ISSN 0023-1584, Kinetics and Catalysis, 2007, Vol. 48, No. 1, pp. 153–161. © MAIK "Nauka/Interperiodica" (Russia), 2007.
Original Russian Text © Yu.Yu. Tanashev, E.M. Moroz, L.A. Isupova, A.S. Ivanova, G.S. Litvak, Yu.I. Amosov, N.A. Rudina, A.N. Shmakov, A.G. Stepanov, I.V. Kharina, E.V. Kul'ko, V.V. Danilevich, V.A. Balashov, V.Yu. Kruglyakov, I.A. Zolotarskii, V.N. Parmon, 2007, published in Kinetika i Kataliz, 2007, Vol. 48, No. 1, pp. 161–170.

Synthesis of Aluminum Oxides from the Products of the Rapid Thermal Decomposition of Hydrargillite in a Centrifugal Flash Reactor:
II. Physicochemical Properties of the Products Obtained by the Centrifugal Thermal Activation of Hydrargillite

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Received June 16, 2005

Abstract—A variety of physicochemical methods were used to characterize the product of the rapid thermal decomposition of hydrargillite in a centrifugal flash reactor under the following conditions: the average particle size of the reactant, 80–120 μm; the temperature of the solid heating surface (plate or cylinder), 300–700°C; hot-zone residence time, ~1 s; transfer of the product to the cooled zone of the reactor. The composition of the product and the extent of decomposition of hydrargillite were determined as a function of the processing temperature. The centrifugal thermal activation (CTA) of hydrargillite affords an X-ray-amorphous, highly reactive product with a developed surface and a disordered and inhomogeneous porous structure. This structure is capable of forming different modifications of aluminum hydroxide and oxide. The properties of the CTA product are compared with the properties of the earlier reported hydrargillite rapid decomposition products obtained using a gaseous heat-transfer agent (thermochemical activation product) or a fluidized bed of a granular heat-transfer agent (thermal dispersion product).

DOI: 10.1134/S002315840701020X

One well-known method of active alumina preparation includes the thermochemical activation (TCA) of aluminum(III) hydroxide (hydrargillite or gibbsite), specifically, thermal decomposition carried out very far from equilibrium by rapidly heating $Al(OH)_3$ crystals to the dehydration temperature (~300°C) followed by cooling (quenching). This way of preparing active alumina was suggested in the 1950s in France [1]. The theoretical foundations of the TCA process were reported in, e.g., [2, 3].

The basic principles of TCA can be briefly formulated as follows. If the aluminum trihydroxide decomposition is carried out under equilibrium conditions, then its constituent processes, namely, (I) the elimination of OH^- groups and (II) lattice transformation yielding χ-Al_2O_3 and some boehmite (γ-AlOOH), will be conjugated, although they will proceed at different rates. The oxide resulting from equilibrium thermal decomposition is much less reactive than γ-Al_2O_3 obtained by the calcination of pseudoboehmite, the hydrargillite reprecipitation product. The heat treatment of hydrargillite far from thermodynamic equilibrium enables one to carry out incomplete decomposition by "quenching" the process at the stage of hydroxide structure breaking, before the structure of the stable low-temperature oxide is formed. By far-from-thermodynamic-equilibrium conditions, we mean a decomposition time as short as a few seconds. Obviously, the rate at which the initial material is heated to the dehydration temperature, the steam pressure, and the rate of subsequent cooling are essential to this process. Flash heating or cooling such that the temperature is changing at a rate of several hundreds of degrees per second can bring the initial aluminum trihydroxide into a metastable state with a heavily disordered structure, yielding the so-called TCA product, which is also called the thermal dispersion (TD) product [4].

Physicochemical characterization of the TCA (TD) product obtained from hydrargillite [2–5] demonstrated that, under some conditions, $Al(OH)_3$ can be completely decomposed to the X-ray-amorphous, weakly hydrated compound $Al_2O_3 \cdot xH_2O$ ($x < 1.5$) with a developed pore structure. In essence, this compound is disordered aluminum hydroxide very active in terms of solubility and sorption properties. The rehydration of the TCA product can yield aluminum hydroxides with a pseudoboehmite or bayerite structure, from which γ- or η-Al_2O_3 can be obtained by calcination [6–8].

Table 1. Properties of initial hydrargillite samples

Initial hydroxide	Impurities, wt %	Dominant size fraction*	Specific surface area, m^2/g
HP	Na_2O – 0.22 Fe_2O_3 – 0.05	50–100 μm, 55 wt %	1.0
HA	$Na_2O + K_2O$ – 0.40 Fe_2O_3 – 0.01 SiO_2 – 0.02	100–150 μm, 50 wt %	0.5

* Sieving data.

