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The decomposition of $Co(NIA)_2(H_2O)_4$ in nitrogen atmosphere

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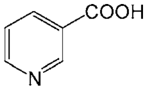
Abstract

The thermal analysis of $Co(NIA)_2(H_2O)_4$ (NIA = nicotinate) in nitrogen has been investigated by thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA). The isoconversional method was applied to estimate the activation energy of decomposition. A comparison between the thermal process corresponding to nitrogen and air atmospheres has also been performed.

Keywords: Cobalt complex; Decomposition kinetics; Isoconversional method

1. Introduction

$Co(NIA)_2(H_2O)_4$ (NIA = nicotinate (see the structure below)) is a transition metal organic–inorganic composite compound with the novel three-dimensional supramolecular structure. It displays remarkably a cavity structure and ladder-type hydrogen bond chains. The formation of this special structure is attributed to such a character that it has two carboxylates and four water molecules, which are strong donor/acceptor in hydrogen bond interactions [1].



nicotinate

Metal complexes with heterocyclic nitrogen compounds as organic ligands are of interest from the chemical and biological points of view. The effect of the structure of these complexes on the thermal decomposition has been studied in recent years. Mojumdar et al. [2–4] have reported the thermoanalytical studies of Mg(II), Cu(II) and Fe(III) complexes with different heterocyclic nitrogen ligands. In our previous paper we investigated the thermodynamic properties of $Co(NIA)_2(H_2O)_4$ in air atmosphere [5]. It is well known that the gas atmosphere is the major factor that affects the thermal behaviour of the complex. Therefore, the present study is concerned with the non-isothermal decomposition of the Co(II) complex with nicotinate in nitrogen atmosphere. In addition, the thermal behaviour of Co(II) complex in nitrogen atmosphere is compared to that in air atmosphere.

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 Mettler Toledo simultaneous thermal analyzer (TGA/SDTA851e) with system interface device and a computer workstation. All the samples were placed in aluminum crucibles. Experiments were performed using sample sizes of 3 ± 0.3 mg. All the experiments were conducted under nitrogen as the purge gas. The flow rate of the gas was 50 ml/min. The range of temperature studied was from 50 to 750 °C, at the heating rates of 5, 10, 15 and 20 °C/min.

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3. Results and discussion

Fig. 1 shows the TG and DTA curves obtained for experiments at 5 °C/min under nitrogen atmosphere. The curves show that the non-isothermal decomposition of the compound in nitrogen undergoes three separate stages. The first weight loss starts at about 90 °C; the decomposition curve achieves constant weight loss of 20.57% due to the loss of water (calculated value is 19.10%). The second stage takes place between 390 and 460 °C and is accompanied by 49.62% mass loss. It is attributed to the decomposition of 1.5 mol nicotinate (calculated value is 48.95%). The final stage starts at about 460 °C reaching a constant weight loss of 15.05% due to the loss of 0.5 mol nicotinate to Co as final solid product (calculated value is 16.31%).

The thermal reaction of complex in nitrogen can be represented as:

$$\mathrm{Co(NIA)_2(H_2O)_4} \xrightarrow{90\text{–}180\,^{\circ}\mathrm{C}} \mathrm{Co(NIA)_2 + 4H_2O}$$

$$\mathrm{Co(NIA)_2} \xrightarrow{390\text{–}460\,^{\circ}\mathrm{C}} \mathrm{Co(NIA)_{0.5} + 1.5NIA}$$

$$\mathrm{Co(NIA)_{0.5}} \xrightarrow{460\text{–}700\,^{\circ}\mathrm{C}} \mathrm{Co + 0.5NIA}$$

The DTA curve for complex shows three endothermic peaks at 150, 422 and 517 °C ascribed to the loss of $4H_2O$, 1.5NIA and 0.5NIA, respectively.

