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The identification of the mechanism function and the kinetic investigation of the energy-storing reaction of ammonium hydrogen sulfate

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Abstract

The kinetics and the mechanism of the thermal decomposition of NH_4HSO_4 were studied by means of thermogravimetry at constant temperature and with increasing temperature. The mechanism function of the reaction was found and identified by a three-stage identification method. Some kinetic parameters were determined. The results of the two methods showed that the thermal decomposition of NH_4HSO_4 is dominated by an R_1 mechanism, i.e. a one-dimensional phase-boundary reaction. The activation energy E obtained by thermogravimetry at constant temperature is 141.25 kJ mol^{-1}. The frequency factor A is 1.563×10^{10} min^{-1}. Its kinetic compensation effect is $\log A = 0.0899E - 2.5143$.

INTRODUCTION

To select a proper chemical-energy storing system, Wentworth and Chen [1] and others [2–7] have suggested ten standards. Evaluated by these standards, the decomposition and synthesis reactions of NH_4HSO_4 form a fairly ideal system for storing energy:

$$NH_4HSO_4 \rightleftharpoons NH_3(g) + H_2O(g) + SO_3(g)$$

Prengle [2] has also reported some theoretical research on the feasibility of applying the above reaction to the energy-storing system of a solar power station, yet the basic investigation of the reaction is far from complete. In particular, there is little published work on the kinetics and mechanism of the decomposition.

This paper describes the kinetics of the thermal decomposition of NH_4HSO_4 by means of thermogravimetry, both at constant temperature and with linearly increasing temperature. The decomposition mechanism

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was obtained in order to provide basic data for practical use in the energy-storing system.

EXPERIMENTAL

The NH_4HSO_4 used (Shanghai Reagent Factory, analytical reagent) was dried for 3 h at 50°C, to remove the absorbed water, and was ground in a mortar and sieved with a 190-mesh sifter.

The following experimental procedure was used. About 10 mg of the reagent were put in a 5 mm × 4 mm aluminium crucible which was placed in a WRT-1 microthermal balance (Shanghai Balancing Instruments Factory). Measurements were made at different β values with a nitrogen flux of 30 ml min^{-1}. The thermogravimetric curves for the isothermal decomposition of NH_4HSO_4 were recorded with the dynamic run under the same conditions; a relevant computer program was written. The kinetics analysis was performed within the transformation range $\alpha = 0.1–0.9$.

RESULTS AND DISCUSSION

Isothermal method

The TG curves of the isothermal decomposition of NH_4HSO_4 are shown in Fig. 1.

The rate of the decomposition reaction can be expressed as [4]

$$\frac{d\alpha}{dt} = Kf(\alpha) \qquad (1)$$

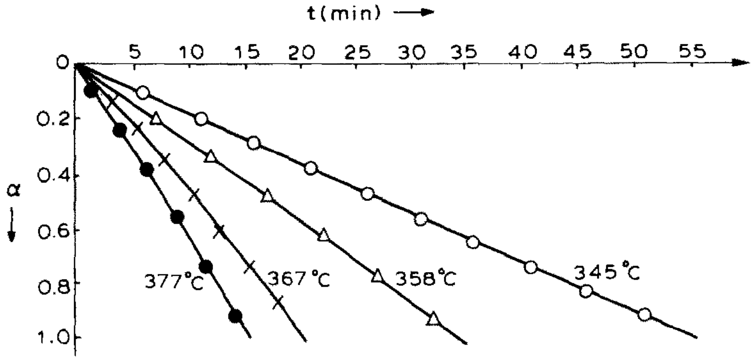

Fig. 1. TG curves of isothermal decomposition of NH_4HSO_4.

