Journal of Crystal Growth 492 (2018) 114–121

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/crys

# The crystallization kinetic model of nano-$CaCO_3$ in $CO_2$-ammonia-phosphogypsum three-phase reaction system

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ARTICLE INFO

*Article history:*
Received 27 October 2017
Received in revised form 3 April 2018
Accepted 16 April 2018
Available online 17 April 2018
Communicated by S. Veesler

*Keywords:*
A1. Nucleation
A1. Growth models
A2. Reactive crystallization
B1. Nanomaterials
B1. Calcium compounds
B1. Phosphogypsum

ABSTRACT

Phosphogypsum (PG) as a low-cost calcium resource was used to prepare nano-$CaCO_3$ in a three-phase system by reactions. Based on the population balance equation, nano-$CaCO_3$ crystal nucleation and growth model in the gas ($CO_2$)-liquid ($NH_3{\cdot}H_2O$)-solid ($CaSO_4$) three-phase system was established. The crystallization kinetic model of nano-$CaCO_3$ in $CO_2$-$NH_3{\cdot}H_2O$-$CaSO_4$ reactions system was experimental developed over an optimized temperature range of 20–40 °C and $CO_2$ flow rate range of 138–251 ml/min as $r_{CaCO_3} = k_n \frac{32\pi M^2\gamma^3}{3R^3\rho^2T^3}\frac{(C-C^*)^{0.8}}{[\ln(C/C^*)]^3} + \frac{\pi\rho}{3M}k_g^3 k_n (C-C^*)^2 t^3$, where nano-$CaCO_3$ nucleation rate constant was $k_n = 6.24\times10^{19}\exp\left(-\frac{15940}{RT}\right)$ and nano-$CaCO_3$ growth rate constant was $k_g = 0.79\exp\left(-\frac{47650}{RT}\right)$ respectively. Research indicated that nucleation rates and growth rates both increased with the increasing of temperature and $CO_3^{2-}$ ion concentration. And crystal growth was dependent on temperature more than that of nucleation process because the activation energy of $CaCO_3$ growth was bigger than that of $CaCO_3$ nucleation. Decreasing the reaction temperature and $CO_2$ flow rate was more beneficial for producing nano-size $CaCO_3$ because of the lower $CaCO_3$ growth rates. The deduced kinetic equation could briefly predict the average particle sizes of nano-$CaCO_3$.



## 1. Introduction

As a kind of important inorganic nano-materials, nano-$CaCO_3$ has been widely used in the fields of rubber, plastic, paper, paint, ink, cosmetics and medical industry [1] because of its small size effect, unique quantum size effect and macroscopic quantum tunneling effect [2]. Besides, the calcium-looping used nano-CaO based $CO_2$ adsorbent is a promising technology for high-temperature decarbonation [3,4] owing to its high capture capacity and fast sorption rate derived from large specific surface area [5,6]. It outperforms many other mature $CO_2$ capture technologies and can be applied to numerous industrial processes, such as flue gas decarbonation [7] and reactive sorption enhanced reforming for hydrogen production [8]. However, the high preparation cost is the normal and restricts its widely industrial applications [9,10].

Preparing nano-$CaCO_3$ from phosphogypsum (PG) might be a potential solution, which is not only reduces the nano-$CaCO_3$ material cost, but also reuses the PG wastes storage. PG is generated during the production of phosphoric acid from phosphate rocks by wet method [11,12]. It primarily consists of calcium sulfate dihydrate (>90 wt%), and has approximately 280 million tons annual output in the worldwide. However, over 80% of the PG is dumped without any treatment [13].

The researches about preparation of $CaCO_3$ derived from PG have been reported in many different systems [14–19]. Among these methods, cogeneration of ammonium sulfate and $CaCO_3$ is the most mature technology. Because the solubility product constant of $CaCO_3$ is 3250 times smaller than that of $CaSO_4$, the conversion of $CaSO_4$ in this reaction can reach 99.97%, and ammonium sulfate could also be used as fertilizer.

Tian Xie et al. [18] disclosed a two-phase preparation method by using solid phosphogypsum (s) and ammonium carbonate solution (l). They added additives and ammonium carbonate into the phosphorus gypsum slurry, the reaction temperature was maintained at 30–60 °C and the reaction time was 0.5–2 h. The purity of the $CaCO_3$ product was 93% and the range of average particle size was 1–5 μm. Baojun Yang et al. [19] proposed a homogeneous preparation method in which the phosphogypsum was converted into soluble calcium ion solution by phase transfer catalyst including ammonium sulfate, ammonium salts of organic acids or sodium salt, then reacted with ammonium carbonate solution. The purity of the $CaCO_3$ product was 97% and the range of average particle size was about 1 μm. Siqi He et al. [20] prepared $CaCO_3$ in the three-phases reaction system of ammonia (l), phosphorus gypsum slurry (s) and $CO_2$ (g) at the temperature of 55–85 °C (Eq. (1)). But

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https://doi.org/10.1016/j.jcrysgro.2018.04.017
0022-0248/

