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Research Article

Influence of the Process Parameters on the Formation of $CaSO_4 \cdot 0.5H_2O$ Whiskers

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This paper discussed the influence of the process parameters such as the temperature, the mixing ways, and the molar ratios of the reactants on the morphology of the $CaSO_4 \cdot 2H_2O$ precursors and the $CaSO_4 \cdot 0.5H_2O$ whiskers. The experimental results indicated that $CaSO_4 \cdot 0.5H_2O$ whiskers with a length of 80–310 μm and a width of 0.8–8.0 μm were produced at hydrothermal condition, using $CaSO_4 \cdot 2H_2O$ fine particles as the precursors which were formed by adding Na_2SO_4 solution into $CaCl_2$ solution at 25°C at the molar ratio of Na_2SO_4 to $CaCl_2$ being 0.5 : 1. A lower supersaturation and a higher $[Ca^{2+}]/[SO_4{}^{2-}]$ molar ratio favored the formation of $CaSO_4 \cdot 2H_2O$ particles with small sizes and the hydrothermal synthesis of $CaSO_4 \cdot 0.5H_2O$ whiskers with high aspect ratios.

1. Introduction

As a kind of environmental friendly material, the calcium sulfate whisker is widely used as the reinforcing material in many fields such as plastics, ceramics, papers, and cements, owing to its high tensile strength, good electronic isolation, and perfect stability at high temperature or in acidic/alkaline media [1–3]. Many methods have been developed to synthesize calcium sulfate whiskers, including the hydrothermal route, the normal acidic synthesis route, the microemulsion route, and the microwave route, [4–9]. The hydrothermal method was getting more and more attention owing to the regular morphology of the product, the moderate condition, and the adjustable process parameters [10, 11].

This paper investigated the possibility of the synthesizing of $CaSO_4 \cdot 0.5H_2O$ whiskers via coprecipitation at room temperature followed by hydrothermal treatment, using Na_2SO_4 and $CaCl_2$ as the raw materials. The influences of the process parameters for the formation of $CaSO_4 \cdot 2H_2O$ precursors such as the temperature, the molar ratio, and the mixing ways of the raw materials on the morphology of the hydrothermal products were investigated, and the optimized synthesizing condition was suggested.

2. Experimental

2.1. Experimental Procedure. 0.2–1.2 $mol \cdot L^{-1}$ Na_2SO_4 were mixed with 0.2–1.2 $mol \cdot L^{-1}$ $CaCl_2$ at room temperature and stirring (350 min^{-1}) conditions via three different routes: adding $CaCl_2$ to Na_2SO_4 or vise versa or adding $CaCl_2$ and Na_2SO_4 simultaneously into a blank container. The molar ratio of $CaCl_2$ to Na_2SO_4 was kept as 0.1–10 : 1, and the dripping speed was 3 $mL \cdot min^{-1}$. The suspension was stirred for 1 h after the mixing of the raw materials, then transferred to a small stainless steel autoclave with an inner volume of 80 mL, heated (3°$C \cdot min^{-1}$) to 120–200°C, and kept in isothermal condition for 1.0–8.0 h. After hydrothermal treatment, the product was cooled to room temperature naturally, filtrated, washed with distilled water and dried at 105°C for 2 h.

2.2. Analysis Method. The morphology of the products was observed by using the field emission scanning electron microscope (FSEM, JSM 7401F, JEOL, Japan). The composition of the products was characterized by X-ray powder diffractometer (XRD, D/Max2500, Rigaku, Japan), using CuKα (λ = 1.54148 Å). The concentrations of Ca^{2+} and $SO_4{}^{2-}$ were analyzed by EDTA titration and barium chromate

