



# Transition mechanism of the reaction interface of the thermal decomposition of calcite

Zhi Li <sup>a,\*</sup>, Zhen Zhao <sup>b</sup>, Qi Wang <sup>a</sup>, Guocheng Wang <sup>a</sup>

<sup>a</sup> School of Materials and Metallurgy, University of Science and Technology Liaoning, Anshan 114051, PR China

<sup>b</sup> School of Chemistry and Life Science, Anshan Normal University, Anshan 114007, PR China



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## ABSTRACT

Even the reaction layer (excited state CaCO<sub>3</sub>) is so thin that it is difficult to detect, it is significantly restrict the orientation of the solid product (excited state CaO) of the thermal decomposition of calcite. Quantum chemical calculation with GGA-PW91 functional reveals that the ground-state (CaCO<sub>3</sub>)<sub>m</sub> clusters are more stable than the hybrid objects (CaCO<sub>3</sub>)<sub>m</sub>-(CaO)<sub>n</sub> clusters. The lowest-energy (CaCO<sub>3</sub>)<sub>m</sub> clusters are more kinetically stable than that of (CaCO<sub>3</sub>)<sub>m</sub>-n(CaO)<sub>n</sub> clusters and then than that of (CaO)<sub>n</sub> clusters except (CaCO<sub>3</sub>)(CaO)<sub>3</sub> clusters from the HOMO-LUMO gaps. (CaCO<sub>3</sub>)<sub>2</sub> clusters should co-exist at room temperature and they prefer to decompose with the temperature increasing.

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## 1. Introduction

Calcite is the most common and widely distributed crystalline mineral in nature and the chemical reactivity of the thermal decomposition product (CaO) is significantly influence on the industrial effect. Up to now, the macroscopic decomposition kinetics of calcite is still reported as a typical crystal transition [1–9]. However, the experimental activation energy  $E_a$  for reaction rate formula ( $\frac{dx}{dt} = A \exp(-\frac{E_a}{RT})(1-x)^n$ ) even ranges from 110 to 1600 kJ/mol [10]. Because the apparent  $E_a$  is determined by the relative contribution of the intermediate processes (the lattice damage, chemical bond fracture, desorption, adsorption and diffusion of gas products, the formation and growth of the crystal nucleus of solid product and so on [11]) in the thermal decomposition of calcite. It is difficult to reasonably distinguish the contribution of certain intermediate step above to the activation energy  $E_a$ . It leads to the apparent mechanism functions as many as 26 species [9]. In a word, the thermal decomposition of calcite is obviously a multi-step reaction.

Croix et al. [12] speculated that there was three outline postulated symmetry-controlled routes (PATH I, PATH II, PATH III) for the decomposition of calcite and in the most feasible path (PATH III) a transition from R-3c to cubic before the thermal decomposition of calcite by the lattice energy theory. It can be confirmed by

the thermogravimetric-differential scanning calorimetry (TG-DSC) method, that is,  $\frac{d\alpha_{DSC}}{dt} = \frac{1}{H_\infty} \frac{dH}{dt} \neq 0$  but  $\frac{d\alpha_{TG}}{dt} = -\frac{1}{m_0 - m_\infty} \frac{dm}{dt} = 0$  before the thermal decomposition of calcite [13,14]. For the reactant CaCO<sub>3</sub>, active sites have been observed in the detail of the microcrystals making up the particle of calcite [15]. The phase transition (calcite crystal → active sites) should start from some active regions of the surface layer. The active sites on the surface layer are abstracted into (CaCO<sub>3</sub>)<sub>m</sub> clusters by the cluster theory. For the product (perfect CaO crystal), in the thermal decomposition process of calcite in vacuum, there is about 6 nm the needle-like products layer (CaO crystal) [16] and massive polyporous small single crystals [15] in the decomposition interface are easy to be obtained. Crystal morphology can be controlled by nucleating crystals on crystalline surfaces [17]. The interface layer can be found in the enlargement of the partially decomposed calcite crystal thermally altered *in situ* in the TEM [16]. According to two-step nucleation [17], the intermediates process aggregate to non-crystal (clusters) and then crystallization. Field emission scanning electron microscopy (FESEM), two-dimensional X-ray diffraction (2DXRD), and transmission electron microscopy coupled with selected area electron diffraction (TEM SAED) analyses of the reactant/product textural relationship have been adopted to the thermal decomposition of Iceland spar single crystals and found that the reaction CaCO<sub>3</sub>(s) → CaO(s) + CO<sub>2</sub>(g) is pseudomorphic and topotactic [18]. However, the reaction layer ((CaCO<sub>3</sub>)<sub>m</sub> clusters or (CaCO<sub>3</sub>)<sub>m</sub>-n-(CaO)<sub>n</sub> clusters) which will restrict the orientation of solid product [18] is so thin that it is difficult to detect. In the thermal decomposition of calcite,

\* Corresponding author.

