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Application of isoconversional calculation procedure to non-isothermal kinetic study: III. Thermal decomposition of ammonium cobalt phosphate hydrate

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ABSTRACT

The single phase $NH_4CoPO_4{\cdot}H_2O$ with layered structure was prepared via solid-state reaction at 60 °C. Based on the iterative isoconversional calculation procedure, the values of activation energy E_a associated with the first, second and third stages of the thermal decomposition of $NH_4CoPO_4{\cdot}H_2O$ were obtained, which demonstrate that the three stages are all a single-step kinetic process and can be adequately described by a unique kinetic triplet. The most probable reaction mechanisms of the three stages were estimated by comparison between experimental plots and modeled plots. The values of pre-exponential factor A of the three stages were obtained on the basis of E_a and the reaction mechanisms.

1. Introduction

Cobalt(II) phosphates and pyrophosphates as a kind of important inorganic multifunctional materials have many industrial and commercial applications and have been used for catalyst, fertilizers, magnetic devices, fire retardants in paints and plastics, and pigments which have good anticorrosion properties and are suitable for coating due to their open framework and diversity of structure types. From a structural point of view, the redox properties of Co(II) sites enhance the catalytic properties of porous materials, and Co(II)–Co(II) magnetic interactions can give rise to interesting magnetic properties; on the other hand, cobalt(II) can adopt a tetrahedral coordination environment identical to that exhibited for silicon and aluminum in the formation of zeolites and create zeolite-like Co(II) frameworks [1–10]. For instance, ammonium cobalt phosphate, which belongs to the series of cobalt(II) phosphates of general formula $MCoPO_4$ ($M = Na^+, K^+, NH_4{}^+, Rb^+$), consists of purely tetrahedral Co^{2+} in structures that is the same as or highly related to aluminosilicate tridymite and zeolite ABW, and shows important porosity characteristics and additional magnetic properties [1].

The preparation of ammonium cobalt phosphate hydrate ($NH_4CoPO_4{\cdot}H_2O$) was reported by various researchers. Carling et al. [7] synthesized $NH_4CoPO_4{\cdot}H_2O$ by precipitation from aqueous solution and determined the crystal structures of $ND_4CoPO_4{\cdot}D_2O$ obtained from $NH_4CoPO_4{\cdot}H_2O$. All these compounds were said to crystallize in the orthorhombic space group $Pmn2_1$. Bramnik et al. [11] also prepared $NH_4CoPO_4{\cdot}H_2O$ as a precipitate by adding $(NH_4)_2HPO_4$ solution to an alkaline solution of $CoCl_2$. And it is well known that cobalt pyrophosphate can be prepared by decomposition reaction of the $NH_4CoPO_4{\cdot}H_2O$ precursor [12].

Kinetic analysis of thermal decomposition process is important and has received considerable attention all along the modern history of thermal decomposition study [13–15]. Kinetic analysis can have either a practical or theoretical application. A major practical application is the prediction of process rates and material lifetime. The theoretical application is the interpretation of experimentally determined kinetic triplets which can mathematically describe the process and determine its thermodynamic properties. However, no kinetic study of thermal decomposition of ammonium cobalt phosphate hydrate has been reported in literature.

The aim of this work is, therefore, to study the kinetics of the thermal decomposition of pure nanocrystalline $NH_4CoPO_4{\cdot}H_2O$ prepared using a novel synthetic technique. Kinetic data were collected using simultaneous TG/DTA technique. Non-isothermal kinetics of the decomposition process was analyzed using a new modified method [16–20]. The values of E_a were obtained from an iterative procedure. The most probable mechanism function $g(\alpha)$ of the thermal decomposition reaction was deduced by comparison between experimental plots and modeled plots. The pre-exponential factor A was calculated using E_a and $g(\alpha)$. The kinetic (A, E_a and $g(\alpha)$) parameters of the thermal decomposition were discussed for the first time.

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2. Experiment

2.1. Preparation of ammonium cobalt phosphate hydrate and characterization

The ammonium cobalt phosphate hydrate ($NH_4CoPO_4{\cdot}H_2O$) was prepared via solid-state reaction at low-heating temperature. This preparation technique has been developed in recent decades and is of simplicity, low cost, high output and little pollution [21–24]. $Co(Ac)_2{\cdot}4H_2O$ was used as the source of cobalt (II) and $(NH_4)_3PO_4{\cdot}3H_2O$ was used as the sources of phosphorus and ammonium. The synthesis procedure was as follows: $(NH_4)_3PO_4{\cdot}3H_2O$ (30.0 mmol, 6.09 g), $Co(Ac)_2{\cdot}4H_2O$ (20.0 mmol, 4.98 g), and surfactant polyethylene glycol-400 (PEG-400) (0.5 mL) were put in a mortar, and the mixture was fully ground for 30 min. The reaction mixture was sealed with preservative film and kept at room temperature for 3 h and then kept at 60 °C for 3 h, washed with deionized water to remove soluble inorganic salts subsequently. The solid was then washed with a small amount of anhydrous ethanol and dried at 80 °C for 3 h to give the single phase $NH_4CoPO_4{\cdot}H_2O$.

