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ARTICLE INFO

ABSTRACT

1. Introduction

2. Methods

 (104) , which are consistent with the literature values of \mathbf{R} $29,36,37$. A sample vacuum region of 20

3. Results and discussion

3.1. Stability of calcite surface with charge-modulated

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\mathbf{F} \qquad \mathbf{W}, \mathbf{F} \quad \mathbf{1a} \qquad \mathbf{1}
$$

3.2. Effect of charge density on adsorption behavior of $CO₂$ on calcite surface

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

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

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

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

S, S_{trans}, S_{rot}, S_{vib}
$$
(\sqrt[1]{\sqrt[3]{K}}, \sqrt[3]{T}, \sqrt[3]{T}
$$

 $\rm H\rm= \rm H_{trans} + \rm H_{rot} + \rm H_{vib} + \rm RT \tag{5}$

H, H_{traps}, H_{rot}, H_{vib}
$$
\begin{array}{ccc}\n & \downarrow & \downarrow & \downarrow \\
 \uparrow & \downarrow & \downarrow & \downarrow \\
 & \uparrow & \downarrow & \downarrow \\
 & & \downarrow & \downarrow\n\end{array}
$$

 fi

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

where G and E(0K) are the Gibbs free energy (kcal/mol) and the zeropoint 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 × 10¹³ [−]/cm² [\(Fig. 6\)](#page-4-0). As shown in [Fig. 6,](#page-4-0) 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 × 10¹³ [−]/cm² can proceed spontaneously at the temperature below 900 K.

3.4. Applications of $CO₂$ capture and separation

3.4.2. Separation performance of CO_2 from calcite surface in gas mixture S CO_2 Since C_2 and C_2 in a multi-gas co-existing of C_2 in a multi-gas co-existing C_3 environment, the CO₂ separation performance is another significant performance is another significant significa criterion. Flue gas (CO2/N2) is the most common exhaust gas which can $\begin{array}{ccc} \text{if} & 4,44 \text{ . T} \\ \text{CO}_2 & \text{f1} \end{array}$ CO_2 find flue gas for \overrightarrow{f} , \overrightarrow{F} and \overrightarrow{F} H_2 is considered as the most promising \mathbf{N} origination product (i) it is possible from \mathcal{H} , \mathcal{H} is policies and shall gas and sh $(\bullet \text{ CH}_4)$ and unconventional clean energy \bullet source have attracted much attracted much attracted much attracted much attracted much \mathbf{f} $r_{\text{46,47}}$. H₂ CO₂ is and r_{H_2} is and r_{H_2} is and r_{H_2} is an H_2 and H_2 and H_3 and H_4 [\[45,48\].](#page-7-5) Consequently, CO2 should be separated from H2 and CH4. I **i** i practical application, the optimal co₂ **c** 8.04×10^{13} 18.56 10^{13} -/² (F . 10). T
8.04 10^{13} -/² 8.04 10^{13} $^{-}/$ ² $\left(\begin{array}{ccc} \text{CO}_2 & \text{N} & \text{N} \end{array} \right)$ or CO_2 $\begin{array}{ccc} \n\text{(F} & 9) & \text{T} & 18.56 & 10^{13} & ^{-} / & ^{2} \\ \n\text{(C)} & 10^{13} & \text{(C)} & 10^{13} & \text{(C)} \n\end{array}$ call charge density at which low concentrations (one \mathcal{CO}_2 molecule)

Fig. 8. A
() T \leftarrow fi \leftarrow CO₂ \leftarrow + \leftarrow fi and $\begin{pmatrix} 0 & 0 \end{pmatrix}$ and $\begin{pmatrix} 0 & 0 \end{pmatrix}$ The initial addition configuration of $\begin{pmatrix} 0 & 0 \end{pmatrix}$ on $\begin{pmatrix} 0 & 0 \end{pmatrix}$ on $\begin{pmatrix} 0 & 0 \end{pmatrix}$ in $\begin{pmatrix} 0 & 0 \end{pmatrix}$ in $\begin{pmatrix} 0 & 0 \end{pmatrix}$ \uparrow calciter surface. (b) The most stability of five CO₂ on calcite surface \uparrow five CO₂ on calcite surface s with the critical charge density.

