Calculation Study of Conversion Nitrate Ions to $N_2$ and $O_2$ by Zinc Oxide Nano-Cage ($Zn_{12}O_{12}$-NC)

Leila Mahdavian

Department of Chemistry, Doroud Branch, Islamic Azad University, Doroud, Iran

ABSTRACT

The aim of this study is to investigate the performance of zinc oxide nano-cages ($Zn_{12}O_{12}$-NC) to detect and reduce nitrate ($NO_3^-$) ions from aqueous media and convert them to oxygen and nitrogen gases by the density functional theory (DFT) method on a B3LYP level with basis set of 6-31+G*. Due to the structure of the nano-cage ($Zn_{12}O_{12}$-NC), there are some location positions with different potential on it. The results showed that the first N atom of nitrate ion strongly prefers to be adsorbed on O atoms and O of nitrate ion is adsorbed on Zn atoms of the 4-membered ring (4-MR). The electronic, structure and thermodynamic properties of these conversions are calculated and investigated. The energy gap ($E_g$) of the $Zn_{12}O_{12}$-NC is dramatically reduced from 3.88 to 1.22 eV upon the adsorption of $NO_3^-$ ion, suggesting that it is transformed to n-type semiconductor ascribed to the large charge transfer from the ion to the nano-cage and ions convert into oxygen and nitrogen on it. The data show that $Zn_{12}O_{12}$ nano-cage can be used to identify and reduce nitrate ions from the environment and may be helpful in several fields of study such as sensors, catalysts, and field emission investigations.

Keywords: DFT Method, Nano-Sensor, Nitrate Ions, Thermodynamic Properties, Zn12O12 Nano-Cage

INTRODUCTION

The nitrate ion is considered as a serious threat to the environment and aquatic ecosystems as one of the main sources of pollution [1]. There are several methods to remove nitrate ions from drinking water. The diluted, ion exchange and reverse osmosis are the most common methods for large-scale nitrate reduction [2]. Nowadays, nanotechnology has attracted the attention of researchers because of its low cost and high efficiency in removing pollutants [3]. The nanoparticles have a high ratio of surface to the volume which increases the reactivity of nanoparticles, therefore, have high sensitivity and fast response time to pollutants [4]. Thus, the development of nano-sensors for identification and reduction of these pollutants is the most important.

The nano-sensors of $C_{60}$, $X_{12}Y_{12}$ (X=Al, B and Y=N, P) nanocluster [9, 10], $B_{12}N_{12}$ nano-cage [11] and so on are used for detection of pollutants and toxic ions. $X_{12}Y_{12}$ nano-cage is magic and is more stable, this nano-cage is formed from six 4-membered rings (4-MRs) and eight 6-membered rings (6-MRs) with $T_h$ symmetry (The optimized structure of $Zn_{12}O_{12}$ nano-cage is in Fig. 1).

$Zn_{12}O_{12}$ nano-oxide sorbents have various structures, $X_{12}Y_{12}$ (X=Al, B and Y=N, P) nanocluster [9, 10], $B_{12}N_{12}$ nano-cage [11] and so on are used for detection of pollutants and toxic ions. $X_{12}Y_{12}$ nano-cage is magic and is more stable, this nano-cage is formed from six 4-membered rings (4-MRs) and eight 6-membered rings (6-MRs) with $T_h$ symmetry (The optimized structure of $Zn_{12}O_{12}$ nano-cage is in Fig. 1).

Zinc oxide is one of the available compounds which can be used to remove pollutants [12, 13], is known as a safe substance [14] and is one of the best options for removal of nitrate ion from the environment. A significant characteristic of zinc oxide is: piezoelectric, semiconductors, being inexpensive, bring non-toxic, bring abundant in nature, being environmentally friendly, having high thermal stability and so on [15-18]. Zinc nano-oxide sorbents have various structures,
Nitrate ions depends on the process of synthesis. They may be zinc oxide nanoparticles (Wurtzite) [19], nanospheres [20], nano boxes [21], hexagonal, tripods [22], tetrapods [23], nanowires, nanotubes, nanorings [24–27], nanocages, and nanoflowers [28, 27]. The Zn-O atoms are a bond of polarity because of a positive charge at Zn and a negative charge at O atom positions; can be an electrophilic or nucleophile molecule. The Zn12O12 nano-cage has been extensively studied at a theoretical level in compared to other its forms. The capacity of the Zn12O12 to adsorption different chemical species has been investigated: NO [28], H2S [29], Cl2 [12] and so on.

