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How does the oxidation state of palladium surfaces affect the reactivity and selectivity of direct synthesis of hydrogen peroxide from hydrogen and oxygen gases? A density functional study

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ABSTRACT: Direct synthesis of H_2O_2 from H_2 and O_2 is an environmentally benign and atom economic process and as such is the ideal pathway in catalysis. However, currently no low-cost pathway of this kind of catalysis exists although it would be an attractive alternative strategy to the common industrial anthraquinone method for H_2O_2 production. Metal-based catalysts are widely employed in such direct synthesis process, but often need to be oxidized, alloyed or supplied with additives to make them selective. To understand the metal-oxidation state in heterogeneous catalysis, we studied the selective oxidation of hydrogen by molecular oxygen on a $\text{Pd}(\text{111})$ and $\text{PdO}(\text{101})$ surface leading to either H_2O_2 or H_2O products. Our results demonstrate, for the first time, that the oxidized $\text{PdO}(\text{101})$ surface clearly shows better performance and selectivity, as compared to the reduced $\text{Pd}(\text{111})$ one. The activation barrier on the oxidized Pd surface is ca. 0.2 eV lower than the one on the reduced Pd surface. On the oxidized surface, the H_2O_2 synthesis route is preferred while on the reduced surface the H_2O route is predominant. The decomposition of H_2O_2 is also greatly inhibited on the oxidized surface. We analyzed the different pathways in detail through thermochemical cycles, which establishes that the oxidized surface shows weaker adsorption ability toward the reagents O_2 and H_2 , the key intermediate OOH and also the product H_2O_2 in comparison with the $\text{Pd}(\text{111})$ surface, which we believe affect the selectivity. The work presented here clearly shows that the oxidation state of metal surfaces is one of the most important factors that tunes the catalysis of a chemical reaction and can affect the selectivity and reaction patterns dramatically.

1. Introduction

Hydrogen peroxide (H_2O_2) is an environmentally benign oxidant due to its green nature that generates harmless H_2O as the only by-product of an oxygenation reaction. Current use of hydrogen peroxide is not only extensive in the textile industry, but also in pulp and paper manufacture, food, aquaculture, water and wastewater treatment processes, etc.¹ Because of the explosive growth in its utilization over the last three decades, the demand for hydrogen peroxide has increased by >5% per year and is expecting to grow further at this rate until 2023.² Currently, most of the H_2O_2 is produced through the indirect anthraquinone auto-oxidation process developed by Riedl and Pfeleiderer.³ Although this method has the advantages of avoiding direct mixture of H_2 and O_2 and as such is suitable for large-scale and continuous operation, it also has several drawbacks. In particular, the yield encounters complex separation and concentration steps, and economic issues.⁴

Scheme 1. Main reactions and side-reactions involved in the direct synthesis of H_2O_2 from H_2 and O_2 . Process labeled with red color denotes the desirable main reactions.

The direct synthesis of H_2O_2 from O_2 and H_2 , however, is seen as an attractive alternative to the anthraquinone auto-oxidation process and has been extensively studied in recent years.⁴⁻¹³ Unfortunately, as shown in Scheme 1, the formation of H_2O_2 directly from H_2 and O_2 is thermochemically less favorable by $105.8 \text{ kJ mol}^{-1}$ than the formation of H_2O from reactants.⁴ In addition, H_2O_2 is

very reactive, and is easy to hydrogenate or decompose into water. Both of these results indicate that the direct synthesis of H_2O_2 from H_2 and O_2 is a challenging process. Thus, an effective catalyst with high selectivity toward H_2O_2 formation that simultaneously prevents product degradation is highly desirable in the Chemical Industry.¹³

Up to now, many catalysts have been developed for the direct synthesis of H_2O_2 .^{6,7} Often these surface catalysts need to be oxidized or doped in order to stimulate and trigger the reaction. Why and how this is needed remains uncertain and controversial. Supported palladium surfaces are the most-used catalysts since the direct synthesis of H_2O_2 from H_2 and O_2 was first reported in 1914.¹⁴ However, Pd catalysts not only have high activity toward the synthesis of H_2O_2 , but also show a large amount of its hydrogenation and decomposition; therefore, the selectivity of Pd toward H_2O_2 formation is very low. Consequently, a number of methods have been developed to overcome the low H_2O_2 selectivity issue of Pd catalyst. The addition of halides (X^-) and mineral acids is taken as an effective method to improve the H_2O_2 selectivity.¹⁵⁻¹⁹ This was rationalized from adsorption of X^- and H^+ pairs on the sites responsible for the undesired by-products and thereby suppressing the generation of H_2O and enhancing the selectivity toward H_2O_2 formation.²⁰ However, the presence of halides and mineral acids can also facilitate metal leaching and requires to be separated from the product after reaction.²¹ Another and even more effective method is the use of bimetallic catalysts, where the addition of the second metal improves H_2O_2 selectivity.²² PdAu alloy catalysts supported on an acid pretreated carbon material (PdAu/C) were shown to effectively inhibit H_2O_2 hydrogenation thereby leading to improved yields of H_2O_2 . However, the high PdAu activity was unable to fully reproduce on commercial support materials such as SiO_2 and TiO_2 , and hence no industrial applications of the PdAu/C catalysts are known.

