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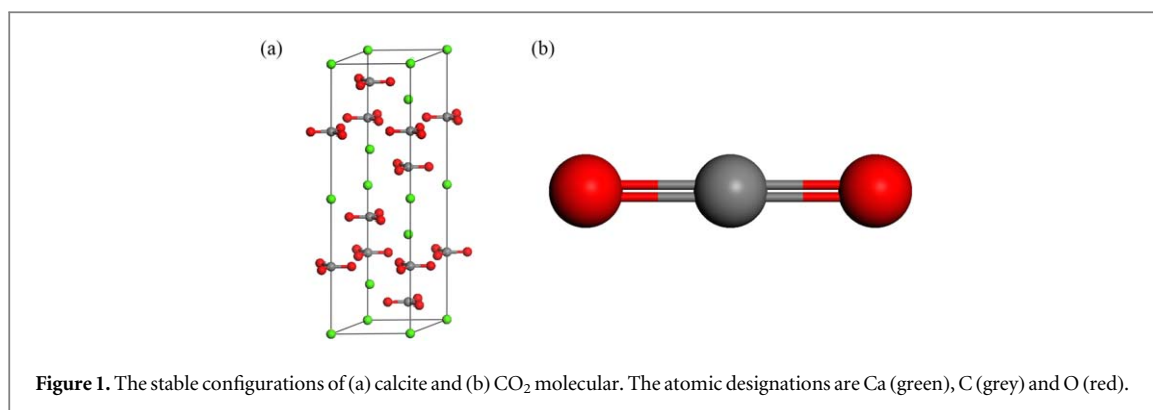
Evolution of calcite surface reconstruction and interface adsorption of calcite-CO₂ with temperatureRECEIVED
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21 November 2018Lin Tao^{1,2}, Zhi Li^{1,2}, Guo-Cheng Wang^{1,2}, Bao-Yu Cui³, Xi-Tao Yin^{1,2,4} and Qi Wang^{1,2,4}¹ The Key Laboratory of Chemical Metallurgy Engineering of Liaoning Province, University of Science and Technology Liaoning, Anshan, Liaoning Province, 114051, People's Republic of China² School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan, Liaoning Province, 114051, People's Republic of China³ School of Resources and Civil Engineering, Northeastern University, Shenyang, Liaoning Province, 110819, People's Republic of China⁴ Authors to whom any correspondence should be addressed.E-mail: yxtaj@163.com and wangqi8822@sina.comKeywords: MD simulation, calcite surface, carbonate groups, CO₂ molecules, adsorption energy**Abstract**

Molecular dynamics (MD) simulation was performed to research the effect of the various temperatures on the calcite (1 0 4) surface reconstruction and the interface adsorption behavior of CO₂ molecules. It is found that the carbonate groups on the surface have opposite rotation directions and the parameters of surface structure are positively related to the temperature. The evolution of surface reconstruction is almost unchanged after the inflection point 673 K. Meanwhile calcite clusters structure should be formed at the crystal surface. According to the surface structure parameters and adsorption energy, the effect of CO₂ molecules on surface structure is eliminated. In addition, CO₂ molecules are adsorbed perpendicularly at the point of Ca ions by electrostatic interaction. And desorption of CO₂ molecules is positively correlated with temperature.

1. Introduction

Calcite is one of the most abundant and widely distributed minerals in nature which is actively involved in variety of industrial processes. The (1 0 4) cleave surface is the most stable thermodynamically crystallographic face of calcite crystal [1–5]. Ca and O in the calcite crystalline structure give the compound some surface properties [6], which make it a star in the development of flotation agents [7, 8], water treatment [4], enhanced oil recovery (EOR) [9], CO₂ capture [10–12] and mechanism of solid thermal decomposition [13–15]. Therefore, it is necessary to understand the surface structure and the interface adsorption behavior of CO₂ molecules on calcite surface at various temperatures, which allows us to deeply explore the above processes.

