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THERMAL TRANSFORMATIONS OF THE PRODUCTS OF PARTIAL HYDROLYSIS OF HYDROUS ALUMINIUM NITRATE

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Abstract

Thermal analysis, mass spectrometry, infrared spectrophotometry, X-ray phase analysis, scanning electron microscopy, and sorption methods were used in the study of thermal transformations of the products of partial hydrolysis of hydrous aluminium nitrate in ammonia medium. It has been found that the process of aluminium nitrate hydrolysis under the conditions applied and in the presence of ammonia gives boehmite as the main product, with some admixture of a basic salt.

Aluminium oxide obtained from the products of partial hydrolysis of hydrous aluminium nitrate in ammonia medium at 550°C has a crystalline γ-Al_2O_3 structure. Its specific surface, as determined by low-temperature adsorption of nitrogen, exceeds 200 $m^2\ g^{-1}$. Features of the products are well developed mesopore structure and considerable ability of benzene adsorption. Calcination of the obtained aluminium oxide for 2 h at 900°C reduces its specific surface to about 110 $m^2\ g^{-1}$.

Keywords: hydrous aluminium nitrate, partial hydrolysis, TA, thermal transformations

Introduction

Aluminium oxide is used widely in catalytic processes, mainly due to its excellent mechanical properties, very high thermal stability in a large temperature range, and high specific surface [1]. When developing methods for the preparation of aluminium oxides of high porosity endeavors are made to delay their sintering on the increase of temperature, since it is of great importance in high-temperature catalytic processes. It is also of great importance to produce aluminium oxides of strictly determined morphology and physical properties suitable in the manufacture of ceramic materials or as components of various composites.

Aluminium oxides are usually produced by the thermal decomposition of aluminium salts or hydroxides obtained in hydrolysis of salts in various media [2–4]. Orientation of the process of synthesis to obtain aluminium oxides of required properties needs the use of a suitable precursor and optimum precipitation conditions. The

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form of aluminium oxide precipitate obtained depends on a number of factors, including the pH value. For example, precipitation at pH lower than 8 gives a gel of aluminium meta-hydroxide (AlOOH) or boehmite [3, 5], from which γ aluminium oxide may be obtained by thermal decomposition at 400–500°C. Precipitation at pH>9 yields $Al(OH)_3$ forms referred to as the tri-hydroxide or bayerite, which can also be used for obtaining aluminium oxide.

In many catalytic reactions the upper process temperature does not exceed 600°C. In some processes of catalytic oxidation the temperature may exceed 1000°C, hence the carrier should be resistant to high temperatures. The high specific surface of the γ and ε modifications of aluminium oxide is greatly reduced on heating at about 800°C because of the sintering processes and the phase transition to the high-temperature α-modification. In order to provide stabilization of the low-temperature modifications of aluminium oxide with high specific surface some additives are used such as silica, phosphoric acid, barium hydroxide, and oxides of cerium and lanthanum [6, 7]. An addition of 10 mol% of silica to aluminium oxide stabilizes its specific surface which does not decrease below 114 $m^2 g^{-1}$ on heating for 5 h at 1200°C [6]. In many authors' opinion such a behaviour is due to the fine-grained form of such preparations, the retardation of the polymorphic transformation, and the formation of micro-cracks in the pre-sintering process [8]. An addition of small quantities of stabilizing substances can modify the original properties of the carrier, such as the surface acidity, melting point, or reactivity. For example [9], an addition of Mn2O3 and Fe2O3 increases the catalytic activity of aluminium oxide; however, at the same time decreases the thermal stability of such systems leading to the crystallization of á-Al2O3 at 100ºC.

According to the authors of the paper [10], the time of aging the precipitate in the mother liquor is a very important factor that also influences the thermal stability. The degree of crystallinity of the product obtained in the hydrolysis reaction of aluminium nitrate in ammonia medium increases, if the hydrolysis is carried out for 264 h at 100ºC, with respect the samples separated from the mother liquor just after completing the dosage of the reagents. Moreover, aluminium oxide, obtained by thermal decomposition of the products of hydrolysis carried out for 264 h at an increased temperature, has a well developed specific surface, stable at high temperatures, amounting to about 100 m2/g, after calcination for 2 h at 1200C.

