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Simple fabrication of polyhedral grain-like microparticle $Cu_{0.5}Zn_{0.5}HPO_4{\cdot}H_2O$ and porous structure $CuZnP_2O_7$

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Abstract

Polyhedral grain-like microparticle $Cu_{0.5}Zn_{0.5}(HPO_4){\cdot}H_2O$ was simply synthesized by heterogeneous reaction using a mixture of $CuCO_3$, ZnO, phosphoric acid and water at room temperature for 30 min. The thermogravimetric study indicates that the synthesized compound is stable below 250 °C and its final decomposed product is $CuZnP_2O_7$. The pure monoclinic phases of the synthesized $Cu_{0.5}Zn_{0.5}(HPO_4){\cdot}H_2O$ and its final decomposed product $CuZnP_2O_7$ are verified by XRD data. The presences of the HPO_4^{2-} ion and H_2O molecule in the $Cu_{0.5}Zn_{0.5}(HPO_4){\cdot}H_2O$ structure and the $P_2O_7^{4-}$ ion in the $CuZnP_2O_7$ structure are confirmed by FTIR data. The thermal stability, the morphology based on polyhedral grain-like microparticles and porous structure of the studied compounds are different from previously reported phosphates, and may affect their activities for potential applications (catalysis, electronics, etc.).

Keywords: Polyhedral grain-like particle; Ceramic pigment; Thermal behaviors; Metal phosphates; Powder synthesis

1. Introduction

Metal phosphates may be classified by its phosphate block units (PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$, $P_2O_7^{4-}$ and $P_4O_{12}^{4-}$) and attract increasing interest for environmental and technological fields [1]. In environmental field, the formation of metal phosphates help remove phosphate from waste waters, while their dissociations help regulate the slow release of fertilizers (P-macronutrient and metal-micronutrients) in acidic soils [2]. In technological field, the interest of metal phosphates is mainly focused on areas such as laser host [3], ceramic [4], dielectric [5], electric [5], magnetic [6], fertilizer [7], and catalytic [8] processes because of their valuable physical–chemical properties and reactivities. Consequently, metal phosphates have become a hot research topic in academic (material and chemical sciences) and industrial fields in the recent years [9–11].

One metal phosphate group, corresponding to the formula $M(HPO_4){\cdot}nH_2O$ (M = Mg, Ca, Mn, Co, Cu, Ni and Zn, $0 < n < 3$)[12–17], is a promising candidate for application in the fields of catalysis, electrics, ion exchange and conductors [3–8]. Because of their acidity and porosity, layered materials represent a vast class of intercalating compounds with useful chemical and thermal properties, which have been extensively used as heterogeneous catalysts [8,18]. Furthermore, thermal treatment of this metal hydrogen phosphate group has a great synthetic potential as it may turn simple compounds into advanced materials, which occur through hydrolysis and dehydration reactions at high temperatures [12–17]. Their final decomposed products belong to the metal pyrophosphate group ($M_2P_2O_7$; M = Mg, Mn, Co, Ni, Cu and Zn), which can be used for wide applications according to above mentioned [1–8]. More recently, many works have been directed towards the synthesis of binary metal hydrogen phosphates ($M_{1-x}A_x(HPO_4){\cdot}nH_2O$ and metal pyrophosphates ($M_{2-y}A_yP_2O_7$) (M or A = Mg, Ca, Mn, Co, Cu, Ni and Zn, $0 < n < 3$; $0 < x < 1$; $0 < y < 2$) [19–21]. Accordingly, it is pertinent to prepare $M_{1-x}A_x(HPO_4){\cdot}nH_2O$, $M_{2-y}A_yP_2O_7$ and their solid solutions, since they may offer some

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excellent physical and chemical properties when the composition is varied. So far, copper zinc hydrogen phosphate has not been reported in the literature. However, copper and zinc have received a great deal of attention due to its friendly environmental character and the associated low costs.

The attempt of this work is to prepare $Cu_{0.5}Zn_{0.5}(HPO_4)\cdot H_2O$ powder by heterogeneous reaction using copper carbonate, zinc oxide, phosphoric acid and water at room temperature for 30 min. Additionally, the $CuZnP_2O_7$ powder has been also obtained from calcination of $Cu_{0.5}Zn_{0.5}(HPO_4)\cdot H_2O$ at 300 °C for 3 h in air atmosphere. This method is a simple, cost- and time-saving route to synthesize $Cu_{0.5}Zn_{0.5}(HPO_4)\cdot H_2O$ and $CuZnP_2O_7$. The studied powders were characterized by thermogravimetry–differential thermogravimetry (TG/DTG), differential scanning calorimetry (DSC), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and scanning electron microscope (SEM) techniques. The data obtained will be important for further studies of the compound.

