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A Computational Study of Carbon Dioxide Adsorption on Solid Boron

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Capturing and sequestering carbon dioxide (CO$_2$) can provide a route to partial mitigation of climate change associated with anthropogenic CO$_2$ emissions. Here we report a comprehensive theoretical study of CO$_2$ adsorption on two phases of boron, α-B$_{12}$ and γ-B$_{28}$. The theoretical results demonstrate that the electron deficient boron materials, such as α-B$_{12}$ and γ-B$_{28}$, can bond strongly with CO$_2$ due to Lewis acid-base interactions because the electron density is higher on their surfaces. In order to evaluate the capacity of these boron materials for CO$_2$ capture, we also performed calculations with various degrees of CO$_2$ coverage. The computational results indicate CO$_2$ capture on the boron phases is a kinetically and thermodynamically feasible process, and therefore from this perspective these boron materials are predicted to be good candidates for CO$_2$ capture.

1 Introduction

Carbon dioxide, CO$_2$, is a greenhouse gas whose concentration in the atmosphere has been increasing since the industrial revolution, and this increase is largely caused by the burning of fossil fuels. Therefore it is essential that this trend be halted, and new technologies aimed at removing CO$_2$ from combustion products to reduce its concentration in the atmosphere are being developed.1,2 An alternative approach to reduction of CO$_2$ from combustion is to select fuels that produce less CO$_2$ on combustion than conventional fossil fuels (e.g., natural gas), or no CO$_2$ (H$_2$). These fuels often contain contaminants including CO$_2$, so CO$_2$ capture from these resources before combustion is necessary and is a well-established process in industry. The most common processes involve treatment with amine solutions or chilled ammonia, however these processes have some problems in that they are not energy efficient, the amine is toxic and solvent can easily be lost.3,4 In both these approaches to reducing CO$_2$ in the atmosphere, it is important that new environmentally friendly and economically feasible processes for CO$_2$ capture be developed.

Solid adsorbents are anticipated to play a key role in new technologies, and there have been many materials considered in recent years.4 To be of practical use the materials must be able to strongly adsorb CO$_2$ and have large surface areas, however many materials only weakly bind CO$_2$. In this work we find that solid boron materials such as α-B$_{12}$ and γ-B$_{28}$ can adsorb CO$_2$ strongly and therefore may be useful materials for CO$_2$ capture.

Boron readily bonds with other boron atoms, forming a variety of different structures with complex features such as three-center two-electron bonds or electron deficient bonds. In the pure boron solids, the B$_{12}$ icosahedron is the basic structural unit which can be flexibly linked or fused to form rigid structures,5,10 and the existence of this unit and it connectivity is associated with the electron deficiency, or hypovalency, of boron. Four reported boron phases correspond to the pure element: rhombohedral α-B$_{12}$,5,11,12 and β-B$_{106}$5 (with 12 and 106 atoms in the unit cell, respectively), tetragonal T-1927 (with 190–192 atoms per unit cell) and γ-B$_{28}$ 8,13,14 (with 28 atoms in the unit cell), whereas there is a large variety of boron-rich compounds. Much work on boron rich compounds has been carried out due to their physical and chemical properties which have resulted in research for their suitability in applications from nuclear reactors to super-hard, thermoelectric and high-energy materials as well as hydrogen storage materials.8,12,15-18 In this study, we will investigate CO$_2$ capture using α-B$_{12}$ and γ-B$_{28}$. The α-B$_{12}$ phase consists of one B$_{12}$ icosahedron per unit cell and γ-B$_{28}$ consists of icosahedral B$_{12}$ clusters and B$_2$ pairs in a NaCl-type arrangement.8 It has been shown that the electronic properties of the B$_3$ pairs and B$_2$ clusters in γ-B$_{28}$, are different, and this results in charge transfer between them.8 For α-B$_{12}$ and γ-B$_{28}$, our study found that there is charge transfer among the atoms on their surfaces and the internal atoms, indicating that the α-B$_{12}$ and γ-B$_{28}$ slabs are amphoteric with acidic and basic sites. The regioselectivity of α-B$_{12}$ and γ-B$_{28}$ indicate CO$_2$ (Lewis acid) might form strong interactions with the basic sites of their B materials due to Lewis acid-base interactions. In order to test this hypothesis, we have carried out DFT calculations of CO$_2$ capture on α-B$_{12}$ and γ-B$_{28}$ surfaces. The primary motivation of the theoretical study is to stimulate further experiments to verify our prediction that CO$_2$ can be captured by these boron materials.
2 Computational methods

