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A rapid synthesis of cobalt cyclotetraphosphate $Co_2P_4O_{12}$ at low temperature

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Abstract

The cobalt cyclotetraphosphate, $Co_2P_4O_{12}$, was synthesized by evaporating a mixture of cobalt chloride hexahydrate, phosphoric acid and water at 70 °C, with further calcinations at 400 °C, 500 °C and 600 °C for 3 h. XRD results indicated that the $Co_2P_4O_{12}$ compounds obtained had only monoclinic phase with space group C^6_{2h} ($Z=4$). From FT-IR spectra, vibrational modes corresponding to internal vibrations of the $P_4O_{12}^{4-}$ anion were identified. The morphologies and crystallite sizes for the $Co_2P_4O_{12}$ obtained from SEM data and X-ray line broadening showed non-uniform particles and 37–68 nm, respectively. All characterization methods showed that the monoclinic phase of $Co_2P_4O_{12}$ could be synthesized at the low temperature of 400 °C with short time consumption. The temperature was about 400 °C lower than that used in the previous synthesis method with $CoCl_2$ as reactant, and resulted in a cost-, energy-, and time-saving method.

Keywords: $Co_2P_4O_{12}$; Cobalt cyclotetraphosphate; Rapid synthesis; Low temperature

1. Introduction

The phosphate systems of type $M_2P_4O_{12}$, in which M is divalent metal elements (M = Mg, Ca, Mn, Co, Ni, Zn, or Cu), have vast industrial properties of interest such as ceramics, catalysts, fluorescent materials, dielectrics, metal surface treatment agents, detergents, food additives, fuel cell materials, pigment, super-fertilizers, etc. [1–4]. Two types of $M_2P_4O_{12}$ compounds are known: (i) cyclotetraphosphates with a ring structure formed by four PO_4 tetrahedra linked by bridging oxygens, and (ii) polyphosphates consisting of helical ribbons formed by corner-sharing PO_4 tetrahedra [5,6]. Most papers devoted to $M_2P_4O_{12}$ have been concerned with metal cyclotetraphosphates because their graining with special inorganic pigments is of interest from both an economic and environmental point of view [7,8]. Previous structure analyses have shown that metal cyclotetraphosphates crystallize in two systems: (i) cubic with space group *I-43d*, and (ii) monoclinic with space group C2/c($Z=4$) [5,6]. Different crystal structures of these inorganic phosphate pigments are affected by synthetic conditions such as selected preparation methods, starting materials, temperature, pH, time, etc. [9–11].

Up to now, some reports have been about synthesis methods for metal cyclotetraphosphate, including the two-step thermal method [3,12], hydrothermal synthesis [11] and thermal decomposition of metal (II) dihydrogenphosphates ($M(H_2PO_4)_2 \cdot nH_2O$; where M is Ca, Mg, Mn, Fe, Co, Ni, Cu or Zn; $0<y<1$; $1<n<4$) [1,9,10]. These previously reported methods are time consuming (>5 h) at high temperature (800–1000 °C) and have been found to evolve toxic gases such as NO_2 and CO_2.

This study was interested in the cobalt cyclotetraphosphate, $Co_2P_4O_{12}$, because it appeared to be advantageous economically, with lower cost, safety, benign

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environmental properties and low toxicity, which influence many properties, for example, a violet–pink hue of pigments, anticorrosion ability, luminescence, and relatively stable compounds—both thermally and chemically [9,10,12]. Cobalt cyclotetraphosphate $Co_2P_4O_{12}$ was synthesized by the high-temperature method [1–4,9–11,13], using mixtures of cobalt chloride and phosphoric acid (85%w/w), cobalt oxide and phosphoric acid (85%w/w) and cobalt carbonate and phosphoric acid (85%w/w) at high temperature (> 500 °C) with long consumption time (20 h). Another method was prepared from calcinations of the cobalt dihydrogen phosphate dehydrate, $Co(H_2PO_4)\cdot 2H_2O$, at > 400 °C for 3 h. However, it was difficult to synthesize $Co(H_2PO_4)_2\cdot 2H_2O$, due to complex procedures, the long time taken and high temperature. There are several disadvantages of the above mentioned syntheses that need to be overcome. For example, synthesis by mixtures of starting materials requires a long reaction time, high-temperature treatment, complicated processing and expensive equipment, and it produces evolving gas (CO_2), and poor yield or pure samples.

