

Preparation of Colloidal Boehmite Needles by Hydrothermal Treatment of Aluminum Alkoxide Precursors

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Fairly monodisperse colloidal boehmite fibrils with a high aspect ratio were synthesized by hydrothermal treatment at 150°C of an acidified aqueous alkoxide solution, prepared by adding an aqueous HCl solution to an aluminum alkoxide precursor. The average particle length could be controlled between about 100 and 500 nm by varying the initial amounts of alkoxide and acid. Using two different alkoxides in a 1:1 molar ratio yielded the most needlelike product, having a particle length standard deviation of 40%. The boehmite particles were polycrystalline and contained 0.14 mol of excess H₂O per mol of AlOOH, bound to the particle surface. [Key words: colloids, boehmite, aluminum, alkoxide, hydrothermal process.]

I. Introduction

DISPERSIONS of submicrometer needlelike boehmite (AlOOH) particles with a narrow size distribution are of interest commercially as well as scientifically. Metal oxide and hydroxide dispersions are used industrially in the production of homogeneous multiphase ceramics.¹ For example, needle-shaped boehmite sols are suitable for application in grain-oriented ceramics. Moreover, sols containing long fibrous boehmite particles show excellent spinnability for fiber drawing.² As for the fundamental science, colloidal boehmite dispersions can serve as model "rigid-rod" systems.³ For industrial applications, as well as for fundamental studies, the properties of the fibrils should be well-defined. Ideally, particles should be noncoagulated with a high aspect ratio (length:width ratio), having a narrow size and shape distribution.

Recently we studied boehmite synthesis by hydrothermal treatment of basic aluminum chloride solutions.⁴ We applied the method of Bugosh⁵ to prepare noncoagulated fairly monodisperse fibrils, about 300 nm long and with an aspect ratio of about 10. A major drawback of the Bugosh method, however, is the time-consuming process of preparing the basic aluminum chloride solution by dissolving aluminum metal powder in a hot aqueous AlCl₃ solution. Also, the maximum achievable Al:Cl molar ratio was limited to 3. Furthermore, it was not possible to affect the size of the hydrothermally grown fibrils systematically by varying the initial Al:Cl molar ratio.

This paper describes the hydrothermal treatment at 150°C of acidified aqueous alkoxide solutions based on various high-

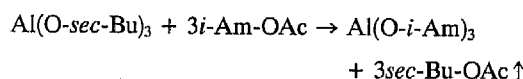
purity aluminum alkoxide precursors. The solutions can be easily prepared on a liter scale, while a wide range of both Al³⁺ and Cl⁻ concentrations can be reached, which allows control of the resulting boehmite fibril length. The hydrolysis of aluminum alkoxides has been widely investigated in recent years in sol-gel preparation, to achieve high-purity powders.^{2,6-8} Al(OR)₃ is readily hydrolyzed by water and produces different hydroxide phases according to temperature. So far to our knowledge no attempt has been made to apply a hydrothermal treatment in the aluminum sol-gel process.

The boehmite is characterized by transmission electron microscopy (TEM), image analysis, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential thermal analysis (DTA).

II. Experimental Procedure

(1) Materials

The alkoxides used were aluminum tri-*sec*-butoxide (ASB) [pract.: 21% Al₂O₃],[‡] aluminum tri-*tert*-butoxide (ATB) [pract.: 90% to 95% Al; 5% Al₂O₃],[‡] aluminum triisopropoxide (AIP) [98+%,[§] and aluminum triisooamyl oxide (AIA). The first three were used as delivered for the boehmite synthesis. AIA was prepared under nitrogen at about 111°C by the exchange reaction⁹ of 25 g of ASB with 40 g of isooamyl acetate,[¶] both freshly distilled under nitrogen, according to



The produced butyl ester was removed easily by distillation because of the large difference between its boiling point (111°C) and that of *i*-Am-OAc (136° to 142°C). The purity of the produced AIA was determined by ¹H NMR** to be in excess of 90%. Its melting point was about 158°C. The yield of AIA was 90% of the theoretical yield. The solid AIA was stored in *t*-BuOH under nitrogen to avoid hydrolysis by moisture in the air. The *t*-BuOH was used because the strong steric hindrance of the *t*-BuO group prevents exchange with alkoxide groups bonded to aluminum.⁹

The HCl solutions were prepared by diluting 37% HCl†† with double-distilled water.

