Theoretical Studies of the Zeolite-Y Encapsulated Chlorine-Substituted Copper(II)phthalocyanine Complex on the Formation Glycidol from Allyl Alcohol

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ABSTRACT: Density functional theory (DFT) used to study the encapsulation of copper(II)phthalocyanine and chlorine-substituted copper(II)phthalocyanine to a zeolite-Y framework. Changes occurring in the redox properties, as well as the red shift of the time-dependent DFT (TD-DFT) spectra, point out the influence of encapsulation on the geometric parameters of the complexes. Also, the TD-DFT calculations show good agreement with the energy changes occurred in the highest occupied molecular orbital and lowest unoccupied molecular orbital. DFT-based descriptors are used for scrutinizing the reactivity of the encapsulated complexes and a mechanism of the glycidol formation is proposed based on the energetics involved in the transformation.

INTRODUCTION

Metallophthalocyanine complexes, widely known as enzyme mimics, have been used for activating peroxides. Phthalocyanine compounds with N4-macrocyanes, an analogue to porphyrin molecule are highly stable owing to their diverse coordination. It exhibits excellent spectroscopic properties and reversible redox chemistry. The catalytic performance of these phthalocyanine catalysts was hindered basically because of two main reasons: aggregation leading to the formation of inactive dimers and oxidative self-destruction at some point in the catalytic oxidation. To minimize these problems various supports, such as zeolites, graphene, carbon nanotube, chitosan, and fibrous materials (silk, cellulose), were utilized to immobilize these catalysts. Among various supports, zeolites were considered as ideal candidates because of their distinctive framework. The geometry and physicochemical properties of the encapsulated complex could be altered by the topology (voids), steric, and electrostatic constraints obliged by zeolite framework walls. The encapsulated complex shows better reactivity than the homogeneous counterparts of the same. These complexes are generally used as an alternative to the most of the biosystem and known as zeozymes.

Recently, metal phthalocyanine-based complexes have been widely used as the catalyst for alkane and alkene oxidation reactions. However, the major drawback of this application is that the mechanism and the species which is actively involved in the process is not well established. To overcome these problems, much effort is focused to design the novel catalyst in the aspect of mechanistic path. However, only some of the reports have been paying attention to the use of these biomimetic catalysts over epoxidation reactions (e.g., allyl alcohol epoxidation). Jana et al. have used Cu(II) complex encapsulated Si-MCM-41 for the epoxidation of a variety of olefinic compounds (styrene and allyl alcohol) using tert-BuOOH as the oxidant. The complex has been reported showing tremendous catalytic activity with a conversion of 73% than Cu(II) complex alone. Ti-MWW and TS-1 ZSM-5 have been utilized for the bis(allyl)ether and allyl alcohol epoxidation, where the catalysts oxidize effectively to their corresponding ethers, allyl glycidyl ether, and bis(glycidyl) ether. The reaction has been supported with 30% aqueous hydrogen peroxide. The allyl alcohol epoxidation is a big challenge in the industrial point of view because of their wide range of applications in the field of organic synthesis and pharmaceuticals.

RESULTS AND DISCUSSION

Geometrical Parameters. Planar complexes such as porphyrins and phthalocyanines show two types of distortions such as saddle and ruffled distortions. In ruffled geometry, because of counter-rotation of different isoindole rings, Nβ and two isoindole carbon atoms are displaced perpendicularly to the molecular plane. However, in saddle-type distortion, each...
pair of isoindole Cβ carbon atoms lies above and below of the molecular plane together with the axis joining pyrrole Cα atoms, and it makes the central CuN8 ring as planar. Because of this distortion, the ruffled geometry was not considered, and the center of inversion of CuPc molecule also preserved as not like the saddle distortion. The isoindole ring displacements were equivalent and upright to the molecular plane; for this reason, only symmetric saddle distortions have been considered. From the optimized saddle-deformed geometry, the isoindole rings tetrahedrally distorted to accommodate into the zeolite framework supercage, and this distortion results in lower interaction energy.23 The geometry of CuPc does not have a center of inversion. The optimized geometry of CuPc, CuPcCl4, CuPc-Y, and CuPcCl4-Y complexes has been shown as follows (Figure 1).

