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Effect of Synthesis Conditions on the Structure and Properties of Ultradispersed Aluminium Oxyhydroxides*

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Abstract

Properties of aluminium oxyhydroxides (AOH) that were obtained through oxidation of electroexplosive ultradispersed (nano-) powder of aluminium by water (55 °C) and subsequent calcination of the initial sample in a temperature range 100–1150 °C have been investigated. These materials were taken up as highly effective adsorbents for special complex water treatment. With the use of X-ray diffraction, thermal analysis, and porosimetry methods, the basic structural characteristics of samples have been determined. It was found that initial AOH contains two modifications: pseudo-boehmite and bayerite. Depending on conditions of heat treatment, the following phase transitions are observed: bayerite $\rightarrow$ η-Al_2O_3 $\rightarrow$ θ-Al_2O_3 $\rightarrow$ α-Al_2O_3 and pseudo-boehmite $\rightarrow$ γ-Al_2O_3 $\rightarrow$ δ-Al_2O_3 $\rightarrow$ θ-Al_2O_3 $\rightarrow$ α-Al_2O_3. The oxyhydroxides that were obtained at relatively low calcination temperatures are characterized by high specific surface and by existence of a microporous structure. A decrease in the calcination temperature leads to disappearance of micropores and to an increase in the volume and size of mesopores.

INTRODUCTION

Ultradispersed powders (UDP) that are produced in various ways are actively investigated and are applied in composites for manufacturing ceramics, catalysts, sorbents, *etc*. Electroexplosive aluminium UDPs can react with the fluid media and, when oxidized by hot water (45–75 °C), they are employed as sorbents for extraction inorganic, organic matter, and microorganisms from water and from air [1–4].

A great number of works deal with studying the structural and textural characteristics of aluminium oxyhydroxides (AOH). Generalized results thereof are presented in [5–12]. However, despite the numerous investigations of AOH, there is no common opinion about the structural and textural characteristics of its numerous modifications, because the properties of AOH depend on many parameters, including method of producing, quality and nature of starting materials, temperature of synthesis, pH of reaction medium, ageing conditions, and temperature of heat treatment.

This work is devoted to investigation of influence of temperature and time of heat treatment on the content of structural water, specific surface, pore space, and phase composition of ultradispersed AOH.

EXPERIMENTAL

Initial sample of ultradispersed AOH was obtained according to the procedure described in [16], by hydrolysis of electroexplosive ultradispersed aluminium at 55 °C for 5–7 h, and then was let to stand under mother solution (pH 10–11) for 1 day at ambient temperature

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TABLE 1

Structural and textural characteristics of aluminium oxyhydroxide samples

Sample number	T_c, °C	τ_c, min	S_{sp}, m^2/g	Pore size (d), nm	Pore volume (V_s), cm^3/g		Micropore volume, cm^3/g ($d < 2$ nm)	Main phases
					N_2 (2 nm < d < 40 nm)	Hg (3.7 nm < d < 40 nm)		
1	250	90	326	4*	0.23	0.18	0.08	Pseudo-boehmite, bayerite, η-Al_2O_3
2	370	160	342	4**, 5.5**	0.28	0.07	0.09	Pseudo-boehmite, η-Al_2O_3
3	550	120	273	3.5**, 5.5**	0.51	0.52	No	γ-Al_2O_3
4	800	180	176	9*	0.60	0.58	«	γ-Al_2O_3

*Monomodal distribution of pores.

