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Thermal transformations of aluminium nitrate hydrate

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Abstract

By means of the thermogravimetric (TG) method, and differential thermal analysis (DTA) with simultaneous chemical analysis of the gaseous reaction products, X-ray diffraction phase analysis, and infrared spectroscopy, stages of decomposition of $Al(NO_3)_3{\cdot}9H_2O$ were studied. It has been found that the thermal decomposition of $Al(NO_3)_3{\cdot}9H_2O$ proceeds in a few stages. First stage is connected with partial dehydration of the compound without decomposition of the nitrate groups. The successive stages comprise the hydrolytic processes, which are connected with further dehydration and loss of the nitrate groups. The process proceeds with the formation of amorphous alumina. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium nitrate hydrate; Thermal transformations

1. Introduction

With total annual production of more than 6.5 million tonnes, the oxides, oxyhydroxides and hydroxides of the elements aluminium, silicon and titanium are undoubtedly among the most important industrial inorganic chemicals. The aluminium oxides, oxyhydroxides and hydroxides are the second most important refined products of the natural mineral bauxite [1,2].

The aluminium oxides are used as catalysts, catalyst supports, adsorbent and ceramic materials. This spectrum of applications requires different properties, such as particle size, morphology, surface, etc. Among the three mentioned metals, aluminium offers the richest variety of Al–O and Al–O–H phases [2,3].

The thermal decomposition of aluminium salt is one of the essential steps in the technology of Al_2O_3 production by the acidic method. A precise recognition of the mechanism of thermal decomposition of the salt is very important for manufacture of alumina of precisely specified properties. The properties of the obtained alumina must be correlated not only with such properties of the starting material, as its crystal structure or grain size, but also with the mechanism of decomposition of the given salt and the recrystallization processes that proceed in alumina as a function of temperature [4].

The aim of this work has been to study the mechanism of thermal decomposition of aluminium nitrate hydrate. The decomposition of this salt proceeds at rather low temperatures. This fact gives a possibility to obtain aluminium oxides of well-developed specific surface, that can be used in catalysis or in sorption processes. Combined thermoanalytical methods, comparative structural and morphological studies show different mechanisms of product formation.

The use of aluminium nitrate as a raw material for the manufacture of hydrous aluminium oxides by hydrolysis has the advantage of easy removal of nitrate

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anion from the reaction mixture and yielding a final product of high purity [5].

2. Experimental conditions and results

The material used in the experimental work was $Al(NO_3)_3{\cdot}9H_2O$, analytical grade, produced by POCH, Gliwice, Poland.

The mechanism of thermal decomposition was studied by thermal analysis coupled with mass spectrometry of the gaseous decomposition products, infrared spectroscopy, and X-ray phase analysis.

The initial samples $Al(NO_3)_3{\cdot}9H_2O$ polythermal differential thermal analysis (DTA) and thermogravimetric (TG) studies were carried out with simultaneous chemical analysis of the gaseous reaction products with the use of a quadrupole mass spectrometer. The instrument was SDT 2960 TA INSTRUMENTS adapted for simultaneous recording of DTA and TG curves, coupled on-line with mass spectrometer QMS Thermostar produced by BALZERS. The samples (20 mg) were heated at the rate of 5 °C/min. The results are shown in Fig. 1.

