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Qiao Sun

University of Queensland

Meng Wang

University of Queensland, mw088@uowmail.edu.au

Zhen Li

University of Wollongong, zhenl@uow.edu.au

Aijun Du

Queensland University of Technology

Debra J. Searles

University of Queensland

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Abstract

Capturing and sequestering carbon dioxide (CO₂) can provide a route to partial mitigation of climate change associated with anthropogenic CO₂ emissions. Here we report a comprehensive theoretical study of CO₂ adsorption on two phases of boron, α -B12 and γ -B28. The theoretical results demonstrate that the electron deficient boron materials, such as α -B12 and γ -B 28, can bond strongly with CO₂ 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 CO₂ capture, we also performed calculations with various degrees of CO₂ coverage. The computational results indicate CO₂ 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 CO₂ capture.

Keywords

dioxide, adsorption, solid, boron, study, computational, carbon

Disciplines

Engineering | Physical Sciences and Mathematics

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A Computational Study of Carbon Dioxide Adsorption on Solid Boron

Qiao Sun^{*,a}, Meng Wang^{a,b}, Zhen Li^{*c}, Aijun Du^d and Debra J. Searles^{*,a,e}

Capturing and sequestering carbon dioxide (CO₂) can provide a route to partial mitigation of climate change associated with anthropogenic CO₂ emissions. Here we report a comprehensive theoretical study of CO₂ adsorption on two phases of boron, α -B₁₂ and γ -B₂₈. The theoretical results demonstrate that the electron deficient boron materials, such as α -B₁₂ and γ -B₂₈, can bond strongly with CO₂ 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 CO₂ capture, we also performed calculations with various degrees of CO₂ coverage. The computational results indicate CO₂ 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 CO₂ capture.

1 Introduction

Carbon dioxide, CO₂, 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 CO₂ from combustion products to reduce its concentration in the atmosphere are being developed.^{1,2} An alternative approach to reduction of CO₂ from combustion is to select fuels that produce less CO₂ on combustion than conventional fossil fuels (e.g. natural gas), or no CO₂ (H₂). These fuels often contain contaminants including CO₂, so CO₂ 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.^{2,3} In both these approaches to reducing CO₂ in the atmosphere, it is important that new environmentally friendly and economically feasible processes for CO₂ capture be developed.

^aCentre for Theoretical and Computational Molecular Science, Australian Institute for Bioengineering and Nanotechnology, The University of Queensland, QLD 4072, Brisbane, Australia. Email: q.sun@uq.edu.au; d.bernhardt@uq.edu.au

^bCenter for Bioengineering and Biotechnology, China University of Petroleum (East China), Qingdao 266555, China.

^cInstitute of Superconducting & Electronic Materials, The University of Wollongong, NSW 2500, Australia. Email: zhenl@uow.edu.au

^dSchool of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4001, Australia.

^eSchool of Chemistry and Molecular Biosciences, The University of Queensland, QLD 4072, Brisbane, Australia.

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 CO₂ and have large surface areas, however many materials only weakly bind CO₂. In this work we find that solid boron materials such as α -B₁₂ and γ -B₂₈ can adsorb CO₂ strongly and therefore may be useful materials for CO₂ 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 B₁₂ 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 its connectivity is associated with the electron deficiency, or hypovalency, of boron. Four reported boron phases correspond to the pure element: rhombohedral α -B₁₂^{6,9,11,12} and β -B₁₀₆⁵ (with 12 and 106 atoms in the unit cell, respectively), tetragonal T-192⁷ (with 190–192 atoms per unit cell) and γ -B₂₈^{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 CO₂ capture using α -B₁₂ and γ -B₂₈. The α -B₁₂ phase consists of one B₁₂ icosahedron per unit cell and γ -B₂₈ consists of icosahedral B₁₂ clusters and B₂ pairs in a NaCl-type arrangement.⁸ It has been shown that the electronic properties of the B₂ pairs and B₁₂ clusters in γ -B₂₈, are different, and this results in charge transfer between them.⁸ For α -B₁₂ and γ -B₂₈, our study found that there is charge transfer among the atoms on their surfaces and the internal atoms, indicating that the α -B₁₂ and γ -B₂₈ slabs are amphoteric with acidic and basic sites. The regioselectivity of α -B₁₂ and γ -B₂₈ indicate CO₂ (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 CO₂ capture on α -B₁₂ and γ -B₂₈ surfaces. The primary motivation of the theoretical study is to stimulate further experiments to verify our prediction that CO₂ can be captured by these boron materials.

