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Synthesis of Aluminum Oxides from the Products of the Rapid Thermal Decomposition of Hydrargillite in a Centrifugal Flash Reactor:

II. Structural and Textural Properties of Aluminum Hydroxide and Oxide Obtained from the Product of the Centrifugal Thermal Activation of Hydrargillite (CTA Product)

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Abstract—The basic properties of aluminum hydroxide compounds, namely, the flash product and the centrifugal thermal activation (CTA) product both before and after heat treatment at 400–1100°C are considered. The hydration conditions for obtaining 100% pseudoboehmite from the CTA product are determined. The structure, morphology, and texture of pseudoboehmite aluminum hydroxide synthesized from the CTA product and of the aluminum oxides obtained from this hydroxide in the temperature range 600–1100°C are described.

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Aluminum hydroxide and oxide are known to be obtained from commercial-grade alumina hydrate (hydrargillite) [1]. Using different processing methods, such as dissolution in an acid or an alkali followed by precipitation, thermal dispersion, and mechanical activation, hydrargillite can be converted into a variety of aluminum-containing products. In particular, thermochemical activation (TCA), specifically, the nonequilibrium thermal decomposition of hydrargillite, which includes heating to the dehydration temperature (~300°C) within a few seconds in counterflowing flue gas and cooling [2–4], yields the TCA product (whose commercial name is the flash product). As compared to hydrargillite, the flash product is more reactive, has a larger specific surface area, and is amorphous to X-rays.

A drawback of the commercial flash product is the low reproducibility of its properties, including phase composition and residual moisture content. As a consequence, pilot batches of catalysts prepared from this product vary in properties. A radically new thermal activation apparatus has been developed in order to eliminate this drawback. This apparatus includes a centrifugal flash reactor (TsEFLAR) [5, 6], in which the centrifugal force establishes a stable contact between hydrargillite powder particles and a rotating hot metallic surface and thereby enhances heat transfer. As applied to the centrifugal thermal activation (CTA) of hydrargillite, this reactor makes it possible to break the hydrargillite structure almost completely to obtain an X-ray-amorphous CTA product under certain process conditions (heating wall temperature >500°C, treatment time 1–1.5 s) [7]. It is, therefore, pertinent to compare the properties of the flash and CTA products and to see whether it is possible to obtain aluminum hydroxide with a pseudoboehmite structure and then alumina via the hydration of the CTA product.

Here, we report the structural and textural properties of pseudoboehmite aluminum hydroxide obtained by the dehydration of the CTA product and of alumina derived from this hydroxide.

EXPERIMENTAL

The object of our study was the CTA product obtained by converting hydrargillite from PO Glinozem (Pikalevo, Russia) in a TsEFLAR-T reactor under the following conditions: heating surface temperature, ~500°C; treatment time, ~1.5 s; reactant mass flow rate, 2.5 g/s. Aluminum hydroxide samples were obtained by hydrating the CTA product with distilled water (solid : liquid = 1 : 10) at a preset temperature for a prescribed time in the presence of nitric acid (N), acetic acid (Ac), or polyvinyl alcohol (PVA). The process was carried out either under hydrothermal conditions [8] or at atmospheric pressure. The resulting samples were designated *T*–τ–*M*–K, where *T* is the process temperature (°C), τ is the process duration (h), *M* is the acid

Table 1. Properties of the starting aluminum-containing materials

Material	Chemical composition			Phase composition**, %				S_{sp}, m^2/g
	Na_2O, %	Fe_2O_3, %	H_2O, mol/(mol Al_2O_3)	HA	Am	Bo	Pbo	
Flash product*	0.30	0.03	1.01	5	+	5	–	90
CTA product	0.16	0.05	0.75	–	+	–	~25	165

* From Achinsk alumina refinery.

** HA = hydrargillite, Am = amorphous phase, Bo = boehmite, and Pbo = pseudoboehmite.

modulus, and K is an acid or PVA. The slurry resulting from the above processing was filtered, and the cake was dried at room temperature and then at 110–120°C in an oven for 12–14 h. Hydroxide samples were calcined at 600 to 1100°C for 4 h.

The starting samples and products were analyzed for impurities by atomic absorption spectroscopy [9]. The constitutional water content was derived from the calcination loss, which was determined as the ratio of the difference between the weight of the sample dried at 110°C for 1 day and the weight of the same sample calcined at 800°C for 4 h to the initial weight.

Thermal analysis was carried out on a Q 1500-D thermoanalytical system in the 20–1000°C temperature range at a heating rate of 10 K/min in air. The sample weight was 0.2 g. Weight losses were determined with an accuracy of ±0.5%.

X-ray powder diffraction patterns were obtained on an HZG-4C diffractometer using monochromated CuK_α radiation ($\lambda = 1.5418$ Å). The coherent-scattering domain size (D) was calculated using the Selyakov–Scherrer formula [10]. Quantitative analysis was carried out using calibration plots. The unit cell parameter a was determined with an accuracy of ±0.005 Å.

Electron microscopic studies were carried out with a JEM-100C transmission electron microscope (resolution 30 nm, acceleration voltage 100 kV).

Specific surface areas were determined by the thermal argon desorption method [11] with an accuracy of ±10%. Texture parameters were derived from low-temperature (–196°C) nitrogen adsorption isotherms recorded on an ASAP-2400 system (Micromeritics).

RESULTS AND DISCUSSION

Comparing the properties of the flash and CTA products. Table 1 lists the most important properties of the flash product from the Achinsk alumina refinery and the CTA product. Clearly, these products differ not only in impurity and constitutional water contents but also in phase composition and, accordingly, specific surface area (S_{sp}). As compared to the CTA product, the flash product contains coarse hydrargillite and boehmite and a larger amount of the amorphous phase. The substances resulting from the heat treatment of the flash and CTA products are still more different.