Recently, a PdSn bimetallic catalyst supported on TiO_2 or SiO_2 was found to achieve very high selectivity toward H_2O_2 (>95%) formation after an appropriate oxidation-reduction-oxidation heat treatment process.⁷ This catalyst was found to be more economic than PdAu. Moreover, it is not necessary to pretreat the supports by acids and no additives (X^- and acids) were required to be added to carry the industrialization of the direct synthesis of H_2O_2 forward. A detailed characterization by X-ray photoelectron spectroscopy (XPS) demonstrated that Pd^{2+} was the predominant surface species. Once these Pd-Sn catalysts were reduced, the high selectivity toward H_2O_2 was lost, which was ascribed to the reduction of Pd^{2+} into metallic Pd^0 – a well-known effective H_2O_2 degradation catalyst.²³ These results indicate the oxidation state of Pd plays important roles for the selective formation of H_2O_2 .

For the above-mentioned bimetallic PdAu/C catalyst, a further detailed characterization using XPS and aberration-corrected scanning transmission electron microscopy indicated that the majority of Pd is present as Pd^{2+} for the acid pretreated PdAu/C catalysts.²³ However,

metallic Pd increases for the catalyst without acid pretreatment. The high H_2O_2 productivity and low H_2O_2 hydrogenation activity is only observed with the acid pretreated PdAu/C, suggesting the catalyst activity is associated with the oxidation state of Pd. In fact, several other groups have also proposed that oxidized palladium could play a more important role than Pd^0 toward the selective generation of H_2O_2 .²⁴⁻³⁰ However, it is still unclear what role the oxidized palladium plays during the generation of H_2O_2 . For instance, what is the difference in adsorption and fragmentation of O_2 and H_2 on the oxidized Pd surface in comparison with metallic Pd? What determines the activity of oxidized Pd toward the formation and the degradation of H_2O_2 ? These challenging topics are pivotal for understanding the active sites and formation mechanism for the direct synthesis of H_2O_2 . If resolved, it will promote the design of more effective catalysts.

Current computational and mechanistic studies so far have mainly focused on the formation and degradation of H_2O_2 on Pd, Au, or PdAu clusters, monometallic Pd surfaces, and bimetallic PdAu, PdAg surfaces.^{20,31-43} Flaherty and coworkers found the formation of H_2O_2 follow proton-electron transfer mechanisms.⁹ No theoretical studies have been reported on the oxidized palladium with respect to its production of H_2O_2 . In this work we present a detailed periodic density functional theory study on the various pathways of H_2 and O_2 adsorption and dissociation on metallic Pd and PdO surfaces as well as the subsequent steps leading to H_2O_2 and H_2O products and the decomposition of H_2O_2 . In addition, a thermochemical and electronic analysis of the reaction mechanisms have been performed, which highlights the origins of the reactivity differences of PdO vs Pd. Our work ultimately leads to predictions on how to develop catalysts for efficient synthesis of H_2O_2 .

2. Computational Methodology

2.1 Surface models. For polycrystalline Pd, (111) and (100) planes are the principally exposed surfaces. Many experimental studies found that the formation of PdO(101) is preferred during the oxidation of Pd(111) and Pd(100) surfaces by means of *in situ* investigations.⁴⁴ Moreover, DFT studies showed that PdO(101) is a stable low-index surface.⁴⁵ The direct synthesis of H_2O_2 is usually carried out with excess O_2 .^{6,7} Hence, it is reasonable to choose PdO(101) as the model of the oxidized Pd catalyst in this work.⁴⁵ The PdO(101) surface has half of the atoms

Figure 1. Pd(111) and Pd(101) surfaces. The top, bridge, fcc, and hcp site for Pd(111), and the O_{cus} and Pd_{cus} atoms and coordinatively saturated (cs) O and Pd atoms were labeled.

coordinatively unsaturated (cus) on the O and Pd atoms (Figure 1), which may be important in oxidation reactions. As above-mentioned, Pd(111) surface is one of the low-index surface of metallic Pd. Our calculations focus on Pd(111) and PdO(101) surfaces only here.

