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DETERMINATION OF THE KINETIC PARAMETERS OF THE MULTI-STAGE THERMAL DECOMPOSITION OF SOLIDS UNDER NON-ISOTHERMAL CONDITIONS BY THE NON-LINEAR ESTIMATION APPROACH

A MODEL OF ALUMINIUM HYDROXIDE DECOMPOSITION

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The activation energy of decomposition of aluminium hydroxide *vs.* weight loss was estimated from thermogravimetric data collected over a wide range of heating rates, without resorting to the model of the reaction mechanism.

These activation energy values were subsequently used to distinguish individual dehydration stages and to determine the best models of the reaction kinetics for these stages.

Finally, the overall decomposition model was formulated, and its parameters were determined by the non-linear estimation approach.

Owing to the development of numerical, computer-based identification method, derivation of a model for the multi-stage thermal decomposition of a solid has become a greatly simplified task [1]. However, a suitable procedure for processing of experimental data to obtain the most information possible on the individual decomposition stages remains of significance. Such a procedure should help to establish a preliminary model structure and determine the activation energy values for the individual stages.

Here, a method is advanced for determining the activation energy and the model structure for the individual thermal decomposition stages, and for developing a kinetic model of overall decomposition that would most accurately account for the experimental data over a wide range of experimental conditions.

Theoretical

In the multi-stage thermal decomposition of a solid under increasing temperature it often happens that the successive stages of the process overlap rather than proceed separately.

Depending on the decomposition mechanism involved, the chemical reactions corresponding to the individual stages can occur either consecutively or simultaneously.

a) Consecutive pattern

$$\begin{aligned} &A_s \rightarrow B_s + C_g && \text{stage I} \\ &B_s \rightarrow D_s + E_g && \text{stage II} \end{aligned} \tag{1}$$

b) Parallel pattern

$$\begin{aligned} &A_s \rightarrow B_s + C_g && \text{stage I} \\ &F_s \rightarrow G_s + H_g && \text{stage II} \end{aligned} \tag{2}$$

The weight loss of the sample undergoing decomposition can be expressed in terms of the conversion degrees achieved in the individual reactions, according to the formulas

$$\text{a) } y = m_C + m_E = m_0(K_1'\alpha_1 + K_2'\alpha_1\alpha_2) = K_1\alpha_1 + K_2\alpha_1\alpha_2 \tag{3}$$

where $\alpha_1 = m_C/m_{C\infty}$; $\alpha_2 = m_E/m_{E\infty}$

$K_1' = M_C/M_A$; $K_2' = M_E/M_A$

$K_1 = m_0K_1'$; $K_2 = m_0K_2'$

$m_{C\infty} = m_0M_C/M_A$; $m_{E\infty} = m_CM_E/M_C$

$m_0 = m_{A0}$

$$\text{b) } y = m_C + m_H = m_{A0}K_1'\alpha_1 + m_{F0}K_2'\alpha_2 = K_1\alpha_1 + K_2\alpha_2 \tag{4}$$

where $\alpha_1 = m_C/m_{C\infty}$; $\alpha_2 = m_H/m_{H\infty}$

$K_1' = M_C/M_A$; $K_2' = M_H/M_F$

$K_1 = m_{A0}K_1'$; $K_2 = m_{F0}K_2'$

$m_{C\infty} = m_{A0}M_C/M_A$; $m_{H\infty} = m_{F0}M_H/M_F$

$m_{A0} + m_{F0} = m_0$.

The meanings of the symbols used in the above formulas are as follows: $m_0 =$ = initial weight of sample; m_C, m_E and m_H = weights of gaseous compounds C, E and H evolved during decomposition in time t; $m_{C\infty}$, $m_{E\infty}$ and $m_{H\infty}$ = weights of compounds C, E and H which correspond to their complete formation; m_{A0} and m_{F0} = weights of compounds A and F before decomposition; M_A, M_C, M_E, M_F and M_H = molecular weights of the respective compounds; α_1 and α_2 = conversion degrees in the individual decomposition stages.

On substituting the values $\alpha_1 = 1$ and $\alpha_2 = 0$ into Eqs (3) and (4), we obtain in both cases

$$y_I = K_1 \tag{5}$$

Thus, constant K_1 accounts for the total weight loss in the 1st reaction stage.

