Research Article

Influence of Activity of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ on Hydrothermal Formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ Whiskers

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The influence of the activity of calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) on the hydrothermal formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers was investigated in this paper, using commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as the raw material. The experimental results indicated that the activity of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was improved after calcination of the commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 150°C for 6.0 h followed by hydration at room temperature for 1.0 h, corresponding to the decrease of the agglomerated particle sizes from $29.7\ \mu\text{m}$ to $15.1\ \mu\text{m}$, the increase of the specific surface areas (BET) from $4.75\ \text{m}^2 \cdot \text{g}^{-1}$ to $19.12\ \text{m}^2 \cdot \text{g}^{-1}$ and the grain sizes from 95 nm to 40 nm. The active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced by the calcination-hydration treatment favored the hydrothermal dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, promoting the formation of hemihydrate calcium sulfate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) whiskers with high aspect ratios.

1. Introduction

The synthesis of calcium sulfate (CaSO_4) whiskers with high aspect ratios and homogeneous morphology has drawn much attention in recent years since they can be used as the reinforcing materials in many fields as plastics, ceramics and paper making, and so forth [1–6].

CaSO_4 whiskers were usually prepared by hydrothermal formation of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers from the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor followed by calcination of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers at elevated temperatures. Wang et al. prepared $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with an aspect ratio of 5–20 at 115°C , using the natural gypsum as the reactant [7]. Wang et al. found that the use of the superfine $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor was essential for the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with small diameters and prepared $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with a diameter of $0.19\ \mu\text{m}$ and an aspect ratio of 98 via hydrothermal conversion of the fine grinded gypsum with an agglomerated size smaller than $18.1\ \mu\text{m}$ at 120°C [8]. Xu et al. prepared $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with a length of 100–750 μm and a diameter of 0.1–3 μm at 110– 150°C from the desulfurization gypsum composed mainly of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (93.45 wt%) and CaCO_3 (1.76 wt%) [9], using H_2SO_4 to change the CaCO_3 impurity to active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Yang et al. prepared calcium sulfate whiskers 50–450 μm by hydrothermal treatment of the desulfurization gypsum at 130°C for 1.0 h in the presence of K_2SO_4 [10]. It was noticed that most of the former work showed that the use of the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor promoted the hydrothermal formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with high aspect ratios.

In this paper a facile calcination-hydration hydrothermal reaction method was developed to synthesize the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor from the commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and to produce the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with high aspect ratios at hydrothermal condition. The influences of calcination and hydration on the morphology and structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor as well as on the morphology of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers were studied.

2. Experimental

2.1. Experimental Procedure. Commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with analytical grade was used as the raw material in the experiments. The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was sintered at 150°C for 3.0–6.0 h, then mixed with deionized water to keep the weight ratio of the solid to water at 1.0–5.0 wt%. After being stirred ($60\ \text{r} \cdot \text{min}^{-1}$) at room temperature for 1.0 h, the suspension

FIGURE 1: Morphology of raw material (a), calcination (b), and calcination-hydration (c) samples.

FIGURE 2: XRD patterns of raw material (1), calcination (2), and calcination-hydration (3) samples. Black square denotes $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, black circle denotes $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.

containing 1.0–5.0 wt% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was then treated in an autoclave at 135°C for 4.0 h. After hydrothermal treatment, the suspension was filtrated and dried at 105°C for 6.0 h.

2.2. Characterization. The morphology of the samples was detected with the field emission scanning electron microscope (JSM 7401F, JEOL, Japan). The structures of the samples were identified by powder X-ray diffractometer (D8 advanced, Bruker, Germany) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The agglomerated particle sizes of the samples were analyzed with the laser particle analyzer (Micro-plus, Germany). The soluble Ca^{2+} and SO_4^{2-} were analyzed by EDTA titration and barium chromate spectrophotometry (Model 722, Xiaoguang, China), respectively.