In the TCA process, the initial powder is usually heated with a gaseous heating medium, such as fuel combustion products. Thermal dispersion is carried out in a catalytic heat generator by bringing hydrargillite into short-term contact with a fluidized bed of a catalyst or another granular heat-transfer agent. Obviously, the powder can be heated using other techniques involving dynamic contact with a heat source. (We will not consider indirect heating techniques, such as high-intensity ionizing radiation [9].) In particular, of interest are apparatuses in which the reagent slides on a hot solid surface owing to a centrifugal force. Such apparatuses, which have recently been designed at the Siberian Branch of the Russian Academy of Sciences and have been commercialized under the name of a centrifugal flash reactor (TsEFLAR^{TM}), have a number of obvious advantages. These include the stability of heat-treatment regimes, rather precise temperature control, the possibility of varying the contact time by controlling the rotational speed of the heating surface, high powder heating and cooling rates, small dimensions, and environmental friendliness [10, 11].

By carrying out the rapid thermal decomposition of hydrargillite in a TsEFLAR, we have demonstrated that, under certain processing conditions, the structure of the starting trihydroxide can be completely broken to obtain an X-ray-amorphous product rehydratable into aluminum hydroxide with a pseudoboehmite or bayerite structure [12]. The thermal decomposition of solids in this reactor received the name of centrifugal thermal activation (CTA), and the material obtained in this reactor was named the CTA product. This name was given for the reason that the TCA and CTA products may somewhat differ in properties, as is demonstrated below.

This article begins a series of publications dealing with the rapid thermal decomposition of aluminum(III) hydroxide in a TsEFLAR reactor and with the reactivity of the resulting products, which are precursors of active alumina. Below, we report physicochemical characterization of the CTA product, including its phase composition; reactivity; and morphological, structural, and textural data.

EXPERIMENTAL

The starting materials were hydrargillite samples produced at PO Glinozem (Pikalevo) and the Achinsk alumina refinery (hereafter, HP and HA, respectively). Some properties of these materials are listed in Table 1. Clearly, the HA particles, whose average size is ~120 μm, are 1.5 times larger than the HP particles, whose average size is ~80 μm. Prior to heat treatment, hydrargillite was dried to constant weight at 110°C and was sieved to remove the agglomerates larger than 0.5 mm.

A detailed description of the plate-type centrifugal flash reactor (TsEFLAR-T) is presented elsewhere [10, 11]. The main element of the reactor (heat-transfer surface) is a plate 1 m in diameter mounted on a vertical shaft. The plate has the shape of a cone diverging upwards. The heaters are mounted under the plate. Hydrargillite is fed through a flow regulator onto the central part of the plate preheated to an appropriate temperature and moves to the plate edge under the action of the centrifugal force. When in contact with the plate, the powder gets heated and undergoes chemical transformations. The contact time (τ) can be varied between 0.5 and 1.5 s by changing the rotational speed of the plate. Falling down from the plate, the powder finds itself in the quenching zone, where the thermal decomposition product is brought into contact with a cold wall and is thus cooled rapidly to 40–80°C. In TsEFLAR-B, another variant of the centrifugal reactor, the thermal decomposition of hydrargillite is carried out on the inner surface of a rotating vertical cylinder (drum) and the material to be processed is fed from above.

This reactor ensures almost instantaneous heating of aluminum hydroxide particles from 20°C to the endothermic dehydration temperature (~300°C). For a particle size of 100 μm and a heating surface temperature of 400°C, the heating time was estimated to be no longer than 0.2 s [10].

The most important hydrargillite processing parameters are readily controllable and are the following: the temperature of the medium near the heating surface (controlled with a few Chromel/Alumel thermocouples), the contact time, the mass feed rate of the reactant (u_r = 0.3–4.2 g/s), and the particle size of the powder.

The partial pressure of the steam resulting from hydrargillite decomposition (P_s) is controlled by fanning the steam–air mixture out of the space between the TsEFLAR-T reactor cover and the plate. If the steam were not removed, the product leaving the reactor would be somewhat wet because of steam condensation in the quenching zone. In TsEFLAR-B, the steam, which flows countercurrently to the powder, is vented through slits in the upper part of the reactor. However, these techniques do not rule out the presence of superheated vapor near the reacting particles.

The powder was fed into the hot zone after the heating surface acquired the preset temperature (300–700°C). The rotational speed of the plate (drum) was adjusted so that the contact time was no shorter than 1 s. Because the heat treatment of the hydroxide is accompanied by dehydration, which is an endothermic process, some decrease in the temperature of the medium is observed near the reactant loaded into the reactor. The temperature drop ΔT depends strongly on the mass flow rate of the reactant and can be as large as 200 K. The thermal decomposition product was sampled for analysis after a steady-state temperature was established. The samples were stored in polyethylene bags at room temperature.

X-ray diffraction patterns from thermally activated samples and from their rehydration products (which will be the subject of forthcoming publications) were recorded on an HZG-4C diffractometer (Germany) using monochromated CuK_α radiation (graphite monochromator in the diffracted beam). The slits were 1 : 2 : 0.35. The vertical divergence was 2.5 and was limited by two Soller slits on the primary and diffracted beams. The diffraction intensity curve was recorded at a scan speed of 1 deg/min. The goniometer was adjusted against the integrated intensities and positions of the 200 and 220 reflections from a standard NaCl powder. Since the monochromator was adjusted to the mean wavelength, we checked that the $K_{\alpha 1}$-to-$K_{\alpha 2}$ intensity ratio for the 220 reflection from NaCl is 2 : 1. Diffraction patterns from the standard sample were taken by scanning the $2\theta = 5°–75°$ range with 0.05° increments and a count time of 10–20 s per point. The following hydroxide references were chosen and characterized for quantitative analysis: hydrargillite, bayerite, crystalline boehmite (Bo), and precipitated pseudoboehmite (Pbo). We prepared mixtures containing preset proportions of these pure phases as references. Samples to be examined were pressed into cells 20 mm in diameter. The calibration plot for each mixture series was based on intensity ratios for certain closely spaced reflections from different phases. The measurement of the intensity ratios makes it unnecessary to standardize the packed density of the sample, the sample weight, the sample preparation procedure, and the X-ray diffraction conditions.