Ab initio DFT calculations are performed with the DMol3 module in Material Studio.\textsuperscript{19,20} The configurations of CO\textsubscript{2} adsorbed on the boron phases are fully optimized using the generalized gradient approximation\textsuperscript{21} treated by the Perdew-Burke-Ernzerhof exchange-correlation potential with long range dispersion correction carried out using the Grimme’s scheme.\textsuperscript{22} This method has been used to successfully determine the geometrical, energetic and electronic structural properties of boron clusters, boron phases and boron containing materials.\textsuperscript{23-29} The basis set employed is an all-electron double-numerical atomic orbital basis set, augmented by d- and p-polarization functions (DNP). The cell parameters of α-B\textsubscript{12} and γ-B\textsubscript{28} in the calculations are all optimized and are consistent with the experimental values.\textsuperscript{8,11} Detailed information on the cell parameters is listed in our previous publication.\textsuperscript{27} The slab thicknesses of α-B\textsubscript{12} and γ-B\textsubscript{28} are 8.012 Å and 6.914 Å (corresponding to two layers of B\textsubscript{12} or B\textsubscript{16} clusters), respectively. The 2 × 2 × 2 boron (001) and γ-boron (001) surfaces were chosen with a 1.5 Å vacuum above the slab in order to avoid interactions between their periodic images, and the Brillouin zone is sampled by 6 × 6 × 1 k-points using the Monkhorst-Pack scheme.

The calculations of CO\textsubscript{2} adsorption on α-B\textsubscript{12} (001) and γ-B\textsubscript{28} (001) surfaces are based on the fully optimized boron surfaces.\textsuperscript{27} The adsorption energy of CO\textsubscript{2} on α-B\textsubscript{12} and γ-B\textsubscript{28} are calculated from Eq. 1:

\[
E_{\text{ads}} = E_{(\text{boron, phase} + \text{CO}_2)} - E_{\text{CO}_2} - E_{(\text{boron, phase})}
\]

where \( E_{(\text{boron, phase} + \text{CO}_2)} \) is the total energy of the boron surface with a CO\textsubscript{2} molecule adsorbed. In order to better clarify the adsorption and the nature of the interaction of CO\textsubscript{2} with α-B\textsubscript{12} and γ-B\textsubscript{28} atoms in molecules (AIM) theory has been employed in the study. Based on the optimized structures at the DFT-D level, we calculate the wavefunctions at the B3LYP/6-31G(d) level of theory.\textsuperscript{23} In the AIM analyses,\textsuperscript{23} the existence of an interaction is indicated by the presence of a bond critical point (BCP), and the strength of the bond can be estimated from the magnitude of the electron density \( \rho_{\text{BCP}} \) at the BCP. Similarly, the ring or cage structures are characterized by the existence of a ring critical point (RCP) or cage critical point (CCP). Furthermore, the nature of the molecular interaction can be predicted from the topological parameters at the BCP, such as the the acian of electron density \( \nabla \rho_{\text{BCP}} \) and energy density \( H_{\text{BCP}} \). The topological analysis of the system was carried out via the AIMALL program.\textsuperscript{33}

The transition states between chemisorbed and physisorbed CO\textsubscript{2} have been investigated using the complete LST (linear synchronous transit)/QST (quadratic synchronous transit) method\textsuperscript{34} implemented in the DMol3 code. The reactants and products correspond to the optimized structures of CO\textsubscript{2} physisorbed and chemisorbed on α-B\textsubscript{12} and γ-B\textsubscript{28} surfaces, respectively. Electron distributions and transfer mechanisms are determined with the Mulliken method.\textsuperscript{34}

