ALUMINIUM NITRATE AS A PRECURSOR OF MESOPOROUS ALUMINIUM OXIDES

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Abstract

The thermal transformations of the products of hydrous aluminium nitrate hydrolysis in ammonia medium were studied by thermal analysis, mass spectrometry, infrared spectrophotometry, X-ray phase analysis, and sorption methods.

Experiments have shown that the hydrolysis of hydrous aluminium nitrate in ammonia medium at pH=6–7 leads to the formation of boehmite. The degree of crystallinity of this product increases, if the hydrolysis is carried out for 264 h at 100°C, with respect the samples separated from the mother liquor just after completing the dosage of the reagents. It has also been found that aluminium oxide, obtained by thermal decomposition of the products of hydrolysis carried out for 264 h at an increased temperature, is characterized by a well developed specific surface, stable at high temperatures, amounting to about 100 $m^2\ g^{-1}$, after calcination for 2 h at 1200°C.

Keywords: digestion, hydrous aluminium nitrate, thermal stability

Introduction

Aluminium oxides are widely applied in catalytic processes owing to their high mechanical strength, thermal stability in wide temperature range, and high specific surface [1, 2]. Many technological processes carried out with the use of aluminium oxides, such as alkylation, isomerisation, reforming and catalytic cracking [3] must be carried out under severe temperature conditions, so much attention is given to the precise recognition of the transformations of aluminium oxides at high temperatures and to the methods of obtaining the oxides of highly developed porous structure, high structural stability, and high resistance to sintering.

Much interest is given particularly to γ aluminium oxide, which is widely applied in catalytic processes due to the relatively high specific surface at temperatures below 800°C. However, their specific surface decreases rapidly at higher temperatures, at which their sintering is accompanied by a phase transformation leading to the formation of the high temperature α modification [4]. Hence there is a need of stabilization of the low temperature forms of aluminium oxides having high specific surface. Various stabilizers used for this purpose include silica and oxides of phospho-

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rus, barium cerium, and lanthanum [3]. However, the use of the modifiers results also in some changes of the primary properties of aluminium oxide, i.e. its reactivity, acid properties of the surface layers, and melting temperature. For this reason more and more attention is given to the development of optimum conditions for obtaining aluminium oxide and hydroxide of required properties.

A very important factor that influences the thermal stability of the materials obtained is the time of digestion [3]. An extension of the time of ageing the precipitate results in elimination of defects in the crystalline structure connected with the limitation of surface diffusion necessary for their growth. The defects in crystal lattice of aluminium hydroxides precipitated are successfully eliminated by increasing the temperature of the reaction medium [5]. This form of treatment probably leads to elimination of water bound in the form of hydroxyl groups and, in consequence, to the condensation of pseudoboehmite layers and development of the crystal structure. An increase of the time of digestion results in a growth of primary particles of aluminium hydroxide with simultaneous increase of crystallinity, decrease of susceptibility to sintering, and reduction of the number of crystal defects.

The aim of the present work was to study the effect of the process conditions in the reaction of hydrolysis of hydrous aluminium nitrate (with particular consideration of the temperature and time of digestion) on the thermal stability of aluminium oxides obtained by thermal decomposition of the hydroxides obtained during the hydrolysis. Investigations, which results are presented in this paper, are the continuation of previous researches on thermal destruction of hydrous aluminium nitrate and the products of its partial hydrolysis in the presence of ammonia [5, 6].

Experimental

The products of hydrolysis of hydrous aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$, anal. grade, produced by POCh Gliwice, were the main object of the studies. The hydrolysis was carried out as follows:

A 0.5 M solution of aluminium nitrate and a 0.5 M solution of ammonia were dosed from 2 burettes to a 1 dm^3 beaker placed in a thermostat. The process of hydrolysis was carried out under controlled pH of 6 or 7, with continuous stirring. A part of the milky-white colloidal precipitate obtained was filtered off, washed with distilled water, dried at 100°C, and powdered in a mortar. The sample thus obtained was used for further studies.

The other part of the reaction mixture was transferred to a round-bottomed flask and heated at 100°C under a reflux condenser for a total of 264 h. The heating was stopped every 16 h for several hours, during which the mixture was kept at a temperature of 50°C. At the end of this process the precipitate was filtered off, dried at 100°C, and powdered in a mortar. The obtained powder sample was used for further studies.