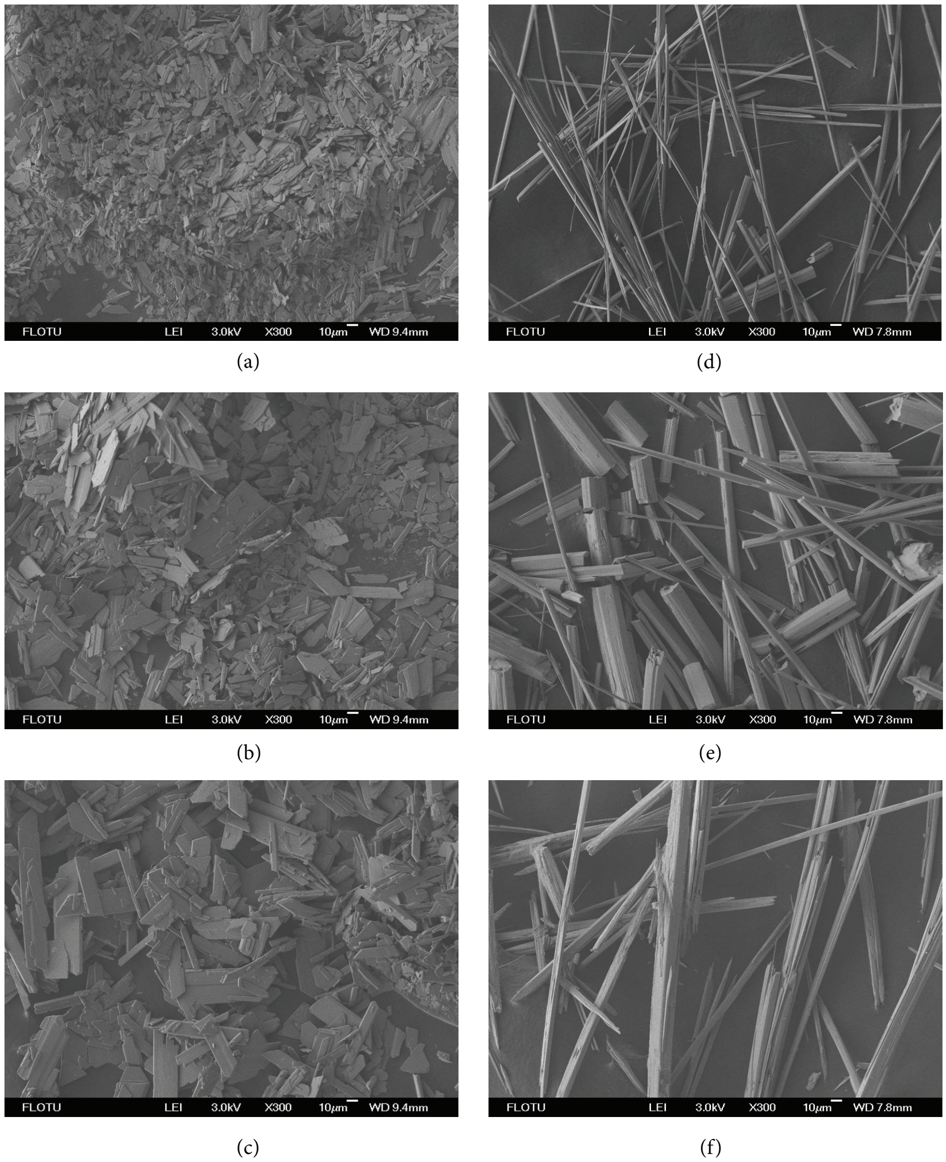


Figure 1: Influence of temperature on the morphology of the precursors ((a)–(c)) and the hydrothermal products ((d)–(f)). Temperature (°C): (a), (d): 25, (b), (e): 60, (c), (f): 90.

spectrophotometry (Model 722, Xiaoguang, China), respectively.

3. Results and Discussion

3.1. Influence of Temperature. Figure 1 shows the morphology of the precursors and the hydrothermal products obtained by adding Na_2SO_4 solution into $CaCl_2$ solution at different temperatures (25°C, 60°C, and 90°C). Figure 2 shows the XRD patterns of the precursor and the hydrothermal product obtained by mixing the reactants at 25°C.