3 Results and discussion

The α-B\textsubscript{12} and γ-B\textsubscript{28} slabs were optimized and the fully relaxed α-B\textsubscript{12} (001) and γ-B\textsubscript{28} (001) surfaces with cell vectors are shown in Fig. 1(a) and (b), respectively. We firstly investigated the Mulliken atomic charge distributions on the α-B\textsubscript{12} (001) and γ-B\textsubscript{28} (001) surfaces and then carried out a study of the mechanism of CO\textsubscript{2} adsorption on the surfaces of the two boron materials. All the possible sites for CO\textsubscript{2} adsorption on α-B\textsubscript{12} and γ-B\textsubscript{28} surfaces have been considered. In this manuscript we will discuss the strongest adsorption sites which we classify as having two different types of interaction: type A and B. In type A interactions, the carbon atom and one oxygen atom in the CO\textsubscript{2} molecule directly connect with two boron atoms, and in type B interactions, two oxygen atoms of the CO\textsubscript{2} molecule directly connect with the boron atoms of the α-B\textsubscript{12} and γ-B\textsubscript{28} surfaces.

3.1 Atomic charge distributions of α-B\textsubscript{12} and γ-B\textsubscript{28}

It is well known that boron phases, such as α-B\textsubscript{12} and γ-B\textsubscript{28}, are electron deficient materials because there is only one electron on the p orbital of each boron atom, while CO\textsubscript{2} is a Lewis acid and it would prefer to gain electrons in reactions. Because of this the electron deficient boron materials might not be expected to be good adsorbents for CO\textsubscript{2} capture. However, from the Mulliken atomic charge distributions of the α-B\textsubscript{12} and γ-B\textsubscript{28} slabs that we modeled we can see that there is electron transfer from the atoms within the slabs to the surface atoms of α-B\textsubscript{12} and γ-B\textsubscript{28}. Fig. 2 shows the optimized α-B\textsubscript{12} and γ-B\textsubscript{28} structures and the Mulliken atomic charges for the atoms labeled in Fig. 2 are listed in Table 1.
The charges on the surface atoms of α-B_{12} are -0.366e (atom B1), -0.321e (atom B2), -0.008e (atom B3 and B4) according to the Mulliken atomic charge analysis, and the atoms in the internal part of the slab have positive charges. The Mulliken atomic charge distributions of γ-B_{24} are similar to those of the α-B_{12} slab: the surface atoms B1 and B2 have negative charges of -0.311e, B3 and B4 have negative charges of -0.098e, and the internal atoms either have positive charges (atoms B9-B14) or are slightly negative (atoms B7 and B8). The charge difference between the atoms on the surfaces and the internal atoms mean that the α-B_{12} and γ-B_{24} slabs are regioselective and amphoteric, with both acidic and basic sites. Similar behaviour in boron materials, such as B_{60}, has been investigated previously by Muya et al., who found the cap atoms of B_{60} act as acid sites and the frame atoms act as basic sites in this regioselective molecule. From the above analysis we have shown that, in principle, CO_{2} (Lewis acid) will form strong interactions with the basic sites of α-B_{12} and γ-B_{24} due to Lewis acid-base interactions. In the following section, we will investigate CO_{2} the mechanism of CO_{2} adsorption on the α-B_{12} and γ-B_{24} surfaces.

Table 1 Atom number and Mulliken atomic charges (e) of the optimized α-B_{12} and γ-B_{24} slabs.