The properties of the aluminium oxide formed depend not only on the properties of the raw material used, its crystal structure, grain size, and content of volatile matter, but they are modified in the course of the thermal decomposition of the raw material. For this reason the knowledge of the mechanism of thermal transformations enables a better understanding of the mechanism of formation of specific properties of the final product. Both hydrous aluminium nitrate and products of its partial hydrolysis in ammonia medium may be good source materials for obtaining aluminium oxides of well developed porous structure. The use of hydrous aluminium nitrate as a raw material provides a possibility of easily removing the unstable nitrate anions from the reaction medium [11, 12] and thus of obtaining the final product with a high purity.

The aim of this work was to study the thermal transformations of the products of partial hydrolysis of hydrous aluminium nitrate in an ammonia medium, with special consideration of the porous structure of the oxides obtained in this way. These studies constitute a part of more general investigations into obtaining aluminium oxides of highly developed porous structure, stable at high temperatures, with the use of hydrous aluminium nitrate as the raw material.

Experimental

Products of partial hydrolysis in ammonia medium of hydrous aluminium nitrate $Al(NO_3)_3{\cdot}9H_2O$ analytical grade, produced by POCH Gliwice, were used in the experiments. The hydrolysis of hydrous aluminium nitrate was carried out as follows:

The starting materials: 0.5 M aluminium nitrate and 0.5 M ammonia were dosed with the same rate from two separate burettes into a 1 dm^3 beaker placed in a thermostat. The process of hydrolysis was carried out under controlled pH=7.0 for 60 min at 90°C under continuous stirring. The obtained milky-white colloidal precipitate was filtered, washed with distilled water, dried at 100°C and ground in a mortar to obtain a white powder. The obtained sample was then subjected to further investigations.

The thermal decomposition of the products of hydrous aluminium nitrate hydrolysis in ammonia medium was studied under dynamic conditions, i.e. under constant temperature increase, as well as under isothermal conditions. Thermoanalytical curves, X-ray diffraction spectra and infrared spectra were recorded for the samples of the starting materials – the products of partial hydrolysis of hydrous aluminium nitrate and for the products of their thermal decomposition under isothermal conditions at specified temperatures and time of reaction.

The partial thermal dissociation of the products of hydrolysis was achieved by heating the samples of the starting material in a high-temperature flow-through reactor Czylok (Poland). The calcination was carried out for 2 h in an air atmosphere at various temperatures. The decomposition temperatures were 150, 300 and 550°C.

The experiments were carried out in the following way: weighed samples of the starting material were spread in a thin layer in a ceramic boat which was then placed in a furnace, previously heated to a required temperature, and were treated for 2 h. The samples of intermediate decomposition products thus obtained under isothermal conditions were then subjected to further studies.

The thermoanalytical curves TG, DTG and DTA obtained for the samples of starting materials and for their decomposition products were recorded in a SDT 2960 thermoanalyser produced by TA Instruments. The measurements were carried out for 5–10 mg samples in an air atmosphere at temperature range 20–1000°C with a heating rate of 10°C min^{-1}.

For some samples the TG and DTA curves were recorded with simultaneous analysis of the gas products by means of a quadrupole mass spectrometer using the SDT 2960 instrument coupled on line with a mass spectrometer QMS ThermoStar produced by Balzers.

The IR spectra of the starting materials and of the products of their decomposition in an air atmosphere were recorded in the wave number range 4000–400 cm^{-1} by means of a 75 IR spectrophotometer produced by Carl Zeiss Jena.

The phase composition of the samples was determined by the X-ray diffraction method. The X-ray diffraction spectra were recorded in an instrument using a Cu cathode with CuK_α radiation with a Ni filter. The measurements were performed in steps of 0.01° with pulse counting in 2 s intervals.

