Pyro and Kinetic Studies of Barium Oxalate Crystals Grown in Agar Gel

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ABSTRACT

Single crystals of barium oxalate have been grown using gel method at ambient temperature. Thermal characteristics and kinetic parameters of barium oxalate crystals were determined by thermo-gravimetric (TG) analysis under non-isothermal heating conditions. The pyrolysis experiments were performed with increasing temperature up to 600°C at heating rate of 5°C, 7°C and 10°C in nitrogen gas atmosphere. The pyrolysis curve showed that loss of mass took place mainly in the range of 220°C - 400°C. At higher temperature there was a significant mass loss due to decomposition of oxalates. Ozawa and Coats & Redfern methods were used to determine the apparent activation energies of material degradation. The apparent activation energies for barium oxalate crystals were obtained 187.42 KJ·mol⁻¹ and 185.4 KJ·mol⁻¹ for the respective methods.

Keywords: Barium Oxalate; Thermo-Gravimetric Analysis; Kinetic Studies; Thermodynamic Parameters

1. Introduction

In the continued demand of materials having more stability even up to high temperature, high resistance to heat and hard, for their applications in pyrotechnic and ceramic industries, the research and development of barium oxalate was a significant step [1]. With its excellent thermal stability and hardness, this material has found a wide range of applications in fire cracker industries as a pyro colorant [2], and to improve hardness of barium titinate in capacitor industries [3]. Nano-particles of barium oxalate [4] and barium titanyl oxalate have shown its effect on semiconducting properties [5].

Well facet prismatic, platy shaped transparent crystals were grown by gel method using agar-agar gel as a media of growth at ambient temperature [6].

Since barium oxalate is a pyro-nature material, which shows great promise in pyrotechnic and high temperature electronic applications. It is therefore interesting to investigate the thermal stability and degradation reaction mechanism of this material.

Pyro and kinetic studies such as decomposition rate and activation energy are important parameters to determine the reaction mechanism in solid phases. The use of thermo-gravimetric data to evaluate the kinetic parameters of solid state reactions involving weight loss has been investigated by many workers [7-11]. If the pyrolysis occurs through a many stepped mechanism, usually, the shape of the curve can be determined by the kinetic parameters of pyrolysis, such as order of reaction, frequency factor and energy of activation. Successful and deliberate attempts to evaluate kinetic and thermodynamic parameters were made by Kotru et al. [12], Arora et al. [13], and Schaube et al. [14]. The kinetics of dehydration of gypsum [15], lithium sulphate monohydrate crystal [16], and the kinetic and thermodynamic parameters of decomposition of chromium chromate in different gas atmospheres have been evaluated [17].

Usually, kinetic parameters can be calculated from the TG curves by applying integral and differential equations [7-9], which are proposed by different authors on the basis of different assumptions to the kinetics of the reaction and the Arrhenius law. However, in the present investigation, the Ozawa [18] and the Coats & Redfern method [7], is an integral approach has been used to elucidate the thermal stability, the nature and extent of the degradation of barium oxalate in nitrogen atmosphere. In addition, thermodynamic parameters were also evaluated.

2. Experimental

The thermo-gravimetric curves were obtained by employing a “TA-2050” thermal analyzer under various heating rates in nitrogen gas atmosphere. About 10 - 14
mg material was used for each measurement. The integral residual weights were recorded in between 30°C to 600°C. However, the kinetic data analysis was performed based on the results obtained between 220°C to 400°C, where the rigorous reaction actually took place. Three heating rates 5°C/min, 7°C/min and 10°C/min were employed as shown in Figure 1. From these TG curves kinetic and thermodynamic parameters were evaluated by applying Ozawa and Coats & Redfern method.

2.1. The Ozawa Method

The Ozawa method has been widely used for kinetic data analysis [19,20]. This integral method compared heating rates with temperatures under the same conversion rates. The kinetic parameters of dehydration process of barium oxalate crystals were evaluated by using Ozawa equation

$$\log \beta = \log \left( \frac{AE}{R} \right) - 2.315 - 0.4567 \left( \frac{E}{RT} \right) - \log(a) \quad (1)$$

where $\beta$ is the heating rate (K·min$^{-1}$), $A$ is the pre-exponential factor (min$^{-1}$), $R$ is the gas constant (8.314 Jmol$^{-1}$·K$^{-1}$), $E$ is the energy of activation, and

$$g(a) = \frac{AE/\beta R}{P(x)} \quad (2)$$

and $\alpha$ is the fraction of decomposed material, which is given by

$$\alpha = \frac{(W_0 - W_t)}{(W_0 - W_f)} \quad (4)$$

where $W_0$ is the initial mass of the sample, $W_t$ is the mass of the sample at temperature $t$ and $W_f$ is the final mass at a temperature at which the mass loss is approximately unchanged.

By plotting graphs between $\log \beta$ versus $1/T$ into a different straight line at different conversion rates as shown in Figure 2, the activation energy $E$ and frequency factor $logA$ could thus be obtained from the slope and the intercept respectively.

Figure 1. The thermogravimetric curves at three different rates.