E-mail address: [lizhi81723700@163.com](mailto:lizhi81723700@163.com) (Z. Li).

the structures of the CaO nanocrystals are evolved as the temperature increased [18]. Even external direct current electric field induced electro-adsorption/electro-desorption of gaseous CO<sub>2</sub> at the surface of calcite particles are observed [19].

Molecular events are analyzed in detail in a way that is currently unfeasible experimentally [17]. In this study, the structure, charge distribution and transition of the interface layer (calcite → (CaCO<sub>3</sub>)<sub>m</sub> clusters → (CaCO<sub>3</sub>)<sub>m-n</sub>(CaO)<sub>n</sub> clusters → (CaO)<sub>m</sub> clusters → CaO crystal) is calculated by GGA-PW91 method.

## 2. Computational details

To avoid missing certain configurations, the stable (CaO)<sub>n</sub> cluster [20,21] is gradually close to a CO<sub>2</sub> molecular to form (CaCO<sub>3</sub>)<sub>m</sub>(CaO)<sub>n</sub> (m = 0–2, n = 0–4) clusters. All the hypothetical configurations of the clusters above are optimized by using the spin polarized density functional theory (DFT) implemented in the DMol<sup>3</sup> package [22,23]. The exchange–correlation potential was considered in the generalized gradient approximation (GGA) [24], combined with the Perdew–Wang (PW91) exchange functional [25]. Effective core potentials were adopted [26]. The double numerical polarization (DNP) basis set was chosen [22]. In the geometry optimization processes, the energy gradient and atomic displacement converged to within 1 × 10<sup>−5</sup> Hartree/Bohr and 5 × 10<sup>−3</sup> Å, respectively. Corresponding to a total energy convergence of 1 × 10<sup>−5</sup> Hartree, the charge density in the self-consistent iterations converged to within 1 × 10<sup>−6</sup> e/Å<sup>3</sup>. Mülliken population analysis was obtained to analyze the atomic charge of the clusters, respectively [27].

The binding energy per atom E<sub>b</sub>(n) for (CaCO<sub>3</sub>)<sub>2</sub> clusters was defined such as [28]

$$E_b = [2E(\text{Ca}) + 2E(\text{C}) + 6E(\text{O}) - E((\text{CaCO}_3)_2)]/10 \quad (1)$$

where E(Ca), E(C) and E(O) are the single atom energies of the Ca, C and O atoms. E((CaCO<sub>3</sub>)<sub>2</sub>) is the total energy of the structure for the (CaCO<sub>3</sub>)<sub>2</sub> clusters.

To study the orientation growth mechanism of the interface layer (CaCO<sub>3</sub>)<sub>m</sub>(CaO)<sub>n</sub>, the association energy is defined as [28]

$$E_{\text{ass}} = E_{(\text{CaCO}_3)_m(\text{CaO})_n} - (E_{(\text{CaCO}_3)_m} + E_{(\text{CaO})_n}) \quad (2)$$

where E<sub>(CaCO<sub>3</sub>)<sub>m</sub>(CaO)<sub>n</sub></sub>, E<sub>(CaCO<sub>3</sub>)<sub>m</sub></sub> and E<sub>(CaO)<sub>n</sub></sub> are the total energy for the (CaCO<sub>3</sub>)<sub>m</sub>(CaO)<sub>n</sub> clusters, (CaCO<sub>3</sub>)<sub>m</sub> clusters and (CaO)<sub>n</sub> clusters, respectively.

To study the thermal decomposition mechanisms (CaCO<sub>3</sub> crystal → (CaCO<sub>3</sub>)<sub>m</sub> clusters → (CaCO<sub>3</sub>)<sub>m-n</sub>(CaO)<sub>n</sub> clusters → (CaO)<sub>m</sub> clusters → CaO crystal) of calcite, the difference in Gibbs free energy is given as

$$\Delta G = G_{\text{Production}} - G_{\text{Reaction}} \quad (3)$$

where Gibbs free energy (G) of them is calculated by vibrational analysis [29].

The temperature dependence of the free energy is given by [29]:

$$F(T) = E_{\text{tot}} + \frac{1}{2} \int F(\omega) h\omega d\omega + kT \int F(\omega) \ln \left[ 1 - \exp\left(-\frac{h\omega}{kT}\right) \right] d\omega \quad (4)$$

where the second item is the zero point vibrational energy, *k* is Boltzmann's constant, *h* is Planck's constant and *F*(*ω*) is the phonon density of states. The value of *PΔV* is so small under constant pressure that the free energy *F* is replaced by the Gibbs free energy *G*.

To evaluate the accuracy of our selected scheme for describing the (CaCO<sub>3</sub>)<sub>m</sub>(CaO)<sub>n</sub> clusters, the calculated bond lengths of (CaO)<sub>1</sub> clusters (R<sub>e</sub> = 1.850 Å) and CO<sub>2</sub> molecular (R<sub>e</sub> = 1.175 Å) are compared which are excellent agreement with experimental results (R<sub>e</sub> = 1.82 Å [30] and R<sub>e</sub> = 1.1625 Å [31]), respectively. Therefore,

the PW91 scheme is reliable and accurate enough for describing the Ca–O–C systems.

