Research Article

Influence of NH₄Cl on Hydrothermal Formation of α-CaSO₄·0.5H₂O Whiskers

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Received 16 November 2014; Revised 28 February 2015; Accepted 4 March 2015

Academic Editor: Yangchuan Xing

The influence of NH₄Cl on hydrothermal formation of CaSO₄·0.5H₂O whiskers from CaSO₄·2H₂O precursor at 135°C was investigated in this paper. Compared with the blank experiment, the presence of 3 × 10⁻² mol·L⁻¹ NH₄Cl led to the increase of the length of the whiskers from 50 to 160 μm or 150 to 300 μm and the decrease of the diameters from 1.0 to 1.5 μm or 0.2 to 0.5 μm. The dissolution of CaSO₄·2H₂O was accelerated by the complex interactions with NH₄Cl and the soluble cations, which led to the decrease of the induction time for the occurrence of α-CaSO₄·0.5H₂O from 46 minutes to 34 minutes and the formation of CaSO₄·0.5H₂O whiskers with high aspect ratios. Furthermore, the critical supersaturation for the formation of α-CaSO₄·0.5H₂O was investigated.

1. Introduction

The formation of calcium sulfate (CaSO₄) whiskers with high aspect ratios has drawn much attention in recent years owing to their nontoxic and perfect mechanical properties and the wide applications in the fabrication of intensified composites [1–4]. Calcium sulfate whiskers were usually prepared by the first formation of α-CaSO₄·0.5H₂O whiskers followed by calcination at 600 to 800°C since the anisotropic –Ca–SO₄–Ca–SO₄–Ca–chains in α-CaSO₄·0.5H₂O favored their growth along c-axis [5].

α-CaSO₄·0.5H₂O whiskers can be prepared by wet processes, including hydrothermal method, microemulsion, or acidification methods, and the hydrothermal method has been widely used owing to its high efficiency and easy control of the formation process [6–9]. α-CaSO₄·0.5H₂O whiskers were usually produced by hydrothermal conversion of CaSO₄·2H₂O at 100 to 150°C, and the hydrothermal dissolution of CaSO₄·2H₂O and the precipitation of CaSO₄·0.5H₂O were connected with the process parameters such as the supersaturation, temperature, pH, and the organic/inorganic additives [10–15]. For example, it was reported that the presence of Sr²⁺ or PO₄³⁻ accelerated the precipitation of CaSO₄·2H₂O while the addition of Cd²⁺, Cu²⁺, Fe³⁺, and Cr³⁺ inhibited the crystallization of CaSO₄·2H₂O. The hydrothermal conversion of CaSO₄·2H₂O to CaSO₄·0.5H₂O was accelerated by the presence of CTAB and inhibited by the presence of arginine, aspartic acid, serine, glycine and sodium dodecyl sulfate, and so forth [16–20].

In this paper, CaSO₄·0.5H₂O whiskers with high aspect ratios were produced by hydrothermal treatment of CaSO₄·2H₂O precursor at 135°C in the presence of NH₄Cl. The influences of NH₄Cl on supersaturation, induction time, and morphology of the CaSO₄·0.5H₂O whiskers were investigated and the corresponding phenomena were discussed.

2. Experimental

2.1. Experimental Procedure. Commercial CaSO₄·2H₂O with analytical grade was sintered at 150°C for 6.0 h, then mixed with deionized water and NH₄Cl at room temperature to get the slurries containing 4.0 (wt/v) % CaSO₄·2H₂O and 0 to 7.48 × 10⁻² mol·L⁻¹ NH₄Cl. The slurries were then transferred to the Teflon-lined stainless autoclaves with an inner volume of 60 mL and kept under isothermal condition at 135°C for 0 to 2.0 h. After hydrothermal treatment, the products were
cooled down to 90°C naturally, filtrated, washed with alcohol for three times, and dried in air at 55°C for 12.0 h until the weight reached a stable value. The precipitates and the filtrates were collected and used for characterizations.

2.2. Characterization. The morphology of the samples were detected with the field emission scanning electron microscopy (SEM, JSM 7401F, JEOL, Japan). The average diameters and the lengths of the hydrothermal products were estimated by direct measuring about 200 particles from the typical FESEM images with magnifications of 250 to 5000. The structures of the samples were identified by powder X-ray diffractometer (XRD, D8 advanced, Brucker, Germany) using Cu Kα radiation (λ = 1.54178 Å). The solution pH was measured by a pH meter (pH meter, Mettler Toledo FE20, China).

