C S D

A S S

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CO_2 -

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A R T I C L E I N F O

Keywords:
CO_2
C
C -
D
A

A B S T R A C T

I , - . T . A 18.56 10^{13} , $^{-}/\ ^{2}$, CO_2 -6.23 V. M , CO_2 / CO_2 , 900 K. I , (4.95 10^{14} $^{-2}$) (8.04 10^{13} $^{-}/\ ^{2}$) - - . I , CO_2 N_2, H_2 CH_4. I , CO_2 8.04 10^{13} 18.56 10^{13} $^{-}/\ ^{2}$. T CO_2 - - .

1. Introduction

T J CO_2, CO_2 fi fi 1,2 . M ,

jV / ,
(5.8 V 17) . S -
, ff - ,
, 18 19 , C_3N 20 , M –N–C
(M = F , C , C) 21 , N- -
22 23 , - -
DFT CO_2 -
. H , - , ,
CO_2 .
T , - ff
CO_2 - . T
24–26 . B , -
13 .
E , , DFT -
CO_2 . F ,
CO_2 fi . T , ,
, CO_2- fi .
M , -
I , , DFT -
CO_2 . F ,
CO_2 fi . T ,
, CO_2- CO_2 . F , CO_2
CO_2 N_2, H_2 CH_4
, CO_2 . T -
, fi CO_2 .

2. Methods

B (DFT), D 3 28
(CO_2, N_2, H_2 CH_4) (1 0 4) (1 0 4)
29,30 . T -
(GGA) P –B -
–E (PBE) 31,32
(DNP) . I -
, - DFT (DFT-D)
G W 33 .
G
- , -
B . 34
. T -
, - ff 4.9
B 3 2 1 -
M -P . B ,
1 10^{-5} H , 0.002 H /
0.005 , . F , M
35
.

3. Results and discussion

3.1. Stability of calcite surface with charge-modulated

F , F . 1**a**

(1 0 4) ,
29,36,37 . A , 20 .
I , - CO_2
. R , S . 16 fi -
BN CO_2 jV
. A BN
5.8 V 17 , BN
10^{13} $^{-2}$ -
, , ,
, 16 . F ,
BN ,
25 . W . 24
. T , -
.
T jV

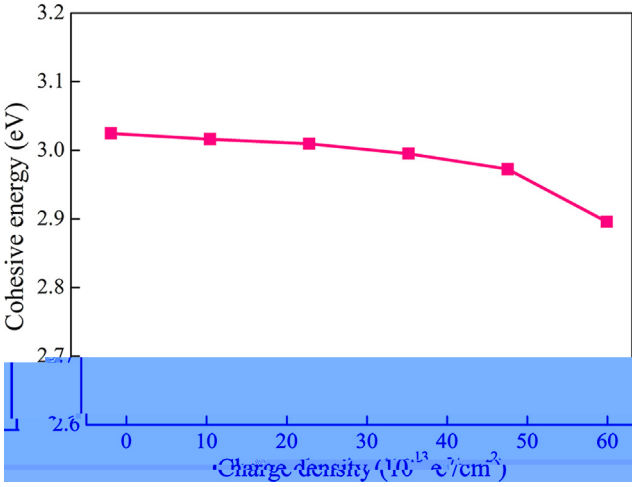

Fig. 2. T .

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

I , fi fi
CO_2
.
N , CO_2
. F , ff
CO_2.
W , ,
19,20,22,39 . C ,
fi -
CO_2
. B
, fi fi -
CO_2 . CO_2
25,29,37,40 , fi CO_2
F . 1**b**. W
0 18.56 10^{13} $^{-}$/ ^{2},
2.69 2.49 (F . 3). I CO_2
. H , CO_2

18.56 10^{13} $^{-}$/ ^{2} (F . S1). T ,
18.56 10^{13} $^{-}$/ ^{2} (1.5 $^{-}$ V)
CO_2 .
F , fi
41 . A F . 3,
CO_2 . T
fi

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

E_{ads} (V), E_{total}
(V), $E_{calcite}$
(V), E_{gas}
(V).
C , -
. I ,
0.52 V 42,43 . F
($\rho = 0$ F . 3), CO_2 −0.38 V.
M CO_2
. T , CO_2
. I , -
,
−6.23 V . T
CO_2 18.56 10^{13} $^{-}$/ ^{2} 16
. M
CO_2 0.61 $^{-}$.
A , CO_2 -
.
D C=O fi 4 ,
ff CO_2. W
CO_2 C=O
F . 3. A F . 3,
CO_2 C=O -
. I
fi
V . F , -
CO_2
CO_2
. T , CO_2

