



CO₂ capture and separation on charge-modulated calcite

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ABSTRACT

In this study, density functional theory calculations were performed to study the CO₂ capture and separation on calcite surface with charge-modulated. The results indicate that calcite surface can be used experimentally for charge modulation and is very stable under charged conditions. At the critical charge density of $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$, the adsorption energy of a single CO₂ on calcite surface can be dramatically enhanced, reaching -6.23 eV . Moreover, reversible processes of CO₂ adsorption/desorption are exothermic without any energy barrier, and thermodynamic properties demonstrate that CO₂ spontaneously adsorbs on the charged calcite surface at the temperature below 900 K. In practical application, calcite can achieve more adsorption capacity ($4.95 \times 10^{14} \text{ cm}^{-2}$) at minimum charge density ($8.04 \times 10^{13} \text{ e}^-/\text{cm}^2$) compared with two-dimensional materials. In addition, charged calcite has highly selective for separating CO₂ from N₂, H₂ and CH₄. Importantly, the optimal charge density range for CO₂ capture and separation is determined from 8.04×10^{13} to $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$. These results not only demonstrate the feasibility of cheap calcite as an excellent reversible CO₂ collector by charge-modulated method but also provide a direction on natural minerals as candidate gas-adsorbent materials.

1. Introduction

The serious environmental problems caused by global warming have become the main focus of climate change around the world. This is because the major by-product of the burning process of fossil fuels is CO₂, and a large amount of CO₂ is emitted into the atmosphere leading to a significant increase in global temperature [1,2]. Meanwhile, ocean acidification caused by increased CO₂ will threaten the survival of marine life and its ecological environment [3]. Therefore, CO₂ capture and separation technologies are considered effective method to mitigate the greenhouse effect [4,5].

Currently, the technology of aqueous amine solutions is the most common way to capture CO₂, which is widely applied in industries [6]. But this method needs to deal with some problems such as corrosive behavior, high regeneration energy requirements, degradability and toxicity [7]. To overcome these problems, membranes have attracted wide attention due to their advantages of simplicity, low energy consumption and environmentally friendly [8,9]. Nevertheless, membrane has good separation performance only for special gases that have large differences in polarity or kinetic diameter. For the separation of CO₂

from N₂, it will be a difficulty because they have a similar kinetic diameter and no dipole moment [10,11]. Besides, membranes are highly costly, and temperature as well as oxidants has a great impact on their adsorption performance [9,12]. To avoid the above problems, solid adsorbents are extensively studied among which calcium oxide is the most representative CO₂-adsorbent material. It has attracted wide attention because of their advantages, such as low cost and high capacities [13,14]. But calcium oxide quickly weakens its efficiency to capture CO₂ during repeated cycles of calcination and carbonation, due to the impenetrable accumulation of calcite on the filling layer surface [15]. To sum up, there are some shortcomings in above-mentioned materials and methods, such as harm to the environment, poor regenerative capacity, high cost and poor selectivity. Therefore, the challenge for CO₂ capture and separation is to obtain high performance adsorbents and technologies.

Recently, a new method of charge-modulated was proposed as a CO₂ capture strategy by Sun et al. [16]. In detail, the authors reported that boron nitride nanomaterials with charge-modulated can achieve CO₂ adsorption/desorption based on density functional theory (DFT) calculations. Furthermore, the CO₂ adsorption/desorption process will

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be simply controlled by injecting/extracting extra electrons, and the charge density applied in boron nitride nanomaterials (the band gap is around 5.8 eV [17]) can be easily achieved experimentally. Subsequently, different two-dimensional materials, such as graphitic carbon nitride, [18] borophene nanosheets [19], C_3N nanosheet [20], Me-N-C (Me = Fe, Cu, and Co) nanosheet [21], N-doped penta-grapheme sheet [22] and nanoporous grapheme [23], were studied by charge-modulated method according to DFT calculations for CO_2 capture and separation. However, two-dimensional materials not only have high production costs and complex manufacturing processes, but also require a high charge density for CO_2 capture and separation.

To solve those problems, calcite was considered as a cost-effective candidate material to capture CO_2 by charge-modulated method. This is because calcite can be polarized and has semiconductor property at a certain temperature [24–26]. Besides, calcite is one of the most thermally stable minerals due to its high decomposition temperature [13]. Economically, calcite has large reserves and is broadly distributed in nature [27]. Therefore, if calcite is feasible, it will not pollute the environment and the cost of CO_2 -adsorbent will be significantly reduced. Moreover, the charge-modulated method will be vastly applied in practical environment due to the operability of low charge density and availability of large temperature range.

In this study, to prove this hypothesis, DFT calculation with dispersion correction method was performed to systematically study the adsorption of CO_2 on neutral and charged calcite surface. First of all, the stability of calcite surface and the critical charge density of calcite surface for CO_2 capture was confirmed. Then, adsorption behavior, adsorption mechanism, kinetic process and thermodynamic properties of CO_2 -calcite interface were studied to illustrate the feasibility of charge-modulated calcite for CO_2 capture. Finally, CO_2 capture capacity and the separation performance of CO_2 from N_2 , H_2 and CH_4 were discussed in detail, among which the optimal charge density range for CO_2 capture and separation is determined. These results not only provide valuable references for the operability of practical applications, but also mean that other natural minerals may have a potential development direction in the field of CO_2 capture and separation.

