

Kinetics of thermal decomposition of nickel oxalate dihydrate in air

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Abstract

Thermal decomposition taking place in solid state complex, $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, has been investigated in air by means of TG–DTG/DTA, DSC, XRD. TG–DTG/DTA curves showed that the decomposition proceeds through two well-defined steps with DTA peaks closely corresponding to the weight loss obtained. XRD showed that the final decomposition product of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was NiO. Kinetics analysis of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ decomposition steps was performed under non-isothermal conditions. The activation energies were calculated through Friedman and Flynn–Wall–Ozawa (FWO) methods, and the most possible kinetic model function has been estimated through the multiple-linear regression method. The activation energies for the two decomposition steps of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were 171.1 ± 4.2 and 174.4 ± 8.1 kJ/mol, respectively.

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1. Introduction

Studies on the thermal analysis and kinetics of thermal decomposition for metal oxalates have attracted more interest for a long time. The first work on PbC_2O_4 decomposition was reported in 1870 [1]. There have been a lot of reports on the thermal decomposition of metal oxalates. Macklen studied the influence of atmosphere on thermal decomposition of nickel oxalates [2] in 1968. El-Wahab et al. reported gamma irradiation effects on the electrical conductivity behavior and thermal decomposition induction period in nickel oxalate [3] in 1996. Majumdar et al. investigated the secondary catalytic reactions during thermal decomposition of oxalate of nickel(II) [4]. There have been few comprehensive reports on kinetics of thermal decomposition of nickel oxalate until 2000. L'vov reported the kinetics and mechanism of thermal decomposition of nickel oxalates in 2000 [5]. A model of dissociative evaporation of the reactant with simultaneous condensation of the low-volatility product was

used in this research. His approach is based on the assumption that decomposition process itself reduces to congruent dissociative evaporation of reactant, so that the kinetics process is determined only by the decomposition of primary decomposition products and experimental conditions, which govern the evaporation mode and reactant self-cooling.

In present study, the kinetics of thermal decomposition of nickel oxalate dihydrate has been reexamined from a fresh point of view in detail. The experiment was carried out in air. Several measurements have been run on nickel oxalate dehydrate at different heating rate from room temperature to 600 °C. Then a model-free value of the activation energy can be made using Friedman or Ozawa–Flynn–Wall (FWO) analysis [6–8]. Friedman plots with multiple peaks or variable activation energy are serious indicators of the presence of a multiple-step process. According to those indications, linear or non-linear regression was run in order to determine the best-fit kinetic model. As a result, reaction order (n), pre-exponential factor (A) and optimized activation energy (E_a) were obtained. In this paper, we studied the thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ using thermal analysis techniques. The product of thermal decomposition was characterized by

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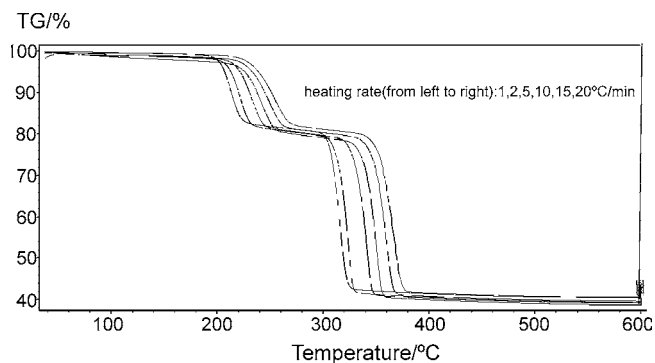


Fig. 1. TG curves of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at different heating rate.

XRD, and the kinetics was studied using above method that proved to be a simple way for kinetic investigation.

2. Experimental

Nickel oxalate dihydrate ($\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) was of analytical grade, obtained from Beijing Reagent Factory.

Thermal analysis measurements (thermogravimetry, TG; differential thermogravimetry, DTG; and differential thermal analysis, DTA) were carried out by means of a Netzsch STA 449C thermal analyzer, German. The differential scanning calorimetry (DSC) measurement was carried out by Netzsch DSC 200 analyzer, German. The thermal analyzer included a data acquisition and handling system.

Thermal analysis experiments TG/DTA were performed in static state air, at heating rate of 1, 2, 5, 10, 15, and 20 °C/min. The sample mass was kept 5.0–5.5 mg. DSC experiment was performed at a heating rate of 15 min⁻¹. The sample mass was 4.82 mg. The decomposition product was collected at the temperature that was showed in TG/DTA curves.

