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Simultaneous thermal analysis of a cobalt(II) complex with nicotinate

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Abstract

Dynamic kinetic analyses were performed on $Co(NIA)_2(H_2O)_4$ (NIA: nicotinate (C_5H_4NCOOH)) using thermogravimetry (TG) and differential thermal analysis (DTA) measurements in air atmosphere. The thermal behavior and the kinetics of decomposition were studied. The effect of the heating rate on the thermal decomposition process was investigated. The Friedman method was applied to estimate the activation energy of decomposition.

Keywords: Cobalt complex; Decomposition kinetics

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1. Introduction

$Co(NIA)_2(H_2O)_4$ (NIA: nicotinate) is a transition metal organic–inorganic composite compound with a novel three-dimensional supramolecular structure. It displays remarkably a cavity structure and ladder-type hydrogen bond chains of carboxylates and water molecules. The designing, synthesizing and determination of the structure of the compound has been reported [1], but no study on thermochemistry, so far as we know, has been done.

Thermogravimetry (TG) and differential thermal analysis (DTA) are valuable techniques for studying the thermal properties of various compounds. Materazzi et al. [2] had reported the thermoanalytical studies of unusual adrenaline complexes with Co(II), Ni(II) and Cu(II). Thermogravimetric analysis of complexes of Co(II) chelates with Schiff base reagents were studied by Madhu et al. [3]. Arshad et al. [4] reported the thermal decomposition pattern of 1,2-dipiperidinoethane complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). The present study is aimed at the thermal decomposition process of $Co(NIA)_2(H_2O)_4$ in air atmosphere. The activation energy for the decomposition of compound was also evaluated.

2. Experimental

The synthesis of $Co(NIA)_2(H_2O)_4$ is described elsewhere [1]. The product was submitted to thermal analysis. All the experiments were performed on a Mettler Toledo simultaneous thermal analyzer (TGA/SDTA851e) with system interface device and a computer workstation. All samples were placed in aluminum crucibles. Experiments were performed using sample sizes of 3 ± 0.3 mg. All the experiments were conducted under air as the purge gas. The flow rate of the gas was 50 ml/min. The range of temperature studied was from 50 to 700 °C, at the heating rates of 20, 30, 40 and 50 °C/min.

3. Results and discussion

Fig. 1 represent TG-DTA curves of the compound, for an experiment carried out at 30 °C/min with a sample size of 3.224 mg in air. The curves show that the non-isothermal decomposition of the compound occurs in two separate steps. The first weight loss starts at about 100 °C; the first decomposition stage ends with weight loss of 20.57% due to the loss of water (calculated value is 19.10%). The second weight loss starts at about 370 °C ending with a weight loss of 59.98% due to the loss of nicotinate and the formation of CoO (calculated value is 61.01%). The DTA curve shows an endothermic peak for the first weight loss and an exothermic peak for the second weight loss.

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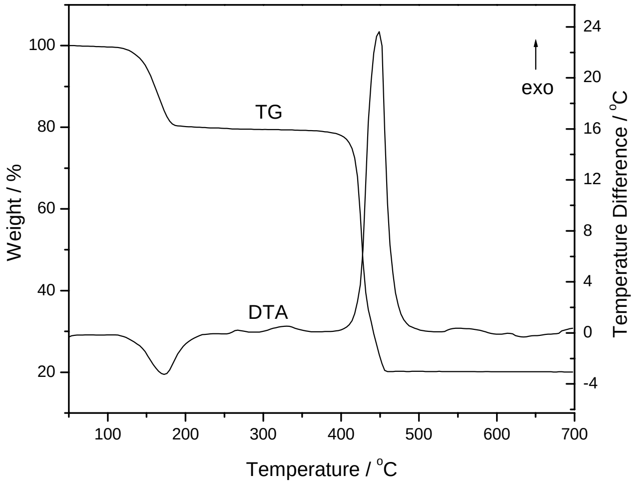

Fig. 1. Typical TG-DTA plot for cobalt(II) complex.

Kinetic studies have been carried out at different temperatures by TG techniques. The apparent activation energy of the decomposition process in non-isothermal conditions can be calculated by isoconversional method [5–14]. The isoconversional method avoids the use of explicit kinetic models. The commonly used equation in the non-isothermal decomposition kinetics is presented as [13]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (1)$$

where α is the fraction decomposed at time t, $d\alpha/dt$ the rate of the reaction, A the pre-exponential factor, E_a the apparent activation energy, and $f(\alpha)$ is an expression describing the kinetic model.

Isoconversional method of Friedman [15] is applied on TG-differential thermogravimetry (DTG) data at different heating rates. From Eq. (1), it follows that

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E_a}{RT} + \ln[Af(\alpha)] \quad (2)$$

Alpha (α) at a particular time or temperature is defined as:

$$\alpha = \frac{w_i - w_t}{w_i - w_f} \quad (3)$$

where w_t is the solid weight at the time t, w_i the initial solid weight, and w_f is the final weight.

The differential form of Eq. (3) gives

$$\frac{d\alpha}{dt} = -\frac{dw_t/dt}{w_i - w_f} \quad (4)$$

The function dw_t/dt can be obtained directly from the differential thermogravimetry plot, and the rate of the reaction can be calculated using Eq. (4). This value of $d\alpha/dt$ obtained from Eq. (4) is substituted into Eq. (2).The slope of $\ln(d\alpha/dt)$ versus $1/T$ for the same value of α gives the value of apparent activation energy. As an illustration, such plots for the first decomposition step are presented in Fig. 2. The apparent activation energy can be calculated for various values of α.

