

## Real Structure of Metastable Forms of Aluminum Oxide

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**Abstract**—Differences in the real structure of  $\gamma$ - $\text{Al}_2\text{O}_3$  samples obtained by the thermal decomposition of pseudoboehmite and boehmite prepared by the hydrothermal treatment of bayerite were found. The transformations of these structures during their conversion to  $\delta$ - $\text{Al}_2\text{O}_3$  as the treatment temperature increased were studied. The rate of conversion of metastable alumina species into the stable  $\alpha$ - $\text{Al}_2\text{O}_3$  phase significantly depends on the real structure of samples. The rate of this transformation is drastically retarded in the presence of extended defects in the oxides originated from boehmite, and the stability of metastable alumina species increased as the degree of surface dehydroxylation increased.

### INTRODUCTION

A wide field of application for aluminum oxide results from structural features of its modifications ( $\gamma$ -,  $\eta$ -,  $\chi$ -,  $\delta$ -,  $\theta$ -,  $\kappa$ -, and  $\alpha$ - $\text{Al}_2\text{O}_3$ ), which, in turn, determine the dispersity and state of an oxide surface. By now, a great body of information on physical and chemical properties of different modifications of aluminum oxide has been accumulated [1–5]; however, the problem of the real structure of low-temperature forms and their transformations during thermal treatment still remains a topic for discussion.

Active aluminum oxide is mainly prepared by the thermal decomposition of aluminum hydroxide. Depending on the conditions of synthesis, the latter is formed in different modifications (amorphous, pseudoboehmite, boehmite, bayerite, and hydrargillite) [1, 3, 4, 6] which differ in chemical composition and crystal structure; therefore, the thermal transformations of each of them proceed via their own pathways. At present, there is no single viewpoint on the mechanism of the thermal decomposition of the corresponding hydroxides [2, 3, 7].

The goal of this work is to study the real structure of low-temperature metastable aluminum oxides obtained under comparable conditions by the thermal decomposition of pseudoboehmite and boehmite prepared by the hydrothermal treatment of bayerite and to examine the effect of the structure on the transformation of the above species to stable oxides.

The distinctive feature of boehmite synthesized by precipitation, as compared to boehmite obtained by hydrothermal treatment, may be its phase inhomogeneity (the presence of an impurity of another hydroxide modification) and the presence of alkaline metal cations. It is known that these factors affect phase transformations and the state of surfaces. Boehmite obtained

from an appropriate initial material by hydrothermal treatment may be rather chemically pure.

### EXPERIMENTAL

Pseudoboehmite was obtained by precipitation from an aluminum nitrate solution with an aqueous ammonia solution at constant pH and temperature followed by filtration and washing of the precipitate with distilled water until a negative reaction for nitrate ions in the filtrate occurred. Boehmite was prepared by the hydrothermal treatment of bayerite at 300°C with an exposure under isothermal conditions for 18 h. The synthesized precipitates were dried at 110°C to constant weight and then calcined at 600, 800, 900, 1000, or 1200°C under isothermal conditions for 4 h.

The impurities in the samples of initial aluminum hydroxides were determined by atomic absorption spectrometry [8] and the Kjeldahl method (nitrates) [9]. The thermal analysis of the samples was carried out on a DQ1500-D derivatograph in the temperature range from room temperature to 1300–1400°C at a heating rate of 7.5 K/min in air. The sample weight was 0.5 g; the accuracy of determining weight losses was  $\pm 0.5\%$ . The micrographs were taken with a JEM-2010 electron microscope. X-ray diffraction was studied using an URD-63 diffractometer. The amount of the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase was determined from the calibration graphs presented in [10]. The IR spectra of the samples were recorded on an UR-20 spectrometer in the range 2000–4000  $\text{cm}^{-1}$ . The samples were pressed in pellets without a binder; the pellets with a density of  $(8\text{--}10) \times 10^{-3} \text{ g/cm}^2$  were evacuated in a cell of the IR spectrometer at 500°C for 2 h. Specific surface areas of the samples were determined by the thermal desorption of argon [11]; texture characteristics were calculated from the isotherms of low-temperature ( $-196^\circ\text{C}$ ) nitrogen

adsorption, which were measured on a DIGISORB 2600 unit.