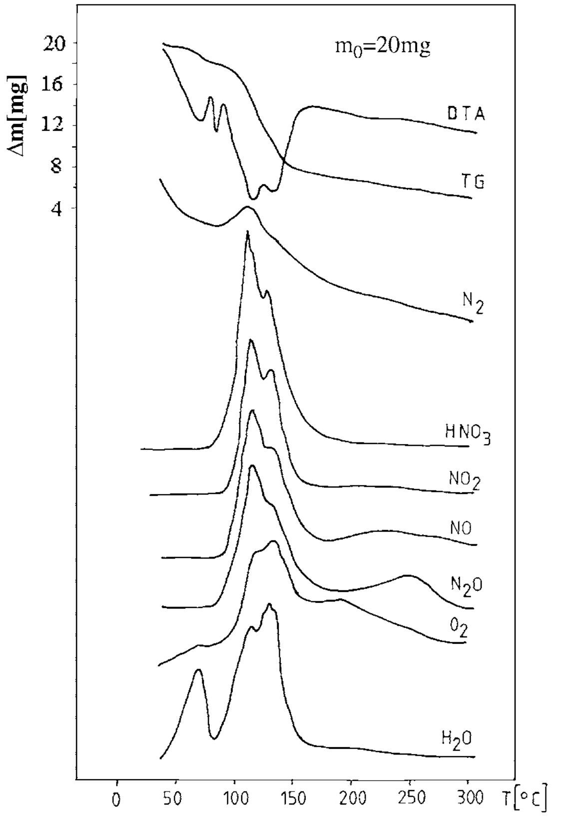

Fig. 1. TG and mass spectrometric analysis of aluminium nitrate hydrate.

Irrespective of the thermal analyses, the X-ray phase analyses, and the IR analyses were performed both for the initial samples and for the products of their decomposition for 1 h, in air, at definite temperatures 120, 200, 400, and 550 °C, in a high-temperature reactor (Czylok).

The thermal analyses involved the TG, differential thermogravimetry (DTG), and DTA measurements using Derywatograf C produced by MOM (Hungary). The samples (100 mg) were heated in air atmosphere at the rate of 10 °C/min in temperature range 20–1000 °C. Pure alumina was used as the reference. The TG, DTG, and DTA curves obtained in the measurements have been shown in Figs. 2–4, respectively.

The IR spectra were taken within 4000–400 cm^{-1} using Specord 75 IR spectrophotometer produced by Carl Zeiss, Jena. The results are shown in Fig. 5.

The phase composition of the samples was determined by qualitative X-ray phase analysis using HZG-4C diffractometer with Cu cathode (Cu Kα radiation) with Ni filter. The measurements were carried out

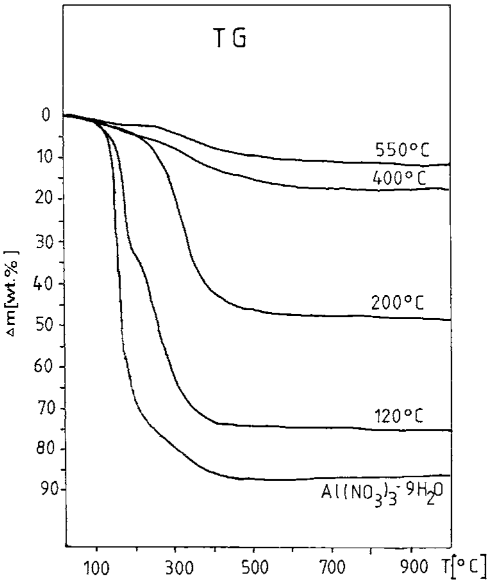

Fig. 2. TG curves of aluminium nitrate hydrate and products of its decomposition at various temperatures.

