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INFLUENCE OF ALUMINIUM PRECURSOR ON PHYSICO-CHEMICAL PROPERTIES OF ALUMINIUM HYDROXIDES AND OXIDES
Part II. $Al(ClO_4)_3·9H_2O$

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Aluminium hydroxide was precipitated during a hydrolysis of aluminium perchlorate in ammonia medium. The materials were studied with the following methods: thermal analysis, IR spectroscopy, X-ray diffraction, low-temperature nitrogen adsorption and adsorption–desorption of benzene vapours.

Freshly precipitated boehmite had a high value of S_{BET}=211 $m^2 g^{-1}$ determined from nitrogen adsorption, good sorption capacity for benzene vapours, developed mesoporous structure and hydrophobic character. After prolonged refluxing at elevated temperature its crystallinity increased which was accompanied by an increase of specific surface determined from nitrogen adsorption up to 262 $m^2 g^{-1}$, decrease of sorption capacity for benzene vapours and stronger hydrophobic character. The calcinations of all boehmites at temperature up to 1200°C resulted in formation of α-Al_2O_3 via transition form of γ-, δ- and θ-Al_2O_3. The samples of aluminium oxides obtained after calcination at 550 and 900°C were characterised with high values of specific surface area of 205–220 and 138–153 $m^2 g^{-1}$, respectively. The S_{BET} values calculated for the oxide samples derived from aged hydroxides and calcined at 1200°C are higher than for the analogous sample prepared without the ageing step. It was concluded that the process of ageing at elevated temperature developed thermal stability of aluminium oxides.

Keywords: *anion, boehmite, metastable aluminium oxides, thermal decomposition*

Introduction

Powders of boehmite/pseudoboehmite play an important role in preparation of catalysts, coatings, alumina and alumina derived materials of desired porosity and mechanical strength. They can be successfully obtained through the precipitation from aqueous solutions of aluminium salts with the use of $NH_3·H_2O$, NaOH, KOH, Na_2CO_3 or urea. During the hydrolysis of aluminium salts, many different monomeric aluminium aquq-ions occur, which subsequently undergo polymerisation/polycondensation processes leading to formation of bigger polynuclear species, in which aluminium is octahedrally and/or tetrahedrally coordinated [1]. According to Trawczynski [2], ions including anions from an aluminium precursor, present in the medium of precipitation affect the Al^{3+} coordination influencing hydrolysis, polymerisation of Al^{3+} and crystallisation of aluminium hydroxide. They may compete with the OH^- ions in coordinating the aluminium cations and block some coordination centers necessary for Al–OH–Al bond formation. The size and structure (steric effect) of coexisting anions are also a matter of consideration as they stabilise or destabilise aluminium complexes. Anions such as SO_4^{2-} or CH_3COO^- are known to easily replace water molecules or OH^- in the first layer of the Al^{3+} coordination and in this way they disturb polymerisation. On the other hand, anions like Cl^- or NO_3^- that show low complexing ability (low affinity to Al^{3+}) are mainly expected to be present in the diffusion layer of the polymeric aluminium cation. In this case, the crystallisation process proceeds without any disturbances.

The effect of the type of aluminium salt used for the precipitation of aluminium hydroxide has arrested some attention of researchers. Prodromou *et al.* [3] investigated the influence of different ions (like Cl^-, NO_3^- and SO_4^{2-}) on the formation of $Al(OH)_3$ polymorphs by promoting stoichiometric reactions between aluminium salts and bases (NaOH, KOH and $NH_3·H_2O$). In all cases, the obtained polymorphs were a mixture of gibbsite, bayerite and nordstrandite or pseudoboehmite with exception of the reaction between KOH and $NH_3·H_2O$ with $Al_2(SO_4)_3$ which produced amorphous gels. The authors explain that in the presence of anions of strong affinity for Al^{3+} (such as SO_4^{2-}) the precipitation occurs rapidly and prevents or at least retards the Al–OH polymers from further hydrolysis and polymerisation into crystal-