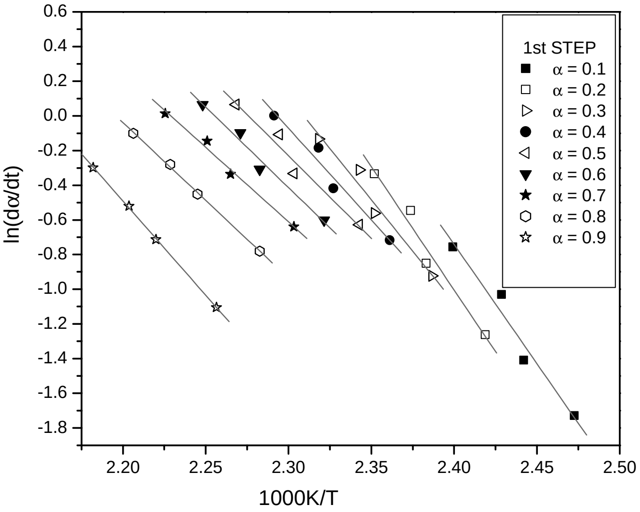

Fig. 2. Illustration for determining activation energy: plots of $\ln(d\alpha/dt)$ vs. $1/T$ for the first decomposition step.

Figs. 3 and 4 present the data on activation energies of two stages decomposition of the compound that was evaluated by isoconversional method. Any point in figures was obtained from the slope of $\ln(d\alpha/dt)$ versus $1/T$ plot. In Fig. 3, we see that the activation energy assumes values varying from about 275.69 to 159.27 kJ/mol in the range of degree of conversion 0.1–0.9. In Fig. 4, the values of activation energy decrease from 400.22 to 13.05 kJ/mol in the range of degree of conversion 0.1–0.9. The above results allows to confirm that more than one reaction occurs in the first and second decomposition process [10].The activation energy obtained in air atmosphere is 188.42±22.43 kJ/mol for the first weight loss and 114.08 ± 10.86 kJ/mol for the second weight loss.

The sequence of processes implies that the water in compound is held less strongly than the nicotinate. But the

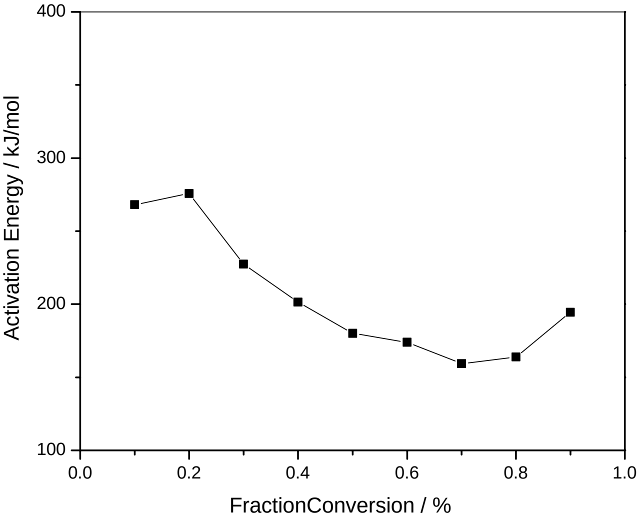

Fig. 3. A plot of E_a as a function of α for the first stage decomposition of the complex in air.

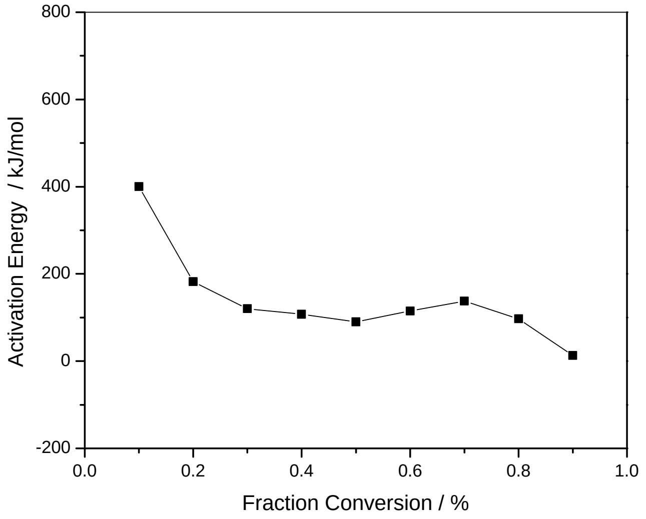

Fig. 4. A plot of E_a as a function of α for the second stage decomposition of the complex in air.

activation energy for the first stage is greater than that of the second stage. This might be due to the second stage comprising of the loss of nicotinate with simultaneous oxidation Co to CoO.

4. Conclusion

$Co(NIA)_2(H_2O)_4$ is a novel organic–inorganic composite compound. The decomposition of the compound has been investigated by simultaneous thermal analysis at different heating rates in air atmosphere. The compound experiences two steps of weight loss. An endothermic peak and an exothermic peak corresponding to two stages of decomposition are observed. Activation energies for the first and the second weight loss are 188.42 ± 22.43 and 114.08 ± 10.86 kJ/mol, respectively.

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