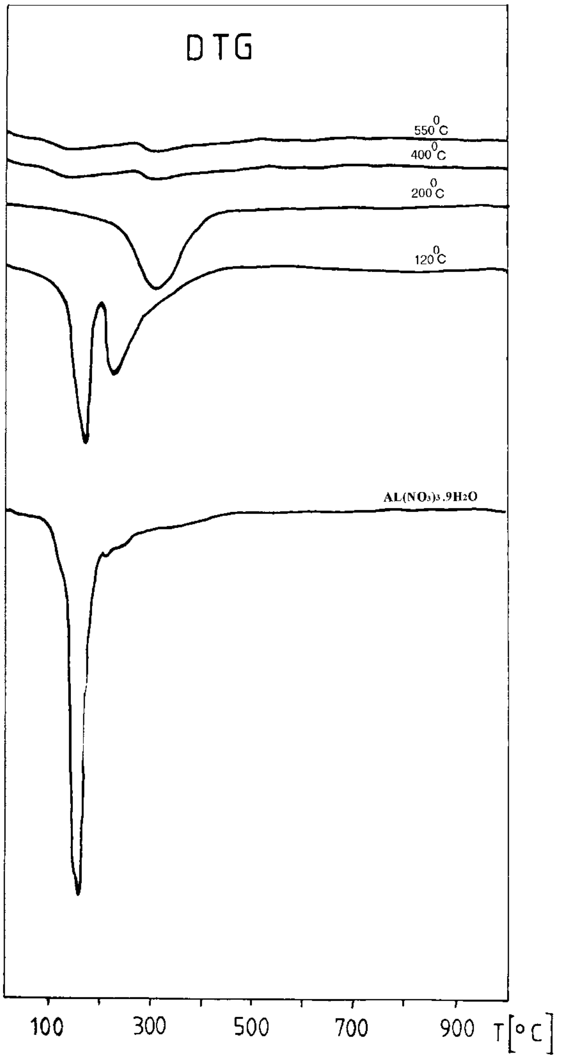

Fig. 3. DTG curves of aluminium nitrate hydrate and products of its decomposition at various temperatures.

in 0.01° steps. The time of pulse counting was 2 s. The results have been shown in Fig. 6.

The specific surface (S_{BET}) determined by the volumetric method of low-temperature adsorption of nitrogen is shown in Fig. 7.

3. Discussion of results

Fig. 1 shows the TG and DTA curves obtained in the thermal decomposition of $Al(NO_3)_3{\cdot}9H_2O$, along with

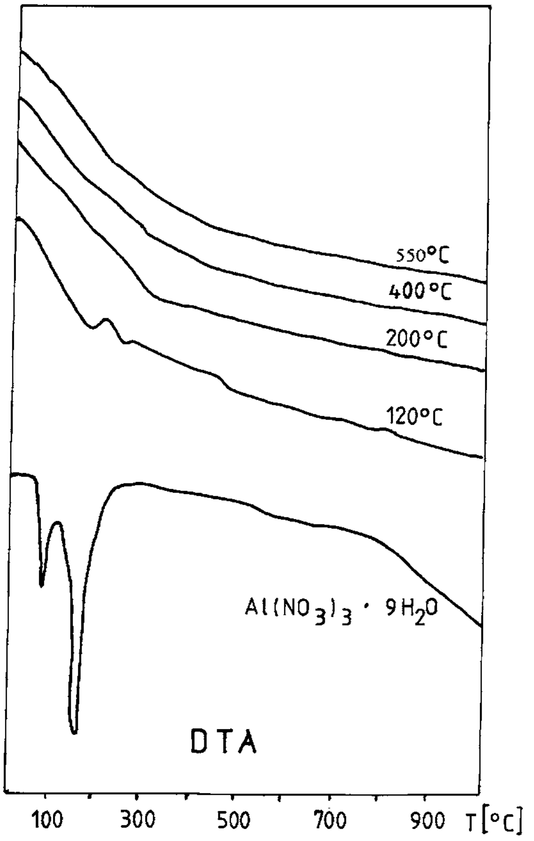

Fig. 4. DTA curves of aluminium nitrate hydrate and products of its decomposition at various temperatures.

the curves that represent the ionic currents in the mass spectrophotometer for the following M/q ratios: 18 (H_2O), 32 (O_2), 44 (N_2O), 30 (NO), 46 (NO_2), 63 (HNO_3), and 28 (N_2) (M: molar mass, q: ionic charge in electron charge units), and this reflects the qualitative composition of the gaseous products of dissociation of the initial compound.

The DTA curve shows four endothermic effects with the extremes at 70, 80, 110, and 130 °C. All these effects (except that at 80 °C being due to melting of the salt) are associated with mass losses.

