DFT study of carbon dioxide capture on functionalized graphane sheets

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Abstract—CO$_2$ capture and storage is a potential means to alleviate global warming and ocean acidification. Herein, CO$_2$ capture with various functionalized graphanes and the effects of functional groups are investigated by density functional theory (DFT). Our results show that CO$_2$ adsorbs weakly on a bare graphane sheet, and absorbs slightly better when functionalized with P-substituted graphane, and increasingly better with PH$_2$-grafted on H atoms. Further, the presence of H$_2$O would provide strong CO$_2$ adsorption and the exothermic adsorption energies could reach about -42 kJ/mol with PH$_2$-grafted on graphane. This computational work provides an atomic-level strategy in the design of functionalized graphane and carbon-based adsorbent materials for CO$_2$ capture and storage.

Keywords—DFT, CO$_2$ capture, Graphane, Functional groups

I. Introduction

The concentration of greenhouse gas carbon dioxide (CO$_2$) in the atmosphere has risen from about 310 to 390 ppm over the past few decades, and the pH value of surface seawater would decrease from 8.2 to 7.8 by 2095 for the accumulation effect of dissolved CO$_2$. Carbon capture and storage (CCS) is a promising approach to capture waste CO$_2$ from large point sources, such as fossil fuel power plants, and has attracted considerable attention during the past several years. CCS transports CO$_2$ to a storage site, or deposits it to, for example, an underground geological formation to avoid it entering the atmosphere. CO$_2$ capture and separation at stationary point source is very important for practical CCS applications. So, one of the key issues to improve CO$_2$ capture performance is to explore efficient capture materials, which should have high CO$_2$ adsorption capacity, excellent adsorption selectivity, and good chemical and mechanical stability. Various adsorbent materials have been proposed for CO$_2$ capture. They include carbon nanotubes, activated carbon, porous organic polymers, covalent organic frameworks, metal organic frameworks, porous graphane membranes, and Zeolites. However, due to their physical characteristics or economic consideration in the processes of synthesis, manufacture and regeneration, they are not fully desirable. Therefore, the development of feasible materials to enhance CO$_2$ capture and separation is still outstanding.

Graphane, a lengthened two-dimensional (2-D) polymer of hydrocarbon, is a burgeoning carbon-based material with attractive properties. Graphane is composed of a monolayer of 2-D sheets of carbon atoms, and the carbon bonds of graphane are in sp$^3$ configuration, as opposed to graphene’s sp$^2$ bond configuration. Unlike graphene, hydrogen grafted to a carbon atom on graphane sheet can be substituted by functionalities without affecting the remaining parts of the graphane structure. Maximizing atomic utilization and tunable composition and functionalities of graphane offer new possibilities for structure of materials based on two-dimensional carbon for applications including adsorption and catalysis. In this paper, we present a DFT investigation of CO$_2$ adsorption over P-substituted/grafted graphanes. CO$_2$ adsorption energies over graphanes with or without P-functionalization are compared to identify the effects of P-site density and position. The effect of moisture addition is also explored. The partial density of states (PDOS) analysis is preformed to elucidate the CO$_2$ adsorption rule. This work therefore contributes to the fundamental understanding of the structural, energetic, and electric properties of substituted/grafted graphanes for CO$_2$ adsorption and may be useful for the design and screening of adsorbent materials for carbon capture and storage.

II. Computational details

DFT calculations were performed with the DMol$^3$ program package in Materials Studio 7.0 of Accelrys Inc., using the exchange-correlation functional of GGA-PW91 approximation. A vacuum layer of 15 Å was added perpendicular to the single layer surfaces. Monkhorst–Pack (MP)$^{26}$ k-point mesh was used for all of the surfaces. The system was modeled as a 4 × 4 supercell of graphane, which contained 32 C atoms plus 32 H atoms, as shown in Fig. 3.1a. The unit cell of graphane was initially optimized as $a = b = 2.46$ Å, which is close to the reported unit cell values of graphane ($a = b = 2.52$ Å). The atomistic models of graphane was built as chair configuration as it is more stable than the boat configuration. The isolated gas phase adsorbates (CO$_2$ and H$_2$O) were optimized separately. All the atoms in the cell were relaxed and all calculations were spin-polarized.

The adsorption energy ($E_a$) is calculated by subtracting the sum of the energy of the isolated adsorbent surface and the energy of the optimized gas-phase adsorbate from the energy of the optimized adsorbate–adsorbent system, which can be expressed by the following equations:

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\[ E_a = E_{\text{adsorbent-adsorbent}} - E_{\text{adsorbent}} - E_{\text{gas}} \]  

where \( E_{\text{adsorbent}} \) is the energy of the bare or functionalized graphene adsorbent, \( E_{\text{gas}} \) is the energy of isolated CO\(_2\) or H\(_2\)O, \( E_{\text{adsorbent-adsorbent}} \) is the total energy of the adsorbent–adsorbent system, such as the adsorbent–CO\(_2\), the adsorbent–H\(_2\)O, and the adsorbent–(CO\(_2\)+H\(_2\)O) system. A more negative \( E_a \) indicates a stronger adsorption.