In this study, for the removal and reduction of nitrate ions from aqueous solution is used zinc oxide nano-cage (Zn12O12-NC). The interaction of nitrate ions with Zn12O12 nano-cage will be theoretically investigated based on analyses of structure, energies, HOMO-LUMO gaps (Eg), stability, electrical and thermodynamic properties and so on. Our results are likely to be useful for further studies related to making of Zn12O12 nano-cage (Zn12O12-NC): as nano-sensor, for investigation of this interaction is used GAMESS-US [30] of the program package in windows.

COMPUTATIONAL METHOD

Computational chemistry includes various mathematical methods which are divided into two groups: 1-molecular mechanics, 2-quantum mechanics. One of the most public computational programs is the quantum chemistry of Gaussian, which is developed by a Sir John Anthony Pople group in Peterborough [31]. Computations can be done on the systems in the gas phase or in the solution, and in the state of base or stimulating. The GAMESS-US program package used a wide range of Density Function theory models and energies decompose ingredients, decompose frequencies computed for all DFT models [32, 33]. All states of similarity of nitrate ion to zinc oxide nano-cage are optimized by B3LYP/6-31+G*. To study the thermodynamic properties, electrical and so on are calculated by this method for stages of conversion NO3 to N2 and O2. As follows:

\[
2\text{NO}_3^- + \text{ZnO-NC} \leftrightarrow 2\text{NO}_3^-\text{ZnO-NC} \\
2\text{NO}_3^-\text{ZnO-NC} \leftrightarrow \text{N}_2 + 3\text{O}_2 + \text{ZnO-NC}
\]

Energy and optimized geometric structure of molecules have a concrete relationship with chemical phenomena and the amounts of other similar atomic loads and border orbitals are less determined by qualitative results. Basically, the catalytic properties of the compositions are totally determined by their electronic structure. Therefore, designing the electronic structure based on the change in composition and physical structure is important. After simulation of Zn12O12-NC structure [34], is optimized by B3LYP/6-31+G* which can be observed in Fig. 1. The Zn12O12 nano-cage includes eight hexagonal rings (6-MRs) and six four-membered rings (4-MRs), Zinc and oxygen atoms have been equally and alternately placed inside the ring with Td symmetry. The heat of formation, geometric form of the molecule, ionization energy, electronic and other properties are calculated for nano-cage and NO3 ions, separately and then converted NO3 ions to N2 and O2 on nano-cage. The binding energy (E_{bind}) of NO3 ions on the nano-cage has been obtained using the following equation:

\[
E_{\text{bind}} = E_{X-\text{ZnO-NC}} - [E_X + E_{\text{ZnO-NC}}] + \delta_{\text{BSSE}}
\]

In this equation, the \(E_{X-\text{ZnO-NC}}\) is the total energy of pollutant energy (X) and (nano-adsorbent is

![Fig. 1. Ball and stick model of the optimized geometric structure of Zn12O12-NC from different views.](image-url)
subtracted from the pollutant complex energy with zinc oxide nano-cage (Zn\(_{12}\)O\(_{12}\)-NC) until the amount of change of thermodynamic and structural parameters of the reaction is achieved in which \(\delta_{BSE}\) is the amount of computational mistake.

RESULTS AND DISCUSSION

The accomplished computations for achieving structural properties are based on B3LYP/6-31+G* method which was performed at 298K temperature in an aqueous medium. In order to study the reaction of nitrate ion with nano-adsorbent for computing thermodynamic parameters, first the computational data from nano-cage and also nitrate ion are computed separately as shown in Table 1. The computed thermodynamic and structural properties of these structures by use of B3LYP/6-31+G* method are: the total energy (\(E_{\text{total}}\)), dipole moment (DM), the root mean square (RMS), the binding energy (\(E_{\text{bin}}\)), the heat of formation (H), the Gibbs free energy (\(G_{\text{ele}}\)), the nuclear energy (\(E_{\text{nuc}}\)) and electric energy (\(E_{\text{elec}}\)).