**Bimodal distribution of pores.

until complete oxidation of large aluminium particles. The obtained product was air dried at 130 °C and then calcined under isothermal regime. Specific surface S_{sp} of samples was determined by argon thermal desorption method in "Sorbtomyetr" analyser (Katakon JSC, Novosibirsk) [17]. Thermal analysis of samples was conducted with Q-1500 D derivatograph in the temperature range 20–1000 °C with a heating rate of 10 °C/min in the air atmosphere; a sample mass was 0.2 g. X-ray scattering curves were recorded in DRON-3 diffractometer in the range of medium and large angles ($2\theta = 3-60°$, MoK_α radiation) with continuous scanning at a rate of 1 deg/min. Sorption of benzene vapour was performed by the exicator method at the vapour pressure $p/p_0 \approx 1$ [18]. Structural and textural characteristics of AOH samples are presented in Table 1.*

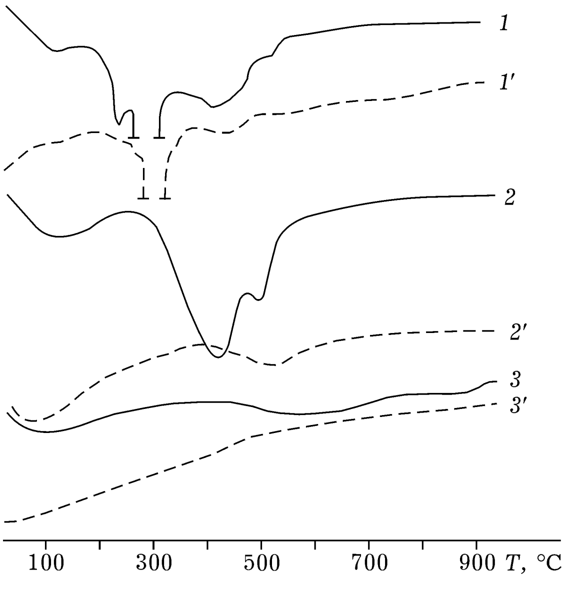

Fig. 1. DTG *(solid)* and DTA *(dotted)* curves of thermal decomposition of aluminium oxyhydroxides: *1, 1′* – initial oxyhydroxide; *2, 2′* – calcinated at 300 °C for 4 h; *3,3′* – calcinated at 450 °C for 4 h.

RESULTS AND DISCUSSION

Oxidation of aluminium UDP at 55 °C by water within several hours yields the powder, light grey in colour, with particles, whose distribution maximum corresponds to 0.2 μm (initial AOH). In the course of linear heating to 1000 °C, initial AOH first loses adsorbed water at 20–170 °C (Fig. 1, curves *1*, *1′*). These losses comprise 1–3 mass %. At 170–220 °C, the removal of so-called bound water occurs (up to 3 mass %). Further rise in temperature leads to structural water removing. Endothermic peaks in DTA and peaks in DTG with minima at a temperature within the limits of 240 and 300 °C can be assigned to bayerite dehydration. The data, which have been obtained by the electron microscopy method, demonstrate that the initial AOH shows polydisperse composition; therefore, bayerite particles can be dehydrated to form boehmite and low-temperature modification of Al_2O_3 [19]. Above 300 °C, decomposition of pseudo-boehmite begins.

In a temperature range 250–350 °C, the sample loses up to 14 mass % of water. Further temperature rise is accompanied by a decrease

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*Determination of pore size by methods of nitrogen sorption and mercury porosimetry and determination of specific surface and phase composition of samples have been performed by N. Ouillon, E. Schweitzer, and E. Kerdavid (France).

TABLE 2

Characteristics of samples of aluminium oxyhydroxides

Sample	T_c, °C	τ_c, h	H_2O/Al_2O_3, mol/mol, at a temperature of, °C		S_{sp}, m^2/g	V_s, cm^3/g	Main phases
			1000	1150			
Initial AOH	130	2	1.77	1.77	261	0.38	Bayerite, pseudo-boehmite, Al
AOH-200(2)	200	2	1.56	–	257	–	Bayerite, pseudo-boehmite
AOH-200(4)	200	4	1.54	–	259	–	Bayerite, pseudo-boehmite
AOH-300(2)	300	2	0.75	0.77	356	0.48	η-Al_2O_3, γ-Al_2O_3, pseudo-boehmite
AOH-300(4)	300	4	0.71	0.70	431	0.53	η-Al_2O_3, γ-Al_2O_3, pseudo-boehmite
AOH-450(2)	450	2	0.31	0.31	417	0.56	η-Al_2O_3, γ-Al_2O_3, boehmite
AOH-450(4)	450	4	0.29	0.28	365	0.56	η-Al_2O_3, γ-Al_2O_3, boehmite
AOH-600(2)	600	2	0.20	0.20	307	0.56	γ-Al_2O_3, η-Al_2O_3
AOH-600(4)	600	4	0.21	0.21	289	0.58	γ-Al_2O_3, η-Al_2O_3
AOH-1150(2)	1150	2	0.07	0.07	76	0.38	θ-Al_2O_3, α-Al_2O_3