The data in Figure 1 indicated that the precursors were plate-like particles. The plates formed at 25°C, 60°C, and 90°C were with a length of 3–45 μm, 8–80 μm, and 12–150 μm and a width of 0.8–15 μm, 1.5–28 μm, and 1.5–45 μm, respectively. The increase of temperature led to the increase of the precursor sizes. The data in Figure 1 also showed that the morphology of the hydrothermal products was connected closely with the formation temperature of the precursors. The hydrothermal products were uniform whiskers with lengths of 80–310 μm and diameters of 0.8–8 μm if the precursor was prepared at 25°C. Being composed of the mixtures of the whiskers and the rod-like particles, the hydrothermal products with a length of 30–240 μm, 30–310 μm and a diameter of 1.5–28 μm, 4.5–22 μm were formed using the precursors formed at 60°C and 90°C, respectively. The hydrothermal products became more ununiform and thicker as increases the precursor temperature, from 25°C to 90°C.

The data in Figure 2 indicated that precursor was composed of $CaSO_4 \cdot 2H_2O$ and the hydrothermal product was composed of $CaSO_4 \cdot 0.5H_2O$.

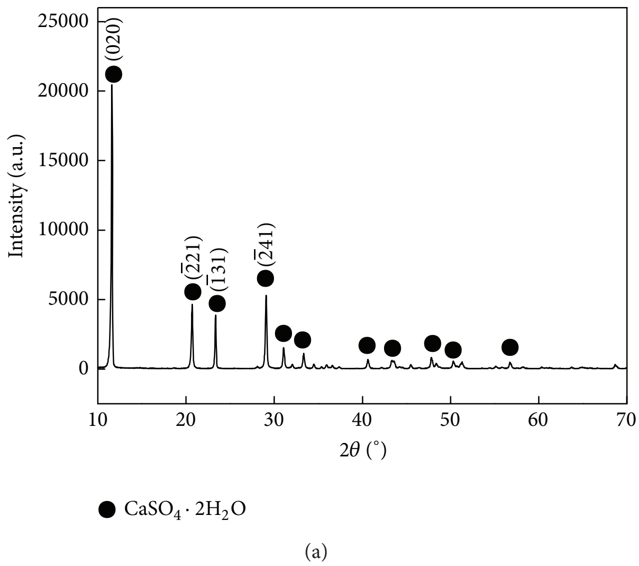


Figure 2: XRD patterns of the precursor (a) and the hydrothermal product (b).

Table 1: Influence of temperature on the supersaturation of $CaSO_4{\cdot}2H_2O$.

Temperature, °C	K_{sp}	$[Ca^{2+}][SO_4{}^{2-}]$	S
25	3.178×10^{-5}	6.5043×10^{-3}	204.7
60	2.375×10^{-5}	6.5043×10^{-3}	273.9
90	1.456×10^{-5}	6.5043×10^{-3}	446.7

The change of the morphology of precursor with temperature may be connected with the varying super-saturations at different temperatures. Super-saturation (S) is defined as follows:

$$S = \frac{\left[Ca^{2+}\right]\left[SO_4{}^{2-}\right]}{K_{sp}}, \tag{1}$$

where S is the super-saturation, $[Ca^{2+}]$ and $[SO_4{}^{2-}]$ are the practical concentrations of the soluble Ca^{2+} and $SO_4{}^{2-}$, respectively, and K_{sp} is the equilibrium constant for the dissolution of $CaSO_4{\cdot}2H_2O$, which can be calculated out from the HSC software [12].

The influence of temperature on the super-saturation is listed in Table 1 at the mixing time of 1 minute. It was supposed that no $CaSO_4{\cdot}2H_2O$ precipitate was formed within 1 minute of mixing time.