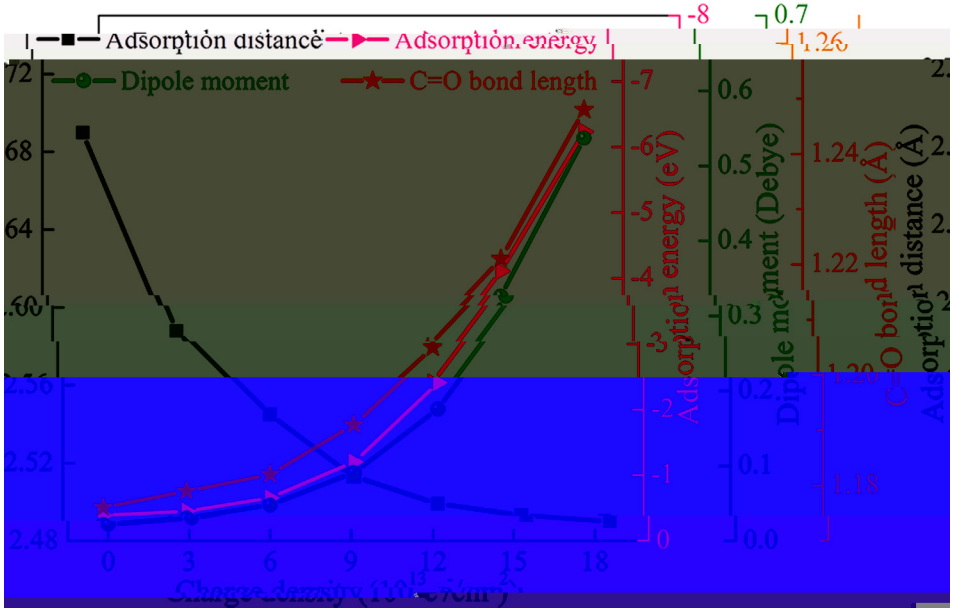

Fig. 3. A , , CO_2 C=O .

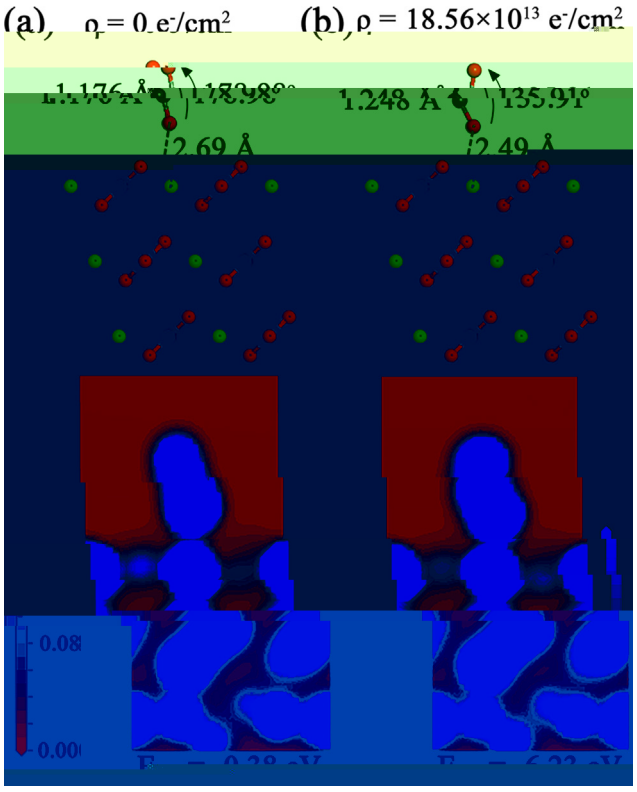

Fig. 4. A CO_2 ( ) ( ) . T , 0 0.16.

J fi CO_2 .