2. Methods

Based on density functional theory (DFT), Dmol³ code [28] was used to calculate all of the adsorption behaviors of gas molecules (CO_2 , N_2 , H_2 and CH_4) on the (104) surface of calcite, since the (104) surface of calcite is the most stable thermodynamically crystallographic plane [29,30]. The exchange-correlation interaction was dealt with by the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) type [31,32] and double numerical basis set with polarization function (DNP) was adopted. In order to accurately describe weak interactions, a dispersion-corrected DFT (DFT-D) method with the Grimme vdW correction [33] was employed in all calculations. Given the incomplete convergence of interlayer interactions across periodic boundaries during the charge-modulated gas capture, a correction procedure proposed by Bal et al. [34] was used to achieve fully converged adsorption processes of gas molecules. To achieve high-quality calculation results, the real-space global cutoff radius was 4.9 Å and the Brillouin zone was sampled by $3 \times 2 \times 1$ k-points using the Monkhorst-Pack scheme. Besides, the convergence tolerances were 1×10^{-5} Ha for the total energy, 0.002 Ha/Å for atomic forces and 0.005 Å for maximum displacement, respectively. Finally, the Mulliken method [35] was chosen to determine the electron distribution and transfer mechanism.

3. Results and discussion

3.1. Stability of calcite surface with charge-modulated

First of all, Fig. 1a shows the structural parameters of the calcite

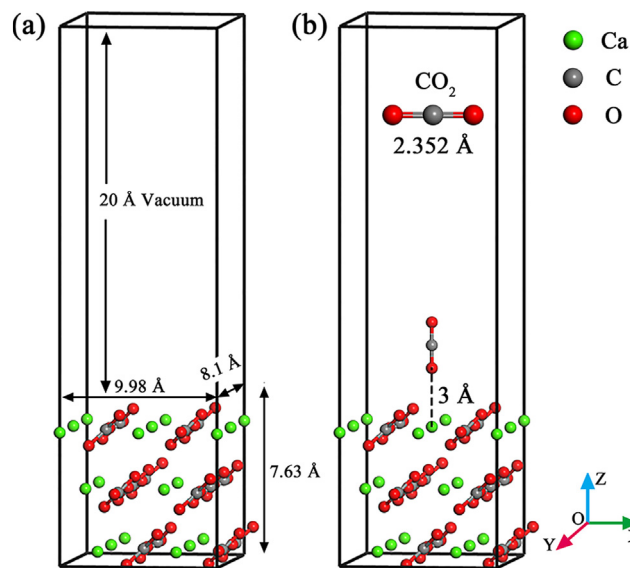


Fig. 1. The (104) surface of calcite. (a) Structure parameters. (b) Initial adsorption configuration of CO_2 .

(104) surface, which are consistent with the literature values [29,36,37]. Among which, the vacuum region of 20 Å vertical to the calcite surface was used to avoid interactions between periodic images. In addition, a good charge-modulated material for CO_2 capture should be easily carried out experimentally. Recently, Sun et al. [16] first reported that BN nanomaterials could be used to capture CO_2 by injecting extra electrons. Although the band gap of BN nanomaterials is around 5.8 eV [17], the author claimed that the charge density applied in BN nanomaterials is of the order of 10^{13} cm^{-2} can be easily realized experimentally using electrochemical methods, namely, electrospray, electron beam, or by gate voltage control [16]. For calcite surface, the band gap is lower than that of BN nanomaterials, especially at high temperatures [25]. Wada et al. [24] also proved that calcite can be polarized. Therefore, calcite can be used for charge-modulated experimentally.

To establish the stability of calcite surface at different charge densities, first, the charge density of calcite surface was defined as

$$\rho = Q/S \quad (1)$$

where ρ is the charge density (e^-/cm^2); Q is the total charge (e^-); and S is the surface area of calcite (104) surface (\AA^2). As shown in Fig. 1a, S is equal to 80.838 \AA^2 . We injected 0 to $5 e^-$ to the calcite surface, which the corresponding charge density ranges from 0 to $61.85 \times 10^{13} e^-/\text{cm}^2$. Secondly, we evaluated stability through its cohesive energy, which was defined as

$$E_{\text{coh}} = (n_1 E_{\text{Ca}} + n_2 E_{\text{O}} + n_3 E_{\text{C}} - E_{\text{calcite}})/(n_1 + n_2 + n_3) \quad (2)$$

where E_{coh} is the cohesive energy (eV); E_{Ca} , E_{O} , E_{C} and E_{calcite} denote the energies of a single Ca atom, a single O atom, a single C atom and calcite surface (eV), respectively; n_1 , n_2 and n_3 are the numbers of Ca, O and C atoms, respectively.

The cohesive energy of calcite surface as a function of charge density is shown in Fig. 2. Based on our computation results, the cohesive energy for neutral calcite is 3.03 eV/atom and 2.9 eV/atom for charged calcite with $61.85 \times 10^{13} e^-/\text{cm}^2$, which suggests that the application of charge density has little effect on the stability of calcite surface. Further, the decomposition temperature of natural calcite is high so that calcite has good thermal stability in a large temperature range [38]. Thus, calcite can be used as a good candidate for charge-modulated CO_2 capture.