The thermal decomposition of the products of hydrolysis was carried out both under dynamic conditions, i.e. under a permanent temperature increase, and under isothermal conditions.

The thermoanalytical curves, X-ray diffraction patterns, and infrared spectra were recorded for the initial samples of partially hydrolysed hydrous aluminium nitrate and for the products of their thermal decomposition under isothermal conditions at definite temperatures and time.

The partial thermal dissociation of the products of hydrolysis was carried out by heating the samples of the starting substance in a high-temperature flow reaction (Czylok, Poland). The calcination was carried out for 2 h in air atmosphere at various temperatures. The decomposition temperatures were 550, 900 or 1200°C.

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

The IR spectra of the starting materials and of the products of their decomposition in air were recorded using a FTIR MATTSON Spectrophotometer.

The phase composition of the samples was determined by the X-ray structural analysis using a diffractometer with a Cu cathode (CuK$_\alpha$, radiation) with a nickel filter. The measurements were carried out in 0.01° steps, and pulse counting was performed every 2 s.

The specific surface of the starting material and of the products of its decomposition was determined by volumetric determination of low temperature nitrogen adsorption and by the adsorption and desorption of benzene vapours. The data obtained from the determination of the adsorption/desorption of benzene vapours were processed by means of the program [7] to calculate the following parameters of the porous structure: specific surface BET (S_{BET}), the surface of mesopores (S_{mez}) from the adsorption and desorption parts of the isotherms using the Kisielev method, and the distribution of mesopore volume and surface by the Dollimore Hill method.

The morphology of the samples was determined using the scanning electron microscope (JOE, Japan) microphotographs.

Results and discussion

Some examples of thermoanalytical curves of the products of aluminium nitrate hydrolysis in ammonia medium are shown in Figs 1 and 2 for the products of hydrolysis carried out at pH=7 and digestion at 100°C for 0 h or 264 h. Figure 3 shows the IR spectra, and Fig. 4 shows some examples of X-ray diffraction patterns of the products of hydrolysis carried out at pH=7 and time of digestion at 100°C of 0 and 264 h, as well as the products of their calcinations at various temperatures.

The thermoanalytical curves of the products of aluminium nitrate hydrolysis carried out in ammonia medium at pH=7 (both not digested and digested for 264 h 100°C) are practically identical (Figs 1 and 2). The decomposition of the samples proceeds essentially in two steps.

In the first step ending at about 170°C the sample loses about 7% of its mass and gives an endothermic effect of the DTA curve, with an extremum at 80°C. In this step the sample loses the humidity water.
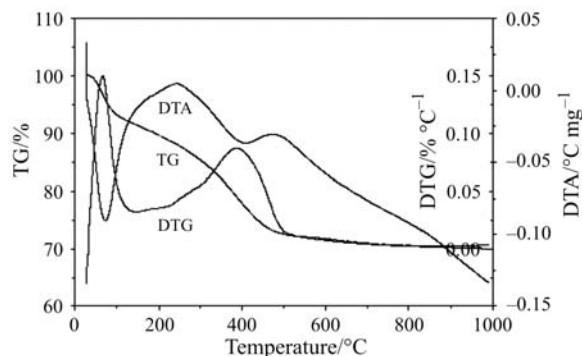
Fig. 1 TG, DTG and DTA curves for the products of hydrolysis of hydrous aluminium nitrate in ammonia medium for pH equals 7 and time of digestion equals 0h
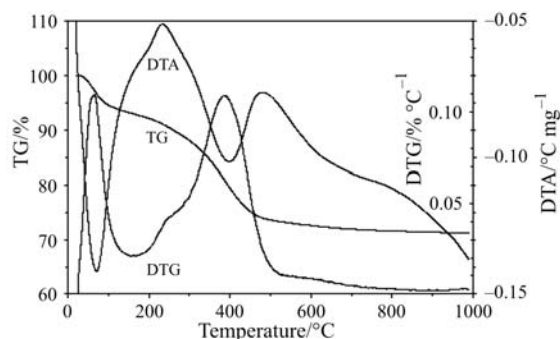

Fig. 2 TG, DTG and DTA curves for the products of hydrolysis of hydrous aluminium nitrate in ammonia medium for pH equals 7 and time of digestion equals 264 h

In the second step, corresponding to the temperature range 170–550°C, the sample loses a further 20% of its mass with an endothermic effect on the DTA curve and an extremum at 400°C. One may suppose that this step is connected with the dehydration of boehmite [8].