3.3. Adsorption mechanism of a single CO_2 on calcite surface at critical charge density

I , . W fi CO_2- . T , CO_2 . F , CO_2

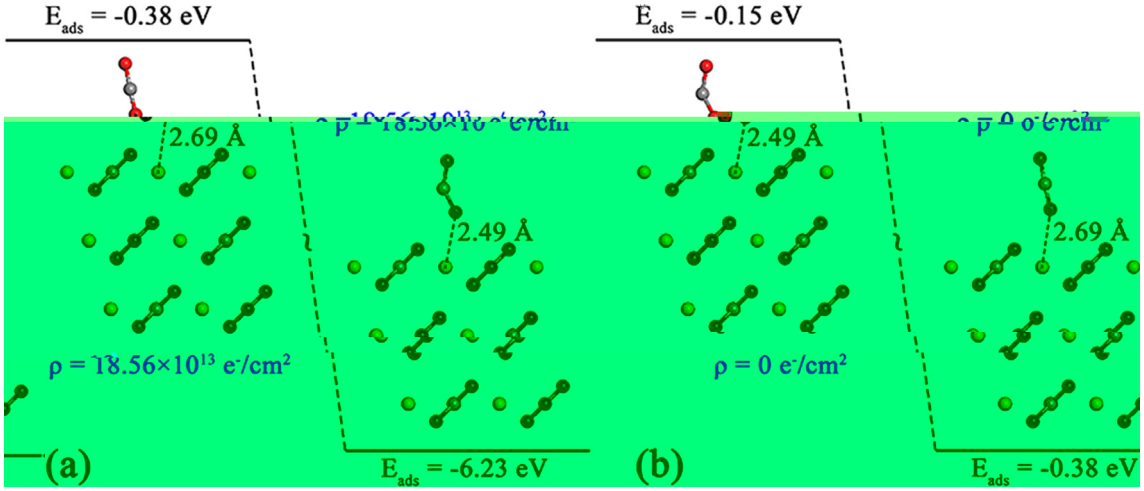

Fig. 5. K CO_2 J . ( ) D CO_2 . ( ) A CO_2 .

. .

3.3.1. Detailed structure and electron density distribution of CO_2-calcite interface

F . 4 CO_2 (18.56 10^{13} $^{-}$/ ^{2}) . O (F . 4**a**), CO_2 (O–C–O 178.98 ; C═O 1.176), . T O CO_2 2.69 , CO_2 CO_2 (O–C–O 180 ; C═O 1.176) 20 . F , CO_2 - (F . 4**a**). T fi CO_2 . H , (18.56 10^{13} $^{-}$/ ^{2}) (F . 4**b**), CO_2 .C fi CO_2 , O - 2.69 2.49 ; O–C–O 178.98 135.91 ; C = O 1.176 1.248 . B , - CO_2 (F . 4**b**), CO_2 . S CO_2 L 16 , CO_2 , - CO_2 . T , CO_2 .

3.3.2. Reversibility of CO_2 adsorption and desorption

S CO_2 fi , CO_2 - J (F . 5). F . 5**a** fi CO_2 . A , CO_2 fi 18.56 10^{13} $^{-}$/ ^{2} . I CO_2 fi , 5.85 V . F , F . 5**b** fi CO_2

fi CO_2 . O , 18.56 10^{13} $^{-}$/ ^{2} , CO_2 fi . F , 0.23 V . H , CO_2 / V / .

3.3.3. Spontaneity of CO_2 adsorbed on calcite surface with critical charge density

E fi CO_2 ff . F , G . H , fi

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

S, S_{trans}, S_{rot}, S_{vib} , (/ /K), ; T ,

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

H, H_{trans}, H_{rot}, H_{vib} , (/), ; R T (8.314 J/ /K) (K), ; F , G fi

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

G E(0K) G (/) (/), . T S M . C , (ΔS, / /K), (ΔH, /), G (ΔG, /) (K) ff CO_2 18.56 10^{13} $^{-}$/ ^{2} (F . 6). A F . 6, ΔS ΔH, ΔG . T ΔG , ΔG 900 K. I CO_2 18.56 10^{13} $^{-}$/ ^{2} 900 K.

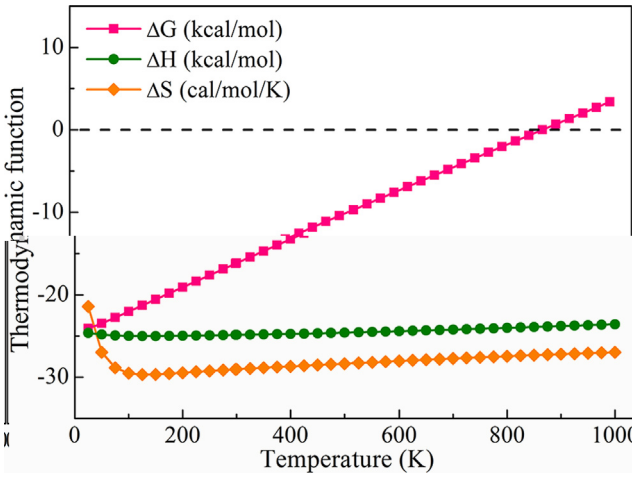

Fig. 6. T CO_2 .