2.2 Computational details. The periodic DFT slab calculations for H₂O₂ formation on Pd(111) and PdO(101) surfaces were carried out employing the ultrasoft pseudopotentials⁴⁶ and the spin polarized generalized gradient approximation (GGA) exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE),⁴⁷ as implemented in CASTEP suite of programs.⁴⁸ For the optimization of H₂, Pd(111) surface, and H₂ adsorption on the Pd(111) surface, only the spin unpolarized functional was employed. The geometry optimizations were performed with fine accuracy. An energy cutoff of 340 eV and 400 eV was applied for the plane-wave expansion of the electronic eigenfunctions of the Pd(111) and PdO(101) surfaces, respectively. The adopted energy cutoffs for Pd(111) and PdO(101) used here have been extensively tested and validated on analogous systems.^{33,34,49,50} Convergence benchmark test calculations were performed for the energy cutoff of the PdO(101) surface (Table S1 Supporting Information), which confirms our selection of $E_{\text{cut}} = 400$ eV is proper. Recent studies comparing the combined pure DFT and the DFT with Hubbard U correction (DFT + U) procedures on the C-H bond activation of CH₄ on a PdO(101) and PdO(100) surface showed that the accuracy of the calculations was affected little by the Hubbard U correction factor.⁵¹ Therefore, all calculations were carried out by employing standard DFT methods.

The surface Brillouin zone was sampled with a $3 \times 3 \times 1$ Monkhorst-Pack k-point grid for Pd(111), a $4 \times 2 \times 1$ grid for PdO(101), and a gamma point for O₂ and H₂ optimization. The Pd(111) and PdO(101) surfaces were modeled with a periodic four-layer slab with 3×3 and 4×1 unit cells, respectively. In the current work, one O-2Pd-O tri-layer of PdO is defined as a monolayer. Previous studies showed that these thicknesses are sufficient to accurately model the experimental Pd(111) and PdO(101) surfaces.⁴⁹ The periodically repeated slabs were separated with a vacuum thickness of 10 Å for Pd(111) and 20 Å for PdO(101) in order to avoid the neighboring slab interactions along z-axis. The convergence criteria for geometry optimization were set to 0.03 (for the local minima) and 0.05 (for transition states) eV Å⁻¹ for maximum force, 1.0×10^{-5} eV atom⁻¹ for energy, 1.0×10^{-6} eV atom⁻¹ for the SCF, and 0.001 Å for maximum displacement. The top two (three) layers for Pd (PdO) were fully relaxed whereas the bottom two (one) layers were fixed at the corresponding bulk positions. The linear and quadratic synchronous transit (LST/QST) complete search method was employed to identify the transition states. A Bader charge analysis was performed using the code developed by Henkelman and co-workers.^{52,53} If there was no special statement, the discussion was based on Mulliken charge analysis. The lattice constant for bulk Pd was predicted to be 3.93 Å, and $a = b = 3.11$ Å and $c =$

5.44 Å for PdO, respectively, which is in good agreement with the experimental values of 3.89 Å⁵⁴ and $a = b = 3.04$ Å, $c = 5.34$ Å.⁵⁵

The adsorption energy (E_{ads}) of X₂, X₂ = H₂ or O₂, on the Pd(111) and PdO(101) surfaces is defined as in Eq 1 with $E(\text{slab-X}_2)$ the bound complex and $E(\text{X}_2)$ and $E(\text{slab})$ the isolated X₂ and slab energies, respectively.

$$E_{\text{ads}} = E(\text{slab-X}_2) - [E(\text{X}_2) + E(\text{slab})] \quad (1)$$

The d-band center was calculated as the first moment of the projected d-band density of states on the surface atoms relative to the Fermi level.

3. Results

3.1 O₂ and H₂ adsorption and dissociation. For the direct synthesis of H₂O₂, the active forms of O₂ and H₂ on surfaces are the first key problem to be considered. Previous isotope labeling experiments have confirmed that the generation of H₂O₂ is derived from molecular oxygen rather than from the dissociated atomic oxygen.⁵⁶ Once O₂ dissociates, it mainly leads to the production of side-product H₂O, which is not desirable for the synthesis of H₂O₂. As such, the dissociation of O₂ is one of the pivotal factors controlling the selectivity of the H₂O₂

Figure 2. O₂ and H₂ adsorption and dissociation on Pd(111) and PdO(101) surfaces with bond distances in angstroms and energies in eV. (a) The most favorable O₂ adsorption geometries; (b) The dissociation of O₂ on Pd(111) surfaces; (c) The most favorable H₂ adsorption geometries; (d) The dissociation of H₂ on a PdO(101) surfaces.

production at the initial stage. On the other hand, H₂ dissociation is essential for the formation of H₂O₂.

Our initial studies focused on the adsorption and dissociation of O₂ and H₂ on the Pd(111) and PdO(101) surfaces and the results are given in Figure 2. We tested many possible binding orientations, see Tables S2 and S3 (Supporting Information), but will only report the lowest in energy here. Thus, the most favorable adsorption of O₂ on Pd(111) is in a top-bridge configuration with one oxygen atom at the top site of Pd and the second one lying in a gap between two Pd atoms. The adsorption energy is estimated to be -1.16 eV. Binding of O₂ leads to elongation of the O–O bond distance to 1.376 Å as compared to the free molecule that has a distance of 1.238 Å. These distances in the bound form match metal-superoxo bond lengths calculated previously and implies that O₂ is highly activated after its adsorption on Pd(111) and binds as a Pd-superoxo.^{57,58} A Mulliken analysis demonstrates that -0.40 e is transferred to O₂ from Pd(111), which further confirms O₂ is highly activated.

