Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 2, 383–393

INFLUENCE OF ALUMINIUM PRECURSOR ON PHYSICO-CHEMICAL PROPERTIES OF ALUMINIUM HYDROXIDES AND OXIDES
Part III. $Al_2(SO_4)_3 \cdot 18H_2O$

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The process of hydrolysis of aqueous aluminium sulfate was carried on in ammonia medium at 100°C and for different time intervals (0, 20, 39 or 59 h). The products thus obtained were calcined at 550, 900 or 1200°C for 2 h with the aim to obtain aluminium oxides. The materials were studied with the following methods: thermal analysis, IR spectroscopy, X-ray diffraction, low-temperature nitrogen adsorption, adsorption–desorption of benzene vapours and scanning electron microscopy.

Freshly precipitated material was an amorphous basic aluminium sulfate which after prolonged refluxing at elevated temperature in a mother liquor underwent a phase transformation into highly crystalline $NH_4Al_{13}(SO_4)_2(OH)_6$ containing tridecameric unit Al_{13}. It was accompanied by a decrease of specific surface area and the formation of a porous structure less accessible for benzene molecules. Regardless of the duration of the hydrolysis process, all products were characterised with poorly developed porous structure and hydrophilic character. Their calcination at the temperature up to 1200°C resulted in the formation of α-Al_2O_3 via transition forms of γ/η- and δ-Al_2O_3. The samples of aluminium oxides obtained after calcination at 550 and 900°C had higher values of specific surface area than starting materials due to processes of dehydroxylation and desulfurization. The process of calcination up to 900°C was reflected in developing of not only porous structure but also hydrophobic character of prepared materials. The S_{BET} values calculated for the oxide samples obtained from aged products of hydrolysis at 1200°C were lower than for the analogous sample prepared without the ageing step. It was concluded that prolonged refluxing at elevated temperature of the products of hydrolysis of aluminium sulfate decreased thermal stability of final aluminium oxides.

Keywords: *metastable aluminium oxides, thermal decomposition, tridecameric Keggin structure*

Introduction

A conventional method of preparing powders of aluminium hydroxides is a process of hydrolysis of aluminium salts carried on in an aqueous solution with the use of $NH_3 \cdot H_2O$, NaOH, KOH, Na_2CO_3, urea, etc. Different aluminium precursors used in the process lead to the formation of products varying from the point of view of their physicochemical properties. A possible reason of this fact is the presence of an anionic counterpart in the medium of precipitation which affects the Al^{3+} coordination, thus influences the polymerisation of Al^{3+} and crystallisation of aluminium hydroxide [1–3]. Anions with a weak affinity towards aluminium, such as Cl^-, ClO_4^- or NO_3^-, are expected to be present mainly in the diffusion layer of aluminium hydroxocomplexes. For this reason, the process of aluminium hydroxide crystallisation proceeds without any disturbances. On contrary, anions with strong complexing ability to Al^{3+}, such as SO_4^{2-}, are known to easily replace water molecules or OH^- in the first coordination layer of aluminium aqua-cation and in this way they disturb the course of polymerisation [1].

Some systematic studies on the influence of co-existing ions in the medium of precipitation of aluminium hydroxide on its physico-chemical properties have been carried on. However, there have been few attempts of finding a relationship between a nature of aluminium precursor and features of aluminium oxides derived from precipitated hydroxide.

The present paper is a fragment of extensive research works concerning the influence of different aluminium salts on the characteristic of aluminium hydroxides and oxides.

Previous works [4, 5] on this subject referred to materials obtained from two aluminium salts $AlCl_3$ and $Al(ClO_4)_3$ containing anions which do not form complexes with aluminium aqua-ions. In both cases, it was observed that the process of hydrolysis resulted in the formation of boehmite whose crystallinity increased after prolonged ageing at elevated temperature. The boehmite samples had high values of S_{BET} determined with the method of low-temperature nitrogen adsorption, good adsorption capacity for benzene vapours and

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1388–6150/$20.00

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developed mesoporous structure. During calcination at temperature up to 1200°C they transformed into α-Al_2O_3 via γ-, δ- and θ-Al_2O_3. It is worth mentioning that the change of an aluminium precursor from chloride to perchlorate, was reflected in an increase of crystallinity of freshly precipitated hydroxide and development of a hydrophobic character. On the basis of the S_{BET} values determined with the method of low-temperature nitrogen adsorption for aluminium hydroxides *vs.* time of ageing, it was found that the process of ageing proceeded faster in the case of materials precipitated from aluminium perchlorate. More advanced ageing process probably resulted in increased thermal stability of obtained aluminium oxides.

This paper describes a similar experiment, nevertheless carried on with the use of aluminium sulfate with the aim to study the effect of an anionic counterpart possessing a strong affinity toward aluminium cation on the properties of precipitated materials and aluminium oxides derived from them.

Experimental

Materials

The products of hydrolysis of hydrous aluminium sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ anal. grade produced by Chemical Company Odczynniki (Lublin), were the main objects of the studies. The hydrolysis process was carried on in ammonia medium as follows.

The substrates (the 0.5 M solution of $Al_2(SO_4)_3$ and 0.75 M solution of $NH_3 \cdot H_2O$) were dosed with a peristaltic pump into a 1000 cm^3 beaker placed in a thermostat. The precipitation was led at 100°C with continuous stirring of reagents. A dosing rate of aluminium sulfate solution was 7 cm^3 min^{-1}, while the pumping rate of $NH_3 \cdot H_2O$ was regulated in such a way to maintain a demanded pH value of 7.

A part of the milky-white colloidal precipitate obtained was filtered off, washed with distilled water, dried at 60°C in a drier and finally 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 20, 39 or 59 h. The heating was stopped for several night hours, during which the mixtures were kept at the temperature of 60°C in a drier. Thus, a total time of keeping them in mother liquors, including night-time spent in a drier at 60°C, was 48, 96 or 192 h, respectively. When the required time was over, the precipitates were filtered off, washed with distilled water, dried at 60°C in a drier and powdered in a mortar. The obtained in such a way powder samples were used for further studies.

The thermal decomposition of the products of hydrolysis of hydrous aluminium sulfate was carried on both under isothermal conditions and under dynamic conditions i.e. under permanent temperature increase.

