Oxygen Reduction Reaction on a CuII Complex of 3,5-Diamino-1,2,4-triazole: A DFT Approach

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ABSTRACT: The high costs for producing catalysts for fuel cells combined with low efficiency in oxygen reduction make metal−organic complexes a promising alternative to noble-metal catalysts. The electrochemical activity of Cu-complex-based catalysts has been reported by many authors, but only a few works are devoted to theoretical studies. In this manuscript, we use density functional theory (DFT) calculations to investigate the oxygen reduction reaction (ORR) on a CuII complex of 3,5-diamino-1,2,4-triazole. The determining steps for the associative and dissociative mechanisms are the oxygen adsorption and the oxygen bond cleavage, respectively. The barrier for breaking the O−O bond in the dissociative mechanism was estimated at 0.7 eV.

INTRODUCTION

Oxygen reduction reaction (ORR) is the cathodic reaction in energy-converting devices such as fuel cells, which are still limited by the absence of efficient catalysts.1−3 Pt-based catalysts are the most used for ORR because of their electrochemical properties, such as high activity and electrochemical stability and durability in acid media.2 However, the high cost of platinum makes commercial production of fuel cells economically nonviable.4 Metal−organic complexes are a promising alternative to Pt-based catalysts. Gewirth and co-workers showed that a copper complex of 3,5-diamino-1,2,4-triazole supported on carbon black has a very high activity for oxygen reduction.5 Although many works report on the activity of Cu-complex-based catalysts,5−11 there is lack of information from the theoretical point of view.

Computational methods based on density functional theory (DFT) afford a convenient and practical means of investigating the thermodynamics of many processes.12−14 Such methods are commonly used in the study of a great variety of materials, as they do not require the preparation and testing of the large numbers of specimens demanded by experimental investigations.15 Besides, these methods can be considered a crucial complement to experimental techniques in which some information is difficult to access. DFT calculations can be used to introduce useful information about the ORR on a copper-based complex employed as the catalyst material. The energetics associated with the interaction between the species are fundamental in the study of electrocatalysis of the reactions involved in fuel cells, and the density of states (DOS) plots enable the evaluation of orbitals participating in this interaction.

To provide relevant information about oxygen reduction, in this manuscript, we use DFT calculations to investigate the mechanisms for ORR on a CuII complex of 3,5-diamino-1,2,4-triazole (Hdatrz).

RESULTS AND DISCUSSION

Geometry and Electronic Structure. A proper understanding of the ORR demands an adequate description of the active sites on the catalytic material, both with regard to the arrangement of atoms and the electronic structure.

The geometry of the [CuII(Hdatrz)·5H2O·2SO4] complex was fully optimized, and the resulting structure is represented in Figure 1A; the complex is pentahydrated and each Cu atom is connected to a sulfate. Water molecules and sulfates are omitted in Figure 1B to provide more clarity. The Cu−Cu distance after optimization is of the order of 3.4 Å, in good

Figure 1. (A) [CuII(Hdatrz)·5H2O·2SO4] complex. (B) Water molecules and sulfates are omitted for clarity.

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agreement with the value reported in ref 5. Computational details are described in Appendix A.

Both species O* and HO* adsorb on one of the Cu atoms with a distance of 2.39 and 2.33 Å, respectively. HOO* adsorbs on a nitrogen atom (Cu–N), 2.78 Å away from it. Also, the molecular species, O2* and H2O*, are somewhat apart from the [CuII(Hdatrz)] complex, 3.54 and 3.84 Å, respectively.

Figure 2 shows the density of states plots projections onto the d orbital of copper and p orbital of nitrogen atoms in the [CuII(Hdatrz)] complex and the p orbital of the oxygen in the adsorbed species. For the projections, we selected the atoms of Cu and N closest to the interacting species, therefore, those with the highest contribution to the DOS. O* strongly interacts with both the d orbital of copper and the p orbital of nitrogen, in which there is a significant change in the structure of these orbitals compared to the pure complex (Figure 2A,C). The shoulder in the range of −1 to 0 eV for the Cu d orbital disappears. Also, for the N p orbital, the structure below −3 eV completely changes. The oxygen 2p orbital in the HO* and HOO* species interacts with the nitrogen 2p of the complex, while no meaningful change in the structure of the copper d orbital is observed. Calculated binding energy of O* is about 5.3 eV, followed by HO* (2.9 eV) and HOO* (0.5 eV). On the other hand, the interaction of molecular species with the complex are weaker, of the order of 0.3 eV.