(2) Preparation of the Acidified Alkoxide Starting Solutions

The preparation of an acidified alkoxide solution was performed by adding an excess amount of aqueous HCl to the alkoxide at room temperature under vigorous stirring. The acidified alkoxide solution used for sample ASB2 was prepared by adding all 100 mL of a 0.060 mol/L HCl solution

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**WP200WB, Bruker, Rheinstätten, FRG.

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directly to 1.9600 g (1.912 mL) of ASB under vigorous stirring. Immediately after the addition of the acid to the alkoxide, a suspension of white material was formed. Yoldas⁶ described the suspended material obtained directly after the addition of ASB to water at 20°C in his experiments as amorphous aluminum hydroxide containing alkoxide groups. X-ray powder diffraction (XRD) obtained for the suspended material in our starting solutions indicated that it was amorphous.

If the Al:Cl molar ratio is less than about 1.5, the suspended and sedimented material dissolves very slowly upon aging for several days, leading to a clear solution. Solutions with Al:Cl molar ratios higher than 1.5 peptize to stable colloidal solutions upon aging. The colloidal phase was determined by XRD to be poorly crystalline gibbsite.

(3) Hydrothermal Treatment

The acidified alkoxide solutions were poured into 8- or 44-mL Teflon liners (80% filled), which fit into stainless steel pressure vessels. The vessels were rotated for 20 h at a constant velocity of 5.75 rpm on a mechanical framework in an oven at 150°C. After hydrothermal treatment the vessels were suddenly cooled in water. The alcohol produced during treatment and the acid anion were removed from the sol by dialysis in a cellophane tube against deionized water at room temperature for 1 week. The dispersions were stored in polystyrene containers to avoid any contamination with silicates from glassware.

(4) Characterization Techniques

A first qualitative indication of the presence of fibrillar particles in the sol is the appearance of a marked birefringence when the sol is stirred. The birefringence is due to spatial anisotropy of the refractive index in the dispersion, caused by the alignment of rodlike particles.¹⁰ The parallel arrangement arises when the hydrodynamic flow field of the medium orients the particles, suppressing their random rotational diffusive motion.

The TEM^{††} specimens were prepared by spraying the sol onto a mica plate. The particles were embedded in a thin

carbon layer and then transferred onto a copper 400-mesh carrier grid in water.⁴ From the micrographs the particle dimensions were determined by image analysis.

The particle size was also determined by X-ray powder diffraction measurements done with a diffractometer^{§§} using monochromatic CuK α_1 radiation. After the sol was dialyzed, dry, fluffy boehmite powder was separated from the solvent by freeze-drying the sol for 15 h at -20°C and 50 Pa. The mean crystallite diameter along the normal to a plane of reflection can be calculated from the broadening of the reflection peak according to the Scherrer equation, $d = (K\lambda)/(B \cos \theta)$,¹¹ where K is a numerical constant on the order of unity, λ is the wavelength of the X-ray beam, θ is the Bragg angle, and B is the peak width measured in radians.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA)^{¶¶} were performed under a nitrogen flow of 50 mL/min. The heating rate in the TGA was 10°C/min, that in the DTA 20°C/min.

The acidity of the dispersions was qualitatively determined by pH-indicator paper.^{†††}

III. Results and Discussion

The boehmite dispersions are clear colloidal solutions exhibiting a weak blue color due to light scattering. The sols show an increase in viscosity with increasing particle length and increasing particle concentration. Removal of alcohol and chloride by dialysis raises the pH from about 1 to about 6, and a marked increase in viscosity is observed.