The partial thermal dissociation of the products of hydrolysis was carried on by their heating in a high-temperature flow reactor (Czylok, Poland), leading the calcination process at 550°C for 2 h in air atmosphere. Aluminium oxides obtained at 550°C were subjected to a further calcination at 900 or 1200°C.

TG, DTA and DTG curves, IR spectra and low-temperature nitrogen adsorption were conducted for the starting product of hydrolysis, as well as for the products of their thermal decomposition under isothermal conditions. For the hydrolysis products, both not subjected to the ageing process and aged for the longest time (59 h), as well as for aluminium oxides derived from them, additional investigations of X-ray powder diffraction and adsorption–desorption of benzene vapours were carried on. The samples of the products of hydrolysis aged for 0 or 59 h and aluminium oxides prepared through their heating at 1200°C were additionally studied by means of scanning electron microscopy.

Methods

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

IR spectra were recorded with a FTIR Matson Spectrophotometer in a wavenumber range of 4000–400 cm^{-1}. Powders were dispersed in KBr matrix and pressed into thin, transparent pallets.

The phase composition of the samples was determined by the X-ray diffraction method. The XRD patterns were recorded in an instrument using a Cu cathode with CuK_α radiation and with a Ni filter. The measurements were performed in steps of 0.01° with pulse counting in 3 s intervals.

The degree of specific surface development was studied by volumetric determination of low-temperature nitrogen adsorption and by the adsorption and desorption of benzene vapours. On the basis of obtained adsorption–desorption isotherms, by means of the programme [6], the following parameters of the porous structure were calculated: specific surface according to BET method (S_{BET}), the surface of mesopores (S_{MEZ}) from the adsorption and desorption part of the isotherms using Kisielev method, and the distribution of mesopore surface by Dollimore–Hill method.

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

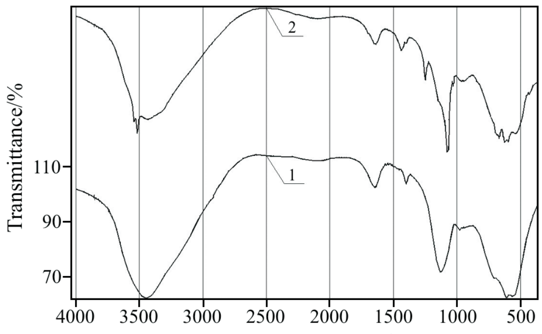

Fig. 1a IR spectra of the products of hydrolysis aged for 0 or 59 h; 1 – PH\0 h, 2 – PH\59 h

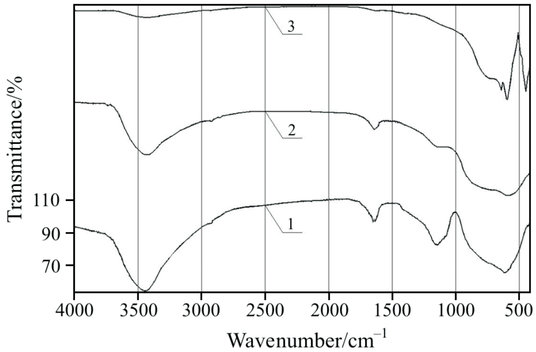

Fig. 1b IR spectra of the products of calcination of the sample PH\0 h at 550, 900 and 1200°C for 2 h;
1 – PH\0 h\550°C, 2 – PH\0 h\550°C\900°C,
3 – PH\0 h\550°C\1200°C

Results and discussion

FTIR spectroscopy

Figure 1a presents the IR spectra recorded for the products of hydrolysis of hydrous aluminium sulfate in ammonia medium aged in the mother liquor for 0 or 59 h. Figure 1b shows the IR spectra of aluminium oxides obtained through the calcination at 550, 900 and 1200°C for 2 h of the product of hydrolysis not subjected to ageing.

The analysis of the IR spectrum of the product of hydrolysis of aluminium sulfate prepared without the ageing step, made on the basis of literature data [7–10] allows stating that obtained material was basis aluminium sulfate (Fig. 1a).

In the spectra of this sample, there is a broad band in the wavenumber range of 3700–2900 cm^{-1} ascribed to stretching vibrations of OH groups structurally bound, as well as from molecular water physically adsorbed [7–10]. A quite intensive band characteristic to the H–O–H bending mode is visible at 1640 cm^{-1}. Very strong vibrations reflected in the sharp peak centered at 1122 cm^{-1} is due to sulfate absorption [7–10]. A weak band at ~700 cm^{-1} probably results from combined absorptions of Al–O stretching vibrations and Al–OH rocking librational mode of molecular water [9]. The band centered at 608 cm^{-1} reflects the combined absorptions of sulfate groups, Al–O stretching vibrations and Al–OH wagging librational mode of molecular water [9, 10].

IR spectrum of the product of hydrolysis of aluminium sulfate aged in the mother liquor for 20 h is very similar to the one described above. However, lengthening of the ageing time over 39 h is reflected in the change of the character of IR spectra (Fig. 1b).

In the spectra of the samples aged for 39 or 59 h, there is still the broad band in the wave number range of 3700–2900 cm^{-1} due to stretching vibrations of OH groups structurally bound, as well as from physisorbed water. Within this band, two other ones are identified. One of them centered slightly over 3500 cm^{-1} is ascribed to the stretching vibrations of Al–OH in the Al_{13} Keggin structure. The second one ~3250 cm^{-1} is due to the stretching vibrations of water molecules combined in the Al_{13} cation [8, 11]. The intensity of these bands becomes stronger together with the lengthening of the ageing time. It may prove that keeping the products of hydrolysis of aluminium sulfate in mother liquors at elevated temperature favoured the formation of a tridecameric structure.

In the IR spectra recorded for the sample aged for 39 or 59 h there is also the peak centered at 1640 cm^{-1} associated with the absorption of OH groups from molecular water [8, 11]. The band visible at ~1090 cm^{-1} is due to hydroxyl groups combined to the Keggin structure. In the spectrum of the sample aged for 39 h, it is of a quite low intensity and it probably overlaps the band ascribed to the stretching vibrations of sulfate groups (1135 cm^{-1} [8, 11]). Prolonged keeping of the precipitate in the mother liquor up to 59 h resulted in splitting these bands and making them stronger.