2 Computational methods

Ab initio DFT calculations are performed with the DMol3 module in Material Studio.^{19,20} The configurations of CO₂ adsorbed on the boron phases are fully optimized using the generalized gradient approximation²¹ treated by the Perdew-Burke-Ernzerhof exchange-correlation potential with long range dispersion correction carried out using the Grimme's scheme²². This method has been used to successfully determine the geometrical, energetic and electronic structural properties of boron clusters, boron phases and boron

containing materials.²³⁻²⁹ The basis set employed is an all-electron double-numerical atomic orbital basis set, augmented by d-polarization functions (DNP). The cell parameters of α -B₁₂ and γ -B₂₈ in the calculations are all optimized and are consistent with the experimental values.^{8,11} Detailed information on the cell parameters is listed in our previous publication.²⁷ The slab thicknesses of α -B₁₂ and γ -B₂₈ are 8.012 Å and 6.914 Å (corresponding to two layers of B₁₂ or B₁₄ clusters), respectively. The 2×2 α -boron (001) and γ -boron (001) surfaces were chosen with a 15 Å vacuum above the slab in order to avoid interactions between their periodic images, and the Brillouin zone is sampled by $6 \times 6 \times 1$ k-points using the Monkhorst-Pack scheme.

The calculations of CO₂ adsorption on α -B₁₂ (001) and γ -B₂₈ (001) surfaces are based on the fully optimized boron surfaces.²⁷ The adsorption energy of CO₂ on α -B₁₂ and γ -B₂₈ are calculated from Eq. 1:

$$E_{ads} = E_{(\text{boron phase}-\text{CO}_2)} - E_{\text{CO}_2} - E_{(\text{boron phase})} \quad (1)$$

where $E_{(\text{boron phase}-\text{CO}_2)}$ is the total energy of the boron surface with a CO₂ molecule adsorbed. In order to better clarify the adsorption and the nature of the interaction of CO₂ with α -B₁₂ and γ -B₂₈, 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,²¹ we then use AIM theory, which has been used to successfully determine intermolecular interactions of different systems.^{27,30,31} In the AIM analyses,³² 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 (ρ_{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 ($\nabla^2\rho_{\text{bcp}}$) and energy density (H_{bcp}). The topological analysis of the system was carried out via the AIMALL program.³²

The transition states between chemisorbed and physisorbed CO₂ have been investigated using the complete LST (linear synchronous transit)/QST (quadratic synchronous transit) method³³ implemented in the DMol3 code. The reactants and products correspond to the optimized structures of CO₂ physisorbed and chemisorbed on α -B₁₂ and γ -B₂₈ surfaces, respectively. Electron distributions and transfer mechanisms are determined with the Mulliken method.³⁴

3 Results and discussion

The α -B₁₂ and γ -B₂₈ slabs were optimized and the fully relaxed α -B₁₂ (001) and γ -B₂₈ (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 -B₁₂ (001) and γ -B₂₈ (001) surfaces and then carried out a study of the mechanism of CO₂ adsorption on the surfaces of the two boron materials. All the possible sites for CO₂ adsorption on α -B₁₂ and γ -B₂₈ 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 CO₂ molecule directly connect with two boron atoms, and in type B interactions, two oxygen atoms of the CO₂ molecule directly connect with the boron atoms of the α -B₁₂ and γ -B₂₈ surfaces.

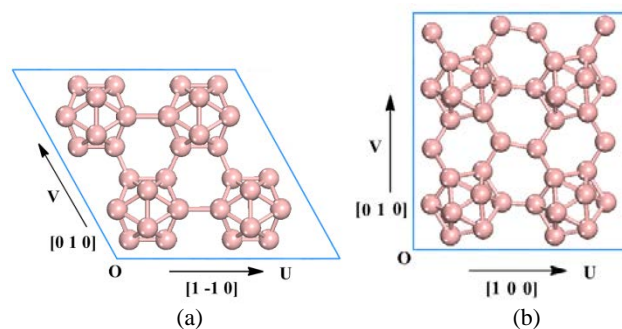


Fig. 1 The top view of the surfaces of fully relaxed α -B₁₂ (001) and γ -B₂₈ (001) slabs with cell vectors shown. Atom color code: pink, boron.

