



Formation mechanism of non-spherical calcium carbonate particles in the solution using cluster-moving Monte Carlo simulation



Kazunori Kadota^{a,b,*}, Ryoichi Furukawa^a, Yuichi Tozuka^b, Atsuko Shimosaka^a, Yoshiyuki Shirakawa^{a,*}, Jusuke Hidaka^a

^a Department of Chemical Engineering and Materials Science, Faculty of Science Engineering, Doshisha University, 1–3, Tatara-Miyakodani, Kyotanabe, Kyoto 610-0321, Japan

^b Osaka University of Pharmaceutical Sciences, 4-20-1, Nasahara, Takatsuki, Osaka 569-1094, Japan

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ABSTRACT

The objective of this work is to elucidate the formation mechanism of spindle shaped calcium carbonate (CaCO_3) clusters using the cluster-moving Monte Carlo (MC) simulation. CaCO_3 primary particles were modeled by the cubic particles with surface charge densities obtained from Molecular Dynamic simulations. The aggregated structure was analyzed using the cluster-moving MC simulation to investigate the formation mechanism from primary particles to spindle-shaped clusters. This algorithm has been successful in the study of aggregation process on ferromagnetic particles or particles with dipole moment. The clusters defined by a separation distance were attempted to move randomly every 10 MC steps, and then the clusters moved according to a transition probability as well as Metropolis's method.

The result of cluster-moving MC simulations revealed that spindle-shaped CaCO_3 clusters were formed by the aggregation of primary particles. The distribution of CaCO_3 cluster width had a sharp peak at smaller region than that of CaCO_3 cluster length. The aspect ratio obtained from cluster-moving MC simulations showed good agreement with the experimental result. The distance between charges on the particle composed of spindle-shaped CaCO_3 clusters indicated that most primary particles aggregated in the same direction since positive and negative charges are attracted to each other.

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1. Introduction

Calcium carbonate (CaCO_3) has been eagerly researched as an essential material used for industrial products over the past years [1]. The control of polymorphs, morphology and particle size distribution of CaCO_3 has been required since the properties of the industrial products are influenced by the characteristics of CaCO_3 [2]. Carbonation process of $\text{Ca}(\text{OH})_2$ aqueous slurry is the most widely used method to produce CaCO_3 particles in industrial fields [3]. This method is able to synthesize CaCO_3 with various shapes (colloidal, spindle shape, whisker, etc.) by controlling the reaction conditions such as temperature, the amount and speed of CO_2 gas [4,5]. It is difficult to clarify the formation mechanism because CaCO_3 has three polymorphs: calcite, aragonite and vaterite [6]. Calcite is the most common and stable crystal among CaCO_3 polymorphs. Calcite particle could be divided into two morphologies. One is the colloidal CaCO_3 particle with rhombic shape and the other is the large spindle shaped CaCO_3 particle. Some researchers reported that the spindle shaped CaCO_3 particles were generated by the

aggregation of the primary CaCO_3 particles with some sort of anisotropy in the same direction [7–9]. However, the phenomena of the aggregation process in the solution are very complicated because the carbonation process is a gas–liquid–solid three-phase reaction. Many researchers tried to solve the aggregation mechanism by means of experimental methods such as an electron diffraction method, Fourier transform infrared spectrophotometer (FT-IR), X-ray photoelectron spectroscopy (XPS), and atomic force microscope (AFM) [10–14]. For instance, Arakawa revealed the formation mechanism of the spindle shaped CaCO_3 particles in the supersaturated CaCO_3 solution using an electron microscope [9]. This research indicated that the spindle shaped CaCO_3 particles were generated by the aggregation of primary CaCO_3 particles in the process of transformation from amorphous to calcite crystals. Yamada and Hara demonstrated that amorphous CaCO_3 was precipitated in the initial growth stage as a precursor of the CaCO_3 particles [15]. Aggregation of calcite particles could arise from a combination of many effects such as solid-state properties, growth habit and crystallization conditions. Detailed surface properties were not obtained only by the experimental approaches because nucleation and aggregation of CaCO_3 were related to specific crystal faces at nano-scale.

Computer simulations are very powerful tools to elucidate the aggregation mechanism of the primary CaCO_3 particles [16–19]. MD simulations make it possible to simulate nano-scale phenomena in nano-

* Corresponding authors at: Osaka University of Pharmaceutical Sciences, 4-20-1, Nasahara, Takatsuki, Osaka 569-1094, Japan. Tel./fax: +81 72 690 1217.

E-mail addresses: kadota@gly.oups.ac.jp (K. Kadota), yshiraka@mail.doshisha.ac.jp (Y. Shirakawa).

seconds and to expose specific crystal faces. In previous researches, MD simulations of the solid–liquid interface were performed to discuss the crystal growth, dehydration, nucleation, etc. [20–23]. Leeuw et al. investigated the stability of crystal surfaces, solubility, and effects of the impurities on the crystal growth of CaCO₃ to simulate the interface between CaCO₃ and water [24]. We also investigated the effect of surface properties including the charge density and the dielectric constant of water on the aggregation process [25]. In addition to MD simulations, MC simulations have advantages of removing particles overlapping and preventing calculation from diverging. These advantages are useful for understanding aggregation in colloidal or suspension systems [26–29]. MC simulations were performed to elucidate aggregation structures with spherical particles in a thermodynamic equilibrium state. We investigated the aggregation of CaCO₃ by MC simulations using the experimental data [30]. In the previous paper, geometric shape and surface charge distribution of the unit particle were the decisive factors for providing the spindle shape of granules. Studies on non-spherical particle are more fascinating because a number of complicated microstructures can be expected to be formed. A conventional metropolis MC simulation is difficult to calculate the aggregation phenomena when the interaction between particles is strong for forming chain-like structure. The chain-like cluster formation was not observed by the conventional MC simulation since it was not suitable for the strong interactions between particles. It is difficult to form larger clusters because the conventional MC simulation prevents particles from separating the cluster [31,32]. The development of algorithm, in which a cluster is moving as a particle, is indispensable for realizing the aggregation phenomena. Aoshima and Satoh proposed a cluster-moving MC algorithm to capture aggregation structures of ferromagnetic particles [29,33]. Their results provided that the thicker chain-like clusters formed in the applied magnetic field with increasing strength of magnetic interactions between particles. Simulation results showed that clusters possess a complicated internal structure as network.