**Nomenclature**

| | |
|---|---|
| $B$ | number rate of nucleation, number/($m^3$·min) |
| $C$ | supersaturation concentration, mol/$m^3$ |
| $C^*$ | equilibrium saturation concentration, mol/$m^3$ |
| [C] | concentration of material C in bulk solution, mol/$m^3$ |
| $g$ | reaction order of crystal growth |
| $G$ | linear crystal growth rate, m/min |
| $L$ | crystal size, m |
| $L_0$ | size of newborn crystal, m |
| $L_i$ | mean size of crystal in range i ($L_i - \Delta L/2$, $L_i + \Delta L/2$), m |
| $k_g$ | growth rate constant, $m^{3g+1}$/($mol^g$·min) |
| $k_n$ | nucleation rate constant, number/($mol^n$·$m^{3-3n}$·min) |
| $K_1$ | equilibrium constant of reaction '5' |
| $K_2$ | equilibrium constant of reaction '7' |
| $K_3$ | equilibrium constant of reaction '8' |
| $k_{sp,CaCO_3}$ | solubility product of $CaCO_3$ |
| $k_{sp,CaSO_4}$ | solubility product of $CaSO_4$ |
| $M$ | molecular weight of $CaCO_3$, g/mol |
| $n$ | reaction order of nucleation |
| $P$ | population density of $CaCO_3$ crystal, number/$m^3$ |
| $P(L_i)$ | population density of crystal with size of $L_i$, number/$m^3$ |
| $r_{CaCO_3}$ | crystallization rate of $CaCO_3$, mol/($m^3$·min) |
| $r_g$ | crystal growth rate, mol/($m^3$·min) |
| $r_n$ | nucleation rate, mol/($m^3$·min) |
| $R$ | gas constant, J/(mol·K) |
| $t$ | time, min |
| $T$ | temperature, K |

*Greek symbols*

| | |
|---|---|
| ρ | density of $CaCO_3$, g/$m^3$ |
| γ | surface tension of $CaCO_3$ |

the conversion was less than 60% and the particle size was around 10–20 μm. Kyungsun Song et al. [21] did the research in the same system at the room temperature, they got $CaCO_3$ with the diameters around 5–10 μm. The three-phase reaction system had more advantages for nano-$CaCO_3$ production due to one step to get the products which could simplify the process. But the particle size of $CaCO_3$ product in these researches never reached nano grade. Based on our recent researches, the nano-$CaCO_3$ could be derived from PG via reactive crystallization in ammonia aqueous under continuous $CO_2$ injection [22]. However, the crystallization kinetics of the nano-size $CaCO_3$ produced from this system has not been reported. Some of the researches about the crystallization mechanism of $CaCO_3$ from different systems have been reported, such as calcium acetate-ammonium carbamate-$CO_2$ batch system [23], a reverse macro emulsion system based on N-stearoyl acid surfactant with head group of serine [24], the stack-like crystallization of calcium carbonate in the presence of hen egg white under direct drying and vacuum freeze drying [25].

$$CaSO_4 \cdot 2H_2O(s) + 2NH_4OH(aq) + CO_2(g) \rightarrow (NH_4)2SO_4 + CaCO_3(s) + 2H_2O(l) \quad (1)$$

The purpose of this paper was to disclose the nucleation and growth process of PG-derived nano-$CaCO_3$ by reactive crystallization in the gas ($CO_2$)-liquid ($NH_3$·$H_2O$)-solid ($CaSO_4$) three-phases system. The nano-$CaCO_3$ prepared in this system referred to calcite nanoparticles with the mean particle sizes of about 100 nm. By analyzing the crystallization mechanism of $CaCO_3$, a new kinetic model would be deduced based on population balance with the favor of Laplace transform and experimental results at a range of reaction temperatures and $CO_2$ flow rates.

## 2. Modeling

### 2.1. Three phases reaction process

The reactive crystallization of PG was a complex process and involves gas ($CO_2$), liquid ($NH_3$·$H_2O$) and solid (PG) three phases. The reactions occurring during the process could be described in the following four steps with equations, which were illustrated in Fig. 1.

a. The dissociation of ammonium in water solution

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (2)$$

b. $CO_2$ absorption and reaction

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \quad (3)$$

$$HCO_3^- + NH_3 \rightleftharpoons CO_3^{2-} + NH_4^+ \quad (4)$$

$$CO_3^{2-} + NH_4^+ \rightleftharpoons H_2NCOO^- + H_2O \quad (5)$$

c. The dissolution of $CaSO_4$

$$CaSO_4(s) \rightleftharpoons Ca^{2+} + SO_4^{2-} \quad (6)$$

d. The conversion of $CaCO_3$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \quad (7)$$

At the initial stage of the reactions, the adsorption of $CO_2$ was relatively small and there was a lot of ammonia in this solution, so the reaction rate of reaction (3) was much bigger than that of reaction(4) and (5). Also, only reaction (4) and (5) were related to the $CO_3^{2-}$ ion concentration in this system. The chemical reaction equilibrium constant expressions for Eqs. (2), (4) and (5) were listed as follow.

$$K_1 = \frac{[NH_4^+][OH^-]}{[NH_3]} \quad (8)$$

$$K_2 = \frac{[CO_3^{2-}][NH_4^+]}{[HCO_3^-][NH_3]} \quad (9)$$

$$K_3 = \frac{[H_2NCO_2^-]}{[CO_3^{2-}][NH_4^+]} \quad (10)$$

The solubility products of $CaSO_4$ and $CaCO_3$ in Eqs. (6) and (7) are as followings.

$$k_{sp,CaSO_4} = [SO_4^{2-}][Ca^{2+}] \quad (11)$$

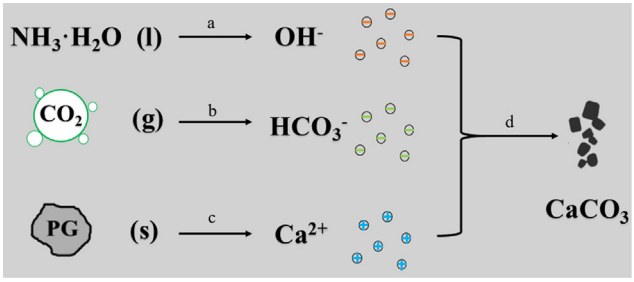


**Fig. 1.** Reaction mechanism of speculation.