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DFT Calculations of the Adsorption States of O₂ on OH/H₂O-Covered Pt(111)

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Abstract

The adsorption of O₂ on Pt(111) was studied with Density Functional Theory calculations. Various adsorbed states of O₂ were evaluated on clean and OH/H₂O-covered Pt(111) surfaces at the solid/gas and solid/liquid interfaces. The results reveal that the adsorption of O₂ on OH/H₂O-covered Pt(111) surface starts with the physical adsorption of O₂. Two other adsorption states are reachable from the physisorbed state, the end-on, and bridging chemisorbed O₂. Analysis of the energetics of these adsorption states shows that O₂ physically adsorbed at the OH/H₂O-covered Pt(111) surface is a high energy state that requires activation to transition to the end-on chemisorbed O₂ state. On the other hand, the end-on chemisorbed state can transition to the bridging chemisorbed state with only a small activation energy when a nearby Pt adsorption site is available. Frequency analysis of the physisorbed, end-on, and bridging adsorption states shows that adsorbed O₂ stretching frequencies are close to 1400, 1300, and 900 cm⁻¹, respectively.

Graphical Abstract

Keywords

Electrochemical adsorption; ORR catalysis; Hydrogen fuel cell; Computational electrochemistry; Physisorbed O₂

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1. Introduction

Many experimental and theoretical works have been conducted to elucidate the reaction mechanism of the Oxygen Reduction Reaction (ORR) over metal surfaces. The research work has been mainly on Pt and Pt-based surfaces due to their high activity and stability toward the ORR.¹ The extensive experimental and theoretical data have revealed many atomic-level details, in particular for the gas-phase adsorption and dissociation of O₂ on Pt surfaces.²⁻⁶ At the Pt-electrode/electrolyte interface, the experimental data concerning the adsorbed state of the initial intermediate species in the ORR (O₂_{ads}, O₂⁻_{ads}, and O₂²⁻_{ads}) are more limited.^{7,8} Adzic and Wang studied the inhibition of ORR on Pt(111) electrodes with Ag adatoms and showed that O₂ adsorbed at a bridge site.⁸ An important step forward to characterize the adsorbed state of the initial intermediate species at the Pt/electrolyte interface has been the identification of an O₂ stretching band at 1005-1016 cm⁻¹.⁷ Employing surface-enhanced infrared reflection and adsorption spectroscopy (SEIRAS) in an attenuated reflection mode (ATR), Shao *et al.* studied the ORR on Pt electrodes in alkaline media.⁷ They assigned the observed band at 1005-1016 cm⁻¹ to superoxide intermediates (O₂⁻_{ads} occupying a bridge site on the Pt surface. Their findings represented the first experimental evidence of O₂-molecular entities adsorbed on Pt-electrodes under electrochemical conditions.

Kunimatsu *et al.* observed an infrared (IR) absorption band at 1400-1403 cm⁻¹ associated with the appearance of ORR current at the Pt/Nafion interface under a humidified O₂ atmosphere.⁹ The band was absent under N₂ atmosphere and insensitive to the change from H₂O to D₂O humidification, leading the authors to assign the band to the O₂ stretching vibration of adsorbed molecular oxygen O₂(_{ads}). The presence of the band at potentials as high as +1.1 V vs. reversible hydrogen electrode (RHE) eliminates the possibility that the band could be due to adsorbed superoxide O₂⁻. The authors proposed a tilted end-on orientation of an adsorbed and partially charged (-0.5e) O₂-molecular entity on the Pt surface as the species responsible for the IR band at 1400-1403 cm⁻¹.⁹ Since such a band has not been observed before on well-defined platinum surfaces, a final assignment was not given. A similar band was reported by Melendres *et al.* in an early work on iron-phthalocyanine adsorbed on copper and gold.¹⁰ Melendres *et al.* also noticed the disappearance of the band during O₂ reduction. More recently, peaks centered at 1400 cm⁻¹ have been reported during the heterogeneous Fenton catalytic reaction of LaFeO₃.¹¹

Density Functional Theory (DFT) calculations have played an important role in identifying the possible adsorbed states of the initial intermediate species in the ORR at the platinum/electrolyte interface.¹²⁻²³ Three adsorption state of O₂ at the Pt/water interface have been identified: i) physisorbed O₂,^{12,13} ii) end-on chemisorbed O₂¹³⁻¹⁵ (so-called Pauling model²⁴), and iii) bridging chemisorbed O₂.^{13,14,16-23,25-27} The first two states have been seen in calculations with micro-solvated environments, where only a few water molecules are employed to simulate the water phase.^{13,15} The bridge chemisorbed O₂ has been found as the most stable adsorbed state in agreement with the experimental data.^{7,8}

In the present work, DFT calculations are employed to study O₂ adsorbed on Pt(111). Several adsorbed states of O₂ were evaluated on clean and OH/H₂O-covered Pt(111)

surfaces under solid/gas and solid/liquid conditions. The computational results reveal a physisorbed state of O₂ on OH/H₂O-covered Pt(111) that exhibits a O-O stretching frequency at 1405 cm⁻¹.