The specific surface of the starting materials and of their decomposition products was determined by the volumetric method and low temperature adsorption of nitrogen. Also, the method of benzene vapour adsorption and desorption was applied to the starting materials and the decomposition products. The adsorption isotherms obtained were used for the determination of the parameters of the porous structure of the sorbents.

The morphology of the samples was determined by means of photographs taken with the use of a scanning electron microscope produced by JOEL (Japan).

Results and discussion

Thermal transformations of the products of partial hydrolysis of aluminium nitrate

The results of thermal studies of the products of aluminium nitrate hydrolysis in an ammonia medium and of the products of their calcination at various temperatures are shown in Figs 1–4.

The thermal decomposition of the products of aluminium nitrate hydrolysis in an ammonia medium proceeds in three stages (Fig. 1).

The first stage, up to a temperature of 100°C, is characteristic by the loss of sample mass of about 6.7% and an endothermic effect on the DTA curve with a minimum at 80°C. This step is connected with the removal of physically bound water from the sample. This fact is confirmed by the results of the thermal analysis of the sample heated to 150°C (Fig. 2). The shape of this thermoanalytical curve is practically identical to that of the sample of the starting material shown in Fig. 1. The reason for this

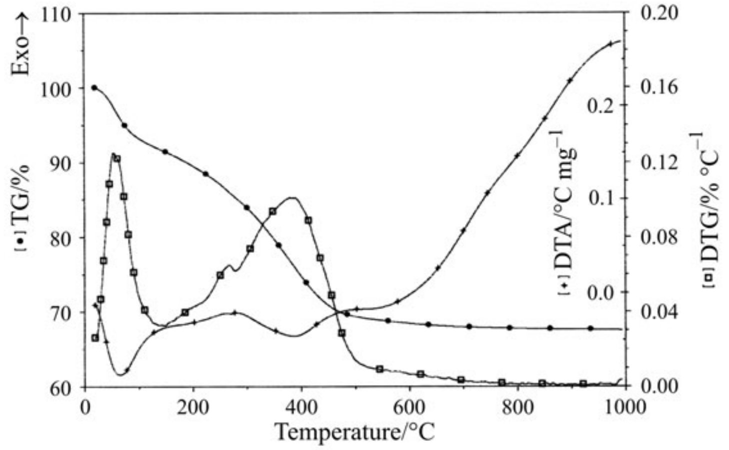

Fig. 1 Thermogravimetric curves of the product of hydrolysis of hydrous aluminium nitrate in an ammonia medium

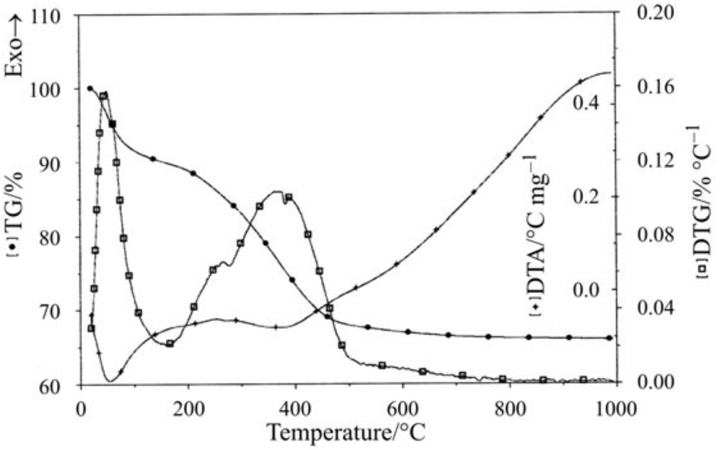

Fig. 2 Thermogravimetric curves of the product of hydrolysis of hydrous aluminium nitrate in an ammonia medium calcined for 2 h at 150°C