<table>
<thead>
<tr>
<th>Atom number</th>
<th>Atomic charge</th>
<th>Atom number</th>
<th>Atomic charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>-0.366</td>
<td>B1</td>
<td>-0.311</td>
</tr>
<tr>
<td>B2</td>
<td>-0.321</td>
<td>B2</td>
<td>-0.311</td>
</tr>
<tr>
<td>B3</td>
<td>-0.008</td>
<td>B3</td>
<td>-0.098</td>
</tr>
<tr>
<td>B4</td>
<td>-0.008</td>
<td>B4</td>
<td>-0.098</td>
</tr>
<tr>
<td>B5</td>
<td>0.139</td>
<td>B5</td>
<td>-0.074</td>
</tr>
<tr>
<td>B6</td>
<td>0.139</td>
<td>B6</td>
<td>-0.074</td>
</tr>
<tr>
<td>B7</td>
<td>0.119</td>
<td>B7</td>
<td>-0.025</td>
</tr>
<tr>
<td>B8</td>
<td>0.119</td>
<td>B8</td>
<td>-0.025</td>
</tr>
<tr>
<td>B9</td>
<td>0.033</td>
<td>B9</td>
<td>0.133</td>
</tr>
<tr>
<td>B10</td>
<td>0.033</td>
<td>B10</td>
<td>0.133</td>
</tr>
<tr>
<td>B11</td>
<td>0.066</td>
<td>B11</td>
<td>0.171</td>
</tr>
<tr>
<td>B12</td>
<td>0.055</td>
<td>B12</td>
<td>0.171</td>
</tr>
<tr>
<td>B13</td>
<td>0.204</td>
<td>B13</td>
<td>0.204</td>
</tr>
<tr>
<td>B14</td>
<td>0.204</td>
<td></td>
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</tr>
</tbody>
</table>

### 3.2 CO_{2} adsorption on the α-B_{12} surface

Currently 16 allotropes of elemental boron have been reported, with the α-boron structure being the simplest. It contains 12 atoms in a rhombohedral unit cell, forming a slightly distorted icosahedral B_{12}. In this section, we will investigate the reaction mechanism of CO_{2} adsorption on α-B_{12}. We have identified two ways in which CO_{2} adsors on α-B_{12}, labelled type A and type B. In type A one O atom and the C atom of CO_{2} bond with one B–B bond of α-B_{12}; and in type B two O atoms of CO_{2} interact with one B–B bond of α-B_{12}.

Fig. 3 (a) shows the optimized structures of the two possible minimum-energy type A configurations, and the transition states for the process of CO_{2} adsorption on the α-B_{12} surface. Corresponding results for type B interactions have been listed in the supporting information, see Fig. S1 (a). The important structural properties, relative energies and the electron transfers from the α-B_{12} to CO_{2} are listed in Table 2 and Table S1 in supporting information. For the two types of interaction of CO_{2} with α-B_{12}, we can see that the chemisorbed type A configuration is the most stable, so the discussion will focus on the adsorption through interactions of type A. For CO_{2} capture on α-B_{12} through type A interactions, we identified two stationary states, corresponding to physisorption and chemisorption. In the physisorbed configuration, CO_{2} interacts with one B–B bond of α-B_{12} and lies parallel to it. The O–C–O angle is 179.9° and B–O distance is approximately 3.1 Å, the long distance indicates the interaction is very weak and the adsorption is mainly due to the van der Waals interaction of CO_{2} and α-B_{12}.

![Fig. 3](image-url)
are aware. Moreover, the calculated barrier between the physisorbed CO\(_2\) molecule and on the boron atoms when CO\(_2\) is adsorbed on \(\alpha\)-B\(_{12}\) and \(\gamma\)-B\(_{28}\) surfaces (chemisorbed configurations). The sum of the charge on the CO\(_2\), the charge on the boron atoms considered, and the charge transfer is also presented. The charge transfer due to adsorption on a \(\alpha\)-B\(_{12}\) surface is listed under CT1 and on a \(\gamma\)-B\(_{28}\) surface is listed under CT2.

<table>
<thead>
<tr>
<th>Atom</th>
<th>SUM/Charge</th>
<th>CO(_2)</th>
<th>CO(_2) on</th>
<th>CT1</th>
<th>CO(_2) on</th>
<th>CT2</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>-0.284</td>
<td>-0.481</td>
<td>-0.197</td>
<td>-0.460</td>
<td>-0.263</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.568</td>
<td>0.246</td>
<td>-0.322</td>
<td>0.278</td>
<td>0.600</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>-0.284</td>
<td>-0.549</td>
<td>-0.065</td>
<td>-0.346</td>
<td>-0.281</td>
<td></td>
</tr>
</tbody>
</table>