According to our data (Table 2), the flash product calcined at 400°C consists largely of an amorphous phase and contains a small amount of crystalline boehmite. Raising the heat treatment temperature favors the crystallization of the amorphous phase into η-Al_2O_3, whose percentage increases with increasing temperature to reach 60% at 900°C. At this temperature, the χ-Al_2O_3 phase first appears among the products and the diffraction pattern indicates the onset of the formation of θ-Al_2O_3. The formation of η-Al_2O_3 rather than γ-Al_2O_3 is indicated by the fact that the parameter B, defined as the 311/222 reflection intensity ratio, is equal to 1.8 [12]. The sample calcined at 1000°C consists of 60% θ-Al_2O_3, 38% κ-Al_2O_3, and ~2% α-Al_2O_3. The sample heat-treated at 1100°C differs only by a higher percentage of the α-Al_2O_3 phase.

As distinct from the flash product, the CTA product partially crystallizes into γ-Al_2O_3 even at 400°C, as is indicated by $B = 1.33$ [12]. Raising the heat treatment temperature causes an increase in the γ-Al_2O_3 percentage, which is 100% at 800°C. At this stage of investigation, it is apparently more correct to call this phase γ-like for the following reasons. It was demonstrated in earlier studies [13, 14] that the formation of low-temperature alumina modifications is controlled by the size and shape of primary particles (the type of the developed face) and by the way these particles are stacked. Since there is no perfect structural order in the CTA product obtained under nonequilibrium (but well-reproducible) conditions, the "low-temperature" oxide resulting from this material can hardly be a pure phase. However, the similarity of this oxide to the γ-modification and the absence of χ-Al_2O_3 (according to X-ray diffraction data) is evidence that hydrargillite undergoes very special structural changes upon nonequilibrium heat treatment.

The formation of γ-like Al_2O_3 upon the thermal treatment of the CTA product is also evident from the observed values of the unit cell parameter a, which decreases from 7.922 Å at 400°C to 7.913 Å at 700–800°C (Table 2). These a values for γ-like Al_2O_3 are substantially smaller than the a values typical of γ-Al_2O_3 synthesized from pseudoboehmite [15], particularly at low temperatures, and coincide closely with reference data [16]. The size of crystallites in the γ-like phase increases from 25 to 40 Å as the temperature is

Table 2. Effect of the calcination temperature on the phase composition of the resulting oxides according to X-ray diffraction data

T_{calcin}, °C	Flash product		CTA product			
	phase composition	$B^* = 311/222$	phase composition	a, Å	D_{440}, Å	$B = 311/222$
400	3–5% crystalline boehmite + amorphous phase	–	Amorphous phase + ~30% γ-Al_2O_3	7.922	25	1.33
500	Amorphous phase	–	Amorphous phase + ~40% γ-Al_2O_3	7.916	30	1.33
600	Amorphous phase + ~10–15% γ-(η-) Al_2O_3	–	Amorphous phase + ~50% γ-Al_2O_3	7.914	35	1.40
700	Amorphous phase + ~25% η-Al_2O_3	1.8	Amorphous phase + ~60% γ-Al_2O_3	7.913	35	–
800	Amorphous phase + ~35% η-Al_2O_3	–	γ-Al_2O_3	7.913	40	–
900	60% η-Al_2O_3 + χ-like Al_2O_3; onset of the formation of θ-Al_2O_3	–	Poorly crystallized δ-Al_2O_3	–	45	–
1000**	60% θ-Al_2O_3 + 38% κ-Al_2O_3 + ~2% α-Al_2O_3	–	Well-crystallized δ-Al_2O_3	–	70	–
1100	~30% θ- + κ-Al_2O_3 65% α-Al_2O_3	–	50% δ- + 50% α-Al_2O_3	–	–	–

* For γ-Al_2O_3, γ^*-Al_2O_3, and η-Al_2O_3, which result from the heat treatment of pseudoboehmite, boehmite, and bayerite, B = 1.2–1.3, 1.05–1.12, and 1.8–1.9, respectively [12].

** The CTA product calcined at 1000°C for 8 h consists of θ-Al_2O_3 + 1% α-Al_2O_3.

raised. The formation of δ-Al_2O_3 begins at 900°C, and thermal treatment at 1000°C yields 100% δ-Al_2O_3. Thermal treatment at 1100°C yields approximately equal amounts of δ-Al_2O_3 and α-Al_2O_3 (Table 2).

As these changes in the phase composition take place, the resulting oxides form their texture. The specific surface areas of the aluminum oxides obtained from the flash and CTA products vary symbatically between 110 and 1100°C (Fig. 1a). However, in the temperature range 110–600°C, the S_{sp} of alumina obtained from the CTA product is 80–100 m^2/g larger than the S_{sp} of alumina obtained from the flash product. As the temperature is raised further, this difference gradually disappears. The way the pore volume of the resulting alumina varies with temperature is also independent of the starting material (Fig. 1b). The average pore diameter of the resulting alumina increases from 30 to 490 Å for the flash product and from 30 to 280 Å for the CTA product as the temperature is raised (Fig. 1c).

Thus, the above comparison of the starting flash and CTA products and their calcination products demonstrates that these materials are markedly different. A specific feature of the CTA product is that it yields γ-like Al_2O_3 upon heat treatment. Note that γ-Al_2O_3 obtained from pseudoboehmite or boehmite is the alumina modification most widely used in the industry [17]. Since γ-like Al_2O_3 obtained from the CTA product contains 0.16 wt % Na_2O (Table 1), it cannot be used in the synthesis of some catalysts without being purified by washing. Furthermore, the average particle size of the CTA product is ~80 μm, making it difficult to produce granular alumina. For certain applications, it is, therefore, necessary to hydrate the CTA product in order to obtain pseudoboehmite aluminum hydroxide containing much smaller amounts of undesired impurities.