Dioxygen dissociation on the Pd(111) surface gives an O–O interaction at 1.837 Å in the transition state (see Figure 2b) with a barrier of 0.70 eV. Previous studies reported a barrier of 0.67 eV, 0.77 eV, and 0.75 eV,^{34,59,60} therefore our result matches the literature well. The O₂ dissociation on a Pd(111) surface is exothermic by -1.03 eV thereby confirming the feasibility of O₂ dissociation on the Pd(111) surface.

On PdO(101) surfaces, we investigated O₂ adsorption on Pd_{cus} and Pd_{cs}, respectively. However, the most favorable adsorption of O₂ is on the bridge Pd_{cus} sites along the Pd row with an adsorption energy of -1.25 eV, which is 0.09 eV higher than that found on the Pd(111) surface. It appears, therefore, that the adsorption of O₂ on PdO(101) surface is a little stronger than that on the Pd(111) surface. However, a short O–O distance of 1.325 Å was obtained. The charge distribution gives a total charge on O₂ of -0.26 e, which is 0.14 e less than the O₂ bound complex on Pd(111). These results suggest that O₂ is less activated on PdO(101) than on Pd(111). Additionally, the Bader charge of adsorbed O₂ is 0.43 e, which implicates that the adsorbed O₂ is in a superoxo-like state.

Subsequently, the dissociation of O₂ on the PdO(101) surface was studied. The dissociation of O₂ on PdO(101) is a high energy process that is endothermic by 1.81 eV and no O₂ dissociation barrier could be calculated. Our calculations imply that the dissociative adsorption of O₂ on Pd(101) is not favorable, which is consistent with previous experimental findings as well as DFT studies.⁶¹

In the case of H₂ adsorption, the calculated results indicate that H₂ prefers dissociative adsorption on Pd(111) with a binding energy of -1.39 eV (Figure 2c), in agreement with previous reports about the spontaneous hydrogen dissociation.⁴³ By contrast, H₂ is adsorbed in molecular form on the top site of Pd_{cus} in PdO(101) surface with an energy of -0.53 eV (Figure 2c, right panel, and Table S3). H₂ lies parallel along the Pd_{cus} row with a H–H

distance of 0.834 Å. Both the adsorption energy and H–H distance indicate the adsorption of H₂ on PdO(101) surface is much weaker than that on Pd(111). Starting with the mentioned favorable adsorption configuration as the reaction entrance (denoted as path I), we investigated H₂ dissociation on the PdO(101) surface and located a transition state (¹TS_{I,PdO}), with its geometry shown in Figure S3. The corresponding barrier and reaction energy are 0.33 eV and 0.23 eV, respectively. The endothermic nature of the dissociation along this pathway implies that the molecularly adsorption is more preferable.

Subsequently, we tested whether the dissociated H atoms can directly migrate to the top site of the O_{cus} atoms. We find this H atom migration process requires an energetic barrier of 0.68 eV with a reaction energy of -1.10 eV. In addition, the alternative dissociation pathway was investigated for comparison (denoted as path II, Figure 2d). This process starts with the adsorption of H₂ perpendicular to the Pd rows which is 0.08 eV higher in energy than the parallel adsorption one. However, the H₂ dissociation pathway occurs through the elongation of the H–H bond where one H atom is kept on the top of the Pd_{cus} site, while the other one transfers to the neighboring oxygen atom. The energy barrier for this process is 0.38 eV, which is comparable with the one for path I. On the other hand, the reaction energy is exothermic with -0.86 eV, indicating that the dissociation of H₂ along this pathway is thermodynamically favorable.

3.2 Formation Mechanism of H₂O₂. Based on the results of H₂ and O₂ adsorption and dissociation, we studied the reaction of H₂ with O₂ on Pd(111) and PdO(101) surfaces. Previous work on the hydroperoxy (OOH) species identified it as a key intermediate during the vapor-phase reaction of H₂ and O₂ on Au/TiO₂ employing inelastic neutron scattering spectroscopy.⁶² Therefore, the OOH species is generally proposed to be the key intermediate for the synthesis of H₂O₂. Here, the hydrogenation of O₂ to generate the OOH species is taken as the first reaction step. As such, the hydrogenation of OOH may lead to the production of H₂O₂ (denoted as H₂O₂ channel). All the processes with respect to the breaking of the O–O bond are acknowledged as the main factors that control the selectivity of the direct synthesis process, for instance, OOH and H₂O₂ decomposition.^{34,41} Therefore, to inspect the H₂O₂ selectivity issues, the dissociation of OOH by O–O bond cleavage resulting in the formation of H₂O (denoted as H₂O channel) and the decomposition of H₂O₂ were both calculated.