Table 1. The structural and thermodynamic parameters of nitrate and zinc oxide nano-cages at 298K.

<table>
<thead>
<tr>
<th>Nano-absorber</th>
<th>(E_{\text{total}}) kcal/mol</th>
<th>Dipole Moment (D)</th>
<th>RMS kcal/ml Å</th>
<th>(E_{\text{bin}}) kcal/mol</th>
<th>H kcal/mol</th>
<th>(G_{\text{ele}}) kcal/mol</th>
<th>(E_{\text{nuc}}) kcal/mol</th>
<th>(E_{\text{elec}}) (kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO(_3^\cdot)</td>
<td>-27176.2</td>
<td>3.418</td>
<td>125.5</td>
<td>-239.17</td>
<td>104.61</td>
<td>-61904</td>
<td>34727.77</td>
<td>0.0003</td>
</tr>
<tr>
<td>Zn(<em>{12})O(</em>{12})-NC</td>
<td>-129957.6</td>
<td>0.62</td>
<td>641.1</td>
<td>1903.66</td>
<td>2930.07</td>
<td>-609651.8</td>
<td>479694.2</td>
<td>0.0032</td>
</tr>
</tbody>
</table>

The obtained results show that greater structural symmetry leads to lower structural dipole moment and less polarity. The zinc oxide nano-cage is more symmetrical and also has a less RMS gradient. The zinc oxide nanocage is used, has twelve zinc and oxygen atoms which can also be shown in the form of Zn\(_{12}\)O\(_{12}\)-NC. Development of nano-cage compounds has caused extreme progress in the sciences, that it is called magical mixes.

As it can be observed in Fig. 2, there are several places for the interaction between pollutant and nano-cage. This nano-adsorbent has been made of two series of 6-RMs ring and 4-RMs ring which have different field and spatial positions to absorb pollutant. These positions are shown in Fig. 2. The nitrate ion can be close to one of these four positions. All probabilities are simulated.

Table 2 shows the computational parameters of all probabilities. Among all positions, first and fourth positions have a high dipole moment in compared to other positions, but thermodynamic

Table 2. The structural and thermodynamic properties of closed nitrate ions to different positions of zinc oxide nano-cage at 298K.

<table>
<thead>
<tr>
<th>Steps</th>
<th>(E_{\text{total}}) kcal/mol</th>
<th>Dipole Moment (D)</th>
<th>RMS kcal/ml Å</th>
<th>(E_{\text{bin}}) kcal/mol</th>
<th>H kcal/mol</th>
<th>(G_{\text{ele}}) kcal/mol</th>
<th>(E_{\text{nuc}}) kcal/mol</th>
<th>(E_{\text{elec}}) (kV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-11252.3</td>
<td>11.62</td>
<td>615.8</td>
<td>-64.08</td>
<td>-64.08</td>
<td>-394262.0</td>
<td>-282047.1</td>
<td>-0.0021</td>
</tr>
<tr>
<td>2</td>
<td>-10668.5</td>
<td>5.67</td>
<td>770.3</td>
<td>-319.73</td>
<td>-221.17</td>
<td>330575.2</td>
<td>-255132.0</td>
<td>-0.0017</td>
</tr>
<tr>
<td>3</td>
<td>-11452.5</td>
<td>6.69</td>
<td>593.4</td>
<td>-264.25</td>
<td>-354.08</td>
<td>315405.1</td>
<td>-252351.3</td>
<td>-0.0016</td>
</tr>
<tr>
<td>4</td>
<td>-11592.0</td>
<td>7.03</td>
<td>599.3</td>
<td>-403.85</td>
<td>-403.86</td>
<td>-217661.0</td>
<td>206369.2</td>
<td>0.0011</td>
</tr>
</tbody>
</table>

Fig. 2. a) the different positions of closed nitrate ion to Zn\(_{12}\)O\(_{12}\) nano-cage and b) the molecular electrostatic potential surface Zn\(_{12}\)O\(_{12}\) nano-cage.
properties calculated for the fourth position show a significant difference compared to other positions, that electrical energy ($E_{elec}$) of this position is much more than other positions in a way that it is 0.0011 kV. The $G_{ele}$ (kcal mol$^{-1}$) and $H$ (kcal mol$^{-1}$) calculated for the 4th position are at their lowest and the total energy for this position is lower. Thus, the possibility of closed nitrate ion to the 4th position of Zn$_{12}$O$_{12}$-NC is more than other positions.