Effect of CTA product hydration conditions on the properties of resulting aluminum hydroxide. The rehydration of the flash product depends on temperature, time, and the pH of the medium and proceeds according to the following scheme: flash product + $H_2O \longrightarrow$ amorphous gel $\longrightarrow$ pseudoboehmite $\longrightarrow$ boehmite $\longrightarrow$ $[Al(OH)_3]$ (bayerite) [18, 19]. Since aluminum hydroxide is amphoteric, varying the hydration conditions will lead to different hydroxide products. Depending on the pH of the medium, the $Al(OH)_3$ molecule is ionized as follows:

in a moderately acidic medium ($2 \le pH \le 5$)

$$Al(OH)_3 \longleftrightarrow Al(OH)_2^+ + OH^-;$$

at low pH ($pH < 2$)

$$Al(OH)_2^+ + OH^- \longleftrightarrow Al^{3+} + 3OH^-;$$

in an alkali medium ($8 \le pH \le 10$)

$$Al(OH)_3 \longleftrightarrow Al(OH)_2O^- + H^+;$$

at high pH ($pH > 10$)

$$Al(OH)_2O^- + H^+ \longleftrightarrow AlO_2^- + H^+ + H_2O.$$

Since the CTA product is amorphous to X-rays and contains a comparatively small amount of constitutional water (Table 1), its hydration likely has some specific features. It was demonstrated for the flash product that the main product of its rehydration in an alkali medium (pH 10) is aluminum trihydroxide (bayerite, hydrargillite, or nordstrandite) and that its proportion increases with increasing rehydration temperature and time [20]. The highest percentage of pseudoboehmite was obtained by the autoclave processing of hydrargillite at 130°C and pH 1.5–3.5 [21]. For this reason, in order to obtain aluminum hydroxide with a pseudoboehmite structure, the hydration of the CTA product was carried out in an acid medium at a certain acid modulus (*M*) and a temperature of 90–150°C either under hydrothermal conditions or at atmospheric pressure.

The aluminum hydroxides obtained by the hydration of the CTA products are characterized in Table 3. Clearly, the hydration of the CTA product changes its chemical and phase compositions and S_{sp}. Furthermore, all of these properties depend on hydration conditions.

It follows from the chemical analysis data (Table 3) that, as compared to the sodium oxide content of the starting CTA product, the Na_2O content of the samples obtained by hydrothermal hydration is approximately one order of magnitude lower (0.007–0.013 wt %) and the Na_2O content of the samples obtained by hydration at atmospheric pressure is lower by a factor of ~3. The iron oxide contents of the starting and hydrated materials do not exceed 0.05%.

The amount of constitutional water in the aluminum hydroxide samples prepared from the CTA product varies between 1.00 and 1.54 (mol H_2O)/(mol Al_2O_3) and is determined by the hydration conditions (Table 3). The constitutional water content of the 140-24-0.1 N sample (Table 3, entry 6) is 1.54 (mol H_2O)/(mol Al_2O_3). This value is comparable with the water content of pseudoboehmite precipitated from an aluminum nitrate solution (Table 3, entry 15).

According to X-ray diffraction data, the hydroxides synthesized consist largely of two phases, namely, an X-ray-amorphous phase and pseudoboehmite, whose ratio is determined by hydration conditions. Raising the hydrothermal synthesis temperature in the order 130 $\longrightarrow$ 140 $\longrightarrow$ 150°C while keeping the other conditions constant increases the pseudoboehmite percentage in the order 47 $\longrightarrow$ 60 $\longrightarrow$ 75%. A similar trend is observed as the hydrothermal processing time is lengthened. Increasing the acid modulus causes a decrease in the pseudoboehmite percentage (Table 3, entries 3, 8). The highest pseudoboehmite content, which is 75%, is observed in the 150-24-0.1 N sample (Table 3, entry 7), but the b (d/n_{020}) value for this sample is 6.16 Å, which is much smaller than the same value for the pseudoboehmite sample obtained by precipitation. The pseudoboehmite percentage can be changed by replacing nitric acid with acetic acid or PVA. This replacement seems to be appropriate because it rules out the evolution of nitrogen oxides during the heat treatment of aluminum hydroxide obtained in the presence of nitric acid. The hydrothermal processing of the CTA product in the presence of acetic acid yields a slightly lower percentage of pseudoboehmite, and the same processing in the presence of PVA leads to a higher pseudoboehmite percentage (Table 3).

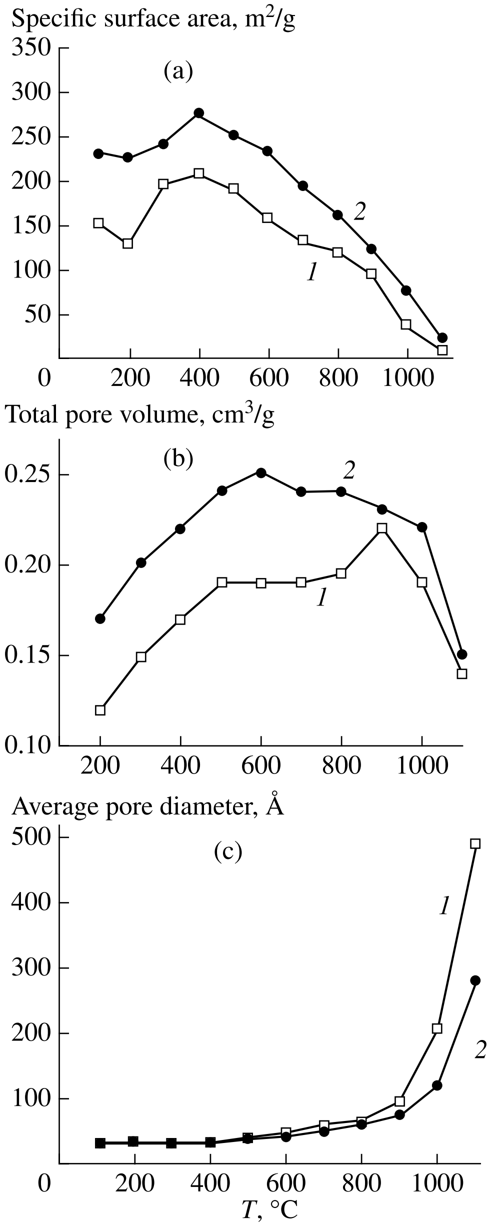

Fig. 1. (a) Specific surface area, (b) total pore volume, and (c) average pore diameter versus calcination temperature for the (*1*) flash and (*2*) CTA products.