By introducing the values $\alpha_1 = 1$ and $\alpha_2 = 1$ into Eqs (3) and (4), we receive

$$y_{I,II} = K_1 + K_2 \tag{6}$$

Constant K_2 can be found from Eqs. (5) and (6) as the weight loss of the sample in the 2nd decomposition stage. From analogous reasoning for the three-stage decomposition process, the following formulas are obtained for the weight loss of the sample

a) $y = K_1\alpha_1 + K_2\alpha_1\alpha_2 + K_3\alpha_1\alpha_2\alpha_3$ (7)

b) $y = K_1\alpha_1 + K_2\alpha_2 + K_3\alpha_3$ (8)

where α_i = conversion degree in the i-th stage, and K_i = total weight loss in the i-th stage.

To determine the weight variation with time, $y(t)$, Eqs (7) and (8) should be supplemented with the kinetic equations, expressed in terms of the conversion rates for the individual stages, *viz.*

$$\dot{\alpha}_i = k_{0i} \exp(-E_i/RT) f(\alpha_i) \tag{9}$$

where E_i = activation energy for the i-th stage (which in general may be different for various conversion values), k_{0i} = pre-exponential factor, T = absolute temperature, $f(\alpha_i)$ = a function that accounts for the reaction mechanism, R = gas constant, and $\dot{\alpha}_i = d\alpha_i/dt$ = rate of the i-th reaction.

The set of Eqs (7) and (9), or (8) and (9), constitutes a model of the multi-stage thermal decomposition process. This model can be used for practical purposes, provided such data are known as the parameters K_i, the form of function $f(\alpha)$ along with its associated parameters, and the parameters of the rate equations, k_{0i} and E_i.

Experimental

As the experimental data required for the evaluation of the parameters and the selection of the model of the reaction kinetics, the values of the temperature and the weight loss with time were used. These values were taken from the thermal curves obtained for decomposition of aluminium hydroxide, the compound produced by ammoniacal hydrolysis of basic aluminium ammonium sulfate. The compound examined, of molar composition $Al_2O_3 \cdot 2.07H_2O$, contained some trace impurities (K_2O 0.022%, NH_3 0.024% and SO_3 0.30%), whose presence was due to incomplete hydrolysis of the starting salt. Measurements were made with a Paulik–Paulik–Erdey MOM derivatograph. The weight of the sample decomposed was 300 mg in all runs. The curves recorded covered a wide range of experimental conditions. Average heating rates were 0.75 to 12°/min, and the final decomposition temperatures ranged from 150 to ca. 1200° (Table 1).

Illustrative thermal curves of the compound under study are given in Fig. 1. Inspection of the TG and DTA curves shows that decomposition of aluminium hydroxide occurs in three stages. The first stage goes up to ca. 200° and corresponds to the liberation of ca. 0.72 mole of adsorption water; in the second stage ca. 1.18 mole of constitutional water is released, nearly all this quantity being evolved at temperatures up to 600°; in the third stage, above 600°, the weight of the sample changes very slowly. This last stage is associated with the removal of the remainder of the water (0.17 mole) and SO_3.

Decomposition of the sulfates starts from 900°. The process, however, could not be brought to completion even by prolonged isothermal calcination (ca. 5 hr) at 1300°. The SO_3 content in the product thus obtained was 0.012% (3% relative to the initial content).

The chemical composition, specific gravity, and dehydration pattern for the compound under study indicate that it is a solid phase with properties similar to

Table 1

Characteristics of the thermal curves of the aluminium hydroxide decomposition

Thermal curves, No.	Average heating rate, °/min	Final temperature, °C	Total, relative weight loss (m_t/m_0), %
1	0.75	150	8.2
2	0.75	150	8.7
3	1.5	300	12.0
4	1.5	600	24.7
5	1.5	600	24.3
6	2.25	900	25.5
7	2.25	900	26.7
8	2.25	900	25.9
9	3.0	300	11.8
10	3.0	600	24.6
11	3.0	600	24.3
12	3.0	1200	25.6
13	3.0	1200	26.2
14	3.0	1200	26.7
15	3.0	1200	25.9
16	4.5	900	24.3
17	6.0	300	11.2
18	6.0	600	23.9
19	6.0	600	24.5
20	6.0	600	24.2
21	6.0	1200	26.0
22	6.0	1200	25.8
23	6.0	1200	25.3
24	6.0	1200	25.7
25	12.0	600	17.7
26	12.0	600	23.6
27	12.0	600	27.0
28	12.0	1200	25.9
29	12.0	1200	26.2