3.4. Applications of CO_2 capture and separation

3.4.1. CO_2 capture capacity of calcite surface at minimum charge density

F - CO_2- , CO_2 fi . B CO_2 - , fi , CO_2 . A F . 7, 4 CO_2 . N , ff fi (2CO_2- 2CO_2-) CO_2 - (F . 7**a and 7b**). B , fi CO_2 , . F , fi CO_2 18.56 10^{13} $^{-}$/ ^{2} (F . 8**a**). A F . 8**b** , fi ff , fi CO_2 . I CO_2 , . T CO_2 , CO_2 ff (F . 9). A , CO_2 . A , ff fi (2CO_2- 2CO_2-) CO_2 . W , CO_2 , . I CO_2 . G , - 0.52 V 42,43 . A F . 9 , 8.04 10^{13} $^{-}$/ ^{2}, CO_2 - . T , fi CO_2 CO_2 . I , CO_2 CO_2 (CO_2) (80.838 ^{2}), , CO_2 4.95 10^{14} $^{-2}$ 8.04 10^{13} $^{-}$/ ^{2}. C - (T 1), CO_2 (8.04 10^{13} $^{-}$/ ^{2}), ffi . I , . T CO_2 .

3.4.2. Separation performance of CO_2 from calcite surface in gas mixture

S CO_2- - - , CO_2 fi . F (CO_2/N_2) ff 4,44 . T , fi CO_2 fl . F , H_2 ( ) - 45 . N (CH_4) ffi , 46,47 . H , CO_2 H_2 CH_4 45,48 . C , CO_2 H_2 CH_4. I , CO_2 8.04 10^{13} 18.56 10^{13} $^{-}$/ ^{2} (F . 10). T 8.04 10^{13} $^{-}$/ ^{2} (CO_2) CO_2 - (F . 9). T , 18.56 10^{13} $^{-}$/ ^{2} (CO_2)

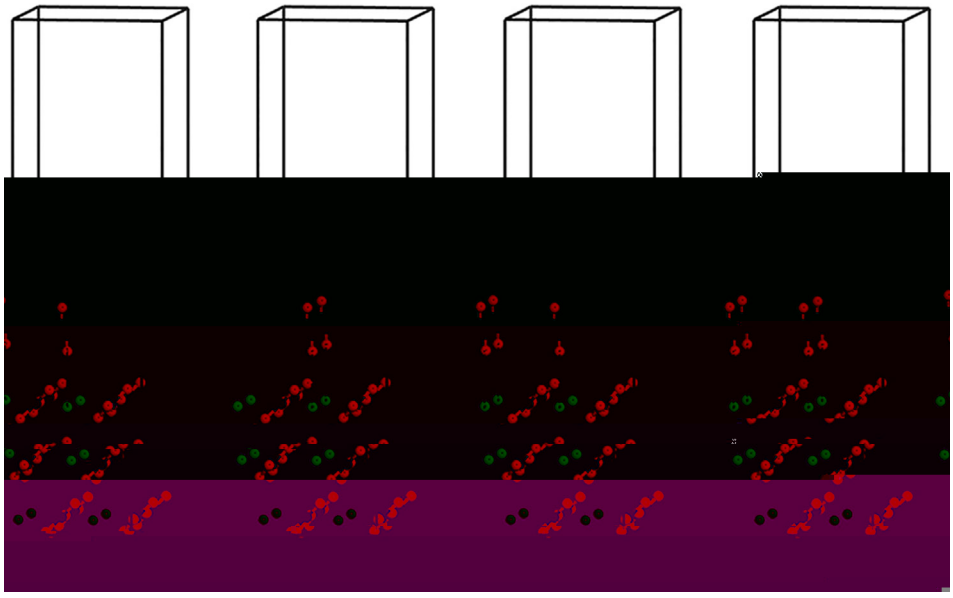

Fig. 7. T fi CO_2 .