The surface structure of calcite will be reconstructed with temperature before thermal decomposition. The reconstruction is largely confined to the top layer of the calcite surface [16–18]. Experiments also demonstrate that calcite decomposition only begins from the surface active sites [14, 19]. Shannon *et al* [15] stated that the activated complex is formed on the calcite surface before the CO₂ is lost, which is agreement with observations of forming metastable calcite structure on calcite surface layer [13]. Calcite surface structural changes before thermal decomposition which was also confirmed by the thermogravimetric-differential scanning calorimetry (TG-DSC) [20, 21], namely, heat flow occurs before weight loss. However, experimental method is difficultly to *in situ* show the evolution of the surface structure reconstruction with temperature. Molecular events are analyzed in detail in a way that is currently unfeasible experimentally [22]. In recent years, MD simulation has become an effective method to explore carbonate minerals surface in the microscopic level [17, 23]. The density functional theory (DFT) is extremely time consuming to be used in large adsorption systems due to its own limitations [24, 25]. CO₂ molecules have a much higher ability than methane to be adsorbed onto calcite surface in calcite slit nanopores, which was demonstrated in MD simulation by Sun *et al* [26]. Santos *et al* [27] concluded that there is a strong polar interaction than methane between CO₂ molecules and calcite surface, which dominate adsorption according to MD simulation, especially at low temperatures. Surface reactivity of calcite is



a key factor in the chemical control of mechanism of reaction in a variety of industrial processes. Wang *et al* [28] found that the calcite surface would be compressed and bond lengths as well as angles have significantly changed due to the adsorption of CO₂ molecules on the (1 $\bar{1}$ 0) surface. Therefore, we must first have an accurate description of the atomic-scale structure of the surface itself. In comparison with the extensive MD simulation investigations about the adsorption of CO₂ molecules, not only is the effect of CO₂ molecules on calcite (1 0 4) surface structure ignored, but also the interface adsorption behaviors of CO₂ molecules at wide temperature range are unclear.

In this study, the calcite surface reconstruction and the interface between calcite and CO₂ molecules are investigated by MD simulation at range from 298 K to 873 K. The surface structure reconstruction parameters and adsorption energy are calculated to elucidate the effect of CO₂ molecules on surface structure. This study provides a new insight into surface reconstruction and gas-solid interface at various temperatures.

2. Computational details

Calcite possesses a rhombohedral crystal structure and belongs to hexagonal crystal system with the space group $R\bar{3}c$. The unit cell of calcite is shown in figure 1(a). In order to make the simulation configurations accurate, the Dmol³ module [29, 30] and CASTEP module [31, 32] were employed to optimize CO₂ molecular and calcite crystal cell, respectively. The calculations for both two modules were performed using the generalized gradient approximation (GGA) [33] with the Perdew-Wang (PW91) [34] to treat the exchange-correlation effects. The calculated parameters of calcite crystal ($a = b = 0.5048$ nm, $c = 1.7199$ nm), which are highly consistent with calculation value ($a = b = 0.5053$ nm, $c = 1.7326$ nm [35]). And the calculated bond lengths of CO₂ molecular ($L_{(CO_2)} = 0.1175$ nm) is compared which is wonderful agreement with experimental value ($L_{(CO_2)} = 0.1163$ nm [36]). The CO₂ molecular configuration is shown in figure 1(b).

