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KINETICS OF ALUMINIUM HYDROXIDE DEHYDRATION

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Non-isothermal thermogravimetric analysis was used for determination of the kinetics of aluminium hydroxide dehydration in an air atmosphere and for processing of the experimental results by the method due to Chatterjee.

Aluminium hydroxide dehydration proceeds according to the following mechanism:

$$Al(OH)_3 \rightarrow AlOOH + H_2O$$
$$2\,AlOOH \rightarrow Al_2O_3 + H_2O$$

Both reactions proceed in the diffusion region, the first up to 526 K and the second up to 700 K, and the corresponding activation energy values are 15.7 and 0.2 kJ/mole, respectively.

By continuous increase of temperature over 526 K in the first, and over 700 K in the second case, the rates of these reactions become limited by the rate of crystallochemical transformation and the activation energy values are 116.9 and 91.9 kJ/mole, respectively.

Results of thermogravimetric analysis, obtained under isothermal [1] and non-isothermal [2, 3] conditions in the course of a reaction, may be used for kinetic research of the processes of thermal decomposition of solid components.

In recent, non-isothermal methods of research the kinetics of thermal decompositions of solid components have found wider and wider application because of the particular advantages they have over the methods of research under isothermal conditions.

The advantages of the determination of reaction kinetics via continuous temperature increase lie in the facts that a significantly smaller number of experimental data is required than for isothermal methods of research and that process kinetics may be studied fully over the complete temperature range in a continuous way. At the same time, this resolves the difficulty always present in isothermal research, at the beginning of the process when the cold sample is put into the heated furnace, during which process, de facto, there are non-isothermal conditions, so that the beginning of the reaction cannot be taken into account in such research.

The process of aluminium hydroxide dehydration was studied by Drobot and Hozanov [4] under isothermal conditions, using high-temperature infra-red spectroscopy for determination of the level of reaction flow with time, which is not applicable for research of this type.

Theory

The method due to Chatterjee [5] for the evaluation of thermogravimetric data in order to calculate the kinetic parameters of thermal decomposition processes may be used successfully for processing of one or more thermogravimetric curves obtained under identical reaction conditions but with different starting sample weights.

A heterogeneous kinetic reaction can be represented by the following general equation for the rate, v:

$$v = -\frac{\mathrm{d}m}{\mathrm{d}t} = k \cdot m^n \tag{1}$$

where k, m, t and n are the rate constant of the reaction, the active weight of the reacting material, the time elapsed from the start of the experiment, and the pseudo order of reaction, respectively.

Mechanisms derived for a heterogeneous reaction from the pseudo order of reaction are of little intrinsic significance and, at best, represent a gross approximation. If k is expressed in terms of an Arrhenius equation, then

$$k = A \cdot e^{-\Delta E^{\ddagger}/RT} \tag{2}$$

where A, $\Delta E^{\ddagger}$, T and R are the frequency factor, the activation energy, the absolute temperature and the universal gas constant, respectively. Substituting Eq. (2) into Eq. (1),

$$v = A \cdot m^n \cdot e^{-\Delta E^{\ddagger}/RT}$$

or

$$n \log m - \log v = \frac{\Delta E^{\ddagger}}{2.303RT} - C \tag{3}$$

Equation (3) gives the relationship between reaction rate and temperature, while the activation energy ($\Delta E^{\ddagger}$) may be determined from the slope of the straight line in the coordinate system ($n \log m - \log v$) *vs.* $1/T$.

Experimental

A Netzsch differential thermoanalyzer, Model 409, was used for the DTA measurements, with Pt/Pt–Rh thermocouples and calcined alumina crucibles for the samples.

Thermogravimetric investigations were performed on a Netzsch thermobalance, Model 409, with the holder and crucible for samples made from calcined alumina. The thermocouple for measuring the temperature of the furnace consisted of Pt/Pt–Rh, and its tip was positioned at the same level as the surface of the sample being investigated.

The aluminium hydroxide powder with a purity of 99% used for these investigations was produced by Riedel de Haën A. G. Seelze, Hanover.