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line $Al(OH)_3$. With Cl^- and NO_3^- anions that weakly affect the Al^{3+} cations, the OH–Al polymers continue to hydrolyse and polymerise into larger units. As they do not disturb the process of crystallisation, the products thus obtained were mixtures of crystalline phases of gibbsite, bayerite and nordstrandite or pseudoboehmite. Ramanathan *et al.* [4] made an attempt to prepare boehmite powders by aqueous aluminium-chloride-urea reaction. A gelatinous precipitate initially produced after further refluxing transformed into a granular powder. According to the authors, the formation of boehmite nuclei from an aqueous solution of aluminium salt containing non-complexing anionic counterpart (Cl^-) above 90°C is attributed to the formation of the compact trimer $Al_3(OH)_9(H_2O)_4$ which after a series of structural rearrangements form the characteristic corrugated boehmite sheets. Ramanathan [5] also describes an experiment whose aim was to demonstrate and compare the role of the anionic part of the aluminium salt ($Al_2(SO_4)_3$ or $Al(NO_3)_3$) on capability to form insoluble precursor powders, their crystallisation into boehmite upon prolonged refluxing and characterisation. It was revealed that the reaction with the use of $Al(NO_3)_3$ produced amorphous gel. Due to the poor coordinate bond forming ability of nitrate anion, it did not interfere in the reaction of hydroxide with the aluminium containing polymeric cation and thus did not disturb this cation to grow into bigger charged species via olation and oxolation involving Al–OH–Al bridges. Because of widely spread and weak binding characteristics of the bridges the resultant precipitate (gel) was porous and voluminous. After ageing at a higher pH it crystallised into boehmite particles of 0.3–0.8 μm size and elongated fibrillar morphology. Due to the better coordinating ability of sulphate ion, the reaction between $Al_2(SO_4)_3$ and NH_4OH formed in situ from urea resulted in the direct formation of amorphous powder consisted of agglomerates of spherical species of composition $Al_4(OH)_{10}SO_4$ and of 2–7 μm size. Since they were neutral, they formed strongly bound compact primary particles, which subsequently agglomerated into granular precipitate. Upon refluxing the agglomerates initially formed remained intact and the material underwent crystallisation into boehmite with a little modification of the particle size distribution and morphology. Mishra *et al.* [6] describe an attempt of hydrothermal precipitation of boehmite from different inorganic aluminium salt solutions under similar conditions using urea as the precipitating agent. It was observed that the hydrolysis of $Al_2(SO_4)_3$ started at a lower temperature due to formation of hydroxy sulphates like $Al_4(OH)_{10}(SO_4)$ in comparison to $AlCl_3$ and $Al(NO_3)_3$ solutions. The boehmite produced from $Al_2(SO_4)_3$ had a lower water content, higher surface area and lower tap density than boehmites obtained from other salts. The higher water content of this material was the reason of a higher temperature of its transformation into γ-Al_2O_3 comparing to the samples prepared from chloride or nitrate. The precipitation of a boehmite colloidal dispersion from aluminium chloride and perchlorate solutions was investigated by the authors of [7]. It was stated that different anions greatly affected the particle shape and phase composition. Diffraction pattern of the dispersed phase of sol in the case of chloride showed peaks corresponding to pseudoboehmite, while in the case of perchlorate anion they corresponded to boehmite.

Most literature works concern the influence of the anion of an aluminium salt used in the precipitation of aluminium hydroxide on its physico-chemical characteristic. However, only a few publications discuss the effect of these anions on the properties of oxides derived from precipitated hydroxides.

The presented paper is a fragment of extensive research works concerning the influence of different aluminium precursors on physicochemical properties of aluminium hydroxides and oxides. The previous paper concerning this subject [8] was to evaluate the preparative conditions (pH, dosing rate of aluminium precursor and duration of precipitate digestion) for preparing aluminium oxo-hydroxide, as a material which could, in turn, be used for obtaining a low-temperature transition alumina (γ-Al_2O_3) of enhanced stability at high temperatures. For this purpose, as the precursor of precipitated hydroxides, aluminium chloride was used which is known to possess an anionic counterpart of weak complexing ability. It was observed that the process of its hydrolysis resulted in formation of boehmite whose crystallinity increased after prolonged ageing at elevated temperature. The boehmite samples had high values of S_{BET} determined by the method of low-temperature nitrogen adsorption (220–300 $m^2\ g^{-1}$), good adsorption capacity for benzene vapours, developed mesoporous structure and hydrophilic character. During calcination at the temperature up to 1200°C they transformed into α-Al_2O_3 via γ-, δ- and θ-Al_2O_3. The samples of aluminium oxides derived from aluminium through the calcinations at 550 or 900°C were characterized with high specific surface values equal 214–220 and 118–145 $m^2\ g^{-1}$, respectively.

This paper describes a similar experiment, nevertheless, with the use of aluminium perchlorate, which is suggested to have an anionic part of a slightly stronger affinity to aluminium.

Experimental

Materials

The products of hydrolysis of hydrous aluminium perchlorate $Al(ClO_4)_3{\cdot}9H_2O$ anal. grade produced by Aldrich Chemical Company, were the main objects of the studies. The hydrolysis process was carried out in ammonia medium as follows

The substrates (the 0.5 M solution of $Al(ClO_4)_3$ 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 perchlorate 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 liquor, 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 perchlorate in ammonia medium was carried out 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 out 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.

Methods

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 samples of aluminium hydroxide 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 benzene vapours were conducted.

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 pellets.

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 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 [9], 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 volume and surface by Dollimore–Hill method.

Results and discussion

Thermal analysis

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

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

The analysis of thermoanalytical curves evidences a two-step decomposition of the samples (Figs 1a and b). In the first step ranging from 20 to 170°C, the samples lost humidity water. This endothermic effect is reflected as a peak on the DTA curve with an extremum at about 60°C. It is accompanied by a mass loss, whose values calculated for particular samples are listed in Table 1. The values for all aged hydroxides are lower than this for the sample not subjected to the process of ageing, which points at smaller amount of physically adsorbed water in them.