*Linear heating.

**Isothermal heating.

in the rate of water loss and by the fuzzy peaks appearing with maxima at 435 and 505 °C, which is related to decomposition of pseudo-boehmite and boehmite, respectively [11]. In response to linear heating to 1000 °C, the initial sample loses 24 mass % of water. Calcination of the initial sample under isothermal regime at 1150 °C for 2 h results also in loss of 24 mass % of water. Thus, the initial sample is practically dehydrated even at 1000 °C, and its structural formula may be written as $Al_2O_3 \cdot 1.77H_2O$.

On the initial stage of oxidizing reaction of aluminium UDP by water, amorphous trihydroxide can be formed on the surface of particles. During ageing in the alkaline (or ammoniac) medium at relatively low (50 °C) or at room temperature, this trihydroxide transforms consecutively to pseudo-boehmite, bayerite, hydrargillite, and boehmite. An oxidation process also goes inside the large aluminium particles (50 μm and less), and this process is associated with generation of a significant amount of heat (up to 7900 J/g) and hydrogen (up to 1.244 cm^3/g of aluminium) [12]. Therefore, it is conceivable that synthesis of oxyhydroxide inside the large particles proceeds under hydrothermal conditions, which is favourable for a crystallized boehmite to form [5]. Spectra of diffraction of Roentgen rays for initial AOH are suggestive of α-$Al(OH)_3$ (bayerite) available in the sample, the substance being detected from the strong lines corresponding to the interplane distances of 0.472, 0.436 and 0.223 nm. Along with bayerite reflexes, initial AOH causes also strongly broadened diffraction lines, the maxima of which coincide with the arrangement of the most intensive lines of well-crystallized boehmite, but for a little displacement. The strongest line for boehmite that matches the interplane distance of 0.612 nm is characterized by a wide profile and is displaced to 0.62 nm that is characteristic of pseudo-boehmite. The presence of pseudo-boehmite is fixed also by lines with d = 0.234 and 0.185 nm. Besides bayerite and boehmite, the sample contains about 5 mass % of unreacted aluminium.

Calcination of the initial sample at various temperatures is followed by change in the content of structural water, in specific surface, pore space, and phase composition of AOH (see Table 1, 2). Low-temperature samples (Nos. 1, 2) are characterized by rather high specific surface and by micropores available. The analysis of diffractograms, which has been performed by N. Ouillon, E. Schweitzer, and E. Kerdavid (France), has demonstrated that these samples are composed of fine crystals, and the sample 1 thereof is represented by pseudo-boehmite and by the decomposition product of bayerite, η-Al_2O_3, as well as by

