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Study on the kinetics of the thermal decompositions of ammonium molybdates

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Abstract

The activation energies and reaction orders of the thermal decompositions of three ammonium molybdates, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_4Mo_5O_{17}$ and $(NH_4)_2Mo_4O_{13}$, were calculated according to Kissinger's method from the DSC measurements of their mixture in air at different heating rates. The activation energies were estimated to be 80.84, 144.83 and 150.48 kJ mol^{-1}, respectively, and the reaction orders one. The reason why the mixture of ammonium molybdates was used in the DSC measurements and the accuracy of the resulting kinetic parameters were also discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: DSC measurement; Ammonium molybdate; Thermal decomposition; Activation energy; Reaction order

1. Introduction

The thermal decompositions of three ammonium molybdate mixtures were studied by authors [1,2] with TGA, DTA and high temperature XRD measurements. For example, a mixture with the mass composition of 4.50% $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, 44.85% $(NH_4)_4Mo_5O_{17}$, 50.65% $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ decomposes in steps as follows:

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \xrightarrow{110^\circ C} (NH_4)_4Mo_5O_{17} \xrightarrow{220^\circ C} (NH_4)_2Mo_4O_{13} \quad (1)$$

$$(NH_4)_2Mo_4O_{13} \text{ and } \beta\text{-}(NH_4)_2Mo_4O_{13} \xrightarrow{290^\circ C} (NH_4)_2Mo_{14}O_{43} \xrightarrow{290^\circ C} (NH_4)_2Mo_{22}O_{67} \xrightarrow{290^\circ C} MoO_3 \quad (2)$$

Other researches finished before are mainly concerned with the thermal decomposition behaviors of the single phases of ammonium molybdates [3–7] .The kinetics of the thermal decompositions of ammonium molybdates, however, has not yet been studied because of the complexation of the processes.

In this paper, the activation energies and reaction orders of the thermal decompositions of three ammonium molybdates, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_4Mo_5O_{17}$ and $(NH_4)_2Mo_4O_{13}$, were calculated for the first time according to Kissinger's method from the DSC measurements of their mixture in air at different heating rates. The reason why the mixture was used in the DSC measurements and the accuracy of the resulting kinetic parameters were also discussed.

2. DSC measurements

The differential scanning calorimetry (DSC) measurements were performed in open air on a Du Pont

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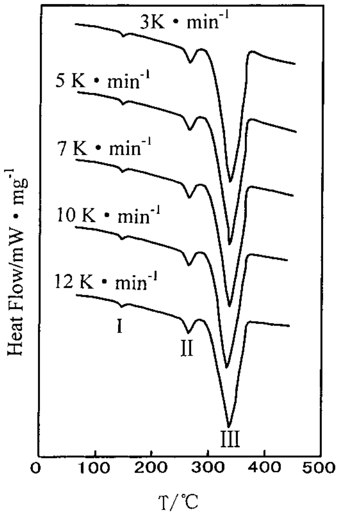

Fig. 1. DSC curves of the sample at different heating rates.

9900 Calorimeter (Du Pont, American) at the heating rates of 3, 5, 7, 10 and 12 K $\min^{-1}$. The sample used in the experiments was a mixture of ammonium molybdates with the mass composition of 4.50% $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, 44.85% $(NH_4)_4Mo_5O_{17}$, 50.65% $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$. The mass of the sample was ca. 30 mg. The DSC curves obtained are shown in Fig. 1.

3. The activation energy of the thermal decomposition

According to Kissinger's method [8–10], the rate of the thermal reaction can be written as

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where α is the fraction of the material decomposed, n the reaction order which is constant for a given thermal decomposition, R the gas constant, T the Kelvin temperature, A a constant that is the property of the material and E_a the activation energy. When the temperature increases at a constant heating rate β and reaches the peak temperature T_m, the following equation is obtained:

$$\frac{d(\ln(\beta/T_m^2))}{d(1/T_m)} = -\frac{E_a}{R} \tag{4}$$

Therefore, the activation energy can be calculated from the slope $-E_a/R$ of the linear regression curve between $\ln(\beta/T_m^2)$ and $1/T_m$. Eq. (4) is independent of the reaction order n.

