Activation of CO$_2$ on the Surfaces of Bare, Ti-Adsorbed and Ti-Doped C$_{60}$

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Abstract: There is a growing interest in finding a suitable catalyst for the adsorption and activation of CO$_2$ molecules to minimize the effect of global warming. In this study, density functional theory-based simulations are employed to examine the adsorption and activation of a CO$_2$ molecule on the pure, Ti-supported and Ti-doped surfaces of C$_{60}$. The adsorption on the pure surface is very weak. Adsorption becomes significant on the Ti-supported C$_{60}$ surface together with significant activation. Such strong adsorption is evidenced by the significant charge transfer between Ti and C$_{60}$. The Ti-doped C$_{60}$ surface adsorbs weakly, but the activation is not significant.

Keywords: activation; DFT; doping; C$_{60}$; adsorption; charge transfer

1. Introduction

Capture and adsorption of CO$_2$ is crucial towards global warming prevention and hydrogen production via purification of gas mixtures. A variety of materials including metal-organic frameworks [1–5], zeolites [6–9], metal oxides [10–12], organic polymers [13–15] and silica [16–18] have been used to investigate the efficacy of adsorbing CO$_2$. Buckminsterfullerene (C$_{60}$) has gathered a lot of interest due to its wide range of properties such as high thermal, chemical and mechanical stability [19]. Both inner and outer surfaces of C$_{60}$ have been thoroughly studied for encapsulation and adsorption of a variety of atoms and molecules respectively [20–25]. Alkali or transition metal adsorbed or doped C$_{60}$ surfaces have been considered for the adsorption and the activation of small molecules such H$_2$, N$_2$ and CO$_2$ [20,22,23,25]. Transition metal-doped C$_{60}$ structures have some special features over alkali atoms-doped C$_{60}$. They are size mismatch between highly charged metal ions and C$_{60}$ and small lattice energies of hypothetical Mn$^{n+}$—C$_{60}^{n-}$—complexes. Titanium doped C$_{60}$ has been studied experimentally and theoretically as a candidate catalyst to adsorb H$_2$ and activate N$_2$ molecules [22,23]. It is anticipated that Ti atom supported on a C$_{60}$ molecule can introduce a charge transfer (Ti to C$_{60}$) due to the larger electronegativity of C$_{60}$. The positively charged Ti is expected to enhance the adsorption of CO$_2$ molecule via strong Ti—O bond formation.

Here, computational modelling based on the density functional theory (DFT) is used to examine the adsorption efficacy of a CO$_2$ molecule on the surfaces of pure, Ti-adsorbed and Ti-doped C$_{60}$. The current methodology enabled us to determine the relaxed configurations together with electronic structures and charges on the adsorbed or doped Ti or CO$_2$ molecule.

2. Computational Methods

A DFT simulation code VASP (Vienna ab initio simulation program) [26] was used to perform all calculations. Projected augmented wave (PAW) potentials [27] and plane wave basis sets (cut-off of 500 eV) were used. The exchange correlation term was modelled using the generalized gradient approximation (GGA) as parameterized by Perdew, Burke, and Ernzerhof (PBE) [28]. All structures were optimized using the conjugate gradient algorithm [29]. The forces on the atoms were less than 0.001 eV/Å. A supercell with a
dimension of 25 × 25 Å × 25 Å was used to ensure that the adjacent molecules do not interact with each other in all directions. A single Ti atom was considered at different positions on the surface of C_{60} for adsorption. The most favorable relaxed structure was allowed to interact a CO_{2} molecule. Doping of Ti was carried out by replacing a C atom on the C_{60} molecule with Ti atom. A 2 × 2 × 2 Monkhorst k-point mesh [30] was used to relax all structures. Semi-empirical dispersive interactions were included as described by Grimme et al. [31] The charges on the atoms were calculated using the Bader charge analysis [32]. Adsorption energy was calculated for a CO_{2} molecule interacting the C_{60} surface using the following equation.

$$E_{ads} = E_{CO_{2}} : C_{60} - E_{C_{60}} - E_{CO_{2}}$$  \hspace{1cm} (1)

where $E_{CO_{2}} : C_{60}$ is the total energy of a CO_{2} molecule interacting the surface of C_{60}, $E_{C_{60}}$ is the total energy of a C_{60} molecule and $E_{CO_{2}}$ is the total energy of a CO_{2} molecule.