Except above mentioned bands, in the spectra of both materials, there is a broad band at about 980 cm^{-1} of a low intensity that may be attributed both to the deformation vibrations of Al–OH in Al_{13} [11] and to sulfate absorption [8].

A comparative analysis of the IR spectra of the samples aged for 39 or 59 h with the spectra recorded for the materials kept in mother liquors for 0 or 20 h reveals the change of the character of the band placed between 600 and 900 cm^{-1}. In the spectra of the products of hydrolysis subjected to ageing for 39 or 59 h, this band is split into several peaks, including 715, 610 and 566 cm^{-1}, confirming the presence of sulfate in analysed samples [11]. It is known that the tridecamer ($AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$) contains a central tetrahedral AlO_4 unit in a cage of twelve aluminium octahedrals [8]. The vibrations of Al–O both from tetrahedrons and octahedrons reveal in the

IR spectra as peaks localised within the wave number range of 600–900 cm^{-1} [12]. According to the opinion of researchers [13] the Al–O vibrations are confirmed by the peaks centered at 494, 549, 606, 648, 706, 750 and 779 cm^{-1}. Thus, it is supposed that in the case of analysed spectra, they overlap the peaks associated with absorption of SO_4^{2-}.

The character of IR spectra recorded for the samples obtained through the calcination process conducted at 550, 900 or 1200°C for 2 h for the products of hydrolysis of hydrous aluminium sulfate subjected to ageing for different time intervals (20, 39, 59 h) is very similar to the character of the spectra of the materials prepared without the ageing step.

The broad band within the wave number range of 3700–2900 cm^{-1} ascribed to the stretching vibrations of OH groups, as well as the peak at 1640 cm^{-1} attributed to the H–O–H bending mode of molecular water become weaker in the spectra of the samples calcined at 550°C (see a representative spectrum in the Fig. 1b). The peak centered at ~1225 cm^{-1} is due to the absorption of sulfate groups. The presence of sulfate is probably reflected in peaks which overlap the broad band at 550–850 cm^{-1}. The character of this band may confirm the formation of γ [9] or η-Al_2O_3 [7, 8, 10] in which Al^{3+} is partly in tetrahedral (AlO_4) and octahedral (AlO_6) coordination. However, an accurate distinction between these two crystallographic forms of aluminium oxide is very difficult because of the significant similarity of the character of their IR spectra. Moreover, opinions of many researchers concerning the aspect of the formation of γ- or η-Al_2O_3 as the first crystallographic forms of aluminas obtained during a thermal decomposition of basic aluminium sulfate are contradictory. For example, Davey *et al.* [14] state that η-Al_2O_3 is the first alumina that appears from basic aluminium sulfate, however it is formed over 800°C. Authors of papers [7, 10] obtained η phase at 900°C. The opinion on the formation of η-Al_2O_3 as the first crystallographic form is also shared by researchers [15], but they do not specify the temperature of the phase transition. Sacks *et al.* [9] carrying on the process of thermal decomposition of basic aluminium sulfate, identified γ-Al_2O_3 at 800°C that was thermodynamically stable even up to 900°C. After exceeding 1050°C it partly underwent a phase transition directly into α-Al_2O_3.

An increase of calcination temperature up to 900°C results in diminishing the peaks at 3450 and 1640 cm^{-1} characteristic to the stretching vibrations of OH groups and the H–O–H bending mode of molecular water (Fig. 1b). The band centered at 1225 cm^{-1} associated with sulfate disappears, which points at a complete process of desulfurization. Simultaneously, the band in the range of 550–850 cm^{-1} becomes a bit broader. A comparison of the character of this band with literature data [12] allows thinking that analysed materials were δ-Al_2O_3. This is against the opinion of authors [9, 14–16], according to which low-temperature phases of aluminium oxide (γ and η) obtained through thermal decomposition of products of hydrolysis of aluminium sulfate, undergo direct transition into corundum.

In the IR spectra of the samples calcined at 1200°C, the band in the range of 3700–2900 cm^{-1} attributed to the stretching vibrations of OH groups becomes weaker (Fig. 1b). Moreover, the character of the broad band at 750–900 cm^{-1} corresponding to Al–O modes in the lattice also changes. In the IR spectra, new peaks at 465, 610 and 645 cm^{-1} appear which are due to vibrations of ‘condensed’ AlO_6 octahedron in α-Al_2O_3. There are no traces of peaks corresponding to θ-Al_2O_3. Similar results were described in [17]. According to authors’ opinion, a precipitate obtained from $Al_2(SO_4)_3$ with the use of $NH_3{\cdot}H_2O$ transforms into corundum either without passing through the θ-phase or the lifetime of this phase is brief in comparison with materials prepared from $AlCl_3$ or $Al(NO_3)_3$.

The comparison of the IR spectra recorded for the samples derived from precipitates aged for different time intervals (20, 39 or 59 h) with the spectrum of aluminium oxide obtained from the product of hydrolysis not subjected to ageing shows that the intensity of the peaks characteristic to α-Al_2O_3 is stronger for the former samples. Thus, it may be supposed that in the case of the precipitates prepared from aluminium sulfate, on the contrary to materials obtained from aluminium chloride [4] and perchlorate [5], the process of ageing in the mother liquor at elevated temperature favoured a rapid transformation into α phase. Moreover, from the products of the hydrolysis of these three aluminium salts, the materials obtained from sulfate underwent the fastest transition into corundum, which might be caused by some quantities of basic aluminium salts contained in these materials facilitating the process of nucleation of α-Al_2O_3 at high temperatures.

A character change of the IR spectra recorded for all products of the hydrolysis, as well as for the products of their calcination at 550, 900 or 1200°C confirms the following sequence of phase transitions that accompanied the heating of the samples:

$$\text{PH}\rightarrow\gamma \text{ or } \eta\text{-}Al_2O_3\rightarrow\delta\text{-}Al_2O_3\rightarrow\alpha\text{-}Al_2O_3$$

where PH stands for ‘product of hydrolysis’.