The adsorption energy of the physisorbed CO\(_2\) is calculated to be 4.95 kcal/mol. The weak interaction is also confirmed by the negligible charge transfer between the \(\alpha\)-B\(_{12}\) and CO\(_2\) molecule (with a value of only -0.004e). Molecular graphs for CO\(_2\) adsorption on \(\alpha\)-B\(_{12}\) are displayed in Fig. 4. We can see from Fig. 4 (a) that the interaction between CO\(_2\) and \(\alpha\)-B\(_{12}\) can be confirmed by the existence of the bond critical point (BCP) of the O–B contact. The calculated topological parameters at the BCPs of the \(\alpha\)-B\(_{12}\) are listed in Table S2 in supporting information. For the physisorbed configurations, the electron densities at the BCPs of the bonds between CO\(_2\) and \(\alpha\)-B\(_{12}\) are small (Table S2), which is consistent with a weak interaction. When CO\(_2\) is chemisorbed on \(\alpha\)-B\(_{12}\), the B–C and B–O bond lengths shorten and a four-membered ring is formed. The O–C–O bond angle is 122.7\(^\circ\), and one C=O double-bond breaks and stretches from 1.176 Å to 1.442 Å due to the bonding interaction that is formed between the B–B bond of \(\alpha\)-B\(_{12}\) and C–O bond of CO\(_2\). Table 3 lists the Mulliken atomic charges (e) when CO\(_2\) is adsorbed on \(\alpha\)-B\(_{12}\) and \(\gamma\)-B\(_{28}\)–CO\(_2\) surfaces (chemisorbed configurations) and the change in charge due to adsorption for the CO\(_2\) atoms and nearby boron atoms using \(\alpha\)-B\(_{12}\) (CT1) and \(\gamma\)-B\(_{28}\) (CT2). A Mulliken charge population analysis shows that there is a -0.584 electron charge transfer from \(\alpha\)-B\(_{12}\) to the CO\(_2\) molecule, and the charge redistributions of the boron atoms at the CO\(_2\)/B interface provide the main contribution to the charge transfer. The CO\(_2\) molecule undergoes structural distortion to a bent geometry and forms a C–O–B–B four-membered ring, in which the B–C and B–O distances are 1.647 Å and 1.477 Å, respectively. The short distance indicates a strong interaction between the CO\(_2\) molecule and \(\alpha\)-B\(_{12}\), with the calculated adsorption binding energy is 47.76 kcal/mol.

Here we note that the interaction between CO\(_2\) and \(\alpha\)-B\(_{12}\) is the strongest value for CO\(_2\) adsorption on substrates so far, as far as we are aware. Moreover, the calculated barrier between the physisorbed and chemisorbed configurations is 4.49 kcal/mol. As shown in Table S2, as we move from the physisorbed configuration (Fig. 4(a)), to the transition state (Fig. 4(b)), to the chemisorbed configuration (Fig. 4(c)) the electron densities at the BCPs for the O1–B bonds increases, which is consistent with the adsorption process resulting in strengthening of the interaction. In addition, the O1–B bond distances decrease from 3.042 Å for the physisorbed structure, 1.967 Å for the transition state structure and 1.477 Å when the CO\(_2\) is chemisorbed, and the C–B bond distances decrease with the values of 3.107 Å, 2.648 Å and 1.647 Å for the three structures, respectively. The strong interaction between CO\(_2\) and \(\alpha\)-B\(_{12}\), and low barrier from the physisorbed to chemisorbed configurations demonstrate that the CO\(_2\) adsorption on \(\alpha\)-B\(_{12}\) is a kinetically favorable process. In addition, we have listed the variation of thermodynamic properties with temperatures (K) for adsorption of free CO\(_2\) on the \(\alpha\)-B\(_{12}\) (a) and \(\gamma\)-B\(_{28}\) (b) surfaces to form chemisorbed configurations (type A) in Figure 5. Fig. 5 (a) shows the temperature dependence of thermodynamic properties ΔG (kcal/mol), ΔH (kcal/mol) and ΔS (cal/mol K) for gaseous CO\(_2\) capture on \(\alpha\)-B\(_{12}\) to form a chemisorbed configuration of type A. It clearly shows that the ΔS of the reaction increases as temperature increases from 200 to 1000 K and ΔH is almost constant over the whole temperature range. The resulting negative ΔG indicates the adsorption reaction process is spontaneous for the temperatures considered.
with type A interactions, where the bond critical points (BCPs), ring critical points (RCPs) and cage critical point (CCP) are denoted as small green, red and blue dots, respectively.