X-ray diffraction patterns for constructing radial electron density distribution (REDD) curves were recorded on a high-resolution diffractometer at the synchrotron radiation station of the Budker Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences ($\lambda = 0.7$ Å, $2\theta = 5°–135°$). The REDD curves were calculated as described in [13].

Thermal analysis was carried out on a Q-1500D thermoanalytical system (Hungary) between 20 and 1000°C in air at a heating rate of 10 K/min. The sample weight was 200 mg, Weight loss was determined with an accuracy of ±0.5%.

Textural properties were studied using an ASAP-2400 Micromeritics instrument. Samples were conditioned in vacuo at 150°C before being examined. The specific surface area (S_{sp}, m^2/g) was determined by the BET method from low-temperature nitrogen adsorption isotherms with an accuracy of 10%.

Electron microscopic studies were carried out with a JEM-100CX transmission microscope (Japan) with a resolution of 0.5 nm at an accelerating voltage of 100 kV.

Magic-angle-spinning ^{27}Al NMR spectra were recorded on a Bruker Avance-400 spectrometer operated at 104.261 MHz. The sample spinning frequency was 11 kHz. The duration of the exciting 90° pulse was 2 μs. The interpulse delay time during data acquisition was 0.3 s. The chemical shift for the ^{27}Al nuclei was measured using an aqueous $AlCl_3$ solution as the external standard.

Reactivity was quantified according to a standard procedure [4] by measuring the extent of dissolution $(m_0 - m_{ins})/m_0$, where m_0 is the weight of the initial sample and m_{ins} is the weight of the insoluble residue) of thermally activated samples (TCA and CTA products) and reference samples (hydrargillite, Bo, Pbo) in 50–100 ml of 20% NaOH at 60°C while stirring for 15–60 min. After separating the insoluble solid, the Al^{3+} concentration in the filtrate was determined by chelatometric titration. Depending on the amount of adsorbed water, the weight of the sample to be analyzed was 12–15 g. The adsorbed water content was determined by drying the sample at 110–115°C for 6 h. These data were taken into account in the determination of the soluble and insoluble fractions of the solid and in the calculation of the dimensionless parameter A, which was defined as the amount of Al^{3+} dissolved in the alkali solution (g) divided by the weight of the initial sample (g). The amount of the insoluble residue was determined by collecting the solid on a filter, washing it with distilled water, and drying it at 110–115°C for 12 h.

The TCA product examined for comparison was produced at the Achinsk alumina refinery. It has a specific surface area of 90 m^2/g and is a mixture of X-ray-amorphous $Al_2O_3 \cdot 0.9H_2O$ and undecomposed hydrargillite and Bo crystals (up to 5 wt % each), as determined by X-ray diffraction. The minor impurities in this product were Na_2O (0.3 wt %) and Fe_2O_3 (0.03 wt %).

RESULTS AND DISCUSSION

According to electron microscopic data, the CTA process, like TCA and TD, yields particles that are a pseudomorphose with respect to the initial hydrargillite; that is, the thermal decomposition process has the character of a pseudomorphic transition (Fig. 1). The particles of the CTA product are large (of size up to

15 μm) and have almost regular shapes. Their projections appear as truncated hexagons or distorted triangles, and their surfaces are slightly angular. Some particles have thin needles about 70–100 Å in size at their edges. Slitlike gaps (pores) are observed on the particle surfaces. Furthermore, the sample contains shapeless aggregates of platelike microporous particles between 0.5 and 2 μm.

According to X-ray diffraction and thermoanalytical data, the samples decomposed in the centrifugal reactor contain the following components (Table 2): crystalline aluminum trihydroxide (usually original hydrargillite) with a dehydration temperature (T_{dehydr}) of about 300°C, crystallized Bo (γ-AlOOH, $T_{\text{dehydr}} \approx$ 520°C), and an X-ray-amorphous phase (aluminum hydroxide oxide) of composition $Al_2O_3 \cdot xH_2O$ ($x <$ 1.0). According to thermoanalytical data, this amorphous phase releases water in a wide temperature range up to 700–800°C (Fig. 2). Note that the CTA product, like the TCA and TD products, contains nearly the same amounts of impurities as the starting hydrargillite.