Results and discussion

Figure 1 shows the DTA curve for the thermal decomposition of aluminium hydroxide in an air atmosphere, obtained at a heating rate of 10° $\min^{-1}$. Aluminium hydroxide dehydration proceeds first to AlOOH, which is shown in the DTA curve by a prominent endothermic peak at 573 K (Fig. 1); AlOOH is then dehydrated to Al_2O_3, as shown by a less prominent peak at 773 K. Certain other changes may be noted at the beginning of dehydration to AlOOH, which are most probably due to the removal of adsorbed humidity. During further heating the

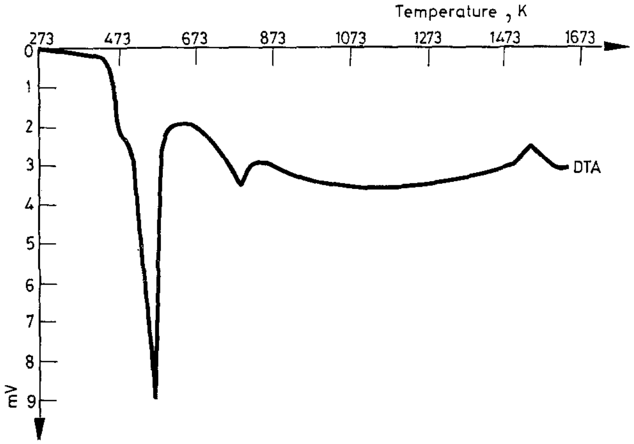

Fig. 1. Differential thermal analysis of aluminium hydroxide in air

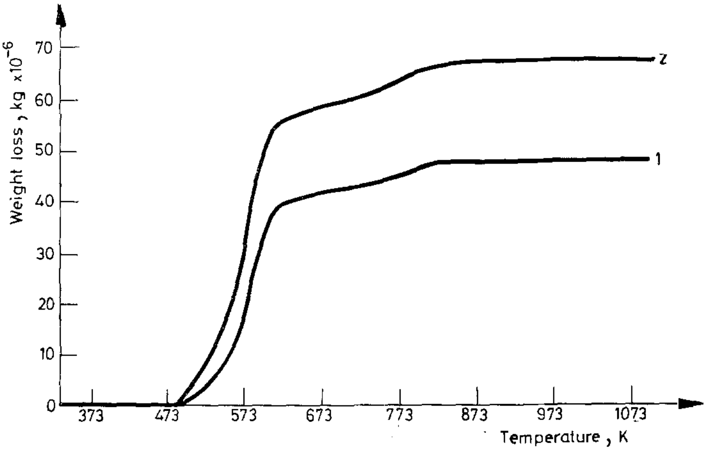

Fig. 2. Thermogravimetric analysis of aluminium hydroxide in air for two samples with different initial weights: 1 sample *a*: 2 sample *b*

DTA curve changes its position in relation to the baseline up to 1573 K, when the process of α-Al_2O_3 crystallization is denoted by a weak exothermic peak, although both reference and studied samples represent Al_2O_3.

For kinetic research of aluminium hydroxide dehydration, two samples of different starting weights were heated in the TG apparatus at a rate of 10° min^{-1}. The results obtained are shown in Fig. 2.

The loss of weight in the temperature interval from 475 K to 600 K corresponds to the process:

$$Al(OH)_3 \rightarrow AlOOH + H_2O \tag{4}$$

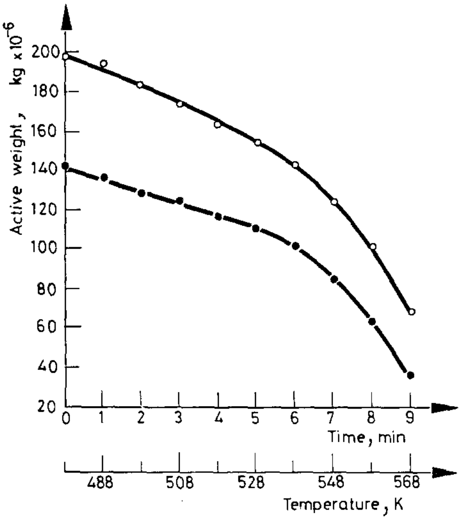

Fig. 3. Variation of active weight of $Al(OH)_3$ with both time and temperature: ● sample *a*: ○ sample *b*