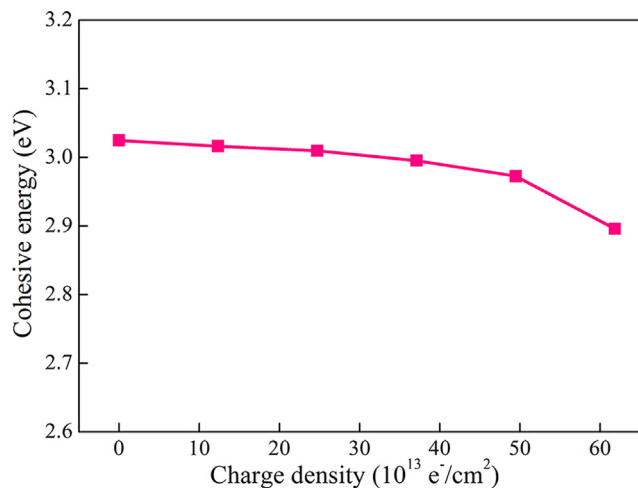


Fig. 2. The cohesive energy of calcite surface as a function of charge density.

3.2. Effect of charge density on adsorption behavior of CO_2 on calcite surface

In this section, we first confirm the critical charge density of calcite surface for a single CO_2 capture by calculating the adsorption distance. Next, we elaborate the adsorption energy of CO_2 at the critical charge density. Finally, we discuss the effect of charge density on adsorption behavior of CO_2 .

When the charge density reaches a critical value, gas molecule will move far away from the adsorbent [19,20,22,39]. Consequently, we needed to confirm the critical charge density by calculating the adsorption distance of a single CO_2 on calcite surface as a function of charge density. Before evaluating the critical charge density of calcite surface, it is very necessary to define the initial adsorption configuration of CO_2 on calcite surface. CO_2 molecule is vertically adsorbed at calcium ion site on calcite surface on the basis of previous studies [25,29,37,40], so the initial adsorption configuration of CO_2 on calcite surface is displayed in Fig. 1b. When the charge density increases from 0 to $18.56 \times 10^{13} e^-/cm^2$, we found that the adsorption distance is reduced from 2.69 Å to 2.49 Å (Fig. 3). It proves that CO_2 is closer to the calcite surface because of the extra electrons. However, CO_2 molecule

unexpectedly moves far away from the calcite surface when the charge density exceeds $18.56 \times 10^{13} e^-/cm^2$ (Fig. S1). Therefore, $18.56 \times 10^{13} e^-/cm^2$ (corresponding $1.5 e^-$ injected to calcite surface) is the critical charge density of calcite surface for CO_2 capture.

Further, adsorption energy is a significant standard to evaluate the interaction between gas and adsorbent [41]. As can be seen in Fig. 3, we calculated adsorption energy of CO_2 as a function of charge density. The adsorption energy was defined as

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{calcite}} + E_{\text{gas}}) \quad (3)$$

where E_{ads} is the adsorption energy (eV), E_{total} is the total free energy of calcite surface with gas molecule (eV), E_{calcite} is the total free energy of calcite surface (eV), and E_{gas} is the total free energy of an isolated gas molecule (eV).

Clearly, a more negative value represents a more powerful interaction between gas molecule and the calcite surface. In general, the adsorption energy of the gas on the adsorbent material must exceed approximately 0.52 eV to ensure chemisorption [42,43]. For neutral surface ($\rho=0$ in Fig. 3), the adsorption energy of CO_2 is -0.38 eV. Mulliken population analysis shows that no charge transfer from CO_2 molecule to calcite surface. Thus, it proves that CO_2 is physisorbed on neutral calcite surface. Interestingly, the adsorption energy is dramatically increased as the charge density of calcite surface increases, reaching -6.23 eV at the critical charge density. The adsorption energy of CO_2 on this $18.56 \times 10^{13} e^-/cm^2$ charged surface is about 16 times of that on neutral surface. Mulliken population analysis shows that the charge transfer from the calcite surface to the CO_2 molecule is $0.61 e^-$. Accordingly, this indicates that the type of CO_2 adsorption on the calcite surface changes from physisorption into chemisorption.

Due to the dipolar of C=O bond in electric field [4], we needed to study the effect of charge density on adsorption behavior of CO_2 . We do the dipole moment of CO_2 molecule and C=O bond length as a function of charge density in Fig. 3. As shown in Fig. 3, the dipole moment of CO_2 molecule and the length of two double C=O bonds increase dramatically as the charge density on calcite surface increases while the adsorption distance decreases. It can be interpreted by the increasing static electric field generated near the charged calcite surface due to increasing injected electrons. Furthermore, the increase of the adsorption energy of CO_2 molecule can be attributed to the increase of the dipole moment of CO_2 molecule and the decrease of the adsorption distance. Therefore, the polarization of CO_2 molecule induced by

