Influence of Different Zeolite Frameworks on the Geometry of Platinum(II)tetraammine Complex

Tamilmani Selvaraj and Rajalingam Renganathan*

School of Chemistry, Bharathidasan University, Tiruchirappalli 620024, Tamilnadu, India

ABSTRACT: The structural changes in the guest platinum(II)tetraammine complex due to the steric and electronic interactions with the host zeolite frameworks LTL, MWW, and Y have been investigated using density functional theory calculations. It is observed that the square planar geometry of platinum(II)tetraammine complex has been distorted to nonplanar geometry when encapsulated in superfages of zeolite framework. The distortion is found to be higher in LTL than that in Y and MWW frameworks, without affecting the nature of the zeolite framework. Geometrical parameters, highest occupied molecular orbital and lowest unoccupied molecular orbital energies, global hardness, and softness were calculated to understand the distortion in the pores of the zeolite matrix. The most plausible active site of the complex was identified using the Fukui functions.

INTRODUCTION

Zeolite-encapsulated transition-metal complexes are interesting candidates for catalysis as their features are analogous to homogeneous and heterogeneous catalytic systems. They create a unique environment by posing steric and electrostatic constraints on voids and walls. These constraints determine the changes in the structural, electronic, redox, and magnetic properties of the encapsulated complexes, thereby contributing to the reactivity of the encapsulated complex.1–12 Zeolite framework has a porous structure that can accommodate a wide range of cations, such as Na+, K+, Ca2+, Mg2+, and others. These cations can readily be exchanged by the incoming cations. Exchanged cation plays a major role in compensating the negative charge and increasing electropositivity thereby strengthening the zeolite framework. It controls the space availability and offers various reactive sites for the guest molecules to interact.13,14 Bulk transition-metal oxides or on nonacidic support were utilized as the first-generation catalysts, which were developed for the alkanes aromatization. Among metal oxides, Cr2O3-based materials show interesting catalytic properties. In spite of their high selectivity, low activity, and fast deactivation, transition-metal oxides have paved the way for discovery of catalysts based on supported noble metals, which comprise second-generation catalyst. Generally, noble metal-supported catalysts are highly active for dehydrogenation of alkanes and hydrogenolysis reactions. However, the drawback of noble metal-supported acidic supports favors the formation of aliphatic hydrocarbons (light alkanes, isoparaffins, alkyl cyclopentanes, and alkyl benzenes) that aliphatic hydrocarbon. The selectivity toward aromatic hydrocarbon strongly depends on metal dispersion, alloying, passivation of metals due to carbon and/or sulfur deposition, acidic properties of the support, temperature, and pressure (hydrogen and alkane). Among the noble metals, Pt has been found to be the best candidate as it possesses excellent catalytic behavior adaptable/stable with solid support.15 Pt clusters (5–12 atoms) supported on basic zeolite (LTL) are found to be highly selective toward dehydrocyclization of alkanes. The reason for higher selectivity is still an unsolved mystery. It could be due to alternating of the redox potential because of confinement or due to the creation of active centers for the adsorption of substrates undergoing reactions. There are few speculations over the selectivity such as nonacidic nature of the support and monofunctional catalyst with platinum, which can provide catalytic sites.16,17 Miller et al. have proposed that cluster size plays an important role along with the presence of a nonacidic support. Furthermore, they reported that the geometry of the LTL zeolite pores is mainly responsible for the adsorption of n-hexane such that they are aligned inside the pore in a special manner, which favors 1–6 ring closure in the alkane.18,19 To resolve the mystery, the present work describes the theoretical investigation of tetraammineplatinum(II) complex encapsulated in various zeolites, such as zeolite Y, MWW, and LTL, and their catalytic activities were reasoned using density functional theory (DFT) studies.

RESULTS AND DISCUSSION

Ground State Geometries. The optimized geometries of the neat and zeolite-encapsulated platinum(II)tetraammine complex are shown in Figure 1. The selected geometric parameters of the optimized neat complex and the zeolite-

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encapsulated complex from B3LYP/LANL2DZ level calculations are tabulated in Table 1.

