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Study of the synthesis and crystallization kinetics of magnesium hydroxide

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HIGHLIGHTS

- Ion conductivity method was used to study nucleation and growth of $Mg(OH)_2$.
- Induction times were determined for various concentrations and temperatures.
- Kinetic parameters were determined from experimental data.
- Particle size of the crystals were in the nanometer range.

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ABSTRACT

The crystallization kinetics of magnesium hydroxide in low concentration solutions has been studied using an electrical conductivity method. Using various experimental relationships, several kinetic factors could be determined during the nucleation and growth process. From measurements of ion concentrations at various temperatures, the induction period of nucleation could be determined. As concentration and temperature increase, the crystallization rate increases affecting the nucleation and crystal growth of $Mg(OH)_2$. The crystal-solution interfacial surface tension was also calculated and shown to be affected by the magnesium anion source. The results show that a uniform particle size distribution of nuclei is formed during the initial homogeneous nucleation process and the nucleation and crystal growth rates can be represented by a first order reaction equation. Through the study of crystallization kinetics, a control strategy is proposed to synthesize a uniform particle size distribution of magnesium hydroxide.

1. Introduction

Magnesium hydroxide ($Mg(OH)_2$) is used in many industries. For example, $Mg(OH)_2$ can be used as a flame-retardant filler in polymer and inorganic materials [1–4], acid neutralizer in the area of environmental protection [5], and one of the raw materials for the production of magnesium oxide [6]. Since the size and morphology of $Mg(OH)_2$ determine its properties, having a controlled synthesis to obtain uniform particle size distribution is important [7]. Study on the crystallization kinetics of $Mg(OH)_2$ can provide important technological parameters for production in industry.

When the ion product of $Mg(OH)_2$ is greater than its solubility product in solution, it is possible to precipitate $Mg(OH)_2$ crystals. However, crystal growth in a saturated solution is a delicate process and the crystallization kinetics is determined by several complex factors [8]. Crystallization of precipitates typically includes four processes: formation of supersaturation, emergence of a new phase, nucleation, and grain growth. In a solution system, various ionic or molecular units do not exist individually but interact with each other to form small molecular clusters. The molecular clusters reach a dynamic equilibrium, and the whole system is thermodynamically stable. When the solution system reaches

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supersaturation, the dynamic equilibrium between the clusters will change and simultaneously form a large number of molecular clusters with varying sizes. These molecular clusters are thermodynamically unstable, and gradually grow to a critical size (r^*) as the energy reaches a maximum. When the cluster size is greater than r^*, excess energy will be released and a new phase will be formed; the newly formed nuclei continue to absorb the molecular clusters and grow to complete the irreversible grain growth process.

The research methods to study crystallization kinetics are generally divided into two categories. The concentration monitoring method measures ion concentrations during the solution reaction process [9,10]. The particle size analysis route measures particle size of the final precipitates [11–15]. However, in the particle size analysis route, $Mg(OH)_2$ particles readily aggregate with each other, leading to difficultly in determining the kinetics during particle formation. Solutions must be precipitated and filtered to analyze. Therefore, the particle size analysis method does not efficiently reflect the crystallization kinetics throughout the nucleation and growth process. In this paper, we studied the crystallization kinetics of magnesium hydroxide in a low concentration solution via an electrical conductivity method, a concentration monitoring method. By monitoring electrical conductivity during the solution reaction process, changes in $[Mg^{2+}]$ and $[OH^-]$ can be measured during nucleation and growth. The induction period of nucleation (t_{ind}), the specific surface Gibbs energy function of nucleation, and the variation of the critical particle size r^*, can be obtained from various experimental relationships. The effect of different anions on the specific surface Gibbs energy of nucleation was investigated by changing the anion sources for magnesium.

2. Experimental

The starting chemicals were reagent grade $MgCl_2 \cdot 6H_2O$, $Mg(CH_3COO)_2$, $Mg(NO_3)_2$, or $MgSO_4$ (>99%) and sodium hydroxide NaOH (>99%). The magnesium salt (i.e. $MgCl_2 \cdot 6H_2O$) and NaOH were first dissolved in distilled water, separately. Then the two solutions were preheated in a water bath. Subsequently, the same volume solutions were mixed together by constant mechanical stirring (300 r/min) and monitored for an electrical conductivity change. Fig. 1 shows the diagram for a typical experimental apparatus.