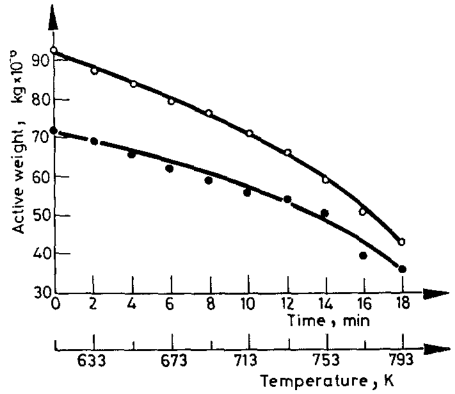

Fig. 4. Variation of active weight of AlOOH with both time and temperature: ● sample *a*; ○ sample *b*

and the loss of weight in the temperature interval from 600 K to 800 K to the process:

$$2\,\mathrm{AlOOH} \rightarrow \mathrm{Al_2O_3} + \mathrm{H_2O} \qquad (5)$$

The loss of sample weight m_t, of 18×10^{-6} kg, due to separation of reaction gas product, based on Eqs (4) and (5), results in the formation of 60×10^{-6} kg of solid AlOOH reaction product in the first, and 120×10^{-6} kg of solid Al_2O_3 reaction product in the second case, both of which remain with the still unreacted part of the sample. Based on these data, the active sample weight, m, was calculated as functions of time and reaction temperature. Values obtained for processes (4) and (5) are shown in Figs 3 and 4, respectively.

Table 1
Thermogravimetric data for calculating the kinetic parameters for the process of $Al(OH)_3$ dehydration

Time, min	Temp., K	Sample	Instantaneous weight, m_t, kg $\times 10^{-6}$	Active weight, m, kg $\times 10^{-6}$	$v = -dm/d_t$, kg·min^{-1} $\times 10^{-6}$	log m	log v	$1000/T$, K^{-1}	log m − log v
0	478	*a*	141.40	141.40	—	—	—	2.092	—
		b	199.40	199.40	—	—	—		—
1	488	*a*	140.03	135.47	5.78	2.132	0.761	2.049	1.314
		b	198.03	193.47	8.27	2.286	0.917		1.371
2	498	*a*	138.73	129.84	6.13	2.113	0.787	2.008	1.326
		b	195.58	182.86	10.24	2.262	1.001		1.262
3	508	*a*	137.20	123.22	6.60	2.090	0.819	1.968	1.271
		b	193.30	172.99	9.90	2.238	0.995		1.243
4	518	*a*	135.68	116.64	6.60	2.066	0.819	1.930	1.247
		b	191.01	163.07	9.16	2.212	0.962		1.250
5	528	*a*	134.15	110.02	8.32	2.042	0.920	1.894	1.122
		b	189.07	154.67	9.92	2.189	0.996		1.193
6	538	*a*	131.86	100.10	13.21	2.000	1.120	1.858	0.880
		b	186.43	143.24	15.63	2.156	1.193		0.963
7	548	*a*	128.05	83.60	18.99	1.922	1.278	1.825	0.644
		b	181.85	123.41	21.48	2.091	1.332		0.759
8	558	*a*	123.09	62.12	23.97	1.793	1.379	1.792	0.414
		b	176.51	100.29	28.11	2.001	1.448		0.553
9	568	*a*	116.98	35.66	24.79	1.552	1.394	1.760	0.158
		b	168.88	67.25	35.51	1.827	1.550		0.277

Table 2
Thermogravimetric data for calculating the kinetic parameters for the process of AlOOH dehydration

Time, min	Temp., K	Sample	Instantaneous weight, m_t, kg × 10^{-6}	Active weight, m, kg × 10^{-6}	$v = -dm/dt$, kg· min^{-1} × 10^{-6}	log m	log v	1000/T, K^{-1}	log m − log v
0	613	*a*	71.99	71.99	—	—	—	1.631	—
		b	93.83	93.83	—	—	—		—
2	633	*a*	71.61	69.64	1.397	1.842	0.145	1.579	1.697
		b	92.84	87.24	2.547	1.941	0.406		1.535
4	653	*a*	71.15	66.40	1.783	1.822	0.251	1.531	1.571
		b	92.30	83.64	2.033	1.922	0.308		1.614
6	673	*a*	70.54	62.33	1.783	1.795	0.251	1.485	1.544
		b	91.62	79.11	1.897	1.898	0.278		1.620
8	693	*a*	70.08	59.27	1.397	1.773	0.145	1.443	1.628
		b	91.16	76.05	2.030	1.881	0.307		1.574
10	713	*a*	69.70	56.74	1.265	1.754	0.102	1.402	1.652
		b	90.40	70.99	2.547	1.851	0.406		1.445
12	733	*a*	69.32	54.21	1.515	1.734	0.180	1.364	1.554
		b	89.63	65.86	2.930	1.818	0.466		1.352
14	753	*a*	68.79	50.68	3.680	1.704	0.566	1.328	1.138
		b	88.64	59.27	3.813	1.773	0.581		1.192
16	773	*a*	67.11	39.49	3.313	1.596	0.520	1.293	1.076
		b	87.34	50.61	4.062	1.704	0.608		1.096

