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PAPER

Evolution of calcite surface reconstruction and interface adsorption of calcite-CO_2 with temperature

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Keywords: MD , , , CO_2 ,

Abstract

M (MD) (1 0 4) CO_2 .I . fl 673 K. M .A , CO_2 .I , CO_2 C .A CO_2 .

1. Introduction

C . (1 0 4) [1–5]. C O [6], fl [7, 8], [4], (EO) [9], CO_2 [10–12] [13–15]. CO_2 , , . . fi [16–18]. E [14, 19]. *et al* [15] CO_2 , [13]. C fi - (G-D C) [20, 21], , fl .H , fi *in situ* .M [22]. I , MD [17, 23]. (DF) [24, 25]. CO_2 , MD *et al* [26]. *et al* [27] CO_2 , MD , .

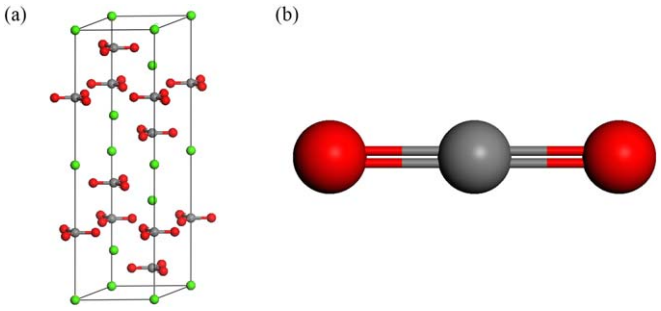

Figure 1. fi ( ) ( ) CO_2 . . C ( ), C ( ) O ( ).

et al [28]
fi
CO_2 $(1\bar{1}0)$. , fi
- .I MD
CO_2 , CO_2 (1 0 4)
, CO_2
.
I , CO_2
MD 298 K 873 K.
CO_2 .
- .

2. Computational details

C
$R\bar{3}c$. fi 1( ). I fi ,
D [3] [29, 30] CA E [31, 32] CO_2
, .
(GGA) [33] (91) [34] -
(= = 0.5048 , = 1.7199),
(= = 0.5053 , = 1.7326 [35]). A CO_2
($L_{(CO2)}$ = 0.1175)
($L_{(CO2)}$ = 0.1163 [36]). CO_2 fi fi 1( ).
I fi (1 0 4) ,
, , $2 \times 2 \times 1, 3 \times 3 \times 1, 4 \times 4 \times 1, 5 \times 5 \times 1, 6 \times 6 \times 1,$
$7 \times 7 \times 1, 8 \times 8 \times 1$ $9 \times 9 \times 1,$ .I $1, 5 \times 5 \times 1$
. fi (1 0 4)
4.1155 × 2.5148 × 0.7769 . F ,
. (1 0 4)
fi 2.
F MD , F [37]
- (COM A) [38] fi
. - E
- , . L -J 9–6
, .
[26, 28, 39]. CO_2
- 350 CO_2
A C C .I (1 0 4) .
fi CO_2 0.45
fi 3.
CO_2 ,
.D , (1 0 4)
.
. fi [28]. fi

Table 1. (10^3 /).

	E (×)							
	2 × 2	3 × 3	4 × 4	5 × 5	6 × 6	7 × 7	8 × 8	9 × 9
E	−1.464 ± 0.012	−1.447 ± 0.017	−1.451 ± 0.010	−1.445 ± 0.009	−1.445 ± 0.013	−1.447 ± 0.011	−1.445 ± 0.015	−1.446 ± 0.010

