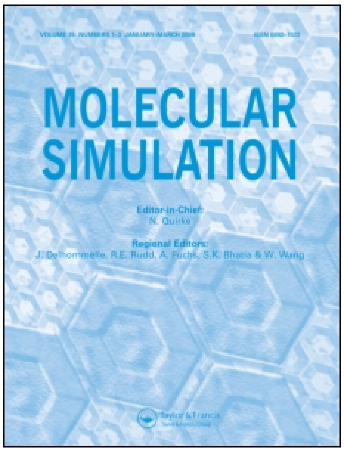

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Density functional theory study of the adsorption of oxygen molecule on iron phthalocyanine and cobalt phthalocyanine

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Iron phthalocyanine (FePc) and cobalt phthalocyanine (CoPc) molecules have been studied in the past as possible catalysts for oxygen reduction reactions. In this work, density functional theory (DFT) computation results of oxygen molecule (O_2) adsorption on FePc and CoPc molecules are reported. For O_2 on FePc, both end-on and side-on configurations are found to be energetically favourable but the end-on adsorption configurations are more stable than the side-on configurations. Moreover, our results predicted that compared to those in the end-on configuration, the adsorbed O_2 molecules in the side-on configuration have weaker O—O bonds, which led us to believe that the side-on configurations would be more active in catalysing oxygen reduction reaction. In contrast, we found that only end-on configurations are energetically stable for O_2 on CoPc. Based on our DFT calculation results and the corresponding experimental observations, we postulate that on the surface of transition metal phthalocyanine catalyst molecules the side-on adsorption of O_2 molecules could promote four-electron oxygen reduction process while the end-on adsorption of O_2 molecules would facilitate two-electron oxygen reduction process.

Keywords: density functional theory; oxygen reduction; adsorption

1. Introduction

It is of great significance to find high-performance electrocatalysts that contain less or no precious metal Pt for low-temperature fuel cell devices [1–3]. Cobalt (Co) and iron (Fe) macrocycles have been studied extensively as catalysts for oxygen reduction [4–16]. Co-phthalocyanine (CoPc) and Co-tetrasufonated phthalocyanine (CoTsPc) adsorbed on carbon surfaces have been found to catalyse two-electron reduction of O_2 to form H_2O_2 in both alkaline and acid solutions, while Fe-phthalocyanine (FePc) and Fe-tetrasufonated phthalocyanine (FeTsPc) catalyse the overall four-electron reduction in alkaline solutions [5–9]. In an acid solution, certain face-to-face Co-porphyrins, which can form a dioxygen bridge between the Co—Co centres on graphite surface, have been shown to catalyse four-electron reduction [10–12]. A planar bi-cobalt complex adsorbed on graphite substrates also catalyses the four-electron reduction of oxygen in alkaline solutions [13]. The catalysis mechanism of transition metal phthalocyanines is assumed as follows: first oxygen molecules are adsorbed on the central metal atoms, then electrons would transfer from that central metal atom to the adsorbed O_2, followed by oxygen reduction reaction (ORR) to form H_2O or H_2O_2 [17]. It was experimentally found that FePc and CoPc exhibit better catalytic performance for ORR than other transition metal phthalocyanines [18]. Prior research suggested that a heat-treated mixture of the two different types of catalyst molecules (FePc and CoPc) could lead to even higher catalytic activity as compared to those of each the components [19]. Despite much progress in developing FePc and CoPc as fuel cell electrocatalysts [20,21], deeper fundamental understanding is needed in order to increase the catalytic activity and structure stability of these catalyst molecules for practical applications [22].

To optimise the catalytic performance of transition metal phthalocyanines in fuel cells, theoretical investigations into the pathways of ORR on these catalysts molecules are essential. Density functional theory (DFT) method has been successfully applied in studying many catalysts and their catalytic activity in fuel cells [23,24]. However, the mechanism of transition metal phthalocyanines for ORR at a molecule level is little studied and not well understood. During the first step of ORR on transition metal phthalocyanine catalyst molecules, an oxygen molecule is adsorbed on one of the catalyst molecules and its O—O bond is stretched (and thus weakens that bond). DFT calculations are able to predict the energetically optimised structure for this essential step. Shi and Zhang [25] have conducted systematical DFT calculations to determine the adsorption structures of oxygen molecule on various metal porphyrins and metal phthalocyanines. They found that the central metal, ligand and substituents are major factors in affecting

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oxygen adsorption on those macrocyclic molecules [25]. Distinct from that prior study, our current work focuses on elucidating the details of the adsorption of oxygen molecule on FePc and CoPc molecules. We find that depending on the orientation of the oxygen molecule there are different optimised and stable adsorption configurations, which were not distinguished in [25]. Moreover, we propose a possible explanation, based on our theoretical results, on why four-electron reduction process is often observed for FePc but not for CoPc catalyst molecules.