TABLE 1

Kinetic models for considering the thermal decomposition of NH_4HSO_4

$g(\alpha)$	Symbol	Rate-controlling process
α^2	D_1	One-dimensional diffusion
$\alpha+(1-\alpha)\ln(1-\alpha)$	D_2	Two-dimensional diffusion
$(1-(1-\alpha)^{1/3})^2$	D_3	Three-dimensional diffusion (Jander function)
$1-(2/3)\alpha-(1-\alpha)^{2/3}$	D_4	Three-dimensional diffusion (Ginstling–Broushtein function)
$\ln(\alpha/(1-\alpha))$	Au	Autocatalytic reaction (Prout–Tompkins function)
$1-(1-\alpha)^{1/n}$	R_n	Phase-boundary reaction; $n = 1, 2$ and 3 (one-, two- and three-dimensional diffusion respectively)
$(-\ln(1-\alpha))^{1/m}$	A_m	Random nucleation, $m = 1$; random nucleation and subsequent growth, $m = 2, 3$ and 4 (Avrami–Erofeev function)

From the Arrhenius equation

$$K = A\ e^{-E/RT} \tag{2}$$

eqn. (1) may be written as

$$\frac{d\alpha}{dt} = A\ e^{-E/RT} f(\alpha) \tag{3}$$

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = K\int_0^t dt \tag{4}$$

$$g(\alpha) = Kt \tag{5}$$

where $f(\alpha)$ and $g(\alpha)$ are functions related to the reaction mechanism, α is the fraction decomposed at time t and K is the rate constant.

The correct $g(\alpha)$ can be preliminarily identified from the linear regression between $g(\alpha)$ and t. The mechanism functions, $g(\alpha)$ of the various theoretical models are listed in Table 1 [6].

Taking data at 345°C as an example, Table 2 lists the analytical results for the linear regression between $g(\alpha)$ and t. In the table, K is the rate constant, r, the correlation coefficient and δ the covariance. From the evaluation of r and δ, R_1 and A_4 were selected as possible $g(\alpha)$ models, with R_1 having the better correlation coefficient.

The related kinetic parameters of the isothermal decomposition of NH_4HSO_4 can be obtained by taking logarithms in eqn. (2) and obtaining the linear regression to $\ln(K-1/T)$, based on the experimental data at 345, 358, 367 and 377°C. The related E, A and r values are listed in Table 3.

TABLE 2

Data for the isothermal decomposition of NH_4HSO_4 at 345°C

Model	K (min^{-1})	r	δ
D_1	0.01843	0.9758	4.2239
D_2	0.01840	0.9472	3.9707
D_3	0.00604	0.8929	1.3838
D_4	0.00401	0.9306	0.9192
Au	0.09103	0.9936	20.8619
R_1	0.01803	1.0000	4.1324
R_2	0.01405	0.9885	3.2191
R_3	0.01103	0.9787	2.5287
A_1	0.04725	0.9489	10.8286
A_2	0.02566	0.9912	5.8806
A_3	0.01806	0.9962	4.1391
A_4	0.01399	0.9968	3.2070

Non-isothermal method

The dynamic TG curves of the thermal decomposition of NH_4HSO_4 at different heating rates are shown in Fig. 2. From eqn. (3) and at a constant heating rate $\beta = \mathrm{d}T/\mathrm{d}t$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\beta}\, \mathrm{e}^{-E/RT} f(\alpha) \tag{6}$$

$$\int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^{T} \mathrm{e}^{-E/RT}\, \mathrm{d}T \tag{7}$$

$$g(\alpha) = \frac{AE}{\beta R} P(x) \ (x = E/RT) \tag{8}$$

TABLE 3

Kinetic parameters of isothermal decomposition of NH_4HSO_4

	E (kJ mol^{-1})	A (min^{-1})	log A (min^{-1})	r
D_1	135.29	5.1121×10^9	9.7086	0.9955
D_2	134.17	3.3443×10^9	9.5243	0.9958
D_3	133.14	1.1397×10^9	9.0568	0.9889
D_4	133.81	8.5173×10^8	8.9303	0.9946
Au	144.68	1.4980×10^{11}	11.1755	0.9976
R_1	141.25	1.5630×10^{10}	10.1864	0.9930
R_2	138.43	7.0843×10^9	9.8503	0.9973
R_3	137.63	4.8029×10^9	9.6815	0.9979
A_1	136.01	1.5255×10^{10}	10.1834	0.9964
A_2	140.77	2.0198×10^{10}	10.3053	0.9984
A_3	143.05	2.1807×10^{10}	10.3386	0.9970
A_4	144.37	2.1632×10^{10}	10.3351	0.9958