X-ray powder diffraction

Figure 2a represents the XRD patterns recorded for the products of hydrolysis of aluminium sulfate, both

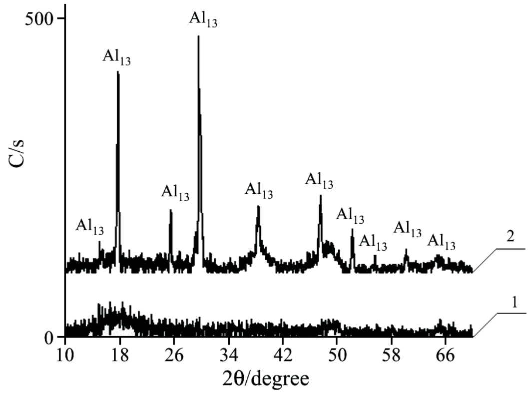

Fig. 2a XRD patterns of the products of hydrolysis aged for 0 or 59 h; 1 – PH\0 h, 2 – PH\59 h

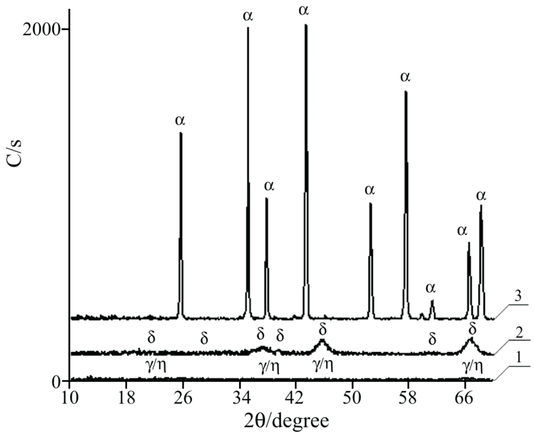

Fig. 2b XRD patterns of the products of calcination of the sample PH\0 h at 550, 900 or 1200°C for 2 h; 1 – PH\0 h\550°C, 2 – PH\0 h\550°C\900°C, 3 – PH\0 h\550°C\1200°C

not subjected to the ageing and aged for 59 h, Fig. 2b shows the X-ray photographs of the samples obtained through a calcination of the product of hydrolysis prepared without the ageing step carried on for 2 h at 550, 900 or 1200°C.

On the basis of XRD analysis results, it may be stated that the precipitate prepared through the hydrolysis of hydrous aluminium sulfate in ammonia medium not subjected to ageing in the mother liquor was amorphous in a significant degree (Fig. 2a). A similar result was obtained by researchers [18] who realised the process of hydrolysis with the use of urea, by Pradhan *et al.* [10] who made a resembling experiment using hydrazine, as well as by Bhattacharya *et al.* [7] who conducted the process of heterogeneous precipitation from $Al_2(SO_4)_3$ with $NH_3{\cdot}H_2O$. Some researchers [2, 3, 19] are of the opinion that the presence of SO_4^{2-} ions in a medium in which a precipitation of aluminium hydroxide is carried on, favours the formation of basic aluminium salts of varying composition e.g. $Al_4(SO_4)(OH)_{10}$. Because of a very strong complexing ability of sulfate anion in relation to Al^{3+}, it easily replaces water molecules in a coordination sphere of aluminium cation forming not only outer-, but also inner-sphere complexes which, in turn, undergo transformation into neutral species of a composition given above. It retards or entirely terminates a polymerization processes leading to the growth of polymeric aluminium cation and to the crystallization into aluminium hydroxide. Basic aluminium salts that are formed in the presence of anions such as SO_4^{2-}, break intramicellar bonds in a structure resulting in amorphous precipitate form [20]. Low-crystallinity of the product of hydrolysis of aluminium sulfate is also favoured by strong affinity of SO_4^{2-} ions in relation to Al^{3+}, which makes all mentioned processes proceed very quickly [21].

XRD analysis evidencs a significant influence of the process of ageing on crystallinity and phase composition of products obtained during hydrolysis of aluminium sulfate. The amorphous freshly precipitated material identified with the use of infrared spectroscopy method as basic aluminium sulfate, after prolonged keeping in the mother liquor at elevated temperature underwent a phase transformation into highly-crystalline $NH_4Al_{13}(SO_4)_2(OH)_6$ containing tridecameric unit Al_{13} $(AlO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+})$, known as the Keggin structure (Fig. 2a).

XRD patterns obtained for the samples prepared without the ageing step and calcined at 550, 900 or 1200°C are very close to analogous ones recorded for the samples derived from materials aged for different time intervals, even though aged products of hydrolysis differed from the material not subjected to this process both in a structure and degree of crystallinity.

The character change of the patterns resulted from the calcination of the samples at higher and higher temperature (550, 900 or 1200°C) confirms the sequence of phase transitions into thermodynamically stable corundum suggested on the basis of IR studies.

All materials heated at 550°C were highly amorphous. In XRD spectra of these samples there are weakly visible diffraction peaks that may be attributed to γ- or η-Al_2O_3 (Fig. 2b). However, it should be underlined that the identification of these phases with the XRD method is very difficult on account of subtle differences between their XRD patterns. According to several studies, including [9, 10], the two phases may be distinguished by a diffraction peak at $d{\approx}0.46$ nm and the relative intensity of diffraction peak for (400) and (440) reflections. Because of the fact that in the case of recorded X-ray photographs, diffraction peaks are very broad and of low intensity, a proper differentiation of γ and η forms is impossible.

An increase of calcination temperature up to 900°C resulted in higher crystallinity of obtained materials. In the XRD patterns of these samples some peaks appear that perhaps evidence the formation of δ-Al_2O_3 (Fig. 2b). However, they are still broad, which is typical for low-temperature transition aluminium oxides [22].

A character of the XRD spectra of products of calcination at 1200°C proves that the materials were α-Al_2O_3. In the patterns of these samples there are no traces of peaks that might be attributed to transition aluminas. This is consistent with the results of IR spectroscopy. A comparative analysis of XRD patterns of aluminium oxides obtained at 1200°C, shows that peaks characteristic of α-Al_2O_3 are of a bit stronger intensity in the case of samples derived from products of hydrolysis subjected to the ageing process in comparison with the material prepared in the analogous way but without the ageing step. It confirms the inference made on the basis of the results of infrared spectroscopy that in the instance of products of hydrolysis carried on for aluminium sulfate, prolonged refluxing at elevated temperature favoured faster formation of a corundum structure. It is contrary to the materials prepared from aluminium chloride and perchlorate, in case of which the ageing process resulted in a delayed formation of α-Al_2O_3 [4, 5].