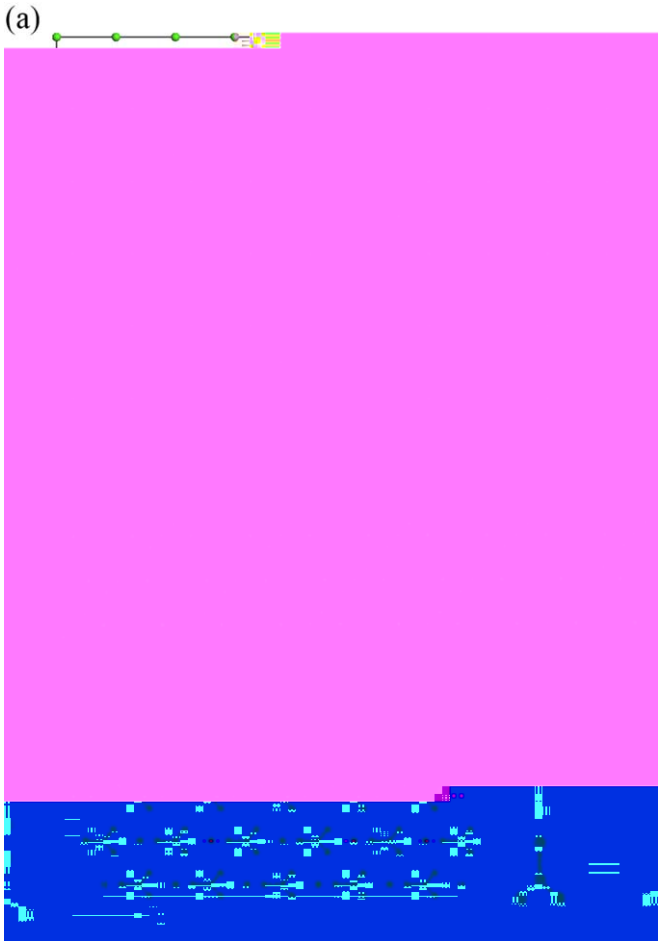

Figure 2. (1 0 4) 5 × 5 × 3 .( ) . ( ).( )A O .( )A O .N 6.5 O .

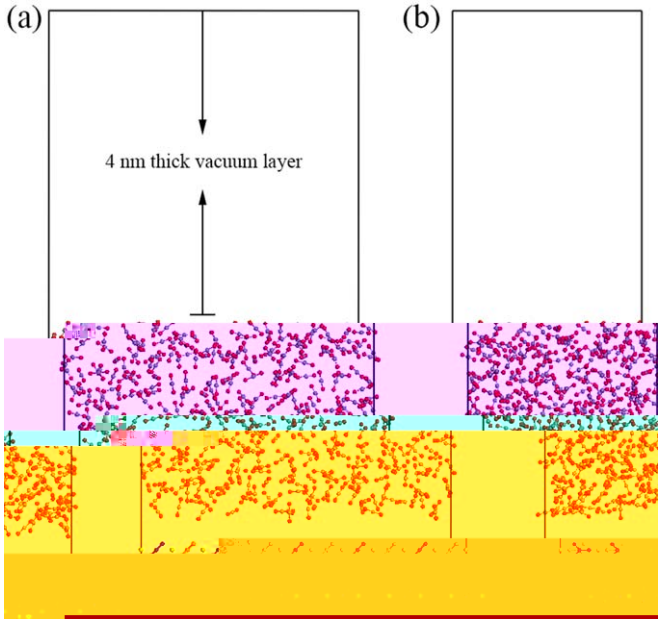

Figure 3. fi CO_2 .( )A O .( ) A O .

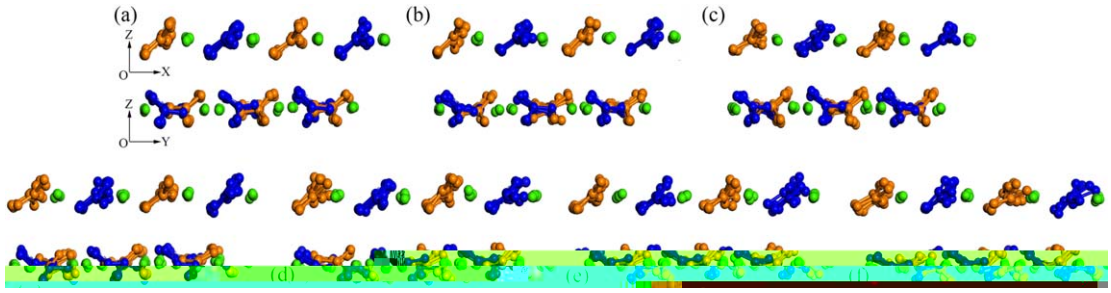

Figure 4. (1 0 4) O O . ( ) 298 K, ( ) 373 K, ( ) 473 K, ( ) 573 K, ( ) 673 K, ( ) 773 K, ( ) 873 K.

, fi [40]. I CO_2 , 4 CO_2 . F , 6.5 fi . fi 2. - , fi [41, 42]. A , (N) N [43]. B . 1 2 , . fi 1 1 MD .I ( ) , , , 298 K, 373 K, 473 K, 573 K, 673 K, 773 K, 873 K, .