The average particle dimensions of boehmite produced by hydrothermal treatment at 150°C for 20 h of various acidified alkoxide-based solutions are shown in Table I. The type of alkoxide used, the Al(OR)₃ concentration, and the Al:Cl molar ratio have a significant effect on the length of the particles, which can be varied roughly between 100 and 500 nm, while the particle width shows only small changes around 20 nm. The fibril thickness differs only slightly from 8 nm. In general, for the hydrothermal treatment of ASB, the average

^{††}CM10 transmission electron microscope, Philips, Eindhoven, Netherlands.

^{§§}Model 1050/25, Philips.

^{¶¶}Model 1090 thermal analyzer, Du Pont, Wilmington, DE.

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Table I. Hydrothermally Treated* Solutions and the Average Particle Dimensions and Aspect Ratios of the Boehmite Products Determined by Electron Microscopy

Sample	Alkoxide precursor	Alkoxide concn (mol/L)	HCl concn (mol/L)	n^{\dagger}	Length (nm)	Width (nm)	Aspect ratio
ASB1	Al(O- <i>sec</i> -Bu) ₃	0.077	0.053	117	367 [39] [†]	23 [30]	17 [41]
ASB2	Al(O- <i>sec</i> -Bu) ₃	0.078	0.059	71	456 [43]	30 [33]	16 [50]
ASB3	Al(O- <i>sec</i> -Bu) ₃	0.076	0.095	105	439 [44]	20 [40]	23 [43]
ASB4	Al(O- <i>sec</i> -Bu) ₃	0.088	0.030	124	136 [40]	17 [24]	8 [38]
ASB5	Al(O- <i>sec</i> -Bu) ₃	0.130	0.038	105	137 [42]	19 [26]	7 [43]
ASB6	Al(O- <i>sec</i> -Bu) ₃	0.192	0.037	120	105 [32]	24 [21]	4 [25]
ASB7	Al(O- <i>sec</i> -Bu) ₃	0.250	0.037	118	113 [39]	21 [24]	5 [40]
ASB8	Al(O- <i>sec</i> -Bu) ₃	0.250	0.192	32	418 [36]	15 [38]	30 [39]
ASB9	Al(O- <i>sec</i> -Bu) ₃	0.296	0.112	65	253 [44]	17 [24]	16 [50]
AIP1	Al(O- <i>i</i> -Pr) ₃	0.176	0.055	144	124 [43]	18 [22]	7 [43]
AIP2	Al(O- <i>i</i> -Pr) ₃	0.181	0.058	127	179 [41]	20 [25]	9 [44]
AIP3	Al(O- <i>i</i> -Pr) ₃	0.076	0.055	119	222 [46]	20 [25]	11 [36]
AIA1	Al(O- <i>i</i> -Am) ₃	0.179	0.054	155	166 [44]	19 [26]	9 [44]
ATB1	Al(O- <i>t</i> -Bu) ₃	0.145	0.058	146	165 [48]	20 [20]	8 [50]
ASBIP1	Al(O- <i>sec</i> -Bu) ₃	0.048					
	Al(O- <i>i</i> -Pr) ₃	0.048	0.059	135	306 [42]	16 [25]	20 [45]
ASBIP2	Al(O- <i>sec</i> -Bu) ₃	0.072					
	Al(O- <i>i</i> -Pr) ₃	0.024	0.049	74	265 [43]	18 [22]	15 [53]
ASBIP3	Al(O- <i>sec</i> -Bu) ₃	0.024					
	Al(O- <i>i</i> -Pr) ₃	0.073	0.049	72	284 [56]	21 [19]	14 [57]
ASBIP4	Al(O- <i>sec</i> -Bu) ₃	0.074					
	Al(O- <i>i</i> -Pr) ₃	0.075	0.087	78	513 [36]	16 [19]	32 [38]
ASBIP5	Al(O- <i>sec</i> -Bu) ₃	0.123					
	Al(O- <i>i</i> -Pr) ₃	0.123	0.142		150-650	±16	±25

*150°C for 20 h. [†]Number of measured particles. [‡]Percentage standard deviations are given in brackets.

fibril length increases if $[\text{Cl}^-]$ increases, keeping $[\text{Al}]$ constant, and the length also increases if $[\text{Al}]$ increases, keeping the Al:Cl molar ratio constant (Figs. 1(A) and (B), Fig. 2). An average aspect ratio of 30 can be reached for particles around 400 nm.

