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Microwave intensified synthesis of regular shaped sodium bisulfate crystal

Hui Liu[a,b], Kaisong Xiang[a], Bentao Yang[a], Shu Yang[a], Qingzhu Li[a,b,*]

[a] Department of Environmental Engineering, School of Metallurgy and Environment, Central South University, Changsha, PR China
[b] Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, Changsha, PR China

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ABSTRACT

Microwave was employed to prepare sodium bisulfate crystal using equimolar quantities of sulfuric acid and sodium sulfate. The effects of microwave on heating behavior and water content changes were studied by monitoring the temperature and weight. To embody the positive effect of microwave on dehydrating speed and crystal transformation, thermal conductive heating was compared. The phase transformation and micro morphology of the product were characterized by X-ray diffraction and scanning electron microscopy. It was observed that crystallization with lower water content obtained higher percentage of sodium bisulfate. Microwave can significantly speed up dehydration and the dehydrating efficiency increase over the output power. According to the phase transformation process, a possible mechanism for H^+-dependent sodium bisulfate crystallization is proposed. Moreover, regular crystal with greater size was obtained under microwave irradiation. The specific phenomenon may be ascribed to the oriented attachment of hydrogen sulfate in alternating electromagnetic field.

1. Introduction

Sodium bisulfate ($NaHSO_4$) is a common chemical material used for mineral decomposition, melt additives, food additives, soil improvement agent and so on. In the past few decades, it has been reported that $NaHSO_4$ was widely used in acid-catalyzed organic reactions such as selective silyl deprotection of sylilethers, selective monoacetylation of diols, etc. [1–3]. Recently, the morphological effects of materials on catalytic activity and selectivity are attracting much attention for organic reaction [4,5] since it can influence organic reaction greatly [6,7]. However, few valid methods were proved to obtain $NaHSO_4$ crystal with a regular shape which is a necessity to investigate the potential morphological effects in acid catalysis.

Conductive heating and electrolysis, conventional but with low-efficiency methods [8–10], are applied to prepare $NaHSO_4$ crystal. However, few researches reported the $NaHSO_4$ crystal in regular shape by using such methods. Microwave heating techniques, offers many advantages in terms of enhanced diffusion processes and significantly reduced processing times [10], are preferable for their high-efficiency in chemical synthesis and dehydration [11,12]. The microwave heating technology has also been applied into some fields such as material sciences [13,14], and pharmaceutical molecule crystallization [15–17].

Microwave can modify the morphology of material crystal in following two aspects: (1) Shape. Microwave can induce a dramatic change in morphology depending on the composition during the synthesis of MFI zeolite [18]. It was also reported that ZnO with various structures from basic to complex could be prepared via microwave irradiation [19]. These effects on morphology depend on the specific groups on surface of the treated materials. (2) Crystal size. It was found that microwave irradiation for evaporative crystallization of niflumic acid results in crystal size reduction due to the high evaporation rates [17]. However, the size of L-alanine crystals increase when utilizing microwave heating [15]. The consequences resulted from the nucleation and crystal growth in microwave were different because the properties of material such as structural and dielectric properties were different [20,21]. Therefore, the mechanism of microwave effects on crystal formation aroused ever-lasting interests and is significant in rational modulation of crystal morphology.

$NaHSO_4$ owned a group of HSO_4^- with O—H bond [22,23], which is significantly beneficial for microwave absorbing. Combining this property and the microwave modifying effects mentioned above, herein, we proposed microwave intensified strategy to prepare $NaHSO_4$ crystal with regular shape. In this work, microwave was used for preparing $NaHSO_4$ crystal from the

* Corresponding author at: Department of Environmental Engineering, School of Metallurgy and Environment, Central South University. Fax: +86 0731 88830875.
E-mail address: qingzhuli@csu.edu.cn (Q. Li).

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mixed solution with equimolar quantities of sulfuric acid and sodium sulfate. Relationship between the phase composition and water content was studied to illustrate the process of phase transformation via X-ray diffraction (XRD). The morphology of $NaHSO_4$ prepared in microwave field was compared with that of sample obtained through conventional conductive heating method. According to the morphology differences, the possible mechanism of the effect of microwave on the crystallization of $NaHSO_4$ was proposed.

2. Materials and methods

2.1. Experimental apparatuses

A computer-controlled microwave synthesizer (XH-100B, Beijing Xianghu Technology Development Co., Ltd.) with a maximum output power of 850 W at 2450 MHz was used for the experiments. The synthesizer is equipped with a controller which allows that the heating process was performed at constant output power and setting temperature. The microwave generator is regulated by the controller on the basis of the inner solution temperature. The temperature was measured by a thermocouple temperature sensor coated with anticorrosive Teflon film. When the temperature or water contents reaches a target value, microwave irradiation automatically decrease to maintain the constant temperature or to cool to room temperature. As a typical equipment of conventional thermal conductive heating, hot-air oven (PHG-9140A, Shanghai Jinghong Laboratory Equipment Co., Ltd.) was applied for comparison tests.