According to thermoanalytical data, the thermolysis of a hydroxide sample depends on whether it is obtained in the presence of nitric or acetic acids or PVA. The nonisothermal processing of the 140-24-0.1 N sample (Table 3, entry 5) gives rise to endotherms at 150 and 460°C (Fig. 2a), which are due to the loss of physically adsorbed water and pseudoboehmite dehy-

Table 3. Effect of CTA product hydration conditions on the chemical and phase compositions and S_{sp} of the resulting aluminum hydroxide

Entry	Sample (T–τ–M–K)*	Chemical composition			X-ray diffraction data**				S_{sp}, m^2/g (110°C)
		Na_2O, %	Fe_2O_3, %	H_2O, mol/(mol Al_2O_3)	Am, %	Pbo			
						%	$b = d/n_{020}$, Å	D_{020}, Å	
1	CTA product	0.16	0.05	0.75	+	~25	–	–	165
	Hydrothermal processing								
2	95–24–0.1 N	–	–	1.44	+	30	–	–	176
3	130–24–0.1 N	0.013	0.04	1.30	53	47	6.24	60	345
4	130–48–0.1 N	–	–	1.28	35	65	–	75	300
5	140–24–0.1 N	0.009	0.05	1.42	40	60	6.24	65	330
6	140–24–0.1 N***	0.013	0.05	1.54	20	80	6.22	60	295
7	150–24–0.1 N	–	–	1.22	25	75	6.16	75	305
8	130–24–0.2 N	–	–	1.37	50	50	6.21	60	260
9	130–24–0.3 Ac	0.007	0.05	1.38	50	50	6.28	45	290
10	140–24–PVA	–	–	1.07	0	100	6.17	105	180
	Hydration at atmospheric pressure								
11	90–24–0.05 N	0.05	0.04	1.00	70	30	6.19	40	210
12	90–24–0.1 N	0.05	0.04	1.06	65	35	6.21	45	260
13	90–24–0.12 N***	–	–	1.16	37	66	6.31	25	315
14	90–24–0.3 Ac	0.067	0.05	1.28	60	40	6.42	40	270
15	Precipitation	<0.001	0.001	1.52	0	100	6.51	25	360

*T is the processing temperature, °C; τ is the processing time, h; M is the acid modulus; K is the component introduced (N = nitric acid. Ac = acetic acid, and PVA is polyvinyl alcohol).

**Am = amorphous phase, and Pbo = pseudoboehmite.

***Aqueous ammonia was added to the slurry that resulted from the hydrothermal process.

dration [13], respectively. In the DTA curves of the 140-24-0.3 Ac and 140-24-PVA samples (Table 3, entries 9, 10), these endotherms are present along with exotherms at 310 and 520°C, respectively (Figs. 2b, 2c), which are due to the oxidation of the organic moieties of the admixtures introduced at the hydration stage. Note that the DTA curves of the materials examined show no exotherm at 800–810°C, indicating that there is no crystallization of amorphous hydroxide, although this exotherm is observed for the initial CTA product (Fig. 2d). Therefore, aluminum hydroxide resulting from the hydration of the CTA product consists only of the pseudoboehmite phase and part of this phase is too fine to be detected by X-ray diffraction. This assumption is confirmed by the fact that the pseudoboehmite percentage increases upon addition of a small volume of aqueous ammonia to the slurry before filtration (Table 3, entries 6, 13).

The above inference is also supported by electron microscopic data for the samples containing 100 and 66% pseudoboehmite (Table 3, entries 10, 14). The morphology of the particles of these samples is typical of pseudoboehmite (Fig. 3), irrespective of the pseudoboehmite content, and can be described as fibers stacked into loose aggregates with various degrees of crystallinity. The 100% pseudoboehmite sample has a high degree of crystallinity: its microdiffraction pattern is a set of thin diffraction rings made up of spot reflections (Fig. 3a). The sample containing 66% pseudoboehmite (according to X-ray diffraction data) has a higher defect concentration or a lower degree of order inside the aggregates, as is indicated by the fact that its microdiffraction pattern shows a set of comparatively broad circular reflections and few, if any, spot reflections (Fig. 3b). No amorphous phase was detected in this sample. Therefore, the thermoanalytical and electron microscopic data suggest that aluminum hydroxide resulting from the hydration of the CTA product consists largely of pseudoboehmite with various degrees of order and crystallinity.

A specific feature of pseudoboehmite resulting from the CTA product is that its b value is smaller than the same value for precipitated pseudoboehmite (Table 3). This is evidence that pseudoboehmite obtained from

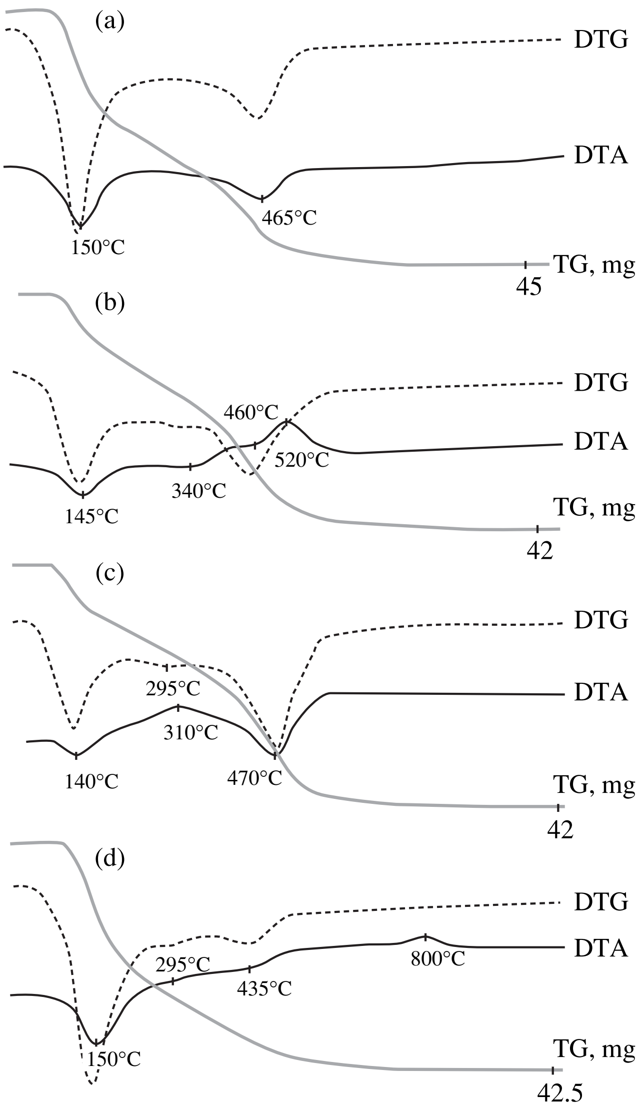

Fig. 2. Thermoanalytical curves for (a) CTA(140-24-0.1 N), (b) CTA(140-24 Ac), (c) CTA(140-24-PVA, and (d) the CTA product.