X-ray powder diffraction patterns of the decomposition product were obtained with a Bruker D8-Advance model X-ray diffractometer with a Ni-filter and graphite monochromator, and Cu K α_1 radiation ($\lambda = 1.54056 \text{ \AA}$, 40 kV, 50 mA).

3. Results and discussion

3.1. TG–DTG/DTA

The series of TG curves in air at different heating rate for thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ are shown in Fig. 1. The curves approximately to each other indicated that the weight loss is independent of the heating rate. TG–DTG/DTA

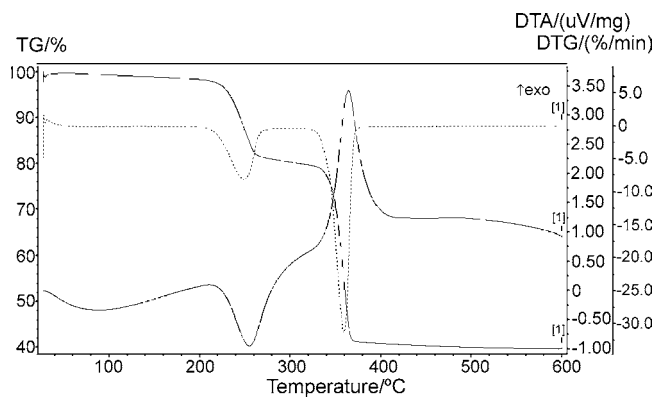


Fig. 2. TG–DTG/DTA curves of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at heating rate of 15 °C/min.

curves of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at heating rate of 15 °C/min are shown in Fig. 2. The DTA peaks closely corresponding to the weight changes observed on the TG curves. The curves showed that the thermal decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ below 500 °C occurs in two well-defined steps. The first step is from 196 to 284 °C, characterized by an endothermic peak at 258 °C in accordance with calculated weight loss of 19.73%, attributed for the dehydration of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and formation of anhydrous oxalate. The anhydrous oxalate is stable up to 316 °C, and then decomposed in the second step. This step shows an exothermic process with DTA peak at 365 °C, indicating a weigh loss of 39.85% due to the decomposition of NiC_2O_4 and the formation of NiO. The exothermic character of the DTA peak accompanying the oxalate decomposition step is due to the air oxidation of CO to CO₂, which is the common fact in thermal decomposition of metal oxalate in air.

3.2. DSC/DDSC

Fig. 3 showed the DSC/DDSC curves of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at heating rate of 15 °C/min. The DSC peaks were in well agreement with DTA peaks. DDSC curves showed that each peak in DSC curve was single. According to the DSC curve, the heat change during decomposition can be calculated as shown in Table 1.

3.3. X-ray diffraction

The X-ray diffraction data of the decomposition product at 400 °C is listed in Table 2. The results indicated that the crystal structure is cube. The calculated parameters are $a = 4.17125 \text{ \AA}$, $V = 72.58 \text{ \AA}^3$, $Z = 4$. The data listed in Table 2

Table 1
Heat change during the decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at heating rate of 15 °C/min

DSC peak	Initial temperature (°C)	Terminate temperature (°C)	Peak temperature (°C)	ΔH (J/g)
1	211.5	257.0	240.1	532.2
2	348.4	357.9	353.2	-776.1

Table 2
The XRD data of solid product from decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at 400°C

<i>H</i>	<i>K</i>	<i>L</i>	D_{OBS} (Å)	D_{CAL} (Å)	$D_{\text{OBS}} - D_{\text{CAL}}$ (Å)	Q_{OBS}	Q_{CAL}	2TH_{OBS}	2TH_{CAL}	DIF.2TH
1	1	1	2.40818	2.40827	-0.00010	0.17243	0.17242	37.309	37.307	0.002
2	0	0	2.08550	2.08563	-0.00013	0.22992	0.22989	43.351	43.348	0.003
2	2	0	1.47528	1.47476	0.00052	0.45946	0.45979	62.950	62.974	-0.025
3	1	1	1.25741	1.25768	-0.00027	0.63248	0.63221	75.554	75.535	0.019
2	2	2	1.20415	1.20414	0.00002	0.68966	0.68968	79.537	79.538	-0.001