The three endothermic peaks I, II and III in Fig. 1 refer to the following thermal decomposition reactions of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $(NH_4)_4Mo_5O_{17}$ and $(NH_4)_2Mo_4O_{13}$, respectively, as in Ref. [2].

$$\begin{aligned}&5(NH_4)_6Mo_7O_{24}\cdot 4H_2O(s)\\&\quad = 7(NH_4)_4Mo_5O_{17}(s) + 2NH_3(g) + 5H_2O(g)\end{aligned} \tag{5}$$

$$\begin{aligned}&4(NH_4)_4Mo_5O_{17}(s)\\&\quad = 5(NH_4)_2Mo_4O_{13}(s) + 6NH_3(g) + 3H_2O(g)\end{aligned} \tag{6}$$

$$\begin{aligned}&(NH_4)_2Mo_4O_{13} \text{ and } \beta\text{-}(NH_4)_2Mo_4O_{13}(s)\\&\quad = 4MoO_3(s) + 2NH_3(g) + H_2O(g)\end{aligned} \tag{7}$$

The peak temperatures T_m at different heating rates β from Fig. 1 are shown in Table 1. The linear regression equations between $\ln(\beta/T_m^2)$ and $1/T_m$ for the three endothermic peaks I, II and III are:

$$\ln\left(\frac{\beta}{T_m^2}\right) = 9.436 - 9.627\times 10^3 \times \frac{1}{T_m}$$
$$\gamma = -0.9463 \tag{8}$$

$$\ln\left(\frac{\beta}{T_m^2}\right) = 19.09 - 17.42\times 10^3 \times \frac{1}{T_m}$$
$$\gamma = -0.9984 \tag{9}$$

$$\ln\left(\frac{\beta}{T_m^2}\right) = 19.09 - 17.42\times 10^3 \times \frac{1}{T_m}$$
$$\gamma = -0.9984$$

$$\ln\left(\frac{\beta}{T_m^2}\right) = 14.43 - 18.10\times 10^3 \times \frac{1}{T_m}$$
$$\gamma = -0.9962 \tag{10}$$

where γ are the regression coefficients.

Table 1
T_m of peaks I, II and III at different β

β/K $\min^{-1}$	3	5	7	10	12
T_m^{I}/K	398.25	399.66	405.91	415.19	416.37
T_m^{II}/K	504.88	511.80	515.73	521.70	524.68
T_m^{III}/K	599.72	608.38	613.99	622.54	626.60

The activation energies of the thermal decomposition reactions (5), (6) and (7) calculated from the slopes of the corresponding regression Eqs. (8)–(10) are:

$$E_a(5) = 9.627 \times 10^3 R = 80.84\,\mathrm{kJ\,mol^{-1}} \quad (11)$$

$$E_a(6) = 17.42 \times 10^3 R = 144.83\,\mathrm{kJ\,mol^{-1}} \quad (12)$$

$$E_a(7) = 18.10 \times 10^3 R = 150.48\,\mathrm{kJ\,mol^{-1}} \quad (13)$$

It is commonly considered [11] that a chemical reaction would take place at room temperature rapidly if its activation energy E_a is <40 kJ $\mathrm{mol^{-1}}$; it would take place at room temperature or a little higher than that if E_a is ca. 100 kJ $\mathrm{mol^{-1}}$ and at ≈200°C if E_a is around 170 kJ $\mathrm{mol^{-1}}$. The decomposition behaviors [1,2] and the activation energies of the thermal decomposition reactions (5), (6) and (7) estimated in this work coincide well with the above considerations. Also, the regression coefficients γ of Eqs. (8)–(10) show that the DSC experimental data used to calculate the activation energies of the thermal decomposition reactions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_4Mo_5O_{17}$ and $(NH_4)_2Mo_4O_{13}$ are well interrelated.