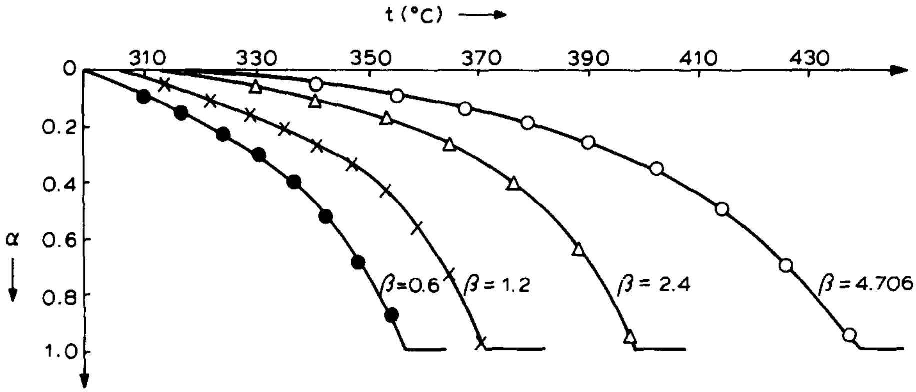

Fig. 2. Dynamic TG curves of the thermal decomposition of NH_4HSO_4.

Solving the right-hand side of eqn. (8) by the Coats–Redfern index integral method, and taking the first two approximate values

$$g(\alpha) = \frac{ART^2}{\beta E}\left(1 - \frac{2RT}{E}\right) e^{-E/RT} \tag{9}$$

Taking logarithms of both sides

$$\log\frac{g(\alpha)}{T^2} = \log\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.303R}\frac{1}{T} \tag{10}$$

From eqn. (10), it is clear that a straight line of slope $-E/2.303R$ should result when plotting log $g(\alpha)/T^2$ against $1/T$; the frequency factor A can be obtained from the intercept.

Table 4 shows the result of the linear regression for the related data when extrapolating β to 0°C min^{-1}. The table also lists the E and A

TABLE 4

Kinetic parameters of the NH_4HSO_4 thermal decomposition when $\beta \rightarrow 0$°C min^{-1}

Model	E (kJ mol^{-1})	log A (min^{-1})
D_1	273.64	21.38
D_2	304.21	23.89
D_3	344.39	26.86
D_4	317.33	24.43
R_1	131.83	9.33
R_2	157.32	11.38
R_3	167.23	12.10
A_1	189.43	14.60
A_2	89.70	5.87
A_3	56.49	4.31
A_4	39.87	4.40

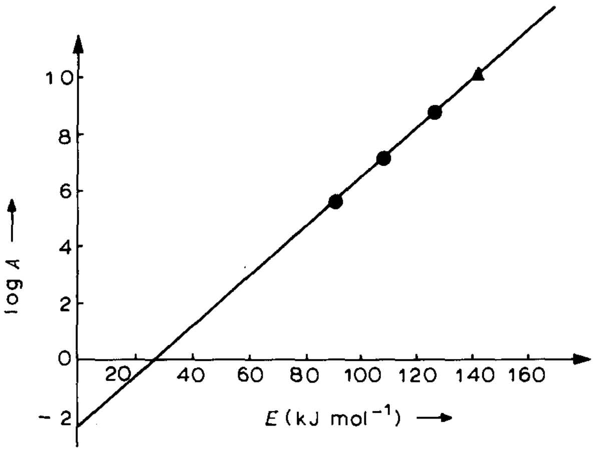

Fig. 3. Kinetic compensation effect on the R_1 mechanism.

values obtained with the different mechanism functions. Comparing the process at constant temperature with the kinetic parameters obtained when $\beta = 0$, and considering the proper E and A values, it is obvious that the R_1 mechanism probably dominates the thermal decomposition process of NH_4HSO_4 and A_4 mechanism should not be considered.