2. Methodology

The binding energies and the site preference of O₂ on Pt(111) at the solid/gas and solid/liquid were determined employing cluster and supercell periodic models. Note that binding energies with positive values indicate that the bound O₂-Pt state is lower in energy than the unbound state. All calculations were carried out using the DMol³ software package.²⁸ Double numerical quality basis sets with polarization functions (DNP)²⁸ were used to expand the Kohn-Sham orbitals. The calculations were performed with spin-polarized Perdew-Burke-Ernzerhof (PBE)²⁹ exchange-correlation functional. The PBE functional does not properly account for weak interactions and the calculated binding energies for O₂ on Pt are expected to be underestimated, particularly for any physisorbed state. There are multiple methods^{30,31} to better account for weak interactions, but such methods are beyond the scope of the present study.

The Pt(111) cluster models have a 54-atom Pt cluster, with 18 atoms per layer. The Pt(111)/water interface was simulated by adding 22 water molecules on top of the Pt cluster (Figure 1), as in our previous studies.³²⁻³⁷ All calculations were performed with charge-neutral conditions, where the total charge of the cluster model was set to $q = 0$. A different number of adsorbed OH (or H₂O) were included in the cluster model to simulate the Pt(111) surface under ORR electrochemical conditions.³⁸ The Pt-Pt bond distances in the metal clusters were initially set at the bulk experimental value (cell parameter $a = 3.92$ Å). Relaxation was allowed for the top Pt layer, the OH, H₂O, and O₂ molecular species. In another set of calculations, the Pt(111)/water interface was simulated with a supercell model containing 18 Pt atoms and 22 water molecules. Calculations with the supercell model were performed to confirm the findings from the cluster models.

3. Results and discussion

First, the adsorption of O₂ on a clean Pt(111) surface at the solid/gas interface was studied. The identified stable adsorption states of O₂ on a clean Pt(111) surface are shown in Figure 2. The three expected adsorption states were found: physisorbed O₂, end-on chemisorbed O₂, and bridging chemisorbed O₂. The bridging chemisorbed O₂ is the top-bridge-top (t-b-t) configuration; the top-fcc-bridge (t-f-b) and top-hcp-bridge (t-h-b) configurations were not stable during geometry optimization and converged to the t-b-t configuration. The calculated binding energies for the physisorbed O₂, end-on chemisorbed O₂, and bridging chemisorbed O₂ states are 0.52, 9.08, and 15.85 kcal/mol, respectively. The end-on and bridging chemisorbed O₂ states are significantly more energetically stable than the physisorbed O₂ state on a clean Pt(111) surface. In the physisorbed state, O₂ is at 4.13 Å from the nearest Pt site; see Table 1. In the chemisorbed states, either one or both oxygens in O₂ is at 2.1 Å from the Pt site. Our results for the binding energy of these adsorption states of O₂ on a clean Pt(111) surface are in reasonable agreement with previous calculations,¹³ where values of 1.66 kcal/mol and 10 kcal/mol were found for the physisorbed O₂ and bridging chemisorbed

O₂, respectively. The physisorbed O₂ has been detected on Pt(111) at the solid/gas phase at temperatures below 45 K.^{2,39-42} The experimental binding energy of physisorbed O₂ on Pt was estimated to be ca. 2.8 kcal/mol at 45 K.⁴⁰ As expected, the calculated binding energy for physisorbed O₂ on Pt is underestimated because the PBE functional does not properly account for weak interactions.

The ORR takes place in the presence of multiple oxygenated adsorbates (e.g., O_{ads}, OH_{ads}, H₂O_{ads}).^{43-45,1,46,38} Therefore, the potential ORR needs to be simulated on metal surfaces that account for the blocking effects of oxygenated adsorbates. The initial step in the ORR, the adsorption of O₂ on an OH_{ads}/H₂O_{ads}-covered Pt(111) surface, has been studied. A hexagonal structure of OH_{ads}/H₂O_{ads} was chosen, because it is the characteristic structure of adsorbed OH and H₂O on the (111) plane of metal surfaces at the solid/gas^{47,48} and solid/liquid interfaces.^{14,38,46,49}