Analysis of the gaseous reaction products shows that only dehydration occurs in the first step of decomposition proceeding below 80 °C. The sample looses about 11.4% of its mass, which corresponds to the loss of 2.5 molecules of water from the outer coordination sphere, without breaking the structure of the nitrate groups. The successive steps of decomposition

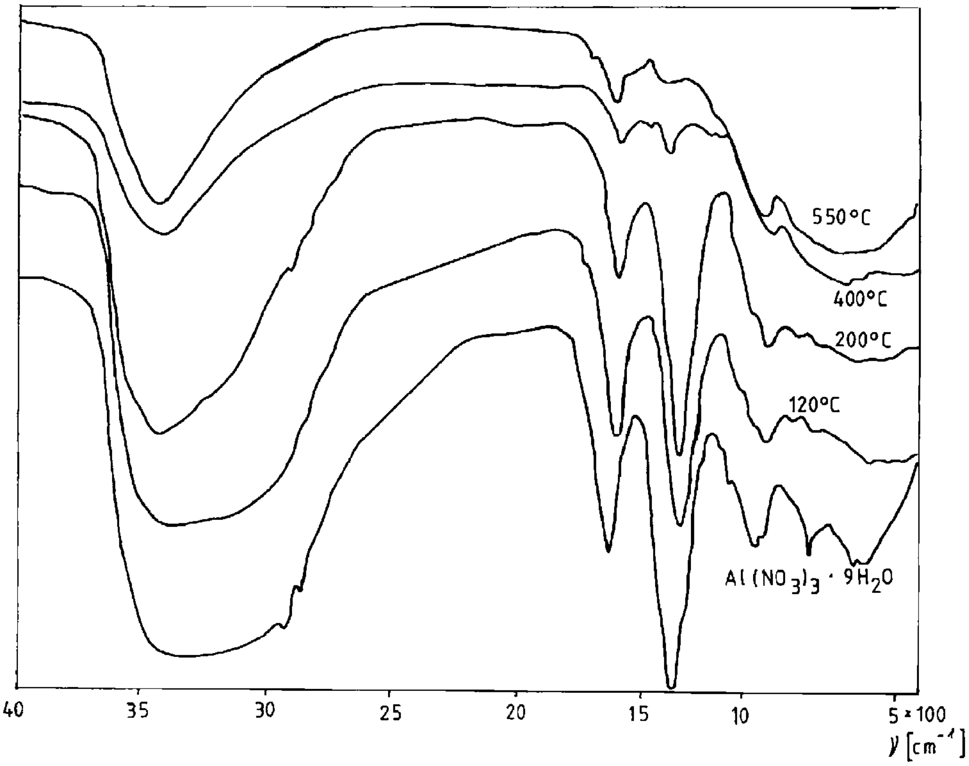

Fig. 5. IR spectra of aluminium nitrate hydrate and products of its decomposition at various temperatures.