The geometrical parameters of the neat complex have been compared with the encapsulated complexes. The optimized geometry of the neat complex has equal Pt−N bond length. The bond angles of N1−Pt−N3, N1−Pt−N2, N2−Pt−N4, and N3−Pt−N4 strongly confirm the square planar geometry.

After encapsulating in LTL, MWW, and Y zeolites, Pt−N bond lengths and bond angles vary. Among the three encapsulated complexes, the LTL zeolite experienced more deviation due to the pore size. These observations support the experimental results reported by Miller et al.18

Table 1 reports the differences in bond length and bond angles of the neat and encapsulated complexes. The covalent character is proven by quantum chemical calculations of Si−O bonds in zeolites.28 Partially delocalized electronic clouds, which are contributed by valence electrons, are seen all over the framework of the zeolite. At short distances, the electron−electron repulsions will be operative between the complex molecule and the walls of cavities present in the zeolite, resulting in deviations in bond lengths.

Table 1. Bond Length and Bond Angle of the Neat and Encapsulated Complexes

| complex      | [Pt(NH3)4]2+ | [Pt(NH3)4]2+−LTL | [Pt(NH3)4]2+−MWW | [Pt(NH3)4]2+−Y |
|--------------|--------------|-----------------|-----------------|----------------|
| Pt−N1        | 2.11         | 3.11            | 2.03            | 2.09           |
| Pt−N2        | 2.11         | 2.08            | 2.11            | 2.11           |
| Pt−N3        | 2.11         | 2.04            | 2.09            | 2.12           |
| Pt−N4        | 2.11         | 2.09            | 2.10            | 2.08           |
| N1∠Pt∠N3    | 179.9        | 38.9            | 176.6           | 175.6          |
| N2∠Pt∠N4    | 179.9        | 170.8           | 169.8           | 177.6          |
| N1∠Pt∠N2    | 89.9         | 108.7           | 88.5            | 89.8           |
| N1∠Pt∠N4    | 90.0         | 92.0            | 93.4            | 88.0           |

Frontier Molecular Orbital Analysis. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of the neat and encapsulated complexes are represented in Figure 2. The HOMO energies are in the order of [Pt(NH3)4]2+ < [Pt(NH3)4]2+−Y < [Pt(NH3)4]2+−LTL < [Pt(NH3)4]2+−MWW and those of LUMOs are in the order of [Pt(NH3)4]2+ < [Pt(NH3)4]2+−Y < [Pt(NH3)4]2+−MWW < [Pt(NH3)4]2+−LTL. It can be observed from Figure 2 that the HOMO and LUMO energies of encapsulated complexes become destabilized. The energies of the frontier orbital of the metal complexes get changed upon encapsulation, leading to a small HOMO−LUMO gap. These changes may be due to (i) the effect of the counterion (two Al atoms in zeolite) and (ii) the steric constraint imparted by the zeolite matrix. When a guest molecule is confined inside zeolite, few types of interaction are considered, such as Coulombic effects, coordination effects, van der Waals interactions, and double-layer effects.29,30 These effects alter the energy levels including the metal complex chemical behavior.

Figure 1. Optimized geometries of the neat (a) [Pt(NH3)4]2+ and encapsulated (b) [Pt(NH3)4]2+−LTL, (c) [Pt(NH3)4]2+−MWW, and (d) [Pt(NH3)4]2+−Y complexes.
The percentages of orbital contribution to each atomic orbital, viz., HOMO and LUMO are given in Table S1. The main contribution to HOMO is from s (15%) and d (85%) orbitals of platinum and to LUMO is only from d orbital of platinum. After encapsulation, the main contribution to HOMO is from s and p orbitals of aluminum and p and s orbitals of oxygen, which are present in the zeolite matrix. The contribution to LUMO is mainly from d orbital of platinum, and a small quantity is contributed by the p orbital of nitrogen; but in the case of zeolite Y-encapsulated complex, the LUMO is coming only from the d orbital of platinum. This shows that the metal complex molecular orbital cannot extend over the entire space and restricts within the dimension of the zeolite cage. Upon substitution of aluminum in zeolite matrix, both HOMO and LUMO levels of platinum(II)tetraammine are stabilized.

