DFT Study of CO2 Adsorption on the Zn12O12 Nano-cage

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Received August 25, 2013, Accepted September 22, 2013

Covalent functionalization of a Zn12O12 nano-cage with CO2 molecule in terms of energetic, geometry, and electronic properties was investigated by density functional theory method. For chemisorption configurations, the adsorption energy of CO2 on the Zn12O12 nano-cage for the first CO2 was calculated −1.25 eV with a charge transfer of 1.00|e| from the nano-cage to the CO2 molecule. The results show that CO2 molecule was significantly detected by pristine Zn12O12 nano-cage, therefore the nano-cage can be used as CO2 storage. Also, more efficient binding could not be achieved by increasing the CO2 concentration. For Physisorption configurations, HOMO–LUMO gap of the configurations has not changed, while slight changes have been observed in the chemisorption configurations.

Key Words : Zinc oxide nano-cage, Adsorption, Functional group, CO2

Introduction

Carbon dioxide (CO2) is known as a greenhouse gas (GHG) and has an important contribution in global climate changes.1,2 The main source of CO2 emission worldwide comes from fossil fuel electric power plants.3 Capture and sequestration of the CO2 emitted from different sources is thus one of the most pressing issues in the environmental protection. Therefore, it is very important to develop a simple, rapid and reliable method for the capture and sequestration of CO2 in many cases. Adsorption of CO2 on zinc oxide (ZnO) surfaces has attracted considerable attention in the last decade. Adsorption of carbon dioxide on the ZnO(0001) surface has been studied by different groups.4,5 Fink6 has studied adsorption of CO2 on the ZnO (0001) surface. Its results showed CO2 dissociation at oxygen vacancy of (0001) surface. Also, Sergio et al.7 have reported CO2 adsorption on polar surfaces of ZnO. They showed a clear interaction between the CO2 molecule and the surface.

Nanostructures due to their novel properties are intriguing in cluster protection, nano-ball bearings, nano-optical magnetic devices, catalysis, gas sensors, and biotechnology.6,7 In recent years, there have been numerous studies of the adsorption of CO2 on solid surfaces4,5; while there are few studies about the adsorption of CO2 on nanostructures surfaces. Therefore, further study of CO2 adsorption on the nanostructures is important task. ZnO nanostructures have been widely investigated both theoretically and experimentally.6,7 Recently, stability of fullerene-like cages of (XY)n nanostructures have been investigated and it has been suggested that the fullerene-like cage (XY)12 is energetically the most stable cluster among different types of (XY)n structures.8,9 Therefore, it can be concluded that the fullerene-like cage (ZnO)12 is energetically the most stable cluster in this family and would thus be an ideal inorganic fullerene-like cage. The aim of this work is to investigate theoretically adsorption of CO2 on Zn12O12 nano-cage based on analyses of structure, energies, stability, electronic properties, etc. Our results are likely to be useful in functionalization of ZnO nanoclusters, construction of a CO2 storage material, nano electronic devices, and other applications.

Computational Methods

Spin-unrestricted B3LYP/6-31G* level of theory has been largely used to describe the adsorption CO2 molecule on surfaces of Zn12O12 nano-cage, specifically the structural and electronic properties. For the Zn atoms, the standard LANL2DZ basis set10 was used. Earlier studies indicated that the computations based on the B3LYP/6-31G* level of theory could yield reliable results in study of different nanostructures.8,11 This method was used to calculate the adsorption energy (Ead) of CO2 molecule on the surface of Zn12O12 nano-cage as follows:

\[ E_{ad} = E_{CO2/ZnO} - [E_{ZnO} + E_{CO2}] \] (1)

Where \( E_{CO2/ZnO} \) is the total energy of an adsorbed CO2 molecule on the pure Zn12O12 nano-cage, \( E_{CO2} \) is referred to the energy of a single CO2 molecule, and \( E_{ZnO} \) is the energy of the pristine Zn12O12 nano-cage. Negative or positive value for \( E_{ad} \) is referred to exothermic or endothermic processes, respectively. All the calculations were carried out by using the GAMESS suite of programs.12

Results and Discussion

Optimized Structure of Zn12O12. The pristine Zn12O12 nano-cage was allowed to relax in the optimization at B3LYP/ LANL2DZ level of theory. Optimized structure of the Zn12O12 nano-cage is formed from eight 6-membered (hexagon) rings and six 4-membered (tetragon) rings with \( T_6 \) symmetry. Optimized structure and geometrical parameters of the Zn12O12 nano-cage is shown in Figure 1. As is shown in Figure 1, two types of Zn–O bonds are computed in...
\(\text{Zn}_{12}\text{O}_{12}\) nano-cage, one with the bond length of 1.91 Å which is shared between two hexagon rings, and the other which is shared between a tetragon and hexagon ring with length of 1.98 Å. The angles in 4-membered and 6-membered rings in \(\text{Zn}_{12}\text{O}_{12}\) nano-cage vary from 88.9 to 90.8 and from 116.2 to 123.6, respectively. The calculated energy gap \((E_g = E_{\text{LUMO}} - E_{\text{HOMO}})\) of the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage was calculated from the total densities of states (DOS) results. As is shown in Figure 1(b), the \(E_g\) of nano-cage is 4.19 eV, indicating that the nano-cage is a semiconductor.