3.1 Atomic charge distributions of α -B₁₂ and γ -B₂₈

It is well known that boron phases, such as α -B₁₂ and γ -B₂₈, are electron deficient materials because there is only one electron on the p orbital of each boron atom, while CO₂ 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 CO₂ capture. However, from the Mulliken atomic charge distributions of the α -B₁₂ and γ -B₂₈ slabs that we modeled we can see that there is electron transfer from the atoms within the slabs to the surface atoms of α -B₁₂ and γ -B₂₈. Fig. 2 shows the optimized α -B₁₂ and γ -B₂₈ structures and the Mulliken atomic charges for the atoms labeled in Fig. 2 are listed in Table 1.

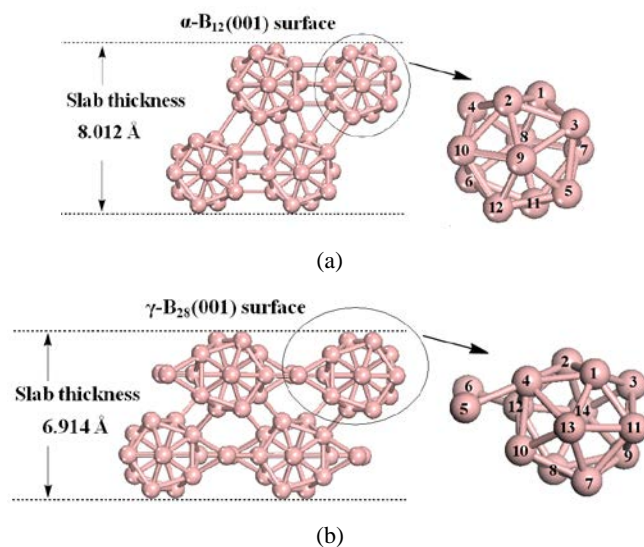


Fig. 2 The side view of the optimized α -B₁₂ (001) and γ -B₂₈ (001) slabs. Mulliken atomic charges of these atoms (with atom numbers in Fig. 2) are listed in Table 1.

The charges on the surface atoms of α -B₁₂ 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 -B₂₈ are similar to those of the α -B₁₂ 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 -B₁₂ and γ -B₂₈ slabs are regioselective and amphoteric, with both acidic and basic sites. Similar behaviour in boron materials, such as B₈₀, has been investigated preciously by Muya et al., who found the cap atoms of B₈₀ act as acid sites and the frame atoms act as basic sites in this regioselective molecule.³⁵ From the above analysis we have shown that, in principle, CO₂ (Lewis acid) will form strong interactions with the basic sites of α -B₁₂ and γ -B₂₈ due to Lewis acid-base interactions. In the following section, we will investigate CO₂ the mechanism of CO₂ adsorption on the α -B₁₂ and γ -B₂₈ surfaces.

Table 1 Atom number and Mulliken atomic charges (e) of the optimized α -B₁₂ and γ -B₂₈ slabs.

α -B ₁₂		γ -B ₂₈	
Atom number	Atomic charge	Atom number	Atomic charge
B1	-0.366	B1	-0.311
B2	-0.321	B2	-0.311
B3	-0.008	B3	-0.098
B4	-0.008	B4	-0.098
B5	0.139	B5	-0.074
B6	0.139	B6	-0.074
B7	0.119	B7	-0.025
B8	0.119	B8	-0.025
B9	0.033	B9	0.133
B10	0.033	B10	0.133
B11	0.066	B11	0.171
B12	0.055	B12	0.171
		B13	0.204
		B14	0.204