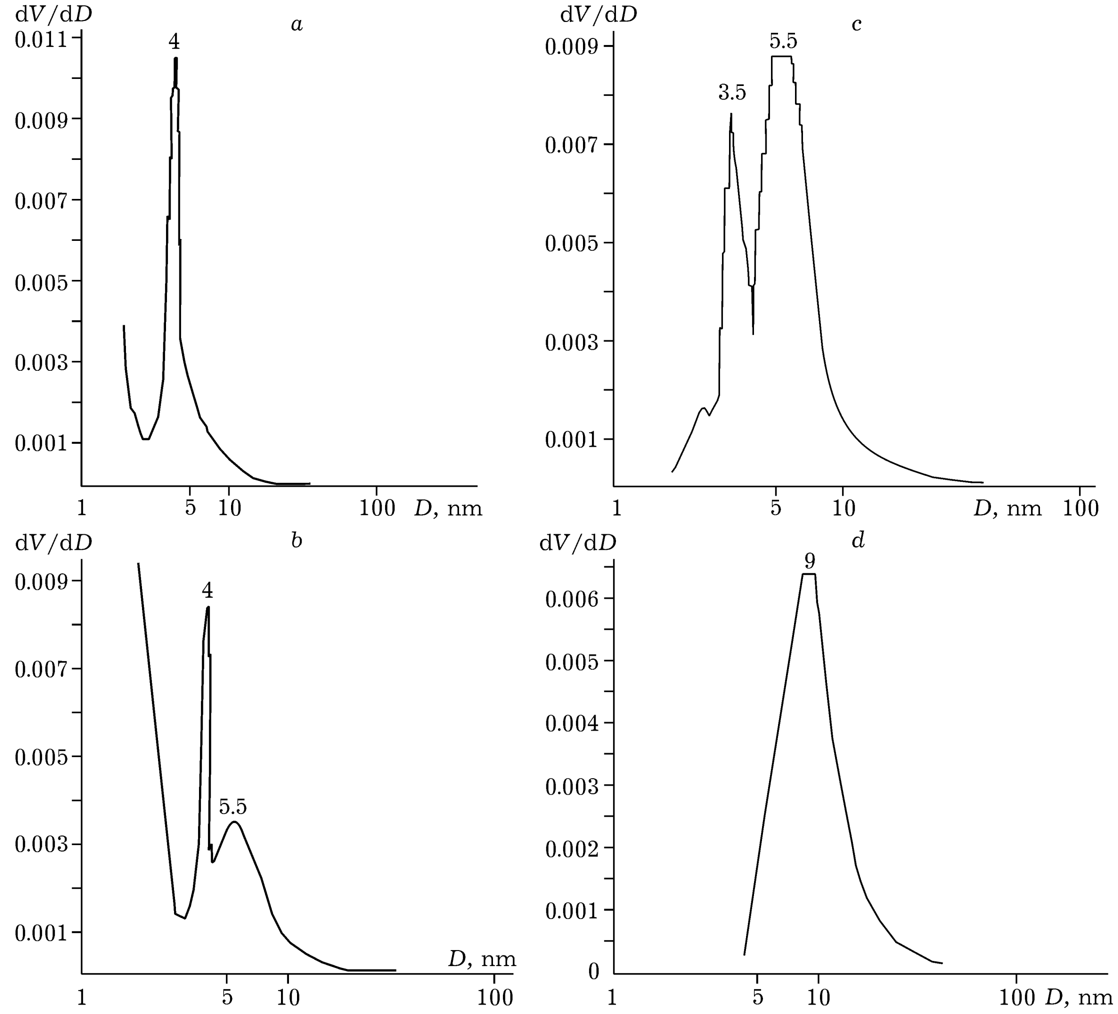

Fig. 2. Pore size distribution curves for AOH samples: *a–d* - samples 1–4, respectively (see Table 1).

residual bayerite. The sample 2 contains pseudo-boehmite and low-temperature η-Al_2O_3 and γ-Al_2O_3 aluminium oxides, which have arisen at dehydration of polydisperse bayerite and pseudo-boehmite. Rise in the calcination temperature causes the mesopore volume to increase, and in the process, the pore size distribution takes first bimodal character, then again monomodal character, and the distribution maxima are displaced in the region of large pore diameters (Fig. 2). Removing water from particles at high temperature causes pseudo-boehmite layers to join and micropores to disappear. We failed to detect micropores even for the sample 3 that was calcinated at 550 °C. High-temperature samples 3, 4 are represented for the most part by γ-Al_2O_3 and it is likely that δ-Al_2O_3 is present in the sample 4.