The compositions of HOMO and LUMO considering the metal complex and zeolite as two segments are calculated and listed in Table S2. As apparent from the MO diagram of \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-LTL, the contributions of the \([\text{Pt(NH}_3\text{)}_4]^{2+}\) and LTL group are around 1.58 and 98.42%, respectively, toward HOMO, whereas LUMO is mainly constituted by metal complex (87%) and zeolite (13%). The HOMO of \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-MWW and \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-Y is composed largely of zeolite, and LUMO is stabilized with the contributions from metal complex.

**Ionization Potential (IP), Electron Affinity (EA), and Binding Energy.** The ionization potential (IP) and electron affinity (EA) values for all of the complexes are calculated and tabulated in Table 2. The values of the ionization potential (IP) of the encapsulated complexes are less than those of the neat complex. This indicates that the encapsulated complexes will act as a better oxidizing agent. This study reports the calculated interaction energy of the encapsulated complexes as the energy differences between the optimized encapsulated complexes and the corresponding fragments (the neat complex and the zeolite). The calculated interaction energies can be ordered as \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-LTL (−22.87 eV) > \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-MWW (−21.27 eV) > \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-Y (−22.23 eV), which indicates that the LTL complex interacts more strongly and is stable than the other two complexes. This interaction energy differences can be attributed to changes in the geometrical parameters.

Global and Local Descriptors. The global and local descriptor’s calculations have been performed as reported by Deka et al.1,2 Deka et al.2 have done calculations on the neat complexes, such as \([\text{Fe(Phen)}_3]^{2+}\), \([\text{Cu(Phen)}_3]^{2+}\), and \([\text{Zn(Phen)}_3]^{2+}\), and their corresponding encapsulated complexes defined as Fe−PhenY, Cu−PhenY, and Zn−PhenY, and their results are given in Table 3. Table 3 reports the chemical hardness (η), the chemical potential (μ), and the electrophilicity index (ω) values computed using B3LYP/LANL2DZ for the neat and encapsulated complexes. The global hardness of \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-LTL is lower in comparison to \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-MWW and \([\text{Pt(NH}_3\text{)}_4]^{2+}\)-Y, whereas it has higher global softness (S) than the other two encapsulated complexes. The maximum hardness and the minimum polarizability principle31–36 state that “hardness measures the stability and softness (polarizability) measures the reactivity”. Following the stated principle, \([\text{Pt(NH}_3\text{)}_4]^{2+}\) encapsulated in LTL zeolite shows higher reactivity with maximum softness and minimum hardness, which makes this complex a better catalyst in comparison with other complexes reported in this article.

Tables S3–S5 present the Fukui functions (FFs, \(f^+_k\) and \(f^-_k\)), local softness (\(S_k^L\) and \(S_k^S\)), and electrophilicity index (\(\omega^L_k\) and \(\omega^S_k\)) of the selected atoms calculated using Hirshfeld population.
M+ and the zeolite framework were revealed by the charge encapsulated complexes, respectively. It is noteworthy that the upon encapsulation, the value of ω ion having the most +ve value of NPA analysis are given in Table 4. The NPA charge of Pt in the system. The charge of nitrogen atoms in the neat complex is +0.604, whereas it has decreased in the zeolite and surrounding zeolite matrix. The interaction energies between the complex and zeolite were found to be reduction of the metal cation.

Table 4. Calculated Hardness (η, in eV), Chemical Potential (μ, in eV), Electroductility Index (ω, in eV), and Global Softness (S, in eV) Values for the Neat and Encapsulated Complexes