The presence of hydrargillite in some of the samples appearing in Table 2 is evidence of the incomplete decomposition of the starting material. This is possible, for example, in the following cases:

(1) The temperature of the heating surface is insufficiently high for the hydrargillite particles (particularly those that are larger than 80–100 μm) to be quickly heated within their residence time in the hot zone of the reactor (Table 2, samples 1 and 2). As a consequence, the large particles of the CTA product are the richest in $Al(OH)_3$, as was determined by the phase analysis of

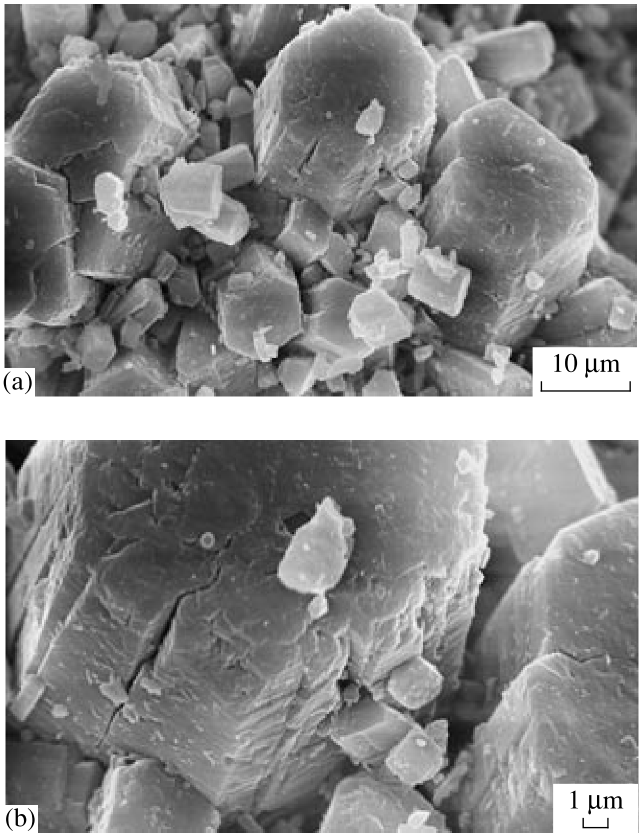

Fig. 1. Electron micrographs of the product of the rapid thermal decomposition of hydrargillite in a centrifugal flash reactor.

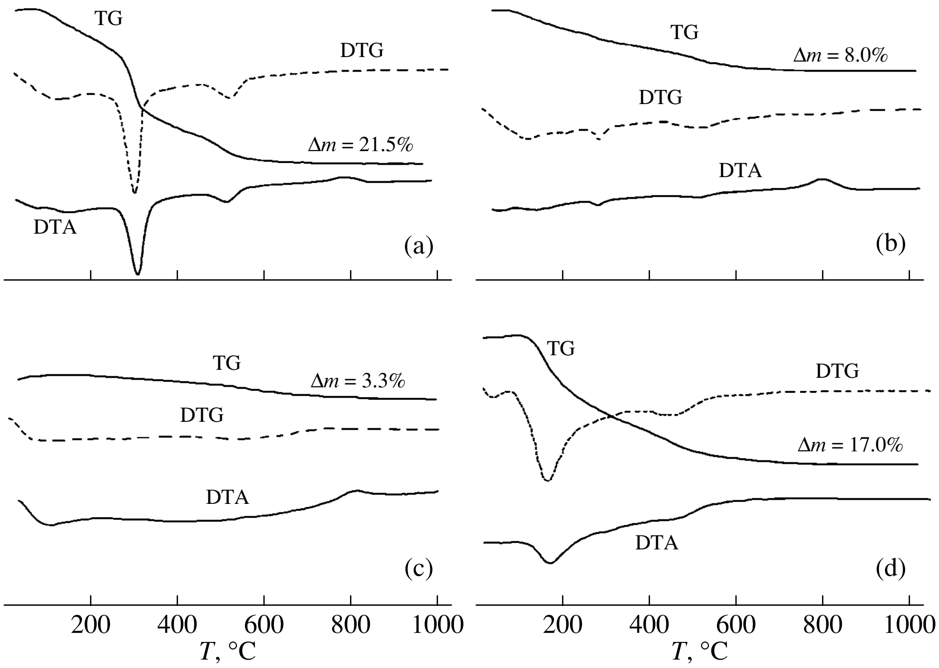

Fig. 2. Thermoanalytical curves for some samples appearing in Table 2. Sample numbers: (a) 1; (b) 12; (c) 14; and (d) 9.

Table 2. Properties of hydrargillite CTA products obtained in TsEFLAR-type reactors under various thermal decomposition conditions

