**A first principles investigation
on the interaction of oxomolybdenum porphyrin with O₂
– Oxomolybdenum porphyrin as a catalyst for oxygen reduction –**

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We investigated the interaction of oxomolybdenum porphyrin (MoO(por)) with O₂ by using first principles calculations. Our calculations indicate that the adsorbed O₂ on MoO(por) does not take an end-on configuration, but a side-on configuration to become more stable. These results can be understood from the differences in the molecular orbital energies and the valence electron densities. The geometric parameters of MoO(por) and MoO(por)(O₂) with a side-on configuration of O₂ are in good agreement with experimental results. [DOI: 10.1380/ejssnt.2006.630]

Keywords: Density functional calculations; Oxygen; Oxomolybdenum porphyrin; side-on; end-on

I. INTRODUCTION

In the 21st century, one of the most important tasks of the international community is to cut back on the emission of gases that cause global warming. Reducing carbon dioxide being emitted to the atmosphere from vehicles directly contributes to the prevention of global warming. The most viable candidate to overcome global warming is to replace gasoline or diesel engines with Polymer Electrolyte Fuel Cells (PEFC). However, PEFCs is not commercially viable at present because of the problems with hydrogen production, hydrogen storage, hydrogen transport infrastructure, and the high cost of a PEFC system. The largest factor is the price of platinum used in both the anode and cathode of PEFCs. We have been studying various alternative catalyst systems for reducing the amount of platinum used in these electrodes [1–4]. One class of catalysts we focus on is metalloporphyrins, which can be artificially synthesized [5, 6].

We have studied metalloporphyrins as a catalyst for non-platinum cathode electrode. In our previous theoretical calculations [1, 7], it has been understood that it is possible to cleave the O-O bond of the adsorbed O₂ on metalloporphyrin by controlling the velocity of the O₂ molecule approaching the complex. However, it is actually difficult to control the velocity of the O₂ molecule, and cleave the O-O bond by interacting the O atom of the adsorbed O₂ molecule with the C atom in the por-

phyrin ring. So, we focus attention on another complex, the oxomolybdenum porphyrin(MoO(por)), which forms the longer O-O bonds after the O₂ molecule is adsorbed. It is experimentally known that oxomolybdenum porphyrins undergo reactions with O₂ to form their dioxygen complexes [8, 9]. Experimental results by X-Ray Diffraction (XRD) clarify that the O₂ adsorbed in oxomolybdenum porphyrins take a side-on configuration, and the O-O bond length of the adsorbed O₂ is longer than that of gaseous O₂ [10]. On the other hand, O₂ adsorbed in metalloporphyrins (without the oxo group) ordinarily takes an end-on configuration, and their O-O bond hardly increases in length [1, 11, 12].

We think that an increase in the O-O bond length weakens the O-O bond and, thus, makes the formation of water by the reaction of the isolated O atoms with protons and electrons easier.

Our interests in this study are why the O₂ adsorbed in oxomolybdenum porphyrins take a side-on configuration, and how the energy levels of molecular orbitals in oxomolybdenum porphyrin change after the adsorption of O₂. To clarify these, first principles calculations are applied to both MoO(por) and its dioxygen complexes. From the calculation results, we discuss the stability of the reaction with respect to the molecular orbitals.

II. COMPUTATIONAL DETAILS

The calculations were performed using the first principles simulation code Vienna *ab initio* simulation package (VASP) [13–16]. Vanderbilt ultrasoft pseudopotentials

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FIG. 1: The structures of MoO(por) (a) and its dioxygen complexes with (b) side-on configuration and (c) end-on configuration. Mo refers to the molybdenum atom in the center of the porphyrin ring, and N1, N2, N3, and N4 are the nitrogen atoms, and O1, O2, and O3 are the oxygen atoms. The white spheres are carbon atoms, and the other small spheres are hydrogen atoms. The optimized structures for the Mo complex with side-on O₂ result in configurations such that N1 is eclipsed by O1, and N3 is eclipsed by the bond between O2 and O3 as shown in the top view of (b). On the other hand, those complexes with end-on O₂ configurations have O1 located between N1 and N2, and a carbon atom eclipsed by O3 as shown in the top view of (c).