In non-isothermal experiments, the change of the sample mass is shown as a function of temperature. The fractional extent of reaction is expressed as:

$$\alpha = \frac{w_\mathrm{i} - w_\mathrm{t}}{w_\mathrm{i} - w_\mathrm{f}} \tag{1}$$

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

The differential kinetic equation can be expressed as [6]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\,\exp\left(-\frac{E_\mathrm{a}}{RT}\right) f(\alpha) \tag{2}$$

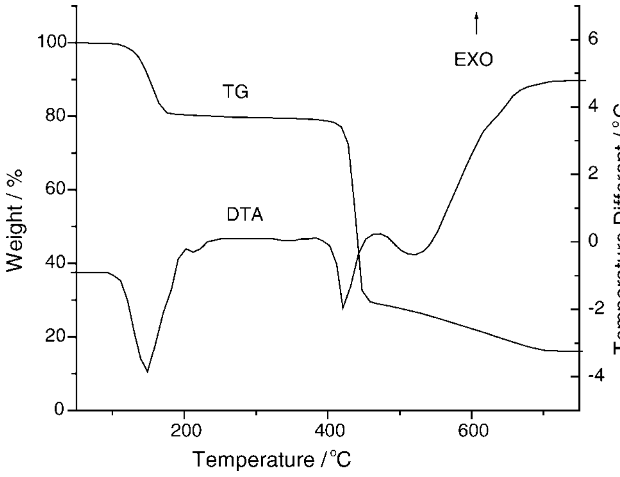

Fig. 1. TG and DTA curves of the complex at heating rate of 5 °C/min in nitrogen atmosphere.

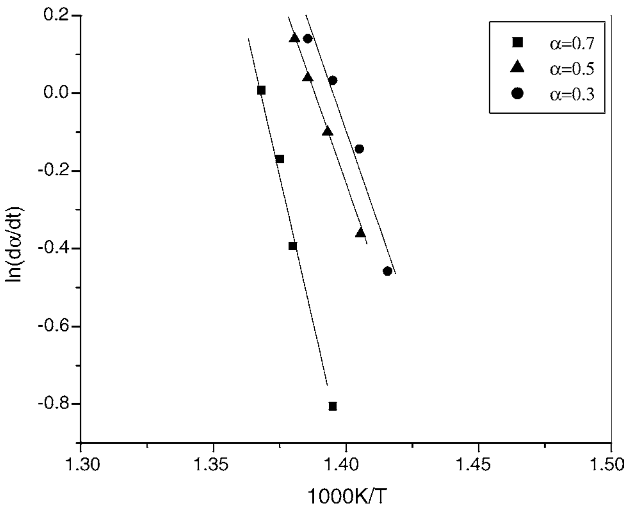

Fig. 2. Illustration for determining activation energy: plots of ln(dα/dt) vs. 1/T for the second step.

where dα/dt is the rate of the reaction, A the pre-exponential factor, E_a the apparent activation energy, and $f(\alpha)$ an expression describing the kinetic model of the studied thermal decomposition process [7].

The apparent activation energy of the decomposition process in non-isothermal conditions can be calculated by the isoconversional method of Friedman. The Friedman method [8] follows from the logarithmic form of Eq. (2):

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\frac{E_\mathrm{a}}{RT} + \ln[Af(\alpha)] \tag{3}$$

Plots of ln(dα/dt) against 1/T should fit to a straight line with a slope of $-E_\mathrm{a}/R$. Such plots for the second decomposition of complex in N_2 atmosphere are presented in Fig. 2. The apparent activation energy can be calculated for various values of α.