Sample ASB2 (Fig. 1(A)) shows polycrystalline boehmite fibrils grown from ASB, being built up of small elongated subunits, which are stuck together with identical crystallographic orientations in the plane formed by their x -axis and z -axis. The particles are therefore flat fibrils which tend to lie with their (010) sides on the TEM grid. This implies that the electron micrograph mainly shows the particle width, while the thickness must be estimated from tilted particles. For the same concentration of alkoxide, AIP gives shorter and thinner particles than ASB (Fig. 1(C)). AIA and ATB show effects similar to those of AIP on the particle morphology.

Hydrothermal treatment of a 1:1 molar mixture of ASB and AIP acidified with HCl leads to a dispersion of very well-defined high aspect ratio needles (Fig. 1(D)). Histograms of particle lengths, widths, as well as aspect ratios of sols prepared by using ASB (sample ASB1), AIP (sample AIP3), and a 1:1 molar ratio of the two alkoxides (sample ASBIP1) are shown in Fig. 3. The average particle width achieved with the mixture is smaller than for either ASB or AIP alone. The aspect ratio distribution of sample ASBIP1 levels out toward very high values of about 55. Using the ASB-AIP mixture, the length of the needles can be increased considerably by raising the initial Al^{3+} and Cl^- concentrations, without varying the Al:Cl molar ratio and keeping the ASB:AIP molar ratio equal to 1. This can be seen in Table I for sample ASBIP4.

An increase of $[\text{Cl}^-]$ results in a higher boehmite yield, irrespective of the $\text{Al}(\text{OR})_3$ concentration. This is indicated by the AlOOH yields of samples ASB4 (65%), ASB7 (65%), and

ASBIP5 (81%). If the initial Cl^- concentration is higher than about 0.08 mol/L, two different types of aggregation of neighboring particles may occur. The first type is a reversible aggregation, which happens when the Al:Cl molar ratio is about 1 and higher, as seen in ASB9 (Fig. 4(A)). The marked turbidity of this dispersion, indicating particle aggregation, can be lowered by Cl^- removal. This reversible aggregation is a consequence of a weak net attraction between the particles. This attraction presumably results from the compression of the electric double layer surrounding the particles, caused by the presence of a relatively large electrolyte concentration. According to the DLVO theory^{12,13} it is possible that the particles then flocculate in a so-called "secondary minimum" of the potential energy between the particles if the thermal energy of the particles is small enough. One can imagine that this is the case while the dispersion cools after hydrothermal treatment. Exact particle size measurement from the electron micrograph of sample ASBIP5 is severely complicated by this aggregation.

When the solution has a low initial Al:Cl molar ratio of about 0.8, the second type of aggregation occurs, which produces skeleton-like intergrown fibrils, illustrated by sample ASB3 (Fig. 4(B)). This irreversible aggregation must have taken place during the particle growth process.

With respect to this growth process, we suggested earlier⁴ a mechanism which seems analogous to that proposed by Sugimoto and Matijević.¹⁴ Very small primary particles nucleate from an open $\text{Al}(\text{OH})_m(\text{OR})_{3-m} \cdot n\text{H}_2\text{O}$ gel network. The gel network retards primary particle growth appreciably while the particle number increases. At the same time larger secondary particles arise by rapid coagulation of the small primary particles. Each secondary particle grows until its vicinity is devoid of primary "feed" particles. The initial