## RESULTS AND DISCUSSION

Because the real structure of metastable alumina species significantly depends on the chemical purity of initial hydroxides, this problem has been given particular attention in the synthesis of samples. First, aluminum nitrate of high-purity grade, which contained no more than 0.005% impurities, was used in the precipitation of hydroxides. Second, according to the data obtained (Table 1), the total impurity of content pseudoboehmite was no higher than 0.022 wt %; in boehmite, 0.60 wt %, of which 0.57 wt % fell on the silicon fraction. Nitrates were not found. The samples of pseudoboehmite and boehmite contained 1.52 and 1.06 mol H<sub>2</sub>O per mole Al<sub>2</sub>O<sub>3</sub>, respectively. The specific surface areas of pseudoboehmite and boehmite were 420 and 2 m<sup>2</sup>/g., respectively

The temperature-programmed heating of the initial hydroxides in air was accompanied by the appearance of low- and high-temperature peaks in the DTA curves (Fig. 1). The endo effects at 130–160°C were caused by the removal of unbonded water; the endo effects at 440 and 510°C were due to the dehydration of pseudoboehmite and boehmite, respectively, to form  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>; and the exo effects at 1195 and 1280°C resulted from the crystallization of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The results obtained are in reasonable agreement with the published data [4, 12]. One of the distinctions is that the exo effects in the DTA curves of pseudoboehmite and boehmite were shifted to higher temperatures (for the pseudoboehmite series, they were shifted from 1140 to 1195°C; for the boehmite series, from 1265 to 1280°C [4]), and the intensity of the boehmite exo peak was very low (Fig. 1). In the case of pseudoboehmite, the temperature shifts observed may have resulted from greater phase homogeneity, because the samples examined in [4] contained an amount of the amorphous phase which transformed to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at a lower temperature. In the case of boehmite, the shifts of temperatures may be due to its higher chemical purity, because boehmite samples used in [4] were obtained by the hydrothermal treatment of hydrargillite.

According to XRD data, after the isothermal treatment of the initial hydroxides in air at 600°C, the samples were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. It was demonstrated by high-resolution electron microscopy that the samples of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (A-I) obtained from pseudoboehmite were aggregates (larger than 100 nm) consisting of highly dispersed (~2 nm) oxide particles (Fig. 2a). The structure of microparticles was rather regular; however, according to XRD data, it contained a great number of layer displacement defects, which caused anisotropic broadening of the diffraction peaks. The particles in an aggregate were disoriented and arranged at large angles to each other. It follows from the adsorption data that the aggregates of particles had a considerable pore volume

**Table 1.** Characteristics of initial hydroxides

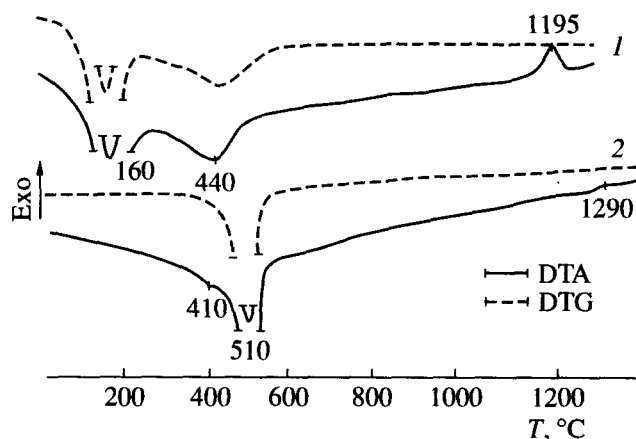
Hydroxide	Impurities (wt %)				H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> , mol/mol	S <sub>sp</sub> , m <sup>2</sup> /g
	NO <sub>3</sub> <sup>-</sup>	Na	Fe	Si		
Pseudo-boehmite	0	<0.001	0.001	0.02	1.52	420
Boehmite	0	<0.001	0.024	0.57	1.06	2

equal to 0.43 cm<sup>3</sup>/g (Table 2). The pore size distribution was rather narrow; the predominant pore diameter was 7 nm; micropores were absent. The specific surface area of sample A-I at the given temperature was 220 m<sup>2</sup>/g.