The composition of the hydrothermal precipitates which were composed of CaSO₄·2H₂O and α-CaSO₄·0.5H₂O was detected by analyzing the contents of the crystalline water in the precipitates using differential thermal-thermogravimetric (DTA-TG) analysis (TGA/DSC1/1600HT, Mettler-Toledo, Switzerland). The soluble Ca²⁺ and SO₄²⁻ were analyzed by EDTA titration and barium chromate spectrophotometry (Model 722, Xiaoguang, China), respectively.

3. Result and Discussion

3.1. Influence of NH₄Cl on Morphology of α-CaSO₄·0.5H₂O. Figure 1 shows the effect of NH₄Cl on the XRD patterns and morphology of the hydrothermal products. XRD analyses showed that all of the hydrothermal products were composed of α-CaSO₄·0.5H₂O and most of the XRD peaks as (200), (020), and (400) were attributed to the planes parallel to c-axis, indicating the possible preferential growth of α-CaSO₄·0.5H₂O along the c-axis. The whiskers with a length of 50 to 160 μm and a diameter of 1.0 to 1.5 μm were prepared in the absence of NH₄Cl (Figure 1(a)); the increase of NH₄Cl from 7.48 × 10⁻³ mol·L⁻¹ to 3 × 10⁻² mol·L⁻¹ led to the increase of the lengths from 100 to 220 μm to 150 to 300 μm, the decrease of the diameters from 0.8 to 1.2 μm to 0.2 to 0.5 μm, and the increase of the average aspect ratios from 180 to 550 (Figures 1(b) and 1(c)). In the case of 7.48 × 10⁻² mol·L⁻¹ NH₄Cl, the lengths and diameters of the whiskers were 160 to 330 μm and 2.2 to 4.0 μm, respectively. The presence of ethanol, potassium sodium tartrate, and sodium citrate lead to the increase in the aspect ratios of CaSO₄·0.5H₂O whiskers from 1.7 to 4.7. Hou and Xiang prepared CaSO₄·0.5H₂O whiskers with average aspect ratio of 325 by hydrothermal treatment of the active CaSO₄·2H₂O precursor [10]. It is reported that the presence of ethanol and potassium sodium tartrate lead to the increase in the aspect ratios of whiskers from 1.7 to 4.8 [21–23].

3.2. Influence of NH₄Cl on Composition of Precipitates and Solutions. Figure 2 shows the influence of NH₄Cl on the conversion of CaSO₄·2H₂O to α-CaSO₄·0.5H₂O. α-CaSO₄·0.5H₂O occurred at about 46 minutes and converted to CaSO₄·0.5H₂O completely at about 60 minutes in the absence of NH₄Cl, while α-CaSO₄·0.5H₂O occurred at 42 minutes, 34 minutes, and 66 minutes in the presence of 7.48 × 10⁻³ mol·L⁻¹, 3 × 10⁻² mol·L⁻¹, and 7.48 × 10⁻² mol·L⁻¹ NH₄Cl, respectively. The above work showed that the formation of α-CaSO₄·0.5H₂O was accelerated with the increase of NH₄Cl up to 3 × 10⁻² mol·L⁻¹ and then slowed down if NH₄Cl ≥ 7.48 × 10⁻² mol·L⁻¹.

Figure 3 shows the influence of NH₄Cl on pH and the concentrations of the total soluble Ca²⁺ and SO₄²⁻ (abbreviated as [Ca²⁺]₀ and [SO₄²⁻]₀, resp.) detected in the experiments. The increase of [Ca²⁺]₀ and [SO₄²⁻]₀ and the decrease of pH with the increase of NH₄Cl should be attributed to the complex interactions of NH₄Cl and the hydrolysis of NH₄Cl, respectively. The possible reactions involved in the hydrothermal solutions at 135°C are listed in Table 1. The solubility products of (NH₄)₂SO₄ and CaCl² in the hydrothermal condition were 10⁻¹⁸ and 10⁻⁰.⁸⁶, respectively, which indicated that (NH₄)₂SO₄ and CaCl² could
Figure 2: Influence of \( \text{NH}_4\text{Cl} \) on formation of \( \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} \). \( \text{NH}_4\text{Cl} \) (mol\( \cdot \)L\(^{-1} \)): 1-0, 2-7.48 \times 10^{-3}, 3-3 \times 10^{-2}, 4-7.48 \times 10^{-2}.

Figure 3: Influence of \( \text{NH}_4\text{Cl} \) on \([\text{Ca}^{2+}]_T\) (a), \([\text{SO}_4^{2-}]_T\) (b), and pH (c). \( \text{NH}_4\text{Cl} \) (mol\( \cdot \)L\(^{-1} \)): 1-0, 2-7.48 \times 10^{-3}, 3-3 \times 10^{-2}, 4-7.48 \times 10^{-2}.