In Zn$_{12}$O$_{12}$-nanocage, Zn atoms are positively charged (green colors) while the O atoms are negatively charged (red colors) in Zn-O bond, indicating the ionic character of these bonds by the molecular electrostatic potential surface in Fig. 2.

So, the closed nitrate ions to the fourth position on zinc oxide nano-cage are simulated in three stages. In Fig. 3, the D stage is a step close pollutants to Zn$_{12}$O$_{12}$-nanocage, the TS$^1$ is the transition state of the complex formed between pollutants and Zn$_{12}$O$_{12}$-NC that occurred exchanging electrons between them and goes into produces and E stage is the formation of produces (N$_2$ and O$_2$ molecules).

After adsorption of nitrate ions and the exchange of electrons between them, they are transformed into gaseous molecules of nitrogen and oxygen. The proposed mechanism after absorption of nitrate ions on Zn$_{12}$O$_{12}$-NC is as follows:

$$\text{NO}_3^- + \text{NO}_3^- \leftrightarrow 2\text{NO}_2 + \text{O}_2 + 2e^-$$
$$2\text{NO}_2 \leftrightarrow 2\text{NO} + \text{O}_2$$
$$2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$$

Computed data of these stages can be observed in Table 3 and the greatest changes in the structure and thermodynamic changes are in the transition state TS$^1$. The $E_{elec}$ for this stage has most changes, is 3.2 V. Because of the symmetry structure of NO$_3^-$ ions changes from $T_h$ to $D_{\infty h}$ and the polarity of Zn$_{12}$O$_{12}$ nano-cage increases.

As it can be seen in obtaining computational data in Tables 3 and 4, the center of zinc oxide nano-cage is the most sensitive position for adsorption of pollutants. Thus, the Gibbs free energy ($\Delta G_{ele}$), the heat of formation ($\Delta H$), entropy ($\Delta S_{ele}$) and the equilibrium constant (K) is calculated between 1st and 2nd steps. The data of Table 4 show that this reaction is spontaneous. The entropy change ($\Delta S_{ele}$) is positive; it is of the entropy increase type. Considering the changes in thermodynamic functions, the reaction is favorable because of the negative Gibbs free energy ($\Delta G_{ele}$), and the positive entropy change ($\Delta S_{ele}$). Therefore, Zn$_{12}$O$_{12}$-nanocage can be used as a sensor for the measurement and reduction of nitrate ions from the environment.

![Fig. 3. The pathway of interaction and the electron transport of nitrate ions with the adsorbent of Zn$_{12}$O$_{12}$ nano-cage.](image)

Table 3. The calculation of electrical energy ($E_{elec}$), Dipole Moment (DM), RMS gradient, total energy ($E_{total}$), heat of reaction formation ($H$), Gibbs free energy ($G_{ele}$), nucleus energy ($E_{nuc}$) and binding energy ($E_{bin}$) for D, TS$^1$, and E by B3LYP/6-31+G* method at 298K.

<table>
<thead>
<tr>
<th>Steps</th>
<th>$E_{total}$ kcal/mol</th>
<th>Dipole Moment (D)</th>
<th>RMS gradient kcal/mol Å</th>
<th>$E_{elec}$ kcal/mol</th>
<th>$H$ kcal/mol</th>
<th>$G_{ele}$ kcal/mol</th>
<th>$E_{nuc}$ kcal/mol</th>
<th>$E_{bin}$ kcal/mol</th>
<th>$E_{elec}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>-50591</td>
<td>10.01</td>
<td>571.5</td>
<td>-1277.68</td>
<td>-3098.76</td>
<td>-572910</td>
<td>-79649</td>
<td>2.9</td>
<td></td>
</tr>
<tr>
<td>TS$^1$</td>
<td>-35151.9</td>
<td>557.4</td>
<td>2427</td>
<td>14161.44</td>
<td>14505.21</td>
<td>-611808</td>
<td>-769554</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>199614</td>
<td>938.5</td>
<td>4406</td>
<td>261152.1</td>
<td>261617.7</td>
<td>-150551</td>
<td>-766773</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>
The structural parameters can be achieved based on the energy levels of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO). The electron-affinity energy of the molecule is a baseline difference with the energy level of LUMO, and the ionization energy of the molecule is the difference in the baseline energy level with the energy level of HOMO. The total energy of the two levels is twice the electronegativity (η) of the molecule, which is a criterion for the hardness and softness of the molecular structure (Fig. 4).