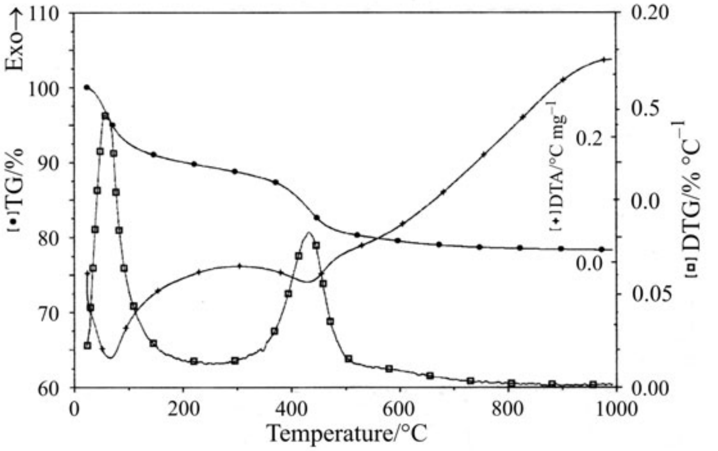

Fig. 3 Thermogravimetric curves of the product of hydrolysis of hydrous aluminium nitrate in an ammonia medium calcined for 2 h at 300°C

is that the sample heated at 150°C undergoes a reversible rehydration due to which it accepts, during the measurements, an amount of physically bound water, which is practically identical to that present in the starting sample.

The second stage corresponding to the temperature range 100 to 300°C is characteristic by further mass loss amounting to about 8% and an endothermic effect on the DTG curve at 280°C. This stage is connected with the further dehydration of the compound and the thermal decomposition of nitrate groups remaining in the sample due to the incompleteness of the reaction of hydrolysis and formation of a basic salt, as confirmed by the results of mass spectrometric studies. The presence of nitrogen oxides is observed in the mass spectrum. The presence of nitrate groups is confirmed by the results of IR absorption analyses [11]. Absorption bands characteristic of the

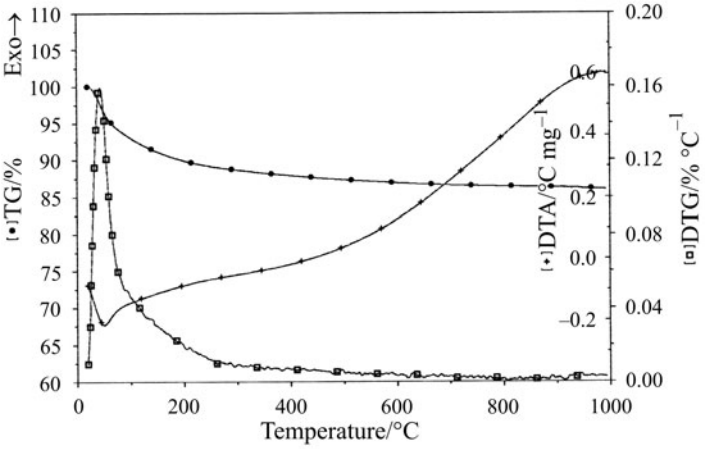

Fig. 4 Thermogravimetric curves of the product of hydrolysis of hydrous aluminium nitrate in an ammonia medium calcined for 2 h at 550°C

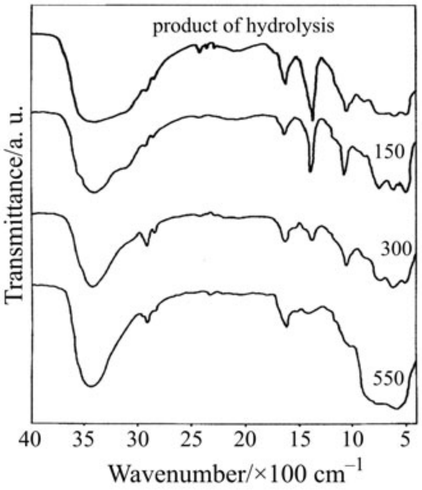

Fig. 5 Infrared spectra of the product of hydrolysis of hydrous aluminium nitrate in ammonia medium and of the products of its calcination for 2 h at various temperatures

nitrate groups at 1360 and 1036 cm^{-1} are present in the IR spectra of both the initial sample and of the sample heated at 150°C (Fig. 5). Identical bands, although of much less intensity, are also present in the IR spectrum of the sample calcined at 300° (Fig. 5). On the other hand, they are not present in the IR spectrum of the sample calcined at 550°C (Fig. 5).