Table 1: Thermodynamic equilibrium reactions.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium Constant</th>
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<tbody>
<tr>
<td>NH₄⁺ + Cl⁻ = NH₄Cl</td>
<td>$K_{eq} = 10^{-1.66}$</td>
</tr>
<tr>
<td>NH₄⁺ + OH⁻ = NH₃(a) + H₂O</td>
<td>$K_{eq} = 10^{-1.66}$</td>
</tr>
<tr>
<td>2NH₄⁺ + SO₄²⁻ = (NH₄)₂SO₄</td>
<td>$K_{eq} = 10^{-10.09}$</td>
</tr>
<tr>
<td>NH₄⁺ + HSO₄⁻ = NH₄HSO₄</td>
<td>$K_{eq} = 10^{-6.866}$</td>
</tr>
<tr>
<td>Ca²⁺ + Cl⁻ = CaCl⁺</td>
<td>$K_{eq} = 10^{-2.57}$</td>
</tr>
</tbody>
</table>

exist stably in the hydrothermal solutions. These reactions would promote the dissolution of CaSO₄·2H₂O due to the shift of chemical equilibrium and the concentration of the total soluble Ca²⁺ (including Ca₂⁺, CaCl⁺, CaCl₂, Ca(OH)²⁻, and Ca(OH)₂) and the total soluble SO₄²⁻ (including SO₄²⁻, HSO₄⁻, (NH₄)₂SO₄, NH₄HSO₄, and H₂SO₄) would increase. Similar phenomena have been reported. Therefore, it was concluded that the critical supersaturation for the formation of $\alpha$-CaSO₄·0.5H₂O became gradually lower than 2 × 10⁻² mol·L⁻¹. The above phenomena confirmed the possible dissolution-precipitation mechanism for the hydrothermal formation of $\alpha$-CaSO₄·0.5H₂O from CaSO₄·2H₂O precursor.

3.3. Thermodynamic Equilibrium Analysis. The equilibrium constants were calculated using reactions listed in Table 1 and the basic data in HSC chemistry 7.0 [24].

The equilibrium concentrations of the soluble species can be calculated based on the above equilibrium equations, [Ca²⁺]₀, [SO₄²⁻]₀, and pH detected in the experiments (Figure 3). Figure 4 shows the influence of NH₄Cl on the concentrations of free Ca²⁺, SO₄²⁻, and HSO₄⁻ (abbreviated as [Ca²⁺], [SO₄²⁻], and [HSO₄⁻], resp.). Free Ca²⁺ and SO₄²⁻ are the simple ion of Ca²⁺ and SO₄²⁻, not including CaCl⁺, Cl⁻, Ca(OH)²⁻, and Ca(OH)₂ or HSO₄⁻, (NH₄)₂SO₄, NH₄HSO₄, and H₂SO₄. [Ca²⁺] increased with the increase of NH₄Cl (Figure 4(a)), indicating that the complex interactions among NH₄Cl and the soluble cations as Ca²⁺ accelerated the dissolution of CaSO₄·2H₂O. Compared with [Ca²⁺] shown in Figure 4(a), [SO₄²⁻] was much lower and decreased with the increase of NH₄Cl (Figure 4(b)), which should be related to the hydrolysis of NH₄Cl. The hydrolysis of NH₄Cl led to the decrease of pH or the increase of [H⁺], which promoted the conversion of SO₄²⁻ to HSO₄⁻ owning to the strong complex between H⁺ and SO₄²⁻. As a result, although the total soluble SO₄²⁻ increased with the increase of NH₄Cl, the free SO₄²⁻ showed an opposite trend and decreased. In the case of the blank experiment without NH₄Cl (Figure 4(c)), [HSO₄⁻] was lower than $2 \times 10^{-2}$ mol·L⁻¹, which was much lower than [SO₄²⁻]. [HSO₄⁻] increased up to $5.3 \times 10^{-2}$ mol·L⁻¹ as the increase of [NH₄Cl] up to $7.48 \times 10^{-2}$ mol·L⁻¹.

3.4. Effect of Supersaturation on Induction Time. Figure 5 shows the influence of NH₄Cl on the supersaturation (S) for the formation of $\alpha$-CaSO₄·0.5H₂O, where $S = [\text{Ca}^{2+}] / [\text{SO}_4^{2-}]$ and $K_{sp}$ for $\alpha$-CaSO₄·0.5H₂O at 135°C was $10^{-5.344}$. $S$ increased with the increase of the reaction time up to 60–70 minutes and then decreased with further prolongation of the reaction time. $S$ also increased with the increase of NH₄Cl up to $3 \times 10^{-2}$ mol·L⁻¹, while S became quite low at $7.48 \times 10^{-2}$ mol·L⁻¹ NH₄Cl. The above work showed that a higher supersaturation favored the faster formation of $\alpha$-CaSO₄·0.5H₂O.