3.2 CO₂ adsorption on the α -B₁₂ surface

Currently 16 allotropes of elemental boron have been reported, with the α -boron structure being the simplest.¹⁸ It contains 12 atoms in a rhombohedral unit cell, forming a slightly distorted icosahedral B₁₂. In this section, we will investigate the reaction mechanism of CO₂ adsorption on α -B₁₂. We have identified two ways in which CO₂ adsorbs on α -B₁₂, labelled type A and type B. In type A one O atom and the C atom of CO₂ bond with one B-B bond of α -B₁₂; and in type B two O atoms of CO₂ interact with one B-B bond of α -B₁₂. Fig. 3 (a) shows the optimized structures of the two possible minimum-energy type A configurations, and the transition states for the process of CO₂ adsorption on the α -B₁₂ 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 -B₁₂ to CO₂ are listed in Table 2 and Table S1 in supporting information. For the two types of interaction of CO₂ with α -B₁₂, 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 CO₂ capture on α -B₁₂ through type A interactions, we identified two stationary states, corresponding to physisorption and chemisorption. In the physisorbed configuration, CO₂ interacts with one B-B bond of α -B₁₂ 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 CO₂ and α -B₁₂.

Table 2 Adsorption energy in kcal/mol, bond distance (r) in Å, bond angle (α) in deg and charge transfer (CT) in electrons for the type A of CO₂ adsorption on α -B₁₂ and γ -B₂₈ surfaces.

Chem		Phys	TS	Chem
α -B ₁₂ surface	Adsorption energy	-4.95	-0.46	-47.76
	r(B-O1)	3.042	1.967	1.477
	r(B-C)	3.107	2.648	1.647
	r(C-O1)	1.176	1.208	1.442
	r(C-O2)	1.176	1.170	1.203
	r(B-B)	1.597	1.636	1.694
	α (O-C-O)	179.9	170.5	122.7
	CT	0.004	0.05	-0.584
γ -B ₂₈ Surface	Adsorption energy	-4.84	-2.50	-29.18
	r(B-O1)	2.896	1.738	1.482
	r(B-C)	3.304	2.616	1.649
	r(C-O1)	1.178	1.216	1.413
	r(C-O2)	1.175	1.166	1.206
	r(B-B)	1.671	1.672	1.740
	α (O-C-O)	179.7	168.8	123.4
	CT	0.007	0.077	-0.528

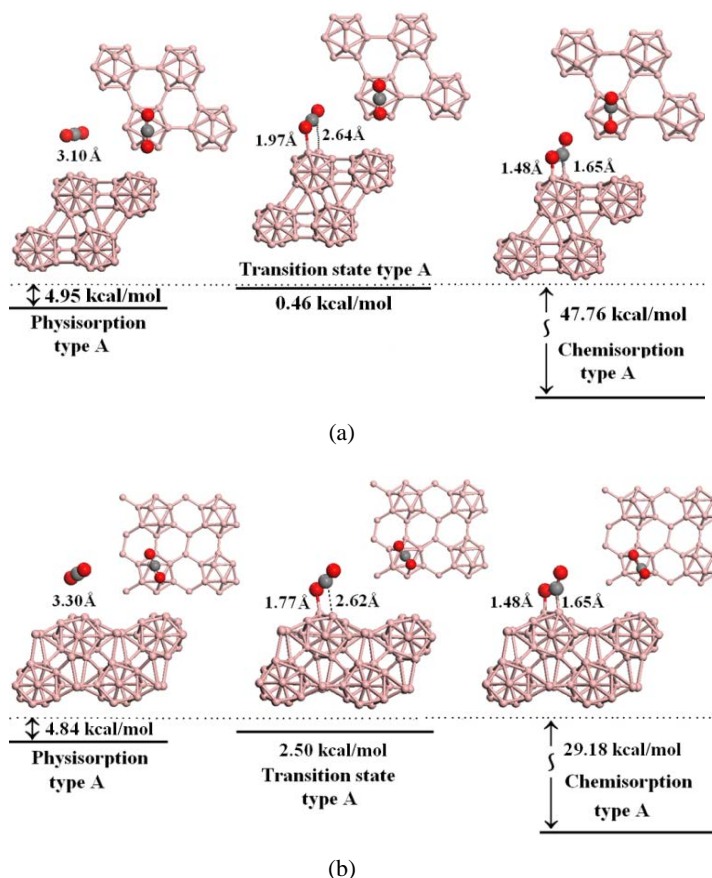


Fig. 3 Computed minimum energy configurations and transition state for CO₂ adsorption on the α -B₁₂ (a) and γ -B₂₈ (b) surfaces involving type A interactions (top and side view of the two minimum energy configurations and transition state).