In the third stage, which occurs in the temperature range 300 to 550°C, the sample loses about 17.4% of its mass. One may suppose that this stage proceeds with dehydration of aluminium compounds (boehmite) and thermal decomposition of the remaining nitrate groups. The total mass loss in all the three stages is 32.2%.

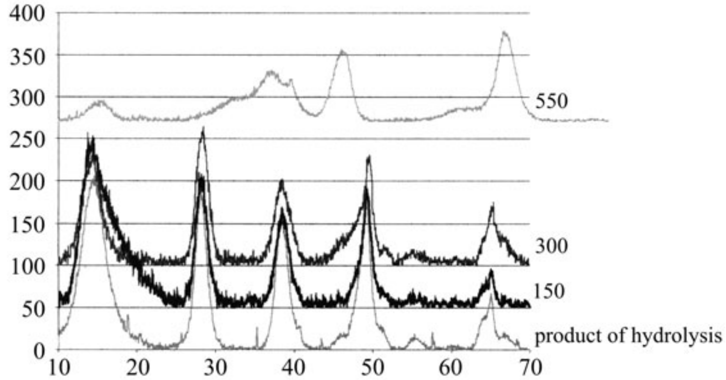

Fig. 6 X-ray diffraction patterns of the product of hydrolysis of hydrous aluminium nitrate in ammonia medium and of products of its calcination for 2 h at various temperatures

The crystal structure of the described product of hydrolytic reaction corresponds to that of boehmite, as can be seen from the results of X-ray phase analysis shown in Fig. 6. A similar shape is observed in the X-ray diffraction patterns of the products of thermal decomposition of the products of aluminium nitrate hydrolysis in an ammonia medium heated at 150 and at 300°C. The intensity of the peaks characteristic of boehmite decreases slightly, as the calcination temperature is increased, and only the peaks characteristic of γ-Al_2O_3 appear for the sample calcined for 2 h at 550°C.

The presence of boehmite in the products of aluminium nitrate hydrolysis in ammonia medium has been confirmed by the results of the spectrometric analyses. The IR spectrum of aluminium nitrate hydrolysed in ammonia medium (Fig. 5) contains absorption bands with peaks at the wavenumbers 470, 610, 750 and 1060 cm^{-1} which are characteristic of pure boehmite [14, 15]. These bands are rather intense for the samples heated at 150 and 300°C, and they disappear in the case of the samples calcined for 2 h at 550°C. This may be accounted for by the fact that boehmite is decomposed in the third stage in the temperature range 300–550°C. This observation is also confirmed by the results of the thermal analysis of the sample calcined at 300°C (Fig. 3). An analysis of the thermoanalytical curve shows thermal decomposition of the sample proceeds in two stages. The sample loses about 10% of its mass in the temperature range 20–200°C. This loss of mass corresponds with an endothermic effect on the DTA curve, having an extremum at 80°C. Physically bound water is also removed from the sample in this temperature range. The other 13% of the sample mass is lost in the second stage of the process, between 200 and 500°C, apparently in consequence of thermal decomposition of boehmite. The IR spectrum of the sample calcined at 550°C contains only the absorption bands characteristic for gamma aluminium oxide (Fig. 6).

The complex overview of the results of thermal analysis and infrared spectroscopy suggests that the hydrolysis of aluminium nitrate in an ammonia medium results essentially in the formation of boehmite with some admixture of a basic salt.

The porous structure of the product of aluminium nitrate hydrolysis in an ammonia medium and of the products of its calcination at various temperatures

Table 1 shows the values of specific surface as calculated by the BET method for the products of aluminium nitrate hydrolysis in an ammonia medium and for the products of its calcination for 2 h at various temperatures. The calculations were based on the results of adsorption of benzene and nitrogen.

The presented results show that both the sample obtained in the hydrolysis of aluminium nitrate in ammonia medium and the products of its calcination at various temperatures are capable of adsorbing considerable amounts of benzene vapours and their specific surface lies within 170–215 $m^2\ g^{-1}$ assuming planar attachment of benzene molecules on the sorbent surface.

