (diagonally adjacent) cus-Pd sites at same calculation accuracy of 0.3 eV/Å. We could not get the calculations converged for these test cases at our standard accuracy of 0.03 eV/Å. In our third test, when the H-atom is placed on the adjacent cus-O atom, the energy barrier for cus-OH group to pop out from the surface decreases significantly to 88.2 kJ (calculation accuracy 0.03 eV/Å). Figure 3-6 shows the initial, transition and final states for all three cases tested as part of this study.

It is observed that presence of H-atom on cus-O atom makes it less bound to the neighboring 4f-Pd and cus-Pd surface atoms as reflected by the increased bond lengths from ~0.203 Å and 0.197 Å to 0.214 Å and 0.208 Å, respectively. The cus-Pd and cus-O bond length increases slightly from 0.208 Å to 0.212 Å in presence of a neighboring hydroxyl group (shown in Figure 3-6C). The loss of most favorable bonding environment lowers the energy barrier for oxidation by facilitating the cus-OH cleavage from the surface. We also notice that the energy barrier for the pathways first described by Blanco-Rey and coworkers reduces significantly from ~187 kJ (168.8 kJ predicted by
our DFT-D3 calculations) at low coverage to 136.5 kJ in presence of neighboring \textit{cus}-OH moieties at high H-atom coverage. These results present a strong case that H$_2$O desorption experimentally observed at lower temperature is facilitated by presence of the adjacent OH group. Our calculations demonstrate a strong case that the presence of adjacent hydroxyl group on PdO(101) surface accelerates the PdO(101) surface reduction by lowering the barrier for \textit{cus}-OH cleavage. H$_2$O formation, though, by disproportionation of \textit{cus}-OH is almost unaffected by presence of more OH groups in the vicinity. Note that the barrier estimated for the configuration shown in Figure 3-6A is \(~115.5 \text{ kJ/mol H}_2\text{ which is significantly lower than the high energy pathway described by Blanco-Rey and coworkers. This lowered barrier may be a result of reduced electronic repulsion between the \textit{cus}-OH and the H-atom adsorbed on the neighboring \textit{cus}-Pd that is observed in the high energy pathway.}
Figure 3-1. Model representation of adsorption of H$_2$ on PdO(101) surface followed by dissociative adsorption and subsequent formation of H$_2$O with adjacent $cus$-vacancy on PdO(101) surface. Atomic color code: blue-Pd, orange-O and white-H. Stable configurations are labeled as C# and transition states as TS# where # = 1,2,3,4,5.
Figure 3-2. Potential energy surface profiling of H₂ activity on PdO(101) surface to produce H₂O at low H₂ coverage. The zero reference is taken as isolated H₂ in gas phase and bare PdO(101) surface. Atomic color codes: blue-Pd, orange-O and white-H.
Table 3-1. Vibrational frequencies (wave numbers) of various stable and transition state configurations. The values are reported in cm$^{-1}$. Frequencies with suffix 'i' and * are imaginary frequencies. See text for more details.

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Table 3-2. Comparison of binding energies of various configurations of H₂ on PdO(101) surface at low coverage on 4x1 and 4x2 PdO(101) slabs. The zero reference is taken as isolated H₂ in gas phase and clean PdO(101) surface. Reference for ZPC is unrestricted H₂ and PdO(101) surface with all atoms but cus-Pd and cus-O atoms involved in H₂O formation fixed. All energies are reported in kJ/mol H₂.

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* The activation barrier is energy difference between C₅ and C₆ states

** C₆ is a bare PdO(101) surface with vacancy at cus-O site.
Figure 3-3. ZPC potential energy evolution of H$_2$ for H$_2$O formation on PdO(101) surface at low H$_2$ coverage. Zero point reference is isolated H$_2$ molecule and clean PdO(101) surface. Stable structures are shown at bottom (C0-C6) where C0 is the bare PdO(101) surface and C7 is PdO(101) surface with a vacancy at cus-O site. Transition structures are shown at the top. Atomic color codes: blue-Pd, orange-O and white-H.
Figure 3-4. H$_2$O formation on PdO(101) surface via high energy pathway. A) H$_2$O formation at low H$_2$ coverage, activation barrier $E_a = 168.8$ kJ/mol H$_2$. The pathway was first discussed by Blanco-Rey et al. See text for details; B) H$_2$O formation at 100% cus site coverage, $E_a = 136.5$ kJ. Potential energy profile comparison of H$_2$O formation by high energy pathway at low coverage against saturation coverage of H$_2$ on PdO(101) surface. Atomic color codes: blue-Pd, orange-O and white-H.
Figure 3-5. H$_2$O formation pathways through disproportionation of 2 adjacent cus-OH at 0.26 ML of H$_2$ coverage on PdO(101) surface. Three possible pathways have been shown for H$_2$O formation at this coverage estimated barriers of 91.4, 96.4 and 91.2 kJ for case-1, case-2 and case-3, respectively. Atomic color codes: blue-Pd, orange-O and white-H.
Figure 3-6. Effect of OH group presence in H₂O formation. A) OH hopping with neighboring cus-Pd H-atom, $E_a = 115.5$ kJ/mol H₂ (accuracy 0.3 eV/A); B) OH hopping on clean surface, $E_a = 101.2$ kJ (0.3 eV/A); C) OH hopping with neighboring cus-OH, $E_a = 88.2$ kJ/mol H₂ (accuracy 0.03 eV/A). Atomic color codes: blue-Pd, orange-O and white-H.
CHAPTER 4
CONCLUSIONS