Table 3 Atom number and Mulliken atomic charges (e) and the sum of charge (e) of CO₂, the boron cell of α -B₁₂-CO₂ and γ -B₂₈-CO₂ complexes (chemisorbed configurations) as well as the charge transfer of α -B₁₂-CO₂ (CT1) and γ -B₂₈-CO₂ (CT2) complexes comparing with those of the isolated forms.

Atom type/Sum	CO ₂	α -B ₁₂	CT1	γ -B ₂₈	CT2
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of charge		CO ₂		CO ₂	
O1	-0.284	-0.481	-0.197	-0.460	-0.263
C	0.568	0.246	-0.322	0.278	0.600
O2	-0.284	-0.349	-0.065	-0.346	-0.281
Sum of charge	0.0	-0.584		-0.528	
B1		-0.186	0.180	-0.192	0.119
B2		0.110	0.431	0.065	0.376
B3		0.001	0.009	-0.011	0.087
B4		0.000	0.008	-0.007	0.091
B5		0.036	-0.103	-0.098	-0.024
B6		0.036	-0.103	-0.057	0.017
B7		0.071	-0.048	-0.010	0.015
B8		0.071	-0.048	-0.018	0.007
B9		0.082	0.049	0.125	-0.008
B10		0.081	0.048	0.126	-0.007
B11		0.069	0.003	0.095	-0.076
B12		0.057	0.002	0.116	-0.055
B13				0.093	-0.111
B14				0.077	-0.127
Sum of charge		0.428		0.304	

The adsorption energy of the physisorbed CO₂ is calculated to be 4.95 kcal/mol. The weak interaction is also confirmed by the negligible charge transfer between the α -B₁₂ and CO₂ molecule (with a value of only -0.004e). Molecular graphs for CO₂ adsorption on α -B₁₂ are displayed in Fig. 4. We can see from Fig. 4 (a) that the interaction between CO₂ and α -B₁₂ 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 α -B₁₂ are listed in Table S2 in supporting information. For the physisorbed configurations, the electron densities at the BCPs of the bonds between CO₂ and α -B₁₂ are small (Table S2), which is consistent with a weak interaction. When CO₂ is chemisorbed on α -B₁₂, 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°, 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 α -B₁₂ and C–O bond of CO₂. Table 3 lists the Mulliken atomic charges (e) of the α -B₁₂-CO₂ and γ -B₂₈-CO₂ complexes (chemisorbed configurations) and the charge transfers of CO₂ and the boron cells which directly connect with CO₂ of α -B₁₂-CO₂ (CT1) and γ -B₂₈-CO₂ (CT2) complexes comparing with those of the isolated forms. A Mulliken charge population analysis shows that there is -0.584 electron charge transfer from α -B₁₂ to the CO₂ molecule, and the charge redistributions of the boron atoms at the CO₂/B interface is the main contribution for the charge transfer. 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 1.647 Å and 1.477 Å, respectively. The short distance indicates a strong interaction between the CO₂ molecule and α -B₁₂, with the calculated adsorption binding energy is 47.76 kcal/mol.

Here we note that the interaction between CO₂ and α -B₁₂ is the strongest value for CO₂ 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 increase, 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 CO₂ 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 CO₂ and α -B₁₂, and low

barrier from the physisorbed to chemisorbed configurations demonstrate that the CO₂ adsorption on α -B₁₂ is a kinetically favorable process. In addition, we have listed variation of thermodynamic properties with temperatures (K) for adsorption of free CO₂ on the α -B₁₂ (a) and γ -B₂₈ (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 CO₂ capture on α -B₁₂ 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.