The relationship between ion concentration and electrical conductivity in the supersaturated solution can be determined by measuring the variation of electrical conductivity (κ) versus time (t). Reaction order of $Mg(OH)_2$, the nucleation rate constant K_1, and the crystal growth rate constant K_2 are determined via curve fitting at different experimental temperatures. By plotting $\ln K$ vs. $-1/T$, the reaction activation energies, E_a, of nucleation and crystal growth were obtained.

3. Results and discussion

3.1. Determination of electrical conductivity and Mg^{2+} concentration

The formation process of $Mg(OH)_2$ crystals is illustrated in Fig. 2, where the control of $Mg(OH)_2$ precipitation is a nucleation and growth process related to its critical particle size and is key for crystallization kinetics. Ions contributing to the electrical conductivity in the solution reaction process include Mg^{2+}, OH^-, Cl^-, Na^+ and trace amounts of impurities. Since the concentration of the solutions is low, the electrical conductivity and concentration meet certain functional relationships, such as the Fuoss–Onsager equation [16–18]. The typical equations are as follows:

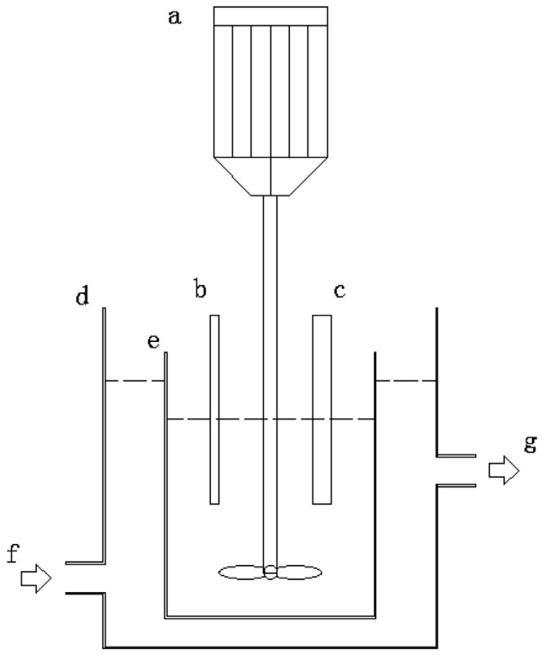

Fig. 1. Schematic for a typical experimental apparatus. (a) stirring motor, (b) thermometer, (c) conductivity electrode, (d) constant temperature water bath, (e) inner container, (f) water inlet, and (g) water outlet.

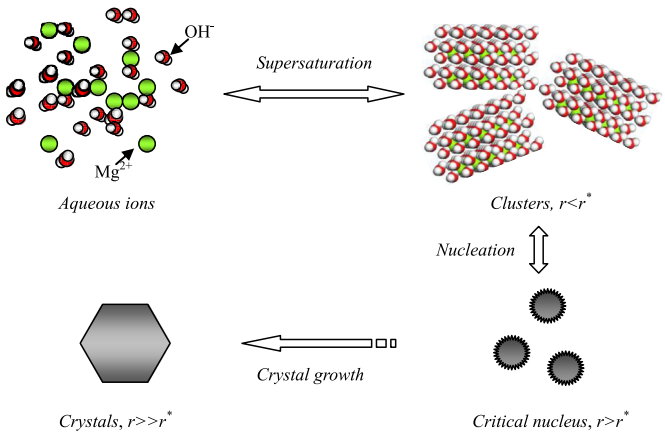

Fig. 2. Formation process of $Mg(OH)_2$ crystals.

The limiting molar conductivity of the electrolyte solution is,

$$\Lambda = \Lambda_0 - \left[\frac{|z_+ z_-| e^2 q \Lambda_0}{3 \times 4\pi\varepsilon_0 \varepsilon k_B (1+\sqrt{q})} + \frac{F^2(|z_+|+|z_+|)}{4\pi\eta_0 N_A}\right]\kappa \quad (1)$$

$$\text{where,} \quad \kappa = \sqrt{\frac{2e^2 N_A}{\varepsilon k_B T}}\sqrt{I} \quad (2)$$

and Λ_0 is the molar conductivity of an infinitely dilute solution, z_+ and z_- denote cation and anion charges, e is the electronic charge, k_B is the Boltzmann constant, $q = 1/2$, N_A is Avogadro constant, F is Faraday constant, ε is the dielectric constant of solution, η_0 is the viscosity of solution, and T is temperature.

I is the ionic strength,

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