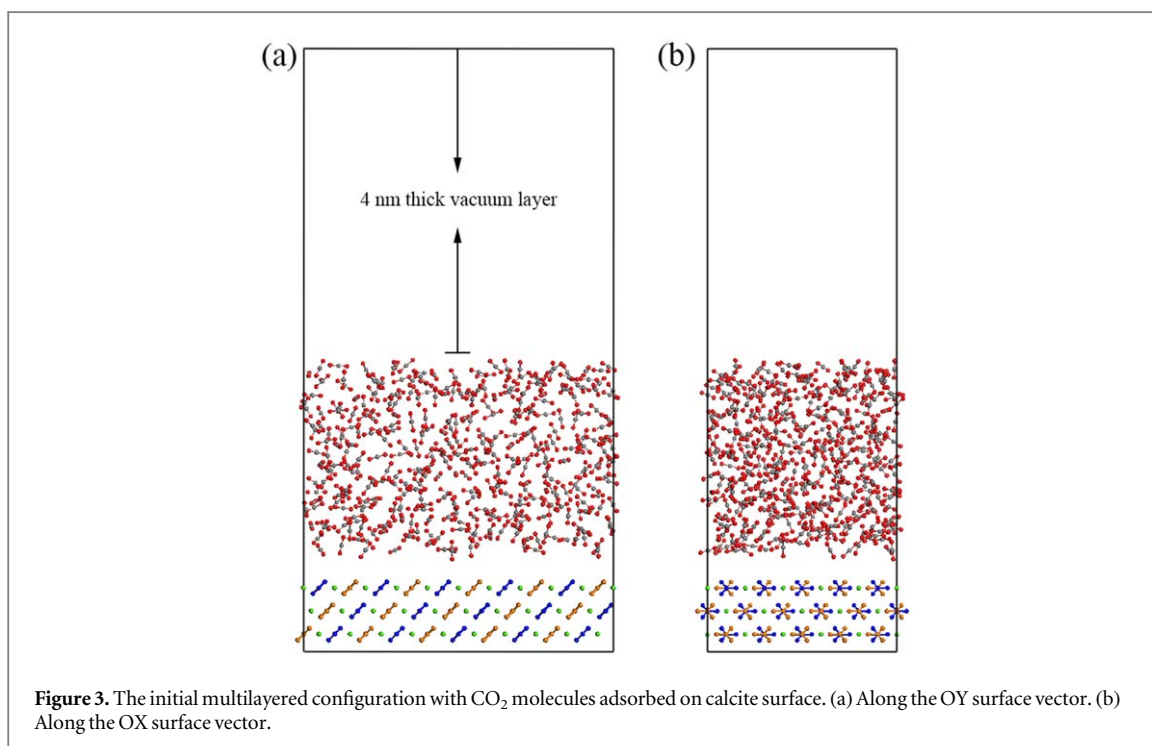
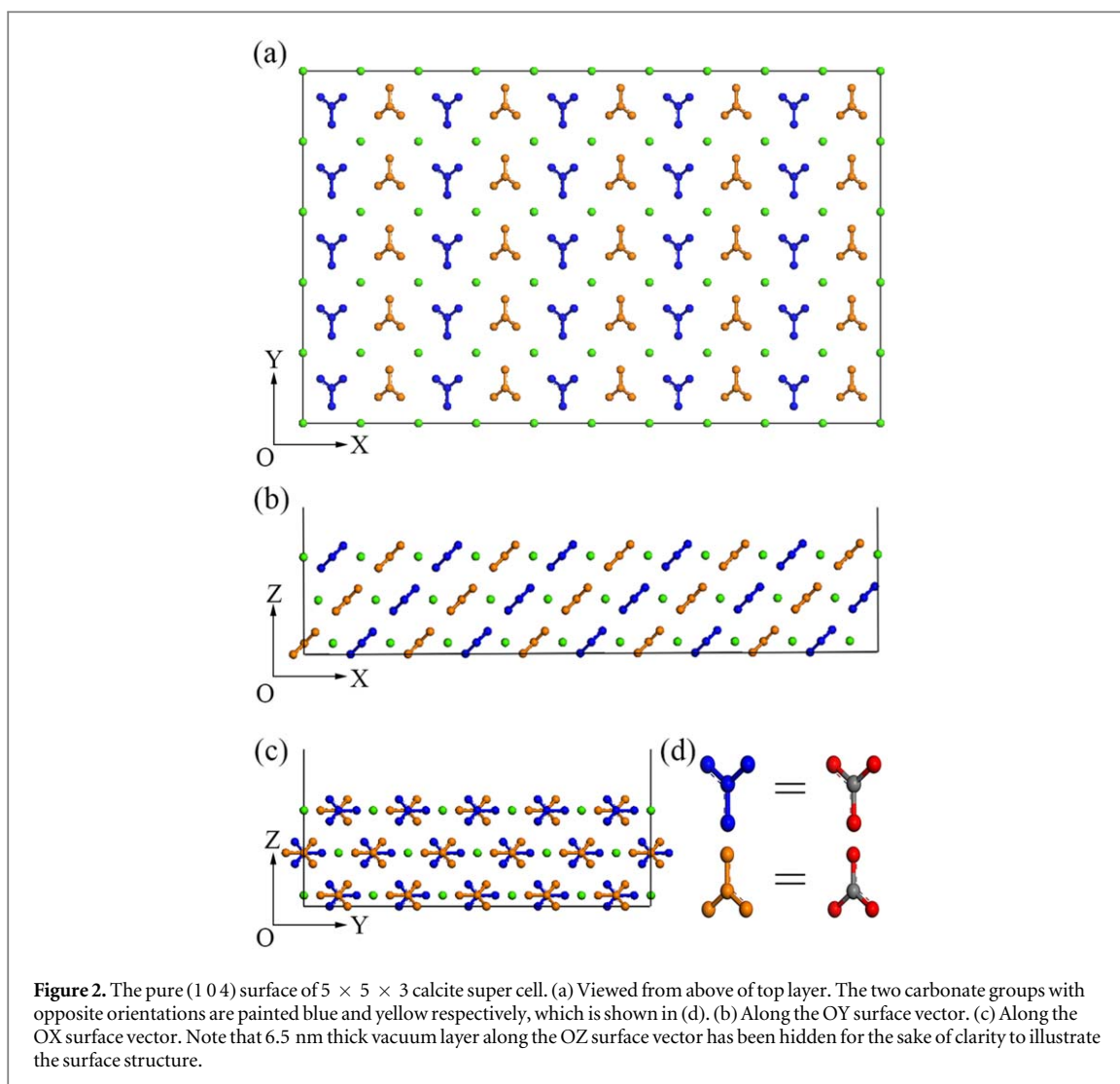
In order to attain the minimum energy and stable configuration for (1 0 4) surface, we constructed eight super cell models and their a, b, c parameters are $2 \times 2 \times 1, 3 \times 3 \times 1, 4 \times 4 \times 1, 5 \times 5 \times 1, 6 \times 6 \times 1, 7 \times 7 \times 1, 8 \times 8 \times 1$ and $9 \times 9 \times 1$, respectively. In terms of the results were shown in tables 1, $5 \times 5 \times 1$ super cell was selected for us to expand as the calcite surface. The final dimension of the pure (1 0 4) surface is 4.1155 nm \times 2.5148 nm \times 0.7769 nm. For the sake of discussion, the two carbonate groups with opposite orientations are painted blue and yellow respectively in this study. The detail of pure (1 0 4) surface is shown in figure 2.