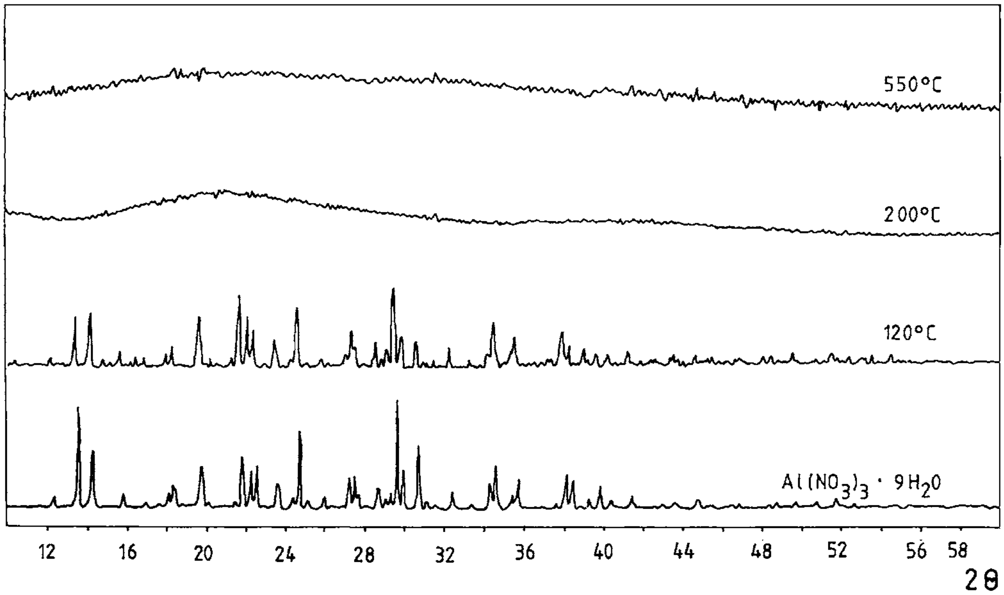

Fig. 6. X-ray diffraction spectra of aluminium nitrate hydrate and products of its decomposition at various temperatures.