The binding energies and O-Pt nearest-neighbor distances for various adsorbed states of O₂ on OH-covered Pt(111) at the solid/gas interface are included in Table 1. Results are included for the adsorption of O₂ when there are either five or six adsorbed OH on the Pt surface. In the case of six adsorbed OH on the Pt surface, only the physisorbed and end-on chemisorbed O₂ states were identified. The physisorbed O₂ is at the center of the OH_{ads}-hexagon at a distance of 2.98 Å from the HO_{ads} groups and at 4.34 Å from the free Pt surface site. The binding energy of the physisorbed state is 0.58 kcal/mol on the Pt surface with six OH_{ads} at the solid/gas interface, which is similar to the binding energy of physisorbed O₂ on the clean Pt surface. The chemisorbed O₂ is on the free Pt atoms at the center of the OH_{ads}-hexagon with a tilted end-on orientation; the O-Pt distance is 2.33 Å, and the O-O distance is 1.242 Å. The end-on chemisorption of O₂ on the free Pt site at the center of the OH_{ads}-hexagon requires an activation energy of 4.35 kcal/mol; see Figure 3a. Such activation energy is higher than the corresponding values for the chemisorption of O₂ on the clean Pt surface, which is close to 1.2 kcal/mol.¹³ Furthermore, the end-on chemisorbed state is 3.39 kcal/mol more energetically stable than the physisorbed state on the Pt surface with six OH_{ads} at the solid/gas interface. On the clean Pt surface, the end-on chemisorbed O₂ state is 8.6 kcal/mol more stable than the physisorbed state. The six OH adsorbed on the Pt surface lowers the binding energy of the end-on chemisorbed state. A reduction of the number of adsorbed OH from six to five results in an end-on chemisorbed state that is more stable than the physisorbed state; see Table 1.

The present results reveal a physisorbed state of O₂ on the OH-covered Pt(111) surface at the solid/gas interface. To study the stability of such state on the metal surface under electrochemical conditions, a water cluster representing a liquid environment was introduced onto the metal cluster model. In the model, the Pt(111) surface is covered by four OH_{ads} and one H₂O_{ads}, providing two free Pt sites for the bridging chemisorbed O₂ state. Figure 4 shows the adsorbed states of O₂ on OH/H₂O-covered Pt surface at the solid/liquid interface. The calculated binding energy for the physisorbed O₂, end-on chemisorbed O₂, and bridging chemisorbed O₂ states are 0.41, 1.07, and 4.45 kcal/mol, respectively. At the electrochemical interface and with fewer OH_{ads} on the Pt surface (four OH_{ads}), the activation energy for the chemisorption of O₂ is 1 kcal/mol (see Figure 3b), which is considerably lower than that of the OH-covered Pt surface at the solid/gas interface (see Figure 3a). The chemisorbed O₂

state is lower in energy than the physisorbed O_2 state on the OH/ H_2O -covered Pt surface at the solid/liquid interface. Physisorbed O_2 is at the center of the OH/ H_2O_{ads} hexagonal ring at 3.70 Å from the free Pt site. The chemisorbed O_2 is on one of the free Pt atoms at the center of the hexagonal OH/ H_2O_{ads} ring with a tilted end-on orientation. The O_2 -Pt distance is 2.24 Å and the O-O distance is 1.24 Å. Both physisorbed and chemisorbed O_2 are nearly neutral with a calculated atomic Mulliken charges of -0.11 and -0.12, respectively. On the other hand, the bridging chemisorbed O_2 has a calculated Mulliken charge of -0.38. The end-on chemisorbed O_2 on the OH/ H_2O_{ads} -covered Pt surface at the solid/liquid interface can transition to the bridging chemisorbed site by a rotating. The activation energy for the rotating transition from end-on to bridging chemisorbed O_2 is estimated to be below 0.6 kcal/mol. The bridge chemisorbed state is 3.38 kcal/mol more stable than the end-on chemisorbed state. The present results agree with the previous results showing the bridging configuration as the energetically lowest state.^{12,13,20,21,26,27}

In Table 1, the calculated O-O stretching frequency is included for the different adsorption states of O_2 on the clean, OH- and OH/ H_2O -covered Pt(111) surface at the solid/gas and solid/water interfaces. For the physisorbed O_2 , the calculated stretching frequencies are in the range of 1452 – 1405 cm^{-1} , depending on the OH/ H_2O -coverage and the type of interface. For the end-on chemisorbed O_2 , the calculated O-O stretching frequency is within the range of 1304 – 1229 cm^{-1} , also depending on the OH/ H_2O -coverage and the type of interface. In the case of the bridging chemisorbed O_2 , the O-O stretching frequency is in the range of 967 – 917 cm^{-1} . The calculated O-O stretching frequency for isolated O_2 in the gas phase is 1568 cm^{-1} , in agreement with the experimental value of 1556 cm^{-1} .⁵⁰ Physisorbed O_2 has been detected on Pt(111) at the solid/gas phase at temperatures below 45 K.^{2,39-42} The vibrational frequency of physisorbed O_2 on Pt (1548 cm^{-1}) is lower, by 8 cm^{-1} , than the gas-phase value.⁴² The calculated stretching frequency of the physisorbed O_2 at different interfaces is in very good agreement with the 1400 cm^{-1} band observed at the platinum/Nafion interface.⁹ The stretching frequency of O_2 in the bridging configuration is in agreement with the observed value 1005 – 1016 cm^{-1} in alkaline solution.⁷