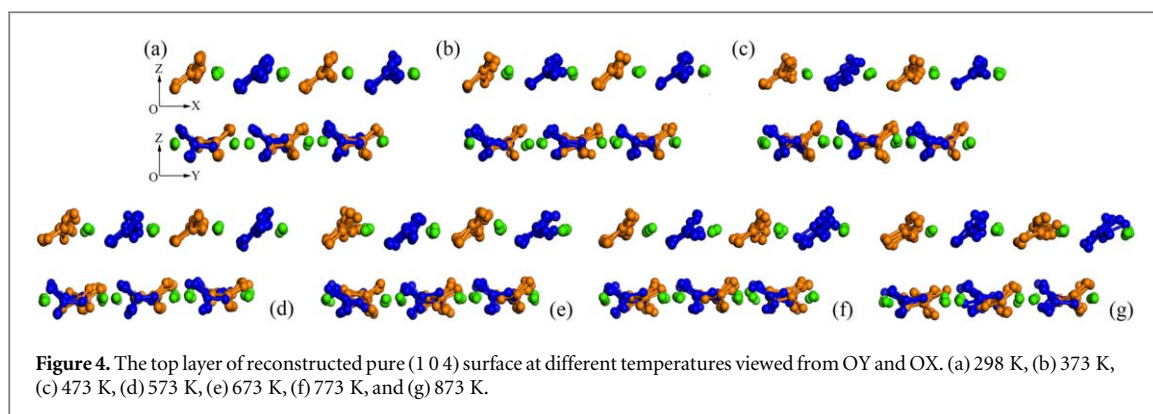
For both pure surface and adsorption behavior MD simulation, the Forcite Tools were used [37] and the condensed-phase optimized molecular potentials for atomistic simulation studies (COMPASS) [38] forcefield was employed for simulation systems. The atom-based and Ewald method were utilized to calculate the van der Waals and electrostatic forces, respectively. The Lennard-Jones 9–6 potential was introduced to describe the van der Waals term, and the coulombic function was used to demonstrate the electrostatic interactions.

The multilayered structure was generated according to the literature [26, 28, 39]. The CO₂ molecules box which is a three-dimensional periodic structure containing 350 optimized CO₂ molecules was constructed by Amorphous Cell Construction task. It has the same parameters of a and b with the calcite (1 0 4) surface. The initial configuration with CO₂ molecules adsorbed on calcite surface at a distance of 0.45 nm from the surface is shown in figure 3. This distance was chosen as optimal because it is not too far where it would take too long for CO₂ molecules to adsorb onto the surface and not too close, where the molecules could be trapped in a local minimum unable to move to more energetically favorable positions. During the simulation, the pure (1 0 4) surface was an ideal cleavage plane. The oxygen atoms and the calcium atoms on the surface were allowed to relax. The rest of the atoms in surface layer was kept fixed [28]. Since the fixed atoms are separately thermostated

Table 1. The energy of the calcite surface (10^3 kcal/mole).