Therefore, this study focused on researching the synthesis of cobalt cyclotetraphosphates, which is important for the development of inorganic material synthesis. Rapid synthesis of the cobalt cyclotetraphosphate, $Co_2P_4O_{12}$, by evaporating mixture of cobalt chloride hexahydrate and phosphoric acid (70% w/v) at 70 °C over a short time period (20 min) has been reported for the first time. Then, dry precursors were calcined at 400 °C, 500 °C and 600 °C and the effect of these temperatures was reported, including the measurement of structure, vibrational modes and morphology for the studied material.

2. Experimental procedure

The starting reagents of cobalt chloride hexahydrate $CoCl_2\cdot 6H_2O$ (99%), phosphoric acid, H_3PO_4 (85% w/v) and acetone were obtained from Merck Co. Ltd., and employed for preparation of the title compounds. As a standard procedure, powder samples of $Co_2P_4O_{12}$ were prepared by evaporating a mixture that contained a slightly excess of H_3PO_4 (3.4 mL) with $CoCl_2\cdot 6H_2O$ (5.00 g), and then heating it at 70 °C for 20 min. The dry precursor obtained was subjected to further heat treatment at 400 °C, 500 °C and 600 °C for 3 h in open air in order to obtain the desired crystalline products. All the final products (violet–pink powders) obtained were crushed, and washed repeatedly with hot water until no PO_4^{3-} or Cl^- was detected in the filtrate. Finally, all violet–pink powder samples were dried completely at 100 °C.

The cobalt content of $Co_2P_4O_{12}$ was determined by dissolving it in 0.0126 M hydrochloric acid using atomic absorption spectrophotometry (AAS, Perkin Elmer, Analyst100). The phosphorus content was determined by colorimetric analysis of the molybdophosphate complex. The structure and crystallite size of the products were studied by X-ray powder diffraction using an X-ray diffractometer (Philips PW3040, The Netherlands) with Cu Kα radiation ($\lambda=0.15406$ nm). The Scherrer method was used to evaluate the crystallite size [14]. Room temperature FT-IR spectrum was recorded in the range of 4000–370 cm^{-1}, with eight scans on a Perkin–Elmer Spectrum GX FT-IR/FT-Raman spectrometer, and a resolution of 4 cm^{-1} using KBr pellets (KBr, spectroscopy grade, Merck). The morphology of the product was examined with a scanning electron microscope using LEO SEM VP1450 after gold coating.

3. Results and discussion

3.1. Chemical analysis of $Co_2P_4O_{12}$

The element contents of the synthesized $Co_2P_4O_{12}$ samples were analyzed according to the methods discussed. The data showed that the mass percentage for all samples (calcined at 400 °C, 500 °C and 600 °C) were found to be in the range of 28–29 wt% and 31–32 wt% for cobalt and phosphorus, respectively. The results obtained were close to those of theoretical data (28% and 32% for Co and P, respectively). This suggests a mole ratio of $Co_{total}:P_{total}=2:4$, which means that the general formula of all synthesized products would be $Co_2P_4O_{12}$.

3.2. XRD analysis of $Co_2P_4O_{12}$

The XRD patterns of the $Co_2P_4O_{12}$ product calcined at 400 °C, 500 °C and 600 °C are shown in Fig. 1. Only $Co_2P_4O_{12}$ peaks were observed, and the peak intensity and width became weak and broad, respectively, with increasing calcining temperatures. All detectable peaks of the calcined $Co_2P_4O_{12}$ were identified at 400 °C, 500 °C and 600 °C as monoclinic phase with space group C2/c ($Z=4$) from PDF no 86-2161 for $Co_2P_4O_{12}$ [15]. The average crystallite size of 37 ± 10, 41 ± 12, and 68 ± 24 nm for the calcined $Co_2P_4O_{12}$ was calculated at 400 °C, 500 °C and 600 °C, respectively, from X-ray line broadening reflections of (112), (311), (312 or 221), (112 or 310) and (113 or 022), using the Scherrer equation (i.e. $D=0.89\lambda/\beta\cos\theta$), where λ is the wavelength of X-ray radiation, D is a