Figure 3 represents some examples of the IR spectra of aluminium nitrate hydrolysed in an ammonia medium at pH=7, both not digested and digested at 100°C. In addition to the absorption band recorded at the wave number of 1360 cm^{-1} and connected with the presence of a small amount of nitrate anions present in the sample, there is a number of absorption bands with peaks corresponding to the wave numbers of 470, 610, 750, 1060, 3090 and 3297 cm^{-1} characteristic for pure boehmite [9, 10]. These bands are more intense, however, for the sample heated at 100°C in the process of hydrolysis. An analogous pattern of the IR spectra was obtained for the samples hydrolysed in a medium of pH=6.

The presence of boehmite in the products of hydrolysis has been confirmed by the results of X-ray phase analysis shown in Fig. 4. However, the boehmite crystal structure is much more developed in the samples that were heated during the hydrolysis for 264 h at 100°C. The digestion of the aluminium hydroxide gel in the mother liquor at an in-
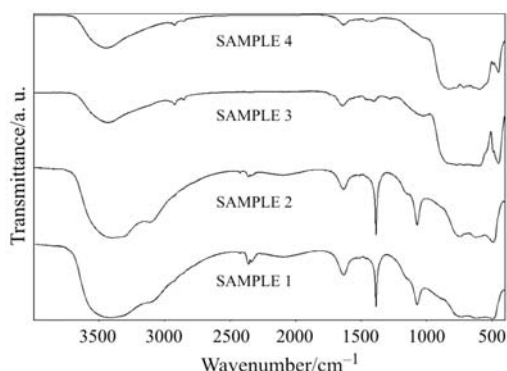
Fig. 3 IR spectra of the product of hydrolysis of hydrous aluminium nitrate in ammonia medium and of the products of its calcination. SAMPLE 1 – product of hydrolysis for pH=7 and t=0 h, SAMPLE 2 – product of hydrolysis for pH=7 and t=264 h, SAMPLE 3 – product of calcination of sample 1 at 1200°C for 2 h and SAMPLE 4 – product of calcination of sample 2 at 1200°C for 2 h
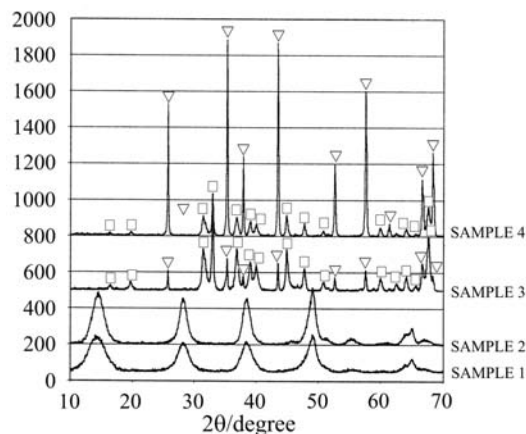
Fig. 4 X-ray diffraction patterns of the product of hydrolysis of hydrous aluminium nitrate in ammonia medium and of the products of its calcination for 2 h. □ – phase θ, ▽ – phase α. SAMPLE 1 – product of hydrolysis for pH=7 and t=0 h, SAMPLE 2 – product of hydrolysis for pH=7 and t=264 h, SAMPLE 3 – product of calcination of sample 2 at 1200°C for 2 h and SAMPLE 4 – product of calcination of sample 1 at 1200°C for 2 h

creased temperature leads to elimination of the water present in the form of hydroxyl groups and, in consequence, to a condensation of the pseudoboehmite layers, growth of primary aluminium hydroxide particles, and formation of a greater number of coarser grains of the precipitate. The recrystallisation processes occurring in the solution during the extended hydrolytic process contribute to a decrease of the number of defects in the crystal structure of boehmite and to higher crystallinity of the samples. The X-ray diffraction patterns of the samples obtained at pH=7 and calcined at 1200°C show that the sample obtained from aluminium hydroxide digested for 264 h at 100°C contains less α

phase, as compared with a sample with a zero time of digestion, which contains mainly the α phase with only a small admixture of the γ phase (data shown in Fig. 4). These facts have also been confirmed by the shape of the IR absorption spectra (Fig. 3). The samples of aluminium hydroxide precipitated at pH=6 contain only the α phase, and the intensity of peaks on the X-ray diffraction pattern is higher in the case of samples not digested, which may be accounted for the prompter formation of that phase. This fact is also confirmed by an abrupt decrease of the specific surface (Table 1), which is probably due to a more rapid sintering of the sample.