	Expand dimension (a × b)							
	2 × 2	3 × 3	4 × 4	5 × 5	6 × 6	7 × 7	8 × 8	9 × 9
Energy	-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





and are not bonded to the surface atoms, we expect that fixing their positions will have a negligible impact on the simulation results [40]. In order to exclude the possibility of CO₂ molecules adsorbed on the other side surface, a vacuum slab measured 4 nm in thickness was added upon the CO₂ molecules layer. For the pure surface, 6.5 nm thick vacuum layer was added upon the surface so that it has the same size as adsorption configuration. The initial structure of pure surface is shown in figure 2. Periodical boundary conditions were applied in three-dimensional spaces, so that the simulation unit repeated infinitely in each direction [41, 42]. All simulations were performed in a constant number, a constant volume and a constant temperature (NVT) ensemble and the temperature was controlled by a Nose thermostat [43]. The initial velocity of molecules was set by Boltzmann function according to relative temperature. The time step and total simulation time were set to 1 fs and 2 ns, respectively. The first 1 ns was used for equilibration and the last 1 ns of the MD simulation was used for data analysis. In order to obtain the intermediate (transition) structure of the surface of calcite before decomposition, seven sets of temperatures, namely, 298 K, 373 K, 473 K, 573 K, 673 K, 773 K, and 873 K, were selected in this study.

3. Results and discussion

3.1. Pure surface reconstruction

Figure 4 shows the final configuration of the top layer of pure surface reaching thermodynamic equilibrium at different temperatures. Compared with figure 2, it is clear that the carbonate groups with alternating orientations are no longer identical, rather the carbonate groups are rotated and distorted in figure 4. The positions of carbonate groups and calcium ions on the surface are almost unchanged along OY, while the orientations of carbonate groups are different from the other two layers. Besides, when the carbonate groups deviate from their initial position along OX, Ca ions follow it forming two rows. Further, the tilt angle of carbonate groups plane with respect to the (1 0 4) surface is decreasing macroscopically with the increase of temperature. This means that carbonate groups tend to lie flat on the surface. An apparent inward displacement is found for the top of calcite surface. According to the MD simulation, a significant rotation of carbonate groups is concluded that the two orientations of carbonate groups have opposite rotation directions, which is shown in figure 5. These similar phenomena on surface are supported by previous studies through the simulation [6, 16, 17] and experiments [18, 44]. However, the evolution rule of the detailed surface structure with temperature is rarely reported.

To better illustrate the effect of temperature on surface structure, we define some parameters as follows. The letter R represents the rotation of the carbonate groups. Firstly, R_C^B and $R_{OO'}^B$ denote the blue carbonate groups rotating around the central C atom and OO' axis, respectively. Secondly, R_C^Y and $R_{OO'}^Y$ denote the yellow carbonate groups rotating around the central C atom and OO' axis, respectively. Thirdly, \angle_{O-C-O}^B and \angle_{O-C-O}^Y represent the blue and yellow carbonate groups with the O-C-O angle of the two O atoms directed out of the surface, respectively. Fourthly, D_{Ca-O}^B and D_{Ca-O}^Y are defined respectively as the distance between Ca ion and O atom in blue and yellow carbonate groups. Fifthly, $\angle CO_3^{2-}$ is the tilt angle of carbonate groups plane with respect to the (1 0 4) surface. Finally, Δ_{surface} denote the downward shift of the top (1 0 4) surface. The average values for the each of the above parameters are obtained every 100 ps from the simulation time 1 ns to 2 ns. The detailed results of the above parameters with the increase of temperature are shown in table 2.

Table 2 shows that all of the rotation of carbonate groups is conspicuous and positively related to the temperature. Notably, at room temperature (298 K), both R_C^B and R_C^Y are quite different from it in ideal lattice (R_C is 0°). This result can be confirmed by Rohl *et al* [16] according to simulation and experimental methods, which carbonate groups are rotated 17° on the relaxed surface. As far as we know, there are few reports about the