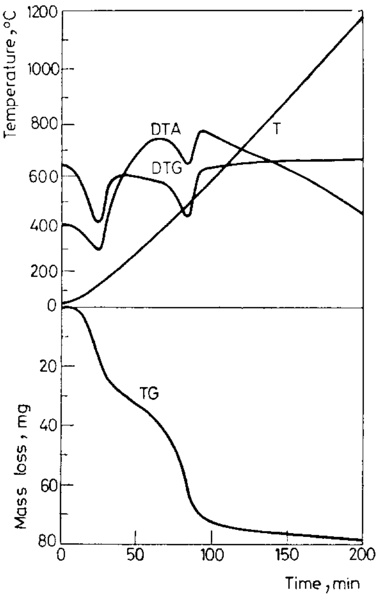

Fig. 1. Thermal curves of the compound under study. Average heating rate 6°/min

those of boehmite (γ-AlOOH). This was confirmed by X-ray analysis of the compound and its decomposition products at 600, 800 and 1300°.

Determination of the kinetic model parameters and structure

The conversion degrees for the individual decomposition stages were evaluated from the formula

$$\alpha = (m - m_s)/m_t \tag{10}$$

where m = weight loss of the decomposed sample,

m_s = weight loss of the sample before the onset of a given decomposition stage, and

m_t = K_i = total weight loss of the sample in a given stage.

The m_s and m_t values for individual stages were preliminarily found from isothermal experiments and from the DTG and DTA curves recorded under non-isothermal conditions.

Stage	m_s/m_0	m_t/m_0
	%	%
I	0	9.3
II	9.3	15.2
III	24.5	2.5

Determination of the activation energy vs. weight loss [2]

By expressing the conversion degree in the kinetic Eq. (9) in terms of the weight loss according to Eq. (10), one obtains

$$(1/m_t)\,\mathrm{d}m/\mathrm{d}t = k_0 \exp\,(-E/RT) f\left(\frac{m - m_s}{m_t}\right). \tag{11}$$

For experimental points with the same weight loss value m and the same m_s and m_t values, taken from the curves recorded at various heating rates, Eq. (11) can be written in the form

$$\mathrm{d}m/\mathrm{d}t = \exp(-E/RT)\ \text{const.} \tag{12}$$

Table 2

The resultant activation energy for the aluminium hydroxide decomposition process *vs.* weight loss

No.	Relative weight loss (m/m_0), %	Activation energy (E), kJ/mole	Relative standard error s.e. $(E)/E$
1	1.3	35	1.34
2	2.0	43	0.98
3	2.7	44	0.96
4	3.3	39	0.99
5	4.0	38	0.95
6	4.7	40	0.88
7	5.3	40	0.89
8	6.0	42	0.84
9	6.7	46	0.77
10	7.3	43	0.76
11	8.0	44	0.74
12	9.3	61	0.56
13	10.7	82	0.50
14	12.0	96	0.47
15	13.3	119	0.43
16	14.7	129	0.44
17	16.0	149	0.41
18	17.3	157	0.41
19	18.7	157	0.42
20	20.0	157	0.43
21	21.3	167	0.41
22	22.7	125	0.48
23	23.3	87	0.63
24	24.7	33	1.14
25	25.0	23	1.29
26	25.3	3	8.67

or, upon taking logarithms

$$\ln \dot{m} = -E/RT + c \tag{13}$$

where E = const. and c = const. for points corresponding to m = const.; $\dot{m} = dm/dt$.

The $\dot{m}(t)$ values were obtained by numerical differentiation of the $m(t)$ curves, i.e. *TG* curves, and their numerical smoothing.