The molecule will have a smooth structure and a high polarization when the two energy levels (above) are close to each other. If the two energy levels are higher distant, the molecule structure will be harder with a lower polarization. The energy difference between the two levels is called the energy gap (Eg), which represents the conductivity level of the molecular structure. The chemical potential or electronegativity (η) [the Eₓa and Eₓi are electron affinity and ionization energy, respectively], chemical hardness (µ), chemical softness (σ), electrophilicity (ω), and molecular charge transfer (ΔN_MAX) were calculated using the following relationships:

\[
E_g = E_{\text{LUMO}} - E_{\text{HOMO}} \\
\eta = (E_{\text{LUMO}} + E_{\text{HOMO}})/2 \\
\mu = (E_{\text{LUMO}} - E_{\text{HOMO}})/2 \\
\sigma = 1 - \mu \\
\omega = \eta/2 \mu \\
\Delta N_{\text{MAX}} = - \eta / \mu
\]

The calculated parameters (Table 5) show that...
the orbital gap energy ($E_g$) is very important to control and detect sensors and filters. The lower the amount of $E_g$, the greater the nano-adsorbent conductivity; in other words, the transmission of electrons between the nitrate ions and the nano-adsorbent increases when the distance between the HOMO and LUMO energy levels is lower in order to generate an electrical signal. The relationship between the electric conductivity ($\mu$) and the orbital gap energy ($E_g$) is shown below:

$$E_g \approx \exp(-E_g/2kT)$$  \hspace{1cm} (8)

where $k$ is the Boltzmann constant and $T$ is the ambient temperature. This equation shows a direct relationship between $E_g$ and $E_g$, indicating a better electrical conductivity for Zn$_{12}$O$_{12}$-NC when ions are close to it.

According to the data in Table 5, The $E_g$ decreases for the TS`$_1$ stage, therefore Zn$_{12}$O$_{12}$-NC is an n-type semiconductor. The $\mu$ and $\sigma$ denote the hardness and softness of the molecules, respectively. HOMOs and LUMOs in hard and soft molecules have large and low gaps, respectively. The molecular charge transfer ($\Delta N_{MAX}$) reflects the electron donority or receivability of the pollutant and the nano-adsorbents.

CONCLUSION

The zinc oxide nanocage was used in this study to remove nitrate ions from the water environment. All of the structures of Zn$_{12}$O$_{12}$-nanocage and pollutant have been optimized using DFT methods by B3LYP/6-31+G*. The structural and thermodynamic properties of these interactions have been calculated by this method and the reason for choosing this computational method are computation speed, obtaining electrical properties and so on. Due to Zn metal using in nano-cage finds this based set of the calculations. The Nanocage interaction with nitrate ions is in the center position of the Zn$_{12}$O$_{12}$-NC and the exchange of electrons between them is better in this position. The results of the thermodynamic show that the conversion of nitrate ions to nitrogen and oxygen molecules on the Zn$_{12}$O$_{12}$-nanocage is possible. The Zn$_{12}$O$_{12}$-NC has semiconducting properties with direct energy gap and is particularly stable at room temperature. The nitrate ions are all chemisorbed on the Zn$_{12}$O$_{12}$-NC with reasonable adsorption energies. The electronic properties of the Zn$_{12}$O$_{12}$-NC present dramatic changes after the adsorption of the nitrate ions, especially their electric conductivity. Therefore, synthetically considering the adsorption energies, charge transfer and the change of electric conductivity can conclude that the Zn$_{12}$O$_{12}$-NC is a potential candidate for nanosensors with high sensitivity for nitrate ions.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

REFERENCES


14. Bagabas A, Alshammari A, Aboud MFA, Kosslick H. Room-temperature synthesis of zinc oxide nanoparticles...