In the second step, corresponding to the temperature range 170–550°C, the samples lost a further 21.8,

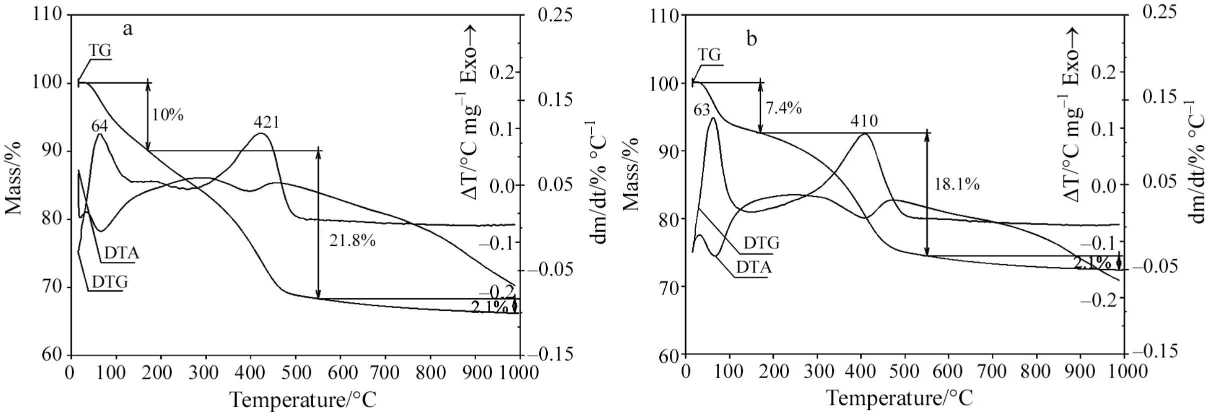

Fig. 1 a – TG, DTG, DTA curves for not aged aluminium hydroxide, b – TG, DTG, DTA curves for aluminium hydroxide aged for 59 h

Table 1 The mass loss values for invidual steps of thermal decomposition calculated for aluminium hydroxide samples both not aged and aged for 20, 39 or 59 h

Sample	Temperature range/°C					
	20–170		170–550		20–1000	
	mass loss/%	$Al_2O_3 \cdot nH_2O$	mass loss/%	$Al_2O_3 \cdot nH_2O$	mass loss/%	$Al_2O_3 \cdot nH_2O$
$Al(OH)_3$\0 h	10.0	0.86	21.8	1.87	33.9	2.91
$Al(OH)_3$\20 h	6.2	0.48	19.1	1.49	27.4	2.14
$Al(OH)_3$\39 h	8.8	0.70	17.8	1.42	28.8	2.29
$Al(OH)_3$\59 h	7.4	0.58	18.1	1.42	27.6	2.16

19.1, 17.8 or 18.1% of their masses, respectively for the hydroxide not subjected to ageing and hydroxides aged for 20, 39 or 59 h (Table 1). These values correspond to the loss of 1.87, 1.49, 1.42 and 1.42 mol of water per 1 mol of Al_2O_3.

Decomposition of boehmite takes place at 410°C [10] according to the reaction:

$$2AlO(OH) \rightarrow \gamma\text{-}Al_2O_3 + H_2O$$

and is accompanied by the loss of 1 particle of water, which corresponds to the theoretical mass loss of 15%. Due to the fact that the values obtained for investigated hydroxides are a bit higher than 15%, one may suppose that the samples were the mixtures of boehmite and pseudoboehmite with the majority of boehmite. These values are lower for all aged hydroxides in comparison with this obtained for the sample prepared without the ageing step. Thus, it may be supposed that hydroxides subjected to the process of ageing for different time intervals contained larger amounts of boehmite. The ageing carried out in mother liquor and at elevated temperature probably favoured the formation of crystal structure of boehmite due to more advanced processes of condensation and dehydration of gels. In consequence, structural defects were removed and the structure became more ordered. The analogous remark was also made in paper [8]. This stage of decomposition is reflected on the DTA curve as an endothermic effect with an extremum ranging from 400 to 420°C.

FTIR spectroscopy

Figure 2a represents the IR spectra recorded for the product of hydrolysis of hydrous aluminium perchlorate in ammonia medium not subjected to the ageing and the products of its calcination for 2 h at 550, 900 or 1200°C; Figure 2b shows the IR spectra of aluminium hydroxide aged for 59 h as well as the products of its calcination for 2 h at different temperatures.

The IR spectra of aluminium hydroxide and the products of its calcination at 550, 900 or 1200°C prepared without the ageing step are similar to the respective IR spectra recorded for analogous samples derived from aluminium hydroxides aged for different time intervals.