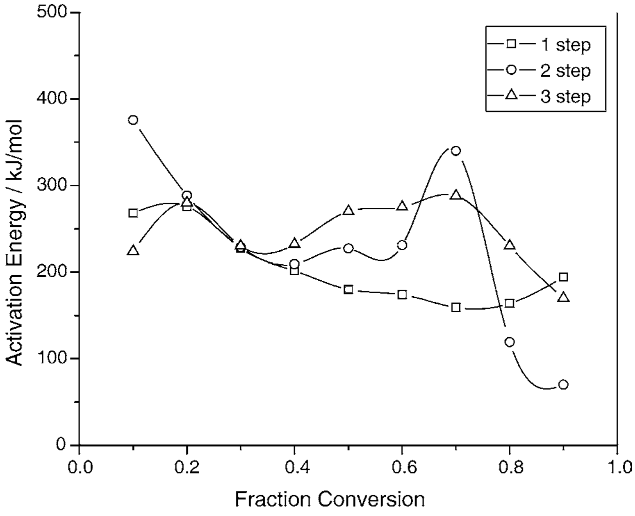

Fig. 3. A plot of E_a as a function of a for three decomposition stages of the complex in nitrogen.

Fig. 3 displays the activation energy obtained by Friedman method for three decomposition stages in nitrogen atmosphere. The activation energies obtained are 186 ± 19, 247 ± 26 and 244 ± 25 kJ/mol for the first, second and third steps, respectively. In Fig. 3, we can see the dependences of the activation energy on the extent of conversion. The observed dependences suggest the occurrence of a multi-step process in every stage of the decomposition of complex [9,10]. In this work, the error limit is higher than 10% for Friedman analysis. The source of error for Friedman analysis may be due to that the temperature and rate of reaction are not exactly defined at the same extent of conversion. Additionally, the basic kinetic equation (2) rests upon the assumption of single-step reaction that disagree with the multi-step nature of reaction in three stages of the decomposition of complex, thus introducing errors for Friedman analyses.

Comparing the results obtained with air [5] and nitrogen, similarity in the first stage and difference in the second and third stages are observed. In air atmosphere, the non-isothermal decomposition of the compound undergoes two separate stages and the second stage is attributed to the decomposition of nicotinate and the formation of CoO, corresponding to a strong exothermic peak in the DTA curve; but in nitrogen atmosphere, it undergoes three decomposition stages and the last two stages are attributed to the decomposition of nicotinate to cobalt metal, corresponding to two weak endothermic peaks. Activation energy of the second decomposition stage in air is much lower than that in nitrogen. This indicates the accelerated effect of air on the second decomposition reaction stage. Compared to in air atmosphere, the intermediate decomposition product of $Co(NIA)_2$ in nitrogen atmosphere is more thermally stable.

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 nitrogen atmosphere. The compound experiences three stages of weight loss, corresponding to three endothermic peaks. Comparing the thermal decomposition in nitrogen and air atmospheres, similar results are obtained for the dehydration process and its activation energy is about 188 kJ/mol.

References

[1] H.B. Jia, J.H. Yu, J.Q. Xu, L. Ye, H. Ding, W.J. Jing, T.G. Wang, J.N. Xu, Z.C. Li, J. Mol. Struct. 641 (2002) 23–27.

[2] S.C. Mojumdar, M. Melinik, E. Jona, J. Anal. Appl. Pyrolysis 53 (2000) 149–160.

[3] S.C. Mojumdar, I. Ondrejkovicova, L. Nevidanska, M. Melnik, J. Anal. Appl. Pyrolysis 64 (2002) 59–69.

[4] S.C. Mojumdar, M. Melnik, E. Jona, J. Anal. Appl. Pyrolysis 46 (1998) 147–156.

[5] Y.H. Liu, J.H. Yu, J.Z. Zhao, H. Zhang, Y.H. Deng, Z.C. Wang, Thermochim. Acta 419 (1–2) (2004) 115–117.

[6] J.H. Suwardie, R. Artiaga, F. Barbadillo, Thermochim. Acta 392/393 (2002) 289–294.

[7] D. Dollimore, P. Tong, K.S. Alexander, Thermochim. Acta 282/283 (1996) 13–27.

[8] H.L. Friedman, J. Polym. Sci.: Part C 6 (1964) 183–195.

[9] S. Vyazovkin, Int. Rev. Phys. Chem. 19 (2000) 45–60.

[10] S. Vyazovkin, New J. Chem. 24 (2000) 913–917.