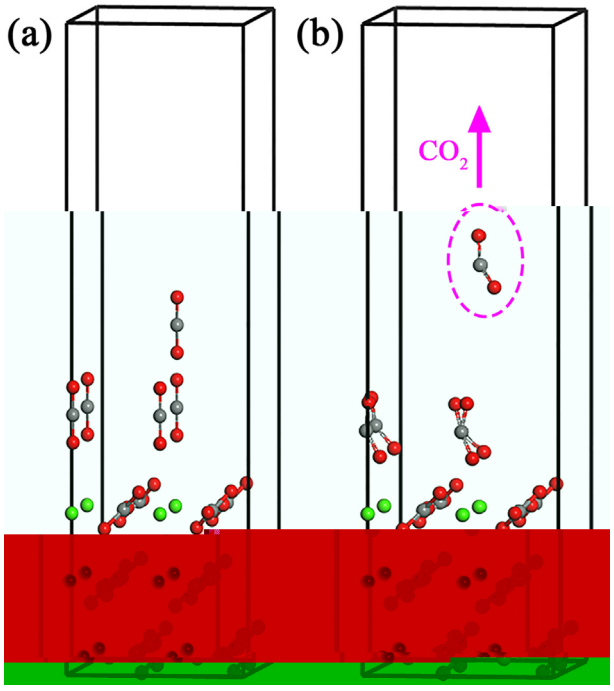

Fig. 8. A fi CO_2 . ( ) T fi fi CO_2 . ( ) T fi fi CO_2 .

CO_2 (F . 3). T fi CO_2 , CO_2, N_2, H_2 CH_4 ff (F . 10), fi - N_2, H_2 CH_4 F . S2. A F . 10, F . S3 F . S3 , H_2 CH_4 . O - 8.66 10^{13} 10.50 10^{13} $^{-}$/ ^{2}, H_2 CH_4 - D ^{3} 19 . B , - N_2

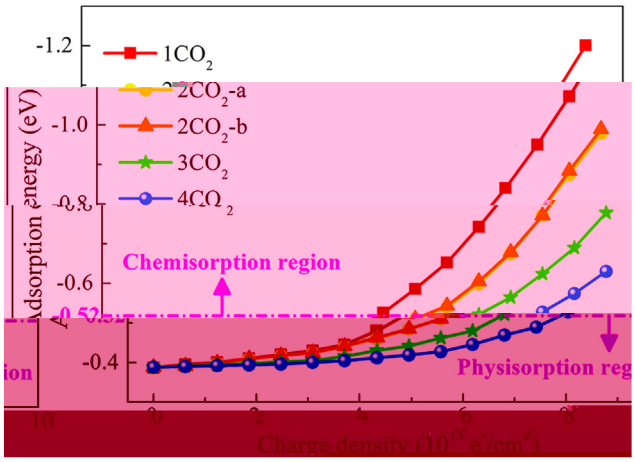

Fig. 9. T CO_2 ff . " " " " ff fi (F . 7**a and 7b**), .

Table 1
C CO_2- .

A	C (10^{13} $^{-}$/ ^{2})	(10^{14} $^{-2}$)
G 18	61.70	7.39
B 19	52.50	6.73
N- - 22	40.90	2.45
C_3N 20	22.00	2.13
Calcite (this study)	**8.04**	**4.95**

, - (F . S3). H , N_2, H_2 CH_4, CO_2 . I CO_2 N_2, H_2 CH_4.

4. Conclusions

I , DFT

CO_2 . T - . T - ff . I , CO_2 18.56 10^{13} $^{-}$/ ^{2}, −6.23 V. T CO_2 L , CO_2 . U , - CO_2 / , CO_2 - 900 K. C - CO_2 , CO_2 4.95 10^{14} $^{-2}$ 8.04 10^{13} $^{-}$/ ^{2}. M , CO_2 N_2, H_2 CH_4. T , fi CO_2 , (CO_2/H_2) , ( ) (CO_2/CH_4), (CO_2/N_2) . T CO_2 fi 8.04 10^{13} 18.56 10^{13} $^{-}$/ ^{2}.

CRediT authorship contribution statement

Lin Tao: C , M , F , W - . **Junchen Huang:** F , W - & . **Davoud Dastan:** F , W - & . **Tianyu Wang:** W - & . **Jing Li:** R , V . **Xitao Yin:** C , S , R . **Qi Wang:** M , W - & , S , R .

Declaration of Competing Interest

T fi fl - .

Acknowledgements

T N N S F C (G N . 51634004, 51874169 51974157) -

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