2. Experimental

The binary $Cu_{0.5}Zn_{0.5}(HPO_4)\cdot H_2O$ compound was prepared by heterogeneous reaction using $CuCO_3$ (99.99%, Merck), ZnO (99.99%, Merck) and H_3PO_4 (86.4%,w/w Merck) as starting materials. Following procedure, 10 mL of acetone were added to mixed solids of 1.24 g of $CuCO_3$ and 0.82 g of ZnO (corresponding to a nominal Mn:Co molar ratio of 1:1) and this suspension was referred to as mixture A. Then, 5 mL of 70% H_3PO_4 (82.02 mL of 86.4%,w/w H_3PO_4 dissolved in 18.98 mL of DI water) was added to the mixture A. The resulting suspension was continuously stirred at room temperature until CO_2(g) was completely evolved and the precipitates were obtained within about 15 min. This process can be explained by the following reaction

$$\frac{1}{2}CuCO_3(s) + \frac{1}{2}ZnO(s) + H_3PO_4(aq) \xrightarrow{\text{acetone, room temperature}} Cu_{0.5}Zn_{0.5}(HPO_4)\cdot H_2O(s) + \frac{1}{2}CO_2(g)$$

The pale blue solid of $Cu_{0.5}Zn_{0.5}HPO_4\cdot H_2O$ product was filtered by suction pump, washed with acetone until free from phosphate ion, dried in air and then kept in desiccator. The water content of the sample was determined by TG data, which reveals the completely decomposed product at temperatures above 250 °C. The dried pale blue solid then was calcined in a box-furnace at 300 °C for 3 h in air and a final decomposed product $CuZnP_2O_7$ was obtained.

The metal contents of the synthesized $Cu_{0.5}Zn_{0.5}H_2PO_4\cdot H_2O$ and its decomposed product $CuZnP_2O_7$ were determined by atomic absorption spectrophotometry (AAS, Perkin Elmer, Analyst100) after dissolution in 0.0126 M hydrochloric acid. The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. Thermal transformation of the synthesized $Cu_{0.5}Zn_{0.5}H_2PO_4\cdot H_2O$ was investigated on a Pyris Diamond TG/DTG Perkin Elmer Instrument and a Diamond DSC Perkin-Elmer apparatus. The experiments were carried out in air atmosphere by increasing temperature at heating rates of 10 °C min^{-1} from 30 to 550 °C with α-Al_2O_3 as the reference material. The room temperature FTIR spectra were recorded in the range of 4000–370 cm^{-1} with eight scans on a Perkin Elmer Spectrum GX FT-IR spectrometer with the resolution of 4 cm^{-1} using KBr pellets (spectroscopy grade, Merck). The structures and crystallite sizes of the prepared product and its decomposed product were studied by X-ray powder diffraction using a D8 Advanced powder diffractometer (Bruker AXS, Karlsruhe, Germany) with Cu Kα radiation (λ = 0.1546 nm). The Scherrer method was used to evaluate the crystallite size (i.e. $D = K\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray radiation, K is a constant taken as 0.89, θ is the diffraction angle and β is the full width at half maximum (FWHM)) [22]. The morphologies of the selected resulting samples were examined by scanning electron microscope (SEM) using LEO SEM VP1450 after gold coating.

3. Results and discussion

The TG/DTG curves of $Cu_{0.5}Zn_{0.5}HPO_4\cdot H_2O$ are shown in Fig. 1. The TG curve of $Cu_{0.5}Zn_{0.5}HPO_4\cdot H_2O$ shows the two weight loss steps in the range of 50–550 °C. The weight loss steps in the TG curve were observed in ranges of 50–150 and 150–400 °C. The corresponding observed weight losses were 4.69 and 14.79% by mass, which correspond to 0.5 and 1.47 mol of water, respectively. The first stage of the weight loss was related to the loss of moisture because it is not stable over 100 °C. While the second stage was due to the loss of water molecules from overlapping reactions: the loss of coordination water (dehydration reaction) and the deprotonation of hydrogen phosphate groups (condensation reaction). These two stages appear in the corresponding DTG and DSC curves as two peaks (55 and 178 °C). The retained mass of about 80.52% is compatible with the value expected for the formation of $CuZnP_2O_7$, which is confirmed by XRD and FTIR data. The thermal decomposition of the studied $Cu_{0.5}Zn_{0.5}H_2PO_4\cdot H_2O$ involves the dehydration of the coordinated water molecule and an intramolecular dehydration (condensation) of

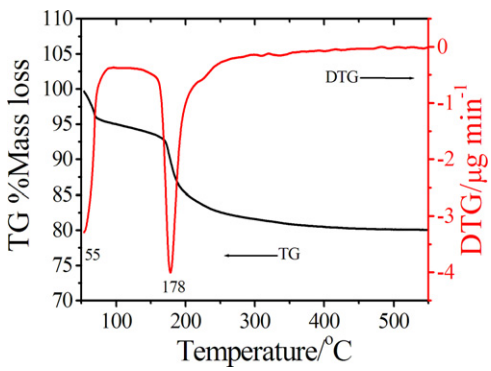

Fig. 1. TG/DTG curves of the synthesized $Cu_{0.5}Zn_{0.5}HPO_4\cdot H_2O$ at the heating range of 10 °C min^{-1}.