**ORR Mechanisms.** In the present work, we investigated two distinct mechanisms for the ORR: associative and dissociative (this with two possible routes). While in the former, the cleavage of the O−O bond does not occur before hydrogenation; in the latter, the bond breaking is an important condition before the hydrogenation process. Both mechanisms start with the chemisorption of the O2 molecule. In the following, we present the reaction steps for the associative mechanism

\[
O_2 \rightarrow O_2^* \quad (1)
\]

\[
O_2^* + H^+ + e^- \rightarrow HOO^* \quad (2)
\]

\[
HOO^* + H^+ + e^- \rightarrow O^* + H_2O \quad (3)
\]

\[
O^* + H_2O + H^+ + e^- \rightarrow HO^* + H_2O \quad (4)
\]

\[
HO^* + H_2O + H^+ + e^- \rightarrow 2H_2O \quad (5)
\]

The free energy diagram for the associative mechanism is depicted in Figure 3. We calculate the free energies using the method outlined in Appendix B. Two configurations were considered: under standard conditions (pH = 0, p = 1 bar, T = 298 K, and U = 0) and changing the electrode potential to U = 1.23 V (the maximum operating potential of fuel cells). The pH was chosen to be zero, hence considering the reaction steps are in acid media.

O2 adsorption precedes hydrogenation, and at potential U = 0.0 V, this step is uphill and all other steps are downhill. As shown in the DOS plots (Figure 2B), HOO is weakly adsorbed to the complex (small interaction with the 2p orbital of nitrogen), thus favoring the breaking of the HO−O bond, which leads to water and O* formation (step 3). Despite the strong binding energy of O*, at low potentials, the hydro-
genation weakens the interaction with the \([\text{Cu}^{II} (\text{Hdatrz})]\) complex, making the reaction instep 4 exergonic. The same holds for hydrating \(\text{HO}^*\) (step 5), the binding energy drops to 0.34 eV and water is formed. Considering the high potential of 1.23 V, only the adsorption of O is downhill and all other steps are uphill.

The reaction steps that were considered in our investigation for the dissociative mechanism are shown below

\[
\begin{align*}
\text{O}_2^* & \rightarrow \text{O}^* + \text{O}^* & (6) \\
\text{O}^* + \text{O}^* + \text{H}^+ + e^- & \rightarrow \text{O}^* + \text{HO}^* & (7) \\
\text{O}^* + \text{HO}^* + \text{H}^+ + e^- & \rightarrow \text{HO}^* + \text{H}_2\text{O} & (8) \\
\text{HO}^* + \text{HO}^* + \text{H}^+ + e^- & \rightarrow \text{HO}^* + \text{H}_2\text{O} & (9) \\
\text{HO}^* + \text{H}_2\text{O} + \text{H}^+ + e^- & \rightarrow 2\text{H}_2\text{O} & (10)
\end{align*}
\]

Alternatively, the dissociative mechanism may occur by a different route, with reactions 11 and 12 replacing reactions 8 and 9, respectively

\[
\begin{align*}
\text{O}^* + \text{HO}^* + \text{H}^+ + e^- & \rightarrow \text{O}^* + \text{H}_2\text{O} & (11) \\
\text{O}^* + \text{H}_2\text{O} + \text{H}^+ + e^- & \rightarrow \text{HO}^* + \text{H}_2\text{O} & (12)
\end{align*}
\]

The two possible routes for the dissociative mechanism are displayed in the free energy diagram in Figure 4. Oxygen dissociation takes place before hydrogenation, and for this step, the barrier was estimated at 0.7 eV. Using the zero cell potential, \(U = 0 \text{ V}\), subsequent steps are downhill. The dissociation barrier of the \(\text{O}_2\) molecule was determined using a series of calculations moving the molecule toward the \([\text{Cu}^{II} (\text{Hdatrz})]\) complex. The \(\text{O}--\text{O}\) interaction weakens during the approach, and the energy reaches a maximum (transition state). The bond length at the transition state is 1.52 Å (against 1.26 Å in the gas phase). The oxygen is parallel to the \([\text{Cu}^{II} (\text{Hdatrz})]\) complex, with each oxygen directing to opposite \(\text{Cu}--\text{N}\) bonds. As previously pointed out, hydrogenation weakens the interaction with the \([\text{Cu}^{II} (\text{Hdatrz})]\) complex at low potentials. At \(U = 1.23 \text{ V}\) and after breaking the oxygen bond, the steps are uphill. Reaction 11 is approximately 0.3 eV more favorable than reaction 8. Through this mechanism, there is no formation of \(\text{HOO}^*\).