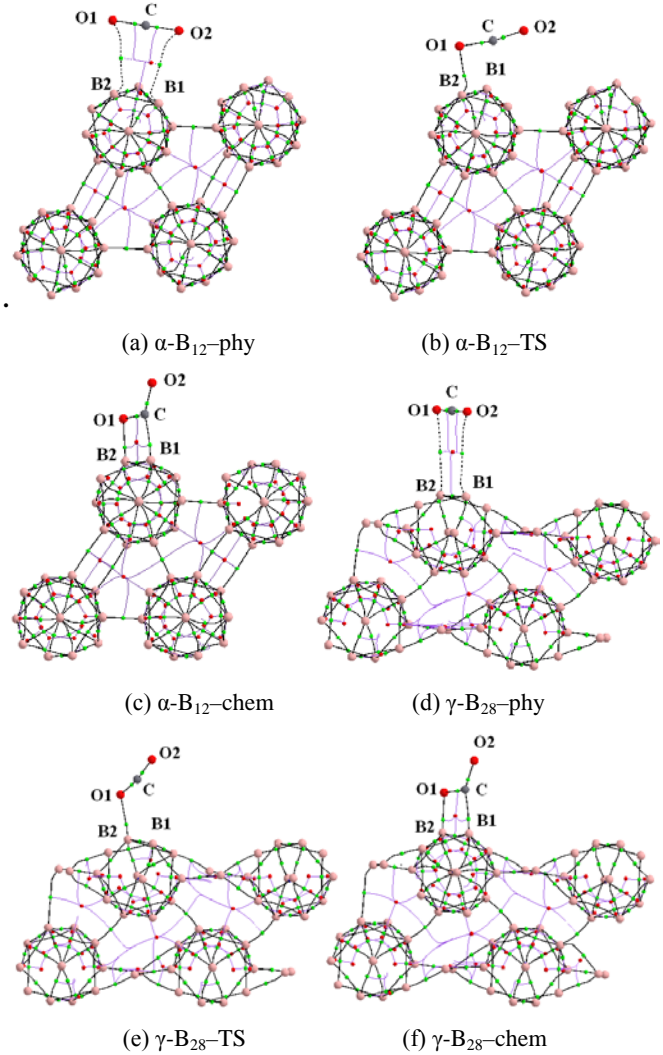


Fig. 4 The molecular graphs of the minimum energy structures and transition states of CO₂ adsorbed on the α -B₁₂ and γ -B₂₈ surfaces with type A interactions, where the bond critical points (BCPs), ring critical points (RCPs) and cage critical point (CCP) are denoted as small green, red and blue dots, respectively.

For type B interactions of CO₂ with α -B₁₂, we also identified two local minima and the transition state between those physisorbed and chemisorbed states. The physisorbed configuration (Fig. S1(a)) of CO₂ on α -B₁₂ is very similar to that observed in the type A physisorbed configuration. The chemisorbed configuration (Fig. S1(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 slight 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 B₁₂ icosahedra. There is debate about whether the two distinct structural units should be partially ionic or not.^{13,24,36} 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 donate 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 physisorbs 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.