In the spectra recorded for all hydroxides, there is a broad band at the wave number range of 3700–2900 cm^{-1} ascribed to stretching vibrations of OH groups in the hydroxide structure, as well as in water physically adsorbed [11]. Within this band, another weaker one is observed at about 3029 cm^{-1} characteristic for stretching vibrations of OH groups in a boehmite structure [12, 13]. A weakly visible band for deformation vibrations of this group is identified at 1155 cm^{-1} [14]. The band at 900 cm^{-1} is due to vibrational modes localised in the surface layer and most likely involving the deformation of surface OH groups in γ-AlOOH [15]. The presence of boehmite in the samples is also confirmed by a very intensive peak ~1070 cm^{-1} [15] ascribed to an Al–O vibrational mode

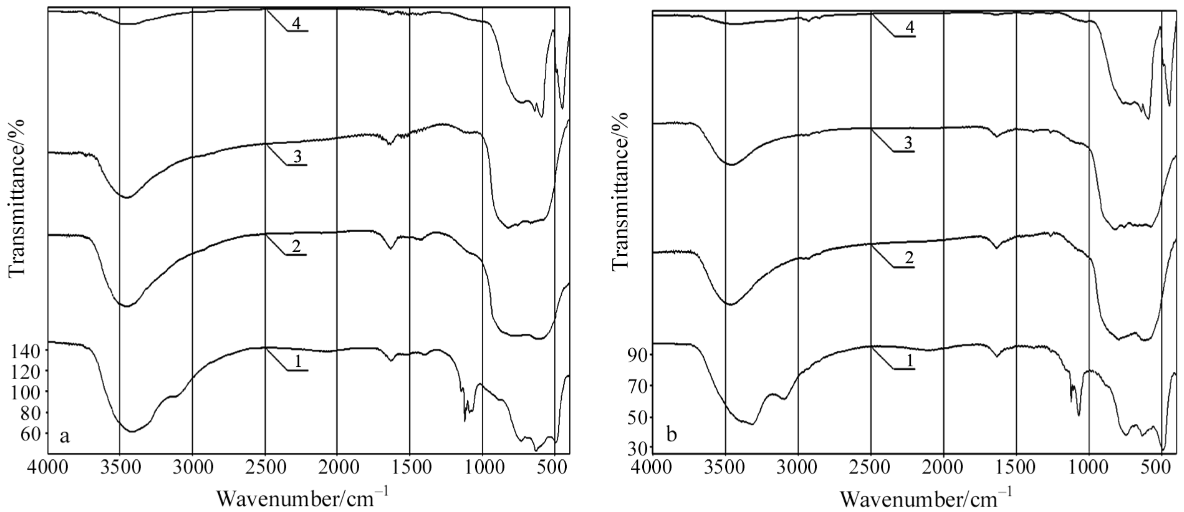

Fig. 2 a – IR spectra of not aged aluminium hydroxide and products of its calcination at 550, 900 or 1200°C. 1 – $Al(OH)_3$\0 h, 2 – Al_2O_3\0 h\550°C, 3 – Al_2O_3\0 h\550°C\900°C, 4 – Al_2O_3\0 h\550°C\1200°C; b – IR spectra of aluminium hydroxide aged for 59 h and products of its calcination at 550, 900 or 1200°C. 1 – $Al(OH)_3$\59 h, 2 – Al_2O_3\59 h\550°C, 3 – Al_2O_3\59 h\550°C\900°C, 4 – Al_2O_3\59 h\550°C\1200°C

[16, 17], as well as a broad band at the wave number range of 480–750 cm^{-1}, consisted of three peaks: 741, 610 and 490 cm^{-1}, attributed to 'condensed' AlO_6 octahedra. The intensity of peaks ascribed to boehmite is stronger for the samples aged in mother liquor at elevated temperature with respect to the sample not subjected to ageing (compare the spectra in Figs 2a and b). It confirms a suggestion made on the basis of the results of thermal analysis and concerning a favourable influence of ageing in mother liquor and at elevated temperature on the formation of boehmite structure. This inference is consistent with a conclusion drawn in the paper [8], as well as with observations of other authors [4, 18, 19]. The formation of boehmite nuclei from aqueous solution of aluminium salt containing a non-complexing anionic counterpart, i.e. a chloride anion investigated by the authors of [8] or an anionic counterpart with a weak complexing ability such as a perchlorate anion, is attributed to the formation of the compact trimer $Al_3(OH)_9(H_2O)_4$, which undergoes a series of structural rearrangements through polymerisation and polycondensation leading to the characteristic corrugated boehmite sheets that are hold together by hydrogen bonding to result in the three-dimensional rigid structure [4]. During a heterogeneous precipitation many of crystallites formed in a reaction medium are entrapped in a gel structure [4, 5]. A prolonged refluxing of the precipitate in mother liquor and at elevated temperature results in dissolution of the gel and further, nearly homogeneous, reprecipitation on liberated boehmite nuclei. The gel structure breaks into fine crystallites that subsequently undergo agglomeration ending with the formation of the granular powder [4].