For type B interactions of CO₂ on α-B₁₂, we also identified two local minima and the transition state between those physisorbed and chemisorbed states. The physisorbed configuration (Fig. 3(a)) of CO₂ on α-B₁₂ is very similar to that observed in the type A physisorbed configuration. The chemisorbed configuration (Fig. 3(a)) has a O–C–O–B–B five-membered ring. In this configuration, the two C–O bonds have stretched from 1.176 Å to 1.330 Å and the O–C–O bond angle is 115.4°. The B–B site is also pulled out of the material and elongated by 0.10 Å. The two B–O distances are 1.494 Å which is slightly longer than the O–B distance in the type A configuration for α-B₁₂ (1.447 Å). The adsorption energy of this chemisorbed configuration is 41.81 kcal/mol, which is slightly weaker than that for type A. The calculated barrier between the physisorbed and chemisorbed configurations is 6.16 kcal/mol. The strong interaction and low barrier between the physisorbed and chemisorbed configurations with type B interactions indicates CO₂ capture is feasible through this mechanism. However, the CO₂ capture process involving type A interactions will dominate because it has a stronger interaction energy and lower barrier to adsorption than type B interactions. Overall, the calculations demonstrate that the α-B₁₂ phase can effectively capture CO₂.

3.3 CO₂ adsorption on γ-B₂₈ surface

The γ-B₂₈ phase with 28 atoms in the orthorhombic unit cell was originally discovered in 1965,14 and is a hard semiconductor with a structure composed of B₂ dumbbells and B₁₂icosahedra. There is debate about whether the two distinct structural units should be partially ionic or not.15,24,36 Our Mulliken charge analysis of the γ-B₂₈ (001) slab indicate that the γ-B₂₈ is amphoteric which contains both acidic and basic sites. This means that the electron deficient boron phase γ-B₂₈ could denote electrons from its basic sites to CO₂ to form a strong bond between CO₂ and the basic sites of γ-B₂₈, and therefore γ-B₂₈ might be a good candidate for CO₂ capture. In this section, we will discuss the absorption of CO₂ on the γ-B₂₈ surface. The computational results indicate that there are two types (A and B) of adsorption of CO₂ on γ-B₂₈ surface, which are very similar to those seen in CO₂ adsorption on α-B₁₂. Firstly, we will discuss CO₂ adsorption on γ-B₂₈ involving type A interactions. We identified two stationary states corresponding to physisorbed and chemisorbed CO₂. The optimized structures of the two configurations as well as the transition state between them are shown in Fig. 3(b). The important structural properties, adsorption energies and the electron transfers from the boron phase to CO₂ are listed in Table 2. From Fig. 3(b) we can see that the CO₂ physisors by interaction with one B–B bond of γ-B₂₈, and is parallel to that bond. The O–C–O angle is 179.7° and the B–O distance is around 2.9 Å. The structure is very similar to that of the configuration of CO₂ physisorbed on α-B₁₂ in a type A interaction (Fig. 3(a)). The adsorption energy of the physisorbed CO₂ is calculated to be 4.84 kcal/mol so the interaction between CO₂ and γ-B₂₈ is very weak.