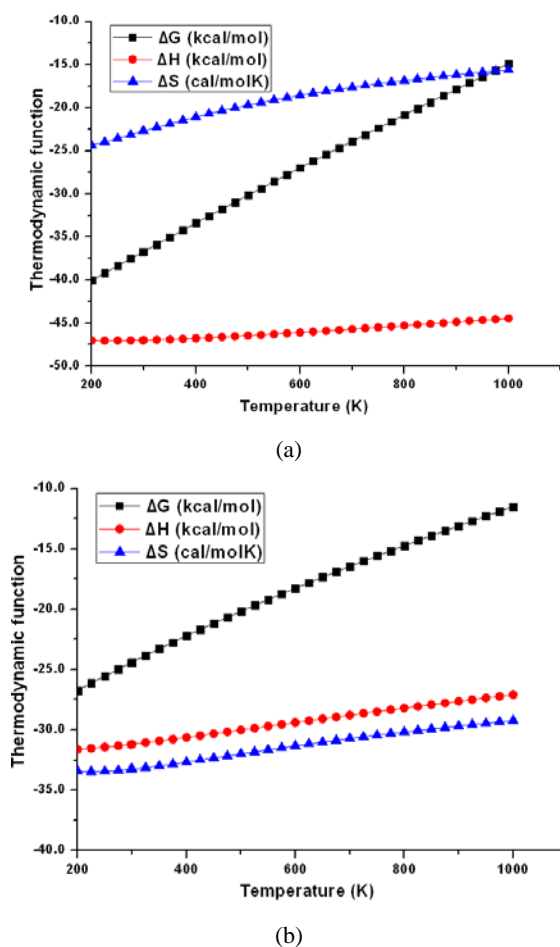


Fig. 5 Variation of thermodynamic properties with temperatures (K) for adsorption of free CO₂ on the α -B₁₂ (a) and γ -B₂₈ (b) surfaces to form chemisorbed configurations (type A). Squares, triangles and circles correspond to the change in Gibbs free energy (kcal/mol), change in entropy (cal/mol K) and 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 C–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 slight 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 the 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 orbitals and nearby molecular orbits are the most important factors determining the stability of molecules. The larger the difference between the frontier orbitals, 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) ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) 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 2×2 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 have been carried out.

The average adsorption energies of CO₂ molecules on boron surfaces are defined as

$$E_{\text{ads}} = (E_{(\text{boron phase}-n\text{CO}_2)} - nE_{\text{CO}_2} - E_{(\text{boron phase})})/n \quad (2)$$

where n is the number of CO₂ molecules adsorbed on the boron surfaces and $E_{(\text{boron phase}-n\text{CO}_2)}$ is the total energy of the boron surface with CO₂ adsorbed.

Table 4 and Figure 6 list the structural properties and the absolute value of average 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

Table 4 The absolute value of average adsorption energies in kcal/mol, average bond distances (r) in Å, bond angles (α) in deg and charge transfer (CT) in electron for two, three and four CO₂ molecules adsorption on α -B₁₂ and γ -B₂₈ surfaces.

Adsorbents	Properties	Two CO ₂	Three CO ₂	Four CO ₂
α -B ₁₂ surface	Ads	-43.19	-38.09	-33.79

γ -B ₂₈ Surface	$r(\text{B-O1})$	1.473	1.479	1.481
	$r(\text{B-C})$	1.650	1.661	1.675
	$r(\text{C-O1})$	1.430	1.407	1.388
	$r(\text{C-O2})$	1.201	1.202	1.201
	$r(\text{B-B})$	1.700	1.703	1.711
	$\alpha(\text{O-C-O})$	123.4	124.6	125.9
	CT	-0.514	-0.444	-0.388
	Ads	-27.61	-25.25	-24.29
	$r(\text{B-O1})$	1.462	1.470	1.471
	$r(\text{B-C})$	1.642	1.662	1.666
	$r(\text{C-O1})$	1.435	1.408	1.198
	$r(\text{C-O2})$	1.200	1.200	1.406
	$r(\text{B-B})$	1.740	1.743	1.744
	$\alpha(\text{O-C-O})$	123.1	124.6	125.1
	CT	-0.489	-0.442	-0.408

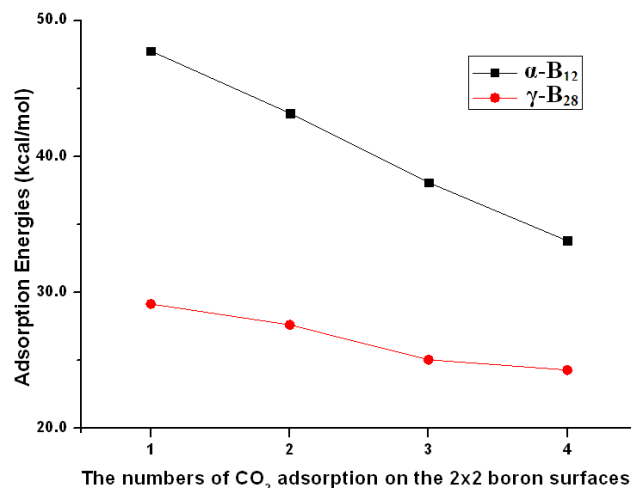


Fig. 6 The absolute value of average adsorption energies (kcal/mol) with two, three and four CO₂ molecules adsorption on 2×2 α -B₁₂ and γ -B₂₈ surfaces.

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 2×2 α -B₁₂ reduce from -47.76 to -33.79 kcal/mol as the number of CO₂ molecules increases 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 2×2 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 absorption energy of CO₂ with their strongest adsorption configurations on α -B₁₂ and γ -B₂₈ boron 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 modelling 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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