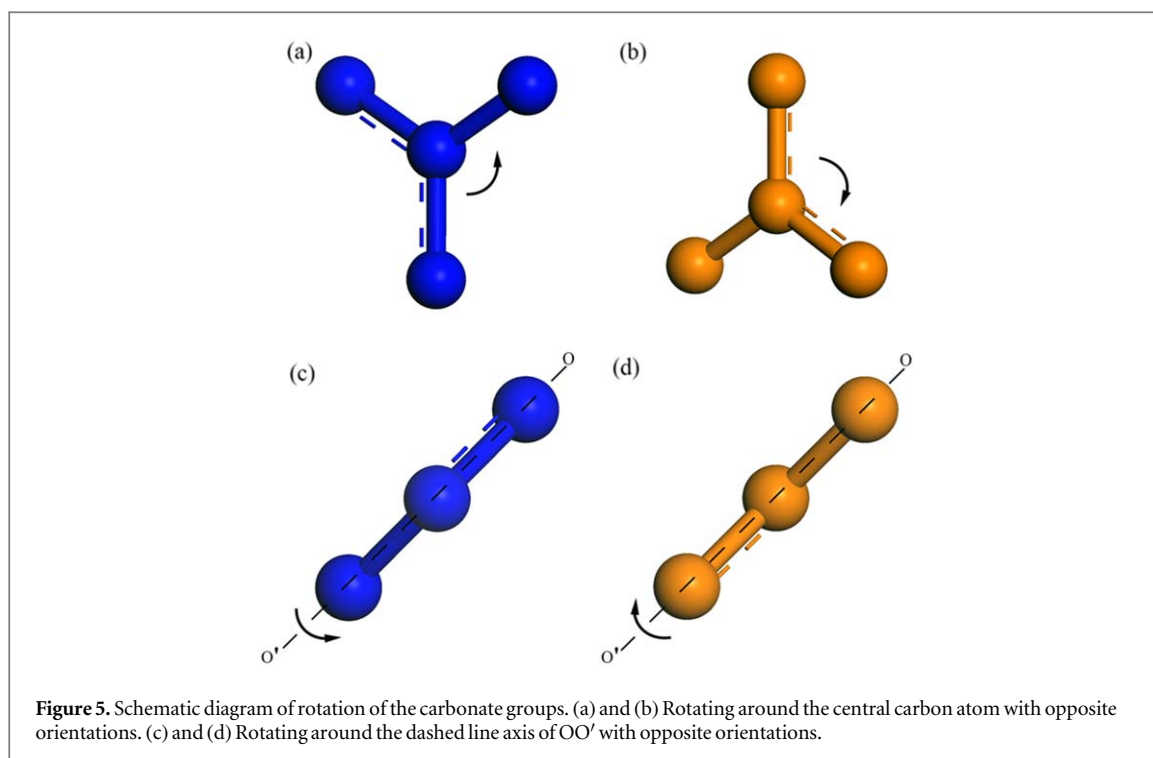


Table 2. Effects of different temperatures on surface structure.

T(K)	Rotation (°)				O–C–O angle (°)		Distance (nm)		Tilt angle (°) $\angle CO_3^{2-}$	Downward shift (nm) Δ_{surface}
	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		
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

carbonate groups rotating around the dashed line axis of OO' in figure 5. It can be found that $R_{OO'}^B$ and $R_{OO'}^Y$ are in opposite orientations and the alternating orientations of carbonate groups planes are not parallel to each other any more with the increase of temperature. Besides, both \angle_{O-C-O}^B and \angle_{O-C-O}^Y increase slightly with the temperature goes up. This result is consistent with previous study [16] which the O–C–O angle of the two O atoms directed out of the surface increasing by 3° on relaxed surface. The temperature has little effect on the O–C–O angle, it could be attributed to the strong C–O covalent bonds [1, 17] and the behavior of a rigid body [45]. What is more, there is little data about the tilt angle of carbonate groups on the pure surface at room temperature (298 K). The tilt angle of carbonate groups is negatively related to the temperature. It indicates that the (1 0 4) surface corrugation will be flattened and the carbonate groups tends to lie flat on the surface. This is in good agreement with the experimental result of Geissbühler *et al* [46] Moreover, the downward displacement of top (1 0 4) surface is positively related to the temperature. Since the surface is the end of periodic arrangement of crystal atoms, there will be some broken bonds on the surface resulting in increasing the surface energy. Nevertheless, atoms may be reconstructed or rearranged in nanoscale due to Jahn-Teller distortion [47, 48], which could reduce the surface energy by lowering the symmetry of the surface structure [1].

Compared with the surface relaxation (D_{Ca-O} is 0.231 nm [49]), the distance between Ca ion and O atom in this study is small due to the rotation and displacement of carbonate groups. With a rising of temperature, the distance between Ca ion and O atom increases slightly. Importantly, the distances what we calculate are almost the same as $(CaCO_3)_2$ clusters [50] and $CaCO_3$ intermediates [51] studied by our group. Therefore, it indicates that similar $CaCO_3$ clusters structure should be formed on calcite surface before thermal decomposition according to the two-step nucleation [22].