![Figure 1. Optimized structure of the (a) CuPc, (b) CuPcCl4, (c) CuPc-Y, and (d) CuPcCl4-Y complexes.](image)

The geometrical parameters from B3LYP/6-31G(d,p) level calculations for CuPc, CuPcCl4, CuPc-Y, and CuPcCl4-Y complexes are given in Table 1. The calculated geometrical parameters of the Optimized CuPc, CuPcCl4, CuPc-Y, and CuPcCl4-Y Complexes are given in Table 1.

| bond distances (Å)/angles (in deg) | CuPc | CuPcCl4 | CuPc-Y | CuPcCl4-Y |
|----------------------------------|------|--------|--------|----------|
| Cu−N8                            | 1.953| 1.954  | 1.908  | 1.908    |
| C7−N21                           | 1.324| 1.324  | 1.373  | 1.390    |
| C7−C3                            | 1.457| 1.456  | 1.481  | 1.482    |
| C4−C3                            | 1.395| 1.396  | 1.379  | 1.377    |
| C4−C5                            | 1.405| 1.405  | 1.437  | 1.440    |
| C1−C2                            | 1.393| 1.392  | 1.415  | 1.419    |
| C1−C2                            | 1.408| 1.408  | 1.393  | 1.386    |
| ∠C9−N8−C7                        | 108.23| 108.27| 107.18| 107.84  |
| ∠N8−C7−N21                       | 127.65| 127.61| 125.63| 124.45  |
| ∠N8−N21−C24                      | 122.91| 122.87| 121.07| 120.64  |
| ∠N8−C7−C4                        | 109.47| 109.48| 110.56| 109.62  |
| ∠C7−C4−C5                        | 106.40| 106.41| 106.13| 106.81  |
| ∠C5−C4−C3                        | 121.20| 120.99| 121.50| 121.34  |
| ∠C4−C3−C2                        | 117.58| 118.00| 117.44| 119.93  |
| ∠N12−Cu−N23                      | 179.24| 179.49| 169.97| 166.98  |

The geometrical parameters from B3LYP/6-31G(d,p) level calculations for CuPc, CuPcCl4, CuPc-Y, and CuPcCl4-Y complexes are given in Table 1. The calculated geometrical

parameters of the CuPc are in good concurrence with the metal phthalocyanine complex reported earlier. After encapsulation, changes are observed in geometrical parameters of the metal complexes, this shows that zeolite encapsulation changes the metal active sites. The bond angle between N12−Cu−N23 is 169.97 and 166.98 for CuPc-Y and CuPcCl4-Y complexes. This shows that chlorine-substituted phthalocyanine complexes undergoes more distortion than unsubstituted phthalocyanine complex.

The CuPc is found to be planar and in concurrence with the available computational and experimental information. In 1935, Robertson reported that the X-ray structural studies of NiPc, CuPc, and PtPc48 and revealed that the metal atom lies in a plane surrounded with the four isoindole nitrogen atoms.

Frontier Molecular Orbitals. It is evident that from the Figures 2 and 3 that the highest occupied molecular orbital (HOMO)—lowest unoccupied molecular orbital (LUMO) patterns were qualitatively equivalent. Spin-unrestricted calculations performed with all the complex systems because of copper(II) open-shell d9 configuration system. The frontier orbital energies (spin-up and spin-down states) of CuPc, CuPcCl4, CuPc-Y, and CuPcCl4-Y were found to be different (Table 2).

The HOMO and LUMO populations of the CuPc, CuPcCl4, CuPc-Y, and CuPcCl4-Y are presented in Figures 2 and 3, and the gap between these two states is found to be 2.19(↑), 2.23(↑) eV, 2.18(↑), 2.21(↑) eV, 3.98(↑), 3.50(↑) eV, and 4.90(↑), 5.39(↑) eV for CuPc, CuPcCl4, CuPc-Y, and CuPcCl4-Y, respectively. The neat complexes have planar geometry. However, the encapsulated complexes have a distorted planar geometry because of the steric hindrance and counterion effect of the zeolite Y framework, and this leads to a change in the frontier orbital energy levels. A Coulombic interaction and coordination effects exist between the zeolite walls and a metal complex. The encapsulation stabilizes the HOMO level to a lower energy and LUMO to a higher energy and leads to higher energy gap, and it is found to be correlated with the absorption spectrum of the encapsulated complex and
the red shift indicates the structural distortion. Global and local descriptors were calculated to understand the reactivity of the molecular system.

Absorption Spectrum. TD-DFT calculations have been performed in various solvents using the B3LYP/6-31G(d,p) basis level. Conductor-like polarizable continuum model (C-}

Figure 2. HOMO−LUMO of CuPc and CuPcCl4 complexes. The arrows represent spin-up (↑) and spin-down (↓) states.