3. Results and Discussion

3.1. Formation of Active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ via Calcination-Hydration Route. The morphology and XRD patterns of the

raw material (a), the calcination sample (b), and the hydration sample (c) are shown in Figures 1 and 2, respectively. The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ raw material was composed of the irregular plates (a length of $1.5\text{--}20.0 \mu\text{m}$ and a width of $3.5\text{--}10.0 \mu\text{m}$) and particles (a diameter of $0.5\text{--}5.5 \mu\text{m}$). After the calcination treatment at 150°C for 6.0 h, the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ raw material was converted to the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ irregular rectangle planes with a length of $1.0\text{--}10.0 \mu\text{m}$ and a width of $0.2\text{--}3.0 \mu\text{m}$. The hydration of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ at room temperature led to the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ irregular rectangle planes with a length of $1.0\text{--}5.0 \mu\text{m}$ and a width of $0.1\text{--}2.0 \mu\text{m}$. The data in Figure 2 showed that the intensities of the XRD peaks in curve c were weaker than those in curve a, revealing that the calcination-hydration treatment promoted the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with poor crystallinity. The grain sizes of the raw material, the calcination sample, and the hydration sample were estimated as 94.9 nm , 37.5 nm and 39.5 nm , respectively, based on the (020) peaks located at $2\theta = 11.6^\circ$ and the Scherrer equation: $D_{hkl} = k\lambda/\beta \cos \theta$, where D_{hkl} , λ , β , and K represent the grain size, the wavelength of the $\text{Cu K}\alpha$ ($1.54178 \text{ \AA}$), the full width at half maximum (FWHM), and the Scherrer constant ($K = 0.89$), respectively.

The BET and the agglomerated particle sizes of the raw material, the calcination sample and the hydration sample, are shown in Figure 3. The BET and the agglomerated particle sizes were $4.75 \text{ m}^2 \cdot \text{g}^{-1}$ and $29.7 \mu\text{m}$ for the raw material, $13.37 \text{ m}^2 \cdot \text{g}^{-1}$ and $15.5 \mu\text{m}$ for the calcination sample, and $19.12 \text{ m}^2 \cdot \text{g}^{-1}$ and $15.1 \mu\text{m}$ for the hydration sample, revealing the increase of BET and the decrease of the agglomerated particle sizes of the samples after calcination and calcination-hydration treatment. The above work showed that the calcination-hydration treatment favored the activation of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor

FIGURE 3: BET (a) and the agglomerated particle sizes (b) of the samples 1: commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 2: calcination sample, and 3: calcination-hydration sample.

FIGURE 4: Variation of $[\text{Ca}^{2+}]$ (a) and $[\text{SO}_4^{2-}]$ (b) with hydrothermal reaction time. Precursor: 1: commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 2: active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Hydrothermal formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers from active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor.

Figure 4 shows the variation of $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ with hydrothermal reaction time. Compared with the commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced by calcination-hydration treatment was easier to be dissolved at hydrothermal condition, so that $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ in the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ system were higher than those in the commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ system. The gradual increase of $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ within 2.0–3.0 h indicated the faster dissolution of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ than the precipitation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, while the decrease of $[\text{Ca}^{2+}]$ and $[\text{SO}_4^{2-}]$ in the later time revealed the faster precipitation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ than the dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

Figure 5 shows the variation of the morphology of the samples with hydrothermal reaction time. The commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was converted to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers

after 2.0 h of hydrothermal treatment, while the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced by calcination-hydration treatment was changed to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers after 1.0 h of hydrothermal reaction owing to the acceleration of the hydrothermal dissolution-precipitation process. It was also noticed that the diameters of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers formed from the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ were much thinner than those from the commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. For example, after 4.0 h of hydrothermal reaction, the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with a diameter of $1.0\text{--}5.0 \mu\text{m}$, a length of $5\text{--}100 \mu\text{m}$, and an aspect ratio of 20–80 were prepared from the commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, while $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with a diameter of $0.1\text{--}0.5 \mu\text{m}$, a length of $30\text{--}200 \mu\text{m}$, and an aspect ratio of 270–400 were produced from the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor (Figures 5(e) and 5(j)).

Figure 6 shows the schematic drawing for the conversion of the commercial/active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O}$

FIGURE 5: Variation of the morphology of the samples with hydrothermal reaction time Precursor: (a)–(e): commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, (f)–(j): active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; Time (h): (a), (f) 0.5; (b), (g) 1.0; (c), (h) 2.0; (d), (i) 3.0; (e), (j) 4.0.

FIGURE 6: Schematic drawing for conversion of commercial/active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers.

whiskers. The active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor with small grain size and high BET was formed by calcination-hydration treatment, which accelerated the hydrothermal dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and promoted the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with high aspect ratios.

4. Conclusion

Active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ precursor improved the morphology of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers. Active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was produced by calcination of the commercial $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 150°C for 6.0 h followed by hydration at room temperature for 1.0 h. The use of the active $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ favored the hydrothermal dissolution of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and the formation of $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with high aspect ratios, producing $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ whiskers with a length of 30–200 μm , a diameter of 0.1–0.5 μm , and an aspect ratio of 270–400.

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