Kinetic compensation effect

In the non-isothermal thermogravimetric experiments, the E and A values will decrease with increasing heating rate. This tendency can be shown by the kinetic compensation effect [3,5]. When the linear heating rates, β were 0.6, 1.2, 2.4 and 4.706°C min^{-1} over several runs, a related kinetic compensation law can be formulated for the dynamic thermal decomposition process of NH_4HSO_4. Figure 3 shows the kinetic compensation effect for the R_1 mechanism.

Table 5 shows the compensation constants a and b in the compensation formula $\log A = a + bE$, and also the correlation coefficient of the linear regression. For the dynamic thermal decomposition of NH_4HSO_4, the kinetic compensation formula is

$$\log A = 0.0899E - 2.5143 \tag{11}$$

It is interesting that the law of compensation can also be used as another criterion in the evaluation of the process mechanism function. For example, Table 5 lists the Arrhenius parameters, the kinetic compensation constants for the eleven $g(\alpha)$ models and the K values obtained at constant temperature according to the compensation law. It is clear that only the two K values from the R_1 mechanism are equal. This confirms

TABLE 5

Comparison of the two rate constants

Model	TG at constant temperature			Compensation constants			Rate constant K [a]	
	E	log A	r	a	b	r	Isothermal	Compensation law
D_1	135.29	9.7086	0.9955	−5.5327	0.09837	0.9999	0.01843	4.0965×10^{-4}
D_2	134.19	9.5243	0.9958	−6.3160	0.09929	0.9997	0.01840	1.0953×10^{-4}
D_3	133.14	9.0563	0.9889	−7.3587	0.09924	0.9992	0.006038	1.1894×10^{-5}
D_4	133.81	8.9303	0.9946	−7.1066	0.09931	0.9994	0.004011	1.9095×10^{-5}
R_1	141.25	10.1864	0.9930	−2.5143	0.08991	1.0000	0.01803	0.01763
R_2	138.43	9.8503	0.9773	−3.1141	0.09211	1.0000	0.01405	0.008984
R_3	137.63	9.6815	0.9979	−3.3867	0.09261	1.0000	0.01103	0.005678
A_1	136.01	10.1834	0.9964	−3.1209	0.09346	0.9998	0.04725	0.01416
A_2	140.77	10.3053	0.9984	−1.6134	0.08322	0.9980	0.02566	0.01584
A_3	143.05	10.3386	0.9970	−3.3899	0.13140	0.7551	0.01806	32.1756
A_4	144.37	10.3351	0.9958	−5.1867	0.22480	0.5681	0.01399	31541.1457

[a] Rate constants of the NH_4HSO_4 thermal decomposition at 345°C.

that the NH_4HSO_4 thermal decomposition process is dominated by an R_1 mechanism, i.e. the reaction is one-dimensional phase-boundary controlled.

CONCLUSION

The identification of the procedural mechanism function is one of the most difficult subjects in the study of solid thermal decompositions. The results of this study, using thermogravimetry both at constant temperature and with programmed increasing temperature show that the thermal decomposition mechanism of NH_4HSO_4 is dominated by a one-dimensional phase-boundary reaction. The activation energy obtained at constant temperature is $E = 141.25$ kJ mol^{-1}. The activation energy obtained by using the increasing temperature program is $E = 131.83$ kJ mol^{-1}. The kinetic compensation formula is log $A = 0.0899E - 2.5143$.

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