3. Results and discussion

3.1. Pure surface reconstruction

F 4 fi fi .C fi 2, , fi 4. O , .B , O , C . F , (1 0 4) . fl .A .A MD , fi , fi 5. [6, 16, 17] [18, 44]. H , . , fi . .F , R_C^B $R_{OO'}^B$ C OO' , . , R_C^Y $R_{OO'}^Y$ C OO' , . , $\angle_{O-C-O}^B$ $\angle_{O-C-O}^Y$ O–C–O O , . F , D_{Ca-O}^B D_{Ca-O}^Y fi C O . F , $\angle CO_3^{2-}$ (1 0 4) . F , $\Delta_{surface}$ (1 0 4) . 100 1 2 . 2. 2 . N , (298 K), R_C^B R_C^Y (R_C 0°). fi *et al* [16] , 17° . A ,

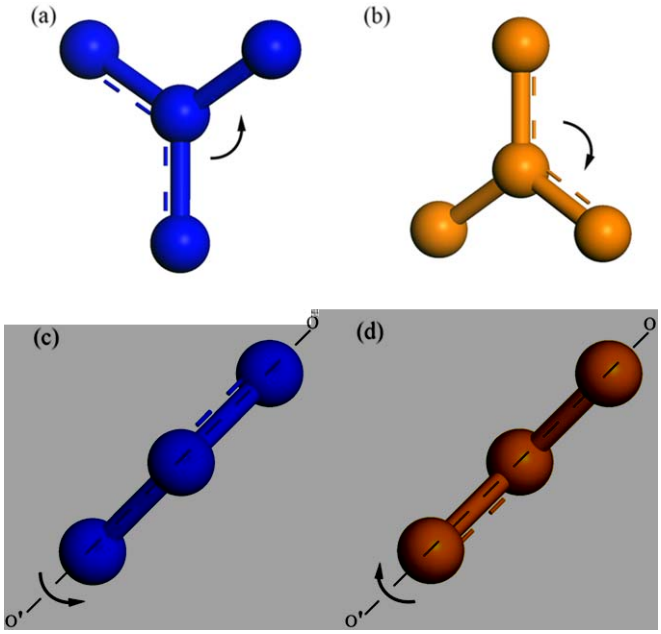

Figure 5. .( ) ( )
.( ) ( ) OO′ .

Table 2. E .

	(°)				O–C–O (°)		D ( )		(°)	D ( )
(K)	R_C^B	R_C^Y	$R_{OO'}^B$	$R_{OO'}^Y$	$\angle_{O-C-O}^B$	$\angle_{O-C-O}^Y$	D_{Ca-O}^B	D_{Ca-O}^Y	$\angle CO_3^{2-}$	$\Delta_{surface}$
298	18.5	19.4	14.2	14.7	122.7	122.8	0.194	0.194	39.4	0.0669
373	19.3	19.1	15.1	14.3	123.0	122.9	0.194	0.195	39.3	0.0727
473	20.0	20.8	15.3	15.4	123.0	122.9	0.196	0.196	39.0	0.0721
573	22.6	21.1	16.6	16.1	123.3	123.0	0.197	0.196	38.9	0.0736
673	24.2	24.0	18.1	18.3	123.5	123.5	0.198	0.198	38.4	0.0715
773	24.3	24.7	18.6	18.7	123.6	123.5	0.198	0.198	38.3	0.0748
873	24.7	24.5	18.5	18.4	123.5	123.6	0.198	0.199	38.4	0.0771

OO′ fi 5. I $R_{OO'}^B$ $R_{OO'}^Y$
. B , $\angle_{O-C-O}^B$ $\angle_{O-C-O}^Y$
[16] O–C–O O
3° . O–
C–O , C–O [1, 17] [45].
,
(298 K). .I (1 0 4)
fl fl .
G *et al* [46] M , (1
0 4) .
, .N ,
J - [47, 48],
[1].
C (D_{Ca-O} 0.231 [49]), C O
,
C O .I ,
$(C CO_3)_2$ [50] $C CO_3$ [51] . ,
$C CO_3$
- [22].