3. Results

3.1. Structure of C_{60}

C_{60} molecule is spherical and is formed by 12 pentagonal and 20 hexagonal molecules (see Figure 1a). It consists of two different carbon-carbon bonds (C–C and C=C) and their experimental values are reported to be 1.43 Å and 1.39 Å respectively [33]. First we optimized the C_{60} molecule to determine the equilibrium bond lengths to validate the pseudo potentials and basis sets used for C, Ti and O in this study. In the relaxed structure, the C–C and C=C bond distances were calculated to be 1.44 Å and 1.40 Å respectively, agreeing well with the corresponding experimental values. The calculated density of the states plot is shown in Figure 1b. The calculated gap between the highest occupied level and the lowest unoccupied level is 1.30 eV in a reasonable agreement with the values (1.55 eV and 1.63 eV) calculated in previous DFT simulations [34,35]. The underestimation of the band gap (E_{gap}) can be attributed to the failure of GGA functionals describing the exchange–correlation effect.

![Figure 1](image.png)

Figure 1. Relaxed structure of (a) C_{60} and (b) its DOS plot.

3.2. Encapsulation of CO_{2} Inside the Pure C_{60}

A single CO_{2} molecule was encapsulated and its encapsulation energy was calculated. Encapsulation is endoergic with and without dispersion (see Table 1). Dispersion improved the encapsulation by ~0.70 eV. A very small amount of charge is transferred between the CO_{2} molecule and the C_{60} showing non-covalent interaction. The total DOS plot shows that the Fermi energy level and the value of the gap are almost unaffected (see Figure 2b). The charge density plot shows that there is no overlap between the CO_{2} molecule and the inner wall of C_{60} (see Figure 2c).
Table 1. Encapsulation and Adsorption energy of a single CO₂ molecule.

<table>
<thead>
<tr>
<th>System</th>
<th>Encapsulation Energy (eV)</th>
<th>Charge Transfer (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vdw-free</td>
<td>vdw</td>
</tr>
<tr>
<td>CO₂@C₆₀</td>
<td>1.60</td>
<td>0.94</td>
</tr>
<tr>
<td>Adsorption energy (eV)</td>
<td>Charge transfer (e)</td>
<td></td>
</tr>
<tr>
<td>CO₂_C₆₀</td>
<td>0.05</td>
<td>–0.05</td>
</tr>
</tbody>
</table>

Figure 2. Relaxed structure of (a) a CO₂ molecule encapsulated inside the C₆₀, (b) its DOS plot and (c) charge density plot showing no interaction between the molecule and the inner wall of the C₆₀. Corresponding information (d–f) is also provided for a CO₂ molecule adsorbed on the surface of C₆₀.

3.3. Adsorption of CO₂ on the Surface of Pure C₆₀

The adsorption of CO₂ molecule was next considered. The relaxed structure is shown in Figure 2d. The adsorption is exoergic with dispersion and endoergic without dispersion, indicating the importance of dispersion (see Table 1). Charge transfer is negligible. The electronic structure is almost unaffected by the adsorption (see Figure 2e) as evidenced by the charge density plot in which there is no interaction of charge density (see Figure 2f).

3.4. Adsorption of CO₂ on the Surface of C₆₀ Supported with Ti

Next, I considered a CO₂ molecule adsorbed on the Ti-supported C₆₀ surface. Five different starting configurations were considered (see Figure 3) for the Ti interacting with C₆₀. In the configurations H and P, the Ti atom is positioned on the hexagonal ring and the pentagonal ring respectively. The configurations 66 and 65 accommodate the Ti atom above the bonds bridging hexagonal–hexagonal and hexagonal–pentagonal rings respectively. In the initial structure C, Ti atom is located above the C atom on the C₆₀ surface. All initial configurations were fully relaxed. Table 2 lists the relative energies of the final configurations. The most stable configuration is found to be the configuration H. The inclusion of dispersion does not affect the trend in the relative energies.
Figure 3. Five different initial sites (H, P, 66, 65 and C) considered for the adsorption of a single Ti atom on the surface of C$_{60}$.

Table 2. Relative energies of five different configurations considered for the adsorption of Ti atom.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Relative Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>vdw-free</td>
</tr>
<tr>
<td>H</td>
<td>0.00</td>
</tr>
<tr>
<td>C</td>
<td>0.42</td>
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<tr>
<td>66</td>
<td>0.42</td>
</tr>
<tr>
<td>P</td>
<td>0.58</td>
</tr>
<tr>
<td>65</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The relaxed structure of Ti adsorbed on the hexagonal ring of C$_{60}$ (H) is shown in Figure 4a. The adsorbed Ti forms strong bonds with C in the hexagonal ring are described by the shorter Ti–C bond lengths (see Figure 4b). The Bader charge analysis shows that there is a significant charge transfer from Ti to the C in the hexagonal ring (see Figure 4b). This is further confirmed by the positive Bader charge on the Ti atom and the negative Bader charges on the C. The adsorption energy was calculated using a Ti atom as a reference state. Adsorption is negative and its value is $-1.71$ eV with dispersion. Exclusion of dispersion reduces the adsorption by 0.04 eV as expected.