In the IR spectra of hydroxides aged for different time intervals (20, 39 or 59 h) any distinct differences in the intensity of peaks characteristic for boehmite are visible, which points at slight influence of ageing time on the formation of boehmite structure.

Except above mentioned bands, in the IR spectra of all hydroxides there is a peak at 1640 cm^{-1} ascribed to bending vibrations of OH groups in structural water [20] and another intensive peak at the wave number range of 1050–1200 cm^{-1} [21] that most likely involves residual perchlorate anions.

The process of calcination at 550°C for 2 h for all starting hydroxides led to creation of γ-Al_2O_3. It is confirmed by a strong broad absorption band in the region 750–900 cm^{-1}, due to stretching vibrations of a lattice of interlinked tetrahedra AlO_4 [15]. Within this band, a peak at about 610 cm^{-1} typical for γ-Al_2O_3 [15] is observed. This is in agreement with thermal analysis results. An increase of calcination temperature up to 900°C probably results in the formation of transition oxides such as δ or θ of higher crystalline order. This is reflected in the character change of the band at 750–900 cm^{-1}, which becomes broader, stronger and partly resolved into several sharp components of small or medium intensity [15]. Simultaneously, the band in the range of 3700–2900 cm^{-1} attributed to stretching vibrations of OH groups in the hydroxide structure, as well as in physically adsorbed water, becomes weaker. The intensity of this band is still weaker in the IR spectra of the samples calcined at 1200°C. 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 octahedra in α-Al_2O_3. Their intensity is weaker for the oxides prepared from aged hydroxides in comparison with the sample derived from the hydroxide not subjected to ageing. However, it hardly changes with lengthening of ageing time from 20 to 59 h. It may prove that the process of ageing of aluminium hydroxides favoured a delayed transformation of γ-Al_2O_3 obtained from them into α phase. This is in agreement with the results of the researchers [8].

A character change of the IR spectra recorded for all examined aluminium hydroxides and 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:

$$\text{boehmite/pseudoboehmite}\rightarrow\gamma\text{-}Al_2O_3\rightarrow\delta\text{-}/\theta\text{-}Al_2O_3\rightarrow\theta\text{-}/\alpha\text{-}Al_2O_3$$

X-ray powder diffraction

Figures 3a and b represent the XRD patterns recorded for the sample of aluminium hydroxide not subjected to the ageing and the products of its calcination for 2 h at 550, 900 or 1200°C, as well as for aluminium hydroxide aged for 59 h and the products of its calcination for 2 h at different temperatures, respectively.

The XRD patterns obtained for the samples prepared without the ageing step are very close to analogous ones recorded for aluminium hydroxide aged for 59 h and oxides derived from it.

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 transitions of aluminium hydroxide into a thermodynamically stable α phase, which was suggested on the basis of IR studies.

The XRD spectra for both hydroxides, not aged and aged for 59 h, reveal peaks characteristic for boehmite [18, 22]. However, in the case of the aged hydroxide, these peaks are sharper and stronger, which may prove a larger amount of boehmite in this sample in comparison with the hydroxide not subjected to ageing. It may be the evidence of a favourable influence of ageing on the formation of boehmite structure and is consistent with the results obtained by authors of other papers [4, 18, 19]. The character of the XRD patterns recorded for both hydroxides makes it possible to suppose that apart from boehmite structure they also contain pseudoboehmite. According to Rousseaux *et al.* [19] the term of ‘pseudoboehmite’ refers to a poorly crystallised boehmite whose low crystallinity degree is reflected with a considerable broadness and weak intensity of the peaks typical for boehmite.

On the basis of a comparative analysis of XRD spectra of both hydroxides it was suggested that the process of prolonged refluxing of the precipitates at elevated temperature favoured a transition of poorly crystallised pseudoboehmite into boehmite, thus an increase of crystallinity of aluminium hydroxides. Above notices were also confirmed by the results of thermal analysis and infrared spectroscopy.

A character of XRD patterns recorded for the products of calcination at 550°C of both hydroxides is typical for the structure of γ-Al_2O_3 (Figs 3a and b) [18, 23–26]. An increase of calcination temperature up to 900°C resulted in formation of subsequent transition aluminas. The spectra of both aluminium oxides reveal peaks characteristic for δ- and θ-Al_2O_3 [23, 24, 27]. A further increase of heating temperature to 1200°C led to the next phase transition resulting in the mixture of θ- and α-Al_2O_3. It is accompanied by disappearing of peaks typical for δ-Al_2O_3 and occurring new peaks ascribed to α phase [10, 18, 23, 24, 26–29]. Comparing