### III. Results and discussion

#### A. CO\(_2\) adsorption over P-Substituted and PH\(_2\)-grafted graphanes

The optimized basic graphene surfaces (a) bare, (b) P-substituted, and (c) PH\(_2\)-grafted are shown in Fig. 1. The substitution of a single C atom in the lattice with a P atom led to P concentration of 3.13 wt %. As shown in Fig. 1a, the bare graphane structure is in a chairlike conformation with the H atoms alternating on both sides of the plane, which is a preferable conformation compared to the boatlike conformer with the H atoms alternating in pairs.\(^{[21,22]}\) All the C atoms form a hexagonal network, and the calculated C–C bond length is 1.50 Å, similar to the sp\(^2\) bond length of 1.53 Å of ethane, and much longer than the typical bond length (1.42 Å) of sp\(^3\) carbon. As shown in Figs. 1b and 1c, the basic graphane structure is well retained with slight distortion of the hexagonal lattice in both P-substituted and PH\(_2\)-grafted structures.

![Fig. 1. Optimized graphane surfaces: (a) bare, (b) P-substituted, and (c) PH\(_2\)-grafted. Color code: gray, C; purple, P; white, H.](image)

**CO\(_2\) adsorption over P-substituted graphanes.** To study the effects of P-site density on P-substituted graphane on CO\(_2\) adsorption, CO\(_2\) adsorption thermodynamics over a 4 × 4 graphene unit cell surface with 0 ~ 2 units of P-sites (0, 3.13, and 6.27 wt% of P-site density) were studied. The optimized interaction configurations and adsorption energies are given in Fig. 2. For the substitution of 2 P-sites per graphene cell, three configurations of P-sites in meta-, para-, and ortho-positions were considered. Doping P atoms into a graphene unit cell strengthens the CO\(_2\) adsorption when compared to adsorption on an undoped surface (adsorption energy changes from -3.313 (undoped) to -4.895 (1-P) and -9.861 (2-P ortho-position) kJ/mol, respectively. The result suggests that higher P-site density gives more exothermic CO\(_2\) adsorption. With 2 P atoms doped in the graphene unit cell, the CO\(_2\) adsorption energy varies with the placement of the P atoms, which increases in the order of ortho > para > meta. Regardless of the concentration of P-doped, all the adsorption of CO\(_2\) over P-substituted graphane is weak, similar to CO\(_2\) adsorption over N-substituted graphane.\(^{[22]}\)

![Fig. 2. Optimized interaction configurations and adsorption energies (\(E_a\) in kJ/mol) for CO\(_2\) adsorption over graphanes: (a) bare graphane; (b) single P-substituted graphane; (c) 2 P-substitutions in meta-position; (d) 2 P-substitutions in para-position; (e) 2 P-substitutions in ortho-position. Color code: gray, C; red, O; purple, P; white, H.](image)

**CO\(_2\) adsorption over PH\(_2\)-grafted graphanes.** Primary phosphino (PH\(_2\)) grafted graphanes are expected to offer stronger basicity,\(^{[27]}\) leading to a stronger CO\(_2\) adsorption (an acidic molecule). This hypothesis was investigated via studying several modes of adsorption on these surfaces. One interaction configuration was CO\(_2\) physisorption, the other hypothesis configuration was the reaction of PH\(_2\) and CO\(_2\).\(^{[28]}\) Figs. 3a and 3b show the proposed interaction configurations and adsorption energies. CO\(_2\) adsorbs weakly on graphane surface-functionalized with single grafted PH\(_2\)-sites, with an exothermic adsorption energy -6.762 kJ/mol. The reaction of PH\(_2\) and CO\(_2\) (Fig. 3b, \(E_a = 42.997 \text{ kJ/mol}\)) is not favorable, comparing with physisorption over a single PH\(_2\)-functionalized surface.

![Fig. 3. Proposed interaction configurations and adsorption energies (\(E_a\) in kJ/mol) for CO\(_2\) adsorption on P-functionalized graphanes: (a) PH\(_2\)-grafted by physisorption; (b) PH\(_2\)-reaction with CO\(_2\); (c) 2PH\(_2\)-grafted by physisorption; (d) one of the 2PH\(_2\) reacting with CO\(_2\); (e) P-substituted with H\(_2\)O; (f) PH\(_2\)-grafted with water. Color code: gray, C; red, O; purple, P; white, H.](image)