In its chemisorbed configuration, the CO₂ molecule undergoes structural distortion to a bent geometry and forms a C–O–B–B four-membered ring in which the B–C and B–O distances are 1.649 Å and 1.482 Å, respectively. The O–C–O bond angle is 123.4°, and one C=O double-bond breaks and stretches from 1.178 Å to 1.413 Å due to the bonding interaction that formed between the B–B bond of the γ-B₂₈ and the C–O bond of CO₂. The shorter distance indicates a stronger interaction between the CO₂ molecule and γ-B₂₈, and the calculated adsorption energy is 29.18 kcal/mol. Compared with the type A energy of adsorption of CO₂ on α-B₁₂ (47.76 kcal/mol), the adsorption of CO₂ on γ-B₂₈ is much lower. The transition state between the physisorbed and chemisorbed configurations has been identified. Adsorption has also been verified by observation of an increase in the energy density at the BCP in going from the physisorbed state (Fig. 4(d)), to the transition state (Fig. 4(e)), and to chemisorbed state (Fig. 4(f)), which is consistent with strengthening of the interaction. In addition, the O1–B bond distances decrease from 2.896 Å to 1.738 Å and then 1.482 Å, and the C–B bond distances decrease from 3.304 Å to 2.616 Å and then 1.649 Å for the three structures, respectively. The calculated barrier between the physisorbed and chemisorbed configurations with type A interactions is 2.34 kcal/mol. The variation of thermodynamic properties has also been calculated (Fig. 5(b)) in order to study the entropic and temperature effects of the chemisorption of gaseous CO₂ on γ-B₂₈. From Fig. 5(b) we can see that ΔS is monotonically increasing when the temperature is above 200 K and ΔH has a slight linear increase over the whole temperature range considered. This results in ΔG increasing almost linearly with an increase in temperature for CO₂ capture on γ-B₂₈, as the free CO₂ is chemisorbed on the surface. Moreover, ΔG is negative in the temperature range considered (200 K to 1000 K), which indicates the adsorption of CO₂ on γ-B₂₈ to form the chemisorbed configuration is a spontaneous process for these temperatures. In summary, the low barrier and the negative ΔG within the temperature range demonstrate that CO₂ adsorption on γ-B₂₈ is a kinetically and thermodynamically favorable process. 

![Graph](image-url)
change in entropy (cal/mol K) and change in enthalpy (kcal/mol), respectively.

For CO₂ capture on γ-B₂₈ with type B interactions, two local minima were also observed (chemisorbed and physisorbed configurations). In the physisorbed configuration, CO₂ weakly interacts with γ-B₂₈ with the adsorption energy of 4.89 kcal/mol. The chemisorbed CO₂ on γ-B₂₈, has one five-membered ring O–C–O–B–B, which is very similar to that of configuration of chemisorbed on CO₂ on α-B₁₂ with type B interactions. In this configuration, the two O–O bonds stretch from 1.176 Å to 1.314 Å and the O–C–O bond angle is 117.6°. The B–B site is also pulled out and elongated by 0.10 Å. The two B–O distances are 1.511 Å, which is slightly longer than that of O–B distance when type A interactions result in CO₂ bonding to γ-B₂₈ (1.482 Å). The adsorption energy of this chemisorbed configuration is 21.78 kcal/mol, which is slightly weaker than the absorption energy of the type A chemisorbed configuration. The barrier from the physisorbed to chemisorbed configurations with type B configuration is low with a value of 9.39 kcal/mol. Moreover, the type A configuration will be the dominant one because it has a stronger adsorption energy and lower barrier than that due to type B interactions. In all, the computational results support the hypothesis that the γ-B₂₈ phase can effectively capture CO₂.

The different adsorption energies between CO₂ and the two boron phases can be understood by analysis of their LUMO-HOMO energy gaps. According to molecular orbital theory, the frontier orbits and nearby molecular orbits are the most important factors determining the stability of molecules. The larger the difference between the frontier orbits, the more stable the molecular structure is. The energy gaps of ΔE between their highest occupied molecular orbitals (HOMO) and their lowest unoccupied molecular orbitals (LUMO) (ΔE = E_{LUMO} – E_{HOMO}) for α-B₁₂ and γ-B₂₈ surfaces are 0.046 and 0.854 eV, respectively. The energy gap of γ-B₂₈ is clearly larger than that of α-B₁₂. The narrower LUMO-HOMO energy-gap indicates that this material is more reactive. The interaction of CO₂ with α-B₁₂ (adsorption energy 47.76 kcal/mol for the type A configuration) is stronger than with γ-B₂₈ (adsorption energy 29.18 kcal/mol for the type A configuration). The energy gaps of the two boron materials explains the relative strength of interactions between them and CO₂.