It was noticed that the NH₄Cl concentrations containing 0 to 7.48 × 10⁻² mol·L⁻¹ NH₄Cl were quite similar, being 209.5 (Point C), 210.2 (Point B), 208.4 (Point A), and 209.2 (Point D) at 0, $7.48 \times 10^{-3}$, $3 \times 10^{-2}$, and $7.48 \times 10^{-2}$ mol·L⁻¹ NH₄Cl, respectively. The points of A, B, C, and D were arranged around a horizontal line, corresponding to $S = 209.5$. Therefore, it was concluded that the critical supersaturation for the formation of $\alpha$-CaSO₄·0.5H₂O at 135°C was 209.5, which was irrelevant to the presence of NH₄Cl. $\alpha$-CaSO₄·0.5H₂O occurred if the solution supersaturation was higher than the critical supersaturation. $S$ increased with the increase of NH₄Cl up to $3 \times 10^{-2}$ mol·L⁻¹, which led to the decrease of the induction time for $\alpha$-CaSO₄·0.5H₂O. In the case of $7.48 \times 10^{-2}$ mol·L⁻¹ NH₄Cl, the low $S$ led to the prolongation of the induction time for the formation of $\alpha$-CaSO₄·0.5H₂O due to the hydrolysis of NH₄Cl and the decrease of [SO₄²⁻].

The morphology of $\alpha$-CaSO₄·0.5H₂O was connected with the solution supersaturation. According to the traditional crystal theories, nuclei with small sizes prefer to be produced in solutions with high supersaturations, which favored the formation of CaSO₄·0.5H₂O whiskers with thin diameters and high aspect ratios. As shown in Figures 1 and 5, CaSO₄·0.5H₂O whiskers formed in the presence of 3 × $10^{-2}$ mol·L⁻¹ NH₄Cl were of the smallest diameter (0.2 μm) and the highest aspect ratio (550) owing to the comparatively high $S$ compared with those in the presence of 0, $7.48 \times 10^{-2}$, and $7.48 \times 10^{-2}$ mol·L⁻¹ NH₄Cl.

4. Conclusion

A facile NH₄Cl-assisted hydrothermal method was developed to synthesize $\alpha$-CaSO₄·0.5H₂O whiskers with high aspect ratios. The presence of 0 to $3 \times 10^{-2}$ mol·L⁻¹ NH₄Cl led to the decrease of the induction period from 46 minutes to 34 minutes and the increase of the aspect ratios of the whiskers from 110 to 550. The critical supersaturation for the formation of CaSO₄·0.5H₂O was 209.5, irrelevant to the presence of NH₄Cl. In the cases of 0 to $3 \times 10^{-2}$ mol·L⁻¹ NH₄Cl, the complex interactions among NH₄Cl and the soluble ions led to the increase of the supersaturation, which favored the quick occurrence of $\alpha$-CaSO₄·0.5H₂O nuclei with small sizes.
Figure 4: Influence of NH$_4$Cl on [Ca$^{2+}$], [SO$_4^{2-}$] and [HSO$_4^-$]. NH$_4$Cl (mol·L$^{-1}$): 1-0, 2-7.48 × 10$^{-3}$, 3-3 × 10$^{-2}$, 4-7.48 × 10$^{-2}$.

Figure 5: Influence of NH$_4$Cl on supersaturation. NH$_4$Cl (mol·L$^{-1}$): 1-0, 2-7.48 × 10$^{-3}$, 3-3 × 10$^{-2}$, 4-7.48 × 10$^{-2}$. 

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<table>
<thead>
<tr>
<th>Concentration (mol·L$^{-1}$)</th>
<th>Time (min)</th>
<th>[Ca$^{2+}$]</th>
<th>[SO$_4^{2-}$]</th>
<th>[HSO$_4^-$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>0.03</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>0.06</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>0.09</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>0.12</td>
<td>0.06</td>
<td>0.04</td>
</tr>
</tbody>
</table>
and promoted the formation of α-CaSO₄·0.5H₂O whiskers with high aspect ratios. In the case of 7.48 × 10⁻⁵ mol L⁻¹ NH₄Cl, the hydrolysis of NH₄Cl led to the decrease of [SO₄²⁻], which reduced the solution supersaturation and prolonged the induction period of α-CaSO₄·0.5H₂O, producing α-CaSO₄·0.5H₂O with comparatively large diameters and low aspect ratios.

Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments
This project is supported by the National Science Foundation of China (nos. 51374138, 51174125, and 51234003) and the National Hi-Tech Research and Development Program of China (863 Program, 2012AA061602).

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