2. Computational method

DFT calculations were performed using the Materials Studio® DMol^3 module from Accelrys (Materials Studio 4.1, DMol^3, Accelrys Inc., San Diego, CA, USA). We used the generalised gradient approximation of Perdew and Wang [26] for exchange and correlation and double numeric basis with polarisation functions as atomic basis set. We employed density functional semi-core pseudopotentials, which were generated by fitting all electron relativistic DFT results, to reduce the computation cost. Spin-unrestricted wavefunctions and Fermi orbital occupations were used in our calculations. The energy convergence for geometry optimisation was set to be 1×10^{-5} eV.

3. Results

3.1 Isolated molecules

First, we conducted a full structure optimisation for isolated FePc, CoPc and O_2 molecules using DFT method. Figure 1 shows the molecule structure of FePc (or CoPc) after optimisation. We found that the isolated FePc and CoPc molecules assume an exactly planar structure at their minimal energy configuration. Table 1 gives some calculated properties of these optimised FePc and CoPc molecules. Compared to experiments [27,28], our calculations over-predict the distance ($D_{\mathrm{M-N}}$) between the central metal atom and its nearest neighboring N atom (atom N9, N18, N27 and N36 as marked in Figure 1) by 1.1% for FePc and 1.0% for CoPc. The agreement between theory and experiments is remarkable, considering that the FePc and CoPc are in crystalline state in experimental samples but are assumed as equilibrium isolated states in our calculations. Shown in Table 1, previous DFT calculations [25] lead to a little better agreement with experiments in predicting $D_{\mathrm{M-N}}$. The difference between our results and those from the previous work is the exchange and correlation parameterisation employed: [25] used VWN-BP functional while we used Perdew and Wang (1991) functional.

Our results in Table 1 indicate that the central transition metal atom in FePc and CoPc molecules are positively charged through Mulliken atomic population analysis [29]. The Fe atom in FePc would have more positive charges than the Co atom in CoPc.

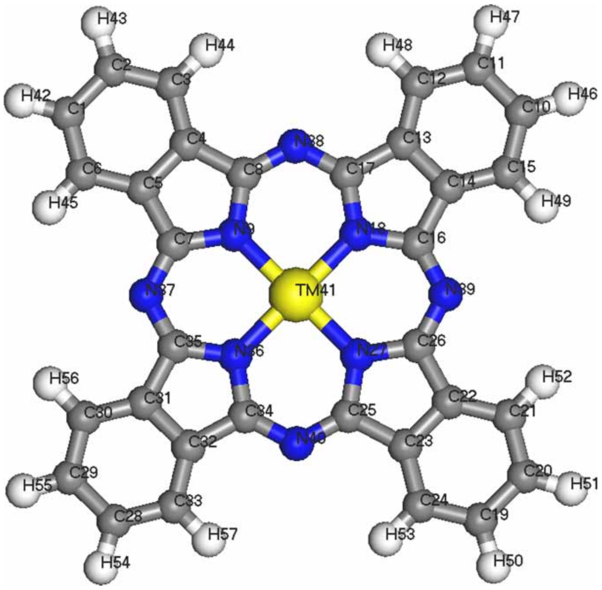

Figure 1. Molecular structure of FePc and CoPc catalysts. The central yellow ball represents metal Fe or Co atom, blue balls represent N atoms, gray balls represent C atoms and light white balls represent H atoms.

For an O_2 molecule, our calculation yields a bond length of 1.225 Å and a bonding energy of 6.77 eV. In comparison, experimental data of gas oxygen molecules are 1.21 Å [30] for bond length and 5.12 eV [31] for bond energy. There is a noticeable difference between our prediction and experimental data of the O_2 bond energy. As pointed out in an early work [32], this problem stems mainly from the error in calculating the energy of the free O atom and hence is not expected to have a significant effect on the calculated energy of O_2 adsorption on catalysts molecules.