3.2.1 Reactivity on the Pd(111) surface. As can be seen in Figure 3, adsorbed O₂ reacts with an adsorbed hydrogen atom at the start of the reaction resulting in the formation of an OOH species. The energetic barrier (TS_I) is estimated to be 0.68 eV, which is comparable with the O₂ dissociation of 0.70 eV. As such, the formation of the OOH species and the dissociation of O₂ are competitive processes on the Pd(111) surface. Consequently, the selectivity toward the generation of H₂O₂ will be low. On the other hand, since the OOH species can be formed, it

Figure 3. The energy profiles for the reaction of O₂ with H₂ on Pd(111) surface. The formation of H₂O₂ is labeled by red color. The energies are in eV unit.

may subsequently abstract another H atom to generate the main product H₂O₂ via **TS2** or alternatively lead to the breaking of the O–O bond via **TS3** and yield a hydroxyl species and atomic oxygen. The barriers of these two steps are estimated to be 0.58 eV (**TS2**) and 0.11 eV (**TS3**), respectively. If atomic hydrogen is present in the vicinity of the OOH species, it will assist the dissociation of the OOH species and lead to the formation of water by one concerted step (via **TS4** in Figure 3) with a barrier of only 0.03 eV. With these results in mind, after the formation of the OOH species, the most favorable step refers to the concerted dissociation of OOH and simultaneously formation of water rather than the formation of H₂O₂. Once H₂O₂ forms, it easily dissociates into two hydroxyl radicals with a barrier (**TS5**) of 0.48 eV. The present results indicate that the minimum energy pathway for the reaction of H₂ and O₂ on a Pd(111) surface leads to the dissociation of OOH and the formation of side product H₂O. Consequently, the calculations predict little or no formation of H₂O₂ on a pure Pd(111) surface, which is consistent with Lunsford's reports that almost no H₂O₂ was formed without the presence of additives.⁶³

3.2.2 Reactivity on the PdO(101) surface. In view of the discussion on O₂ and H₂ adsorption of the PdO(101) surface, it follows that the preferential binding will be on the Pd_{cus} sites. Although the dissociation of H₂ may be feasible, it will require a barrier of 0.38 eV. Therefore, we only consider molecularly adsorbed O₂ and H₂ on the Pd_{cus} sites. The reaction of O₂ and H₂ on the PdO(101)

surface is displayed in Figure 4. As can be seen, the formation of the OOH species has a negligible barrier (**TS6**) of only 0.03 eV, which is 0.65 eV lower in energy than the one calculated for the Pd(111) surface. Therefore, the PdO(101) surface is more favorable for the formation of OOH species with respect to the Pd(111) surface. The reaction energy for this step is –0.39 eV. The formed OOH species is preferentially located on the top site of Pd_{cus} on the PdO(101) surface with the hydroxyl group positioned over an adjacent bridge site and the O–H bond pointing away from the surface (structure **IM6** in Figure 4). For the subsequent formation of H₂O₂, we considered the participation of a second molecule of H₂ on an adjacent Pd_{cus} site neighboring the non-hydrogenated oxygen atom. The energy barrier for the second hydrogen atom transfer is estimated to be 0.46 eV via **TS7**, which is higher in energy than the one found for the OOH formation step. However, it is still 0.09 eV lower in energy than the analogous transition state found for the Pd(111) surface. Moreover, the released energy that accompanies the adsorption of O₂ and H₂ will compensate for the high energy barrier. For the decomposition of the OOH species into atomic oxygen and a hydroxyl radical, a barrier (**TS8**) of 1.33 eV was determined. By contrast, on the Pd(111) the barrier was only 0.11 eV (**TS3** in Figure 3). In the case of OOH decomposition in the presence of adsorbed H₂, similar to the results on the Pd(111) surface, the break of O–O bond and the formation of H₂O happens simultaneously. The barrier for concerted H₂ insertion into OOH via **TS9** has a barrier of 1.40 eV, while a much

lower value was obtained on a pure Pd(111) surface. These results indicate that OOH decomposition will not be favored on the PdO(101) surface and H₂O will be an unlikely product. Decomposition of H₂O₂ requires a barrier of 0.77 eV, which is well higher in energy than both the formation of OOH and H₂O₂ reactions. In summary, the main reaction leading to the production of H₂O₂ is the most favorable pathway on PdO(101) surface.

