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Thermodynamics and kinetics of the dehydration reaction of $FePO_4 \cdot 2H_2O$

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ABSTRACT

The thermal decomposition kinetics of $FePO_4 \cdot 2H_2O$ in dynamical air atmosphere was studied by mean TG–DTG–DTA. The stage and product of the thermal decomposition were determined. A number of kinetic models and calculation procedures were used to determine the kinetic triplet and thermodynamic parameters characterizing the dehydration process. The obtained activation energy and most kinetic model indicate the single kinetic mechanism and three-dimension diffusion as "Ginstling–Brounstein equation (D4 model)", respectively. The thermodynamic functions (ΔH^*, ΔG^* and ΔS^*) of the dehydration reaction are calculated by the activated complex theory and indicate that the process is non-spontaneous without connecting with the introduction of heat. The kinetic and thermodynamic results were satisfactory which present good correlation with a linear correlation coefficient close to unit a low standard deviation.

1. Introduction

Iron (III) phosphate, $FePO_4$ has long been used in many fields such as catalysts, wastewater purification systems, ferroelectrics, lithium batteries and steel and glass industries [1]. It has recently been proposed as the cathode in lithium batteries and lithium metal phosphates can be used as cathode or anode electrodes in lithium batteries because it is the next generation of positive-electrode material for lithium batteries and offer additional advantages in practical applications due to its lower cost, safety, benign environmental properties, stability and low toxicity [2]. The existence of several crystalline iron phosphate phases was reported in the literatures: the orthorhombic heterosite $FePO_4$, obtained from the delithiated $LiFePO_4$, the monoclinic $FePO_4$, and the orthorhombic $FePO_4$, hydrated phases include the phosphosiderite (or metastrengite) $FePO_4 \cdot 2H_2O$ monoclinic and the $FePO_4 \cdot 2H_2O$ orthorhombic forms [3–6]. The successful application of the required material depends on the morphology and purity, which depend mainly on the conditions of synthesis. Different synthetic routes have so far been reported for synthesizing $FePO_4$, $LiFePO_4$ and some of the synthesis conditions reported in the literature [5–7]. It is well known that $FePO_4$ was prepared by many phases of $FePO_4 \cdot 2H_2O$ and $FePO_4 \cdot 3H_2O$ precursors at high temperatures (>800 K) [5–7]. Consequently, the mechanisms, kinetic and thermodynamic studies of thermal decomposition reactions are needed in order to take advantage of this potential, which is a beneficial effect on the manufacturing cost [8,9]. The results obtained can be directly applied in materials science for the preparation of various metals and alloys, cements, ceramics, glasses, enamels, glazes, polymer and composite materials because the great variety of factors with diverse effects such as reconstruction of solid state crystal lattices, formation and growth of new crystallization nuclei, diffusion of gaseous reagents or reaction products, materials heat conductance, static or dynamic character of the environment, physical state of the reagents—dispersity, layer thickness, specific area and porosity, type, amount and distribution of the active centers on solid state surface, etc [5–8].

The aim of the present work is to study the mechanisms, kinetics and thermodynamics of the decomposition of $FePO_4 \cdot 2H_2O$ using TG–DTG–DTA. Non-isothermal kinetic of the decomposition process of $FePO_4 \cdot 2H_2O$ was interpreted by the Flynm–Wall–Ozawa (FWO) [9] and the Kissinger–Akahira–Sunose (KAS) [10,11]. The possible conversion function has been estimated using the Coats and Redfern method which gives the best description of the studied decomposition process and allows the calculation of reliable values of kinetic triplet parameter [12]. The thermodynamic (ΔH^*, ΔS^*, ΔG^*) and kinetic (E, A, mechanism and model) parameters of the decomposition reaction of $FePO_4 \cdot 2H_2O$ have attracted the interest of thermodynamic and kinetic scientists and are discussed for the first time.

2. Experimental

2.1. Synthesis and characterization

$FePO_4 \cdot 2H_2O$ crystalline powder was synthesized by wet chemistry method [1,2]. In this study, $FePO_4 \cdot 2H_2O$ was prepared

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by precipitation from aqueous solution of $FeCl_3 \cdot 6H_2O$ and H_3PO_4 (86.4% w/w) at pH=6.5 at the "precipitation end point", with ammonium hydroxide solution. During the synthesizing procedure, iron chloride was dissolved in distilled water followed by adding an equivalent amount of the phosphoric acid (86.4% w/w) with vigorous stirring at room temperature. Finally, the gel solution was obtained by adding 2 M ammonia solutions until pH 6.5. The white powder was isolated by filtration, then washed with deionized water and dried in air for 24 h.