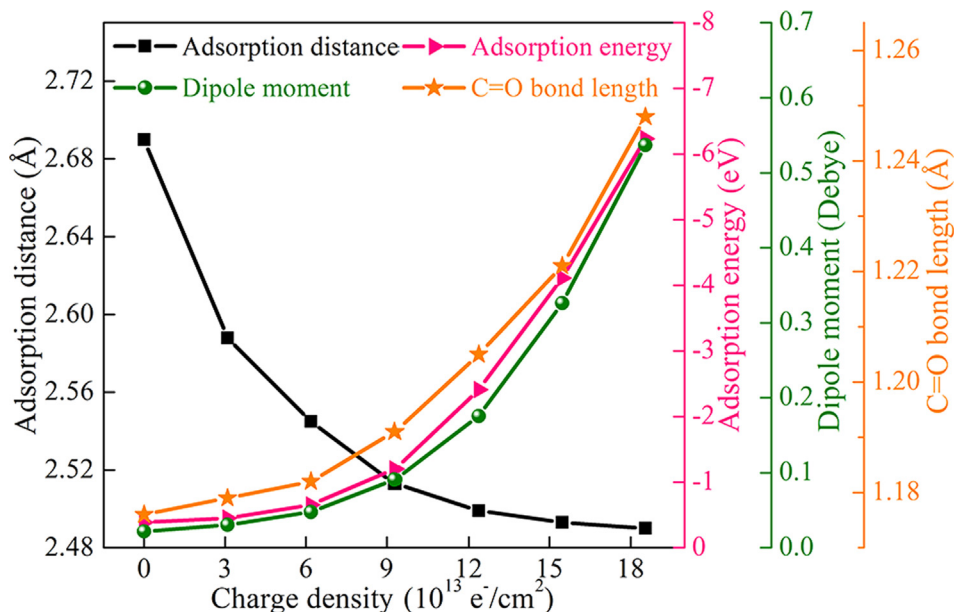


Fig. 3. Adsorption distance, adsorption energy, dipole moment of CO_2 molecule and C=O bond length as a function of charge density of calcite surface.

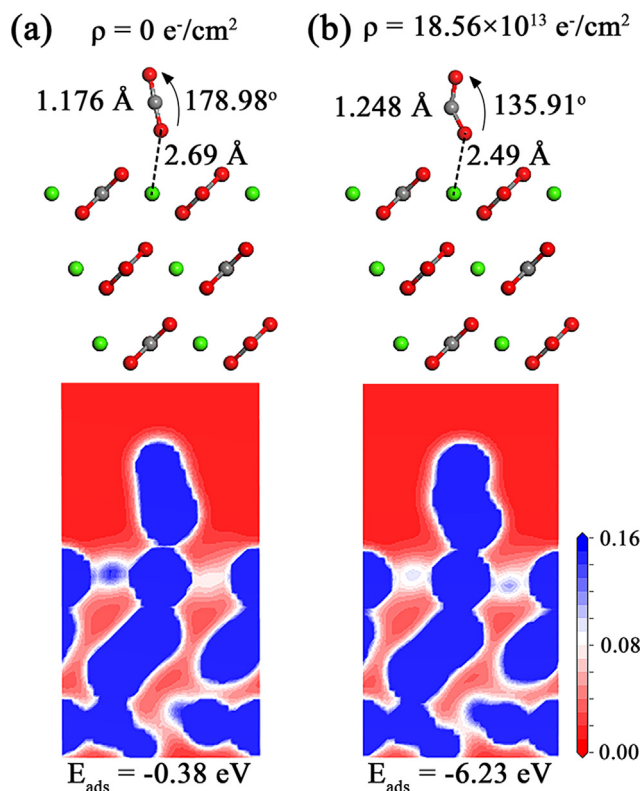


Fig. 4. Adsorption structure and electron density distribution of CO₂ on (a) neutral surface and (b) calcite surface with critical charge density. The densities are drawn with an isosurface, the range of isovalue is set to be 0 to 0.16.

injecting electrons plays a significant role in the adsorption energy of CO₂ molecule.

3.3. Adsorption mechanism of a single CO₂ on calcite surface at critical charge density

In this section, we take the critical charge density of calcite surface as an example to fully understand the adsorption mechanism. We first exhibit detailed adsorption structure and depict electron density distribution of CO₂-calcite interface. Then, we explore the kinetic process to illustrate reversible of CO₂ adsorption and desorption. Finally, we calculate thermodynamic properties to determine whether CO₂

spontaneously adsorbs on the calcite surface.

3.3.1. Detailed structure and electron density distribution of CO₂-calcite interface

Fig. 4 shows the detailed adsorption structures of CO₂ on neutral and the critical charge density ($18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$) calcite surface. On neutral calcite surface (Fig. 4a), the CO₂ molecule has a linear shape (the O-C-O angle is 178.98°; two double C=O bonds are 1.176 Å), which is vertically to surface and adsorbed at calcium ion site. The distance between the O atom of CO₂ and the calcium ion on calcite surface is 2.69 Å, and the geometry of the linear CO₂ molecule is similar to a free CO₂ molecule (the O-C-O angle is 180°; two double C=O bonds are 1.176 Å) [20]. Furthermore, there is no electrons overlap between CO₂ molecule and neutral calcite surface in the light of electron density distribution map (Fig. 4a). The results confirm that the CO₂ molecule shows weak physisorption on neutral surface. However, on calcite surface with the critical charge density ($18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$) (Fig. 4b), the linear CO₂ molecule is obviously distorted due to the extra electrons. Compared with the configuration of CO₂ physisorbed on the neutral calcite surface, the distance between the O atom and the calcium ion is shortened from 2.69 Å to 2.49 Å; the O-C-O angle is bent from 178.98° to 135.91°; the two double C = O bonds are elongated from 1.176 Å to 1.248 Å. Besides, an evident electron density distribution overlap is manifested between CO₂ molecule and charged calcite surface (Fig. 4b), demonstrating CO₂ molecule interacts more strongly with charged calcite surface. Since CO₂ is a Lewis acid and prefers to gain electrons during reaction [16], charged calcite surface would donate electrons to CO₂ molecule, resulting in a new bond between CO₂ molecule and calcite surface. Therefore, charged calcite surface exhibits strong chemisorption with CO₂ molecule at the critical charge density.