Table 1 presents the values of specific surface obtained for the products of aluminium hydrolysis in ammonia medium and for the products of their calcination for 2 h at various temperatures, as calculated from the results of low temperature adsorption of nitrogen.

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

|	Calcination temperature/°C	S_{BET} N$_2$/m^2 g^{-1}	
		Time of digestion in mother liquor/h	
		0	264
pH=6	Starting hydroxide	200	260
	550	210	260
	900	135	248
	1200	10	50
pH=7	Starting hydroxide	210	233
	550	260	233
	900	140	200
	1200	56	95

An analysis of the data collected in Table 1 shows that aluminium oxides obtained from the boehmite formed in the course of hydrolysis and prolonged digestion in the mother liquor at an increased temperature are characterised by the highest thermal stability of the specific surface. For example, aluminium oxide obtained from boehmite formed in the hydrolysis of aluminium nitrate at pH=7, with extended time of reaction at an increased temperature retains its specific surface of about 100 m^2 g^{-1} after 2 h calcinations at 1200°C. The reason lies probably in the small number of defects in the well developed boehmite crystal structure of the precursor. The smaller number of lattice defects in the boehmite may be a reason for the delayed transformation of aluminium oxide into the α form and for the reduced surface diffusion of ions in the course of sintering. The two phenomena: phase transition to the more stable α modification and sintering processes lead, in consequence, to a considerable decrease of specific surface of the aluminium oxides tested with increasing temperature. The sample of aluminium hydroxide precipitated at pH=6, like that obtained at pH=7, digested for 264 h in the mother liquor at 100°C, has a higher thermal stability as compared with that of the zero time of digestion. At the same time, the values of specific surface of aluminium oxide obtained at pH=7 are higher than those of the samples obtained at lower pH values.

Also the values of specific surface determined from benzene adsorption studies by the methods of Kisielev and Dollimore & Hill [11–13] and BET (Table 2, Figs 5 and 6) point to the higher thermal stability of the samples retained in the hydrolytic solution at an increased temperature. The specific surface values determined from the benzene adsorption for aluminium oxide precipitated at pH=7 and not subjected to digestion exhibit higher variations in calcinations, than a similar digested sample. For example, the S_{des} surface determined by the Kisielev method for a sample not digested, changes on calcination from 170.1 to 545.9 m^2 g^{-1}, then the increase is about 25 times as high as that calculated for a sample obtained in the extended hydrolysis. This fact may also be accounted for a change in the porous structure of the samples obtained without digestion in the mother liquor at an increased temperature.

The high values of mesopore surface, as determined by the Dolimore & Hill and Kisielev methods for the samples digested in the mother liquor at 100°C show that this type of pores prevails in the materials under study. On the other hand, no micropores were found in the samples.

Table 2 Parameters of porous structure of the product of aluminium nitrate hydrolysis in ammonia medium and of the products of its calcination for 2 h