Processing conditions				Product composition (thermoanalytical and X-ray diffraction data)					S_{sp}, m^2/g	Reactivity**, %	A***
sample no.*	initial material	u_r, g/s	T, °C	H_2O, wt %	$Al(OH)_3$, wt %	Boehmite, wt %	$Al_2O_3 \cdot xH_2O$, wt %	x			
1 (T)	HA	1.3	300	21.5	33	10	57	0.98	–	53.1	0.213
2 (T)	HA	1.4	350	16.0	13	8	79	0.85	58	62.1	0.276
3 (T)	HA	1.7	400	9.5	3	7	90	0.51	106	61.6	0.286
4 (T)	HA	1.4	450	8.0	3	6	91	0.43	88	59.9	0.284
5 (T)	HA	4.2	450	11.0	10	7	83	0.54	–	58.9	0.270
6 (T)	HP	1.9	460	9.5	2	4	94	0.56	97	57.2	0.264
7 (T)	HA	1.1	500	6.3	3	<1	96	0.35	108	54.7	0.279
8 (T)	HP	2.1	500	6.8	2	–	98	0.38	–	–	0.279
9 (T)****	HP	2.0	500	12.9	<1	–	75	0.65	230	45.5	0.213
10 (B)	HP	1.4	520	7.0	2	1	97	0.39	187	55.2	0.269
11 (T)	HP	2.1	540	5.9	–	–	100	0.36	122	–	0.245
12 (T)	HA	1.9	580	5.4	1	–	99	0.30	168	47.1	0.233
13 (B)	HP	1.4	580	4.8	2	–	98	0.26	218	–	0.241
14 (B)	HA	0.8	650	3.3	–	–	100	0.18	139	28.6	0.154

*The parenthesized letter following the number stands for the reactor modification in which the sample was processed: T = TsEFLAR-T, and B = TsEFLAR-B.

**Determined as the extent dissolution of a 12-g sample in 100 ml of 20% NaOH within 15 min.

***Calculated using the formula presented in EXPERIMENTAL.

****The sample was obtained in the presence of steam in the cooling zone of the reactor and contains ~25 wt % pseudoboehmite.

samples that had been sieved to separate out the >90 μm fraction.

(2) The mass flow rate of the solid exceeds the u_r^{max} value specific to the given reactor, which is determined by the geometry of the heating surface and by the particle size of the reactant. At $u_r < u_r^{max}$, the powder particles move on the heating surface as a thin layer. At $u_r > u_r^{max}$, the particles pile up, hampering heat transfer to the reactant layer. As a consequence, most of the powder does not reach the dehydration temperature within the residence time (Table 2, entry 5).

(3) The contact time is shortened as a result of a change in the rotational speed of the heating plate. This case is not included in Table 2. For all samples, the reactant particles and the heating surface were in contact for ~1 s.

The formation of Bo during CTA is obviously due to the fact that hydrargillite decomposes under hydrothermal conditions in the bulk of large particles [14]. As the processing temperature is raised, the proportion of Bo in the sample decreases down to zero. As a whole, the effect of the processing temperature on the number of crystalline phases in the CTA product ($Al(OH)_3$, AlOOH) is the same as in the case of TCA using a gaseous heat-transfer agent [7].

The proportion of the X-ray-amorphous component in the products examined can be as large as 100%. The properties of this component depend on hydrargillite decomposition conditions and dictate the way in which the desired oxides should be synthesized. Many of the observed properties of the X-ray-amorphous CTA products are similar to or even coincide with the properties of the TCA and TD products known from the literature [2–5, 7]. First of all, this is true for the above-mentioned pseudomorphism. Furthermore, the above products have similar texture parameters. Like TCA and TD, the thermal decomposition (dehydration) of hydrargillite in a TsEFLAR reactor causes the formation of a developed pore structure in primary particles and dramatically increases the specific surface area of the sample to 200 m^2/g or above. According to adsorption data, the CTA product generally has a uniform pore texture with an average pore diameter of ~35–40 Å. Note that S_{sp} depends not only on processing conditions in the centrifugal reactor but also on the conditions under which the sample was pretreated before surface area measurements. Table 2 lists S_{sp} data for samples conditioned in vacuo at 150°C. Raising the conditioning temperature to 300°C usually leads to an increase in the observed S_{sp} value.

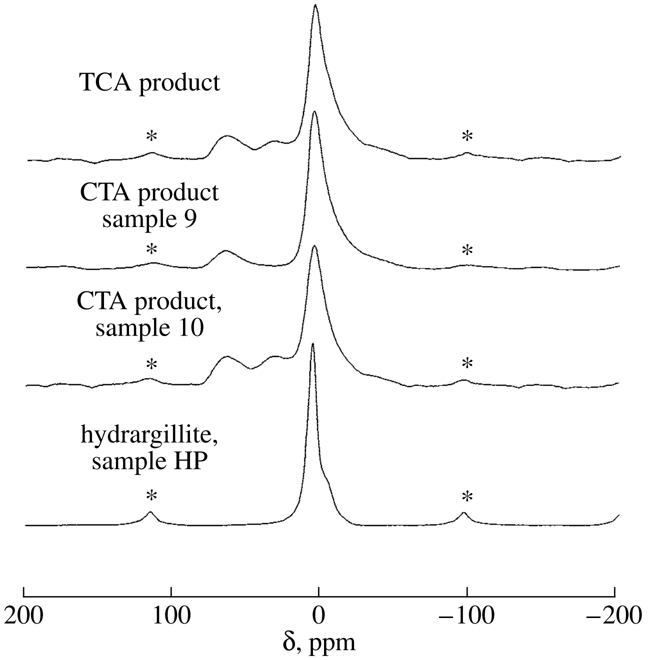

Fig. 3. ^{27}Al NMR spectra of initial thermally activated hydrargillite samples. The symbol * labels the satellites arising from the spinning of the sample.