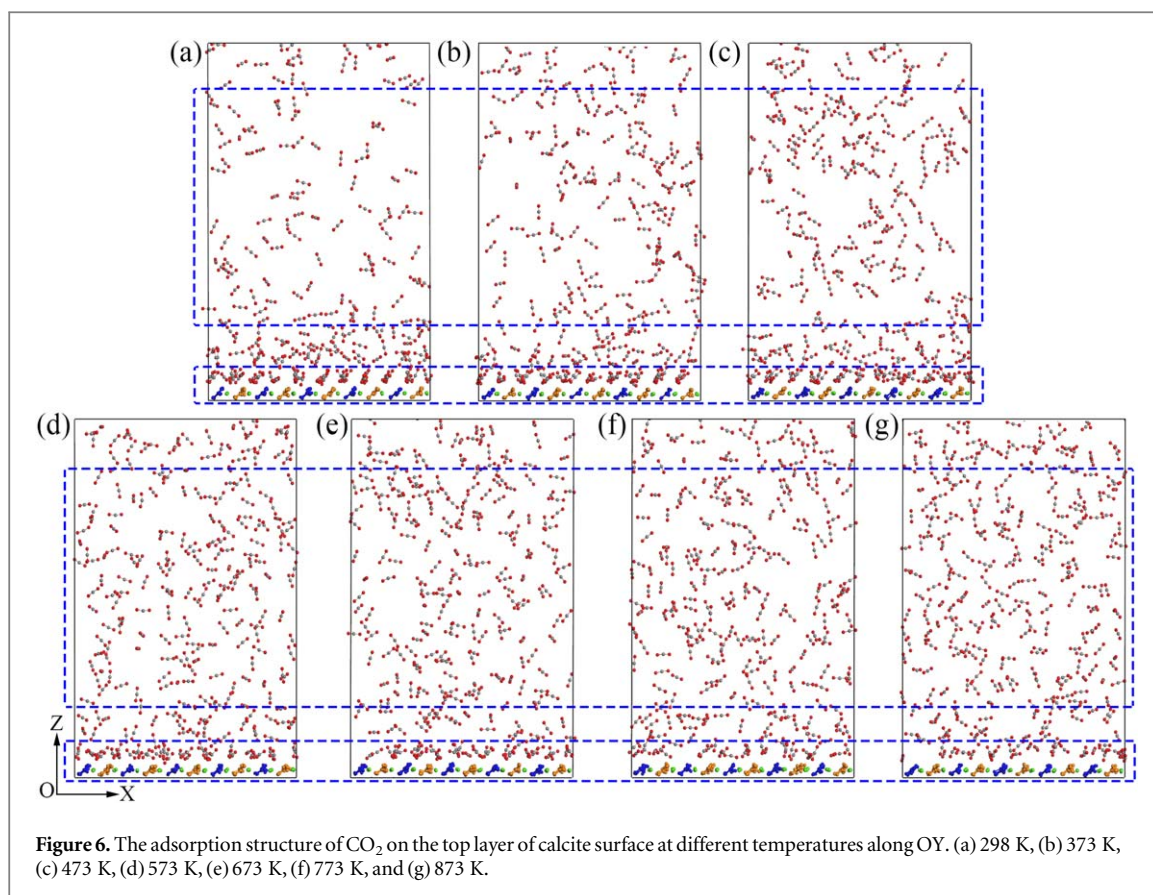


Table 3. Effects of different temperatures on the adsorption structure of CO₂ on calcite surface.

T(K)	Rotation (°)				O–C–O angle (°)		Distance (nm)		Tilt angle (°) $\angle \text{CO}_3^{2-}$	Downward shift (nm) Δ_{surface}
	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		
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

According to the results of MD simulation, the rotation, the O–C–O angle, the distance and the tilt angle are basically stable after 673 k. It is proved that there is an inflection point in the evolution of surface structures. It means that there is a critical value of surface structure reconstruction before thermal decomposition. Once this critical value is exceeded, the decomposition reaction occurs.

3.2. CO₂ adsorption behavior

The evolution rule of the pure surface structure has been discussed. When CO₂ molecules are adsorbed on the surface, the final adsorption configurations of the top layer of calcite surface at thermodynamic equilibrium are shown in figures 6(a)–(g). Before the adsorption behavior of CO₂ molecules is analyzed, the effect of CO₂ molecules on the surface structure is investigated in the first step. The structure parameters of the adsorption surface are measured, which is shown in table 3. Compared with table 2, it can be found that there is no different between each of the parameters at various temperatures. It suggests that the adsorption surface reconstruction is the same as that of the pure surface even if the CO₂ molecules are adsorbed.