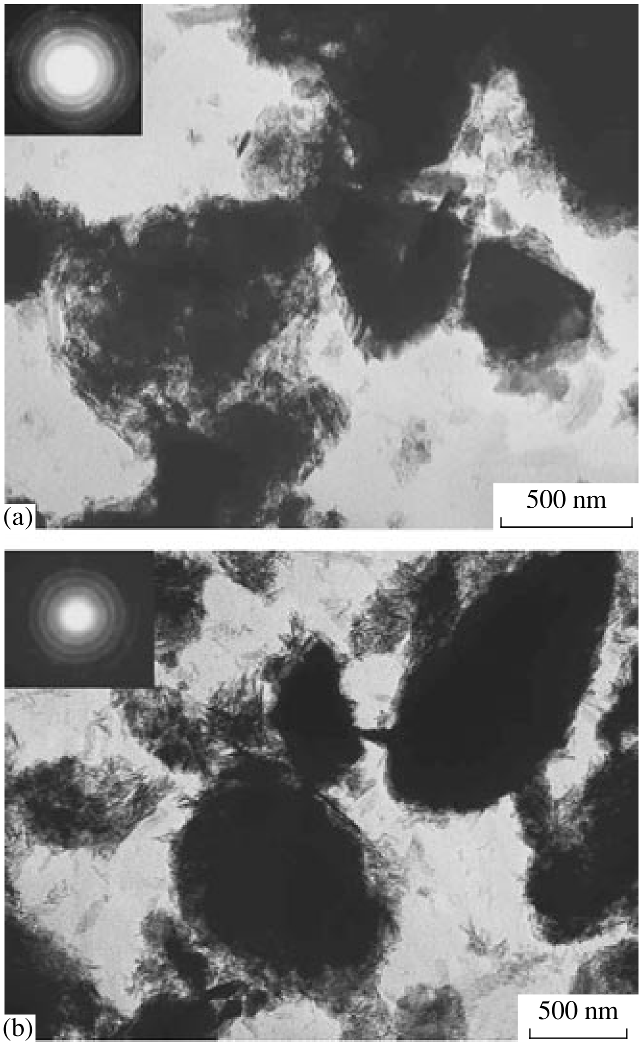

Fig. 3. Electron micrographs of the starting materials (a) 140-24-PVA and (b) 90-24-0.1 N obtained by the hydration of the CTA product.

the CTA product has a smaller proportion of interlayer water and a higher degree of crystallinity [17]. Indeed, as compared to pseudoboehmite obtained by precipitation, most of the samples have a lower constitutional water content (Table 3) and a larger crystallite size (Table 4). Note that, for pseudoboehmite synthesized by precipitation (Table 4, entry 15), the crystallite size increases in the order $\langle 020\rangle \longrightarrow \langle 120\rangle \longrightarrow \langle 031\rangle$, the average being (30 ± 5) Å. A similar trend of the particle size is observed for the CTA pseudoboehmite samples 3 and 5 (Table 4). In the other two samples (nos. 9 and 10), the crystallites grow primarily in the $\langle 120\rangle$ direction; that is, acetic acid and PVA alter the way the particles form.

This difference between the particle sizes of forming aluminum hydroxides determines the S_{sp} value. It is clear from Table 3 that S_{sp} ranges between 180 and 350 m^2/g; depends on the CTA product hydration conditions; and, for some samples, takes a value characteristic of precipitated pseudoboehmite. However, for the sample that is prepared in the presence of PVA and consists of 100% pseudoboehmite, S_{sp} is as small as 180 m^2/g. This small S_{sp} value is possibly due to PVA blocking up part of the pore space, thus making part of the internal surface of the sample inaccessible.

Figure 4 shows typical nitrogen adsorption isotherms and the corresponding pore size distributions for the samples dried at 110°C. The starting CTA product has a narrow pore size distribution (Fig. 4a). Its pore volume is 0.12 cm^3/g, and its average pore diameter is 30 Å, which are smaller than the corresponding parameters of precipitated aluminum hydroxide (0.3 cm^3/g, 40 Å). The hydrothermal processing of the CTA product causes an increase in the total pore volume and gen-

Table 4. Crystallite sizes along different crystallographic directions for pseudoboehmite samples obtained under different conditions

Entry*	Sample	Pbo**, %	D_{020}, Å	D_{120}, Å	D_{031}, Å
3	130–24–0.1 N	47	45	50	50
5	140–24–0.1 N	60	50	65	70
9	140–24–0.3 Ac	50	60	80	70
10	140–24–PVA	100	105	130	120
15	Precipitated Pbo	100	25	30	35

* The samples are numbered in the same way as in Table 3.

** Pbo = pseudoboehmite.

erally alters the volumetric pore size distribution (Fig. 4b). For the 140-24-0.1 N sample containing 60% pseudoboehmite (Table 3), the pore size distribution is bimodal, the pore volume is 0.25 cm^3/g, and the average pore diameter is 40 Å.