3.3.2. Reversibility of CO₂ adsorption and desorption

Since reversibility of CO₂ adsorption and desorption is significant for renewable materials, we explored the kinetic process of CO₂ adsorbed on calcite surface after electrons were injected or extracted (Fig. 5). Fig. 5a shows the most stable configuration of CO₂ physisorbed on neutral calcite surface in the adsorption process. Afterwards, the interaction between CO₂ molecule and charged calcite surface was significantly enhanced at the charge density of $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$ when compared with the neutral calcite surface case. It illustrates that the physisorbed CO₂ molecule spontaneously changes to chemisorption configuration, and the adsorption process is exothermic by 5.85 eV without any energy barrier. For the desorption process, Fig. 5b shows the initial configuration of CO₂ chemisorbed on charged calcite surface

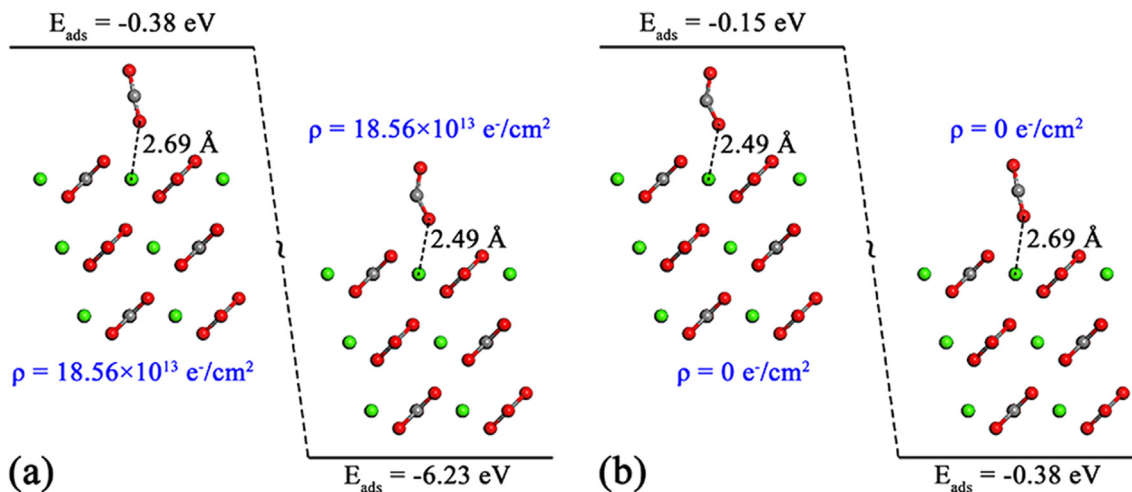


Fig. 5. Kinetic processes of adsorption and desorption of CO₂ on calcite surface with critical charge density. (a) Adsorption process of CO₂ on calcite surface during charge injection. (b) Desorption process of CO₂ on calcite surface during charge removal.

and the most stable configuration of CO₂ physisorbed on neutral calcite surface. Obviously, when the charge density of $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$ was removed from charged calcite surface, CO₂ molecule spontaneously desorbed from calcite surface and transferred to the weakly physisorption configuration. Furthermore, the desorption process is also exothermic by 0.23 eV without any energy barrier. Hence, the CO₂ adsorption/desorption processes on charged calcite surface are reversible and can be easily modulated via injecting/extracting extra electrons.

3.3.3. Spontaneity of CO₂ adsorbed on calcite surface with critical charge density

Evaluating thermodynamic properties is beneficial to determine whether CO₂ adsorbed on the charged calcite surface at different temperatures. For the calculation of thermodynamic properties, we need to calculate the entropy and enthalpy to get the Gibbs free energy. Hence, entropy was first calculated by

$$S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} \quad (4)$$

where S , S_{trans} , S_{rot} , and S_{vib} are the entropy, translation entropy, rotation entropy, and vibration entropy (cal/mol/K), respectively; Then, enthalpy was given by

$$H = H_{\text{trans}} + H_{\text{rot}} + H_{\text{vib}} + RT \quad (5)$$

where H , H_{trans} , H_{rot} , and H_{vib} are the enthalpy, translation enthalpy, rotation enthalpy, and vibration enthalpy (kcal/mol), respectively; R and T are the ideal gas constant (8.314 J/mol/K) and the absolute temperature (K), respectively; Finally, the Gibbs free energy was defined as

$$G = E(0\text{K}) + H - T \cdot S \quad (6)$$

where G and $E(0\text{K})$ are the Gibbs free energy (kcal/mol) and the zero-point energy (kcal/mol), respectively.