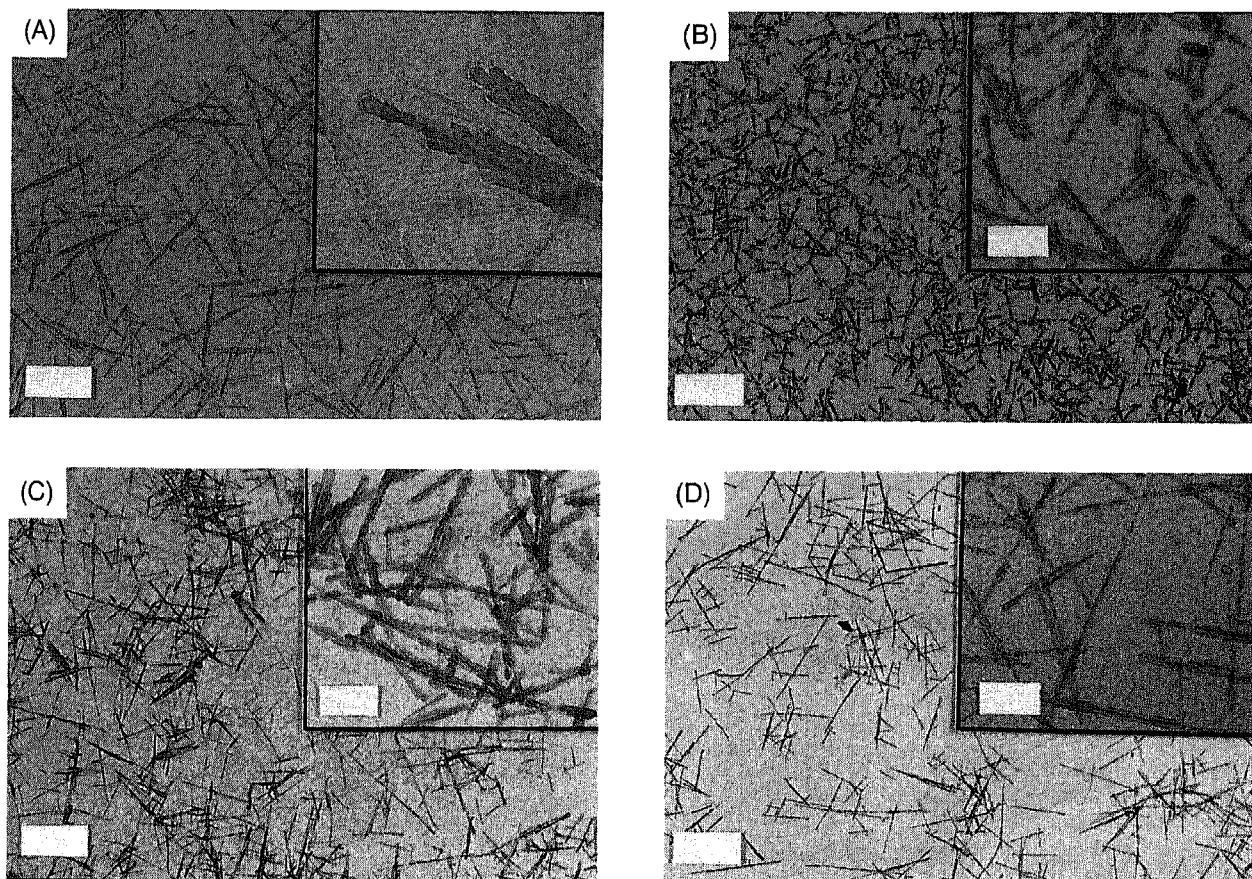


Fig. 1. Transmission electron micrographs of boehmite obtained as listed in Table I: (A) sample ASB2, (B) sample ASB5, (C) sample AIP3, and (D) sample ASBIP1. The lengths of the bars at low magnification represent 0.5 μm ; those at high magnification (in the inserts) 0.1 μm .

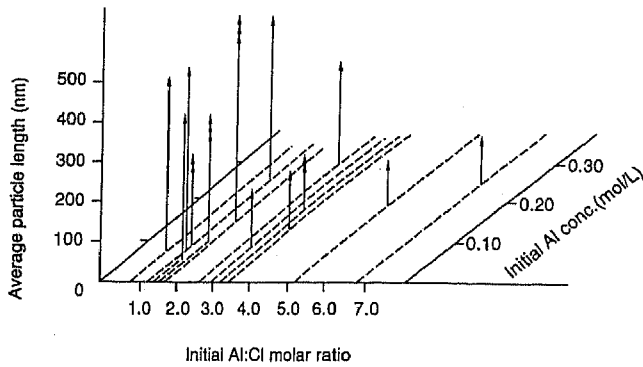


Fig. 2. Average length of boehmite particles determined with electron microscopy as a function of initial aluminum concentration and Al:Cl molar ratio (three-dimensional plot). Temperature of synthesis 150°C, duration 20 h. Single arrow: Al(O-*sec*-Bu)₃; double arrow: Al(O-*i*-Pr)₃; and triple arrow: 1:1 molar ratio of Al(O-*sec*-Bu)₃ and Al(O-*i*-Pr)₃.

amounts of alkoxide and chloride may have an effect on the structure of the network and thus on the final particles.