Thus, our study of the effect of hydration conditions on the formation of pseudoboehmite aluminum hydroxides from the CTA product has demonstrated that nearly pure pseudoboehmite can be obtained under certain conditions, but the properties of this material will differ from the properties of precipitated aluminum hydroxide. The difference is that the pseudoboehmite obtained by the hydrothermal processing of the STA product is better crystallized (b = 6.16–6.28 Å) and can be viewed as so-called microcrystalline pseudoboehmite [17]. The hydrothermal processing of the CTA

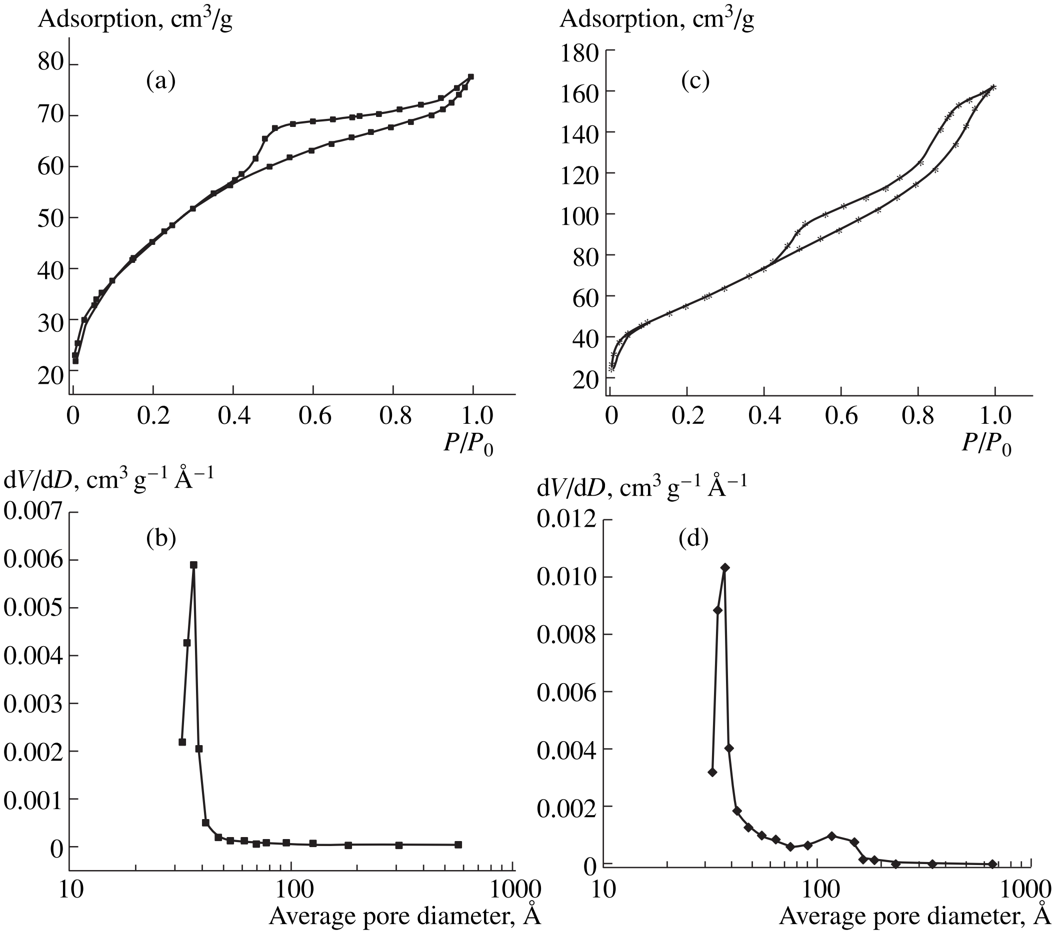

Fig. 4. Adsorption isotherms and pore size distribution functions for (a, b) the CTA product and (c, d) aluminum hydroxide obtained by the hydration of the CTA product (sample 140-24-0.1 N).

Table 5. Effect of the calcination temperature on the phase composition of alumina

Sample no.	Starting aluminum hydroxide	Processing temperature, °C	Phase composition				S_{sp}, m^2/g
			phase	%	a, Å	D_{440}, Å	
1	140–24–0.1 N	600	γ-$Al_2O_3^{**}$	50	7.914	45	234
	(40% Am–60% Pbo)	800	γ-Al_2O_3	100	7.905	60	182
		900*	γ-Al_2O_3	~100	7.903	60	170
		1000	δ-Al_2O_3	100	–	75	114
		1100	δ- + 58% α-Al_2O_3	–	–	–	26
2	150–24–0.1 N	600	γ-$Al_2O_3^{**}$	65	7.911	50	250
	(25% Am–75% Pbo)	800	γ-Al_2O_3	100	7.907	60	184
		900*	γ-Al_2O_3	~100	7.903	60	160
		1000	δ-Al_2O_3	100	–	80	115
		1100	δ- + 22% α-Al_2O_3	–	–	–	68
3	140–24–PVA	600	γ-$Al_2O_3^{**}$	80	7.913	50	222
	(100% Pbo)	800	γ-Al_2O_3	100	7.903	60	178
		900*	γ-Al_2O_3	~100	7.901	60	146
		1000	δ-Al_2O_3	100	–	90	88
		1100	δ- + 85% α-Al_2O_3	–	–	–	15
4	Precipitated pseudoboehmite (100% Pbo)	600	γ-Al_2O_3	100	7.932	40	283
		800	γ-Al_2O_3	100	7.913	50	235
		900	γ-Al_2O_3	100	7.911	55	196
		1000	γ- + δ-Al_2O_3 (traces)	–	–	70	134
		1100	δ- + 13% α-Al_2O_3	–	–	–	60

* T = 900°C is the temperature at which the formation of δ-Al_2O_3 begins.

** The balance is an X-ray-amorphous phase.

product at atmospheric pressure yields aluminum hydroxide similar in properties (b = 6.31–6.42 Å) to precipitated pseudoboehmite.

Effects of the nature of the starting hydroxide and of the processing temperature on the properties of the resulting alumina. In order to elucidate the effect of the nature of the starting hydroxide (obtained by the hydration of the CTA product) on alumina structure and texture formation, we selected samples (Table 5) differing in terms of preparation conditions and, accordingly, the ratio of the amorphous phase to pseudoboehmite (as determined by X-ray diffraction).