of CO2 would not leave the calcite surface ([Fig. 3\)](#page-2-0). To confirm the high $\begin{matrix} \text{CO}_2 & \text{O}_3 \\ \text{CH}_4 & \text{ff} \end{matrix}$ capture, the adsorption of $\begin{matrix} \text{CO}_2 & \text{O}_4 \end{matrix}$ CQ_2 , N_2 , H_2 CH_4 ff $\begin{array}{ccc} \n\text{C}\n\text{C}\n\text{C}\n\text{C}\n\text{C}\n\text{C}\n\text{C}\n\text{C}\n\text{C}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{D}\n\text{F}\n\text{D}\n\text{F}\n\text{D}\n\text{F}\n\text{D}\n\text{F}\n\text{D}\n\text{F}\n\text{D}\n\text{F}\n\text{D}\n\text{F}\n\text{D}\n\text{F}\n\$ $_{1}N_{2}$ $_{1}H_{2}$ and $_{1}N_{2}$ and $_{1}N_{2}$ are shown in Fig. S2. A \overrightarrow{F} in [Fig. 10,](#page-6-17) Fig. S3 and Fig. S3 and H₂ CH₄ physisorbed on calcite surface. Once the charge densities are respectively. Once the charge densities are respectively. **t** 8.66 10^{13} 10.50 10^{13} $\frac{10^{13}}{2}$ 10^{13} -/ 2 , H₂ CH₄ keep away from the charged calcite surface surface surface surface so that the adsorption end of \mathcal{A} $\begin{array}{ccccc}\n\downarrow & & & \downarrow & & \downarrow & \downarrow & \downarrow & \downarrow \\
N_2 & & \downarrow & & \downarrow & & \downarrow & \downarrow & \end{array}$ N_2 on calcite surface increases surface increases surface increases surface increases surface increases surface in

 -1.2 $-1CO₂$ \degree ₂CO₂-a $\frac{1}{2}$ dsorption energy (eV)
 $\frac{1}{2}$ = $\frac{1}{2}$ = $\frac{1}{2}$ = $\frac{1}{2}$ $-2CO₂-b$ $3CO₂$ $4CQ$ **Chemisorption region** -0.6 -0.4 Physisorption

Fig. 9. The number and the average adsorption energies of CO_2 and CO_2 ifferentially different differential energies of CO_2 and H charge densities. " \mathbf{f} and \mathbf{f} represent added \mathbf{f} figurations configuration configurations of \mathbf{f} $(F.7a$ and 7b), $\qquad \qquad \downarrow$.

Table 1				
C	CO ₂			
$\boldsymbol{\mathsf{A}}$		C 2 $\overline{}$	$(10^{13}$ $^{-2}$	$(10^{14}$
G $\, {\bf B}$ $N-$ 22	18 19	61.70 52.50 40.90	7.39 6.73 2.45	
C_3N 20 Calcite (this study)		22.00 8.04	2.13 4.95	
\cdot I	$(F.S3)$. H CO ₂	H , ,	N_2 , H_2 ₁ N_2 , H_2	CH_4 , CO_2 $CH4$.

4. Conclusions

 I , DFT

CRediT authorship contribution statement

Lin Tao: Conceptualization, Methodology, Formal and Terms in Writing and Methodology, Writing and Methodology, W \overrightarrow{A} Junchen Huang: F_c \overrightarrow{A} , W \overrightarrow{B} edition Davoud Dastan: Formal and $W = \begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$ and $W = \begin{bmatrix} 0 & 1 \\ 0 & 1 \end{bmatrix}$ Tianyu Wang: W_c · Resources, Wang Li: Resources, 2014 V \overrightarrow{V} . X_itao Yin: C \overrightarrow{S} , R . 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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