[17, 18] supplied with the code were used to represent the ion core of the atoms. Pseudopotentials for molybdenum, where the semi-core *p* states are treated as valence, were used. Well-converged cutoff energies of 400 eV were used to expand the plane wave basis. The Perdew-Burke-Ernzerhof (PBE) functional [19, 20] was adopted for gen-

eralized gradient approximation (GGA). Self-consistent structure relaxations were performed with respect to total energy by conjugate-gradient (CG) [21, 22] optimization for all atomic coordinates as well as for the supercell volume. The supercell containing MoO(por) or its dioxygen complexes was constructed as 20 Å × 20 Å × 20 Å unit cells,

TABLE I: Structural parameters and binding energies of MoO(por) and its dioxygen complexes. The bond lengths are in Å, angles in degrees, and binding energy in eV. "Cal" gives the calculated structural parameters in this work and "Exp" gives the experimental structural parameters by XRD [10, 24]. The symbols Mo, O1, N1, N2, N3, and N4 are the same meaning as Fig. 1(a). M-N_p shows the average of the distances between M and the planes formed by all 3-atom combinations of the 4 nitrogen atoms, N1, N2, N3, and N4.

Complex	MoO(por)		MoO(por)(O ₂)		
			Side-on		End-on
Bond lengths	<i>Cal</i>	<i>Exp</i> [24]	<i>Cal</i>	<i>Exp</i> [10]	<i>Cal</i>
Mo-O1	1.69	1.656(6)	1.71	1.697(13)	1.71
Mo-O2			1.98	1.945(18)	1.98
Mo-O3			1.98	1.948(19)	3.08
Mo-N1	2.14	2.113(9)	2.27	2.256(7)	2.20
Mo-N2	2.14	2.110(11)	2.17	2.116(7)	2.18
Mo-N3	2.14	2.104(9)	2.43	2.320(6)	2.21
Mo-N4	2.14	2.115(10)	2.17	2.121(7)	2.19
Mo-N _p	0.635	0.6389(8)	1.04	1.00	0.86
O2-O3			1.42	1.42(3)	1.32
Bond angles	<i>Cal</i>	<i>Exp</i> [24]	<i>Cal</i>	<i>Exp</i>	<i>Cal</i>
<O1-Mo-N1	107	105.54(41)	78		84
<O1-Mo-N2	107	109.57(41)			
<O1-Mo-N3	107	107.73(42)			
<O1-Mo-N4	107	107.55(40)			
<O2-Mo-N3			73		79
<O3-Mo-N3			73		
<Mo-O2-O3					137
Binding energy	0.000		0.611		-0.153

so that the molecules are not influenced by molecules in the neighboring unit cells. In order to estimate the total energy of the isolated system in a vacuum from the small supercell calculations, we made all direction dipole and quadrupole corrections in the total energy [23].

III. RESULTS AND DISCUSSION

We performed full geometry optimizations for MoO(por), MoO(por)(O₂) with side-on O₂, and MoO(por)(O₂) with end-on O₂. Optimized geometries of these complexes are shown in Fig. 1. N1, N2, N3, and N4 are the nitrogen atoms, and O1, O2, and O3 are oxygen atoms. The white spheres are carbon atoms, and the other small spheres are hydrogen atoms. The optimized structures for the MoO(por) with side-on O₂ result in a configuration such that N1 is eclipsed by O1, and N3 is eclipsed by the bond between O2 and O3 as shown in the top view of Fig. 1(b). On the other hand, the complex with end-on O₂ configuration has O1 located between N1 and N2, and a carbon atom eclipsed by O3 as shown in the top view of Fig. 1(c).