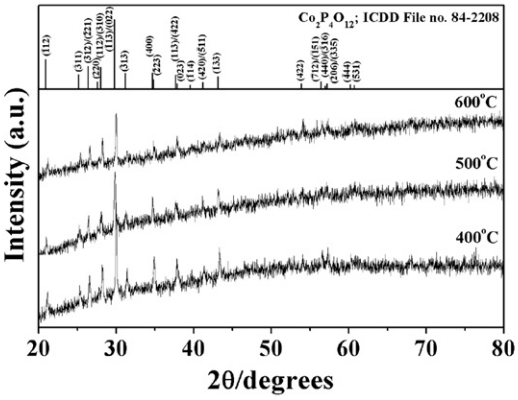

Fig. 1. XRD patterns of $Co_2P_4O_{12}$ calcined at 400 °C, 500 °C and 600 °C.

constant taken as 0.89, θ is the diffraction angle and β is the full width at half maximum (fwhm) [14]. The crystallite sizes and lattice parameters are calculated, in which the lattice parameters of the calcined $Co_2P_4O_{12}$ are very close to those of the standard data PDF no 86-2161 (a=1.1809 nm, b=0.8297 nm, c=0.9923 nm, β=118.72°) at temperature of 400 °C (a=1.1729 nm, b=0.8238 nm, c=0.9837 nm, β=118.75°), 500 °C (a=1.1745 nm, b=0.8273 nm, c=0.9988 nm, β=118.82°) and 600 °C (a=1.1853 nm, b=0.8318 nm, c=0.9938 nm, β=118.64°). The crystallite sizes increased when the calcined temperatures intensified. These results confirmed that different crystallite sizes of synthesized $Co_2P_4O_{12}$ depends on calcining temperatures.

3.3. FT-IR spectroscopic analysis of $Co_2P_4O_{12}$

Fig. 2 shows the FT-IR spectra of calcined $Co_2P_4O_{12}$ at 400 °C, 500 °C and 600 °C, which were caused mainly by vibration of the $P_4O_{12}^{4-}$ group [1,16]. The absorption peaks became slightly small and broad by increasing calcining temperatures. The crystal structure was a three-dimensional framework of polyhedral CoO_6 linked with P_4O_{12} rings by Co–O–P. The basic structure unit was the centrosymmetric cyclotetraphosphate P_4O_{12} cyclic ring, formed by joining the vertices of four tetrahedral PO_4s. The vibrational modes of $P_4O_{12}^{4-}$ ion observed in the frequency range of 370–1400 cm^{-1} were assigned according to the literature [16]. The $P_4O_{12}^{4-}$ anions containing a P−O−P bridge, and the PO_2^{2-} radical, were divided into two groups, as they differed in their bond strength and resulted in a vibrational mode. As the P−O strength in the P−O−P bridge was weaker than that in the PO_2^{2-} radical, stretching frequencies of the P−O−P bridge were expected to be lower than those in the PO_2^{2-} radical. Three types of P−O−P bridge: asymmetric stretching, symmetric stretching and bending frequencies, were observed at around 1100–1000 cm^{-1}, 800–700 cm^{-1} and 400–150 cm^{-1}, respectively, whereas, the same three types of PO_2^{2-} radical were observed at around 1340–1277 cm^{-1}, 1123–1100 cm^{-1} and 600–400 cm^{-1}, respectively. Co–O stretching usually appears in the bending mode region (400–300 cm^{-1}), as the bending modes of the P–O–P bridge and absorption bands associated with these vibrations are very weak as a rule. A weaker IR band at 328–300 cm^{-1} is probably due to this mode. The observation of strong double ν_s POP bands (740 cm^{-1} and 710 cm^{-1}) is known to be the most striking feature of cyclotetraphosphate spectra, along with the presence of the $\nu_{as}OPO^-$ band, which indicates that the crystal structure is monoclinic (space group C2/c) with a cyclic structure of the $[P_4O_{12}]^{4-}$ anion. This FT-IR result is consistent with X-ray diffraction data [15].