Figure 4. Optimized structure of (a) Ti atom adsorbed on the hexagonal ring of C$_{60}$, (b) bond lengths (Ti-C and C-C) and Bader charges on the Ti atom and the adjacent C atoms directly bonded to it.

The total DOS plot exhibits that the Ti-supported C$_{60}$ is metallic (see Figure 5a). This is due to strong perturbation of C$_{60}$ with Ti. The atomic DOS plots shows that the Fermi energy level is mainly populated with $d$ states of Ti (see Figure 5b).
A single CO$_2$ molecule was allowed to adsorb on the surface of Ti-supported C$_{60}$. The relaxed configuration is shown in Figure 6a. In this structure, the CO$_2$ molecule exhibits a nonlinear structure. There is a significant elongation in the bond lengths of C-O in comparison with those found in molecular CO$_2$ (1.18 Å) (see Figure 6b). This indicates that depletion of CO$_2$ can be enhanced by the support of Ti on the surface of C$_{60}$. The Bader charge analysis shows that the net charge on the CO$_2$ molecule is $-1.19$.

Adsorption energy of the CO$_2$ molecule was calculated. Adsorption is exoergic with an adsorption energy of $-1.57$ eV. Adsorption becomes less negative (by 0.06 eV) without dispersion. Adsorption is exoergic as confirmed by the strong bonding between Ti and oxygen in the CO$_2$ molecule. The resultant configuration exhibits a narrow-gap semiconductor (see Figure 6c). The states appearing around the Fermi level are contributed to by the $d$ states of Ti (see Figure 6d).
3.5. Adsorption of CO\textsubscript{2} on the Surface Ti-Doped C\textsubscript{60}

The efficacy of Ti-doped surface for the adsorption of CO\textsubscript{2} was next considered. The relaxed structure of Ti-doped C\textsubscript{60} is shown in Figure 7a. In the relaxed structure, the Ti atom is displaced forming longer Ti–C bond lengths compared to C–C bond lengths (see Figure 7b). There is a significant distortion in the relaxed structure. The Bader charge analysis exhibits a significant charge transfer between Ti and three C atoms directly bonded to it. The Bader charge on the Ti is +2.21. The loss of 2.21 electrons is gained by three nearest neighbor C atoms. The total DOS plot exhibits that the resultant structure is a semi-conductor with a band gap of 0.6 eV. This value is lower than that found for the pure C\textsubscript{60}. The atomic DOS plots shows that states near the Fermi level are mainly associated with the d states of Ti.

Adsorption of CO\textsubscript{2} was next considered on the surface of Ti-doped C\textsubscript{60}. The relaxed structure is shown in Figure 8a. In the relaxed structure, one of the oxygen atoms in the CO\textsubscript{2} molecule forms a strong bond with Ti (see Figure 8b). In the relaxed structure, the CO\textsubscript{2} molecule is slightly bent. The net charge on the CO\textsubscript{2} molecule is $-0.23$ according to the Bader charge analysis. The activation of the C-O bond is not significant as its bond lengths are not significantly elongated with respect to its isolated molecule. The energy required to adsorb a CO\textsubscript{2} molecule is $-0.41$ eV with dispersion, indicating that Ti-doped C\textsubscript{60} can accommodate a CO\textsubscript{2} molecule. Adsorption is endothermic without dispersion and its adsorption energy is $+1.71$ eV, again indicating the importance of dispersion. There is a small band gap of 0.50 eV observed in the total DOS plot. The states associated with the d orbitals of Ti are mainly localized near the Fermi energy level.
Figure 8. Relaxed structure showing (a) a CO₂ molecule adsorbed on the Ti-doped surface, (b) bond distances and Bader charges on the atoms, (c) total DOS plot and the (d) atomic DOS plot of Ti.

4. Conclusions

Computer simulations based on the DFT together with dispersion were applied to examine the efficacy of the pure, Ti-supported and Ti-doped C₆₀ surface for the adsorption of a CO₂ molecule. The results show that there is no significant adsorption on the surface of pure C₆₀. Adsorption becomes significantly stronger once the Ti is supported on the surface of C₆₀. Such adsorption distorts and activates the CO₂ molecule significantly. The enhancement of adsorption is confirmed by the significant charge transfer between the Ti and the C₆₀ molecule. Thus, the Ti-supported C₆₀ molecule is the most efficient for CO₂ adsorption. The Ti-doped C₆₀ surface has the ability to adsorb the CO₂ molecule. However, the activation is not significant.

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