The rates of the dehydration reactions of $Al(OH)_3$ to AlOOH and AlOOH to Al_2O_3, v, were calculated by graphical differentiation of the thermal curves given in Figs 3 and 4. The required thermogravimetric data for the calculation of the kinetic parameters of these processes are shown in Tables 1 and 2.

Based on the calculated values in Tables 1 and 2, Figs 5 and 6 show the corresponding relationship ($n \log m - \log v$) as a function of the reciprocal reaction temperatures.

The results in Fig. 5 show that two different reaction rates correspond to the dehydration of $Al(OH)_3$ in the given temperature interval; there is a break in the straight line at 526 K. Analogous reasoning applies to the dehydration of AlOOH to Al_2O_3, the difference being that the change of reaction rate is observed at 700 K, as is shown in Fig. 6. In both cases, the results obtained for samples *a* and *b* show a good correlation.

The statistical method of least squares [6] was used to determine the slopes

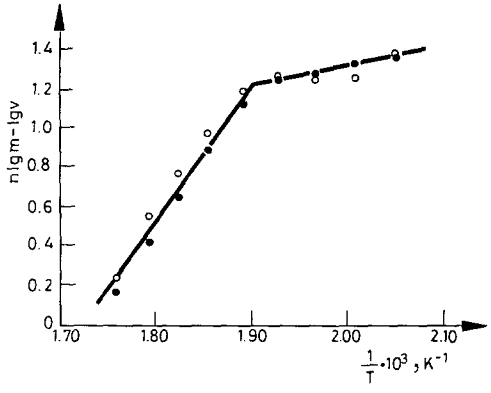

Fig. 5. Temperature dependence of ($n \log m - \log v$) for the dehydration of $Al(OH)_3$ in air: ● sample *a;* ○ sample *b*

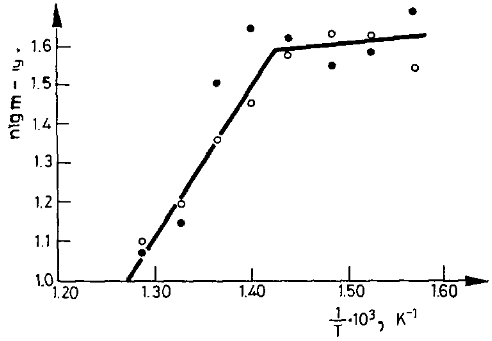

Fig. 6. Temperature dependence of ($n \log m - \log v$) for the dehydration of AlOOH in air: ● sample *a;* ○ sample *b*

of the most probable straight lines shown in Figs 5 and 6, and these slopes were used for calculation of the corresponding values of the activation energies of the given processes:

a) for reaction (4)
  - temperature interval up to 526 K
    $\Delta E_1^{\ddagger} = 15.70$ kJ/mole
  - temperature interval from 526 to 570 K
    $\Delta E_2^{\ddagger} = 116.97$ kJ/mole;

b) for reaction (5)
  - temperature interval up to 700 K
    $\Delta E_1^{\ddagger} = 0.20$ kJ/mole
  - temperature interval from 700 to 790 K
    $\Delta E_2^{\ddagger} = 91.92$ kJ/mole

Based on calculated slopes, the temperature relationships of the rates of the given processes in an air atmosphere at a constant heating rate of 10° min^{-1} may be described in the following way:

a) for reaction (4)
– temperature interval up to 526 K

$$n \log m - \log v_1 = \frac{0.820}{T} - 0.345 \tag{6}$$

– temperature interval from 526 to 570 K

$$n \log m - \log v_2 = \frac{6.108}{T} - 10.469 \tag{7}$$

b) for reaction (5)
– temperature interval up to 700 K

$$n \log m - \log v_1 = \frac{0.0109}{T} + 1.582 \tag{8}$$

– temperature interval from 700 to 790 K

$$n \log m - \log v_2 = \frac{4.800}{T} - 5.151 \tag{9}$$

where $n = 1$, m and $v = -\mathrm{d}m/\mathrm{d}t$ are the order of the reaction, the active weight of the reactant and the thermal decomposition rate, respectively.