Equations (11) through (13) are valid in relation to a definite decomposition stage, under the assumption that the activation energy is constant. If stages overlap, the E value found from these equations must be regarded as a resultant of the overlapping reactions. Such values of the activation energy were determined from the experimental data by the linear regression method according to Eq. (13). Results are collected in Table 2.

The s.e. $(E)/E$ values in the last column of Table 2 are relative standard errors of the activation energy estimates and represent the precision of the estimation. Calculations were made using the data from the following thermal curves:

points 1 to 23: curves nos. 4, 5, 11, 18, 19, 20, 26 and 27;
points 24 to 26: curves nos. 7, 8, 12, 14, 21, 28 and 29.

Table 2 shows that the activation energy is nearly constant over the range m/m_0 = 1.3 to 8.0% and in the region $\dot{m}/m_0$ = 16.0 to 21.3%. In the former range it is ca. 42 kJ/mole, and in the latter ca. 155 kJ/mole. The two regions mentioned correspond to the predominance of the first and the second decomposition stage, respectively. The intermediate range m/m_0 = 8.9 to 16.0% corresponds to overapping of stages I and II.

Stage III has a much lower activation energy than stage II, but very large values of the relative error s.e. $(E)/E$ indicate that the data in this region are not accurate, and therefore cannot be reliably used for estimation of the activation energy.

Determination of the average activation energies for the individual decomposition stages

If, in a given area of weight loss, a certain decomposition stage is predominant, as described by the general Eq. (11), for sets of experimental points selected in that area that correspond to successive constant values of the weight loss, the following equations are valid

$$\ln \dot{m}_i = -E/RT + c_i, \text{ where } i = 1, \ldots, n. \tag{14}$$

Subscript i in these equations refers to a set of data that corresponds to a constant weight loss; n = number of sets; and E = average activation energy in the weight loss range of interest.

The average values of the activation energy for the selected ranges of weight loss calculated by the linear regression method according to Eq. (14) are shown in Table 3.

Table 3

The average resultant activation energy for the individual stages of the aluminium hydroxide decomposition evaluated independently of the form of kinetic model

Stage	Average activation energy (E_{av}),	Relative standard error s.e. $\frac{(E_{av})}{E_{av}}$	Range of weight loss (m/m_0),	Number of exptl. points	Curves used for calculations
	kJ/mole	—	%		
I	43.5	0.25	1.3 - 8.0	121	4, 5, 10, 19, 20, 25, 26, 27
II	124.8	0.14	10.7 - 22.7	100	4, 5, 10, 11, 18, 19, 20, 26, 27
III	9.6	1.45	24.7 - 25.7	40	7, 8, 12, 13, 14, 15, 21, 24, 28, 29

Since the regions where stages are distinctly separated are too narrow to be suitable for formulating a kinetic model, the selected ranges of data also included measurements that corresponded to overlapping of neighbouring stages. As a result, the average activation energy for the region $m/m_0 = 10.7$ to 22.7% is much lower than in the region $m/m_0 = 16.0$ to 21.3% where stage II is distinct (see previous section).

However, after the evaluation of kinetic models for the individual stages (see next section), the overall decomposition model is developed which accounts for all the stages concerned and allows one to adjust the values of the average activation energies.

Selection of the best models for the individual stages of aluminium hydroxide decomposition

The estimated values of the activation energy, as found independently of the form of function $f(\alpha)$, can be used in the derivation of a suitable model structure. Of a few alternative equations, the best model of a given decomposition stage is the equation in which the activation energy value is closest to the average, independently-evaluated activation energy.

The logarithmic form of kinetic Eq. (9) with incorporation of function $f(\alpha)$ in the forms listed in Table 4 [3] is linear with respect to the estimated kinetic parameters; these parameters can therefore be evaluated by the linear regression method on the basis of the data corresponding to the given stage.