2.2. Microwave irradiation of mixed solution

All chemicals used were of analytical grade. 7.1 g Na_2SO_4 (Sinopharm Chemical Reagent Co., Ltd., China) was dissolved in 12 ml deionized water and the solution was mixed with 2.7 ml H_2SO_4 (98 wt%, Sinopharm Chemical Reagent Co., Ltd., China). The molar ratio of Na_2SO_4 to H_2SO_4 is 1:1. For each experiment, the prepared solution was filled into a Teflon jar in the heating chamber of microwave synthesizer. According to the experiment requirements, the solution was heated at the constant output power of 200, 400 and 600 W or constant heating temperature of 120, 140, and 160 °C. After cooling to room temperature, the crystal was obtained by filtration using water circulation pump (SHB-III, Henan Aibo Technology Co., Ltd.) when the water content is relatively high. Due to the high temperature, the crystals were recrystallized from melt in annealing process. In order to observe the micromorphology, the as-prepared samples were grinded to powder. The powder samples were stored in the vacuum dryer filled with allochroic silica gel to protect from moist until characterization assays.

The weighing processes were completed within 10 s with the aid of electronic balance (AUY-220, Shimadzu). The water contents were calculated according to weight changes using the following calculation formula:

$$\theta = \frac{m - m_a}{m_a} \quad (1)$$

where θ is the water content, m is the real-time weight of matter in Teflon jar respectively, m_a is the weight of dry weight of Na_2SO_4 and H_2SO_4. The end points of heating were based on the target water contents.

2.3. Characterization of crystal

XRD data were collected by Rigaku D/Max-RB diffractometer with Cu–Kα radiation (λ = 0.15406 nm, 35 kV, 40 mA). Measurements of each test were performed in the scattering 2θ range from 7° to 50° with a step of 0.02°. Rietveld method was applied to the quantitative phase analysis for the crystal samples.

Scanning electron microscopy (SEM, JSM-6360LV) was used to characterize the morphology of the obtained crystal. All the as-prepared crystal samples were treated by spray-gold before the SEM tests.

3. Results and discussion

3.1. Effect of water contents on crystal products

Water content is an important factor for formation of $NaHSO_4$ crystal. Fig. 1 shows the XRD patterns of the as-prepared crystal powders obtained at different water contents. Samples were prepared by microwave synthesizer with the output power of 400 W at maximum temperature of 160 °C.

XRD results (Fig. 1) and Rietveld calculations (Table 1) indicated that the phase composition varied with the water content. When water content was 40%, $Na_3H(SO_4)_2$ accounted for 85.3% of product composition (Fig. 1a). As the water content decreased to 20%, the intensity of $Na_3H(SO_4)_2$ characteristic diffraction peaks decreases but that of $NaHSO_4{\cdot}H_2O$ is just reverse (Fig. 1b). Specifically, the proportion of $Na_3H(SO_4)_2$ decreases from 85.3% to 6.4% while that of $NaHSO_4{\cdot}H_2O$ increases from 14.2% to 87.4%. As the water content is further decreased to 3% (Fig. 1d), the characteristic diffraction peaks of $Na_3H(SO_4)_2$ disappear, indicating complete conversion of $Na_3H(SO_4)_2$ to $NaHSO_4$ and $NaHSO_4{\cdot}H_2O$. In the case of $NaHSO_4{\cdot}H_2O$, the intensity of characteristic diffraction peak decreases and the proportion of $NaHSO_4{\cdot}H_2O$ decreases from 87.4% to 17.8% when the water content was reduced from 20% to 3%. On the other hand, the peak of $NaHSO_4$ at 12.87° continues to be enhanced, corresponding to the ratio of $NaHSO_4$ increases from 6.2% to 82.2% with the water contents varied from 20% to 3%. As a conclusion,

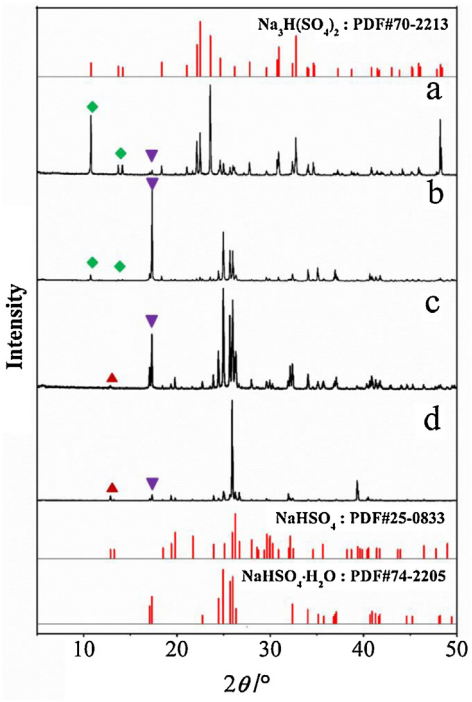

Fig. 1. XRD patterns of crystal with different water content. (a) θ = 40%; (b) θ = 20%; (c) θ = 10%; (d) θ = 3%. ◆ stand for characteristic peak of $Na_3H(SO_4)_2$ at 10.80°, 13.73° and 14.18°; ▲ stand for characteristic peak of $NaHSO_4$ at 12.87°; ▼ stand for characteristic peak of $NaHSO_4{\cdot}H_2O$ at 17.08° and 17.31°.