| complex                | μ      | η      | ω      | S      |
|-----------------------|--------|--------|--------|--------|
| [Pt(NH3)4]2+          | −12.755| 2.805  | 29.00  | 0.178  |
| [Pt(NH3)4]2+−LTL      | −3.875 | 1.725  | 4.352  | 0.289  |
| [Pt(NH3)4]2+−MWW      | −3.760 | 1.770  | 3.993  | 0.282  |
| [Pt(NH3)4]2+−Y        | −3.865 | 1.975  | 3.781  | 0.253  |
| [Fe(Phen)]3+          | −9.568 | 0.974  | 46.995 | 0.513  |
| Fe−PhenY (ref 2)      | −4.264 | 0.758  | 11.993 | 0.659  |
| [Cu(Phen)]3+          | −9.142 | 0.605  | 69.071 | 0.826  |
| Cu−PhenY (ref 2)      | −9.607 | 0.2875 | 160.529| 1.740  |
| Cu−PhenY(↑) (ref 2)   | −9.425 | 0.834  | 53.255 | 0.560  |
| Cu−PhenY(↓) (ref 2)   | −3.949 | 0.456  | 17.084 | 1.095  |
| Cu−PhenY(↑) (ref 2)   | −4.418 | 0.324  | 30.121 | 1.543  |
| Cu−PhenY(↓) (ref 2)   | −4.1785| 0.647  | 13.482 | 0.772  |
| [Zn(Phen)]3+          | −9.963 | 1.467  | 33.831 | 0.340  |
| Zn−PhenY (ref 2)      | −5.044 | 0.606  | 20.978 | 0.824  |

Table 3. Calculated Hardness (η, in eV), Chemical Potential (μ, in eV), Electroductility Index (ω, in eV), and Global Softness (S, in eV) Values for the Neat and Encapsulated Complexes

higher than that for MWW (21.27 kcal/mol) and Y (22.23 kcal/mol). Theoretical studies confirmed that the zeolite framework walls enforce space constrain to the metal complexes, which modifies their geometrical and catalytic behavior. The encapsulation changes the value of redox potential, which in turn causes altered catalytic behavior.

Supporting Information is drawn from DFT calculations, which shows the reduced distance between the HOMO and LUMO levels that is influenced by space constraint and Coulombic electrostatic field forced by the zeolite framework. On the whole, DFT calculations report that encapsulation (i) reduces the global hardness, (ii) increases the softness and (ii) the Fukui function values of the complexes, leading to higher catalytic activity. Taking the Fukui functions into account and evaluating the reactivity indexes, we conclude that the platinum atom is the most prone site for the attack of both nucleophile and electrophile.

COMPUTATIONAL DETAILS

All of the calculations were carried out using Gaussian 09 program with B3LYP correlation functional using LANL2DZ basis set. Three different zeolite frameworks (zeolite Y, MWW, and Linde type L) were created by taking 40 tetrahedral units (40T), where the supercage was saturated with hydrogens. First, crystallographic positions of Si and O atoms of the clusters were fixed and the positions of terminal H atoms were optimized. Following Lowenstein’s rule, two aluminum atoms were replaced in the position of two silicon atoms in the six-member ring to compensate two +ve charges of the complexes. The gas-phase-optimized Pt complex is then encapsulated inside the supercage. All geometric optimizations were performed without point group constraints.

The chemical potential (μ) and global hardness (η) can be expressed by Koopman’s theorem22 as

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

and

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

where $E_{\text{LUMO}}$ is the energy of the lowest unoccupied molecular orbital and $E_{\text{HOMO}}$ is the energy of the highest occupied molecular orbital.

The ionization potential (IP) and electron affinity (EA) of the system defined by the finite difference approximation are as follows.23

$$IP = E_{N-1} - E_{N}$$

$$EA = E_{N} - E_{N+1}$$

where $E_{N}$, $E_{N+1}$, and $E_{N-1}$ are the energies of the $N$, $N + 1$, and $N - 1$ electron systems, respectively.

The global electrophilicity defined by Parr et al.24 is given as

Table 4. Atomic Charge Distribution Calculated from the Natural Population Analysis (NPA) for the Neat and Encapsulated Complexes

| atom       | [Pt(NH3)4]2+ | [Pt(NH3)4]2+−LTL | [Pt(NH3)4]2+−MWW | [Pt(NH3)4]2+−Y |
|------------|-------------|------------------|------------------|----------------|
| Pt         | +0.604      | +0.592           | +0.576           | +0.567         |
| N1         | −1.029      | −1.013           | −1.049           | −1.032         |
| N2         | −1.029      | −1.018           | −1.012           | −1.030         |
| N3         | −1.029      | −1.152           | −1.046           | −1.025         |
| N4         | −1.029      | −1.042           | −1.043           | −1.023         |