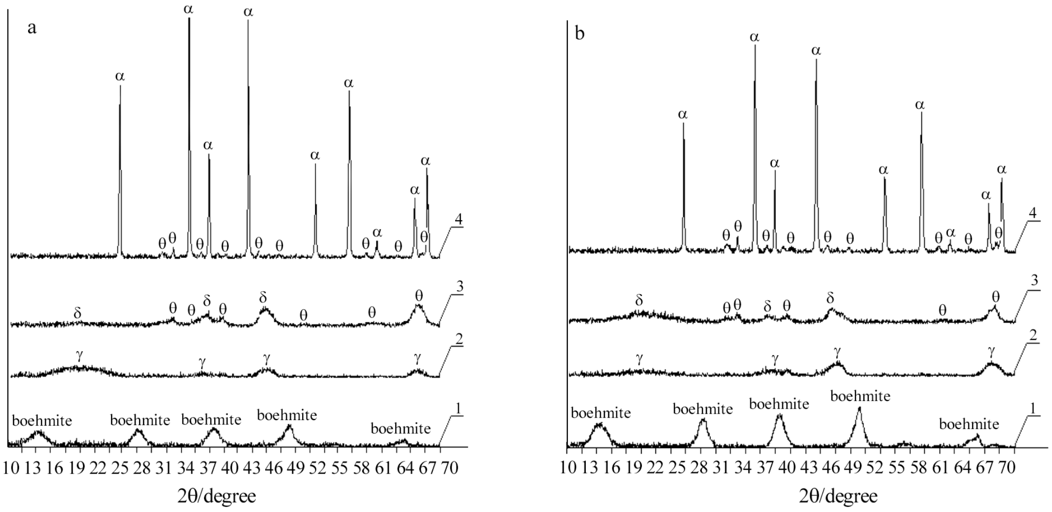

Fig. 3 a – XRD patterns of not aged aluminium hydroxide and products of its calcination at 550, 900 or 1200°C. 1 – $Al(OH)_3$\0 h, 2 – Al_2O_3\0 h\550°C, 3 – Al_2O_3\0 h\550°C\900°C, 4 – Al_2O_3\0 h\550°C\1200°C; b – XRD patterns of aluminium hydroxide aged for 59 h and products of its calcination at 550, 900 or 1200°C. 1 – $Al(OH)_3$\59 h, 2 – Al_2O_3\59 h\550°C, 3 – Al_2O_3\59 h\550°C\900°C, 4 – Al_2O_3\59 h\550°C\1200°C

the XRD patterns for both aluminium oxides obtained through calcination at 1200°C (Figs 3a and b), one may notice that the peaks attributed to α-Al_2O_3 are slightly less intensive in the case of the sample derived from the hydroxide subjected to ageing. Thus, it can be supposed that the process of prolonged refluxing at elevated temperature favoured a delayed formation of a corundum structure. Probably, during this process, a number of surface defects is decreased, which in consequence limits an ion diffusion and retards a sintering of particles while calcination [18].

Low-temperature nitrogen adsorption

Table 2 presents the values of specific surface determined by the method of low-temperature nitrogen adsorption for the samples of aluminium hydroxide, both not aged and aged for different time intervals (20, 39 or 59 h), as well as the products of their calcination at 550, 900 or 1200°C for 2 h.

An analysis of the data collected in Table 2 shows that freshly precipitated aluminium hydroxides are characterised by relatively high values of specific surface (211–262 $m^2\ g^{-1}$). All hydroxides subjected to ageing have higher values of specific surface in comparison with the respective hydroxide prepared without the ageing step. This is consistent with the results of investigations presented in paper [8]. During the process of ageing, the hydrolysis of basic aluminium salts takes place together with the removal of OH groups resulting in developing of crystal structure [11, 18]. When water is removed from the interlayer space pores develop, bigger and more ordered primary particles of aluminium hydroxide are formed, which consequently leads to the increase of specific surface for the samples of aged hydroxides.

Musić *et al.* [30] investigating an influence of ageing time on the crystallinity of boehmite and its surface development noticed the decrease of the specific surface value from 164 to 146 $m^2\ g^{-1}$ with lengthening time of ageing from 1 to 6 h. Samples aged for longer time intervals (24, 72 or 86 h) had better and better formed crystal structure, however lower and lower value of specific surface (S_{BET}=91 $m^2\ g^{-1}$ for the sample digested for 86 h). Similar results were obtained for examined hydroxides, investigations of which are presented in this paper. The sample of aluminium hydroxide aged for 20 h is characterised with the specific surface value of 262 $m^2\ g^{-1}$, while the samples subjected to ageing for longer time intervals (39 or 59 h) have a bit lower values of specific surface, 243 and 244 $m^2\ g^{-1}$ respectively.