3.2 Adsorption of O_2 on FePc and CoPc

The first step of ORR is the adsorption of O_2 on the central transition metal atoms of the FePc and CoPc molecules. The adsorption energy (E_{ad}) of O_2 on FePc (or CoPc) molecule is defined as follows:

$$E_{\mathrm{ad}} = (E_{\mathrm{O_2}} + E_{\mathrm{Ml}}) - E_{\mathrm{Ml-O_2}}, \quad (1)$$

where $E_{\mathrm{Ml-O_2}}$ is the energy of the optimised structure of O_2 adsorbed on FePc (or CoPc) molecule, while $E_{\mathrm{O_2}}$ and E_{Ml} are the energies of the isolated O_2 and FePc (or CoPc) molecules. Therefore, positive adsorption energy indicates that the O_2 molecules would be energetically favourable to be adducted to the surface of the FePc or CoPc catalysts, while negative adsorption energy indicates that O_2 molecules would not prefer contacting with the FePc

Table 1. Calculated distance ($D_{\mathrm{M-N}}$) between the central metal atom and its nearest neighbouring N atom and calculated Mullikan charge of the central metal atom for the equilibrium FePc and CoPc molecules.

	$D_{\mathrm{M-N}}$ (Å)			
	This work	Expt.	Other works	Mullikan charge of metal atom
FePc	1.949	1.928[a]	1.923[b]	0.475
CoPc	1.930	1.910[c]	1.917[b]	0.215

For comparison, experimental measurements ([27,28]) and other theoretical results ([25]) are also included in the table.[a] [27]. [b] [25]. [c] [28].

or CoPc catalysts. Consequently, positive adsorption energy of O_2 is a requirement for the catalysts to promote ORR.

There are two possible fashions for O_2 to be adsorbed on those molecules: end-on configuration (Pauling model [33]) and side-on configuration (Griffiths model [34]). In an end-on configuration (see Figure 2(a) and (b)), one oxygen atom lies right above the central metal atom over the catalyst molecule plane and the other oxygen atom is farther away from the metal atom. In a side-on configuration