In addition to the structural information, the surface energy of the pure surface (E_{pure}) and the adsorption surface (E_{Ads}) were calculated in table 4. It can be found that the error is quite small. Therefore, it's reasonable to conclude that the adsorption of CO₂ molecules has no effect on the surface reconstruction. Since we exclude the

Table 4. The energy of calcite surface at different temperatures. (10^3 kcal/mole).

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

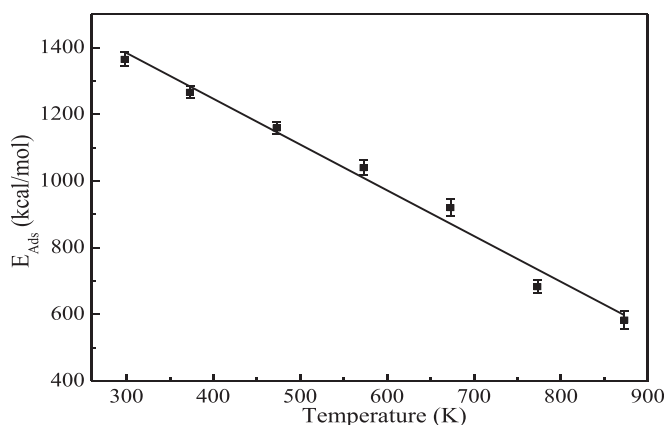


Figure 7. The adsorption energy of CO₂ molecules on calcite surface at different temperatures.

influence of CO₂ molecules on the surface structure, the temperature is considered to be an important parameter dominating the surface reconstruction.

As can be seen from figure 6, CO₂ molecules are adsorbed on the surface at the point of Ca ions by the highly oriented arrangement. This result can be confirmed by previous study [26]. CO₂ molecules are adsorbed perpendicularly on the surface by electrostatic interaction. This could be explained by electrostatic force between Ca ions on the surface with positive charge and one of the O atoms of the CO₂ molecule with negative charge. As the temperature goes up, the number of CO₂ molecule adsorbed on the surface decreases, while the number of CO₂ molecule in the vacuum layer increases. It means that increasing the temperature will lead to CO₂ molecule desorption. Further, to better characterize the adsorption capacity of CO₂ molecule on surface, the adsorption energy can be calculated at different temperatures by the following equation:

$$E_{Ads} = E_{Sur} + E_{Gas} - E_{Tot} \quad (1)$$

where E_{Tot} , E_{Sur} and E_{Gas} are the energy of adsorption system, surface and CO₂ molecules respectively. The higher the adsorption capacity of CO₂ molecules on surface, the greater value of the adsorption energy. Note that the adsorption energy can provide a basic quantitative description of the interactions between CO₂ molecules and calcite surface. The trend of the adsorption energy with the temperature increasing is shown in figure 7.

As figure 7 displays, at low temperature, the adsorption energy of CO₂ molecules on the calcite surface is approximately twice as high as it at high temperature, which is consistent with the illustrative diagram in figure 6. To our knowledge, rarely related experiments have been carried out at high temperatures before thermal decomposition. The results indicate that the decomposition temperature would be increased due to the adsorption of CO₂ molecules. Even at the beginning of thermal decomposition (873 K), the adsorption energy between CO₂ molecules and calcite surface is quite large. Therefore, it is difficulty to using inert gas to blow completely away the adsorption of CO₂ molecules on surface. The ultra high vacuum turbo molecular pump can as close as possible achieve the pure surface to study intrinsic reaction. It is confirmed in a experiment study by Dash *et al* [52]. Given no effect of CO₂ molecules on surface reconstruction before thermal decomposition, it means that the formation of calcite clusters structure is independent of gas partial pressure.

4. Conclusion

In this study, we used MD simulation to research the effect of temperature on the pure (1 0 4) surface and the adsorption behavior of CO₂ molecules. We observed that temperature promotes surface structural reconstruction and the carbonate groups on the surface have opposite rotation directions. The parameters of surface structure are positively related to the temperature. When the temperature exceeds the inflection point 673 K, the surface rearrangement reaches equilibrium. Once equilibrium is broken, the decomposition reaction occurs. What is more, calcite clusters structure should be formed at the crystal surface. Importantly, when CO₂ molecules are adsorbed on the surface, the surface structure is no longer change so that the effect of CO₂ molecules is eliminated. CO₂ molecules are preferentially adsorbed at the point of Ca ions and arranged in ordering orientation. In addition, CO₂ molecules desorption occurs with increasing of the temperature. According to adsorption energy, the amount of CO₂ molecules desorption is positively correlated with temperature.

Notes

The authors declare no competing financial interests.

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