Moreover, from the Mulliken charge analysis we know that the charges of the surface atoms B1 and B2 of α-B₁₂ which interact directly with CO₂ are -0.366e and -0.321e, while the charges of two boron atoms of γ-B₂₈ which interact directly with CO₂ with are -0.311e and -0.311e, respectively, which also indicate the base sites of the α-B₁₂ surface are more basic than those of γ-B₂₈ surface. The charge analysis is also consistent with the Lewis acid-base interaction of CO₂ on the α-B₁₂ surface being stronger than that of CO₂ with the γ-B₂₈ material.

### 3.4 Coverage of CO₂ on α-B₁₂ and γ-B₂₈ surfaces

In the previous calculations, adsorption of one CO₂ molecule on the 2 x 2 α-B₁₂ and γ-B₂₈ surfaces was considered. In order to investigate the capacity of these boron materials for CO₂ capture, calculations with higher coverage of CO₂ were carried out. The average adsorption energies of CO₂ molecules on boron surfaces are defined as

\[ E_{\text{ads}} = \frac{n E_{\text{surf-phase of CO₂}} - n E_{\text{surf - phase}}}{n} \]

where \( n \) is the number of CO₂ molecules adsorbed on the boron surfaces and \( E_{\text{surf-phase of CO₂}} \) is the total energy of the boron surface with CO₂ adsorbed.

Table 4 and Figure 6 list the structural properties and the average value of adsorption energies (kcal/mol) with different coverage of CO₂ on α-B₁₂ and γ-B₂₈ surfaces with up to four molecules of CO₂. We find that the α-B₁₂ and γ-B₂₈ surfaces can effectively capture up to four CO₂ molecules through chemisorption with configurations which are similar to those when one CO₂ is adsorbed on these surfaces. However, the average adsorption energies reduce with increasing of CO₂ coverage. In detail, the adsorption energies for CO₂ molecules adsorbed on 2 x 2 α-B₁₂ reduce from -47.76 to -33.79 kcal/mol as the number of CO₂ molecules increase from one to four, with the energy required to remove one CO₂ molecule from the system with four adsorbed being -20.89 kcal/mol. As the number of CO₂ molecules adsorbed on 2 x 2 γ-B₂₈ increases from one to four, the average adsorption energies reduce from -29.19 to -24.29 kcal/mol, with the energy required to remove one CO₂ molecule from the system with four adsorbed being -21.41 kcal/mol. These results indicate that the binding of additional CO₂ molecules will be weaker. This means that although the energy required to completely regenerate the clean boron would be high, boron solid which is partly covered by CO₂ molecules would be a useful material for CO₂ capture. Therefore pure solid boron could be used a material for permanent capture of CO₂, or alternatively the solid boron functionalised with CO₂ could be used as a material for capture of further CO₂ and release of the additional CO₂.

### 4 Conclusions

Using DFT calculations we have investigated the reaction mechanisms for CO₂ capture on α-B₁₂ and γ-B₂₈ surfaces. We found that these “electron deficient” boron solids perform well in capturing CO₂ on the basic sites of these boron surfaces due to Lewis acid-base interactions. The adsorption energy of CO₂ with their strongest adsorption configurations on α-B₁₂ and γ-B₂₈ phases are 47.76 and 29.18 kcal/mol, respectively, and the barriers of these adsorption processes from their physisorbed to chemisorbed configurations are very low. Moreover, the values of the changes of Gibbs free energy for capture of free CO₂ on α-B₁₂ and γ-B₂₈ surfaces to form chemisorbed configurations are negative over the temperature range 200 ~ 1000 K, which indicate the reactions are spontaneous within this temperature range. The calculations also show the binding between CO₂ and the materials become weaker as the CO₂ coverage increases. In addition, the modeling suggests that the solid boron materials can effectively capture CO₂ and should stimulate some further experiments to verify our theoretical prediction.
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Notes and references