The X-ray powder diffraction peaks of sample ASBIP5 (Table II) show the considerable broadening of typical sub-micrometer fibrillar boehmite. From the broadening of the basal 020 reflection the fibril thickness is calculated to be 8.1 nm, supposing that the particles do not have strain. This value matches well with the thickness of about 8 nm, determined by electron microscopy. The 020 spacing of 6.14 Å approaches that calculated for an ideally ordered γ -AlOOH lattice,¹⁵ which shows that interlayer water is absent. So the excess water must be present on the surface of the well-crystallized AlOOH subunits.

TGA and DTA patterns (Fig. 5(A)) of the powder of sample ASBIP5 are as expected for polycrystalline boehmite.⁴ About 5 wt% of the powder ASBIP5 at room temperature is physisorbed atmospheric water, which is completely released at about 95°C. The amount of excess water is calculated, from the gradual weight loss between 100° to 330°C, to be 0.14 mol of H₂O per mole of AlOOH. The dehydration to Al₂O₃ begins at 330°C with a sharp endothermic heat effect.

The weight loss as a function of time, heating at a constant rate from 25° to 1000°C, and holding the temperature for 1 h at 100°C and 1 h at 330°C, is displayed in Fig. 5(B). Prolonged

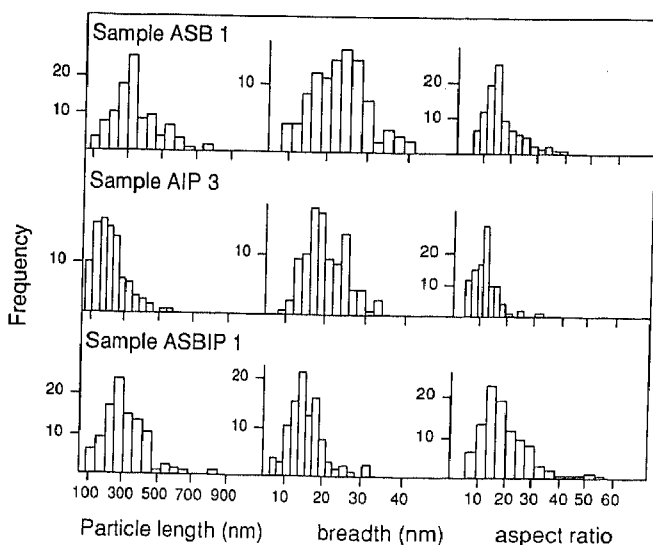


Fig. 3. Histograms of the particle length, breadth, and aspect ratio distributions of samples ASB1, AIP3, and ASBIP1 (Table I), obtained from electron micrographs.

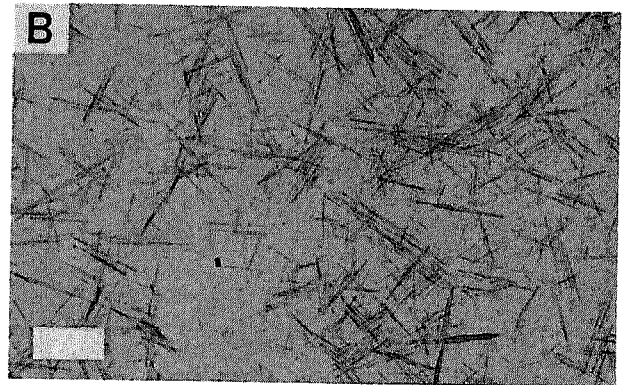


Fig. 4. Transmission electron micrographs of strongly aggregated boehmite particles of sample ASB9 (A), and "skeletal" coagulated boehmite of sample ASB3 (B). The lengths of the bars correspond to 0.5 μ m.

heating at 100° or 330°C does not generate more weight loss, suggesting that the excess water is firmly bound to the boehmite surface. A striking feature in the DTA pattern for ASBIP5 (Fig. 5(A)) is the two partly superposed endothermic effects at about 190° and 295°C, which distinguish two successive, overlapping excess water releases with increasing temperature.