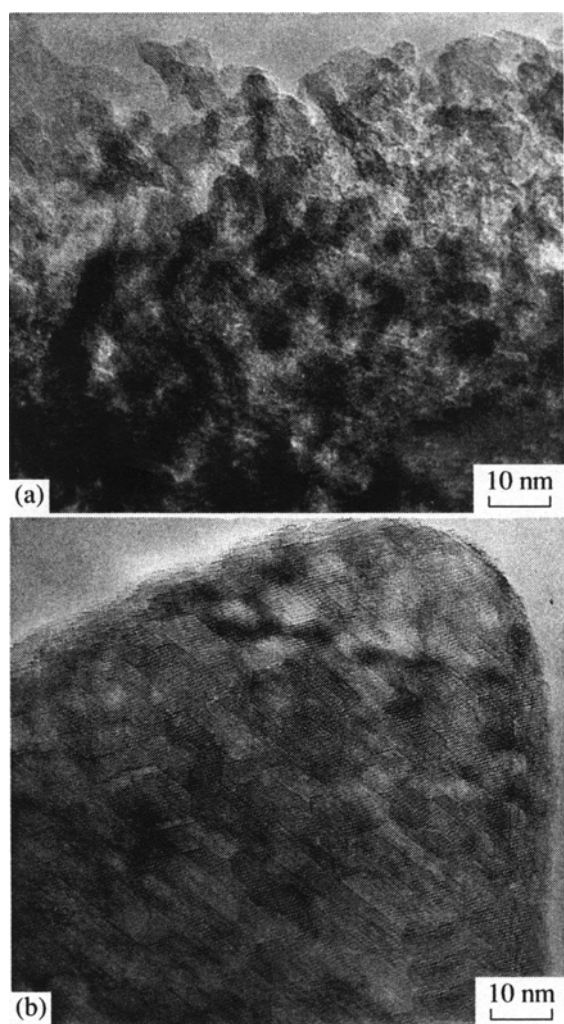
The particles of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (A-II) obtained from boehmite had a shape of extended (~100 nm) thin single-crystal plates with the most developed (110) face (Fig. 2b). An important specific feature of their microstructural arrangement is the presence of specific closed-type defects formed by extended dislocation walls. The latter resulted from the coalescence of lattice vacancies during the formation of the structure of samples A-II. The samples of this series possess almost the same pore volume as samples A-I (Table 2). However, the pore size distribution is absolutely different: the fraction of pores with  $2 \leq d \leq 10$  nm is insignificant; pores with  $d \geq 10$  nm represent the major fraction; and the predominant pore diameter is 150 nm. The specific surface area of this sample is 90 m<sup>2</sup>/g (Table 2).

A further increase in the temperature of calcination of the initial hydroxides to 800–900°C was not accompanied by considerable structural changes; only a decrease in the specific surface area of the samples was observed (Table 2); this fact is in agreement with the decrease in the volume of fine pores ( $2 \leq d \leq 10$  nm), though no pore size redistribution occurred.

The XRD analysis of the samples calcined at 1000°C showed that the structure of  $\delta$ -Al<sub>2</sub>O<sub>3</sub> began to form in them, while, for the major part, the structure of



**Fig. 1.** DTA and DTG curves for (1) pseudoboehmite and (2) boehmite.



**Fig. 2.** Electron micrographs of the  $\gamma\text{-Al}_2\text{O}_3$  samples obtained by the thermal treatment of (a) pseudoboehmite and (b) boehmite at 600°C.

$\gamma\text{-Al}_2\text{O}_3$  was retained in both the pseudoboehmite and boehmite series of samples. The electron-microscopic studies of these samples demonstrated that, at the specified temperature, the structure of the oxide originated from boehmite changed in the bulk of a microcrystal, and these changes were accompanied by the rearrange-

ment of the extended defects. The formation of  $\delta\text{-Al}_2\text{O}_3$  in the pseudoboehmite series occurred discretely in isolated microparticles, whereas the  $\gamma\text{-Al}_2\text{O}_3$  structure in other microparticles of the same polycrystalline aggregate remained unchanged.