Figure 3. HOMO−LUMO of CuPc-Y and CuPcCl4-Y complexes. The arrows represent spin-up (↑) and spin-down (↓) states.

| complex       | HOMO  | LUMO  | μ    | η    | ω    | S    |
|---------------|-------|-------|------|------|------|------|
| CuPc(↑)       | −4.94 | −2.75 | −3.845 | 1.095 | 6.750 | 0.456 |
| CuPc(↓)       | −4.96 | −2.73 | −3.845 | 1.115 | 6.629 | 0.448 |
| CuPcCl4(↑)    | −5.39 | −3.21 | −4.300 | 1.090 | 8.481 | 0.458 |
| CuPcCl4(↓)    | −5.40 | −3.19 | −4.295 | 1.105 | 8.347 | 0.452 |
| CuPc-Y(↑)     | −5.87 | −1.89 | −3.884 | 1.991 | 3.788 | 0.251 |
| CuPc-Y(↓)     | −5.87 | −2.37 | −4.126 | 1.750 | 4.863 | 0.285 |
| CuPcCl4-Y(↑)  | −6.60 | −1.70 | −4.155 | 2.452 | 3.521 | 0.203 |
| CuPcCl4-Y(↓)  | −6.60 | −1.21 | −3.911 | 2.697 | 2.835 | 0.185 |
PCM) was used for solvation effects. Copper(II)-phthalocyanine exhibits Soret bands ($n \rightarrow \pi^*$) around 330–370 nm and Q ($\pi \rightarrow \pi^*$) bands around 600–780 nm. These bands have been assigned to $a_{2u} \rightarrow e_g$ and $a_{2u} \rightarrow e_u$ transitions. In gas phase, the CuPc and CuPcCl$_4$ complexes show Q bands at 318, 592 nm and 523, 597 nm, respectively. These bands are red-shifted to 556, 778 nm and 592, 718 nm in the encapsulated complexes. The Soret bands are also red-shifted from 334 and 357 nm to 347 and 364 nm for CuPc and CuPcCl$_4$, respectively. The solvent effects on absorption properties were studied using different solvents. Table 3 shows that the largest red shift of the Q band was observed for both neat and encapsulated complexes in dimethyl sulfoxide (DMSO). The LUMO gets stabilized, if the transition shift to longer wavelength. According to that, the metal complex LUMO gets stabilized while it interacts with coordination solvents. From this, it is evident that the zeolite supercage effectively accommodates the complexes. In consequence, the encapsulation results in the distortion of the structure of CuPc and CuPcCl$_4$ because of steric hindrance.

**Global Descriptors.** The global descriptors values are in Table 2. The maximum hardness principle reveals that the complex stability increases with its hardness. The chemical hardness of CuPc, CuPcCl$_4$, CuPc-Y, and CuPcCl$_4$-Y complexes are observed at 1.095 eV; 1.115 eV; 1.090 and 1.105 eV; 1.991 and 1.750 eV; and 2.452 and 2.697 eV, respectively. Thus, the encapsulated complexes show better stability corresponding to that of the neat complexes. The electrophilicity index of the encapsulated complexes shows that the minimum electrophilicity and maximum hardness are responsible for its higher reactivity. The higher chemical potential value of the encapsulated complexes makes it more active toward electron transfer reactions compared with the neat complexes.

**Local Descriptors.** Hirschfeld population analysis has been carried out to evaluate the Fukui function ($f_i^+$ and $f_i^-$) values of copper and four nitrogens present in the complexes CuPc, CuPcCl$_4$, CuPc-Y, and CuPcCl$_4$-Y (Table 4). A site having a minimum value of Fukui function favors the hard—hard interaction, whereas that of maximum value favors the soft—soft interaction. Because the central copper atom of the encapsulated complex shows a minimum Fukui function value, the zeolite framework influences the metal reactivity and enhances the hard—hard interaction.

**Energy and Spin Density.** The energies of the CuPc, CuPcCl$_4$, CuPc-Y, and CuPcCl$_4$-Y complexes are tabulated in Table 5. The spin densities are calculated for CuPc and CuPcCl$_4$ complexes, and they are presented in Figure 4. The central Cu atom has high Mulliken charge density, and the four coordinated N atoms have lesser density. The high charge density on central Cu atom implies that the unpaired d electrons carry out to evaluate the Fukui function ($f_i^+$ and $f_i^-$) values of copper and four nitrogens present in the complexes CuPc, CuPcCl$_4$, CuPc-Y, and CuPcCl$_4$-Y (Table 4). A site having a minimum value of Fukui function favors the hard—hard interaction, whereas that of maximum value favors the soft—soft interaction.51−53 Because the central copper atom of the encapsulated complex shows a minimum Fukui function value, the zeolite framework influences the metal reactivity and enhances the hard—hard interaction.