By comparison of the activation energy values and the degree of fit of the model to the experimental data, expressed by the sums of the squared deviations, the following tentative models for the individual decomposition stages were taken:

$$\begin{aligned}
&\text{stage I:} && \dot{\alpha}_1 = k_{01} \exp(-E_1/RT)(1-\alpha_1)^{m_1} \\
&\text{stage II:} && \dot{\alpha}_2 = k_{02} \exp(-E_2/RT)(1-\alpha_1)^{m_2}\alpha_2^{n_2} \\
&\text{stage III:} && \dot{\alpha}_3 = k_{03} \exp(-E_3/RT)(1-\alpha_3)^{m_3}
\end{aligned} \tag{15}$$

Table 4

Forms or function $f(\alpha)$ considered in the selection of the kinetic model

Model No.	$f(\alpha)$
1	$(1-\alpha)^{2/3}$
2	$(1-\alpha)^{m}$
3	$(1-\alpha)^{m}\alpha^{n}$
4	$(-\ln(1-\alpha))^{p}$
5	$(1-\alpha)^{m}(-\ln(1-\alpha))^{p}$
6	$\alpha^{n}(-\ln(1-\alpha))^{p}$
7	$(1-\alpha)^{m}\alpha^{n}(-\ln(1-\alpha))^{p}$
8	$(1-\alpha)^{1/3}/(1-(1-\alpha)^{1/3})$
9	$(1-\alpha)^{2/3}/(1-(1-\alpha)^{1/3})$

The values of the model parameters found on the basis of the selected experimental points are given in Table 5 as starting values for an iterative non-linear estimation procedure.

Overall decomposition model

The conclusive selection of the model and the estimation of the parameters were carried out by the non-linear estimation approach [4]. This approach consists in matching the results calculated from models (15), and (7) or (8), with non-transformed experimental data, by a suitable optimization of the model parameters. The optimization procedure employed in this work was the linearization method with Marquardt's modification [1, 5].

The differential equation set (15) was integrated by the 5th-order Runge–Kutta method. Complete data from thermal curves Nos 2, 4, 14 and 29 were utilized in the calculations. As the starting parameters for the iterative estimation process, the values obtained from approximate decomposition models for the individual stages were taken. Results of the parameter estimation for the alternative decomposition models (7) and (8) are listed in Table 5.

Application of the non-linear estimation approach permitted one to account for the effects of overlapping of successive stages, and to eliminate the simplification introduced in evaluating the values of the parameters for the individual stages.

The value of the activation energy for stage II, 153.2 kJ/mole, compares well with the values found independently for the region where stage II distinctly prevails. The results obtained lends validity to the previously made conclusion that the observed change in activation energy during aluminium hydroxide decom-

Table 5

The values of parameters in the alternative forms of the overall model

	Stage I			
	K_1/m_0	E_1, kJ/mole	$\ln k_{01}$	m_1
Starting values	0.093	44.0	12.0	1.8
Estimated values				
a) consecutive reactions model	0.091	56.5	16.7	2.5
b) parallel reactions model	0.092	68.2	15.9	2.2

position (Table 2) is actually a resultant of the overlapping of two stages with different activation energy values.

The sum of squares criterion for the consecutive reaction model was about one-third less than the value for the parallel reactions model. Therefore, the best model of the thermal decomposition of aluminium hydroxide has the form:

$$\begin{aligned} y &= m_0(0.091\,\alpha_1 + 0.152\,\alpha_2 + 0.025\,\alpha_1\alpha_2\alpha_3) \\ \mathrm{d}\alpha_1/\mathrm{d}t &= \exp(-56.5/RT + 16.7)(1-\alpha_1)^{2.5} \\ \mathrm{d}\alpha_2/\mathrm{d}t &= \exp(-153.2/RT + 20.0)(1-\alpha_2)^{0.14}\,\alpha_2^{-3.6} \\ \mathrm{d}\alpha_3/\mathrm{d}t &= \exp(-31.0/RT - 1.5)(1-\alpha_3)^{1.1} \end{aligned} \tag{16}$$

where activation energies are expressed in kJ/mole.