The detailed thermodynamic calculations were shown in Supplementary Material. Consequently, changes in the thermodynamic functions of entropy (ΔS , cal/mol/K), enthalpy (ΔH , kcal/mol), and Gibbs free energy (ΔG , kcal/mol) with temperature (K) could be calculated to study the effect of temperature on CO₂ adsorption on the calcite surface with charge density of $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$ (Fig. 6). As shown in Fig. 6, based on the values of ΔS and ΔH , the values of ΔG are achieved. The ΔG increases linearly with increasing temperature, among which the ΔG value is negative until approximately 900 K. It indicates that the chemisorption of CO₂ on the calcite surface with critical charge density of $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$ can proceed spontaneously at the temperature below 900 K.

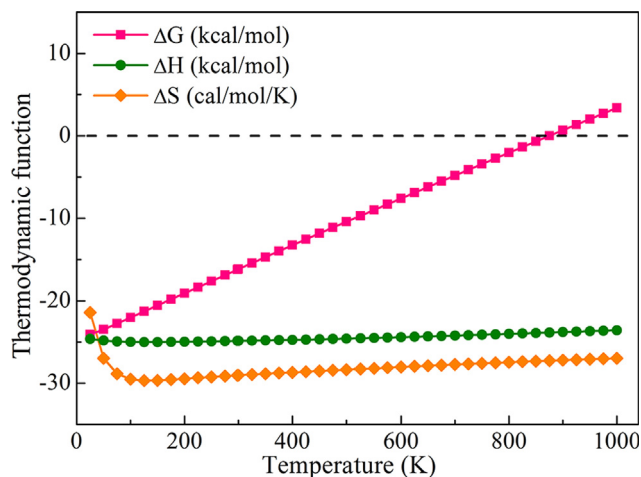


Fig. 6. Thermodynamic properties of CO₂ adsorbed on calcite surface as a function of temperatures.

3.4. Applications of CO₂ capture and separation

3.4.1. CO₂ capture capacity of calcite surface at minimum charge density

For high-performance CO₂-adsorbent materials, CO₂ capture capacity is an significant criterion. Before evaluating the CO₂ capture capacity, first, we need to consider the adsorption sites of multiple CO₂ molecules on calcite surface. As shown in Fig. 7, the supercell of calcite has 4 sites of calcium ion for CO₂ adsorption. Notably, two different adsorption configurations (2CO₂-a and 2CO₂-b) were designed for two CO₂ molecules co-adsorbed on calcite surface (Fig. 7a and 7b).

Besides, to confirm if there is a second layer of CO₂ adsorbed on calcite surface, we need to study it at critical charge density to ensure maximum adsorption energy. For this reason, we examined the adsorption behavior of the fifth CO₂ molecule on calcite surface with the critical charge density of $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$ (Fig. 8a). As the Fig. 8b suggests, when the first layer is filled, the fifth CO₂ molecule will no longer be adsorbed on charged calcite surface. It concludes that CO₂ molecule can only form a monolayer on charged calcite surface, even at the critical charge density.

To get a deeper studying of CO₂ capture capacity, we elaborated the average adsorption energies and the number of CO₂ molecules on charged calcite surface with different charge densities (Fig. 9). As the charge density increases, the adsorption energy of all CO₂ molecules increase. Among which, two different configurations (2CO₂-a and 2CO₂-b) of CO₂ adsorbed on calcite surface exhibit similar adsorption energy. When the charge density is constant, the larger the amount of CO₂ adsorbed on calcite surface, the smaller the adsorption energy. It is worth noting that the saturated chemisorption of CO₂ of calcite surface should be ensured in practical application. Generally, adsorption energy greater than 0.52 eV is considered chemisorption [42,43]. As the Fig. 9 displays, when the minimum charge density is $8.04 \times 10^{13} \text{ e}^-/\text{cm}^2$, four CO₂ molecules are chemisorbed on the charged calcite surface. Therefore, we define the saturation CO₂ capture coverage of charged calcite surface as four chemisorbed CO₂ molecules. In detail, CO₂ capture capacity can be calculated by dividing the number of CO₂ molecules (four CO₂ molecules) by the surface area (80.838 \AA^2), that is to say, CO₂ capture capacity is $4.95 \times 10^{14} \text{ cm}^{-2}$ at the charge density $8.04 \times 10^{13} \text{ e}^-/\text{cm}^2$. Compared with the optimal charge density of two-dimensional materials (Table 1), calcite surface can capture large amounts of CO₂ molecules at lower charge density (only $8.04 \times 10^{13} \text{ e}^-/\text{cm}^2$), which can obviously reduce the charge energy consumption and improve the adsorption efficiency. In addition, the production cost is very low because of the large reserves and wide distribution of calcite. The above advantages demonstrate that charged calcite surface is a wonderful sorbent for CO₂ capture.

3.4.2. Separation performance of CO₂ from calcite surface in gas mixture

Since CO₂-adsorbent materials often work in a multi-gas co-existing environment, the CO₂ separation performance is another significant criterion. Flue gas (CO₂/N₂) is the most common exhaust gas which can lead to the greenhouse effect [4,44]. Therefore, it is very significant to capture CO₂ from flue gas for mitigating global warming. Furthermore, H₂ is considered as the most promising alternative fuel because its oxidation product (water) is pollution-free [45]. Natural gas and shale gas (mainly CH₄) as conventional and unconventional clean energy source have attracted much attention due to their high efficiency, richness and environmental protection [46,47]. However, CO₂ is an undesirable impurity in the manufacturing processes of H₂ and CH₄ [45,48]. Consequently, CO₂ should be separated from H₂ and CH₄.

