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Studies on synthesis and mechanism of nano-$CaZn_2(PO_4)_2$ by chemical precipitation

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Abstract

Calcium zinc phosphate nano-powder was prepared from phosphoric acid and the media—calcium zincate was synthesized in supersonic field by chemical precipitation using zinc oxide and calcium hydroxide as raw materials. The compositions and morphologies of media and product were investigated by XRD, SEM and TG. The mechanism of formation of $CaZn_2(PO_4)_2$ nano-powder has been studied, and the effects of supersonic radiation on the formation and reunion of media have also been discussed.

Keywords: Chemical precipitation; Calcium zinc phosphate; Nano-powder; Reaction mechanism

1. Introduction

Zinc phosphate, as a new type of non-toxic, ecological anticorrosive pigment with excellent properties, has been employed in the coating industry. However, owing to its low activity resulting from weaker solubility and hydrolysis, it cannot completely replace traditional toxic anticorrosive pigment, for example: zinc chromate and red lead [1]. As a consequence, many attempts have been made to modify zinc phosphate so as to realise a new generation of zinc phosphate pigments of high performance. It is known from the literature that one way is to add a cation (such as Ca^{2+}, K^+, Al^{3+}, etc.) [2–6] or new anion (such as SiO_4^{4-}, MoO_4^{3-}, OH^-, etc.) [7–10] to the zinc phosphate pigment, i.e. chemical modification to improve its activity. Up to now, such products have been micrometer powders and, as there has been no well-dispersing nanometer modified product, this constrains further improvement of the anticorrosive properties of the pigment.

The object of this paper is to prepare highly active nanometer, anticorrosive calcium zinc phosphate which possesses good dispersity, by using chemical precipitation involving the reaction of zinc oxide and calcium hydroxide in a supersonic field. In this work, the effect of supersonic radiation, stirring speed, reaction time and reactant dropping rate on the structure and morphologies of the new zinc phosphate media are discussed.

2. Experimental

2.1. Materials

ZnO, $Ca(OH)_2$ and H_3PO_4 of analytical grade were used as received without further purification. Deionized water was used.

2.2. Preparation of $CaZn_2(PO_4)_2$ nano-powder

Firstly, the media was synthesized by chemical reaction between 0.06 mol zinc oxide and 0.03 mol calcium hydroxide with quantitative double-distilled water under violent and consecutive stirring in a supersonic field for a given time. Secondly, a stoichiometric amount of dilute phosphoric acid was added to the mixture with simultaneous stirring. The reactive

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system was then heated to a certain temperature and reaction was maintained for some time. Finally, the white precipitate was filtered, washed with double-distilled water and then dried in an oven at a certain temperature.

2.3. Characterization

The crystal structure and composition of the media and product were analyzed by powder X-ray diffraction (Y-2000 XRD made in China) using a Rigaku D_{max} γA X-ray diffractometer with Cu Kα radiation ($\lambda = 0.154178$ nm), using an accelerating voltage of 30 kV. Powder morphology and size were characterized by KYKY-1000B scanning electron microscope made in America.

3. Results and discussion

3.1. XRD analysis of the product

As shown in Fig. 1, the X-ray diffraction pattern of the product has matched that of $CaZn_2(PO_4)_2 \cdot 2H_2O$ in JCPDS file (card no. 35-0495). Diffraction peaks of the reactants and media are not found in Fig. 1. These results show that chemical reaction has taken place completely and the obtained product is indeed calcium zinc phosphate. Furthermore, the average crystallite size of synthesized $CaZn_2(PO_4)$ is 52 nm, as estimated by the Scherrer's formula.

3.2. SEM analysis of the product

The SEM image of as-synthesized $CaZn_2(PO_4)_2$ sample of Fig. 1 is shown in Fig. 2. It shows that the nanoparticles have spherical morphology with the diameters of ca. 45–55 nm, which is consistent with the result calculated for the half-width of diffraction peaks using the Scherrer's formula. It can be seen that the morphology of the particles is homogeneous but some nanoparticles agglomerate seriously owing to small particle size and high surface energy.