Using DFT-D3, we studied H\(_2\) adsorption process on PdO(101) surface and H\(_2\) reaction with lattice *cus*-O to yield H\(_2\)O. We learn that H\(_2\) adsors onto *cus*-Pd sites of PdO(101) surface and readily dissociatively chemisorbs through precursor mediated mechanism with energy barrier of 33.5 kJ/mol H\(_2\) wherein the molecularly adsorbed H\(_2\) serves as the precursor. Our calculations predict that diffusion barrier for H-atom along the *cus*-O row is 117.5 kJ/mol H\(_2\) whereas barrier for H-atom diffusion from one *cus*-Pd site to another is only 20.5 kJ/mol H\(_2\) which is lower than dissociation barrier of molecularly adsorbed H\(_2\) on the surface. This implies that the H-atom can diffuse freely along the *cus*-Pd row of the PdO(101) surface but the diffusion barrier along *cus*-O row is high enough to restrict H-atom diffusion from one *cus*-O to another. The barrier for H-atom from *cus*-Pd to *cus*-O is estimated to be 82.4 kJ/mol H\(_2\) which yields the chemisorbed structure of H\(_2\) with binding energy of 114.0 kJ/mol H\(_2\). Observe that even though the binding energy of H-atom chemisorbed on adjacent *cus*-O is the highest among all other chemisorbed configurations, at very low temperatures, the H\(_2\) will prefer to be dissociatively chemisorbed on *cus*-Pd adjacent *cus*-O, being this the stable configuration with low energy barrier of formation.

Earlier experimental studies have shown possibility of multiple pathways for water formation. Using DFT-D3, we confirm the presence of more than one pathway for water formation on PdO(101) surface leading to its reduction. Our calculations predict the presence of a low barrier pathway for H\(_2\)O formation. We find that H\(_2\)O can form on the PdO(101) by disproportionation of two adjacent OH group on the surface. The barrier for this reaction is predicted to be 82.8 kJ/mol H\(_2\). The energy barrier for H\(_2\)O
formation through this pathway is very close to the barrier for H-atom to diffuse from cus-Pd to cus-O. The low energy barrier is attributed to the presence of neighboring hydroxyl group which weakens the bond between cus-OH and the surface facilitating the cus-OH cleavage from the PdO(101) surface. Existence of this pathway also suggests the possibility that as the temperature of the H$_2$ adsorbed PdO(101) surface is increased, most of the hydrogen on the surface will combine with lattice cus-O to produce water. This conclusion matches well with experimental results which suggest that approximately 76% of H$_2$ is released from the PdO(101) surface as water. Another high energy pathway described by Blanco-Rey and coworkers is also confirmed by our DFT-D3 calculations, though the 168.8 kJ/mol H$_2$ barrier estimated by our calculations is lower than that reported in Blanco-Rey’s paper. We believe this difference may be due to taking dispersion effects into consideration.

Our calculations to understand the coverage effects of H$_2$ on the surface reveal that only the high energy Blanco-Rey pathway will be viable at the saturation coverage, however, the barrier for the pathway reduces significantly to 136.5 kJ/mol H$_2$ compared with the low coverage barrier. Once again the neighboring hydroxyl groups lower the barrier for cus-OH cleavage from surface but the presence of H-atom on the adjacent cus-Pd increases the electronic repulsion between H-and OH moieties leading to a high energy barrier for H$_2$O formation at saturation coverage. We find that if the H$_2$ coverage on PdO(101) is slightly reduced to 0.26 ML, the hydroxyl disproportionation pathway once again becomes viable. Agreeing to experimental results, our calculations predict that the H$_2$O formation barrier is almost independent of the H$_2$O coverage, the energy barrier for H$_2$O formation at 0.26 ML H$_2$ coverage lies between 91.4 kJ/mol H$_2$ to 96.2
kJ/mol H\textsubscript{2} (not ZP corrected). These results suggest that at saturation coverage, chemisorbed hydrogen will prefer to desorb from the surface as molecular H\textsubscript{2} creating vacant \textit{cus} sites than to oxidize and produce water due to its high formation barrier. Since the Pd-H bond weaker than the O-H bond, H\textsubscript{2} desorption will be preferred from \textit{cus}-sites.
LIST OF REFERENCES


BIOGRAPHICAL SKETCH

Rahul, born in the state of Uttar Pradesh in India, completed bachelor’s degree in chemical engineering from Sardar Vallabhbhai National Institute of Technology, Surat. After gaining experience in information technology in banking and finance domain, he pursued master’s degree in chemical engineering at University of Florida. He graduated from UF in summer 2013 majoring in chemical engineering with thesis.