Non-isothermal Kinetics of the Dehydration Process of Na$_2$MoO$_4$•2H$_2$O

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The dehydration process of Na$_2$MoO$_4$•2H$_2$O and its kinetics have been studied by TG-DTG. Using Malek method, SB(m,n) was defined as the kinetic model of the dehydration process. The corresponding kinetic and thermodynamic parameters were obtained.

Keywords   Na$_2$MoO$_4$•2H$_2$O, non-isothermal kinetic, dehydration process, TG-DTG

Introduction

In the field of thermal analysis kinetics, there have been many kinetic models and methods of processing the corresponding data, which can depict the most probable kinetic mechanism of solid state reactions, such as the method combining differential and integral methods,[1-6] the method combining isothermal and non-isothermal processes[7,8] and method of TA curve shape,[9,10] and so on. Recently, based on the predecessor's work, a more complete kinetic method of processing thermal analysis data was put forward by Malek *et al.*[11-13] The advantage of this method is that without considering the kinetic models, first, the activation energy *E* can be calculated by the multiple scanning method, then, the probable kinetic model function can be determined through the characteristic values of two functions [$Y(\alpha) = (d\alpha/dt)e^x$ and $Z(\alpha) = \pi(x)(d\alpha/dt)T/\beta$] obtained by the calculation with simple experimental data, and at last, pre-exponential factor *A* can be obtained. The complete kinetic result is thus obtained. In this way, the trouble of calculating with every *f*(*α*) one by one and the influence of the kinetic compensation effect made when the activation energy, *E*, pre-exponential factor *A* and kinetic model function *f*(*α*) are obtained simultaneously can be avoided.

In this paper, the method suggested by Malek[11-13] was used to study the kinetic parameters and mechanism model for the dehydration process of the title compound. The sodium molybdate is more and more valued by people because of its solid-solid phase transition in the process of temperature change and its usage in the storage of heat energy,[14,15] but few studies on the non-isothermal kinetics of its thermal decomposition mechanism have been reported in literature.

Experimental

Sample

The Na$_2$MoO$_4$•2H$_2$O used in the present investigation was of an analytical grade.

TG and DTG analysis

The TG and DTG experiments for the title compound were performed using a Perkin-Elmer TGA-7 thermogravimetric analyzer. The heating rates used were 3, 5, 7 and 10 ℃•min^{-1} from the ambient to 325 ℃, and the sample mass was 6.5±0.2 mg. Air was used as a static atmosphere.

Theory of kinetic investigation

The kinetic investigation method proposed by Malek and coworkers[11-13] was described as follows.

Calculation of the activation energy *E*

Multiple-scan methods can be applied to the calculation of activation energy *E* from several sets of TG-DTG curves at various heating rates. Ozawa[16,17] and Kissinge[18] methods were used to obtain the value of *E*. Ozawa and Kissinger equations are as follows:

$$\text{Log } \beta + 0.4567E/RT = C \tag{1}$$

$$d\{\ln(\beta/T_P^2)\}/d(1/T_P) = -E/R \tag{2}$$

where β, *E*, *R*, *T* and T_P have the usual meanings, and *C* is the constant.

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Determination of the kinetic model

The special functions $Y(\alpha)$ and $Z(\alpha)$ are defined as follows and can be easily obtained by simplified transformation of the experimental data:

$$Y(\alpha) = (d\alpha/dt)e^x \tag{3}$$

$$Z(\alpha) = \pi(x)(d\alpha/dt)T/\beta \tag{4}$$

where $x = E/RT$, and $\pi(x)$ is the approximate function of temperature integration proposed by Sinum-Yang:[11,19]

$$\pi(x) = (x^3 + 18x^2 + 88x + 96)/(x^4 + 20x^3 + 120x^2 + 240x + 120) \tag{5}$$

By combination of the shape of function $Y(\alpha)$ with parameters α_m, α_P and α_p^∞, at which the function $Y(\alpha)$, TG-DTG curve and $Z(\alpha)$ have a maximum, respectively, the most suitable kinetic model function $f(\alpha)$ can be determined from Figure 1. The usually used functions $f(\alpha)$ are listed in Table 1.[11,12]
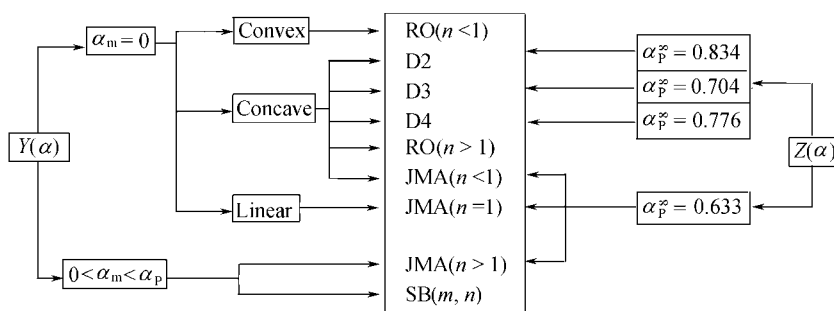

Figure 1 Schematic diagram of the kinetic model determination.