**CONCLUSIONS**

Few theoretical works report on the use of copper-based complexes as catalyst materials for ORR. The \([\text{Cu}^{II} (\text{Hdatrz})]\) complex is presented as an alternative to noble-metal-based catalysts providing good activity at affordable prices. The theoretical method employed in our investigation constitutes a highly useful tool to assist in the elucidation of processes occurring in the electrochemical environment. DFT calculations were performed to describe the geometric properties and the electronic structure of the complex, and its interaction with some species. Our results show that oxygen adsorption is the determining step for the associative mechanism. On the other hand, for the dissociative mechanism, the process should overcome a barrier of the order of 0.7 eV to cleavage the oxygen bond before hydrogenation.

**APPENDIX A. COMPUTER METHODS**

All DFT calculations were carried out using the SIESTA code. SIESTA uses a numerical linear combination of atomic orbitals as the basis set and describes the core–electron interaction using norm-conserving pseudopotentials in the Kleinman–Bylander form. Exchange and correlation interactions were treated with the PBE\textsuperscript{18,19} generalized gradient approximation functional. For comparison, the PW91 exchange–correlation functional\textsuperscript{20,21} was also used for geometry optimization. We considered the PBE functional more suitable and employed it to the rest of the calculations.

First, we performed the geometry optimization of the \([\text{Cu}^{II} (\text{Hdatrz})]\cdot5\text{H}_2\text{O}\cdot2\text{SO}_4\)] complex and the convergence criterion was achieved when the force on each atom was less than 0.04 eV/Å. To calculate the interaction with \(\text{O}_2\), \(\text{HOO}\), \(\text{O}, \text{HO}, \text{H}_2\text{O}\), each species was placed close to the complex and the optimization procedure was repeated with all atoms free to move.

To calculate the barrier to break the \(\text{O}--\text{O}\) bond in the dissociative mechanism, we bring the \(\text{O}_2\) molecule closer to the \([\text{Cu}^{II} (\text{Hdatrz})]\) complex, in steps of 0.1 Å, fixing the oxygen atoms on the orthogonal axis only. While approaching the molecule to the complex, the bond length increases and the energy rises to a maximum. After that, the energy decreases and each oxygen atom adsorbs to a site. The nudged elastic band (NEB) method could be also an option to calculate the transition state since both the initial (\(\text{O}_2\)) and final (2\(\text{O}^*\)) states are well-known. We used the NEB method elsewhere.\textsuperscript{14} Details on the method used to calculate the differences in the free energies presented in this manuscript can be found in the next appendix.


**APPENDIX B. FREE ENERGY CALCULATION**

Here, we summarize the method used for calculating the differences in the free energy for the ORR. The procedure was proposed by Nørskov et al.\(^{12}\)

The reference potential is set to be that of the standard hydrogen electrode, and the chemical potential for the reaction \(H^\dagger + e^-\) can be related to that of \(1/2H_2\) in the gas phase, which is in equilibrium under standard conditions (\(pH = 0\), \(p = 1\) bar, \(T = 298\) K, and \(U = 0\))

\[
\frac{1}{2}H_2 \rightarrow H^\dagger + e^-
\]  

(13)

Differences in the free energy, \(\Delta G\), are calculated using the equation

\[
\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_{PH} + \Delta G_U
\]  

(14)

where \(\Delta E\) is the interaction energy obtained directly from DFT calculations, \(\Delta ZPE\) is the change in the zero-point energy, and the values used in the present study are taken from ref \(^{12}\). \(T\Delta S\) is the entropic term whose values were obtained from standard tables for gas-phase molecules.\(^{15,22}\) \(\Delta G_{PH}\) is the contribution of the \(H^\dagger\) concentration to the free energy (in our study we considered \(pH = 0\)), and \(\Delta G_U\) is the shift in energy at specific electrode potential for all states involving an electron in the electrode (\(-eU\)).

For \(pH\) other than zero, one can correct the free energy of \(H^\dagger\) ions using the equation

\[
\Delta G_{PH} = -k_B T \times \ln[H^\dagger] = pH \times k_BT \ln 10
\]  

(15)

In eq 15, \(k_B\) is the Boltzmann constant.

At standard conditions \(\Delta G (pH = 0 \text{ and } U = 0) = \Delta G_0\) and eq 14 becomes

\[
\Delta G_0 = \Delta E + \Delta ZPE - T\Delta S
\]  

(16)

Change in the free energy of \(O_2, \Delta G_0 = 4.92\) eV, was derived from the reaction \(2H_2O \rightarrow O_2 + 2H_2\) using experimental values. Besides, the entropy for gas-phase water was taken at \(p = 0.035\) bar and \(T = 298\) K, in which this is in equilibrium with liquid water.

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**Notes**

The authors declare no competing financial interest.

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