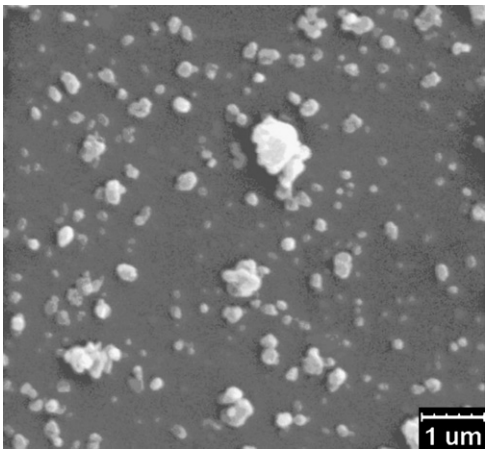

Fig. 2. SEM images of the product.

3.3. TG analysis

According to the TG curve of the product in Fig. 3, the loss of water molecules from the product can be divided into two stages. For the first stage from 335 K to 423 K, the mass-loss is about 4.90%. In this stage, the mass-loss of 0.25% between 335 K and 363 K may be due to the removal of adsorptive water in the precipitate, while the mass-loss of 4.65% between 363 K and 423 K is due to the removal of the first structural water molecule, which is very approximate to the theoretical value from $CaZn_2(PO_4)_2 \cdot 2H_2O$. For the second stage from 423 K to 773 K, the mass-loss is 4.70%. It is due to the removal of the second structural, which approaches to the theoretical value from $CaZn_2(PO_4)_2 \cdot 2H_2O$. Above this temperature, the removal of all water molecules indicates that anhydrous $CaZn_2(PO_4)_2$ phase is established. The process is as follows:

$$CaZn_2(PO_4)_2 \cdot 2H_2O \overset{-H_2O}{\rightarrow} CaZn_2(PO_4)_2 \cdot H_2O \overset{-H_2O}{\rightarrow} CaZn_2(PO_4)_2$$

This result further proves that $CaZn_2(PO_4)_2 \cdot 2H_2O$ was prepared by means of chemical precipitation from zinc oxide, calcium hydroxide and dilute phosphoric acid, and drying temperature of samples should be fixed between 363 K and 373 K on the basis of the mass-loss curves (Fig. 3).

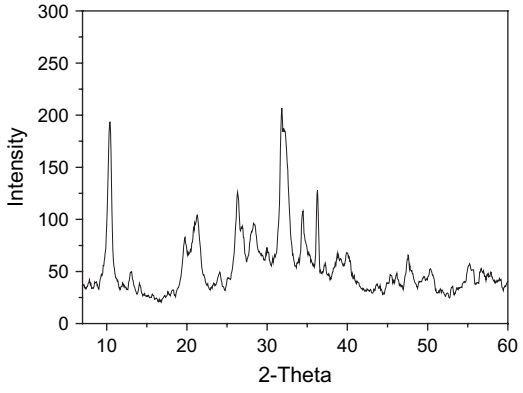

Fig. 1. XRD pattern of the product.

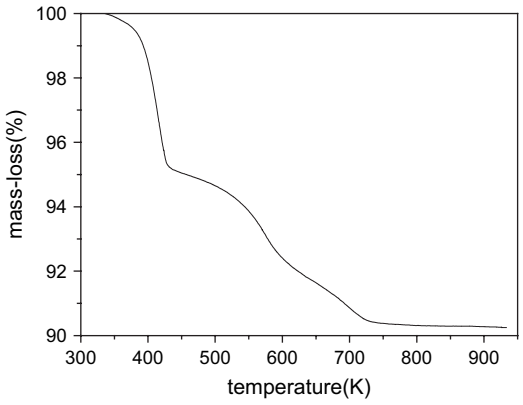

Fig. 3. TG curve of the product.

3.4. Study on reaction mechanism

3.4.1. Composition analysis of the media

The crystallinity and phase of the media were examined by XRD. Fig. 4 is the X-ray diffraction of the obtained media with the help of supersonic radiation. From Fig. 4, it can be found that some new strong peaks occur in addition to the diffraction peaks of ZnO and $Ca(OH)_2$. This shows that new compound was synthesized by the chemical reaction from zinc oxide and calcium hydroxide in supersonic field. The XRD pattern of the media is coincident with the reported data of $Ca[Zn(OH)_3]_2\cdot 2H_2O$ in JCPDS 24-0222. All the diffraction peaks corresponding to the compound are labeled in Fig. 4. The high intensity of peaks of media in the XRD pattern indicates that it has high crystallinity. Therefore, these results show that the obtained mixture consists of media—calcium zincate and reactants with supersonic radiation.