For an understanding of the mechanism of structural changes in the aluminum oxides formed from pseudoboehmite and boehmite, we comprehensively investigated the thermal behavior of aluminum oxides precalcined at appropriate temperatures. Both the pseudoboehmite and boehmite series of samples (Fig. 3), as well as the initial hydroxides (Fig. 1), exhibited no thermal effects due to the transitions of  $\gamma\text{-Al}_2\text{O}_3$  to  $\delta\text{-}$  and  $\theta\text{-Al}_2\text{O}_3$ . In the case of samples of the pseudoboehmite series, well-defined exothermic peaks corresponding to the transformation to  $\alpha\text{-Al}_2\text{O}_3$  were observed at 1180 and 1175°C for the samples calcined at 600 and 1000°C, respectively. For the samples that originated from boehmite, again, only an insignificant (trace) exothermic peak caused by the transition to  $\alpha\text{-Al}_2\text{O}_3$  was detected at 1280°C. Water losses for the test samples heated to certain temperatures were calculated from the thermal analysis data (Table 3).

The samples of both series calcined at 600 and 1000°C rehydrated in air, as demonstrated by the water losses measured. The character of changes in the water losses within each series was identical: as the calcination temperature increased up to 600°C, the water losses monotonically decreased and passed through maximum values at 800 and 1000°C. The samples of the pseudoboehmite series lost greater amounts of water than the samples of the boehmite series at all of the temperatures, all other factors being the same. As mentioned above, the  $\alpha\text{-Al}_2\text{O}_3$  phase appeared at a lower temperature (Figs. 1, 3). It should be noted that samples A-I calcined at 600 and 1000°C and were dehydrated to a greater extent than the initial hydroxide; evidently, for this reason, the temperature at which  $\alpha\text{-Al}_2\text{O}_3$  appeared (the position of the exo peak) was shifted to lower temperatures (Figs. 1, 3).

The difference in the removal of water from the samples could have resulted from the nature of bonding between hydroxyl groups and corresponding fragments of the surface and from the parameters of the real structure of metastable alumina species, including the particle size and shape and the pore sizes.

The IR-spectroscopic study of samples A-I and A-II calcined at 600°C demonstrated (Table 4) that the spectra of the hydroxyl coverage of  $\gamma\text{-Al}_2\text{O}_3$  obtained from both pseudoboehmite and boehmite exhibited eight absorption bands. In accordance with the present view, these bands ( $\text{cm}^{-1}$ ) correspond to the following structures: (I)  $\text{Al}_i\text{OH}$  (3795); (II)  $\text{Al}_o\text{OH}-\text{Al}_s\text{OH}$  (3775–3750); (III)  $\text{Al}_o\text{OHAl}_o$  (3735); (IV)  $\text{Al}_s\text{OHAl}_o$  (3710); (V)  $\text{Al}_s\text{OHAl}_i$  (3685); (VI)  $\text{Al}_s\text{OHAl}_i-\text{Al}_i\text{OHAl}_o$  (3675); and (VII)  $\text{Al}_i\text{OHAl}_o$  (3670), where  $\text{Al}_i$ ,  $\text{Al}_o$ , and  $\text{Al}_s$  are tetrahedral, octahedral, and pentacoordinated Al atoms, respectively. The band at  $3590\text{ cm}^{-1}$

**Table 2.** Texture characteristics of  $\gamma\text{-Al}_2\text{O}_3$  obtained from pseudoboehmite (A-I) and boehmite (A-II)

Sample	$T_{\text{calcin}}, ^\circ\text{C}$	$S_{\text{sp}}, \text{m}^2/\text{g}$	$V_{\text{pore}}, \text{cm}^3/\text{g}$	Pore size distribution, $\text{cm}^3/\text{g}$		
				pore diameter, nm		
				2–10	10–100	100–1000
A-I	600	220	0.43	0.37	0.05	0.01
	800	160	0.38	0.29	0.09	0
A-II	600	90	0.40	0.07	0.14	0.20
	800	50	0.40	0.04	0.15	0.21

relates to hydrogen-bonded OH groups. As can be seen in Table 4, the concentration of these OH groups in samples A-II is an order of magnitude higher than that in samples A-I.