To a first approximation, the CTA products retain the layered structure of hydrargillite (Fig. 1), indicating that it is possible to carry out dehydration without restructuring the oxygen sublattice into an oxide structure as in the case of the TCA process [7]. According to ^{27}Al NMR data (Fig. 3), most of the aluminum cations of the resulting products are octahedrally coordinated, giving rise to a resonance at δ = 5–6 ppm. In the light of the conceptions developed by Buyanov et al. [2, 7], this finding is evidence that the thermal decomposition of crystalline aluminum trihydroxide in the centrifugal reactor yields metastable intermediate structures, which result primarily from the elimination of part of the structural elements (OH^- groups) from the stable layered structure of hydrargillite. The layers in the resulting product are split, and the structure of the product, as distinct from the initial structure, is porous and heavily disordered. Furthermore, as is demonstrated below, this structure is significantly inhomogeneous, containing nuclei of various hydroxides (so-called hydroxide constituents) and low-temperature alumina phases (oxide constituents). The disorder in the structure of the CTA product is indicated by the NMR spectra shown in Fig. 3. These spectra exhibit not only peaks due to octahedrally and tetrahedrally coordinated aluminum ions at 5–6 and 64–66 ppm, respectively, but also an intermediate peak at 31–32 ppm. According to earlier data [7], this peak is evidence that the CTA products, like the TCA products, contain pentacoordinated aluminum.

The presence of χ-Al_2O_3-like structural units in the CTA products is indicated by X-ray diffraction data (broad halo in the region of $2\theta = 67°$ (CuK_α); see also Fig. 4) and by the interatomic distances derived from the REDD curves (Fig. 5). The TCA product examined for comparison contains this phase along with 5–7% hydrargillite and a small amount of Bo. It is clear from Fig. 4 that, not considering the undecomposed hydrargillite, the CTA and TCA products are identical and are both χ-alumina-like, at least to some extent. At the same time, the TCA product (more precisely, its X-ray-amorphous component) crystallizes as η-Al_2O_3 upon calcination [4, 15]. It is, therefore, of interest to study the heat-induced phase transitions in the CTA product. According to thermoanalytical data, the X-ray-amorphous component crystallizes at 800 ± 20°C, giving rise to an exotherm in the DTA curve (Fig. 2) [16].

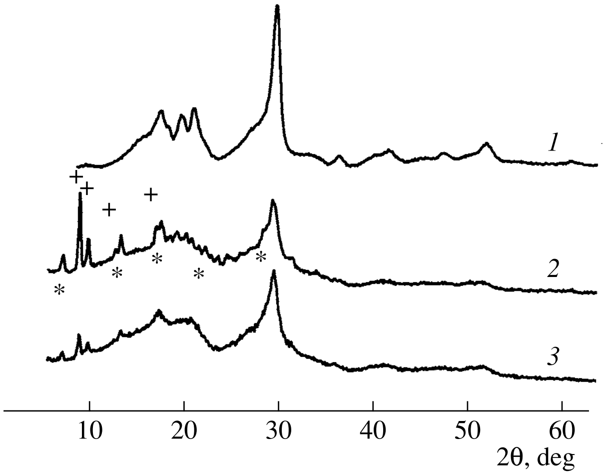

Fig. 4. X-ray diffraction patterns from (*1*) χ-Al_2O_3, (*2*) the TCA product, and (*3*) the CTA product (sample 12, λ = 0.7 Å). Diffraction peaks from hydrargillite are labeled with +; those from boehmite, with *.

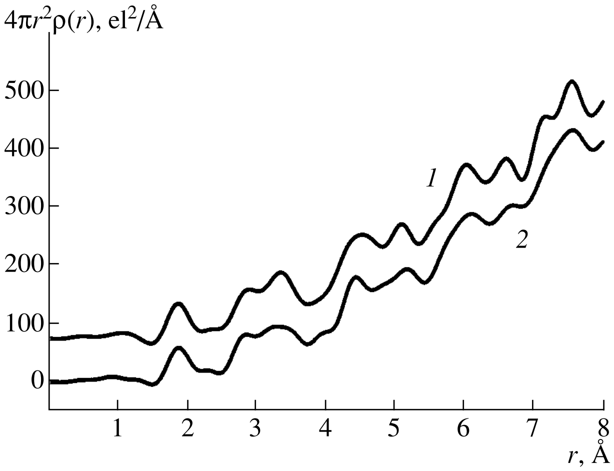

Fig. 5. REDD functions for (*1*) TCA and (*2*) CTA samples.

Note that the exothermic event is observed only for samples from which steam was removed during their thermal decomposition. In order to elucidate the nature of the resulting oxide, we carried out X-ray diffraction phase analysis of the CTA products calcined at 800°C for 4 h (samples 10 and 11). The parameter B, defined as the intensity ratio of the 311 and 222 reflections, ranges between 1.75 and 2.0 for the samples examined, indicating the presence of η-Al_2O_3 [17], as in the case of the TCA products [4, 15]. The unit cell parameter a of this phase is 7.901 Å. The sample calcined at ≤800°C contains an X-ray-amorphous χ-like component along with η-Al_2O_3, as is indicated by the presence of the above-mentioned halo at $2\theta = 67°$ (CuK_α) in the diffraction pattern.