As mentioned above, the elementary steps for the formation of H₂O₂ involve the hydrogenation of O₂ to yield the key intermediate OOH, and the further hydrogenation of OOH to generate the product H₂O₂. A comparison of the H₂O₂ formation potential energy surfaces of the processes on either the PdO(101) or Pd(111) surface reveals that both steps proceed on the PdO(101) surface with lower energy barriers. These results implicate that the formation of H₂O₂ on a PdO(101) surface will be much easier than that on a Pd(111) surface. The main side reactions accompanying the generation of H₂O₂ refer to the breaking of the O-O bond, i.e., the dissociation of O₂, the decomposition of the key intermediate OOH, and the decomposition of the main product H₂O₂. The barrier for the dissociation of O₂ on the Pd(111) surface is 0.70 eV, which is competitive with its hydrogenation process (0.68 eV). By contrast, the dissociative adsorption of oxygen on the PdO(101) surface is well higher in energy than the most stable adsorption state, so that the dissociation of O₂ on the PdO(101) surface will be unlikely. Consequently, the Pd(111) and PdO(101) surfaces are fundamentally different and react with substrates to form different products. In the Discussion section we will analyze the differences between the surfaces in detail.

4. Discussion

As shown in this work Pd(111) and PdO(101) surfaces efficiently react with O₂ and H₂ gas to form products; however, on the Pd(111) surface the reaction mostly gives water, whereas on the PdO(101) surface H₂O₂ is obtained in significant amounts. The formation of H₂O₂ was experimentally observed by Adzic and co-workers when catalysts with lower binding activity toward O₂ were employed in oxygen reduction reaction,⁶⁴ which is consistent with our computational results. The balance of the pathways leading to either H₂O or H₂O₂ will depend on the adsorption of reactants (O₂ and H₂), the cleavage energy of the O-O bond in O₂/OOH/H₂O₂ and their binding strength to the metal surface.

Nørskov and co-workers proposed that the weighted center of the d-band (ϵ_d) (the average energy of the d electrons) of surface metal plays a vital role in determining the surface reactivity.^{65,66} Previous DFT and experimental studies established that the adsorption energies and reactivity of small adsorbents correlate well with the position of ϵ_d on metal surfaces.^{67,68} A surface with ϵ_d closer to the Fermi level generally gives a higher activity towards the binding of adsorbents. By contrast, a surface with ϵ_d shifting away from Fermi level often shows lower activity toward the adsorption of molecules. As such, we compared the ϵ_d value of Pd atoms on Pd(111) and PdO(101) surfaces. Our calculations give ϵ_d values of -2.01 eV and -2.84 eV relative to Fermi level for Pd(111) and PdO(101), respectively. According to the d-band center theory, it is easier to infer that PdO(101) has lower activity toward the binding of reactant substrates and species formed during the reaction. This is in line with our calculated results that both O₂ and H₂ are less activated on PdO(101) in comparison with on Pd(111).

Similarly, we find that the OOH species on PdO(101) are

Figure 4. The energy profiles for the reaction of O₂ with H₂ on PdO(101) surface. The formation of H₂O₂ is labeled by red color. The energies are in eV unit.

also less activated than on Pd(111). The O–O bond distance of OOH is only 1.410 Å (see **IM6** in Figure 4) on PdO(101) while it is elongated to 1.516 Å (see **IM1** in Figure 3) on Pd(111). Moreover, the charge of OOH is –0.20 e on PdO(101) and –0.31 e on Pd(111), which further confirms a lesser activation of OOH on PdO(101). For the H atoms adsorbed on Pd(111) and PdO(101), we find a charge-transfer of –0.13 e and –0.10 e, respectively (see Tables S7 and S9). The present results suggest less electron transfer from the PdO(101) surface to the adsorbed H atoms as compared to the Pd(111) surface. This can be rationalized by a comparison of the work functions for the two surfaces. Values of 5.083 eV for PdO(101) and 4.971 eV for Pd(111) are found, hence the work function for PdO(101) is 0.112 eV higher than that of Pd(111). Consequently, the escape of electrons from PdO(101) surface will more difficult than that from Pd(111) making PdO(101) less active than Pd(111). The change in work function is beneficial to inhibit the O–O bond cleavage in O₂/OOH/H₂O₂ and results in the favorable formation of H₂O₂. Moreover, the electron transfer from the Pd/PdO substrate to the anti-bonding orbitals of the O–O species promotes the splitting of O–O bonds. The higher d-band energy corresponds to the stronger electron donating ability and thus the higher O–O splitting activity. The higher d-band center of Pd(111) which denotes the higher d-band energy in comparison with PdO(101) confirms its high activity toward the splitting of O–O bonds, which is adverse for the selective formation of H₂O₂. The passivation of Pd by oxygenation will weaken its activity toward O–O species and thus facilitate the selective formation of H₂O₂.