It is known [13] that closely spaced hydroxyl groups can stabilize their state by forming hydrogen bonds between each other. It takes higher energy to rupture these hydrogen bonds as compared to the energy necessary for breaking a hydrogen bond formed by the proton of an isolated hydroxyl group and surface oxygen. This arrangement of hydroxyl groups can occur in fine pores, and it can probably affect the formation and stability of extended defects characteristic of the  $\gamma$ - $\text{Al}_2\text{O}_3$  samples of the boehmite series. Although the  $\gamma$ - $\text{Al}_2\text{O}_3$  obtained from boehmite has larger pores than that obtained from pseudoboehmite (Table 2), these pores are slot-shaped in samples A-II, whereas they are cylindrical in samples A-I. This conclusion follows from an analysis of the shapes of hysteresis loops obtained by the adsorption and desorption of nitrogen on samples A-I and A-II. The presence of slot-like pores in samples A-II was additionally confirmed by electron microscopy.

Among the types of hydroxyl groups observed in the IR spectra, type I ( $\nu_{\text{OH}} = 3795 \text{ cm}^{-1}$ ) exhibits the highest basicity. According to the model proposed in [14], dehydroxylation of the  $\text{Al}_2\text{O}_3$  surface is controlled by the relative acidity and basicity of the adjacent OH groups. It is believed that more basic hydroxyl groups (of type I) will be removed first by the interaction with neighboring hydroxyl groups to form various anionic vacancies. The concentration of the hydroxyl groups of type I is much higher in samples A-I (Table 4).

Taking into account the particle size and the pore shape of  $\gamma$ - $\text{Al}_2\text{O}_3$  samples obtained by dehydrating pseudoboehmite and boehmite (Fig. 2), it can be suggested from the aforesaid that metastable oxide species obtained from boehmite (sample A-II) will be dehydroxylated at a slower rate than the oxide species obtained from pseudoboehmite (sample A-I). Hence, it follows that the fraction of hydroxyl groups eliminated from the samples with increasing temperature will be greater in the samples of the pseudoboehmite series under comparable conditions (as confirmed by the thermal analysis data). In turn, this facilitates the transformation of metastable species into stable  $\alpha$ - $\text{Al}_2\text{O}_3$ . Correspondingly, in the samples of the pseudoboehmite series after their temperature-programmed heating to  $1200^\circ\text{C}$  in the derivatograph, only the  $\alpha$ - $\text{Al}_2\text{O}_3$  phase was observed by XRD.

At the same time, we found that the higher the initial degree of dehydroxylation of the surface of samples of the boehmite series, the slower the structural rearrangement. Thus, the XRD analysis of samples of the boehmite series after heating the samples in an derivatograph demonstrates (Table 5) that an increase in the pretreatment temperature was accompanied by a decrease in the fraction of  $\alpha$ - $\text{Al}_2\text{O}_3$ . The samples cal-

**Table 3.** Water losses by the samples

Sample*	Losses of $\text{H}_2\text{O}$ , mol/(mol $\text{Al}_2\text{O}_3$ )**		
	600°C	800°C	1000°C
Pseudoboehmite (initial)	1.50	0.06	0.02
A-I (600°C)	1.46	0.11	0.04
A-I (1000°C)	0.83	0.05	0.03
Boehmite (initial)	1.04	0.05	0.01
A-II (600°C)	0.55	0.06	0.02
A-II (1000°C)	0.19	0.01	0