Table 1 summarizes the structural parameters of MoO(por), MoO(por)(O₂) with side-on O₂, and MoO(por)(O₂) with end-on O₂. The bond lengths are in Å, angles in degrees, and binding energy in eV. The "Cal" column gives the calculated structural parameters, and the "Exp" column gives the experimental structural parameters determined by X-Ray Diffraction (XRD). The symbols Mo, O1, N1, N2, N3, and N4 have the same

meaning as in Fig. 1. Mo-N_p shows the average distances between M and the planes formed by all 3-atom combinations of the 4 nitrogen atoms (N1, N2, N3, and N4). Experimental structural parameters in MoO(por) are from MoO(tpp) [24, 25]. It is found that the calculated geometry of MoO(por) is in good agreement with the experimental results by XRDs. For MoO(por)(O₂) with side-on O₂, the two bonds, Mo-N1 and Mo-N3, are eclipsed by the oxo and peroxy ligands, and these bond lengths are slightly longer than those of the other two bonds, Mo-N2 and Mo-N4. The bond length of Mo-O2 and that of Mo-O3 are completely equal, and both are longer than that of Mo-O1. The O2-O3 bond length is 1.42 Å. We think that MoO(por) may serve as potential catalysts for O-O bond cleavage since this bond length is longer than that of gaseous O₂. Compared with MoO(por), the Mo atom moves about 0.4 Å out of the N-plane because of attraction to O₂. These bond lengths and the configuration are almost equal to those of MoO^{IV}(tmp)(O₂) obtained by XRD [10, 25] though the complex used in their experiment has four mesityl groups. The structural parameters of MoO(por)(O₂) with end-on O₂ are also shown in Table 1 for reference.

Figure 2 gives molecular orbital energy diagrams and schematic valence electron densities for MoO(por), MoO(por)(O₂) with a side-on O₂, and O₂ in the order from left to right. Fig. 3 gives those for MoO(por), MoO(por)(O₂) with an end-on O₂, and O₂. The energy is measured from the vacuum level. For each molecule, the left hand side of the molecular orbital energy diagram shows molecular orbitals for α -spin electrons, and

FIG. 2: Molecular orbital energy diagrams and schematic valence electron densities for MoO(por), MoO(por)(O₂) with a side-on O₂, and O₂ in the order from left hand side to right hand side. The energy is measured from vacuum level. For each molecule, the left hand side of the molecular orbital energy diagram shows molecular orbitals for α -spin electrons, and the right hand side shows molecular orbitals for β -spin electrons. The schematic electron densities of $\alpha(\beta)$ -HOMO, $\alpha(\beta)$ -HOMO-1, and $\alpha(\beta)$ -HOMO-2 of MoO(por) and MoO(por)(O₂) are drawn with a contour surface cutoff of 0.003 electrons/Å³.

FIG. 3: Same as Fig. 2 but for MoO(por), MoO(por)(O₂) with an end-on O₂, and O₂.

the right hand side shows molecular orbitals for β -spin electrons. The schematic electron densities of $\alpha(\beta)$ -HOMO, $\alpha(\beta)$ -HOMO-1, and $\alpha(\beta)$ -HOMO-2 of MoO(por) and MoO(por)(O₂) with a side-on O₂ are drawn with a contour surface cutoff of 0.003 electrons/Å³.

We now analyze the results by molecular orbitals. For

MoO(por), it was found that the $\alpha(\beta)$ -HOMO are mainly made of the d -orbitals of Mo atom, the $\alpha(\beta)$ -HOMO-1 are mainly made of the p -orbitals of C the atoms and the N atoms in the porphyrin ring. For MoO(por) (O₂) with a side-on O₂, the $\alpha(\beta)$ -HOMO are mainly the π^* orbitals of the adsorbed O₂, and the $\alpha(\beta)$ -HOMO-1 are the p -orbitals