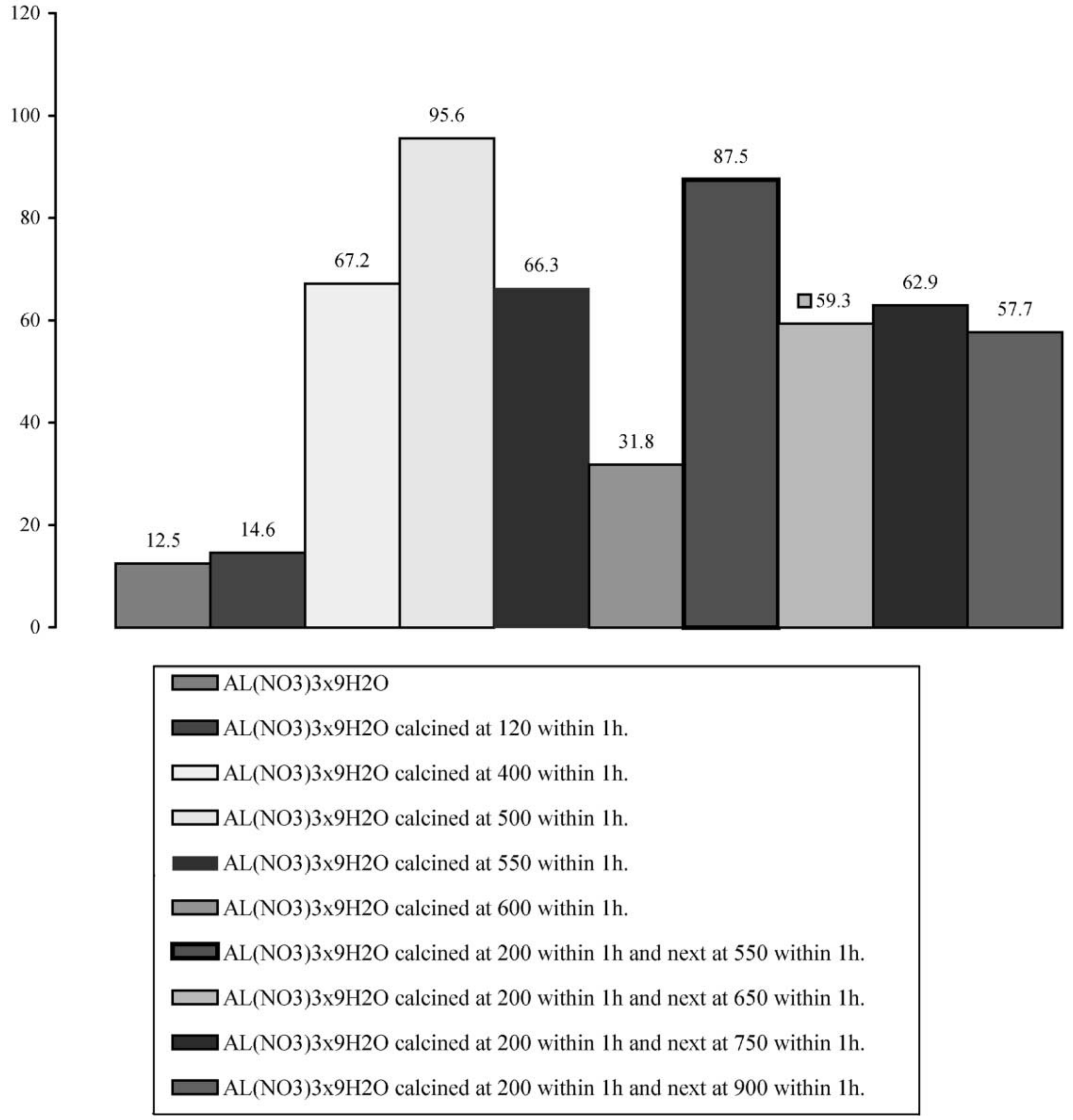

Fig. 7. S_{BET} of aluminium nitrate hydrate and products of its decomposition at various temperatures.

proceeding above 80 °C are connected with further dehydration of the salt, and simultaneous destruction of the nitrate groups. The salt melts at 80 °C. The mechanism of the stepwise dehydration may be explained by assuming the following formula to the initial hydrate $[Al(H_2O)_6](NO_3)_3{\cdot}3H_2O$ [6].

Like other hydrous nitrates, mainly of the group 'd' of the elements [4,7], aluminium nitrate hydrate cannot give anhydrous salt in thermal decomposition process. In the case of aluminium cation, having small atomic radius and large electric charge (3+), the neutralization of the charge by the nitrate anions would require a too high coordination number (assuming the formal charge of oxygen to be equal to 1/3). Such a number is neither observed in practice nor possible from the geometrical viewpoint.

The problem of charge neutralization at the small radius of the Al^{3+} cation may be resolved by creation of the hydrated ion, with the electric charge distributed on its surface, that can be neutralized by a suitable number of oxygen atoms proceeding from the nitrate groups. Thus, the structure of aluminium nitrate hydrate is featured by the presence of two kinds of water, which is reflected in the stepwise dehydration of the compound.

The mechanism of decomposition of the hydrous salt changes upon changing the experimental conditions: the larger the sample mass, the higher the heating rate (see Figs. 2–4).

Thermal decomposition of $Al(NO_3)_3{\cdot}9H_2O$ is preceded by melting, which manifests itself by endothermic effect on the DTA curve (Fig. 4), with an extremum at 80 °C, and no change in the sample mass (see TG curve in Fig. 2).

Thermal dissociation of the hydrate proceeds in a rather narrow temperature range within 150–400 °C, practically as a one-stage process. The overall mass loss of the sample is about 85%, which corresponds roughly to theoretical contents of volatile components in $Al(NO_3)_3{\cdot}9H_2O$ (see TG and DTG in Figs. 2 and 3, respectively). The loss in mass is accompanied by a sharp peak on the DTA curve, with the extremum at 170 °C (Fig. 4).

An analysis of the TG and DTG curves shows that the rate of the mass loss is variable (Figs. 2 and 3). The rate observed at temperatures below 170 °C is much higher than that in higher temperature range, between 170 and 400 °C. The process of the salt decomposition ends practically at 400 °C. The initial stage of decomposition, below 170 °C, comprises probably a series of simultaneous reactions such as dehydration, hydrolysis, and destruction of nitrate groups, whereas such processes as dehydroxylation of hydroxy salts, formed during the decomposition as a consequence of hydrolytic processes, occur at temperatures above 170 °C. The hydrolytic process and formation of solid hydroxy salts can be observed when the process is carried out under isothermal conditions.