The heat treatment of these aluminum hydroxide samples at 600°C favors the formation of γ-Al_2O_3 (Table 5). The percentage of this phase varies in the same way as the pseudoboehmite content of the starting hydroxide. The unit cell parameter a of this phase is 7.911–7.914 Å, while a for γ-Al_2O_3 obtained from pseudoboehmite has a much larger value of 7.932 Å. This difference can be due to these oxides differing either in the degree of crystallinity or in the distribution of aluminum cations among the tetrahedral and octahedral sites of the cubic lattice. The crystallite size is 45–50 Å for γ-Al_2O_3 samples 1–3 (Table 5) and 40 Å for alumina obtained from pseudoboehmite.

It was demonstrated by electron microscopy (Fig. 5) that alumina calcined at 600°C consists of ~200-nm aggregates of fine fiberlike particles (d = 3.5–4.0 nm), no matter what the ratio of the amorphous phase to pseudoboehmite in the starting hydroxide, obtained by the hydration of the CTA product. The microdiffraction pattern from an isolated γ-Al_2O_3 particle (see the inset in Fig. 5) is circular, with diffuse broad reflections. This may be due to the development of a pore structure inside the particle during the hydroxide-to-oxide phase transition. At the same time, the γ-Al_2O_3 particles resulting from pseudoboehmite are known to be aggregates (with a size of >100 nm) consisting of finer (2-nm) particles [13]. The particles in such an aggregate are oriented at large angles relative to one another.

Raising the heat treatment temperature to 800°C favors the buildup of γ-Al_2O_3 up to 100% and the

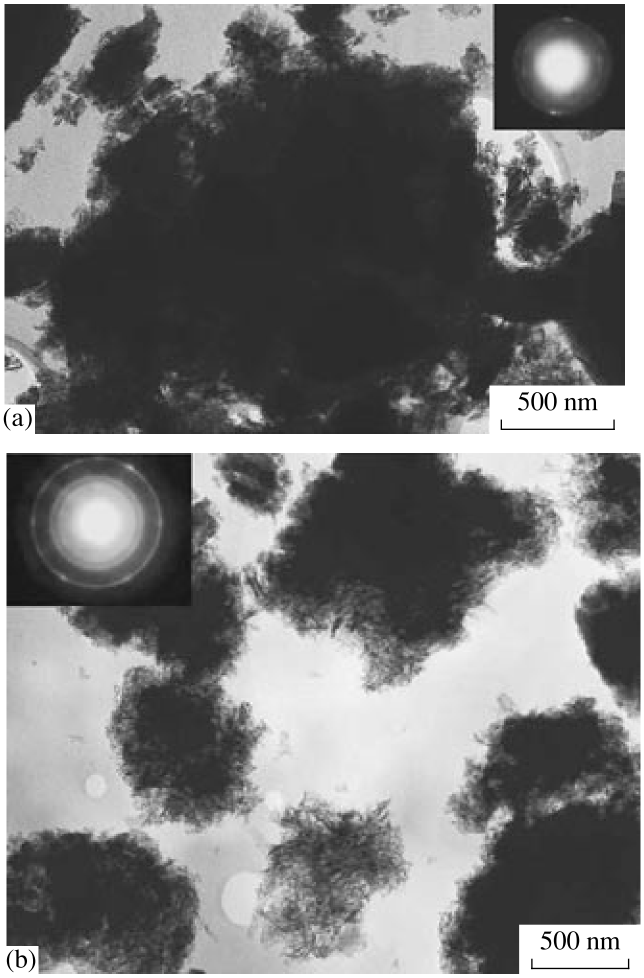

Fig. 5. Electron micrographs of alumina samples obtained by the calcination of the (a) CTA(140-24-PVA) and (b) CTA(90-24-0.12 N) aluminum hydroxides at 600°C.

growth of its crystallites up to 60 Å, reducing the unit cell parameter *a* to 7.905 ± 0.002 Å (Table 5). The δ-Al_2O_3 phase begins to form upon the heat treatment of the hydroxides at 900°C, and its formation is almost complete at 1000°C. Raising the temperature to 1100°C favors the crystallization of α-Al_2O_3, whose percentage increases in the order Pbo (precipitated) < CTA(150-24) < CTA(140-24) < CTA (140-24-PVA). Thus, the α-Al_2O_3 crystallization rate depends on the temperature of the hydrothermal synthesis of the initial hydroxide.

If the phase transitions occurring during the heat treatment of precipitated pseudoboehmite are taken into consideration, it will be clear that the structural transformation of the γ-oxide into the α-oxide in the CTA sample series proceeds at a higher rate than the same transformation in the precipitated pseudoboehmite series; in the latter case, δ-Al_2O_3 begins to form only upon heat treatment at 1000°C. Moreover, among the samples examined, precipitated pseudoboehmite yields the lowest α-Al_2O_3 percentage at 1100°C (Table 5).

During the nonisothermal heat treatment of pseudoboehmite, α-Al_2O_3 crystallization occurs at 1195°C [13]. The isothermal heat treatment of aluminum hydroxide at 1100°C for 4 h speeds up the crystallization of α-Al_2O_3. The percentage of α-alumina in this case is determined by the nature of the starting hydroxide. In particular, sample 3 (Table 5), obtained in the presence of PVA, contains the largest amount of α-Al_2O_3 after heat treatment at 1100°C. This is possibly due to the fact that PVA burnout causes local overheatings, which can initiate the formation of α-alumina nuclei. As the temperature is raised, these nuclei can become crystallization centers to accelerate the process.

An unexpected result was provided by the heat treatment of hydroxides hydrothermally synthesized at different temperatures (140 and 150°C; samples 1 and 2 in Table 5), which, therefore, contained different percentages of pseudoboehmite (60 and 75%, respectively). After these samples were calcined at 1100°C, their α-Al_2O_3 contents were found to be 58 and 22%, respectively (Table 5). This effect may be due to the specific structural features of the pseudoboehmite phase in these samples. Indeed, the interplanar spacing *b* for pseudoboehmite present in samples 1 and 2 (Table 3) is 6.24 and 6.16 Å, respectively. As mentioned above, the smaller the *b* value, the lower the interlayer water content of the pseudoboehmite and the higher the degree of crystallinity of this phase.