The CTA product may contain pseudoboehmite-like structural units. It was mentioned above that the properties of the flash decomposition products of hydrargillite depend strongly on steam partial pressure P_s. We did not measure P_s in this study, but it can be assumed that, since the free space near the reactant is small, the reactant moves in a medium containing a large percentage (up to 100%) of steam being continuously released. The role of steam removal is to prevent steam condensation in the quenching zone and, accordingly, the impairment of the reactor performance, specifically, product caking and sticking to cooled surfaces. Some products were obtained under weak steam fanning or without fanning at all, so that considerable amounts of steam entered the quenching zone of the TsEFLAR-T reactor. The resulting materials were identified by X-ray diffraction and thermal analysis. It was found that the interaction between steam and the product being cooled causes partial rehydration of the CTA product, producing fine-particle Pbo ($T_{dehydr} \approx 430°C$) in 20–30 wt % yield (Table 2, entry 9). The ^{27}Al NMR spectrum of this sample (Fig. 3) shows no signal assignable to pentacoordinated aluminum, and the DTA curve indicates no exotherm at 800°C (Fig. 2d). The calcination of this sample at 400–800°C yields γ-like alumina. This is indicated by X-ray diffraction data: for the crystalline phase resulting from calcination, B = 1.3–1.4 and a = 7.913–7.922 Å. This a value is nearly equal to the reference a value for γ-Al_2O_3 obtained by the calcination of standard Pbo [18].

Figure 5 plots the REDD curves for the samples thermally activated by two different methods (TCA and CTA). The first coordination peak (r = 1.85–2.00 Å) is assignable to the Al–O distance typical of low-temperature aluminum oxides [19]. The Al–O distances characteristic of the hydroxide phases pseudoboehmite and bayerite also fall in this range [20]. The second coordination peak (r = 2.85–2.95 Å) is assignable to the distance between aluminum cations occupying adjacent octahedral sites in either an oxide or a hydroxide phase. A specific feature of the pseudoboehmite structure is the Al–O distance elongated from 3.4 to 3.6 Å because of the presence of water molecules between layers of octahedra. It is likely that the CTA product contains the Pbo phase that is not detected by X-ray diffraction because of its low content and small crystallite size (<30 Å). In the REDD curve for this sample, the second peak is broadened and shifted.

Information concerning the reactivity of the products is presented in Table 2. While making measurements, we modified the standard activity determination procedure [4]. In particular, in order to see whether it is possible to shorten the analysis time, we increased the amount of alkali from 50 to 100 ml. The observed dissolution kinetics (Fig. 6a) suggest that most of the so-called reactive phase of the CTA and TCA products dissolves under these conditions within the first 15 min and the extent of dissolution is similar to that observed for the solution volume of 50 ml in 60 min. Therefore, the standard analytical test can indeed be quickened. It should only be taken into consideration that the "$NaOH/Al_2O_3$" ratio varies from sample to sample at a fixed weight of the CTA product because of the variability of the parameter x (Table 2). This is the reason why the parameter A and the extent of dissolution vary from sample to sample in a nonsymbatic way. Therefore, reactivity in terms of solubility in NaOH should be considered together with phase and chemical composition data. Note that the data presented in Table 2 indicate that the parameters measured during the dissolution of a sample are sensitive to the completeness of hydrargillite decomposition and to the proportion of the oxide constituent in the X-ray-amorphous component: the reactivity is markedly reduced both in the case of incomplete hydrargillite decomposition (sample 1) and in the case of a high extent of dehydration (sample 14).

Partial dissolution can be considered to be a technique distinguishing the less reactive and the more reactive components of the CTA product. The alkali-insoluble solid was collected on a filter, washed, dried, and then examined by X-ray diffraction. The difference between this solid and the initial CTA product is that the $2\theta = 67°$ reflection from the latter has a lower integrated intensity.

It is significant that the reactivity of the CTA product somewhat declines in the course of time (Fig. 6b). Apparently, the relaxation of the metastable state of the substance resulting from flash decomposition needs careful examination. On the one hand, there are data suggesting that the phase composition of the hydrargillite TCA and CTA products does not change considerably in time; that is, the X-ray-amorphous component remains unchanged for a long (apparently infinite) time. According to X-ray diffraction data, its stability to crystallization (a kind of thermal stability) persists up to rather high temperatures of 300–400°C. On the other hand, consideration of the systems obtained by pulse heating from the standpoint of structural imperfection suggests that short-lived defects can exist in CTA products. This is indicated by the reactivity decreasing in time and by the following facts:

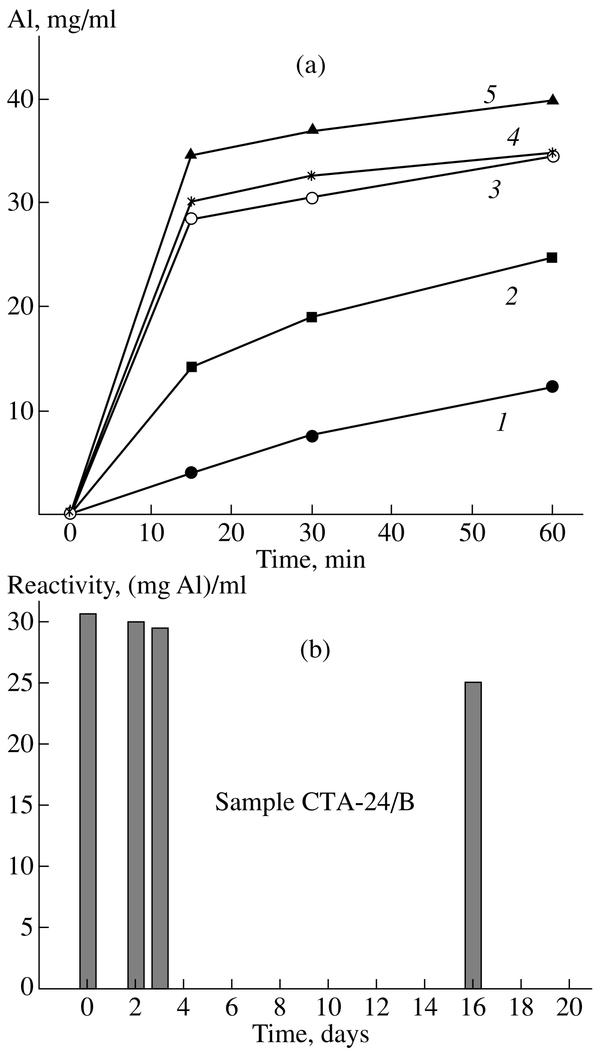

Fig. 6. (a) Kinetics of dissolution in 20% NaOH (solution volume 100 ml, sample weight 12 g): (*1*) hydrargillite HP; (*2*) precipitated pseudoboehmite; (*3*) TCA product; (*4*) CTA product, sample 10; (*5*) CTA product, sample 8. (b) Variation of the reactivity index of the CTA product during storage.

(1) Like the TCA product, the CTA product interacts readily with atmospheric moisture and CO_2 during the hours immediately following thermal activation. This interaction manifests itself as a weight gain, which can be as large as 13–15% at an air humidity of 50–70% and $T = 20°C$ (sample 14). A fresh sample gains weight even if it is held at 110°C. The adsorption of CO_2 is also indicated by IR spectroscopic data [12].

(2) As mentioned above, the reaction between the CTA product and steam in the quenching zone yields pseudoboehmite. This rehydration can be considered to be a kind of stabilization of short-lived defects, since, after long-term storing, the samples not treated with steam react with water to yield Pbo only under special conditions. This point will be considered in forthcoming publications.

CONCLUSIONS

Thus, the results of this study suggest that the products of the centrifugal thermal activation of hydrargillite are similar in many respects to the well-known TCA and TD products. The rapid thermal decomposition of hydrargillite in a TsEFLAR reactor yields, in a very short time, a substance in an energy-rich, highly reactive, metastable state. CTA process conditions can be varied in wide ranges in order to control the extent of hydrargillite decomposition and the properties of the resulting materials. The CTA products have a developed surface and a disordered and inhomogeneous microporous structure, from which different modifications of aluminum hydroxide and oxide can be formed, in particular, by subsequent hydration and heat treatment.

A specific feature of the above method of rapid hydrargillite decomposition is that the gas phase in both the activation and quenching zones can contain much more water vapor than the gas phase in the TCA or TD process. Furthermore, the properties of the resulting product may depend on the rate at which the starting material is heated to its dehydration temperature. According to earlier calculations [10, 11], replacing the gaseous heat-transfer agent with a solid heating surface allows the heating time and, accordingly, the overall processing time to be shortened several times. The actual energy consumption in the thermal activation in a TsEFLAR reactor is not higher than 4 kJ per gram of hydrargillite, while the same parameter estimated for the TCA process using flue gas is 7–10 kJ/g.

These specific features of the CTA process can lead to differences between the pulse thermal decomposition products of hydrargillite samples obtained by different methods. This is indicated by pseudoboehmite appearing in the CTA product, by the CTA and TCA products differing in terms of solubility and reactivity in the hydration reaction [12], and by these products having different balling capacities. In forthcoming publications, we will consider some properties of the CTA products in greater detail. We are going to focus on the phase transitions in these products caused by hydration and/or heat treatment, as well as on finding the conditions under which the CTA product can be converted into aluminum hydroxide with a pseudoboehmite or bayerite structure.

ACKNOWLEDGMENTS

We are grateful to V.S. Lakhmostov and D.N. Sokolov, researchers of the Boreskov Institute of Catalysis, for technical assistance in the experiments carried out in the TsEFLAR-B reactor.

This work was supported by grants from the Presidium of the Siberian Branch of the Russian Academy of Sciences (integrated project no. 176) and from the Chemistry and Materials Sciences Division of the Russian Academy of Sciences (Program 4.8, “Laying the

Scientific Foundations of New Chemical Technologies and Producing Samples and Pilot Batches of Compounds and Materials").

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