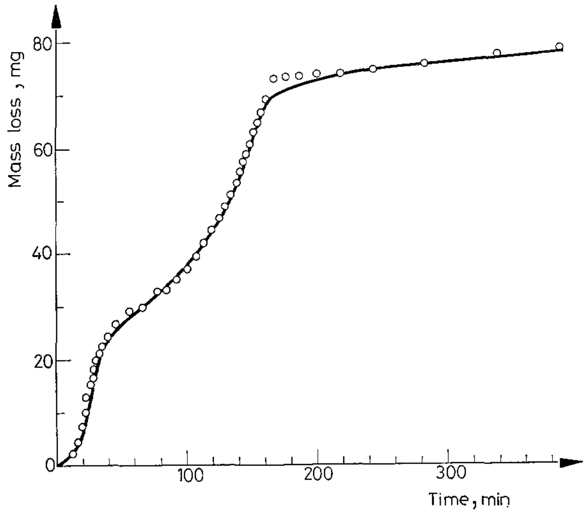

Fig. 2. Simulation of the experimental TG data from thermal curves 15 using the overall decomposition model (16). Solid line denotes the experimental curve. Circles denote calculated values

of aluminium hydroxide decomposition (Eqs 7, 8 and 15)

Stage II					Stage III			
K_2/m_0	E_2, kJ/mole	$\ln k_{02}$	m_2	n_2	K_3/m_0	E_3, kJ/mole	$\ln k_{03}$	m_3
0.152	120.6	14.8	0.13	−2.8	0.025	9.2	−2.9	2.3
0.151	153.2	20.0	0.14	−3.6	0.028	31.0	−1.5	1.1
0.154	153.2	19.9	0.13	−3.4	0.024	14.2	−4.7	2.7

No attempt was made to give any physical interpretation to the models of the individual decomposition stages. The aim of the study was to obtain an adequate mathematical description of the process, valid over a wide range of conditions of the decomposition reaction. In this connection model (16) was checked on 29 experimental curves recorded under various conditions of temperature rise (Table 1).

Comparison of the experimental values with the weight loss values calculated from the model is illustrated in Fig. 2.

The agreement of the model with the experimental data in the region corresponding to the first two decomposition stages is satisfactory. As expected from the scatter of the data, the region corresponding to the third decomposition stage shows a poorer fit of the model to the data.

Conclusions

Estimation of the activation energy as a function of the weight loss of the sample subjected to thermal decomposition allows one to point out the experimental data with the prevalent effects on the individual decomposition stages. From these data, reaction kinetic models can subsequently be derived in suitable forms and approximate values of the parameters of these models can be evaluated.

The non-linear estimation approach used is good to account for the overlapping effects of the successive stages and to estimate the values of the kinetic parameters from complete experimental data taken under various conditions of temperature rise.

For a correctly chosen decomposition model the activation energy values determined by the non-linear estimation approach show a satisfactory agreement with the corresponding values found independently of the form of the kinetic model.

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Résumé — On a estimé l'énergie d'activation de la décomposition de l'oxyde d'aluminium en fonction de la perte de poids à partir de données thermogravimétriques obtenues avec un large intervalle de vitesses de chauffage, sans avoir recours au modèle du mécanisme de la réaction.

On a utilisé ensuite ces valeurs de l'énergie d'activation pour distinguer les étapés individuelles de la déshydratation et pour déterminer les meilleurs modèles de cinétique réactionnelle correspondant à celles-ci.

Enfin, on a formulé un modèle général de décomposition et déterminé ces paramètres par approximations non linéaires.

Zusammenfassung — Die Aktivierungsenergie der Zersetzung von Aluminiumhydroxid wurde in Abhängigkeit vom Gewichtsverlust aus einen weiten Bereich von Aufheizgeschwindigkeiten umfassenden thermogravimetrischen Daten gesammelt, ohne auf das Modell des Reaktionsmechanismus einzugehen.

Diese Werte der Aktivierungsenergien wurden daraufhin zur Unterscheidung einzelner Dehydratisierungsstufen und zur Bestimmung der besten Modelle der Reaktionskinetik dieser Stufen eingesetzt.

Schließlich wurde ein allgemeines Zersetzungsmodell formuliert und seine Parameter durch nichtlineare Schätzungsnäherung bestimmt.

Резюме — Энергия активации разложения гидроокиси алюминия в зависимости потери веса была оценена по термогравиметрическим данным, собранным в широкой области скоростей нагрева, не прибегая к модели механизма реакции. Эти значения энергии активации были впоследствии использованы для разделения индивидуальных стадий разложения и для определения наилучших моделей кинетики реакций для этих стадий. Представлена также полная модель разложения и определены ее параметры с помощью нелинейного оценочного приближения.