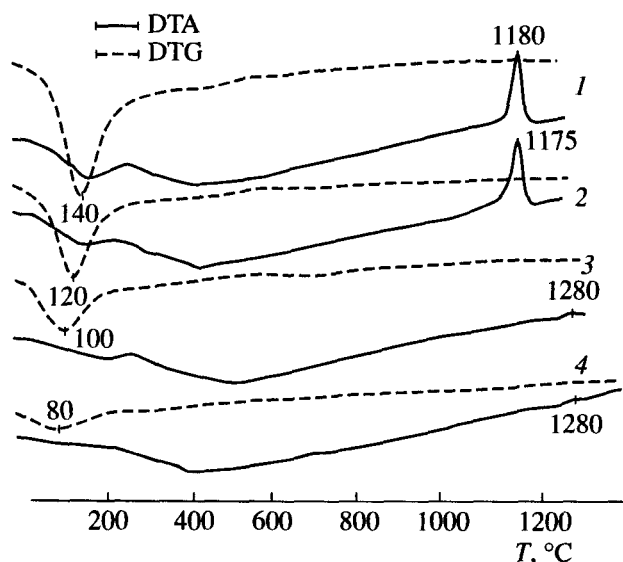
\* The temperature of precalcination is given in parentheses.

\*\* Samples were consecutively calcined at 600, 800, and  $1000^\circ\text{C}$ .

**Table 4.** IR absorption band maximums and concentrations of hydroxyl groups in aluminum oxides

Sample	$\nu_{\text{OH}}$ , $\text{cm}^{-1}$							
	3590	3670	3685	3710	3735	3750	3775	3795
	Concentration of OH groups, $\mu\text{mol/g}$							
A-I	1.2	20	24	22	24	16	11	7
A-II	10	19	0	13	16	7	4.5	0.6

cined under isothermal conditions at 600 and  $800^\circ\text{C}$  contained 55%  $\delta$ - $\text{Al}_2\text{O}_3$  and 45%  $\alpha$ - $\text{Al}_2\text{O}_3$  after nonisothermal treatment to  $1240$ – $1280^\circ\text{C}$ , whereas the sample precalcined at  $1000^\circ\text{C}$  consisted of only  $\delta$ - $\text{Al}_2\text{O}_3$  after nonisothermal treatment. An increase in the final temperature of the nonisothermal calcination from  $1240$  to  $1420^\circ\text{C}$  changed the  $\alpha$ - $\text{Al}_2\text{O}_3$  content from 45 to 60%; the nature of the second phase ( $\delta$ - or  $\theta$ - $\text{Al}_2\text{O}_3$ ) depends on the temperature of the isothermal pretreatment of samples. This behavior of aluminum oxide



**Fig. 3.** DTA and DTG curves for alumina samples obtained by the precalcination of (1, 2) pseudoboehmite and (3, 4) boehmite at (1, 3)  $600^\circ\text{C}$  and (2, 4)  $1000^\circ\text{C}$ .

**Table 5.** Phase composition of samples of the boehmite series as a function of thermal treatment conditions

Sample	Precalcination, °C	Final temperature of nonisothermal treatment, °C	Phase composition of Al <sub>2</sub> O <sub>3</sub>	Concentration of $\alpha$ -Al <sub>2</sub> O <sub>3</sub> , %
Boehmite A-II	20	1400	$\theta + \alpha$	59
	600	1280	$\delta + \alpha$	45
		1310	$\delta + \alpha$	52
		800	$\delta + \alpha$	45
	1000	1240	$\delta$	0
Boehmite*	1200	1420	$\theta + \alpha$	50
		—	$\delta + \alpha$	48

\* The sample was calcined under isothermal conditions for 4 h.

samples obtained by dehydrating boehmite is obviously associated with the real structure, which is characterized by the presence of rather stable extended defects, which are probably stabilized by hydrogen-bonded hydroxyl groups. It is likely that the structure of defects in these samples favors the retarded rearrangement of the lattice and the formation of  $\delta$ - and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. The absence of the above defects from the oxides of the pseudoboehmite series is probably responsible for the accelerated transformation of metastable species into  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Therefore, under comparable conditions of thermal treatment, different sets of Al<sub>2</sub>O<sub>3</sub> phases occurred in the samples obtained from pseudoboehmite and boehmite prepared by hydrothermal treatment of bayerite.

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