Thermal analysis measurements (thermogravimetry, TG; differential thermogravimetry, DTG; and differential thermal analysis, DTA) were carried out on a Pyris Diamond Perkin Elmer apparatus by increasing temperature from 323 to 1073 K with calcined α-Al_2O_3 powder as the standard reference. The experiments were carried out in air atmosphere at heating rates of 5, 10, 15, and 20 K min^{-1}. The sample mass was added about 6.0–10.0 mg in an aluminum crucible without pressing. The structures of $FePO_4 \cdot 2H_2O$ and its final decomposition products ($FePO_4$) were studied by X-ray powder diffraction using X-ray diffractometer (Phillips PW3040, The Netherland) with Cu Kα radiation (λ=0.1546 nm). The morphology of the selected resulting samples was examined by scanning electron microscope (SEM) using LEO SEM VP1450 after gold coating. The room temperature FTIR spectra were recorded in the range of 4000–370 cm^{-1} with 8 scans on a Perkin-Elmer Spectrum GX FT-IR/FT-Raman spectrometer with the resolution of 4 cm^{-1} using KBr pellets (KBr, Merck, spectroscopy grade).

2.2. Kinetics and thermodynamics

Decomposition of crystal hydrates is a solid-state process of the type [13–16]: A (solid)→B (solid)+C (gas). The kinetics of such reactions is described by various equations taking into account the special features of their mechanisms. The reaction can be expressed through the temperatures corresponding to fixed values of the extent of conversion ($\alpha=(m_i-m_a)/(m_i-m_f)$, where m_i, m_a and m_f are the initial, actual and final sample mass at moment time, t) from experiments at different heating rates (β). The FWO [9] and the KAS [10,11] methods are two representative ones of model-free, which are convenient to calculate the activation energy. The activation energy (E_α) of the dehydration reaction of $FePO_4 \cdot 2H_2O$ can be calculated according to the FWO and the KAS equations.

The FWO equation:

$$\ln\beta = \ln\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - 5.3305 - 1.0516\left(\frac{E_\alpha}{RT}\right) \tag{1}$$

The KAS equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_\alpha}{Rg(\alpha)}\right) - \left(\frac{E_\alpha}{RT}\right) \tag{2}$$

where A (the pre-exponential factor) and E (the activation energy) are the Arrhenius parameters and R is the gas constant (8.314 J mol^{-1} K^{-1}). The $g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}$ is the integral form of the $f(\alpha)$, which is the reaction model that depends on the reaction mechanism.

For one dehydration reaction of $FePO_4 \cdot 2H_2O$, the estimation of kinetic function model can be turned into a multiple linear regression problem through the Coats–Redfern method [12] as follows:

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E_\alpha}\right)\left(1-\frac{2RT}{E_\alpha}\right) - \left(\frac{E_\alpha}{RT}\right) \cong \ln\left(\frac{AR}{\beta E_\alpha}\right) - \left(\frac{E_\alpha}{RT}\right) \tag{3}$$

Hence, $\ln(g(\alpha)/T^2)$ calculated for different α values at the single β value on $1000/T$ must give rise to a single master straight line, so the activation energy and the pre-exponential factor can be calculated from the slope and intercept through ordinary least square estimation. The activation energy and the pre-exponential factor can be calculated from the slope and intercept through ordinary least square estimation, which combined with nine conversion functions (Table 1) with the best equation [13]. Comparing the kinetic parameters from the Coats and Redfern equation, the probable kinetic model may be selected, where the values of E_α and A were calculated with the better linear correlation coefficient and the activation energies obtained from the Coats and Redfern equation above were showing good agreement to those obtained from the KAS and the Ozawa methods with a better correlation coefficient (r^2). Hence, the

Table 1
Algebraic expressions of functions $g(\alpha)$ and $f(\alpha)$ and its corresponding mechanism [13,21].

No.	Symbol	Name of the function	$f(\alpha)$	$g(\alpha)$	Rate-determination mechanism
1. Chemical process of mechanism non-invoking equations					
(1)	$F_{3/2}$	One and a haft order	$2(1-\alpha)^{3/2}$	$[1-(1-\alpha)^{-1/2}-1]$	Chemical reaction
2. Sigmoid rate equations or random nucleation and subsequent growth					
(2)	A_1, F_1	Avrami-Erofeev equation	$(1-\alpha)$	$-\ln(1-\alpha)$	Assumed random nucleation and its subsequent growth, n=1
(3)	$A_{3/2}$	Avrami-Erofeev equation	$(3/2)\ (1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$	Assumed random nucleation and its subsequent growth, n=1.5
3. Deceleratory rate equations					
3.1. Phase boundary reaction					
(4)	R_3, $F_{2/3}$	Power law	$3(1-\alpha)^{2/3}$	$[1-\ln(1-\alpha)]^{1/3}$	Contracting volume (spherical symmetry) or two-thirds order
3.2. Based on the diffusion					
(5)	D_1	Parabola law ($\alpha=kt^{1/2}$)	$1/2\alpha$	α^2	One-dimension diffusion
(6)	D_2	Valensi equation	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	Two-dimension diffusion
(7)	D_3	Jander equation	$(3/2)(1-\alpha)^{2/3}/[\ln(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$	Three-dimension diffusion
(8)	D_4	Ginstling–Brounstein Equation	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$[1-(2/3)\alpha-(1-\alpha)^{2/3}]$	Three-dimension diffusion
(9)	D_5	Zhuravlev Lesokhin Tempelman Equation	$(3/2)(1-\alpha)^{4/3}/[1-(1-\alpha)^{-1/3}]$	$[(1-\alpha)^{-1/3}-1]^2$	Three-dimension diffusion