From the results obtained it may be concluded that the dehydration processes of Al(OH)_3 and AlOOH from their beginning up to 526 K and 700 K, respectively, are in the extremal diffusion phase, i.e. resistance to the diffusion of reaction gas product through the laminar layer of gas which envelopes the particles of solid reagent limits the rates of the processes as a whole. By continuous temperature increase, the resistances to chemical reaction become larger and larger, so that at 526 K for Al(OH)_3 dehydration and 700 K for AlOOH dehydration they become the largest, as compared to other resistances to reaction flow, as a consequence of which, in both cases, the rate of the process as a whole is limited by the crystal-chemical transformation at the reagent-solid reaction product boundary surfaces.

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RÉSUMÉ — On détermine la cinétique de la déshydratation de l'hydroxyde d'aluminium dans l'air, par thermogravimétrie non-isotherme, en dépouillant les résultats suivant la méthode proposée par P. K. Chatterjee.

Le processus de la déshydratation de l'hydroxyde d'aluminium s'effectue suivant le mécanisme:

$$Al(OH)_3 \rightarrow AlOOH + H_2O$$
$$2\,AlOOH \rightarrow Al_2O_3 + H_2O$$

Les deux réactions ont lieu par diffusion, la première jusqu'à la température de 526 K et la seconde jusqu'à 700 K, les valeurs correspondantes des énergies d'activation étant 15.70 kJ · mol^{-1} pour la première et 0.20 kJ · mol^{-1} pour la seconde réaction.

Lors d'une élévation continue de la température au-dessus de 526 K dans le premier cas et au-dessus de 700 K dans le deuxième cas, les vitesses de ces réactions deviennent limitées en raison des transformations cristallochimiques et les valeurs des énergies d'activation sont 116.97 pour la première et 91.92 kJ · mol^{-1} pour la seconde réaction.

ZUSAMMENFASSUNG — Die nicht-isotherme thermogravimetrische Analyse wurde zur Bestimmung der Kinetik der Dehydration von Aluminiumhydroxid in Luft-Atmosphäre eingesetzt und die Methode von P. K. Chatterjee zur Verarbeitung der Versuchsergebnisse angewendet.

Der Dehydratisierungsvorgang von Aluminiumhydroxid verläuft nach folgendem Mechanismus:

$$Al(OH)_3 \rightarrow AlOOH + H_2O$$
$$2\,AlOOH \rightarrow Al_2O_3 + H_2O$$

Beide Reaktionen spielen sich in der Diffusionszone ab, die erstere bis zur Temperatur von 526 K und die zweite bis zur Temperatur von 700 K. Die entsprechenden Aktivierungsenergien sind 15.70 kJ/Mol für die erste und 0.20 kJ/Mol für die zweite Reaktion.

Bei kontinuierlicher Erhöhung der Temperatur über 526 K im ersten und über 700 K im zweiten Fall werden die Geschwindigkeiten dieser Reaktionen durch kristallchemische Umwandlungen begrenzt und die Aktivierungsenergie beträgt 116.97 kJ/Mol für die erste und 91.92 kJ/Mol für die zweite Reaktion.

Резюме — Неизотермический термогравиметрический анализ был использован для определения кинетики дегидратации гидроокиси алюминия, а для обработки экспериментальных результатов — метод Чэттерье. Процесс дегидратации протекает по следующему механизму:

$$Al(OH)_3 \rightarrow AlOOH + H_2O$$
$$2AlOOH \rightarrow Al_2O_3 + H_2O$$

Обе реакции протекают в диффузионной области, причем первая до температуры 526 К, а вторая — до 700 К. Соответствующие энергии активации для первой и второй реакций составляли 15,70 и 0,20 кдж/моль. При непрерывном увеличении температуры сверх 526 К в первом случае и сверх 700 К — во втором, скорость этих реакций лимитировалась скоростью кристалло-химического превращения, а значения энергии активации для первой и второй реакции, соответственно составляли 116,97 и 91,92 кдж/моль.