Adsorption of CO\textsubscript{2} on the \(\text{Zn}_{12}\text{O}_{12}\). In order to determine the minimum adsorption energy structure of adsorbed CO\textsubscript{2} on the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage, various possible initial adsorption geometries including both the carbon and oxygen atoms of CO\textsubscript{2} close to hexagon and tetragon rings, oxygen atom close to Zn atom, two oxygen atoms locating top of the two Zn atoms of a hexagon or tetragon rings and one of the oxygen atoms above the center of 4-hexagon or tetragon rings. After careful structural optimizations without any constraints, re-orientation of the molecule has been observed in some states, and finally it was found that only three kinds of the considered configurations are stable and are shown in Figure 2.

As shown in Figure 2(a), the C atom of CO\textsubscript{2} molecule is bonded to O atom of the nano-cage, so that the plane of CO\textsubscript{2} has bent due to the intramolecular steric repulsion. In configuration (a), length of the newly formed C-O bond is 1.36 Å. The adsorption of CO\textsubscript{2} shows an apparent local structural deformation on both the CO\textsubscript{2} and the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage. In the configuration, O–C–O angle of CO\textsubscript{2} molecule is reduced from 180° to 128.6° and the bond length of C-O is increased from 1.17 Å in isolated CO\textsubscript{2} to 1.27 Å in the adsorbed state. In addition, the length of Zn–O bonds in adsorbed ring increased from 1.91 and 1.98 Å to 2.14 and 2.39 Å in the configuration. Further indication of the deformation degree in the geometry of CO\textsubscript{2} due to the adsorption process is given by the bond reorganization energy \((E_{br})\). \(E_{br}\) is as the calculated energy difference between the full relaxed CO\textsubscript{2} molecule and its adsorbed state, in which for each state is summarized in Table 1. \(E_{br}\) of CO\textsubscript{2} molecule for this configuration is 2.5 eV and the \(E_{\text{ad}}\) is −1.25 eV, indicating a strong interaction and chemisorption process. Natural bond orbital (NBO) analysis shows a charge transfer of −1.00|e| from the nano-cage to the CO\textsubscript{2} molecule. In the configuration, the vacant \(\pi^*\) orbital of C=O in the CO\textsubscript{2} molecule accepts the electrons from the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage and CO\textsubscript{2} \(\pi\)-bond breaking due to electron backdonation from the \(\text{Zn}_{12}\text{O}_{12}\) to CO\textsubscript{2} and the CO\textsubscript{2} molecule undergoes the structural distortion to a bent structure. Therefore, the O-C-O angle is reduced to 128.6°, and the broken C-O bond is significantly elongated to 1.27 Å.

In configuration (b) (Fig. 2(b)), one of the oxygen atoms of CO\textsubscript{2} molecule is close to a Zn atom of the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage by an interaction distance of 2.37 Å. The \(E_{\text{ad}}\) and \(E_{br}\) of CO\textsubscript{2} molecule for this configuration are −0.40 and 0.01 eV, respectively and a charge of 0.03|e| is transferred from the CO\textsubscript{2} molecule to the nano-cage. The results indicate that this interaction is weak and should be considered as a physisorption. Another CO\textsubscript{2} physisorption approach is shown in Figure 2(c), in which the interaction distance between both of the oxygen atoms of CO\textsubscript{2} molecule and the Zn atoms of a tetragon ring of the nano-cage is about 2.80 Å. This configuration has an \(E_{\text{ad}}\) of −0.37eV and does not show charge transfer to take place between the CO\textsubscript{2} and \(\text{Zn}_{12}\text{O}_{12}\) nano-cage. Also, \(E_{br}\) of CO\textsubscript{2} molecule for this configuration is zero.

There are several hexagon and tetragon rings in structure of the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage as potential adsorption site; therefore the possibility of the second adsorption is interesting for consideration. In this configuration (Fig. 3(d)), two CO\textsubscript{2} molecules are adsorbed on the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage. The \(E_{\text{ad}}\) and \(E_{br}\) of CO\textsubscript{2} molecule for this process is about −1.03 and 2.44 eV per CO\textsubscript{2} molecule with a charge transfer of −0.98|e|, which are slightly lower than that of one CO\textsubscript{2} adsorption due to the steric repulsion between two CO\textsubscript{2} molecules. In the next step, three and four CO\textsubscript{2} molecules are adsorbed on the \(\text{Zn}_{12}\text{O}_{12}\) nano-cage (Fig. 3(e) and (f)). The \(E_{\text{ad}}\) for these configurations are about −1.05 and −1.12 eV per CO\textsubscript{2} molecule for three and four molecules adsorption. \(E_{br}\) of CO\textsubscript{2} molecule for these processes are 2.43 and 2.45 eV per CO\textsubscript{2},
respectively. In comparison with the one CO$_2$ adsorption model (Fig. 2(a)), the $E_{ad}$ and $E_{br}$ of CO$_2$ molecule due to the steric repulsion between the CO$_2$ molecules is reduced. 