## 3. Results and discussion

### 3.1. Structures

The electronic distributions and the total binding energies of the typical stable isomers for (CaCO<sub>3</sub>)<sub>m</sub>(CaO)<sub>n</sub> clusters are shown in Fig. 1. Two calcium carbonate molecules which are included in the primitive cell are utilized to abstract the interaction between calcium carbonate molecules. For the lowest-energy structure (C<sub>2h</sub>) of (CaCO<sub>3</sub>)<sub>2</sub> clusters, the Ca atoms are distorted to neither on the plane of CO<sub>3</sub> such as only one CaCO<sub>3</sub> molecule [32] nor perpendicular to the plane of CO<sub>3</sub> such as the configuration of the primitive cell of calcite. However, two Ca atoms and four O atoms are occurred on the same plane. Then two Ca atoms and other two O atoms constitute a narrower (75.538°) diamond structure than that (86.762°) of the lowest-energy structure (C<sub>1</sub>) of (CaO)<sub>2</sub> clusters. The binding energy of the low-lying isomer (C<sub>2v</sub>) of (CaCO<sub>3</sub>)<sub>2</sub> clusters which has the mirror symmetry structure is slightly higher (0.36 eV) than that of the ground state structure (C<sub>2h</sub>) of (CaCO<sub>3</sub>)<sub>2</sub> clusters. The binding energy of the low-lying isomer (C<sub>1</sub>) of (CaCO<sub>3</sub>)<sub>2</sub> clusters which have one CO<sub>2</sub> molecule tend to leave is significantly higher (2.333 eV) than that of the ground state structure (C<sub>2h</sub>) of (CaCO<sub>3</sub>)<sub>2</sub> clusters. Similarly, the angle of O–Ca–O (81.550°) of the ground state structure (C<sub>1</sub>) of (CaCO<sub>3</sub>)(CaO) cluster is between that of the lowest-energy structure (C<sub>2h</sub>) of (CaCO<sub>3</sub>)<sub>2</sub> clusters and the lowest-energy structure (C<sub>1</sub>) of (CaO)<sub>2</sub> clusters.

For the lowest-energy and low-lying isomers of (CaCO<sub>3</sub>)<sub>2</sub>(CaO) clusters, the structural transformation law is the same as that of (CaCO<sub>3</sub>)<sub>2</sub> clusters. The hexagonal ring (O–Ca–O–Ca–O–Ca) in the ground-state (CaCO<sub>3</sub>)<sub>2</sub>(CaO) clusters is slightly distorted by two CO<sub>2</sub> molecular. The angle of O–Ca–O near the CO<sub>3</sub> in the lowest-energy structure (C<sub>2</sub>) of (CaCO<sub>3</sub>)<sub>2</sub>(CaO) clusters (94.045°) successively less than those (105.865° and 115.632°) in the lowest-energy structure (C<sub>1</sub>) of (CaCO<sub>3</sub>)(CaO)<sub>2</sub> and (CaO)<sub>3</sub> clusters. The formation of the structure of CO<sub>2</sub> is away from the CO<sub>3</sub> rather than that is adjacent CO<sub>3</sub> need to consume slightly more energy (0.017 eV) by analyzing the two isomers of (CaCO<sub>3</sub>)<sub>2</sub>(CaO) clusters.

For the lowest-energy structure (C<sub>s</sub>) of (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters which are a mirror symmetry structure, one CaCO<sub>3</sub> molecule is a plane structure and the other CaCO<sub>3</sub> molecule is a distorted configuration. The following three low-lying isomers of (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters which binding energies are equal to −76.261 eV, −76.222 eV and −76.207 eV retain the distorted (CaO)<sub>4</sub> configuration. As for the low-lying isomer of (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters which binding energy is equal to −76.050 eV, the distorted (CaO)<sub>4</sub> configuration is damaged by a CO<sub>2</sub> molecule which is similar to that of the ground state (C<sub>s</sub>) (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters. The binding energy of the low-lying isomer (C<sub>1</sub>) of (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters which has one linear CO<sub>2</sub> configuration and one plane CaCO<sub>3</sub> molecule is significantly higher (2.208 eV) than that of the ground-state structure (C<sub>s</sub>) of (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters. While the binding energy of the low-lying isomer (C<sub>1</sub>) of (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters which has one plane CaCO<sub>3</sub> molecule and one special structure of O–O atom proximity is unusually higher (5.420 eV) than that of the ground-state structure (C<sub>s</sub>) of (CaCO<sub>3</sub>)<sub>2</sub>(CaO)<sub>2</sub> clusters.

### 3.2. Stability

Further the binding energies per atom of the considered (CaCO<sub>3</sub>)<sub>m</sub>(CaO)<sub>n</sub> clusters are displayed in Table 1. This calculated binding energies per atom of the lowest-energy of (CaO)<sub>2</sub>, (CaO)<sub>3</sub> and (CaO)<sub>4</sub> clusters are agreement with the BL3YP and 6-311G(d)

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