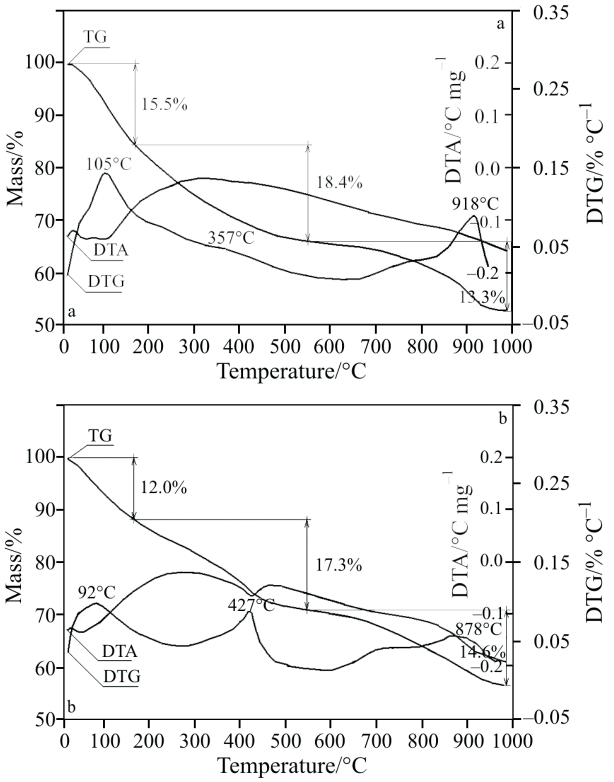

Fig. 3 TG, DTG, DTA curves for the products of hydrolysis a – not subjected to ageing and b – hydrolysis aged for 59 h

Thermal analysis

TG, DTG and DTA curves recorded for the products of hydrolysis of aluminium sulfate, both not subjected to the ageing process and aged at 100°C for 59 h, are presented in Figs 3a and b; whereas Table 1 reveals the values of mass loss for each step of thermal decomposition calculated for all products of hydrolysis.

The thermal analysis results show that all materials, regardless of the ageing process and its duration, decomposed in a similar way.

Unlike the products of hydrolysis of aluminium chloride and perchlorate, the materials prepared from sulfate underwent a three-step thermal decomposition (Figs 3a and b).

In the first step, ranging from 20 to 170°C, the samples lost humidity water. Thus, it was accompanied by a mass loss, whose values calculated for particular samples are listed in Table 1. This endothermic effect is reflected as a peak on the DTA curve with an extreme at about 88–105°C.

The second step, corresponding to the temperature range 170–550°C, was accompanied by a further mass loss (Table 1). For this temperature range, there is one endothermic effect with an extreme centered at about 357–427°C. It is noticeable that the temperature of this process increased together with an increase of sample crystallinity. This decomposition step conformed to the processes of dehydration and dehydroxylation. Some literature data [8, 23, 24] suggest that thermal decomposition carried on at the temperature extending ~500°C for the products obtained during the hydrolysis of aluminium sulfate should lead to a total loss of water. For example, basic aluminium

Table 1 The mass loss values for individual steps of thermal decomposition calculated for the products of hydrolysis aged for different time intervals

Sample	Temperature range/°C							
	20–170		170–550		550–1000		20–1000	
	Mass loss/%	$Al_2O_3 \cdot nH_2O$	Mass loss/%	$Al_2O_3 \cdot nH_2O$	Mass loss/%	$Al_2O_3 \cdot nSO_3$	$Al_2O_3 \cdot nH_2O$	$Al_2O_3 \cdot nSO_3$
PH/0 h	15.5	1.66	18.4	1.98	13.3	0.32	3.64	0.32
PH/20 h	13.0	1.34	18.5	1.90	13.4	0.31	3.24	0.31
PH/39 h	11.1	1.10	18.5	1.85	13.8	0.31	2.95	0.31
PH/59 h	12.0	1.21	17.3	1.75	14.6	0.33	2.96	0.33

sulfate prepared by Kara and Sahin [23] underwent nearly entire dehydration up to ~400°C, while dehydration and dehydroxylation of the material containing the Keggin structure and described with the formula $Na_{0.1}[Al_{13}O_4(OH)_{24}(H_2O)_{12}](SO_4)_{3.55}\cdot xH_2O$, according to [8] ended below 360°C. Wang and Muhammed [24] observed a complete dehydration and dehydroxylation of basic aluminium sulfate with the tridecameric structure at the temperature not exceeding 350°C. However, Sacks *et al*. [8] mentioned that the loss of hydroxyl groups may take place even up to 700°C.

A total mass loss of the first and second step of thermal decomposition is 33.9, 31.5, 29.6 and 29.3% for the products of hydrolysis, not aged and subjected to ageing for different time intervals (20, 39 or 59 h), respectively. As it may be seen, the values are lower for aged samples in comparison with the value for freshly precipitated material, which betokens smaller amount of water physically and chemically bound (Table 1). Thus, it suggests an inference that the prolonged refluxing at elevated temperature favoured removal of water, both molecular and in the form of hydroxyl groups. Similar result was described in the paper [25].

The values of mass loss for the second step of thermal decomposition, associated with removal of structural water, are higher than the values obtained for the samples prepared from aluminium chloride or perchlorate [4, 5]. It may prove the highest degree of hydration of the products of hydrolysis of aluminium sulfate. As it was mentioned, the sulfate ion forms stable complexes with hydrate aluminium cation by replacing water molecules in its coordination sphere. It makes the processes of hydroxyl group condensation and water removal quite difficult.

The third step of decomposition (550–1000°C) was accompanied by a mass loss ranging from 13.3 to 14.6% (Table 1). It was associated with a desulfurization of the hydrolysis products i.e. removal of SO_4^{2-} groups. This endothermic effect is reflected as a peak on the DTA curve with an extreme at about 862–918°C.