Table 1 The specific surface values as calculated by the BET method of the product of hydrolysis of aluminium nitrate in an ammonia medium and of the products of its calcination for 2 h at various temperatures

Sample	$S_{BET}\ C_6H_6/m^2\ g^{-1}$		$S_{BET}\ N_2/m^2\ g^{-1}$
	S_{BET} planar	S_{BET} vertical	
Product of hydrolysis	212	132	122
Product of hydrolysis/150°C	170	106	199
Product of hydrolysis/300°C	246	154	263
Product of hydrolysis/550°C	215	135	213
Product of hydrolysis/550°C/900°C			110

It should be pointed out that it is only in the case of the product of hydrolysis, that the specific surface determined from adsorption of benzene vapours with assumption of planar disposition of benzene molecules on the surface is about 1.7 times higher than the surface determined from the sorption of nitrogen. In all of the other samples, calcined at various temperatures, the specific surface calculated from the sorption of benzene is either lower than, or else comparable to that calculated from the sorption of nitrogen. The nature of the temperature dependence of the sorption of the two adsorbates is also different. In the case of benzene sorption the calcination of aluminium hydroxide at 150°C results in a considerable decrease of the specific surface with respect to that of the initial sample, from 212 to 170 $m^2\ g^{-1}$. An increase of the calcination temperature to 300°C increases again the specific surface up to 246 $m^2\ g^{-1}$, and a further increase of temperature up to 550°C reduces the specific surface to a value of 215 $m^2\ g^{-1}$. A slightly different nature of the changes is observed for the specific surface determined from the sorption of nitrogen. When the calcination temperature is increased, the specific surface increases from 122 to 263 $m^2\ g^{-1}$, and only a small decrease (down to 213 $m^2\ g^{-1}$) is observed on further temperature increase up to 550°C. When aluminium oxide obtained by calcinations at this temperature is heated for 2 h at 900°C, its specific surface decreases only to 110 $m^2\ g^{-1}$. Thus the obtained oxide exhibits some in-

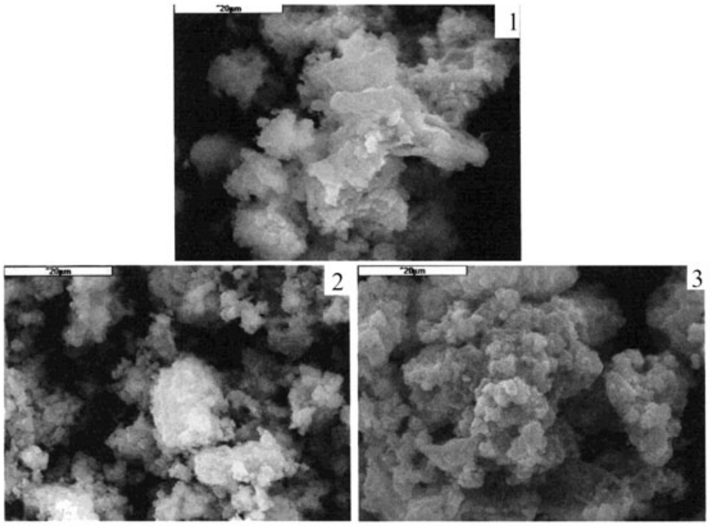

Fig. 7 Microscope photographs of the product of hydrolysis of hydrous aluminium nitrate in ammonia medium and of products of its calcination for 2 h at various temperatures: 1 – product of hydrolysis, 2 – sample (1) calcined at 550°C, 3 – sample (2) calcined at 900°C