The data in Table 1 showed that the increase of temperature led to the decrease of the K_{sp} of $CaSO_4{\cdot}2H_2O$. Therefore, the super-saturation at high temperature is bigger than the super-saturation at low temperature. According to the crystallinity theory, the super-saturation is connected closely with the growth rate of the crystals. The bigger the super-saturation, the faster the nucleation rate and the growth rate. It is known from Figure 1 that smaller precursors were formed at lower temperature, indicating that the formation of the $CaSO_4{\cdot}2H_2O$ precursor may be connected mainly with the growth of the crystals: a lower temperature led to a smaller super-saturation and a slower growth rate of crystals, which favored the formation of $CaSO_4{\cdot}2H_2O$ precursors with smaller particles as well as the formation of uniform $CaSO_4{\cdot}0.5H_2O$ whiskers at hydrothermal condition. Therefore, compared with 60°C and 90°C, 25°C was more favorable for the formation of $CaSO_4{\cdot}2H_2O$ precursors with small sizes.

3.2. Influence of the Mixing Ways of the Reactants. The influences of the mixing ways of the reactants at 25°C on the morphology of the precursors and the hydrothermal products are shown in Figure 3.

The particle sizes of the plate-like precursors connected closely with the mixing ways of the reactants. The lengths of the plates were 15–140 μm, 3–45 μm, and 10–60 μm and the widths of the particles were 1.5–35 μm, 0.8–15 μm, and 1.5–30 μm in the cases of the following mixing ways of the reactants: adding $CaCl_2$ to Na_2SO_4, adding Na_2SO_4 to $CaCl_2$ and adding Na_2SO_4 and $CaCl_2$, simultaneously, respectively. The particle sizes of the precursors formed by adding Na_2SO_4 to $CaCl_2$ were much smaller than those formed by adding $CaCl_2$ to Na_2SO_4. The aspect ratios of the corresponding hydrothermal products-$CaSO_4{\cdot}0.5H_2O$ whiskers changed with the precursor sizes. The smaller the particle sizes of the precursors, the higher the aspect ratios of the whiskers. $CaSO_4{\cdot}0.5H_2O$ whiskers with a length of 80–310 μm and a diameter of 0.8–8.0 μm were formed at hydrothermal condition using the precursor formed by adding Na_2SO_4 to $CaCl_2$.

The data in Figures 3 and 4(a) indicated that all of the practical super-saturations of the solutions were much bigger than K_{sp}, which favored the quick nucleation and crystal growth. The super-saturations in line a were bigger than those in line b, and the particle sizes of the corresponding precursors in line a were also bigger than those in line b, indicating that a higher super-saturation system favored the formation of bigger precursors. Compared with the case of