Analysis of thermoanalytical curves of the decomposition product of aluminium nitrate hydrate carried out for 1 h at 120 °C shows that the process proceeds in two stages (Figs. 2–4). In the first step, below 220 °C, the sample loses about 33.5% of its weight. The process is associated with a peak on the DTG curve and an endothermic effect on the DTA curve, with an extremum at 170 °C. A further 42.2% loss in mass is observed in the second stage, which proceeds at 220–450 °C. The rate of the mass loss is, however, much slower in this step and it decreases with increasing temperature. The thermal decomposition is here not preceded by the melting of the salt. Stoichiometric calculations show that the composition of the product of partial dehydration at 120 °C corresponds to the formula $Al(OH)(NO)_3{\cdot}2H_2O$.

An analysis of the results of X-ray diffraction studies shows that in both the initial salt and the sample heated for 1 h at 120 °C (see Fig. 6) the crystalline phase, corresponding to $Al(NO_3)_3{\cdot}9H_2O$ (ASTM 24-0004) is present. The products obtained from partial decomposition of the salt have amorphic structure. The aluminium nitrate hydrate, occurring in the both samples, has a different degree of crystallinity. The size of crystals present in the sample calcined at 120 °C is much finer.

The infrared absorption spectra of the hydrate heated for 1 h at 120 °C do not especially differ from those obtained for the starting salt (Fig. 5). The IR absorption spectra show only some change in the shape of the absorption band within wave numbers 400–800 cm^{-1}, probably indicated for variety of Al–O–Al bonds [10,11].

The thermoanalytical curves of the intermediate product, obtained by heating the hydrate for 1 h at 200 °C do not substantially differ from those obtained at 120 °C. Only the height of the effect connected with the first stage of decomposition is markedly reduced.

The greatest mass loss, amounting to about 40%, takes place in the temperature range 220–450 °C. It is probably due to the dehydration of the hydrolysis products formed during the isothermal heating of the salt.

On changing the process conditions from non-isothermal to isothermal ones it is possible to observe the reactions of hydrolysis associated with the decomposition. The shape of the DTG and DTA curves of the intermediate reaction products of aluminium hydrate decomposition, carried out for 1 h at temperatures 120, 200, 400 and 550 °C, as compared with identical curves obtained for the starting salt, is shown in Figs. 3 and 4. The DTG curves (Fig. 3) show the decrease of the effect observed at 170 °C, as the temperature of heating increases. The weakening of this effect is accompanied by the appearance of a new effect at 220 °C. The new effect increases and shifts toward higher temperatures as the temperature of isothermal heating increases. The new effect is probably due to the dehydroxylation of the hydroxy salts, formed in the hydrolysis associated with the decomposition of the hydrate. An endothermic effect at 80 °C, observed for the initial sample and connected with the melting of the substance (Fig. 4), is absent on the DTA curves of the samples heated at higher temperatures, in which the processes of thermal decomposition and hydrolysis had been much more advanced. The course of the hydrolytic reactions and the decomposition of the hydrate has been confirmed by the results of spectrophotometric analyses.

The IR absorption spectra (see Fig. 5) show a distinct change in the shape of the absorption band within wave numbers 2800–3600 cm^{-1}. A broad asymmetric band observed for the sample of the initial salt may prove the presence of water bound differently in the hydrate. The band narrows markedly as the temperature of isothermal heating increases. This fact points to the presence of hydroxy groups in the sample compounds. The band at 1370 cm^{-1}, characteristic for the nitrate anion, decreases steadily with increasing temperature of isothermal heating [11,12]. The IR spectra of the samples heated at 400 and 550 °C are similar to each other and are characteristic of aluminium oxide [8,9].