The objective of the present study is to elucidate the aggregation mechanism of the primary CaCO₃ particles at molecular level. We performed the aggregation structure of CaCO₃ particles using a cluster-moving MC simulation. Then, a cluster-moving MC simulation has been carried out to investigate the dispersion and aggregation state of primary particles using the surface charge density determined by the results of MD simulation [25]. Hybrid simulations between MD simulations and cluster-moving MC simulations would give us the promising design methods for aggregation process.

2. Simulation details

We have already reported the effect of surface properties of CaCO₃ on aggregation process using MD simulations [25]. Table 1 shows the surface charge density calculated by the previous MD simulations. These results of charge density on the crystal surface were utilized to perform the cluster-moving MC simulation.

The conventional MC simulation as mentioned above is difficult to duplicate the aggregation phenomena where particles formed chain-like structure owing to the strong interaction between particles. The clusters are slow to grow because the algorithm prevents particles from separating from the cluster. The cluster-moving MC algorithm

was applied to calculate the aggregation structure of CaCO₃ particles. Satoh proposed this algorithm to capture aggregate structures of particles [34]. This algorithm has been successful in simulating the aggregation of ferromagnetic particles [29,33]. The clusters defined by a separation distance is attempted to move randomly every 10 MC steps. The clusters move with a transition probability as well as Metropolis's method. Aggregated particles are regarded as a cluster in this algorithm. The potential function in this algorithm is based on the DLVO theory which took into account van der Waals and electrostatic interaction [35,36]. Thus, the dispersion and aggregation state of particles were determined by the sum of two interactions. Van der Waals interaction V_A between two particles is given by [37]:

$$V_A = -\frac{A}{6} \left\{ \frac{2a^2}{r^2 - 4a^2} + \frac{2a^2}{r^2} + \ln \frac{r^2 + 4a^2}{r^2} \right\} \quad (1)$$

where a is the particle radius and r is the center-to-center particle distance. A is the Hamaker constant calculated using Lifshitz's theory [38]

$$A = \frac{3kT}{4} \left(\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^2 (2\kappa s) \exp(-2\kappa s) + \frac{3h\nu_e}{16\sqrt{2}} \frac{(n_{R1}^2 - n_{R2}^2)^2}{(n_{R1}^2 + n_{R2}^2)^{3/2}} \quad (2)$$

where s is the separation distance, k is the Boltzmann constant, T is the absolute temperature, h is the Planck's constant, n_R is the refractive index, ε is the dielectric constant, and ν_e is the main electronic absorption frequency in ultraviolet region. Subscripts 1 and 2 denote CaCO₃ and water, respectively. The first term in Eq. (2) is the screening effect of the electrolytes on van der Waals interaction and the second term in Eq. (2) is the dispersion energy contribution. We used $\nu_e = 3 \times 10^{15} \text{ s}^{-1}$ as a typical value [18,39]. According to the DLVO theory, the electrostatic interaction with low surface charge ($\psi_0 < 100 \text{ mV}$) is given by:

$$V_c = 4\pi\varepsilon\varepsilon_0 a \psi_0^2 \exp(-\kappa s) / r \quad (\kappa a < 10) \quad (3a)$$

$$V_c = 2\pi\varepsilon\varepsilon_0 a \psi_0^2 \ln[1 + \exp(-\kappa s)] \quad (\kappa a > 10) \quad (3b)$$

where ε_r is the permittivity of vacuum, ψ_0 is the surface potential, and κ is the Debye screening factor. In the present calculation, we assumed the primary particle as a cubic model with the heterogeneously charged

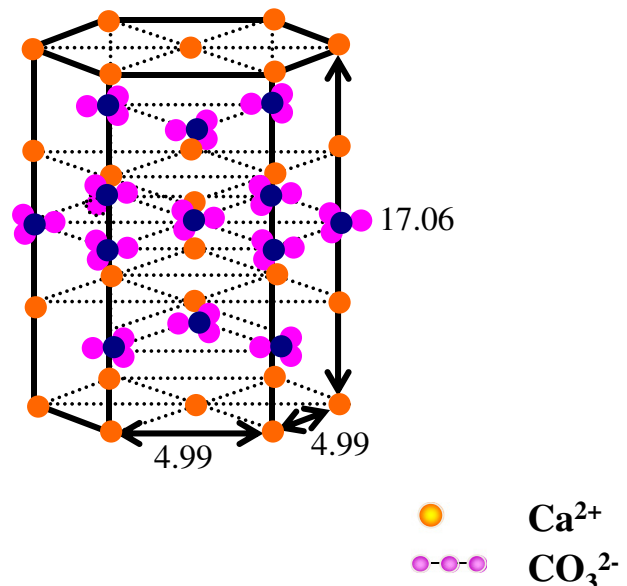


Fig. 1. Crystalline structure of calcite in rhombic system.

Table 1
Charge density at each surface calculated by MD simulation [25].

Surface	Charge density (C/m ²)
(001)Ca	0.711
(001)CO ₃	-0.637
(100)	-0.258
(104)	-0.190

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