In addition, the spatial arrangement of the PdO(101) surface is probably also relative to the lower activity towards the breaking of the O–O bond. Our calculations reveal that the dissociation of OOH and H₂O₂ is easier on surfaces with hollow Pd sites, which are more prevalent on Pd(111) than PdO(101) surfaces. As a consequence, the PdO(101) surface gives selectivity towards H₂O₂ formation, while on Pd(111) the dioxygen bond breaks and water is the dominant product. Indeed, the high selectivity of PdAu alloy catalyst reported before is also attributed to the spatial arrangement of the surface atoms.³¹ Thus, DFT calculations showed that an active Pd atom surrounded by lesser active Au atoms gives enhanced reaction barriers for O–O bond cleavage.³¹ Furthermore, addition of hydrogen halides as additives were also shown to block the active site for H₂O₂ degradation and hence enhanced the selectivity for H₂O₂ product formation.²⁰ However, we will emphasize that half of the O and Pd atoms on the PdO(101) surface are coordinatively unsaturated. Pd_{cus} possesses a coordination vacancy which plays a decisive role in oxidation chemistry. This unique structure of Pd_{cus} is only found in the oxidized Pd surfaces. Looking back at Figure 4, every elementary step takes place at these Pd_{cus} sites. Previous studies had also confirmed that PdO surface shows superior activity toward alkane oxidation, CO oxidation and methanol oxidation.⁴⁴ Hence, it is reasonable to infer that the oxidation state instead of

other factors in PdO(101), e.g., steric hindrance, plays a key role in improving its H₂O₂ selectivity.

To gain further insight into the mechanistic details of the reaction of O₂ and H₂ on Pd(111) and PdO(101) surfaces, we calculated thermochemical cycles for substrate (O₂ and H₂) binding, their dissociation into bound-atoms and their coupling into products. Figure 5 displays calculated energetics for O₂ and H₂ binding to either Pd(111) and PdO(101). In all cases O₂ and H₂ bind with high exothermicity to the metal surfaces and hence are strongly bound. Subsequently, we calculated the dissociation of O₂ on the metal surfaces. On the Pd(111) surface the O₂ dissociation is exothermic with 258.2 kJ mol^{–1}; however, it is endothermic by 174.9 kJ mol^{–1} on the PdO(101) surface. Consequently, dioxygen on a Pd(111) surface will quickly decompose into atoms, whereas it will not decompose on the PdO(101) surface. The same is seen for H₂ binding to these two surfaces, whereby the Pd(111) gives highly exothermic hydrogen splitting into atoms. On the other hand, H₂ dissociation is endothermic by only 22.6 kJ mol^{–1} on the PdO(101) surface and hence may be feasible. Therefore, dioxygen and hydrogen binding to Pd(111) or PdO(101) will lead to completely different adsorption patterns. In particular, the Pd(111) will lead to quick decomposition of O₂ and H₂, which will not be the case on the PdO(101) surface.

Figure 5. Binding energies (in kJ mol^{–1}) of O₂ and H₂ on Pd(111) (top) or PdO(101) (bottom) and the subsequent atomization.

Subsequently, we investigated the pathways leading to H₂O₂ and H₂O formation on the Pd(111) and PdO(101) surfaces and the results are given in Figure 6. As mentioned above in Figure 5, on the Pd(111) surface both O₂ and H₂ will decompose into atoms. Thus, a surface bound H-atom at the Pd(111) surface can react with an incoming O₂ molecule to form HOO radicals. It is endothermic by 234.8 kJ mol^{–1}. This OOH radical can then attack another surface-bound H-atom to form H₂O or H₂O₂. The former reaction is exothermic by 276.9 kJ mol^{–1}, while the latter is endothermic by 95.2 kJ mol^{–1}. Consequently, on the Pd(111) surface an OOH radical will react with surface bound H-atoms to form H₂O and no hydrogen peroxide should be formed through this pathway. These thermochemical values of isolated species are in line with the full reaction mechanism reported above in Figure 3.

Figure 6. Thermochemical pathways for the synthesis of H_2O and H_2O_2 from O_2 and H_2 on Pd(111) (top) and PdO(101) surfaces. Reaction energies are given in kJ mol^{-1} .

Next, the formation of H_2O and H_2O_2 on the PdO(101) surfaces was investigated. On this surface, dioxygen will not dissociate and will be present as Pd-superoxo form. Thus in a reaction with free H_2 products OOH and surface bound H-atoms in an endothermic reaction step. However, it is much less energetically demanding by 130.9 kJ mol^{-1} than those on Pd(111). In the following step this pair splits into H_2O and surface bound oxygen-atoms with an exothermicity of 254.7 kJ mol^{-1} or alternatively pair up to form hydrogen peroxide with an exothermicity of 122.5 kJ mol^{-1} . These thermochemical cycles are consistent with the DFT studies reported above, and indicate the formation of H_2O on PdO is still the thermodynamically more favorable process than H_2O_2 . However, it needs to conquer a much higher barrier (1.40 eV) compared with H_2O_2 (0.46 eV). Therefore, H_2O formation on PdO is kinetically unfavorable. As such, on the PdO(101) surface we predict dominant hydrogen peroxide products and lesser amount of water.