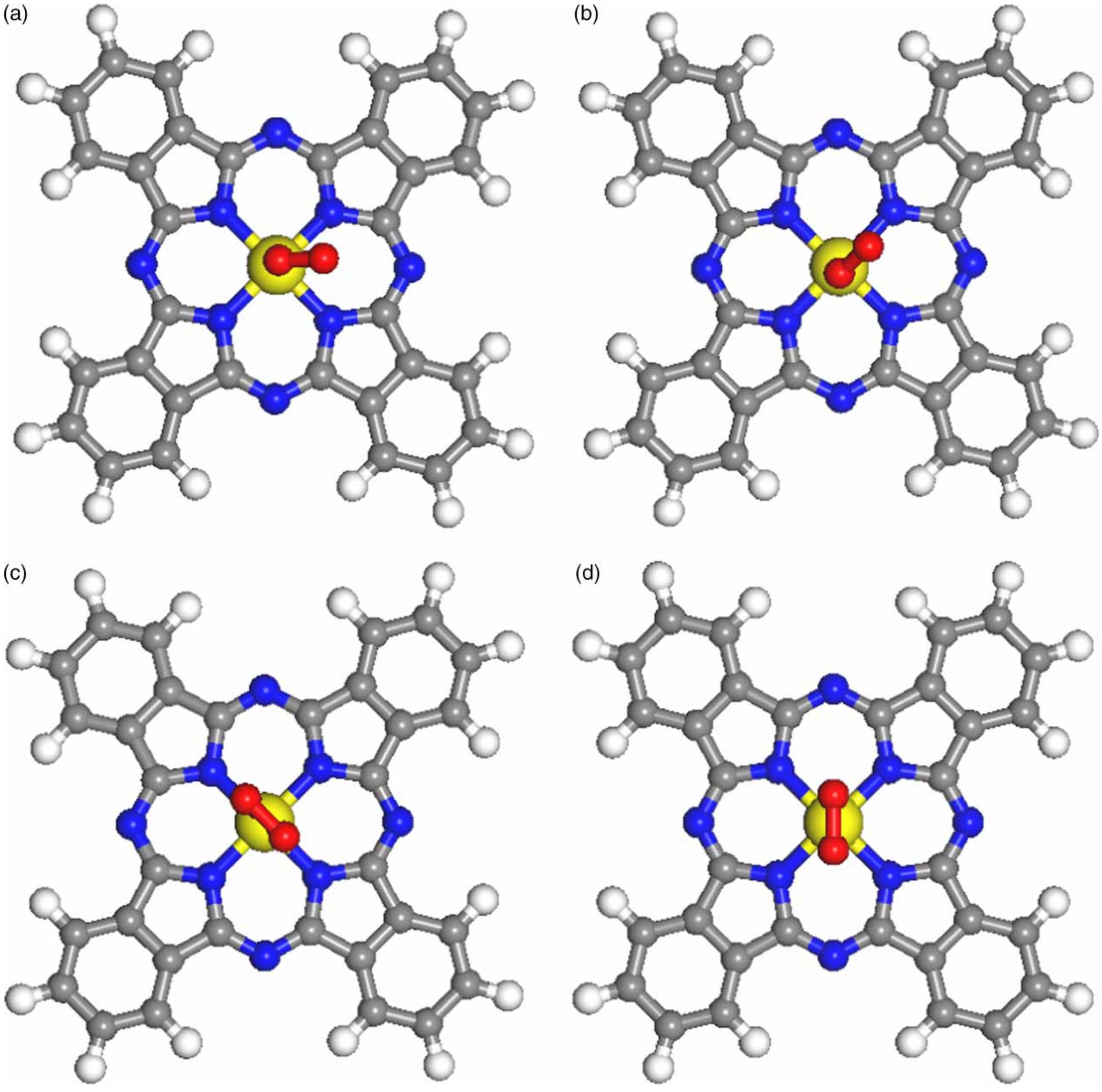

Figure 2. Optimised structural configurations for oxygen molecule adsorbed on FePc and CoPc molecules. (a) and (b) are two end-on configurations; (c) and (d) are two side-on configurations. The central yellow ball represents metal Fe or Co atom, the central two red balls represent the adsorbed O_2 molecule, blue balls represent N atoms, gray balls represent C atoms and light white balls represent H atoms.

(see Figure 2(c) and (d)), the adsorbed O_2 molecule extends parallel to the catalyst molecule plane and the two oxygen atoms are in equal distance from the central metal atom.

In the present work, we discovered that there are two stable structures each for both the end-on and side-on configurations of oxygen molecule adsorption. In one case (see Figure 2(b) and (c)), the projection of the oxygen bond in the catalyst molecule plane is aligned with the bond between the central metal atom and its nearest N atoms. In the other case (see Figure 2(a) and (d)), the projection of the oxygen bond on the catalyst molecule plane is aligned with the bisecting line of the two neighbouring bonds between the central metal atom and two nearest N atoms. As a result, we have identified four possible ways for O_2 adsorption on the FePc or CoPc catalyst molecules. Figure 2 displays the molecular structures of these adsorption states. We denote these adsorption structures as end-on A (Figure 2(a)), end-on B (Figure 2(b)), side-on A (Figure 2(c)), and side-on B (Figure 2(d)).

The optimal adsorption structure and the adsorption energy of O_2 on FePc or CoPc were obtained through an energy optimisation process using the DFT method (the energies are given in Supplementary Materials, available online). We found that all four structures shown in Figure 2 are stable (positive adsorption energy) for the O_2 on FePc; their adsorption energy and structural properties are given in Table 2. In contrast, we found that only the end-on configurations are energetically stable for O_2 on CoPc molecule. Hence, we listed in Table 3 only the energy and structural properties of O_2 adsorbed on a CoPc molecule for the end-on configurations.

4. Discussion

The results in Table 2 show that the O_2 adsorption energy on FePc is about 0.77 eV higher (more stable) for the end-on configurations than for the side-on configurations. This implies that the end-on configurations would be dominant in the experimental sample of O_2 adsorption on FePc molecules.

Based on Mullikan charge analysis, the charge transfers from the catalyst molecules to the adsorbed O_2 molecules are 0.145e (end-on A), 0.135e (end-on B), 0.334e (side-on A) and 0.398e (side-on B). Hence, there is more charge transfer from the catalyst molecules to the adsorbed O_2 molecule in the side-on configurations than the end-on configurations. It is also noticeable that the O—O bond lengths of the adsorbed O_2 molecule in the side-on configurations are about 7.3% larger than those of the adsorbed molecules in the end-on configurations and 11.6% larger than that of the isolated O_2 molecule. These results strongly suggest that the O—O bonds in the adsorbed O_2 molecules are much weaker in the side-on configurations than in the end-on configurations. In other words, the adsorbed O_2 molecules in side-on configurations are conceivably more active in participating ORR.