Table 1 The mathematical expressions of the kinetic models

Model	Symbol	$f(\alpha)$
Šesták-Berggren eqn.	SB(m,n)	$\alpha^m(1-\alpha)^n$
Johnson-Mehl-Avrami eqn.	JMA(n)	$n(1-\alpha)[-\ln(1-\alpha)]^{1-1/n}$
Reaction order eqn.	RO(n)	$(1-\alpha)^n$
Two-dimensional diffusion	D2	$1/[-\ln(1-\alpha)]$
Jander eqn.	D3	$3(1-\alpha)^{2/3}/2[1-(1-\alpha)^{2/3}]$
Ginstling-Brounshtein eqn.	D4	$3/2[(1-\alpha)^{-1/3}-1]$

Calculation of the kinetic exponents *n* (or *m*)

Once the kinetic model has been determined, the corresponding kinetic exponents n (or m) can be calculated.

Calculation of the pre-exponential factor *A*

Knowing the value of E and the kinetic exponents, the value of A can be calculated using the equation

$$A = -\beta x_p \exp(x_p)/[T_P f'(\alpha_p)] \tag{6}$$

Results and discussion

Thermogravimetric decomposition data

TG and DTG curves of $Na_2MoO_4 \cdot 2H_2O$ are shown in Figure 2. The first stage starts from 79.86 to 128.48 ℃ with a mass loss of 14.61% which corresponds to the loss of 2 mol of water (theoretical loss is 14.88%).

Kinetics

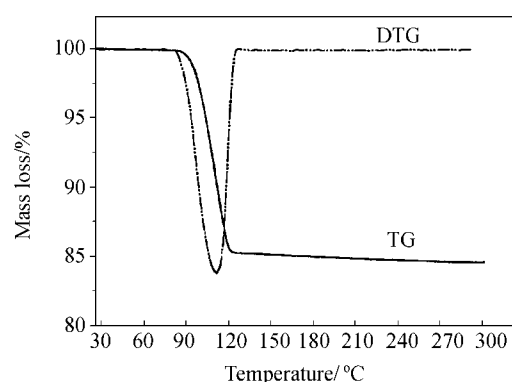Activation energy E is the most important factor for

Figure 2 TG-DTG curves for the dehydration of $Na_2MoO_4 \cdot 2H_2O$

the determination of the function $f(\alpha)$,[11] so without touching the kinetic function, values of E of the first-stage thermal decomposition were calculated by Ozawa equation[16,17] using the multiple-scan method. The results are listed in Table 2, from which it can be seen that the average value of E is 78.55 kJ•mol^{-1}. In order to verify the reliability of this result, Kissiger

Table 2   The activation energy for the first-stage decomposition of Na$_2$MoO$_4$•2H$_2$O obtained by Ozawa method

No.	α	T_3 ℃/min/K	T_5 ℃/min/K	T_7 ℃/min/K	T_{10} ℃/min/K	E/(kJ•mol^{-1})	E^a/(kJ•mol^{-1})	r
1	0.15	362.38	370.98	369.48	376.96	85.85	78.55	0.9306
2	0.20	364.03	372.79	371.59	379.22	83.89		0.9390
3	0.25	365.59	374.6	373.69	380.84	85.09		0.9455
4	0.30	366.79	375.95	375.45	382.78	82.78		0.9548
5	0.35	368.00	377.31	376.5	384.39	80.94		0.9491
6	0.40	369.20	378.67	378.61	386.01	80.47		0.9620
7	0.45	370.81	379.57	380.02	387.62	82.08		0.9699
8	0.50	371.61	380.93	381.78	389.24	78.93		0.9749
9	0.55	372.81	382.29	383.18	390.85	77.76		0.9753
10	0.60	374.02	383.55	384.59	391.82	79.18		0.9763
11	0.65	374.82	384.55	385.64	393.43	76.42		0.9775
12	0.70	376.03	385.45	387.05	395.05	75.66		0.9821
13	0.75	377.23	386.81	388.45	396.02	76.94		0.9831
14	0.80	378.03	387.72	389.86	397.63	74.35		0.9866
15	0.85	379.24	389.53	391.26	399.25	73.15		0.9827
16	0.90	380.44	390.43	393.02	400.86	72.40		0.9891
17	0.95	381.65	392.24	395.13	403.13	69.41		0.9904