Low-temperature nitrogen adsorption

Table 2 presents the values of specific surface determined with the method of low-temperature nitrogen adsorption for the samples of products of hydrolysis, both not aged and aged for different time intervals (20, 39 or 59 h), as well as the samples obtained through their calcination at 550, 900 or 1200°C for 2 h. Figure 4 shows changes of the values of specific surface area as a function of calcination temperature for all products of hydrolysis.

An analysis of the data collected in Table 2 shows that precipitated materials were characterised by low values of specific surface area (5–19 $m^2\ g^{-1}$) – Table 2. It was probably caused by a very strong affinity of SO_4^{2-} anion to aluminium hydroxocomplexes, which retarded their growth by means of polymerisation and polycondensation usually leading to the formation of a highly porous structure. All materials subjected to ageing had lower values of specific surface in comparison with the respective sample prepared without the ageing step. Keeping a freshly precipitated product in the mother liquor up to 39 h resulted in lowering the S_{BET} value. However, lengthening the ageing time to 59 h caused a slight increase of specific surface area. Sulfate ions can be considered to act as a chemical 'glue'

Table 2 Porous structure parameters for selected samples determined by low-temperature nitrogen adsorption and adsorption–desorption of benzene vapours

Sample	Specific surface (nitrogen)	Specific surface (benzene)		Surface of mesopores (Kisielev method)	
		$S_{BET\ (vertical)}$/ $m^2\ g^{-1}$	$S_{BET\ (planar)}$/ $m^2\ g^{-1}$	$S_{MEZ\ (adsorption)}$/ $m^2\ g^{-1}$	$S_{MEZ\ (desorption)}$/ $m^2\ g^{-1}$
PH/0 h	19	43	27	24	50
PH/0 h/550°C	42	48	30	25	43
PH/0 h/550°C/900°C	117	46	29	47	64
PH/0 h/550°C/1200°C	17	10	6	*	*
PH/20 h	8	–	–	–	–
PH/20 h/550°C	40	–	–	–	–
PH/20 h/550°C/900°C	115	–	–	–	–
PH/20 h/550°C/1200°C	9	–	–	–	–
PH/39 h	5	–	–	–	–
PH/39 h/550°C	40	–	–	–	–
PH/39 h/550°C/900°C	97	–	–	–	–
PH/39 h/550°C/1200°C	10	–	–	–	–
PH/59 h	10	23	14	28	62
PH/59 h/550°C	79	69	43	66	146
PH/59 h/550°C/900°C	88	49	31	76	112
PH/59 h/550°C/1200°C	10	7	4	*	*

*lack of hysteresis loop

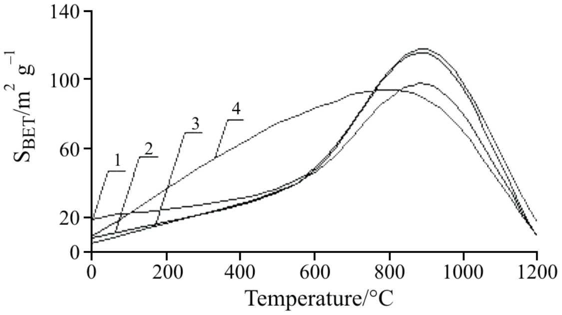

Fig. 4 The specific surface area as a function of calcination temperature for the products of hydrolysis aged for different time intervals; 1 – PH\0 h, 2 – PH\20 h, 3 – PH\39 h, 4 – PH\59 h

affecting, hindering or suppressing dissolution [25]. In their presence, a precipitate may undergo only structural rearrangement. Thus, the changes of the S_{BET} values reflected a transformation of precipitate structure leading to the formation of $NH_4Al_{13}(SO_4)_2(OH)_6$.

Calcination at 550 or 900°C of all hydrolysis products resulted in developing of specific surface area (Table 2 and Fig. 4). That was contrary to the materials derived form aluminium chloride and perchlorate [4, 5]. Researchers [8, 9] are of the opinion that the extension of specific surface area accompanying a calcination process in terms of increasing temperature is usually connected with the decomposition of a precursor material and the current formation of internal porosity. In the case of samples heated at 550°C, pores formation was primarily associated with dehydration and dehydroxylation. An increase of the calcination temperature up to 900°C additionally resulted in the process of desulfurization. This was the reason of higher S_{BET} values for the samples obtained at 900°C in comparison to materials calcined at 550°C.

Subsequent decrease of specific surface development (9–17 m^2 g^{-1}), in the case of aluminium oxides prepared at 1200°C (α-Al_2O_3 as it was proved by means of IR and XRD methods), indicated pore closure and/or pore coarsening (i.e. sintering processes). The analysis of data collected in Table 2 allows noticing that the values of specific surface area determined from low-temperature nitrogen adsorption for the samples prepared taking the ageing process into account were generally lower than the respective value for the analogous material obtained without the ageing step. Thus, it may be suggested that prolonged refluxing of the products of hydrolysis of aluminium sulfate in mother liquors at elevated temperature did not lead to improving their thermal stability, but on the contrary, favoured their faster transformation into corundum. This is consistent with results of IR and XRD analysis.

Adsorption and desorption of benzene vapours

The exemplary adsorption and desorption isotherms of benzene vapours obtained for the product of hydrolysis not subjected to the process of ageing, as well as for the oxides derived from this sample, are shown in Fig. 5. Figures 6a and b present the distribution of mesopore surface as a function of effective radii determined by the Dollimore–Hill's method with an assumption of the model of cylindrical pores, open from both sides, for quartz as the adsorption layer, obtained for the products of hydrolysis (not aged and aged for 59 h) and the samples of oxides derived from them. The parameters of the porous structure of these materials are revealed in Table 2.