Calcination at 550, 900 or 1200°C of all hydroxides resulted in a decrease of specific surface development. However, aluminium oxides obtained by heating at 550 or 900°C maintain relatively high values of S_{BET}, from 205 to 222 $m^2\ g^{-1}$ for the samples calcined at 550°C, and from 128 to 153 $m^2\ g^{-1}$ for the samples calcined at 900°C. Such high values of specific surface are typical for metastable aluminium oxides [15], whose formation was proved by the results of IR spectroscopy and X-ray powder diffraction. The analysis of the data collected in Table 2 shows that S_{BET} measured for the oxides prepared from aged hydroxides are very similar to the values for the respective samples obtained without the ageing step. An in-

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

Sample	Specific surface/$m^2\ g^{-1}$			Surface of mesopores/$m^2\ g^{-1}$	
	(nitrogen)	(benzene)		(Kisielev method)	
		$S_{BET(vertical)}$	$S_{BET(planar)}$	$S_{MEZ(adsorption)}$	$S_{MEZ(desorption)}$
$Al(OH)_3$\0 h	211	128	206	201	303
Al_2O_3\0 h\550°C	205	129	207	148	174
Al_2O_3\0 h\550°C\900°C	138	54	87	71	92
Al_2O_3\0 h\550°C\1200°C	13	7	11	*	*
$Al(OH)_3$\20 h	262	–	–	–	–
Al_2O_3\20 h\550°C	220	–	–	–	–
Al_2O_3\20 h\550°C\900°C	153	–	–	–	–
Al_2O_3\20 h\550°C\1200°C	25	–	–	–	–
$Al(OH)_3$\39 h	243	–	–	–	–
Al_2O_3\39 h\550°C	213	–	–	–	–
Al_2O_3\39 h\550°C\900°C	138	–	–	–	–
Al_2O_3\39 h\550°C\1200°C	17	–	–	–	–
$Al(OH)_3$\59 h	244	112	180	99	118
Al_2O_3\59 h\550°C	222	120	192	120	141
Al_2O_3\59 h\550°C\900°C	139	63	101	49	59
Al_2O_3\59 h\550°C\1200°C	19	11	17	*	*

*lack of hysteresis loop

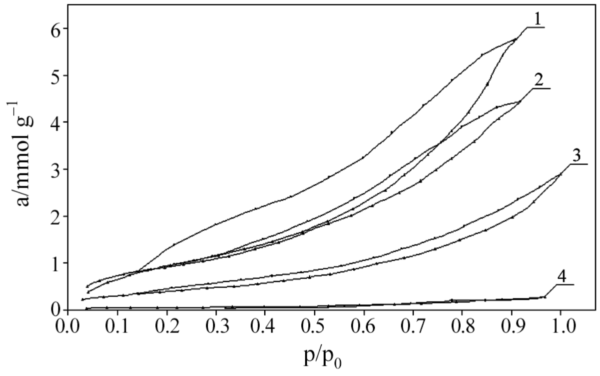

Fig. 4 The adsorption–desorption isotherms of benzene vapours for the samples of not aged aluminium hydroxide and products of its calcination at 550, 900 or 1200°C. 1 – $Al(OH)_3$\0 h, 2 – Al_2O_3\0 h\550°C, 3 – Al_2O_3\0 h\550°C\900°C, 4 – Al_2O_3\0 h\550°C\1200°C

crease of calcination temperature up to 1200°C resulted in a prominent decrease of specific surface values. The IR spectra, as well as XRD patterns denoted that at this temperature high-temperature transition aluminium oxides such as θ- or α-Al_2O_3 were formed (Figs 2 and 3), which was accompanied by the sintering of powder particles, as well as devastation of their internal porosity. Aluminium oxides prepared through calcination at 1200°C of aged hydroxides have slightly higher values of specific surface in relation to the analogous sample derived from the hydroxide not subjected to ageing.

Adsorption and desorption of benzene vapours

The exemplary adsorption and desorption isotherms of benzene vapours obtained for the aluminium hydroxide not subjected to the process of ageing, as well as for the oxides derived from this hydroxide, are shown in Fig. 4. Figures 5a 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 samples of aluminium hydroxides (not aged and aged for 59 h) and the samples of oxides derived from them. Table 2 reveals parameters of the porous structure of these materials.

The shape of isotherms obtained for all samples of aluminium hydroxides and oxides may be classified according to IUPAC nomenclature as the H3 type [31]. For the materials of this kind, a hysteresis loops 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 calcined 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 aluminium hydroxides have good adsorption capacity for benzene vapours. It should be noticed that the process of ageing at elevated temperature resulted in a decrease of adsorption capacity. S_{BET} values, calculated supposing planar orientation of benzene molecules in adsorption monolayer, are 206 and 180 m^2 g^{-1} for the starting hydroxide and the hydroxide aged for 59 h, respectively. At the same time, the values of mesopore surface are lower in the case of the sample subjected to ageing. An increase of a crystallinity degree and an arrangement of crystal structure of aluminium hydroxide that accompany the ageing process result in formation of pores which are less accessible for large benzene molecules.