creased thermal stability. A microscope photograph of the sample does not show any distinct effect of sintering processes (Fig. 7). The increased thermal stability is apparently due the development of the boehmite crystal structure while aluminium nitrate is hydrolysed in an ammonia medium. When continuing our studies we shall endeavour to obtain boehmite preparations of a higher degree of crystallinity, which should greatly improve the thermal stability of the aluminium oxide obtained. Comparing the results of benzene and nitrogen adsorption makes it possible to suppose that the thermal decomposition of the product of hydrolysis of aluminium nitrate results in a change of the nature of its surface. The fact that the specific surface of the initial sample, calculated from the adsorption of benzene with the assumption of planar orientation of benzene molecules, is by a factor of 1.5 higher than the S_{BET} for nitrogen and is similar to the value calculated for the vertical stacking of benzene molecules enables it to see assumed that benzene molecules adsorbed on the initial sample surface are fixed in the vertical orientation. It may be accounted for by the liophilic nature of the surface. On the other hand, smaller values of specific surface calculated for a planar distribution of benzene molecules, as compared with the value obtained from nitrogen adsorption would show that the nature of the surface has changed to the liophobic one. One cannot exclude, however, that the distribution of benzene molecules on the sorbent surface changes because of a change in the adsorption mechanism.

The results of the calculation are shown in Fig. 8. All the samples exhibit a well developed mesopore structure with a small amount of micropores [16]. The change in porosity of the samples depends mostly on the developed structure of the mesopores. A large hysteresis loop may be accounted for by the developed porous structure of the preparation, in which the pores of irregular shape are of high importance.

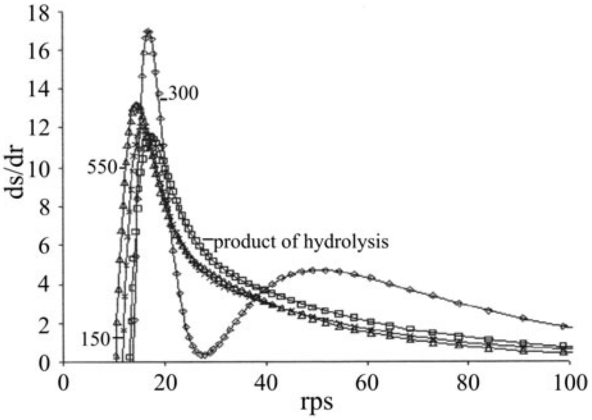

Fig. 8 Pore surface distribution according to their effective radius for samples of the product of hydrolysis of aluminium nitrate in an ammonia medium and of the products of its calcination for 2 h at various temperatures

An analysis of the shape of the distribution curves shown in Fig. 8 leads to a conclusion that the porous structures of the samples of the initial product of aluminium nitrate hydrolysis in ammonia medium and of the products of its calcination at temperatures of 150 and 550°C are similar and that the shape of their curves of distribution according to the pore volumes and surfaces as a function of effective radium is monodisperse. The porous structure of the samples is characterised by a considerable majority of pores with an internal radius in the range of 10–100 Å, but with a distinct maximum on the distribution curve for the pore radius of 20 Å. With increasing calcination temperature the maximum shifts slightly toward the smaller pore radii. A different behaviour is only observed for the curve of surface distribution according to the effective radius in the case of the sample calcined for 2 h at 300°C. This curve has two maxima for the pore radii of 18 and 60 Å. It should be noted that the nitrate groups of the basic salts are removed before this temperature has been attained.

The morphology of the samples of partly hydrolysed aluminium nitrate practically does not change as the temperature is raised (comp. the photographs in Fig. 7).

Conclusions

Complex analysis of the results of the studies performed leads to the following conclusions:

- Under the experimental conditions of this work the hydrolysis of aluminium nitrate in an ammonia medium results in the formation of boehmite with a rather well developed crystal structure accompanied by small admixtures of a basic salt.
- Aluminium oxide obtained from the products of partial hydrolysis of hydrous aluminium nitrate in ammonia medium at 550°C has the crystal structure of γ-Al_2O_3. Its specific surface determined by the low temperature adsorption of nitrogen exceeds 200 $m^2 g^{-1}$. It retains the specific surface of 110 $m^2 g^{-1}$ on calcinations for 2 h

at 900°C . The oxide has a fairly well developed mesopore structure and it exhibits a considerable ability to adsorb benzene.

- The morphology of the samples of the partial hydrolysis of hydrous aluminium nitrate practically does not change with increasing temperature.

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