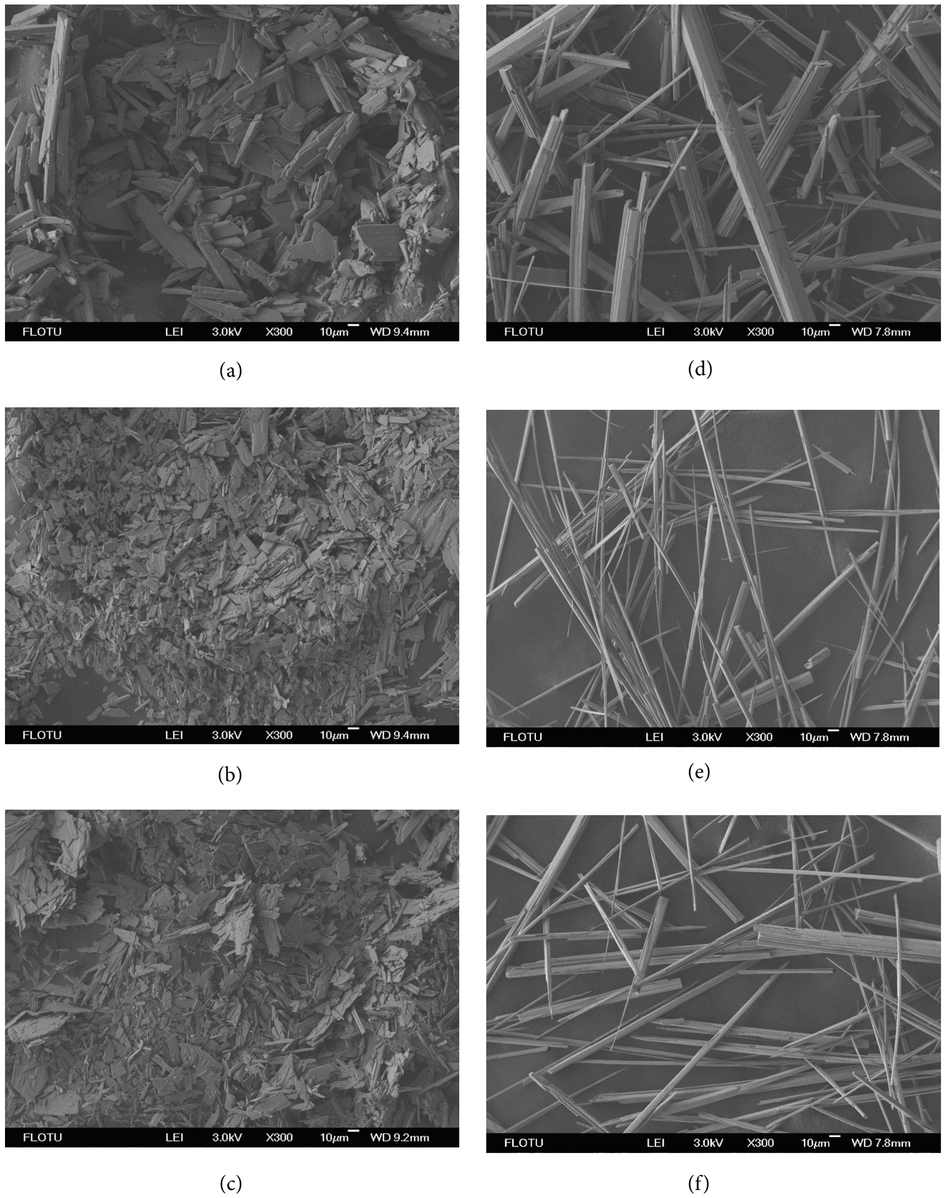


Figure 3: Influence of the mixing ways of the reactants on the morphology of the precursors ((a)–(c)) and the hydrothermal products ((d)–(f)). Mixing of reactants: (a), (d): adding $CaCl_2$ to Na_2SO_4, (b), (e): adding Na_2SO_4 to $CaCl_2$, (c), (f): adding $CaCl_2$ and Na_2SO_4 simultaneously to a blank container.

line a, smaller precursors were obtained despite the bigger super-saturation in the case of line c, which may be connected with the difference of the solution compositions. Figure 4(b) shows the variation of $[Ca^{2+}]/[{SO_4}^{2-}]$ with reaction time. The order of the values of $[Ca^{2+}]/[{SO_4}^{2-}]$ in lines a–c (line b > line c > line a) was in accordance with the order of the particle sizes of the precursors, indicating that a high value of $[Ca^{2+}]/[{SO_4}^{2-}]$ favored the formation of the $CaSO_4{\cdot}2H_2O$ with small particles. The above phenomena indicated that the particle sizes of the precursors were influenced by both the super-saturation and the value of $[Ca^{2+}]/[{SO_4}^{2-}]$. Adding Na_2SO_4 to $CaCl_2$ was considered to be a suitable mixing way of reactants for the formation of fine precursor and the whiskers with higher aspect ratios.