3.4.2. Study on the reaction mechanism

In the experiment, it was necessary for the suspension of zinc oxide and calcium hydroxide to be stirred for a period of time in supersonic field. Because of strong alkalinity of calcium hydroxide and OH^- ions released in its aqueous solution, amphoteric property of zinc oxide, with the assistance of supersonic radiation and stirring, the OH^- ion could destroy the dense structure of ZnO and form complicated complex with it, i.e. the media—calcium zincate. Furthermore, supersonic radiative energy can accelerate the formation of media. The reaction process is as follows:

$$Ca(OH)_2 + H_2O = Ca^{2+}(aq) + 2OH^-$$

$$OH^- + H_2O + ZnO = Zn(OH)_3^-$$

$$2Zn(OH)_3^- + Ca^{2+}(aq) + 2H_2O = Ca[Zn(OH)_3]_2\cdot 2H_2O$$

From Fig. 4, it can be noted that the diffraction peaks of $Ca(OH)_2$ are very weak, indicating that $Ca(OH)_2$ in the mixture has almost reacted completely; furthermore, the molar ratio of $Ca(OH)_2$ and ZnO is 1:2, which is consistent with that of Ca and Zn in the newly synthesized media, indicating that ZnO also reacts basically. But from Fig. 4, it can be seen that the diffraction peaks of ZnO are very strong because of its perfect crystal structure. Besides, owing to strong alkalinity of calcium hydroxide, it cannot react with zinc oxide completely. Therefore, there are only a little of $Ca(OH)_2$ and ZnO in the obtained the media—$Ca[Zn(OH)_3]_2\cdot 2H_2O$.

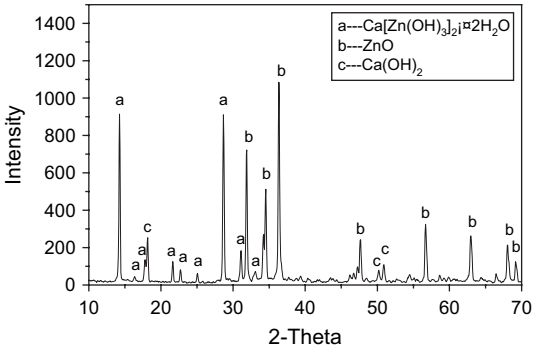

Fig. 4. XRD pattern of the media.

3.4.3. Discussion on the supersonic radiation mechanism

In the supersonic field, the formation rate and amount of nucleation increased by several orders of magnitude because the conditions of high temperature and high pressure from supersonic cavitational effect provided energy for the formation of particles, so that nano-sized particles could be obtained. The millions of air bubbles, provided by supersonic cavitational effect, reduce to micro-vortex motion of reactant solution on the surface of particles and played a stirring-up role in the reactant system. This micro-stirring avoided the ununiformity of partial concentration in reactant system, made ZnO and $Ca(OH)_2$ commingle more uniformly in the mesostructure and accelerated the diffusion of reactant system and so controlled synchro growth of crystal particles. Besides, a powerful shock wave, resulting from breaking down plentiful air bubbles by a supersonic cavitational effect, can repeatedly destroy the agglomeration of media and reactant so as to demolish the surface adsorption of particles on each other, make agglomeration exfoliate, result in disconnection of chemical bonds such as the hydrogen bond, and make the agglomerates separate from each other. Lots of air bubbles, owing to synchro expansion and constriction with ultrasonic pressure, infiltrated clearance and interspace of particles and smashed the agglomeration, which inhibited secondary agglomeration of particles effectively [11,12].

4. Conclusions

In the process of preparing $CaZn_2(PO_4)_2$ nano-powder by chemical precipitation, the media—calcium zincate containing a little reactants was synthesized with aids of ultrasonic radiation, which could accelerate nucleation of the media and restrain the growth and agglomeration of crystal nucleus effectively; then nanometer spherical calcium zinc phosphate with well dispersity and uniform distribution of gain sizes was prepared by precipitation reaction.

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