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electron is presented on the metallic center and not over the ligands aromatic rings.54

**Possible Mechanism for the Conversion of Allyl Alcohol to Glycidol in the Presence of CuPc and tBuOOH.** A possible catalytic cycle for allyl alcohol transformation into glycidol in the presence of CuPc and tBuOOH is presented in Scheme 1. The mechanism involves a direct electrophilic attack of the peroxo group of the allyl alcohol. DFT studies focused on the allyl alcohol epoxidation mechanism including the location of transition states and activation barriers of oxygen transfer. The calculations disclose that direct nucleophilic attack of the allyl alcohol at electrophilic peroxo oxygen center is preferred. An active species CuPc* is generated via electron transfer between CuPc and tBuOOH. This leads to the formation of CuPc−O•− intermediate by the interaction of peroxo O to Cu2+. Finally, the transfer of oxygen from peroxide to allyl alcohol resulted in the formation of glycidol.

The addition of tertiary butyl hydrogen peroxide to the CuPc complex through the axial position forms a weakly bound Cu(II)Pc−tBuOOH complex via TS1. The transition step is associated with an energy barrier of 11.8 kcal/mol. In the TS1, the oxygen atom of tBuOOH moves toward the metal center and leads to the formation of the Cu−O linkage. The optimized intermediate state geometries show the weakly bound complex formed via the interaction of the metal center with one of the peroxide−oxygen moiety. The oxidation state of Cu in the intermediate remains as Cu(II). Cu(III) intermediates were proposed by Hamilton et al. in galactose oxidase base. However, later it was found to be copper(II). The experimental reports indicate that without forming high valent copper center, Cu(II)−hydroperoxo complexes which are present in biological system directly oxidize the substrates.55−58 The Cu−O distance is 2.09 Å. If allyl alcohol inserts to the metal peroxide complex, oxygen from peroxide transferred to allyl alcohol (TS2), leading to the formation of product and CuPc subsequently regenerated. This transition step TS2 has an energy barrier of 7.2 kcal/mol. The energy profile diagram for this conversion is as follows (Figure 5).

![Scheme 1. Possible Reaction Path for Glycidol Formation](image)

**CONCLUSION**

Square planar phthalocyanine and tetra-chlorine substituted phthalocyanine complexes of Cu(II) are encapsulated with zeolite-Y and studied using different DFT studies. It revealed that zeolite framework walls impose steric hindrance and modify the overall behavior of the complex. DFT calculation further supports that encapsulation changes the values of the global, local, and Fukui function values of the complexes, resulting in the higher catalytic ability. The electron-transfer process is responsible for the interaction of tBuOOH with metal complexes. The encapsulated complexes show better catalytic activity than the free complexes.

**COMPUTATIONAL METHOD**

G09 program is used to perform the density functional calculations with B3LYP/6-31G(d,p) level.39−43 The Faujasite zeolite framework has been chosen, and the cluster dimension was reduced to 40 tetrahedral units (40T). In zeolite framework, Si and O atoms were held on their respective crystallographic positions, and all the terminal positions were optimized using H atoms. Al atoms were substituted with two Si atoms, in the six-member ring satisfying Lowenstein’s rule. The starting geometry of CuPc is taken from the X-ray diffraction data from the literature.44 The free neat complex was first optimized in the gaseous state followed by encapsulation inside supercage. Geometric optimizations were done eliminating the point group constraints.

The chemical potential (μ) and global hardness (η) can be calculated as follows

\[ \mu = \frac{E_{\text{LUMO}} + E_{\text{HOMO}}}{2} \]  

\[ \eta = \frac{E_{\text{LUMO}} - E_{\text{HOMO}}}{2} \]

where \( E_{\text{LUMO}} \) is the LUMO energy and \( E_{\text{HOMO}} \) is the HOMO energy.

The global electrophilicity is calculated by Parr et al. as follows

![Figure 5. Simple energy profile diagram for the catalytic conversion.](image)
\[ \omega = \frac{\mu^2}{2\eta} \]

The calculation of the global softness is done by
\[ S = 1/2\eta \]

The Fukui function\(^{47}\) of an atom, \( k \), is calculated using the following equations.

\[ f^+_k = [q_k(N + 1) - q_k(N)] \quad \text{(for nucleophilic attack)} \]
\[ f^-_k = [q_k(N) - q_k(N - 1)] \quad \text{(for electrophilic attack)} \]
\[ f^0_k = \frac{[q_k(N + 1) - q_k(N - 1)]}{2} \quad \text{(for radical attack)} \]

where \( q_k(N) \), \( q_k(N + 1) \), and \( q_k(N - 1) \) are the charges of the \( k \)th atom for the \( N, N + 1 \), and \( N - 1 \) electron systems, respectively.

TD-DFT calculations were performed at the B3LYP/6-31G(d,p) level from the ground-state optimized geometry. C-atom effects. We have computed 100 excitation energies. Transition states were confirmed by frequency analysis.

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**Notes**
The authors declare no competing financial interest.

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