3.3. Influence of the Molar Ratio of the Reactants. The influence of the molar ratios of the reactants on the morphology of the precursors and the hydrothermal products is shown in Figure 5. The precursors were prepared by adding Na_2SO_4 to $CaCl_2$ at 25°C.

The precursors were plate-like particles with lengths of 3–45 μm, 3–60 μm and 4.5–55 μm, and widths of 0.5–15 μm, 1.5–18 μm, and 1.5–20 μm in the cases of the molar ratios of Na_2SO_4 to $CaCl_2$ being 0.5 : 1, 1 : 1 and 2 : 1, respectively. A low

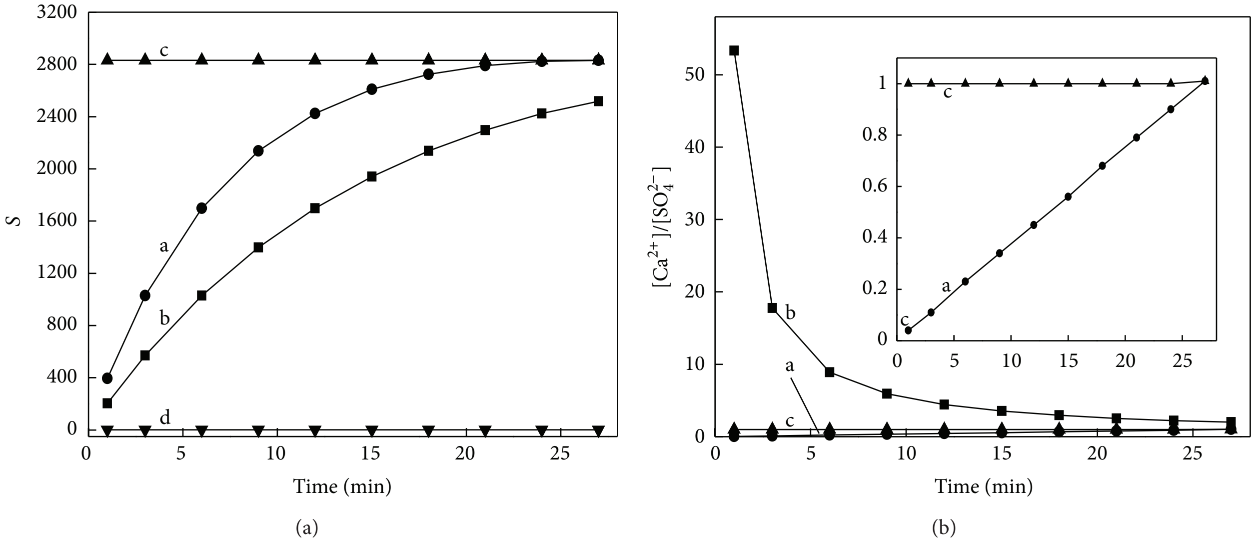


Figure 4: Influence of the mixing ways of reactants on the super-saturation (I) and $[Ca^{2+}]/[SO_4^{2-}]$ (II). (a): adding $CaCl_2$ to Na_2SO_4, (b): adding Na_2SO_4 to $CaCl_2$, (c): adding $CaCl_2$ and Na_2SO_4 simultaneously to a blank container, and (d): K_{sp} of $CaSO_4 \cdot 2H_2O$.