The experimental error is considered to be due to the temperature gradient across the sample when DTA or DSC measurements are carried out to calculate the activation energy according to Kissinger's method. To reduce the temperature difference to a minimum extent, samples are usually 'diluted' [8]. The sample in our DSC measurements was a mixture of three ammonium molybdates. When measuring the heat flow of the endothermic peak I or II, the rest compounds, which did not decompose under certain conditions, could act as the 'diluents'. This would make the DSC measurement results of the mixture more accurate and interrelated to calculate the kinetic parameter than those of the single phases.

The thermal decomposition reactions of $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ occur at almost the same temperature as in Eq. (2). Their endothermic peaks can not be identified separately by DSC measurements so that their activation energies can not be calculated individually by this method. The activation energy calculated from peak III is, therefore, the apparent activation energy of ammonium tetramolybdate.

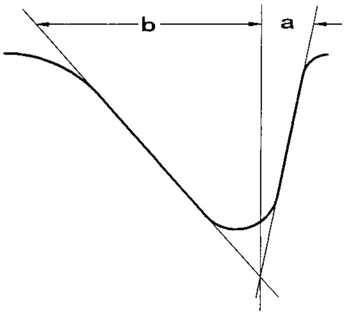

Fig. 2. Shape index for DSC and DTA peak.

4. The reaction order of the thermal decomposition

Fig. 2 is a typical endothermic DTA or DSC peak. The shape index S is defined as

$$S = \frac{a}{b} \quad (14)$$

Kissinger indicated [9] that the reaction order n of the thermal decomposition can be calculated from the shape index S of the endothermic peak as

$$n \approx 1.26 S^{1/2} \quad (15)$$

The reaction orders n of the thermal decompositions (5), (6) and (7) of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $(NH_4)_4Mo_5O_{17}$ and $(NH_4)_2Mo_4O_{13}$ calculated from the shape indexes S of the three endothermic peaks I, II and III of the DSC curves at different heating rates β according to Eq. (15) are listed in Table 2.

From Table 2, it can be seen that the reaction orders n of the thermal decompositions (5) and (6) of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $(NH_4)_4Mo_5O_{17}$ are estimated to be one which are independent of the heating rates of the DSC measurements. The apparent reaction order n of the thermal decomposition (7) of $(NH_4)_2Mo_4O_{13}$ and β-$(NH_4)_2Mo_4O_{13}$ is approximately

Table 2
The reaction orders n of the thermal decompositions (5), (6) and (7) at different β

K $\mathrm{min^{-1}}$	3	5	7	10	12
Reaction (5)	1.1	1.2	0.8	0.9	0.9
Reaction (6)	0.9	1.0	1.0	1.0	1.0
Reaction (7)	0.7	0.7	1.0	0.6	0.8

equal to one, which may be caused by the interaction of the two phases during the decomposition processes.

5. Conclusions

The activation energies and reaction orders of the thermal decompositions of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, $(NH_4)_4Mo_5O_{17}$ and $(NH_4)_2Mo_4O_{13}$ are calculated according to Kissinger's method from the DSC measurements of their mixture as follows:

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O \overset{80.04\,\mathrm{kJ\,mol^{-1}}}{\rightarrow} (NH_4)_4Mo_5O_{17} \quad n = 1$$

$$(NH_4)_4Mo_5O_{17}\cdot 4H_2O \overset{144.83\,\mathrm{kJ\,mol^{-1}}}{\rightarrow} (NH_4)_2Mo_4O_{13} \quad n = 1$$

$$(NH_4)_2Mo_4O_{13} \text{ and } \beta\text{-}(NH_4)_2Mo_4O_{13} \overset{150.48\,\mathrm{kJ\,mol^{-1}}}{\rightarrow} MoO_3 \quad n \approx 1$$

The mixture used in the DSC measurements would make the experimental results well interrelated to calculate the considerably accurate kinetic parameters.

Acknowledgements

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