The influence of dehydration temperature on specific surface, on the content of structural water, and on the phase composition has been studied with the second AOH series as an example. These AOH have been obtained by calcination of initial AOH at the temperatures of 200, 300, 450, 600, and 1150 °C in the isothermal regime for 2 or 4 h (see Table 2, Fig. 3).

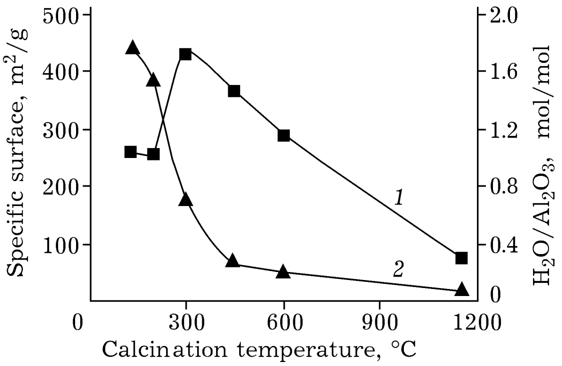

Fig. 3. Effect of calcination temperature on specific surface *(1)* and the content of structural water *(2)* in aluminium oxyhydroxides.

During linear heating, all samples lose sorbed water in the same temperature range as the initial sample. DTA and DTG curves of thermodecomposition of the samples calcinated at 200 °C show intensive peaks at 300 °C, wide peaks at 437 °C, and very weak peaks at 500 °C. Loss of structural water in a temperature range 170–1000 °C amounts to 21 %, which correlates with the $Al_2O_3 \cdot 1.56H_2O$ (2 h) and $Al_2O_3 \cdot 1.54H_2O$ (4 h) structural formulae of samples. AOH-300 (2) and AOH-300 (4) (see Fig. 1, curves *2*, *2'*) are characterised by uniform decrease of mass. An increase in the dehydration rate, which is present in the interval 350–500 °C, reflects on the emergence of wide minima in the DTA curves at 430 and 505 °C that are characteristic of pseudo-boehmite and boehmite, respectively. As was highlighted in the foregoing, boehmite can form in the course of oxyhydroxide synthesis and during decomposition of pseudo-boehmite and polydisperse bayerite. In addition, crystallized boehmite can form upon calcination of the initial AOH as a result of hydrothermal synthesis conditions created inside the large particles [5]. The samples calcinated at 300 °C lose about 11 mass %, which correlates with the composition $Al_2O_3 \cdot 0.77H_2O$ (AOH-300(2)) and $Al_2O_3 \cdot 0.70H_2O$ (AOH-300 (4)).

DTG curves of decomposition of the samples obtained at 450 °C show two fuzzy peaks, which reflect the removal of adsorbed water (above 100 °C) and interlayer water (above 500 °C) from boehmite. Decomposition of pseudo-boehmite is nearly finished. Losses of structural water are of about 4 mass %. Composition of samples can be represented as $Al_2O_3 \cdot 0.31H_2O$ (AOH-450 (2)) and $Al_2O_3 \cdot 0.28H_2O$ (AOH-450 (4)).

Heat treatment of initial AOH in the isothermal regime at 600 °C gives rise to the product of composition $Al_2O_3 \cdot 0.21H_2O$. The quantity of the removed water is independent of the heat treatment time and heat treatment procedure for initial AOH. Removing the interlayer water and formation of γ-Al_2O_3 goes on. The sample calcinated at a temperature of 1150 °C contains 0.07 mol of structural water.

Specific surface of the samples that were subjected to air-drying at 130 and 200 °C remains a constant, then peaks at a temperature range 300–450 °C.