2.2. The Coats & Redfern Method

Coats & Redfern method is also an integral method, and it involves the thermal degradation mechanism [21,22]. The kinetic parameters of dehydration process can be evaluated by using the relation as

$$\log_{10} \left[ \frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n)} \right] = \log_{10} \left[ \frac{AR}{\beta E} \frac{1 - \frac{2RT}{E}}{T^2} \right] - \left( \frac{E}{2.303RT} \right) \quad (5)$$

for $n \neq 1$

To determine the value of activation energy and order of reaction “$n$”, a plot of $\frac{1 - (1 - \alpha)^{1-n}}{T^2 (1-n)}$ versus $1/T$ is drawn for different values of $n$ (Figure 3). The best linear fit gives the correct value of $n$. The value of activation energy can be calculated from the slope of a linear plot. The value of frequency factor can be obtained from Equation (5). Equation (5) is applied for all values of $n$, except $n = 1$. For $n = 1$, the modified equation has been proposed [7].

$$\log_{10} \left[ \frac{-\log(1-\alpha)}{T^2} \right] = \log_{10} \left[ \frac{AR}{\beta E} \frac{1 - \frac{2RT}{E}}{T^2} \right] - \left( \frac{E}{2.303RT} \right) \quad (6)$$

for $n = 1$

The other kinetic analysis parameters such as enthalpy of activation ($\Delta H^\circ$), entropy of activation ($\Delta S^\circ$) and free energy change of decomposition ($\Delta G^\circ$) were evaluated [23] using equations

$$\Delta H^\circ \text{ (KJ·mol}^{-1}) = E + \Delta nRT \quad (7)$$
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Figure 3. \( \frac{-\log(1-a)}{T^2} \) as a function of 1000/T.

where \( \Delta n \) = Number of moles of product – number of moles of reactant in the reaction

\[
\Delta S^* (JK^{-1} \cdot mol^{-1}) = 2.303 R \left( \log \left( \frac{A h}{K T} \right) \right) \tag{8}
\]

\[
\Delta G^* (KJ \cdot mol^{-1}) = \Delta H^* - T \Delta S^* \tag{9}
\]

where \( A \) is (Arrhenius constant) determined from the intercept, \( K \) is Boltzmann and \( h \) is Plank’s constant.

3. Results and Discussion

Figure 1 shows the non-isothermal degradation behavior of barium oxalate crystals at the various heating rates. It has been clearly evidenced that the sample displayed excellent thermal stability. When the heating rate was chosen 10°C/min, the residual weight along testing temperature can be used to depict the thermal properties. The initial decomposition temperature or the onset weight loss of sample was about 220°C. The temperature that corresponds to the maximum weight loss rate was around 320°C. The decomposition process slowed down after reaching 370°C. The residual weight was 48% when heated upto 400°C. The reaction appeared to be a one stage reaction in nitrogen atmosphere.

The analysis of reaction kinetic parameters was performed on the thermo-gravimetric curves, obtained between 220°C to 400°C, using Ozawa and Coats & Redfern methods.

In Ozawa method, the plot of log (heating rate) versus 1000/T is provided in Figure 2. Five different conversion rates ranging from 0.1 to 0.6 were used for data analysis. Three different heating rates were used in this analysis, including 5°C, 7°C, and 10°C/min. The slopes of these five straight lines have been used to calculate activation energy (\( E \)) and their intercepts were used to calculate frequency factor (log\( A \)). The other kinetic parameters such as enthalpy of activation (\( \Delta H^* \)), entropy of activation (\( \Delta S^* \)), and free energy change of decomposition (\( \Delta G^* \)) were calculated using Equations (7)-(9) and are represented in Table 1.

Figure 3 is the best linear fitted plot obtained using Equation (6) for Coats & Redfern method. The slopes of these straight lines have been used to calculate activation energy (\( E \)) and their intercepts were used to calculate frequency factor (log\( A \)). The average calculated activation energy, frequency factor and other thermodynamic parameters were also depicted in Table 1.

Table 1. Kinetics and thermodynamic parameters of dehydration of barium oxalate.

<table>
<thead>
<tr>
<th>Method</th>
<th>( K (\text{min}^{-1}) )</th>
<th>( E (\text{KJ/mole}) )</th>
<th>( \Delta H (\text{KJ/mole}) )</th>
<th>( \Delta S (\text{J/mole} \cdot \text{K}) )</th>
<th>( \Delta G (\text{KJ/mole}) )</th>
<th>Frequency factor (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozawa</td>
<td>1.12 \times 10^{10}</td>
<td>187.42</td>
<td>183.4</td>
<td>63.1</td>
<td>152.6</td>
<td>2.02 \times 10^{16}</td>
</tr>
<tr>
<td>Coats &amp; Redfern</td>
<td>1.8 \times 10^{10}</td>
<td>185.4</td>
<td>181.1</td>
<td>62.7</td>
<td>148.7</td>
<td>7.7 \times 10^{16}</td>
</tr>
</tbody>
</table>

According to Table 1, the activation energy values calculated from Ozawa and Coats & Redfern methods were found to be 187.4 KJ·mol\(^{-1}\) and 185.4 KJ·mol\(^{-1}\) respectively, which seem to be in good agreement with each other. The positive value of \( \Delta H^* \) indicate that the dissociation processes are endothermic in nature and enhanced with the rise of temperature. \( \Delta G^* \) values are positive, thus dissociation processes are non-spontaneous [24]. The positive values of \( \Delta S^* \) indicate that the activated complex has a less ordered structure than the reactants [25] and further the high values of \( A \) indicate the fast nature of the reaction [25].

4. Conclusions

In summary, the kinetic and thermodynamic parameters evaluated from the thermodynamic curves by applying Ozawa and Coats & Redfern relations were performed between 220°C to 400°C. Following are the point wise conclusions:

1) The major thermal degradation reaction appeared to be a one stage reaction.
2) In the decomposition reaction, the main reason of mass loss corresponding to decomposition of oxalates into barium carbonate by releasing carbon monoxide. This carbonate is used as a pyro-colorant to produce green colour in fire crackers as well as in signaling [2].
3) High activation energy, thus explained high degree of thermal stability and resistance to heat, which lead its application to improve hardness of barium titanate in
4) The thermodynamic parameters suggest that the enthalpy increases during the process is of endothermic in nature, whereas fast and nonspontaneous type nature of reaction.

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REFERENCES