In practical application, the optimal charge density range for CO₂ capture and separation is determined from 8.04×10^{13} to $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$ (gray region in Fig. 10). This is because $8.04 \times 10^{13} \text{ e}^-/\text{cm}^2$ is the minimum charge density at which high concentrations (four CO₂ molecules) of CO₂ can be saturated chemisorbed on the calcite surface (Fig. 9). Then, $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$ is the critical charge density at which low concentrations (one CO₂ molecule)

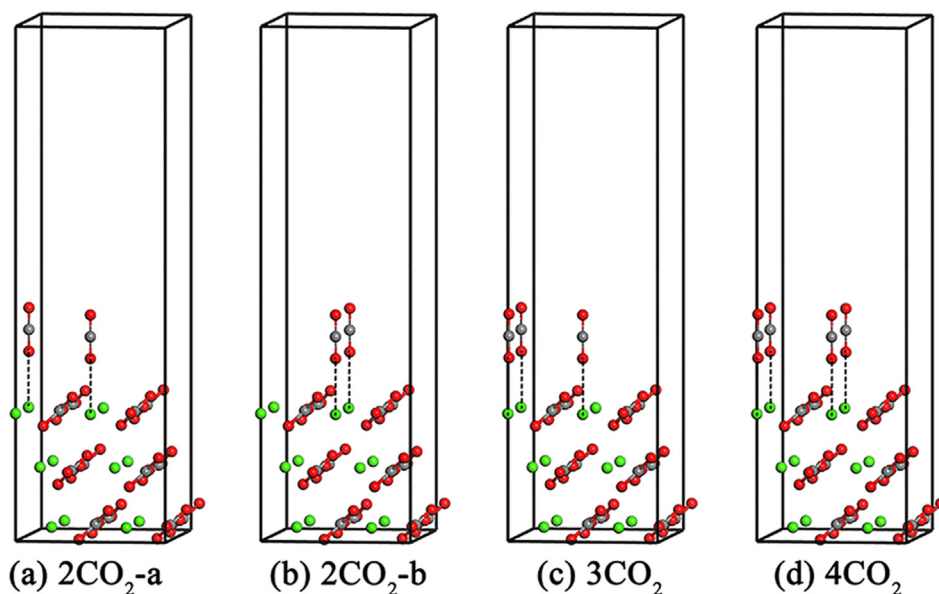


Fig. 7. The initial adsorption configurations of multiple CO₂ molecules on calcite surface.

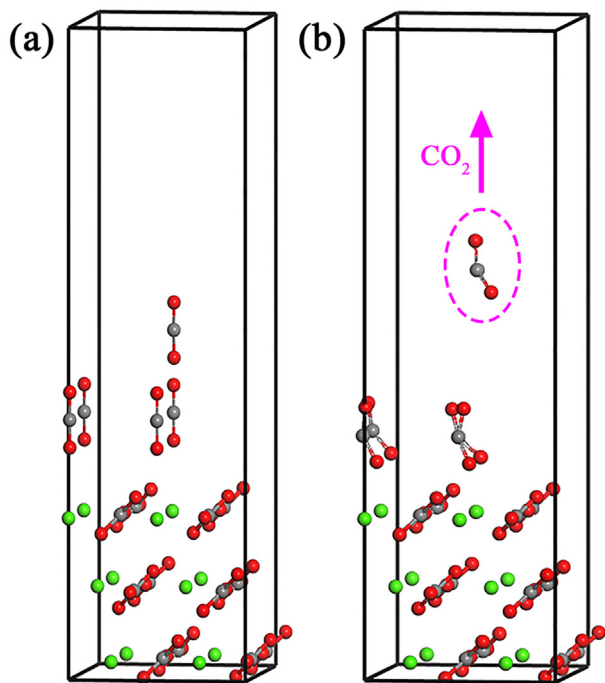


Fig. 8. Adsorption behavior of five CO₂ molecules on calcite surface with the critical charge density. (a) The initial adsorption configuration of five CO₂ on calcite surface. (b) The most stable configuration of five CO₂ on calcite surface with the critical charge density.

of CO₂ would not leave the calcite surface (Fig. 3). To confirm the high selectivity of charged calcite surface for CO₂ capture, the adsorption energies of CO₂, N₂, H₂ and CH₄ on different charge densities of calcite surface are calculated (Fig. 10), which the initial adsorption configurations of N₂, H₂ and CH₄ on the calcite surface are shown in Fig. S2. As shown clearly in Fig. 10, Fig. S3a and Fig. S3b, both H₂ and CH₄ are physisorbed on calcite surface. Once the charge densities are respectively greater than 8.66×10^{13} and $10.50 \times 10^{13} \text{ e}^-/\text{cm}^2$, H₂ and CH₄ keep away from the charged calcite surface so that the adsorption energy cannot be calculated in the Dmol³ code [19]. Besides, the adsorption energy of N₂ on calcite surface increases slowly with the