On transition metal phthalocyanine molecules, the oxygen reduction can proceed via four-electron reduction to yield water or via two-electron reduction to produce peroxide. Four-electron reduction process is more desired in fuel cell applications since more energy is released during the four electron ORR process. It was found that a single FePc adsorption site can promote four-electron ORR but a single CoPc adsorption site only promotes two-electron ORR [16]. However, no clear understanding at the atomistic level has ever been achieved on how the four-electron reduction process occurs on the surface of FePc. In this work, we propose the following explanation to this phenomenon based on our DFT results (Tables 2 and 3): on the surface of transition metal phthalocyanines four-electron reduction would take place if the O_2 molecules are adsorbed in the side-on configurations while two-electron reduction would happen if the O_2 molecules are adsorbed in the end-on configurations. Thus, FePc can promote four-electron ORR because side-on O_2 adsorption is energetically permitted. In contrast, only end-on O_2 adsorption is possible and only two-electron ORR can occur on CoPc.

Our proposed explanation can be justified by the following two observations.

(1) In the end-on O_2 adsorption configurations, one O atom is closer to the transition metal atom than the other. The results in Tables 2 and 3 show that the O atom closer to the transition metal atom gets much less transferred charge from the catalyst

Table 2. Calculated adsorption properties of oxygen molecule on FePc molecule.

	End-on A	End-on B	Side-on A	Side-on B
E_{ad} (eV)	1.16	1.12	0.40	0.35
D_{Fe-O_1} (Å)	1.744	1.741	1.893	1.874
$D_{O_2-O_1}$ (Å)	1.274	1.275	1.356	1.378
$\angle O_2O_1Fe$ (°)	120.6	124.4	69.0	68.4
Mullikan charge of Fe	0.339	0.339	0.381	0.435
Mullikan charge of O_1	−0.002	0.002	−0.167	−0.199
Mullikan charge of O_2	−0.143	−0.137	−0.167	−0.199

The listed properties includes: adsorption energy (E_{ad}), distance (D_{Fe-O_1}) between the central Fe atom to its nearest neighbouring O atom (denote as O_1), bond length of O_2 molecule ($D_{O_2-O_1}$), angle ($\angle O_2O_1Fe$) formed by the central Fe atom with the two adsorbed O atoms, and Mullikan charges of the central Fe atom and the two adsorbed O atoms. End-on A corresponds to Figure 2(a), End-on B corresponds to Figure 2(b), side-on A corresponds to Figure 2(c), and side-on B corresponds to Figure 2(d).

Table 3. Calculated adsorption properties of oxygen molecule on CoPc molecule.

	End-on A	End-on B
E_{ad} (eV)	0.40	0.38
D_{Co-O_1} (Å)	1.906	1.915
$D_{O_2-O_1}$ (Å)	1.267	1.266
$\angle O_2O_1Co$(°)	117.2	117.9
Mullikan charge of Co	0.170	0.172
Mullikan charge of O_1	− 0.037	− 0.037
Mullikan charge of O_2	− 0.091	− 0.087

The listed properties includes: adsorption energy (E_{ad}), distance (D_{Co-O_1}) between the central Co atom to its nearest neighbouring O atom (denote as O_1), bond length of O_2 molecule ($D_{O_2-O_1}$), angle ($\angle O_2O_1Co$) formed by the central Co atom with the two adsorbed O atoms, and Mullikan charges of the central Co atom and the two adsorbed O atoms. End-on A corresponds to Figure 2(a) and end-on B corresponds to Figure 2(b).

molecules than the other O atom. This may allow the O atom that is far away from the transition metal atom to react first to form peroxide via two-electron reduction. In the side-on O_2 adsorption configurations, the two O atoms have equal distance to the transition metal atom and are equally charged. Thus, it is possible that the ORR takes place at the same time on the two O atoms and proceeds via a four-electron process.

(2) The results in Table 2 show that O—O bonds in the side-on adsorbed O_2 molecules are much weaker and easier to break in the reduction reaction than those in the end-on adsorbed O_2. Thus, the side-on adsorbed O_2 would determine the main characteristics of ORR even though the end-on adsorbed O_2 are energetically more stable.

5. Summary

We studied the adsorption of O_2 on FePc and CoPc catalyst molecules using DFT simulation. We identified four stable adsorption configurations for the system of O_2 on transition metal phthalocyanines. Specifically, we found that both the end-on and side-on configurations are energetically favourable for the O_2 on FePc but only the end-on configurations are energetically allowable for O_2 on CoPc. Furthermore, we proposed that the side-on adsorbed O_2 molecules promote the four-electron reduction process while end-on adsorbed O_2 molecules promote the two-electron reduction process on the surface of transition metal phthalocyanine catalyst molecules. The proper adsorption of O_2 on the catalyst surface is the first step of ORR. To find a high-performance fuel cell electro-catalyst, it is necessary to elucidate the detailed reaction pathway for O_2 on the molecule catalysts in future work.

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