^{a} Averrage value of E.

method[18] was   also used to calculate the value of E of the first-stage thermal decomposition, and the result is shown in Table 3. The value of E of 69.49 kJ mol^{-1} by Kissinger method is approximate to that of E by Ozawa method. The average value of 74.24 kJ•mol^{-1} was used to calculate the functions $Y(\alpha)$ and $Z(\alpha)$. The experimental data of T, α and dα/dt can be obtained from TG-DTG curves. Functions $Y(\alpha)$ and $Z(\alpha)$ can be obtained by the transformation experimental data and activation energy E from Eqs. (3) and (4). Figures 3 and 4 show the dependence of $Y(\alpha)$ and $Z(\alpha)$ on α, respectively. In order to obtain the accurate values of α_m and α_p^∞, at which functions $Y(\alpha)$ and $Z(\alpha)$ have a maximum, respectively, Mathematica 3.0 software was used for fitting the curves of $Y(\alpha)$ and $Z(\alpha)$ values vs. the values of α. It is found that the equation obtained by six time-fitting was the most accurate. The fitted equation at various heating rates are described as follows:

β＝3 ℃•min^{-1}

$$Y(\alpha)=0.145133+1.43869\alpha-5.66696\alpha^2+11.2655\alpha^3-13.5146\alpha^4+9.08418\alpha^5-2.72784\alpha^6$$
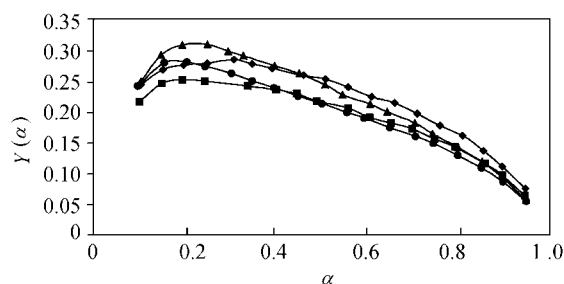
$$Z(\alpha)=-0.00111273+1.85932\alpha-7.41454\alpha^2+20.757\alpha^3-33.6623\alpha^4+28.3667\alpha^5-9.82912\alpha^6$$

β＝5 ℃•mol^{-1}

$$Y(\alpha)=0.0608572+2.62962\alpha-13.8159\alpha^2+36.3696\alpha^3-52.8595\alpha^4+36.7687\alpha^5-1.42506\alpha^6$$

Table 3   Kinetic parameters for the first-stage decomposition of Na$_2$MoO$_4$•2H$_2$O obtained by Kissinger method

β/(℃•mol^{-1})	T_p/K	E(kJ•mol^{-1})	r
3	374.34	69.49	0.9611
5	384.23		
7	384.60		
10	393.94		

Figure 3   The relation between $Y(\alpha)$ and α (β＝3 ℃•mol^{-1}, ◆; β＝5 ℃•mol^{-1} ■; β＝7 ℃•min^{-1}, ▲; β＝10 ℃•mol^{-1}, ●).

$$Z(\alpha)=0.0236415+1.66187\alpha-5.80339\alpha^2+15.1622\alpha^3-24.1015\alpha^4+20.0253\alpha^5-12.1483\alpha^6$$

β＝7 ℃•mol^{-1}

$$Y(\alpha)=-0.03484116+4.67337\alpha-23.964\alpha^2+60.3348\alpha^3-82.8287\alpha^4+58.642\alpha^5-16.8164\alpha^6$$

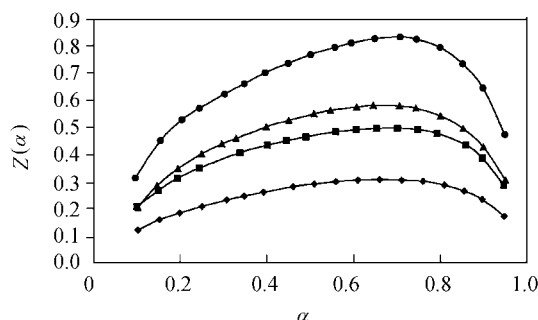**Figure 4** The relation between $Z(\alpha)$ and α ($\beta=3$ ℃•min^{-1}, ◆; $\beta=5$ ℃•min^{-1}, ■; $\beta=7$ ℃•min^{-1}, ▲; $\beta=10$ ℃•min^{-1}, ●).