**Figure 2.** Models for three optimized structure of CO$_2$/Zn$_{12}$O$_{12}$ configurations and their density of state (DOS) plots. Distances are in angstrom.

**Adsorption of CO$_2$ on the Electronic Properties of Zn$_{12}$O$_{12}$ Nano-cage.** Finally, to better understand the interaction between CO$_2$ with the Zn$_{12}$O$_{12}$ nano-cage, the influence of
CO$_2$ adsorption on the electronic properties of the nano-cage was studied. The difference in energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), $E_g$, was calculated from DOS plots. As shown in Table 1, with comparison of DOS of the free ZnO nano-cage and the physisorption configurations (Fig. 2(b) and (c)), it is found that their $E_g$ value have changed about 0.24-0.72% after the CO$_2$ adsorption. In the physisorption configurations the valence and conduction level energies are relatively the same as for the pristine Zn$_{12}$O$_{12}$ valence and conduction level energies. Therefore, the results show that the CO$_2$ adsorption through these configurations has not sensible effects on the electronic properties of the nano-cage. For functionalization or chemisorption cases (Fig. 2(a) and Fig. 3(d)-(f)), it is revealed from DOS plots that their valence level energies in the cases are approximately similar to that of the Zn$_{12}$O$_{12}$, while the conduction level energies some shift downwards. As

![Figure 3. Model for 2CO$_2$, 3CO$_2$, and 4CO$_2$ chemisorbed-Zn$_{12}$O$_{12}$ configurations and their density of states (DOS) plots. Distances are in angstrom.](image)
shown in Table 1, upon the CO₂ adsorption on the Zn₁₂O₁₂ nano-cage, the $E_g$ value of the nano-cage are more changed compared to the physisorption cases, in other words, when number of CO₂ molecules increased from 0 to 3, band gap of the ZnO nano-cage has changed about (1.6-7.978%). However, when 4CO₂ molecules are adsorbed, the band gap has changed about 0.95% due to the steric repulsion between the CO₂ molecules. In fact, with increasing of CO₂ numbers, the $E_g$ of CO₂ molecules is decreased (see Table 1) and increasing of CO₂ molecules has no sensible effects on the electronic properties of the nano-cage. Therefore, Change of $E_g$ value in the configuration F (with 4CO₂ molecules) is reduced.

In a molecule at 0 Kelvin, Fermi level lie approximately middle of the $E_g$. Table 1 indicates that the Fermi level energy ($E_{FL}$) of the physisorption configurations is increased from $-4.84$ eV in the pristine Zn₁₂O₁₂ nano-cage to $-4.75$ and $-4.81$ eV in the (b) and (c) configurations. This increasing of $E_{FL}$ with CO₂ adsorption leads to a decrement in the work function which is important in field emission applications. The work function is the minimum energy required for one electron to be removed from the Fermi level to the vacuum. The decrement in the work function shows that the field emission properties of the configurations are improved upon the CO₂ adsorption. While, the $E_{FL}$ of the chemisorption configurations is shifted down (see Table 1) which leads to an increment in the work function. The increment in the work function shows that the field emission properties of the configurations are impeded upon the CO₂ adsorption and have a disadvantageous effect on the field emission properties of Zn₁₂O₁₂ nano-cage.

Conclusions

Physisorption and chemical functionalization of CO₂ molecule on the Zn₁₂O₁₂ nano-cage were studied using density functional calculations. Binding energy corresponding to adsorption of CO₂ on the Zn₁₂O₁₂ in the most stable configuration was calculated to be $-1.25$ eV with a charge transfer of 1.00 e from the nano-cage to the CO₂ molecule. On the basis of our calculations, it seems that attachment of the CO₂ molecule on the walls of the Zn₁₂O₁₂ nano-cage induces some changes in electronic properties of the cluster and its $E_g$ is slightly reduced after covalent functionalization process. The results show that pristine Zn₁₂O₁₂ nano-cage can significantly detect CO₂ molecule. Also, more efficient binding could not be achieved by increasing the CO₂ concentration. The strong adsorption of the CO₂ on the Zn₁₂O₁₂ nano-cage shows the potential application of the ZnO-based materials for CO₂ capture and storage.

Acknowledgments. The publication cost of this paper was supported by the Korean Chemical Society.

References