 Density functional theory (B3LYP/LANLD2ZZ) studies report the influence of different zeolites on platinum(II)tetraammine complex. Three different frameworks, such as LTL, MWW, and Y zeolites, were studied. The framework of the LTL zeolite can stabilize the adsorption between the complex and the cage. The interaction energy for LTL zeolite is −22.87 kcal/mol, which is

analysis scheme. The $f_{\mu}$, $S_{\mu}$ and $ω_{\mu}$ values are analyzed in the context of an electrophilic attack, and the larger values of $f_{\mu}$, $S_{\mu}$ and $ω_{\mu}$ correspond to the most evident reaction site available for receiving an electrophile. It is observed from Tables S3−S5, upon encapsulation, the values of the FFs at the metal centers decrease. Reported calculations37−39 have shown that a minimum Fukui function site is preferred for hard−hard interactions and maximum for soft−soft interactions. However, upon encapsulation, the value of $f_{\mu}$ is changed with the metal ion having the most +ve value of $f_{\mu}$. The values of $f_{\mu}$, $S_{\mu}$ and $ω_{\mu}$ suggest that encapsulation alters the reaction site.

Natural Population Analysis (NPA). The results of the NPA analysis are given in Table 4. The NPA charge of Pt in the neat complex is +0.604, whereas it has decreased in the zeolite system. The charge of nitrogen atoms in the neat complex is −1.029, which shows the compensation between the complex and surrounding zeolite matrix. The interaction energies between the complex and zeolite were found to be −22.87, −21.27, and −22.23 kcal/mol for LTL-, MWW-, and Y-encapsulated complexes, respectively. It is noteworthy that the interaction energies with the amount of charge transfer between M+ and the zeolite framework were revealed by the charge reduction of the metal cation.

CONCLUSIONS

Density functional theory (B3LYP/LANLD2ZZ) studies report the influence of different zeolites on platinum(II)tetraammine complex. Three different frameworks, such as LTL, MWW, and Y zeolites, were studied. The framework of the LTL zeolite can stabilize the adsorption between the complex and the cage. The interaction energy for LTL zeolite is −22.87 kcal/mol, which is
The global softness $S$ is defined as

$$S = 1/2\eta$$

The condensed Fukui function of an atom, $k$, in a molecule with $N$ electrons is defined by a finite difference approximation as

$$f^+_k = [q_k(N + 1) - q_k(N)]$$ (for nucleophilic attack)

$$f^-_k = [q_k(N) - q_k(N - 1)]$$ (for electrophilic attack)

$$f^0_k = [q_k(N + 1) - q_k(N - 1)]/2$$ (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.

Equations 1–6 were used to calculate the global and local reactivity descriptors. Eqs 7 and 8 were used to calculate the Fukui functions ($f^+_k$ and $f^-_k$). The local softness value of an atom $k$ can be defined as the product of the Fukui function, and the global and softness values of selected atoms were calculated using eqs 10–12.

$$S_k^+ = [q_k(N + 1) - q_k(N)]S$$

$$S_k^- = [q_k(N) - q_k(N - 1)]S$$

$$S_k^0 = [q_k(N + 1) - q_k(N - 1)]/2$$

A generalized concept of philicity associated with a site $k$ in a molecule was defined by Chattaraj et al., as below

$$\omega_k^\alpha = \omega f^\alpha_k$$

where $\alpha = +, -, 0$ represent nucleophilic, electrophilic, and radical attacks, respectively.

The charge distribution in the complexes has been analyzed in the natural population analysis (NPA).

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**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b02069.

Orbital contribution (in %) to HOMO and LUMO for the neat and encapsulated complexes (Table S1); Frontier molecular orbital compositions (in %) in the ground state for the neat and encapsulated complexes (Table S2); Hirshfeld population analysis of the Fukui functions for the selected atoms of the neat and encapsulated complexes (Table S3); Hirshfeld population analysis of local softness for the selected atoms of the neat and encapsulated complexes (Table S4); Hirshfeld population analysis of local philicity indices for the selected atoms of the neat and encapsulated complexes (Table S5) (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: rrengas@gmail.com.

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