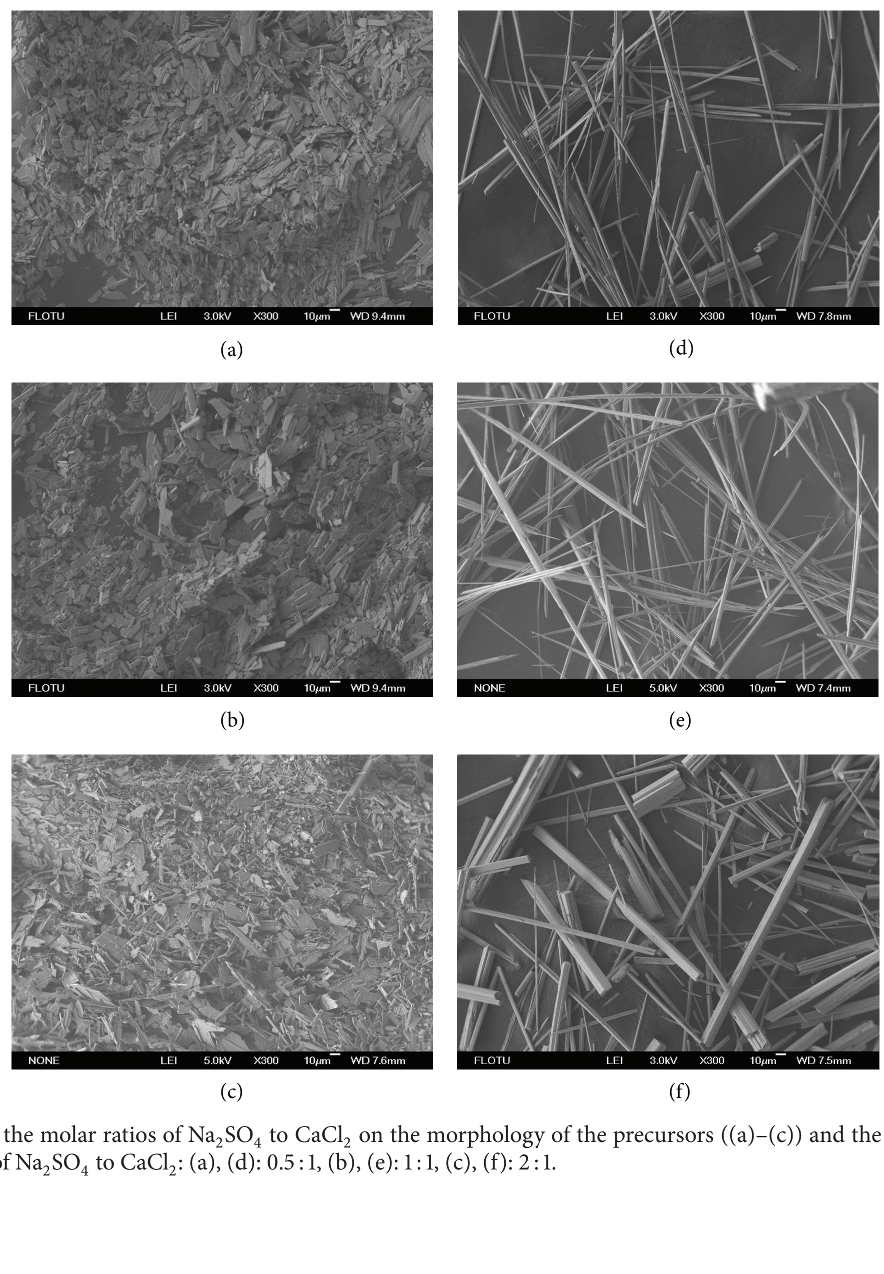
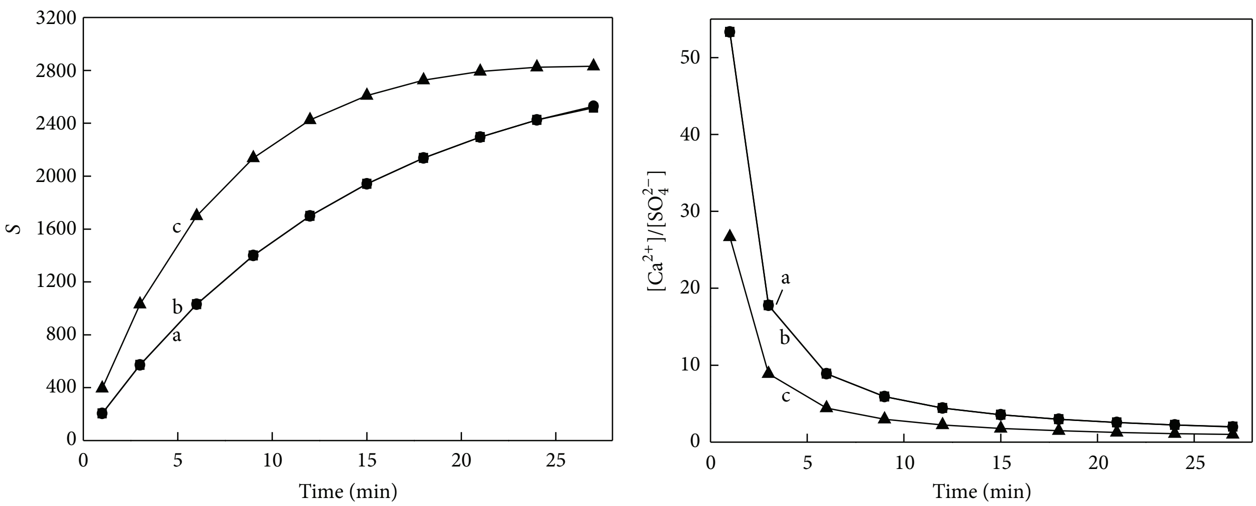