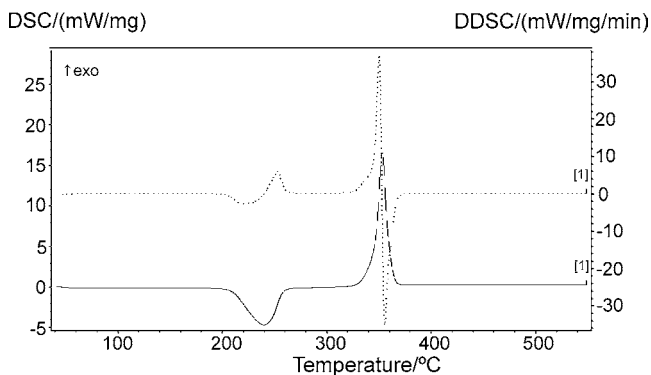


Fig. 3. DSC/DDSC curves of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in air at heating rate $15^\circ\text{C}/\text{min}$.

is in accordance with that in PDF card 471049. The product is NiO.

3.4. Kinetic studies

The aim of the kinetic studies of TA data is to find the most probable kinetic model which gives the best description of the studied process and allows the calculation of reliable values for the parameters E_a and A . The Arrhenius parameters E_a , A together with the reaction model, are sometimes called the kinetic triplet. The correlation of kinetic parameters and the apparent kinetic models does not allow the correct analysis to be performed by using only one experimental TG curve [6]. This problem can be solved, however, if multiple-

scan method was employed. In our paper, model-free and model-fitting approached was used to investigate the kinetics under multiple-scan non-isothermal conditions, which was described as below.

3.4.1. Calculation of the activation energy

As one of the non-isothermal multiple-scan methods for studying of kinetics, isoconversion method is also called model-free method because no kinetic model was set before the calculation of energy. FWO method and Friedman method are two representative ones of model-free methods, which are convenient to calculate the activation energy.

The reaction proceeds in accordance with the usual kinetic formula:

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

where α , A , E_a , R , T are the conversion rate, pre-exponential factor, activation energy, gas constant and temperature, respectively. The function $f(\alpha)$ represents the mathematical expression of kinetic model. With dynamic techniques, temperature rate dT/dt is set to be a constant β . Thus, the kinetic equation of non-isothermal heterogeneous reaction is obtained as follow.

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (2)$$

Friedman method [7] and Flynn–Wall–Ozawa [8,9] method therefore derived from the above, which is described

Table 3
Activation energies calculated using different methods during the decomposition of $\text{NiC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ at multiple-scan rate

Conversion rate α	Dehydration reaction		Decomposition reaction	
	Friedman method E_a (kJ/mol)	FWO method E_a (kJ/mol)	Friedman method E_a (kJ/mol)	FWO method E_a (kJ/mol)
0.20	153.96	200.05	148.69	187.42
0.25	148.86	190.78	212.21	184.87
0.30	145.26	183.93	138.96	184.34
0.35	143.43	178.62	183.91	182.24
0.40	141.28	174.07	176.77	182.40
0.45	138.79	170.19	153.44	180.66
0.50	139.20	166.88	154.11	179.00
0.55	138.06	164.00	177.34	177.37
0.60	138.31	161.49	180.88	178.00
0.65	140.70	159.53	149.98	176.67
0.70	144.77	157.80	175.85	175.17
0.75	150.42	156.65	175.41	175.69
0.80	158.37	156.46	153.78	174.30
Average	148.8 ± 10	177.73 ± 23	165.04 ± 12	182.28 ± 5.2

as following, respectively.

$$\ln \left[\left(\frac{d\alpha}{dT} \right) \beta \right] = \ln[Af(\alpha)] - \frac{E_a}{RT} \quad (3)$$

$$\ln \beta = \left[\frac{AE_a}{RG(\alpha)} \right] - 5.3305 - 1.0516 \frac{E_a}{RT} \quad (4)$$

These two methods are usually used to calculate activation energy. Friedman method is very sensitive to experimental noise, and tends to be numerically unstable because of employing instantaneous rate value. But FWO method produces a systematic error in E_a when varies with α . This error does not appear in Friedman method [10]. In our present study, they were used to calculate activation energy listed in Table 3.

It is shown that the values including activation energy calculated by FWO method are higher than that of Friedman method (in the range $0.2 \leq \alpha \leq 0.8$). It is due to that Friedman method is very sensitive to experimental noise, but FWO method leads to meaningful result assuming that E_a invaries with α . It also can be seen that activation energies change little with α , which is just for FWO method. It also suggested that each reaction correspond to the two steps probably obey a single kinetic mechanism.

3.4.2. Determination of kinetic model

For one-step reaction, the determination of kinetic parameters can be turned into a multiple linear regression problem through suitable transformations and simultaneous conversion of Eq. (1).