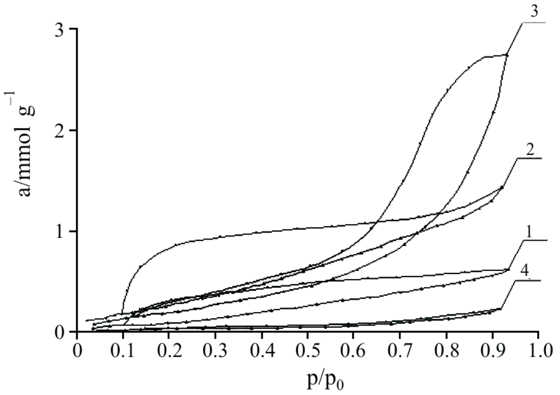

Fig. 5 The adsorption–desorption isotherms of benzene vapours for the sample PH\0 h and products of its calcination at 550, 900 or 1200°C for 2 h; 1 – PH\0 h, 2 – PH\0 h\550°C, 3 – PH\0 h\550°C\900°C, 4 – PH\0 h\550°C\1200°C

The shape of isotherms obtained for both products of hydrolysis for all the samples obtained through the calcination at 550 or 900°C may be classified according to IUPAC nomenclature as the H3 type [26]. For the materials of this kind, a hysteresis loop is qualified by capillary condensation between two layers, as a consequence of which bottle shape pores predominate in these samples. The exceptions are the samples of aluminium oxides heated at 1200°C, in case of which the isotherms become flattened and narrowed, and the hysteresis loops disappear. It is the evidence of low adsorption capacity of these samples.

The values of specific surface presented in Table 2, show that both hydrolysis products had poor adsorption capacity for benzene vapours, which is evidenced by low values of S_{BET} (Table 2) and down placed hysteresis loops (exemplary Fig. 5). The S_{BET} values, calculated supposing planar orientation of benzene molecules in adsorption monolayer, are 43 and 23 m^2 g^{-1} for the starting product of hydrolysis and the material aged for 59 h, respectively. The

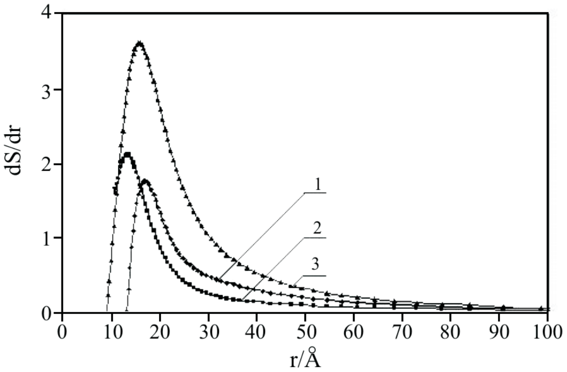

Fig. 6a The distribution of mesopore surface area as a function of the effective radii for the sample PH\0 h and products of its calcination at 550 or 900°C for 2 h;
1 – PH\0 h, 2 – PH\0 h\550°C, 3 – PH\0 h\550°C\900°C

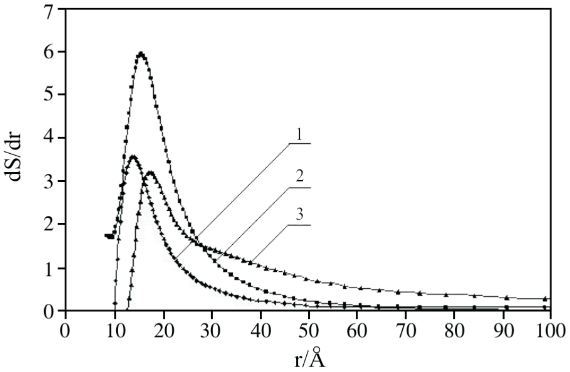

Fig. 6b The distribution of mesopore surface area as a function of the effective radii for the samples PH\59 h and products of its calcination at 550 or 900°C for 2 h;
1 – PH\59 h, 2 – PH\59 h\550°C,
3 – PH\59 h\550°C\900°C

character of changes of S_{BET} values determined with the 'benzene' method arising from keeping the hydrolysis product in the mother liquor at elevated temperature is consistent with the changes of S_{BET} values obtained with the 'nitrogen' method (compare data in Table 2). Lower values for the hydrolysis product aged for 59 h in comparison with the sample not subjected to ageing, perhaps resulted from structural rearrangement leading to the formation of the high crystalline material $NH_4Al_{13}(SO_4)_2(OH)_6$ containing a porous structure less accessible for large benzene molecules.

The S_{BET} values for the samples obtained through the calcination at 550 and 900°C of not aged hydrolysis product were very close to the values for the precursor. In this case, the calcination process had a slight effect on the changes of the general porosity, however caused an increase of the surface of mesopores, especially for the oxide prepared at 900°C, which was reflected in increasing values of S_{MEZ} and widening hysteresis loops. As it was suggested, these phenomena were the consequence of the process of desulfurization.

In the case of the hydrolysis product aged for 59 h, during heating at 550°C the dehydroxylation caused a development of porous structure, which was evidenced by increasing of the S_{BET} and S_{MEZ} values. However, rising in temperature up to 900°C contributed to a decrease of porosity, thus, this sample was characterised with the value of S_{BET} determined with the 'benzene' method very close to the value of the analogous sample of aluminium oxide prepared without the ageing step (Table 2).

Aluminium oxides calcined at 1200°C had significantly lower adsorption capacity for benzene vapours, which was confirmed by vanishing or emphatic narrowing of hysteresis loop, the lowest placed adsorption isotherms, and in consequence, low values of specific surface. Within oxides calcined at 1200°C, the sample prepared from the hydrolysis product subjected to prolonged refluxing in the mother liquor at elevated temperature had slightly lower value of S_{BET}, which might prove its poorer thermal stability. This was consistent with the results of both IR and XRD analysis, as well as of low-nitrogen adsorption.

A comparative analysis of nitrogen and benzene adsorption results gives the possibility of estimating the hydrophilic–hydrophobic properties of aluminium hydroxides and oxides [27, 28]. These properties depend on the surface functional groups that may altar the orientation of adsorbed benzene molecules and change the degree of their packing in the adsorption layer. The nitrogen molecule (inert gas) has a small seating surface (0.16 nm^2) as compared with that of benzene molecule (0.25 nm^2 in the vertical orientation and 0.40 nm^2 in the planar orientation). For this reason, if the surface structure is favourable for the planar orientation of benzene molecule, the specific surface $S_{BET\ (planar)}$ should be smaller or equal to the S_{BET} value determined from the adsorption of nitrogen. Excessive values of $S_{BET\ (planar)}$ with respect to the specific surface values determined from nitrogen adsorption may be accounted for the decrease of the seating surface of benzene molecule, which can be a result of the change of its orientation in adsorption layer. The deviation of benzene molecules on the surface of hydroxides and oxides is likely to be caused by surface hydroxyl groups.