of C atoms and N atoms -just as in the case of MoO(por). On the other hand, for MoO(por) (O₂) with end-on O₂, both the $\alpha(\beta)$ -HOMO and the $\alpha(\beta)$ -HOMO-1 are mainly the π^* orbitals of the adsorbed O₂. The electron densities of $\alpha(\beta)$ -HOMO-2 in MoO(por), MoO(por) (O₂) with a side-on O₂, and MoO(por) (O₂) with an end-on O₂ are almost same. These observations suggest that electron charge is transferred from MoO(por) to O₂, thereby populating the antibonding states of O₂ and weakening the O-O bond. Electrons transfer from the *d*-orbitals of the Mo atom to the π^* orbitals of the coming O₂ occurs during the side-on adsorption of O₂ on MoO(por), whereas electrons transfer from both the *d*-orbitals of the Mo atom and the *p*-orbitals of C atoms and N atoms to the π^* orbitals of the O₂ coming occurs during the end-on adsorption of O₂. This is explained by the symmetry between the orbitals of MoO(por) and the π^* orbitals of the coming O₂ with the orientation. For MoO(por) with a side-on O₂, the resonance integral between the $\alpha(\beta)$ -HOMO of MoO(por) and the π^* orbitals of the coming O₂ hybridizes into the new orbitals by the symmetry of their molecular orbitals, whereas those between the $\alpha(\beta)$ -HOMO-1 or the $\alpha(\beta)$ -HOMO-2 and the π^* orbitals become zero. For MoO(por) with an end-on O₂, the resonance integral between the $\alpha(\beta)$ -HOMO or the $\alpha(\beta)$ -HOMO-1 of MoO(por) and the π^* orbitals of the coming O₂ hybridizes into the new orbitals by the symmetry of their molecular orbitals, whereas those between the $\alpha(\beta)$ -HOMO-2 and the π^* orbitals become zero.

Next, we discuss the difference in energy between MoO(por) and two kinds of Mo dioxygen complexes. In comparison with the $\alpha(\beta)$ -HOMO of MoO(por), the α -HOMO of MoO(por) (O₂) with a side-on O₂ becomes more stable by about 0.924 eV after adsorption of O₂ and β -HOMO stabilizes by about 1.190 eV as shown in Fig. 2. With regards to the $\alpha(\beta)$ -HOMO-1 and the $\alpha(\beta)$ -HOMO-2, the energy levels after adsorption of O₂ hardly change. On the other hand the α -HOMO of MoO(por) (O₂) with end-on O₂ becomes more stable by about 0.744 eV after adsorption of O₂ and β -HOMO stabilizes by about 1.000 eV as shown in Fig. 3. However, the α -HOMO-1 of MoO(por) (O₂) with end-on O₂ becomes more unstable by about 0.462 eV after adsorption of O₂ and the β -HOMO-1 destabilizes by about 0.490 eV. The energy levels of the $\alpha(\beta)$ -HOMO-2 after adsorption of O₂ hardly change. We think that the difference in the bonding energies between MoO(por) (O₂) with a side-on and an end-on O₂ results primarily from the difference in the change of energy levels of the $\alpha(\beta)$ -HOMO-1. These results explain from the aspect of the molecular orbital energetics that O₂ take a side-on configuration upon reaction with MoO(por) to become more stable.

We are currently investigating the reactions of other oxometalporphyrins with O₂. Our calculation results confirmed that some other oxometalporphyrins also adsorb O₂ with a side-on configuration, and the O-O bond

length also increases after adsorption.

IV. CONCLUSION

We investigated the interaction of MoO(por) with O₂ by using first principles calculations. Our calculated geometries for MoO(por) and MoO(por)(O₂) with a side-on O₂ agree with experimental results by XRD. Our calculations further indicate that the adsorbed O₂ on MoO(por) does not take an end-on configuration, but a side-on configuration to become more stable. This result is in agreement with XRD experiments on oxomolybdenum porphyrin dioxygen. These results are explained as follows: for MoO(por) with a side-on O₂, the electrons in $\alpha(\beta)$ -HOMO, which are mainly made of the *d*-orbitals of the Mo atom, transfer to the π^* orbitals of the coming O₂ to become more stable, but the electrons in other orbitals stay the same. On the other hand, for MoO(por) with an end-on O₂, both the electrons in $\alpha(\beta)$ -HOMO and $\alpha(\beta)$ -HOMO-1 transfer to the π^* orbitals of the coming O₂; in the process, the $\alpha(\beta)$ -HOMO becomes more stable but the $\alpha(\beta)$ -HOMO-1 becomes unstable. We think that the difference of the bonding energies between MoO(por) (O₂) with a side-on and an end-on O₂ results primarily from the difference in the change of energy levels in the $\alpha(\beta)$ -HOMO-1. We think that MoO(por) is a potential cathode for PEFC since it increases the bond length and increases electron density in the antibonding states of O₂.

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