First, the experimental values (such as TG data) are differential or integrated and then transformed into the degree of conversion. Application of Friedman equation yields Eq. (5) for reaction type Fn, Eq. (6) for nucleation process of the n th dimension (An), described by Avrami–Erofeev equation [11–13], Eq. (7) for the complex reaction type, Bna (Prout–Tompkins n th-order, a th autocatalysis) [14] as well as the modified Friedman Eq. (8) for the remaining reaction type.

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + n \ln(1 - \alpha) \quad (5)$$

$$\ln \frac{d\alpha/dt}{1 - \alpha} = \ln(nA) - \frac{E}{RT} + \frac{n - 1}{n \ln[-\ln(1 - \alpha)]} \quad (6)$$

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + n \ln(1 - \alpha) + a \ln \alpha \quad (7)$$

$$\ln \frac{d\alpha/dt}{f(\alpha)} = \ln A - \frac{E}{RT} \quad (8)$$

Replaced the data of experiments into the equations corresponding to different kinetic models [15], then we used multiple linear regression method to determine the best-fit kinetic model. Generally speaking, the one with highest correlation coefficient (>0.99) is the best-fit kinetic model. The optimized value is the data of activation energy and $\ln A$, which was calculated with the best equation. Experimental results are shown in Table 4.

Table 4

Comparison of the results obtained from the model-fit and the different calculation methods

	First step	Second step
Activation energy (kJ/mol)		
Friedman method	148.8 ± 10	165.0 ± 12
FWO method	177.7 ± 23	182.3 ± 5.2
Model-fitting method	171.1	174.4
$\log A$ (S ⁻¹)	15.1	11.6
Reaction type	CnB	C ₁ B
Reaction order	1.746	1
$\log K_{\text{cat}}$ ^a	0.7923	1.5186
Correlation coefficient	0.998596	0.997371
Function	$f(\alpha) = (1 - \alpha)^n$ (1 + $K_{\text{cat}}\alpha$)	$f(\alpha) = (1 - \alpha)(1 + K_{\text{cat}}\alpha)$

^a Logarithm of the balance constant for autocatalysis reaction.

According to Table 4, it was seen that the value calculated by FWO method was close to the optimized value. That is because the FWO kinetic equation was obtained by integrating the Arrhenius equation after assuming that the kinetic model and the kinetic parameters were invariant all over the process, which nearly accord with the fact in the range $0.2 \leq \alpha \leq 0.8$. We can conclude that the kinetic model for the dehydration is CnB, and the corresponding function is $f(\alpha) = (1 - \alpha)^n(1 + K_{\text{cat}}\alpha)$. The correlated kinetic parameters are $E_a = 171.1$ kJ/mol, $\log A = 15.1$, $n = 1.75$, respectively. The kinetic model for the second reaction is C₁B. The function is $f(\alpha) = (1 - \alpha)(1 + K_{\text{cat}}\alpha)$. The optimized activation parameters are $E_a = 174.4$ kJ/mol, $\log A = 11.6$, $n = 1.0$.

In previous works, L'vov also studied the kinetics of thermal decomposition of nickel oxalate using a model of dissociative evaporation of the reactant with simultaneous condensation of the low-volatility product. In his opinion, the average activation energy for the steady-state decomposition of nickel oxalate in vacuum is 220 ± 5 kJ/mol, which was mainly used for the selection of appropriate schemes of thermal decomposition of nickel oxalate. In our study, the kinetics of the thermal decomposition of nickel oxalate was investigated under non-isothermal conditions in air using multiple linear regression method. The optimized value of activation energy was 171.1 kJ/mol (dehydration), 174.4 kJ/mol (decomposition). Obviously, the value of activation energy calculated by L'vov is higher than that calculated by us. We attempted to explain this as due to the difference between the true scheme decomposition of nickel oxalate. These differences consisted of in primary gasification of all decomposition products and the methods that were used to calculate E_a and $\log A$ to obtain the topochemical equation.

4. Conclusions

By properly choosing the primary product composition, we have succeeded in getting the final data of E_a and $\log A$,

determining the best-fit reaction model for the thermal decomposition of nickel oxalate dihydrate in air under non-isothermal condition using multiple linear regression method. Multiple linear regression is a process that the data of experiments into the equations corresponding to different kinetic model firstly, then the best-fit kinetic model was determined, the value of E_a and A was calculated subsequently. The method was proved to be convenient for investigating thermal analysis of inorganic compounds.

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