Both products of hydrolysis, as well as the sample obtained through calcination at 550°C of not aged material, had higher values of $S_{BET\ (planar)}$ and $S_{BET\ (vertical)}$ than S_{BET} determined from low-temperature of nitrogen adsorption. It proved not only their hydrophilic character, but also a significant compression of an adsorption film. All other sample were characterised with hydrophobic properties. Moreover, much higher values of both $S_{BET\ (planar)}$ and

$S_{BET\ (vertical)}$ than S_{BET} calculated with the 'nitrogen' method also pointed to a significant distance from particular benzene molecules in the adsorption layer and so, to a considerable rarefaction of the adsorption film. It is probable that in the case of these materials, a localised adsorption on unsaturated aluminium cations took place.

Both products of hydrolysis of aluminium sulfate (not aged and aged for 59 h) were characterised with monodispersive distribution of mesopore surface area as a function of effective radii (Figs 6a and b). It can be observed that the pores of radii of about 17 and 14 Å contributed the most to their porosity, respectively. Thus, it was additionally proved that the process of ageing resulted in the structural rearrangement leading to the formation of highly crystalline $NH_4Al_{13}(SO_4)_2(OH)_6$ of a porous structure less accessible for benzene molecules.

The samples obtained at 550 or 900°C were also characterised with monodispersive distribution of mesopore surface area as a function of effective radii, with the exception of aluminium oxide prepared at 900°C from the hydrolysis product aged for 59 h, in the case of which a slight bimodal nature of the curve could be noticed. The calcination process carried on at 550 or 900°C for the product of hydrolysis not subjected to ageing caused the formation of smaller pores, contrary to the samples derived from aged hydrolysis product, in the case of which pores of radii bigger than in their precursor predominated (Figs 6a and b). Generally, all aluminium oxides prepared at 550 or 900°C had a similar porous structure of the highest contribution of pores with radii within 13–20 Å.

Scanning electron microscopy

Figures 7a and b show exemplary microscopic photographs of the product of hydrolysis not subjected to ageing and of the aluminium oxide obtained by its heating at 1200°C.

All materials precipitated from aluminium sulfate were hard and compact masses difficult to grind. While breaking down, they cracked forming fragments of different size and of distinct edges and shapes visible with the magnification of ×500 (the exemplary Fig. 7a). The representative photo taken with the magnification of ×10000 shows that they were composed with closely adhering particles of nearly spherical shape and size ~1 μm which formed agglomerates differing in size. Such a structure resulted in poorly developed porosity. The formation of round particles during hydrolysis of aluminium sulfate was also documented in papers [3, 9, 18, 22, 23, 29]. The morphology of the hydrolysis products remained unchanged while their keeping in mother liquors at elevated temperature. It is consistent with observations of researchers [25]. According to their opinion, the transformation of amorphous material precipitated from $Al_2(SO_4)_3$ into highly crystalline product taking place during prolonged refluxing is a phenomenon occurring inside particular particles.

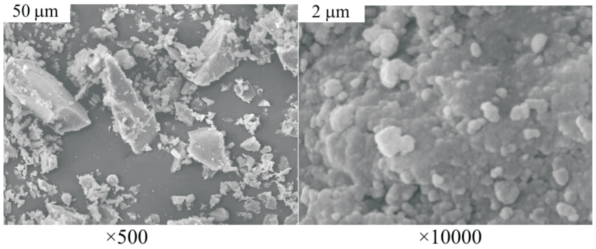

Fig. 7a SEM photographs for the product of hydrolysis not subjected to ageing

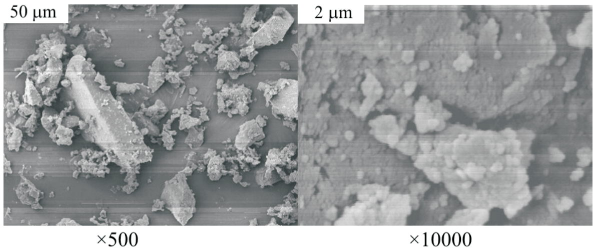

Fig. 7b SEM photographs for the product of calcinations at 1200°C for 2 h of the sample PH\0 h

The results of SEM analysis do not point to an increase of particles of materials aged in mother liquors in comparison with particles of the hydrolysis product subjected to ageing. As it was suggested, anions such as SO_4^{2-}, are known to take part in a specific adsorption to particle surface hindering the course of the ageing process. Thus, the precipitate may only undergo structural rearrangement that retards the subsequent ageing step leading to an increase in particle size.

Calcination at 1200°C carried on for both products of hydrolysis did not result in considerable changes of morphology (exemplary Fig. 7b). The samples of obtained aluminas were still consisted of spherical particles. However, heating at 1200°C was reflected in sintering and coarsening of material particles which certainly caused the decrease of specific surface area.

Conclusions

- The hydrolysis of hydrous aluminium sulfate in ammonia medium results in the formation of amorphous basic aluminium sulfate.
- Prolonged refluxing of freshly precipitated product leads to a phase transformation into highly-crystalline $NH_4Al_{13}(SO_4)_2(OH)_6$ containing tridecameric unit Al_{13}, which is accompanied by a decrease of

specific surface area and the formation of a porous structure less accessible for benzene molecules.

- All products of hydrolysis, both not subjected to ageing and aged for different time intervals (20, 39 or 59 h), during calcination at the temperature up to 1200°C become transformed to α-Al_2O_3 via γ/η- and δ-Al_2O_3.
- An increase of calcination temperature up to 900°C results in developing of a porous structure of obtained oxides due to processes of dehydroxylation and desulfurization.
- The process of ageing at elevated temperature of the products of precipitation decreases thermal stability of aluminium oxides.

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Received: July 25, 2006
Accepted: August 10, 2006

DOI: 10.1007/s10973-006-7898-2