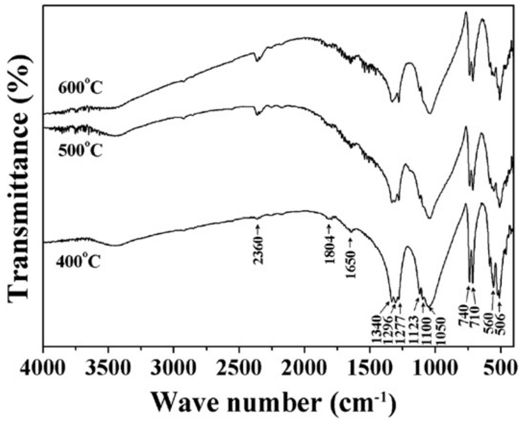

Fig. 2. FT-IR spectra of $Co_2P_4O_{12}$ calcined at 400 °C, 500 °C and 600 °C.

3.4. SEM analysis of $Co_2P_4O_{12}$

The SEM micrographs of $Co_2P_4O_{12}$ calcined at 400 °C, 500 °C and 600 °C are shown in Fig. 3. The particle shape and size change throughout the whole range of calcining temperatures. The SEM micrograph of the calcined $Co_2P_4O_{12}$ at 400 °C (Fig. 3a) illustrates many small and large non-uniform particles, with sizes of about 1–3 μm and 3–6 μm for small and large particles, respectively. The SEM micrograph of the calcined $Co_2P_4O_{12}$ at 500 °C (Fig. 3b) shows many small and large non-uniform polyhedral particles, with sizes of about 10–20 μm and 20–60 μm for small and large particles, respectively. The SEM

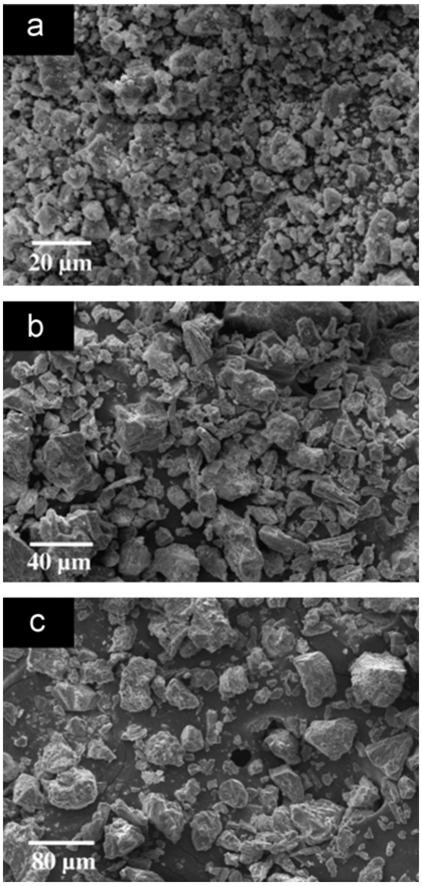

Fig. 3. SEM micrographs of $Co_2P_4O_{12}$ calcined at (a) 400 °C, (b) 500 °C and (c) 600 °C.

micrograph of the calcined $Co_2P_4O_{12}$ at 600 °C (Fig. 3c) shows coalescence in aggregates of non-polyhedral particles, with sizes in the range of 20–60 μm. The SEM images indicate that particle sizes increase by increasing calcining temperature. The SEM result indicates that the grain sizes of $Co_2P_4O_{12}$ compounds are consistent with the crystallite sizes in the XRD analysis, which affects the exact particle nucleation and growth mechanisms.

4. Conclusion

This study successfully achieved a rapid synthesis of monoclinic $Co_2P_4O_{12}$ cobalt cyclotetraphosphate obtained by evaporating mixtures of $CoCl_2 \cdot 6H_2O$, H_3PO_4 and H_2O at 70 °C for 30 min, with further calcinations at or below the temperature of 600 °C. XRD data shows that the $Co_2P_4O_{12}$ structure is monoclinic (space group C2/c) with a cyclic structure of $P_4O_{12}^{4-}$ anion in the precursor calcined at 400–600 °C, which is confirmed by FT-IR spectroscopy measurements. The morphologies of $Co_2P_4O_{12}$ show a high agglomerate of non-uniform particles and polyhedral crystallite sizes of 2–60 μm, as estimated by SEM. This research displays the low temperature and short time period to synthesize cobalt cyclotetraphosphate compared with other works. The results are necessary for academic scientists to elaborate technology and produce cyclotetraphosphate of transition metals, which may be useful as potential applications for super phosphate and micronutrient fertilizers, inorganic ceramic pigment, and catalyst and corrosion-proof compositions.

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