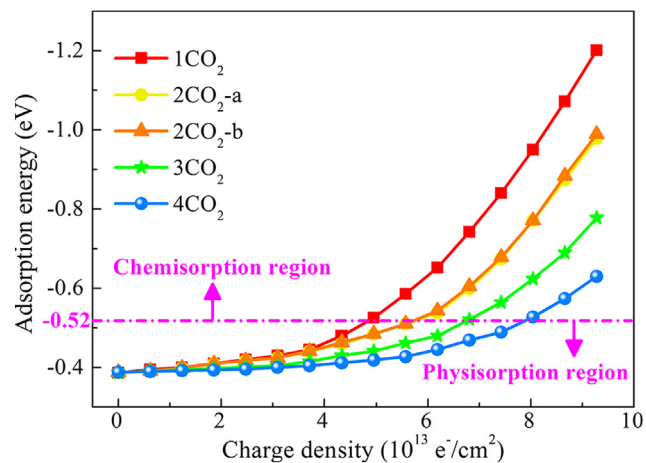


Fig. 9. The number and the average adsorption energies of CO₂ with different charge densities. “a” and “b” represent two different adsorption configurations (Fig. 7a and 7b), respectively.

Table 1

Comparison of CO₂-adsorbent performance of present and previous results.

Adsorbent materials	Charge density ($10^{13} \text{ e}^-/\text{cm}^2$)	capture capacity (10^{14} cm^{-2})
Graphitic carbon nitride [18]	61.70	7.39
Borophene nanosheet [19]	52.50	6.73
N-doped penta-grapheme sheet [22]	40.90	2.45
C ₃ N nanosheet [20]	22.00	2.13
Calcite (this study)	8.04	4.95

increase of charge density, but it is still in the state of weak physisorption (Fig. S3c). However, compared with N₂, H₂ and CH₄, CO₂ is strongly chemisorbed on calcite surface in the optimal charge density range. It evidently indicates that the charged calcite surface shows high selectivity for CO₂ separate from mixtures of N₂, H₂ and CH₄.

4. Conclusions

In summary, DFT with dispersion correction method was used to

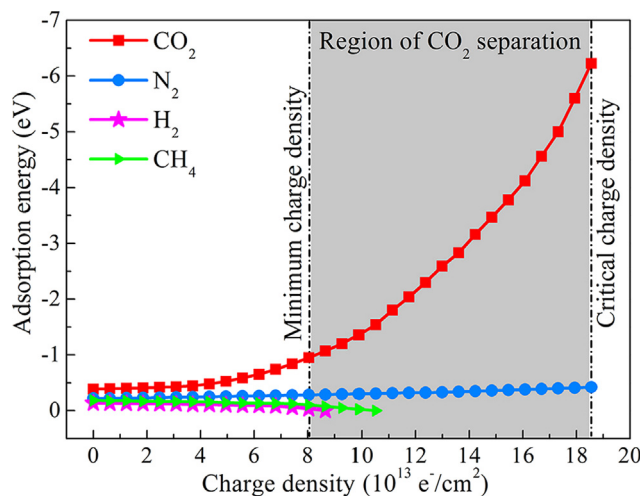


Fig. 10. Adsorption energies of CO₂, N₂, H₂ and CH₄ on different charge densities of calcite surface.

investigated adsorption properties of CO₂ on neutral and charged calcite surface. The results show that charge-modulated calcite is experimentally feasible and the charge density has little effect on the stability of calcite surface. In addition, adsorption energy of a single CO₂ is drastically enhanced at the critical charge density of $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$, reaching -6.23 eV . This is because CO₂ is a Lewis acid and prefers to gain electrons during adsorption, resulting in a new bond between CO₂ molecule and calcite surface. Under critical charge density, reversible processes of CO₂ adsorption/desorption are exothermic without any energy barrier, and thermodynamic properties prove that CO₂ spontaneously adsorbs on the charged calcite surface at the temperature below 900 K. Compared with the optimal charge density of two-dimensional materials for CO₂ capture, calcite surface can easily achieve CO₂ capture capacity up to $4.95 \times 10^{14} \text{ cm}^{-2}$ at minimum charge density of $8.04 \times 10^{13} \text{ e}^-/\text{cm}^2$. Meanwhile, charged calcite surface has highly selective for separating CO₂ from N₂, H₂ and CH₄. Therefore, the above results suggest that the charged calcite surface will have significant applications in currently the most interesting for CO₂ capture technologies, such as precombustion (CO₂/H₂) capture, natural gas (or shale gas) sweetening (CO₂/CH₄), and postcombustion (CO₂/N₂) capture. The optimal charge density range for CO₂ capture and separation is defined from 8.04×10^{13} to $18.56 \times 10^{13} \text{ e}^-/\text{cm}^2$.

CRediT authorship contribution statement

Lin Tao: Conceptualization, Methodology, Formal analysis, Writing - original draft. **Junchen Huang:** Formal analysis, Writing - review & editing. **Davoud Dastan:** Formal analysis, Writing - review & editing. **Tianyu Wang:** Writing - review & editing. **Jing Li:** Resources, Visualization. **Xitao Yin:** Conceptualization, Supervision, Resources. **Qi Wang:** Methodology, Writing - review & editing, Software, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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