Thermogravimetry (TG) and differential thermal analysis (DTA) measurements were made using a Netsch 40PC thermogravimetric analyzer. High purity nitrogen gas (99.999%) was used as protective atmosphere, flowing at 20 mL min^{-1}. The samples were loaded without pressing into an alumina crucible. (The results presented in this paper were calculated by the programs compiled by ourselves). X-ray powder diffraction (XRD) was performed at a scanning rate of 5° min^{-1} from 5° to 70° for 2θ at room temperature using a Rigaku D/max 2500 V diffractometer equipped with a graphite monochromator and a Cu target. Fourier transform infrared (FT-IR) spectra was recorded on a Nicolet IS10 spectrometer in the wavenumbers range of 4000–500 cm^{-1} for samples made in KBr pellet form. The morphology of the product and its calcined residues were examined by S-3400 scanning electron microscopy (SEM) on samples mounted on an alumina slice and coated with Au.

3. Theoretical

According to non-isothermal kinetic theory, kinetic equation of thermal analysis [13] can be expressed as follow:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{1}$$

where α is the extent of conversion, β is the heating rate (K min^{-1}), E_a is the apparent activation energy, A is the pre-exponential factor, R is the gas constant (8.314 J mol^{-1} K^{-1}).

3.1. Calculation of the values of E_a by the iterative procedure

The iterative procedure [16–19] is used to calculate the approximate value of E_a approaching to the exact value, the equations are expressed:

$$\ln\frac{\beta}{h(x)T^2} = \ln\frac{AR}{g(\alpha)E_a} - \frac{E_a}{RT} \tag{2}$$

where $h(x)$ is expressed by the fourth Senum and Yang approximation formulae [25]:

$$h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \tag{3}$$

where $x = E_a/(RT)$.

The iterative procedure is performed including the following steps: (i) assume $h(x) = 1$ to estimate the initial value of the activation energy E_{a1}. The conventional isoconversional methods stop the calculation at this step; (ii) using E_{a1}, calculate a new value of E_{a2} for the activation energy from the plot of $\ln[\beta/(h(x)T^2)]$ vs. $1/T$; (iii) repeat step (ii), replacing E_{a1} with E_{a2}. When $|E_{ai} - E_{a(i-1)}| < 0.01$ kJ mol^{-1}, the last value of E_{ai} is considered to be the exact value of the activation energy of the reaction. These plots are model independent since the estimation of the activation energy does not require selection of particular kinetic model (type of $g(\alpha)$ function). Therefore, the activation energy values obtained by this method are usually regarded as more reliable than those obtained by the Coats–Redfern method.

3.2. Determination of the most probable reaction models [13]

3.2.1. Determination parameters of compensation effect

The compensation effect can be observed when a model-fitting method, such as the Tang equation (Eq. (4)) [26], is applied to a single heating rate run.

$$\ln\left[\frac{g_i(\alpha)}{T_\alpha{}^{1.894661}}\right] = \left[\ln\left(\frac{A_iE_i}{\beta R}\right) + 3.63504095 - 1.894661\ \ln E_i\right] - 1.00145033\frac{E_i}{RT_\alpha} \tag{4}$$

The different pairs of the Arrhenius parameters, $\ln A_i$ and E_i, which are yielded by substitution of different models $g_i(\alpha)$ [27] into the Tang equation and fitting it to experimental data, all demonstrate a strong correlation known as a compensation effect [13]:

$$\ln A_i = aE_i + b \tag{5}$$

Different models $g_i(\alpha)$ [27] combined with the temperature T corresponding to conversions α are put into Eq. (4), the slope (k) and intercept (B) are obtained from the plot of $\ln[g_i(\alpha)/(T^{1.894661})]$ vs. $(1/T)$. First, the E_i and $\ln A_i$ can be estimated from the slope (k) and intercept (B). Then, the parameters of compensation effect (a and b) can be calculated from Eq. (5) with the E_i and $\ln A_i$.

3.2.2. Determination $\ln A_0$

Eq. (6) is used to estimate $\ln A_0$:

$$\ln A_0 = aE_0 + b \tag{6}$$

where a and b are obtained from Eq. (5), E_0 is average value of the apparent activation energy E_a calculated from Eq. (2).

3.2.3. Determination of reaction models

For constant heating rate conditions, integration of Eq. (1) leads to Eq. (7) [13].

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_0^T \exp\left(\frac{-E}{RT}\right)dT \tag{7}$$

The temperature integral in Eq. (7) can be replaced with various approximations, $h(x)$ as follows [19,25]:

$$g(\alpha) = \frac{AE}{\beta R}\exp(-x)\frac{h(x)}{x^2} \tag{8}$$

where $A = A_0$, $E = E_0$. A, E, β and the temperature T corresponding to conversions α are put into the right hand side of Eq. (8). And the experimental plot of $g(\alpha)$ vs. α is obtained. The analytical form of the reaction model (i.e., equation) can then be established by comparison between the experimental plot and the theoretical plots obtained from the $g(\alpha)$ equations representing the reaction models [27,28] and finding the best matching theoretical plot.