The process of calcination at 550–900°C led to a gradually decrease of S_{BET} values and the values of mesopore surface. Moreover, the samples of aluminium oxides obtained by calcination of not aged hy-

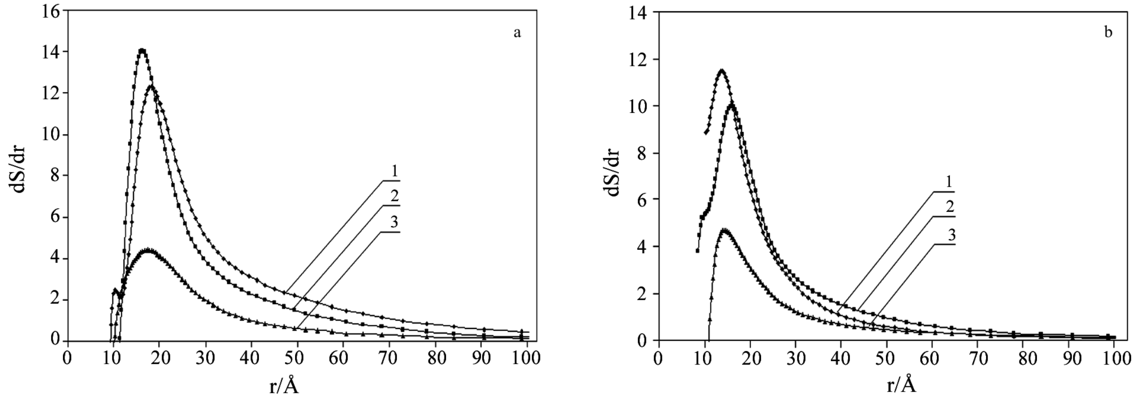

Fig. 5 a – The distribution of mesopore surface area as a function of the effective radii for the samples of not aged aluminium hydroxide and products of its calcination at 550 or 900°C. 1 – $Al(OH)_3$\0 h, 2 – Al_2O_3\0 h\550°C, 3 – Al_2O_3\0 h\550°C\900°C; b – the distribution of mesopore surface area as a function of the effective radii for the samples of aluminium hydroxide aged for 59 h and products of its calcination at 550, 900°C or 1200°C. 1 – $Al(OH)_3$\59 h, 2 – Al_2O_3\59 h\550°C, 3 – Al_2O_3\59 h\550°C\900°C

droxide maintain more developed surfaces of transition pores in relation to analogous samples derived from the hydroxide aged for 59 h. Aluminium oxides calcined at 1200°C have significantly lower adsorption capacity for benzene vapours, which is 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 hydroxide subjected prolonged refluxing in mother liquor at elevated temperature has slightly higher value of S_{BET}, which may prove its higher thermal stability.

A comparative analysis of nitrogen and benzene adsorption results gives the possibility of estimating the hydrophilic-hydrophobic properties of aluminium hydroxides and oxides [32, 33]. These properties depend on the surface functional groups that may alter 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 $S_{\mathrm{BET(planar)}}$ should be smaller or equal to the S_{BET} value determined from the adsorption of nitrogen. Excessive values of $S_{\mathrm{BET(planar)}}$ 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.

The samples of aluminium hydroxide not subjected to ageing as well as of aluminium oxide obtained through its calcination at 550°C are characterised with $S_{\mathrm{BET(planar)}}$ value close to that determined from the adsorption of nitrogen. In case of other materials, the values of specific surface calculated from adsorption of benzene supposing its planar orientation in a monomolecular layer are much lower than analogous ones obtained from nitrogen adsorption. It may be suggested that all investigated materials had a low concentration of surface hydroxyl groups enabling deviation of adsorbed benzene molecules from planar orientation. Thus, the hydroxides possessed hydrophobic character that became stronger in case of samples of higher crystallinity, thus aged in mother liquor at elevated temperature.

All the samples of aluminium hydroxides and oxides are characterised with monodispersive distribution of the pores. It can be observed that the pores of radii of about 15 Å contribute the most to their porosity. It may also be found that in case of aluminium hydroxide subjected to ageing the pores were a bit smaller (13 Å) in comparison with the analogous sample prepared without the ageing step (17 Å). However, generally the process of prolonged ageing at elevated temperature of aluminium hydroxides and an increase of calcination temperature had hardly any effect on the pore size of investigated materials.

Conclusions

- The hydrolysis of hydrous aluminium perchlorate in ammonia medium results in the formation of boehmite.
- Prolonged refluxing of freshly precipitated aluminium hydroxide develops its crystallinity, increases its specific surface determined from nitrogen adsorption and hydrophobic character, as well as decreases its sorption capacity for benzene vapours.
- Extending of ageing duration (from 20 to 59 h) has a slight effect on the properties of boehmites.
- Obtained aluminium hydroxides during calcination at the temperature up to 1200°C transform to α-Al_2O_3 via γ-, δ- and θ-Al_2O_3.
- The samples of aluminium oxides obtained after calcination at 550 and 900°C are characterised with high values of specific surface area of 205–220 and 138–153 m^2 g^{-1}, respectively.
- The process of ageing at elevated temperature develops thermal stability of aluminium oxides.

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