The analysis of X-ray diffraction spectra demonstrates that the samples calcinated at 300 °C are represented mostly by pseudo-boehmite. Bayerite and low-temperature aluminium oxide, which constitutes a product of bayerite disintegration and a product of the started pseudo-boehmite decomposition, are identified too. Phase composition of AOH-450(2) and AOH-450(4) samples varies in the direction of the decreased concentration of pseudo-boehmite and the increased γ-Al_2O_3 content. Based on XRD spectra, AOH-600(2) and AOH-600(4) samples contain for the most part low-temperature aluminium oxides. Since initial AOH is composed of bayerite and pseudo-boehmite, it should be expected that the above aluminium oxides must be η-Al_2O_3 and γ-Al_2O_3. However, unambiguous identification of a mixture of badly crystallized phases from broadened diffractogram lines was troublesome. Isothermal heating of initial AOH at a temperature of 1150 °C precludes the obtaining a pure α-Al_2O_3 phase. This is suggested by rather high value of specific surface (see Table 2). The sample contains θ-Al_2O_3, which is a product of phase transitions bayerite $\rightarrow$ η-Al_2O_3 $\rightarrow$ θ-Al_2O_3 and pseudo-boehmite $\rightarrow$ γ-Al_2O_3 $\rightarrow$ δ-Al_2O_3 $\rightarrow$ θ-Al_2O_3.

Determination of integral intensity of the diffraction maxima, which correspond to the interplanar distances (*d*) of 0.62 nm (pseudo-boehmite) and 0.139–0.140 nm, 0.198 nm (η-Al_2O_3 and γ-Al_2O_3, respectively), demonstrates that as the dehydration temperature of initial AOH increases, the

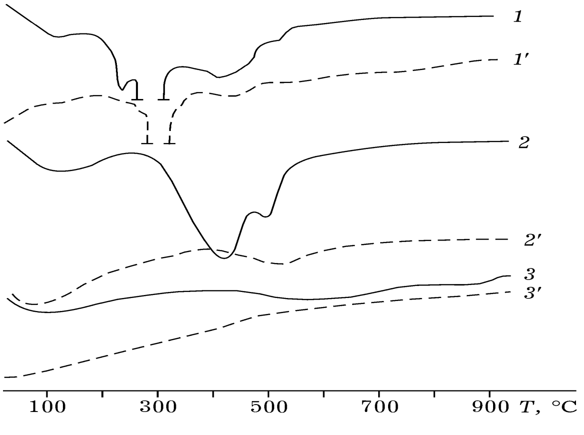

Fig. 4. Dependence of integral intensity of diffraction maxima on the dehydration temperature of initial AOH. *d*, nm: 0.62 *(1)*, 0.198 *(2)*, 0.139–0.140 *(3)*.

content of pseudo-boehmite drops and the proportion of Al_2O_3 rises (Fig. 4).

The sorption activity of the produced materials is estimated from the magnitude of the limiting adsorption pore volume, which was determined from the benzene vapour sorption at $p/p_0 \approx 1$. The limiting adsorption volume, as well as specific surface, reaches the maximum value (more than 0.55 cm^3/g) in the interval 450–600 °C (see Table 2) and it is practically unaffected by the time of heat treatment. The maximum sorption capacity with respect to benzene vapour is exhibited by dehydrated AOH composed of low-temperature aluminium oxides.

CONCLUSIONS

The investigations performed demonstrate that an oxidate of ultradispersed aluminium by water at 55–60 °C is of composition $Al_2O_3 \cdot 1.77H_2O$. It is represented by bayerite and pseudo-boehmite. Thermal decomposition of an initial sample proceeds with formation of low-temperature oxides (η-Al_2O_3 and γ-Al_2O_3), which transform to θ-Al_2O_3 and α-Al_2O_3 at a temperature above 1000 °C. It is significant that only the synthesis temperature was under rigorous control; therefore, this work does not discuss an effect of ageing conditions on the synthesised products.

Thus, structural and phase transformations of AOHs, which were produced by thermohydrolysis of the aluminium ultradispersed powders and by subsequent calcination, are in a perfect agreement with current theoretical concepts. Ultradispersed AOHs retain small particle size (0.2 μm and less) and possess the developed surface and high mesopore volume, which ensure that they can be used as effective adsorbents, catalysts, or their carriers. Authors intend to report about an effect of ageing conditions, about the character of active sites, as well as about the adsorption properties of ultradispersed AOH in the subsequent publications.

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