4. Conclusions

In the present work, DFT calculations have been performed to study the adsorption of O_2 on the Pt(111). Pt(111) was simulated as OH/ H_2O -covered surfaces. The computational results reveal three adsorbed states of O_2 on OH/ H_2O -covered platinum surfaces: physisorbed O_2 , tilted end-on chemisorbed O_2 , and bridging chemisorbed O_2 . The physisorbed O_2 displays a stretching frequency close to 1400 cm^{-1} , in line with the band observed by Kunimatsu *et al.*⁹ at 1400-1403 cm^{-1} . The physisorbed state of O_2 is favorable only when the Pt surface is covered with adsorbed OH/ H_2O . As the surface coverage decreases, the tilted end-on chemisorption of O_2 becomes energetically favorable because there is less repulsion between O_2 and the adsorbed OH/ H_2O . Our results suggest that the tilted end-on chemisorbed state of O_2 should have an IR-band around 1300 – 1200 cm^{-1} . However, the tilted end-on chemisorbed state of O_2 is expected to be an extremely short-lived intermediate that transitions to a bridging chemisorbed state via a low energy rotation. These results show the blocking effects of adsorbed OH/ H_2O on the ORR. Adsorbed OH/ H_2O blocks the Pt pair active sites, preventing the O_2 adsorption in the bridging site.

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Figure 1. Cluster models of the a) Pt(111)/water interface with b) absorbed OH_{ads} and H₂O_{ads} and two available adsorption sites.

Figure 2.

a) Physisorbed, b) end-on chemisorbed, and c) bridging chemisorbed O_2 states at the Pt(111)/gas interface. The binding energy (kcal/mol) is included for each state.

Figure 3. Interaction energy O_2 on covered Pt(111) surface at the a) solid/gas and b) solid/water interface as a function of the Pt- O_2 distance. Inserted figures display the end-on chemisorbed and physisorbed O_2 states.

Figure 4.

a) Physisorbed, b) end-on chemisorbed, and c) bridging chemisorbed O_2 states at the Pt(111)/water interface with four adsorbed OH_{ads} and one adsorbed $\text{H}_2\text{O}_{\text{ads}}$. The end-on chemisorbed and bridging chemisorbed O_2 states are more strongly bound than the physisorbed state.

Table 1.

Calculated O₂ stretching frequency, binding energy, and O-Pt distance for various adsorbed states of O₂ on OH/H₂O-covered Pt(111) at the solid/gas and solid/water interfaces. Note that at the solid/water interfaces, calculations were performed with cluster models and models under periodic boundary conditions.

Adsorbed state of O ₂	Adsorbed OH and H ₂ O	O ₂ stretching frequency (cm ⁻¹)	Binding Energy (kcal/mol)	Pt-O ₂ distance (Å)
Pt(111)/Gas interface				
Physisorbed O ₂	0 OH _{ads}	1450	0.52	4.13
End-on chemisorbed O ₂	0 OH _{ads}	1229	9.08	2.13
Bridge chemisorbed O ₂	0 OH _{ads}	967	15.85	2.12
Physisorbed O ₂	6 OH _{ads}	1452	0.58	4.34
End-on chemisorbed O ₂	6 OH _{ads}	1301	-2.81	2.33
Physisorbed O ₂	5 OH _{ads}	1440	1.05	4.06
End-on chemisorbed O ₂	5 OH _{ads}	1277	1.96	2.33
Bridge chemisorbed O ₂	5 OH _{ads}	930	13.23	1.34
Pt(111)/water interface				
Physisorbed O ₂ ^a	6 OH _{ads}	1414	0.25	4.24
End-on chemisorbed O ₂ ^a	6 OH _{ads}	-	-8.74	2.33
Physisorbed O ₂	4 OH _{ads} , 1 H ₂ O _{ads}	1405	0.41	3.70
End-on chemisorbed O ₂	4 OH _{ads} , 1 H ₂ O _{ads}	1304	1.07	2.30
Bridge chemisorbed O ₂	4 OH _{ads} , 1 H ₂ O _{ads}	917	4.45	2.10

^aCalculations performed with the Solid/water interface modeled with periodic boundary conditions.