The difference between the Pd(111) and Pd(101) surfaces in H_2O_2 synthesis can be easily understood from a comparison of Figures 5 and 6. HOO reacts with a surface-bound H-atom by H-atom abstraction. However, in the case of Pd(111) the binding energy of H-atoms is considerably stronger than for the PdO(101) surface. Thus, H_2 easily dissociates into surface-bound H-atoms on Pd(111) and hence are strongly bound to the surface. By contrast, the reaction is endothermic on the PdO(101) surface. Then, the reaction of HOO with a surface-bound H-atom (Figure 6) will require the cleavage of a very strong Pd-H bond on the Pd(111) surface to form H_2O_2 . On the other hand, HOO can react with a surface-bound H-atom to form H_2O and form a stronger surface-bound O-atom.

It is worth to note that many factors can affect the oxidation state of Pd beyond oxygenation. Hutchings and co-workers²³ reported that predominant Pd^{2+} species can be obtained after calcination of PdAu catalysts supported on the acid pre-treated carbon. However, on the acid untreated supports, the catalysts exhibit both Pd^{2+} and

Pd^0 . With different electronegativity, alloying is another method to modify the oxidation state of Pd.³² The heat treatment procedure with different atmosphere (H_2 , O_2 or air) can also change the oxidation state. With appropriate oxidation-reduction-oxidation heat treatment cycle, Pd^{2+} is confirmed as the predominant surface species for PdSn catalysts. These Pd^{2+} species was found play important roles for the selective generation of H_2O_2 . However, the anion associated with Pd^{2+} is not clear. Usually, the catalysts used for the direct synthesis of H_2O_2 were calcined in air at the last preparation step. Moreover, the synthesis of H_2O_2 is performed in excess O_2 . XRD verified the formation of PdO.⁶⁹ Thus, PdO may be one of the important oxidized forms of Pd. Recently, employing operando X-ray absorption spectroscopy (XAS) and online flow injection analysis, Selinsek and co-workers observed that H_2 can dissolve in Pd resulting in the PdH_x formation.⁷⁰ The added mineral acids combined with halides (X^-) can oxidize Pd by dissolving nanoparticles.^{56,71} Thus, the oxidized Pd may also exhibit as PdH_x , PdX^- or else.¹⁰ All these oxidized Pd may contribute to the improvement of the H_2O_2 selectivity with new mechanistic features. Additionally, the effect of the coverage species on catalyst surface, such as the adsorbed X^- , toward the selectivity of H_2O_2 is not well understood. All these issues will be further investigated in our future work.

Finally, a point should be made regarding the change of palladium into a different oxidation state. Thus, for iron containing monooxygenases, such as the cytochromes P450, molecular oxygen on an iron-heme center is selectively converted to water and a high-valent iron(IV)-oxo heme cation radical species.⁷²⁻⁷⁴ However, by selective protonation and reduction, an uncoupling reaction leading to hydrogen peroxide becomes available. This pathway is energetically unfavorable over the water formation pathway,⁷⁵ similar to what is seen here for the Pd(111) vs PdO(101) system. By affecting the kinetics of the proton transfer, it was shown that the uncoupling reaction could become kinetically feasible.⁷⁵ The same applies to the palladium systems described here. Furthermore, modeling of the P450 reactivity patterns showed that oxygen atom transfer is faster for the iron(IV)-oxo heme cation radical species than its one-electron reduced species,^{74,76} which is in support of the calculations reported here that efficient H_2O_2 formation is achieved through the oxidized form of the catalyst.

5. Conclusion

In conclusion, we studied the reaction of O_2 and H_2 gas on Pd(111) and PdO(101) surfaces using density functional theory methods. We obtain completely different reactivity patterns on the two surfaces, whereby the reaction on the Pd(111) surface leads to the formation of H_2O products, whereas on the PdO(101) surface H_2O_2 is the dominant product. Furthermore, not only the activity toward the H_2O_2 production is higher but this pathway also shows much lower activity toward the undesirable side reactions,

such as the dissociation of O₂, and OOH and H₂O₂ products. This indicates that PdO(101) has higher activity and selectivity toward H₂O₂ as compared to Pd(111). We attribute this high performance of PdO(101) to its special electronic and geometrical structures. The down-shift of ϵ_d of Pd atoms in PdO(101) results in their weak interaction with binding adsorbents (whether O₂, H₂, OOH, or H₂O₂), and further suppresses these adsorbents from dissociation and promotes the formation of hydrogen peroxide. The special geometrical structures isolate unsaturated Pd atoms as arrays and thus block the O-O bond break process. Additionally, the high performance of PdO(101) could also be understood by thermodynamical differences of the Pd(111) and Pd(101) surfaces toward the binding of reaction substrates and the pathways for the synthesis of H₂O and H₂O₂. The present results provide new insights into the active oxidation state of palladium for the direct synthesis of H₂O₂ from H₂ and O₂ and have more implications for the catalyst design.

ASSOCIATED CONTENT

Supporting Information. Supporting Information containing detailed absolute and relative energies as well as geometric data and Cartesian coordinates are given and is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.

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