$$Z(\alpha) = -0.145455 + 4.98132\alpha - 20.0193\alpha^2 + 50.7454\alpha^3 - 74.466\alpha^4 + 58.1236\alpha^5 - 19.1094\alpha^6$$

$$\beta = 10 \ ℃•min^{-1}$$

$$Y(\alpha) = 0.0421481 + 3.54599\alpha - 19.3478\alpha^2 + 50.0581\alpha^3 - 69.6193\alpha^4 + 49.7235\alpha^5 - 14.3981\alpha^6$$

$$Z(\alpha) = -0.157267 + 7.37867\alpha - 33.211\alpha^2 + 89.2612\alpha^3 - 133.646\alpha^4 + 104.481\alpha^5 - 33.9166\alpha^6$$

The values of α_m and α_p^∞ at various heating rates can be obtained by derivation of above equations (data see Table 4). From Table 4 it can be seen that the values of α_m at various heating rates are all more than zero and less than those of α_p at various heating rates, and values of α_p^∞ at various heating rates are not equal to 0.633. By combination with the Figure 1, the kinetic model of the first-stage thermal decomposition can be determined to be SB(*m,n*).

Table 4 The characteristic values of the functions $Y(\alpha)$ and $Z(\alpha)$

$\beta/(℃•min^{-1})$	Shape of $Y(\alpha)$	α_m	α_p^∞	α_P
3	Convex	0.2678	0.6691	0.6340
5	Convex	0.2231	0.6860	0.6290
7	Convex	0.2194	0.6669	0.6070
10	Convex	0.1914	0.6920	0.6680

The kinetic exponents *m* and *n* were calculated using the equations:

$$\ln[(d\alpha/dt)e^x] = \ln A + n\ln[\alpha_p(1-\alpha)] \tag{7}$$

$$m = pn \tag{8}$$

$$p = \alpha_m/(1-\alpha_m) \tag{9}$$

The pre-exponential factor *A* can be calculated using Eq. (6) and the results are listed in Table 5. The thermodynamic parameters of activation can be calculated from the equations:[20,21]

$$A\exp(-E/RT) = v\exp(-\Delta G^{\neq}/RT) \tag{10}$$

$$\Delta H^{\neq} = E - RT \tag{11}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{12}$$

Table 5 Kinetic parameters and mechanism of the dehydration reaction of $Na_2MoO_4 \cdot 2H_2O$

$\beta/(℃•min^{-1})$	KM^a	m	n	$\ln A/(s^{-1})$	$E/(kJ•mol^{-1})$
3	SB(*m,n*)	0.0183	0.0501	24.91	74.02
5	SB(*m,n*)	0.0095	0.0332	24.60	
7	SB(*m,n*)	0.0146	0.0521	24.23	
10	SB(*m,n*)	0.0046	0.0195	24.35	

^{a} Kinetic model.

The values of the entropy, enthalpy and free energy of activation at the peak temperature obtained by Eqs. (10)—(12) are listed in Table 6.

Conclusions

Using Malek method, SB(*m,n*) was defined as the kinetic model of the dehydration process of $Na_2MoO_4 \cdot 2H_2O$. The activation energy of the dehydration reaction is 74.02 kJ•mol^{-1}. The entropy of activation $\Delta S^{\neq}$ is -51.45 J•mol^{-1}•K^{-1}. The free energy of activation $\Delta G^{\neq}$ is 90.61 kJ•mol^{-1}, the enthalpy of activation $\Delta H^{\neq}$ is 70.83 kJ•mol^{-1}, and the pre-exponential factor is e$^{24.52}$ s^{-1}.

Table 6 The thermodynamic parameters of the title compound

$\beta/(℃•mol^{-1})$	$E/(kJ•mol^{-1})$	$\ln A/s^{-1}$	$\Delta H^{\neq}/(kJ•mol^{-1})$	$\Delta G^{\neq}/(k J•mol^{-1})$	$\Delta S^{\neq}/(J•mol^{-1}•K^{-1})$	T_P/K
3		24.91	70.91	88.88	-48.01	374.34
5		24.60	70.83	90.35	-50.81	384.23
7		24.23	70.82	91.55	-53.89	384.60
10		24.35	70.74	91.66	-53.09	393.94
Mean	74.02	24.52	70.83	90.61	-51.45	

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