Figure 5: Influence of the molar ratios of Na_2SO_4 to $CaCl_2$ on the morphology of the precursors ((a)–(c)) and the hydrothermal products ((d)–(f)). Molar ratio of Na_2SO_4 to $CaCl_2$: (a), (d): 0.5 : 1, (b), (e): 1 : 1, (c), (f): 2 : 1.



(a) (b)

FIGURE 6: Influence of the molar ratios of Na_2SO_4 to $CaCl_2$ on the super-saturation and $[Ca^{2+}]/[SO_4{}^{2-}]$.

molar ratio of Na_2SO_4 to $CaCl_2$ favored the formation of the precursor with small particle size and the formation of the hydrothermal product with high aspect ratio. $CaSO_4{\cdot}0.5H_2O$ whiskers with a length of 80–310 μm and a width of 0.8–8.0 μm were formed in the case of the molar ratio of Na_2SO_4 to $CaCl_2$ being 0.5 : 1.

The variations of the super-saturation and $[Ca^{2+}]/[SO_4{}^{2-}]$ with reaction time are shown in Figure 6. Compared with the data of the molar ratios of Na_2SO_4 to $CaCl_2$ being 1 : 1 and 2 : 1, the super-saturations of the solutions were smaller and the values of $[Ca^{2+}]/[SO_4{}^{2-}]$ were bigger at the molar ratio of Na_2SO_4 to $CaCl_2$ being 0.5 : 1, which favored the formation of the $CaSO_4{\cdot}2H_2O$ precursors with smaller sizes.

4. Conclusion

$CaSO_4{\cdot}0.5H_2O$ whiskers were formed via co-precipitation at room temperature followed by hydrothermal treatment, using $CaCl_2$ and Na_2SO_4 as the raw materials. The particle sizes of the $CaSO_4{\cdot}2H_2O$ precursors formed at room temperature connected closely with the process parameters as temperature, the mixing way and the molar ratios of the reactants. The $CaSO_4{\cdot}2H_2O$ precursors with small particle sizes can be formed at the following condition: 25°C, adding Na_2SO_4 to $CaCl_2$ and keeping the molar ratio of Na_2SO_4 to $CaCl_2$ as 0.5 : 1 owing to the comparatively low super-saturations and the high values of $[Ca^{2+}]/[SO_4{}^{2-}]$, which favored the hydrothermal formation of the $CaSO_4{\cdot}0.5H_2O$ whiskers with high aspect ratios.

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