| Sample | BET | | | | Kisielev [12] | |
| | S/m^2 g^{-1} | | a_m/mmol g^{-1} | | S_{ads}/m^2 g^{-1} | S_{des}/m^2 g^{-1} |
	planar	vertically				
0.5OH, pH=7, t=0 h	151.1	94.4	0.627		133.6	170.1
0.5OH, pH=7, t=264 h	213.9	133.7	0.888		199.1	296.7
0.5OH, pH=7, t=0 h/550°C	229.9	143.7	0.954		346.7	545.2
0.5OH, pH=7, t=264 h/550°C	213.6	133.5	0.886		262.1	282.9
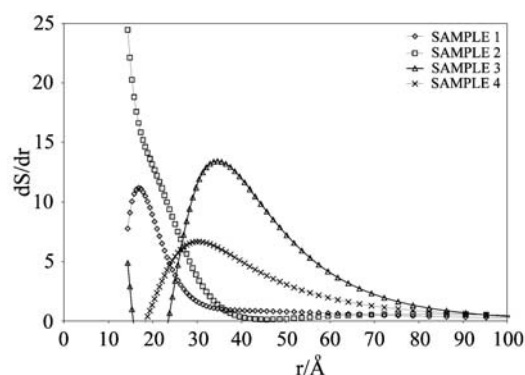
Fig. 5 Pore surface distribution in relation to their effective radius for the product of hydrolysis of aluminium nitrate in ammonia medium and of the products of its calcination. SAMPLE 1 – product of hydrolysis for pH=7 and t=0 h, SAMPLE 2 – product of hydrolysis for pH=7 and t=264 h, SAMPLE 3 – product of calcination of sample 1 at 550°C for 2 h and SAMPLE 4 – product of calcination of sample 2 at 550°C for 2 h
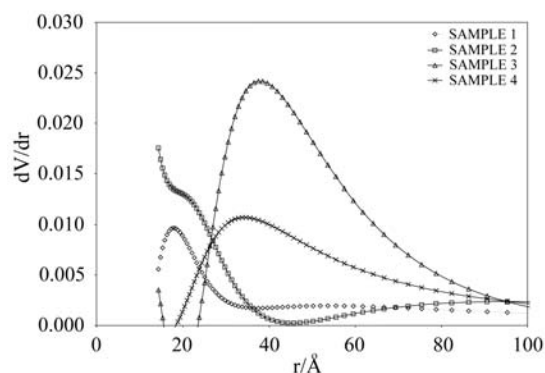
Fig. 6 Pore capacity distribution in relation to their effective radius for the product of hydrolysis of aluminium nitrate in ammonia medium and of the products of its calcination for 2 h. SAMPLE 1 – product of hydrolysis for pH=7 and t=0 h, SAMPLE 2 – product of hydrolysis for pH=7 and t=264 h, SAMPLE 3 – product of calcination of sample 1 at 550°C for 2 h and SAMPLE 4 – product of calcination of sample 2 at 550°C for 2 h

Basing on the distribution of the mesopore surface and volume (Figs 5 and 6), calculated from the adsorption branch of the isotherm basing on the model of cylidrical pores open at both sides, the presence of the pores of similar radius about 18Å was ascertained both in the digested samples and those not digested. However, owing to the lower thermal stability, the calcination of the sample with zero time of digestion resulted in a strong reconstruction and formation of pores of much larger radius ~35Å. No such strong structural changes were observed in the samples digested in the mother liquor at 100°C, which can be considered as a higher resistance to sintering.

Scanning electron microscope photographs (Fig. 7) show a morphological characteristic of digested aluminium oxide obtained after the hydrolysis at pH=7, both in the crude form and after calcinations at 1200°C. The photographs reveal the presence of small changes that suggest a surface sintering of the samples, but the values of specific surface point to their stable internal morphological structure.
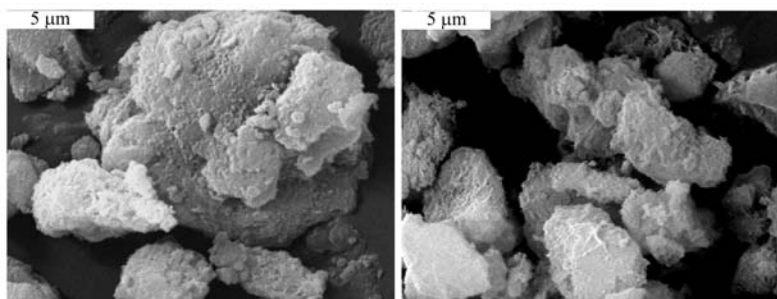
Fig. 7 Microscopic photographs of the product of hydrolysis of hydrous aluminium nitrate in ammonia medium and product of its calcination. 1 – product of hydrolysis for pH=7 and t=264 h, 2 – sample 1 calcined at 1200°C for 2 h

Conclusions

It has been ascertained that the process of aluminium nitrate hydrolysis in ammonia medium at a pH of 6 or 7 leads to formation of boehmite. The degree of crystallinity of this product increases largely for the products of hydrolysis digested for 264 h in the mother liquor at 100°C, as compared with the samples not subjected to the digestion. It has also been found that aluminium oxide obtained by thermal decomposition of the digested samples is characterised by a highly developed specific surface, stable at high temperatures, and amounting to about 100 m^2 g^{-1} after a 2 h calcination at 1200°C.

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