To further survey the effect of –PH\(_2\) functional group on CO\(_2\) adsorption, a second –PH\(_2\) functional group proximate to the –PH\(_2\) site is added. Also, two interaction configurations were studied: CO\(_2\) adsorption by (a)
physiosorption, (b) one of the 2PH$_2$- reaction with CO$_2$. The optimized interaction configurations and adsorption energies are shown in Figs. 3c and 3d. Physiosorption occurs with an adsorption energy of -6.504 kJ/mol, while adsorption energies for PH$_2$- reaction with CO$_2$ were also positive. The positive values of $E_a$ in two reaction configurations indicate that the structures are unstable relative to desorption. Bending the CO$_2$ molecule or transferring a H atom to CO$_2$ creates a local minimum energy structure, thus forming the instability.\cite{22} Compared to one –PH$_2$ grafted, two proximate –PH$_2$ functional groups on graphane hinder the CO$_2$ adsorption, which is probably due to the geometrical restrictions. Overall, similar to P-substituted graphane, the density of phosphorus sites only slightly affects the CO$_2$ adsorption energy. The adsorption of CO$_2$ over PH$_2$-graphane is relatively weak, and PH$_2$- reaction with CO$_2$ is not favorable. Therefore, neither P-substitution nor directly grafted PH$_2$-groups on graphane provide favorable sites for CO$_2$ adsorption.

B. CO$_2$ adsorption over P-Substituted and PH$_2$-grafted graphanes in present of H$_2$O

The content of water is 8-20% in power station off-gas,\cite{21} so the effect of H$_2$O on CO$_2$ adsorption should be taken into consideration. Figs. 3e and 3f show the proposed interaction configuration and adsorption energies for CO$_2$ adsorption over P-substituted/directly grafted PH$_2$-graphanes in the presence of H$_2$O. In Fig. 3e, the H$_2$O molecule is weakly bonded to the P-site, and the measured OH–P bond distance is 5.15 Å. The water molecule adsorbs CO$_2$ strongly through a C–O water electrostatic interaction, as reflected by the adsorption energy $E_a$ of -31.787 kJ/mol. In Fig. 3f, CO$_2$ adsorption to PH$_2$-grafted graphene with H$_2$O, the H$_2$O molecule is bonded to the PH$_2$ group with the OH–P bond distance 2.507 Å, with $E_a$ of -42.3 kJ/mol. The presence of H$_2$O strongly enhances CO$_2$ adsorption over both P-substituted and PH$_2$-grafted graphanes. This result shows that as water is present in the flue gas,\cite{21} and the process can be completed without the introduction of additional water, the extraction of CO$_2$ from power station exhaust gas would be viable. However, the presence of water leads to an impure CO$_2$ stream upon desorption, which needs to be further dried.\cite{22} Our results of CO$_2$ adsorption over P-substituted/directly grafted PH$_2$-graphanes in the presence of H$_2$O are also similar to N-substituted/directly grafted NH$_2$-graphanes.\cite{23}

To better understand the change in the electronic structure of the gas adsorption system with the presence of water, the electron density for CO$_2$+H$_2$O+GAPH$_2$ adsorption system was analyzed. The results are shown in Fig. 4. It can be seen that there is no electron distribution among the CO$_2$ molecule, the H$_2$O molecule and the GAPH$_2$ sheet. This indicates that the adsorption is physical. Also, the partial density of states (PDOS) of P-substituted/PH$_2$-grafted, CO$_2$ on GAP+CO$_2$+H$_2$O and GAPH$_2$+CO$_2$+H$_2$O adsorption system were analyzed, respectively. Fig. 5a shows the PDOS for P-substituted configuration in GAP+CO$_2$+H$_2$O adsorption system. There is no obvious change around the Fermi level. However, the p orbital has slight change after adsorption. This may be caused by the transfer between some electrons. Fig. 5b illustrates that the significant PDOS difference for CO$_2$ in the adsorption system may also be caused by electrons transferring. Then, in Fig. 5c, the PDOS reveals the change of PH$_2$-grafted in GAPH$_2$+CO$_2$+H$_2$O adsorption system. There exists mild shift of both s and p orbitals. The change of CO$_2$ in GAPH$_2$+CO$_2$+H$_2$O system is similar with GAP+CO$_2$+H$_2$O. The large charge transfer is expected to induce the change.

iv. Conclusions

CO$_2$ adsorption over various types of P-substituted/grafted graphanes was studied using DFT. P-substituted/grafted graphanes were constructed by substitution of lattice carbon or surface hydrogen with P-functional groups. CO$_2$ adsorbs weakly on a graphane surface functionalized with single substituted P- or grafted PH$_2$-sites. The adsorption of P-substituted/grafted graphanes can be strengthened with the presence of co-adsorbed H$_2$O. This theoretical work provides an atomic-level strategy in the design of functionalized graphane and carbon-based adsorbent materials for CO$_2$ capture and storage.
Fig. 5. Partial density of state (PDOS) for GAP+CO$_2$+H$_2$O and GAPH$_2$+CO$_2$+H$_2$O systems (a) PDOS of P in GAP+CO$_2$+H$_2$O; (b) PDOS of CO$_2$ in CO$_2$+H$_2$O+GAPH$_2$; (c) PDOS of PH$_2$ in GAPH$_2$+CO$_2$+H$_2$O; (d) PDOS of CO$_2$ in GAPH$_2$+CO$_2$+H$_2$O.

References