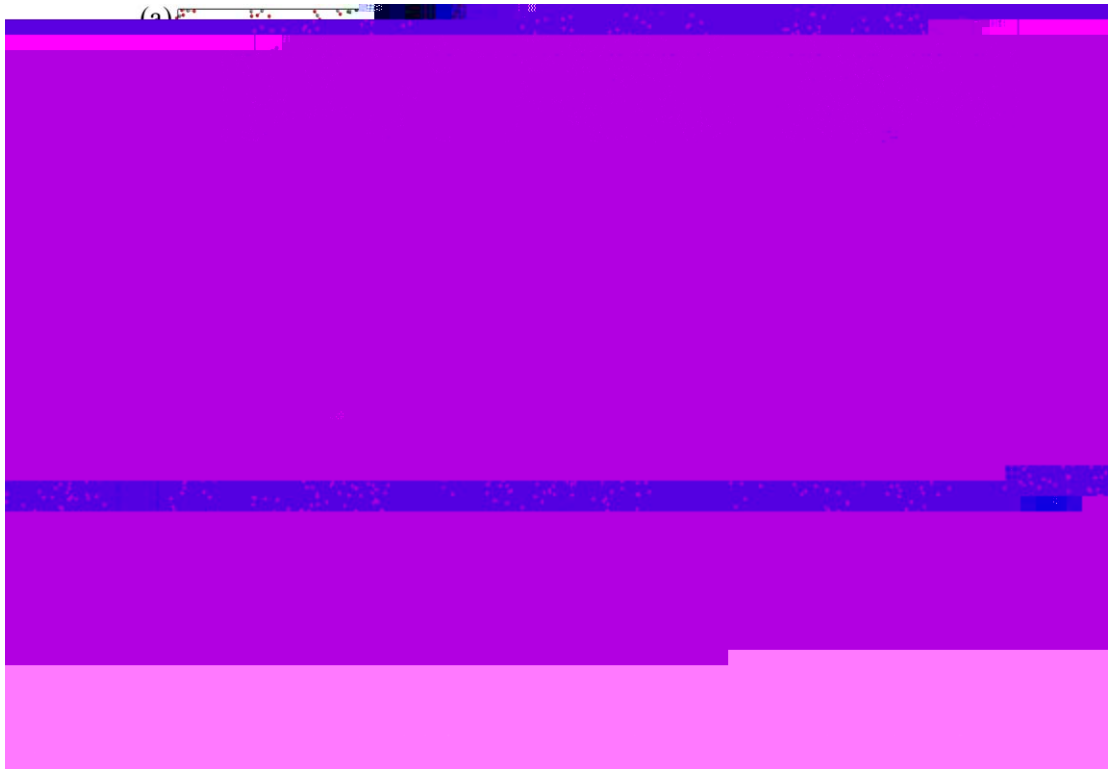

Figure 6. CO_2 O . ( ) 298 K, ( ) 373 K, ( ) 473 K, ( ) 573 K, ( ) 673 K, ( ) 773 K, ( ) 873 K.

Table 3. E CO_2 .

	(°)				O–C–O (°)		D ( )		(°) D ( )	
(K)	R_C^B	R_C^Y	$R_{OO'}^B$	$R_{OO'}^Y$	$\angle_{O-C-O}^B$	$\angle_{O-C-O}^Y$	D_{Ca-O}^B	D_{Ca-O}^Y	$\angle CO_3^{2-}$	$\Delta_{surface}$
298	18.5	19.4	14.4	14.7	122.6	122.7	0.193	0.194	39.6	0.0670
373	19.4	19.2	15.1	14.3	123.0	122.9	0.194	0.196	38.7	0.0722
473	20.1	20.9	15.4	15.4	123.1	123.0	0.196	0.196	39.0	0.0734
573	22.6	21.4	16.6	16.1	123.3	123.0	0.197	0.197	38.9	0.0740
673	24.1	23.8	18.0	17.9	123.5	123.4	0.198	0.197	38.1	0.0720
773	24.3	24.4	18.2	18.1	123.6	123.5	0.198	0.198	37.8	0.0748
873	24.5	24.6	18.3	18.4	123.5	123.6	0.197	0.198	37.9	0.0769

A MD , , O–C–O , 673 . I fl . I . O , .

3.2. CO_2 adsorption behavior

CO_2 , fi fi fi 6( )–( ). B CO_2 , CO_2 fi . , 3. C 2, . I CO_2 . I , (E_{Pure}) (E_{Ads}) 4. I . , , CO_2 .

Table 4. . (10^3 /).

	(K)						
	298	373	473	573	673	773	873
E_{Pure}	−109 451 ± 75	−109 411 ± 81	−109 313 ± 84	−109 237 ± 78	−109 199 ± 85	−109 101 ± 92	−109 005 ± 95
E_{Ads}	−109 442 ± 72	−109 424 ± 77	−109 309 ± 80	−109 228 ± 79	−109 203 ± 88	−109 086 ± 97	−108 997 ± 94

800

fl CO_2 ,

A fi 6, CO_2

[2

C CO_2

. A

$+ E_{Gas} - E_{Tot}$

E_{Tot}, E_{Sur} ,

A fi 7 , , CO_2

,

,

CO_2 . F (873 K

, fi

. I fi

C

ion

I

۷۳

. O ۷۳

,

۷۳ ,

CO_2

O_2

. CO_2 C

I CO_2

CO_2

Notes

ii

Acknowledgments

fi N N F C (G N .51634004 G N .51874169).

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