According to earlier data [13], the crystallization of α-Al_2O_3 from boehmite (AlOOH) occurs ~100°C higher than the crystallization of the same phase from pseudoboehmite ($AlOOH \cdot 1.5H_2O$); that is, boehmite, a better crystallized phase, recrystallizes into alumina at a lower rate. Therefore, the structural transformation of pseudoboehmite with $b = 6.16$ Å would be expected to proceed at a lower rate and to yield a lower percentage of α-Al_2O_3 than the structural transformation of pseudoboehmite with $b = 6.24$ Å. This deduction is indeed confirmed by our experimental data.

The specific surface area of the oxides obtained at 600–1000°C is independent of the amorphous phase/pseudoboehmite ratio in the starting hydroxide (Table 5) and is determined by the calcination temperature. As the temperature is raised, S_{sp} decreases from 250 to 110 m^2/g. The specific surface area of the oxides calcined at 1100°C is determined by the percentage of α-Al_2O_3 formed and decreases as the alumina content increases:

Pbo_{precip} < CTA(150–32) < CTA(140–24) <
CTA(140–24–PVA)

α-Al_2O_3, %	13	22	58	85
S_{sp}, m^2/g	60	68	26	15

The changes in S_{sp} are accompanied by changes in the pore structure of alumina. Figure 6 plots the nitrogen

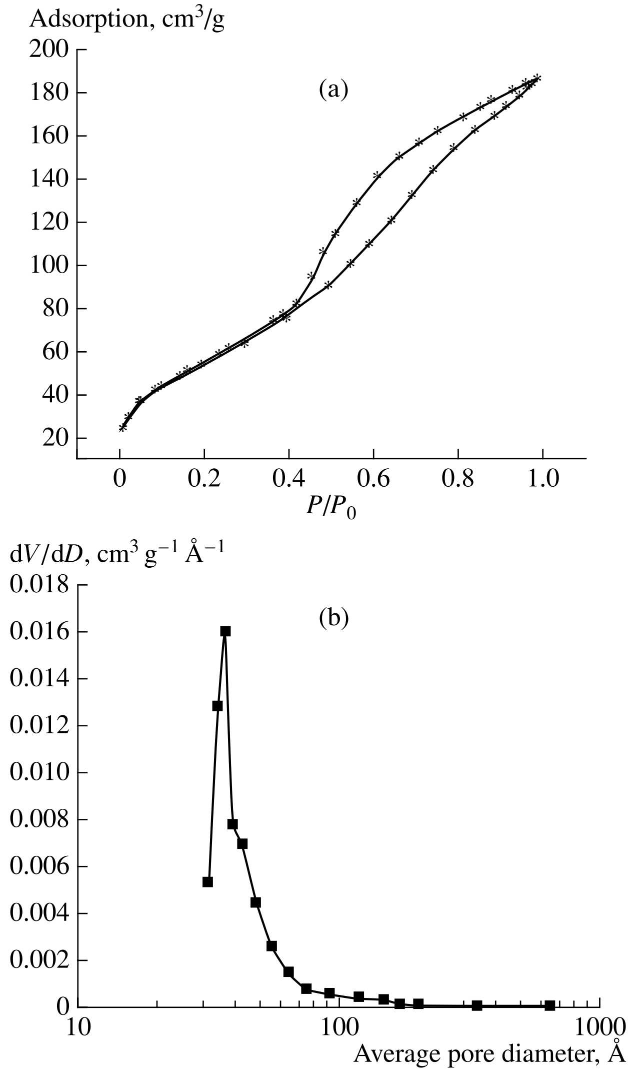

Fig. 6. (a) Adsorption isotherm and (b) pore size distribution for alumina obtained by the heat treatment of the CTA(140-24-0.1 N) hydroxide at 600°C.

adsorption isotherm and the pore size distribution derived from this isotherm for the CTA(140-24-0.1 N) sample calcined at 600°C. The pore size distribution is definitely bimodal, and the average pore diameter is 58 Å. The pore volume in this oxide is 0.29 cm^3/g (Table 6).

Table 6. Textural properties of aluminum oxides obtained at 600°C

Sample	Low-temperature N_2 adsorption data		
	S_{sp}, m^2/g	Pore volume, cm^3/g	Average pore diameter, Å
CTA(140–24–0.1 N)	200	0.29	58
CTA(140–24–0.3 Ac)	206	0.27	52
CTA(140–24–PVA)	220	0.27	49
CTA(150–24–0.1 N)	185	0.37	81

The aluminum oxides obtained from hydroxides synthesized under different conditions were found to have similar textural properties (Table 6). The only exception is alumina obtained by the calcination of CTA(150-24-0.1 N). This material has a larger pore volume and a larger average pore diameter. Thus, the pore structure of alumina can be controlled by varying the conditions of hydroxide synthesis from the CTA product.

The hydration of the CTA product in an acid medium affords nearly 100% fine-particle pseudoboehmite with a specific surface area of 180–350 m^2/g, a pore volume of 0.14–0.27 cm^3/g, and an average pore diameter of 26–56 Å. The degree of crystallinity of the resulting pseudoboehmite depends on the CTA product hydration conditions. Hydrothermal processing yields a better crystallized pseudoboehmite phase (b = 6.16–6.28 Å), which can be regarded as microcrystalline, while hydration at atmospheric pressure yields worse crystallized alumina (b = 6.31–6.42 Å) similar in properties to precipitated pseudoboehmite (b = 6.51 Å).

The heat treatment, at 600°C, of pseudoboehmite obtained by the hydration of the CTA product favors the crystallization of γ-Al_2O_3 with S_{sp} = 220–260 m^2/g; the amount of γ-Al_2O_3 increases to 100% as the temperature is raised to 800°C. The texture of γ-Al_2O_3 is determined by the heat treatment temperature and by the nature of the initial aluminum hydroxide obtained by hydrating the CTA product.

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