The thermal decomposition of aluminium nitrate hydrate proceeds in a rather narrow temperature range and at low-temperatures. Besides, the decomposition is associated with a considerable loss in mass, exceeding 80%. The simultaneous processes of dehydration and of elimination of nitrogen compounds result in rapid collapse of the hydrate structure and amorphization of the obtained product. The samples obtained in calcination for 1 h in air atmosphere at 200 and 550 °C are amorphous according to X-ray studies (Fig. 6). The reactions of decomposition and hydrolysis occurring under the conditions of the experiment are associated with destruction of crystal structure of the hydrate. Owing to the low decomposition temperatures no recrystallization processes take place, and use can be made of this fact in obtaining aluminium oxides of highly developed porous structure. Fig. 7 shows the values of specific surface S_{BET} of the products of thermal decomposition of aluminium nitrate hydrate and of aluminium oxides obtained by calcination of these products at various temperatures.

Analysis of these results shows that the degree of surface development of the products of thermal decomposition aluminium nitrate hydrate depends largely on the history of the sample used. When the thermal decomposition of the hydrate is carried out under isothermal conditions the value of specific surface first increases to 95.6 m^2/g for the product obtained at 500 °C, then it decreases rapidly down to 31.8 m^2/g for a product obtained by heating the initial salt at 600 °C.

It is to be pointed out that the product obtained by thermal decomposition of the hydrate at 500 °C is amorphous (see Fig. 6).

Changes of different kind are observed on two-stage calcination of the starting salt. Samples heated for 1 h at 200 °C, then for 1 h at 550 °C, are characterized by relatively high specific surface of 87.5 m^2/g, similar to S_{BET} of aluminium oxide obtained in a one-stage calcination of the salt at 550 °C.

Increasing the temperature of isothermal calcination in the second stage up to 900 °C does not lead to a substantial decrease of specific surface of aluminium oxides obtained by this procedure. The value of S_{BET} does not fall below 60 m^2/g when the calcination temperature is increased up to 900 °C. The results of X-ray diffraction show that the samples are amorphous. Some amount of crystallinity can only be detected in samples obtained in two-stage temperature treatment: first at 550 °C, then at 900 °C.

The changes in the porous structure of aluminium oxides, hence, also in the degree of development of the specific surface, during the heating at various temperatures, can be explained as a result of sintering. In the temperature range 550–1000 °C, this process may be due to dehydroxylation of the surface of primary crystallites leading to the formation of Al–O–Al bonds and due to mass transfer by surface and bulk diffusion processes.

The surface diffusion transfers the mass from free surface of primary crystallites to the points of their contact. This process leads to increase of the effective pore size diameter and closing the contacts between neighboring particles. As a result, the pore volume and the specific surface of the sample decrease. Increasing the calcination temperature accelerates probably the recrystallization processes and leads to the growth of crystallites and to their sintering.

The results of the studies on thermal decomposition of aluminium nitrate hydrate, in particular of its two-stage decomposition, obtained until now, are not convincing proof of these phenomena. A fact of primary importance is probably, whether the process proceeds in the liquid phase, after the salt has been molten, or in the solid phase in the second stage of the calcination.

A detailed description of the phenomena occurring will be possible after precise studies of the porous structure of the oxides and its changes provoked by the increase of temperature.

4. Conclusions

Analysis of the results of the studies performed enables to make the following conclusions:

- The process of thermal decomposition of $Al(NO_3)_3 \cdot 9H_2O$ is connected with dehydration and elimination of nitrate groups, accompanied by hydrolysis.
- These reactions can proceed in successive stages or in parallel depending on the conditions, in particular, on the rate of temperature increase and composition of the gas phase in the reaction medium.
- The physical properties of the aluminium oxides depend on the method and the parameters of thermal decomposition of aluminium nitrate hydrate.
- The two-stage process of decomposition of the salt is more advantageous for obtaining aluminium oxides of highly developed specific surface.

Further studies on the kinetics of thermal decomposition and on the porous structure of aluminium oxides obtained are necessary for better understanding of the phenomena occurring in the formation of the structure of these materials.

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