In previous work⁴ we found a morphological change with increasing temperature of hydrothermal treatment toward particles built up of fewer subunits of larger size. The decreasing polycrystallinity correlated with a decreasing amount of excess water, which suggests that the excess water is located between the subunits of the fibril. Once the polycrystalline boehmite fibrils have lost their "intercrystallite water" at 330°C in TGA, they start to convert to Al₂O₃.

Table II. X-ray Powder Diffraction Data of Sample ASBIP5, with Crystallite Diameter Calculated from Peak Broadening

<i>hkl</i>	<i>d</i> _{<i>hkl</i>} (Å)	<i>I</i> _{rel}	2 θ _{<i>hkl</i>} (deg)	HPW* (rad)	<i>d</i> [†] (nm)
020	6.14	100	14.42	0.0096	8.1
120	3.16	97	28.22	0.0113	7.0
200	1.85	80	49.10	0.0122	6.9
031	2.34	74	38.41	0.0079	10.3
002	1.43	28	65.18	nd [‡]	
231	1.45	26	64.17	nd	
122	1.31	25	72.02	0.0096	9.9
151	1.66	24	55.36	0.0105	8.3
220	1.76	21	51.91	nd	
171	1.38	18	67.86	nd	
131	1.97	16	46.03	nd	
080	1.53	15	60.45	nd	

*Half peak width. [†]Mean diameter according to Scherrer's equation with the peak width as 2 times the half peak width. [‡]Not determined.

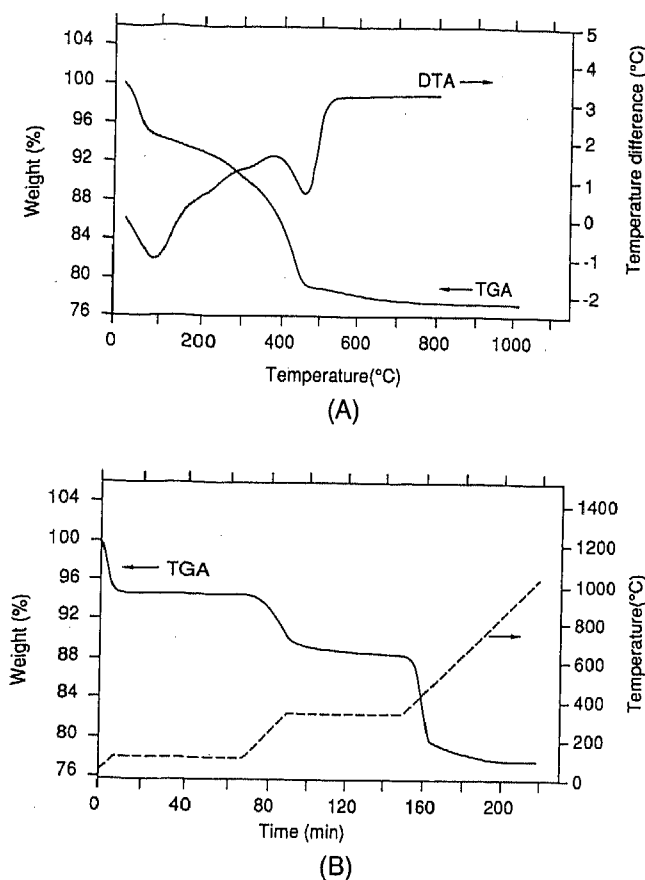


Fig. 5. (A) DTA and TGA curves of boehmite powder obtained from sample ASBIP5 by freeze-drying; (B) TGA with weight loss as function of time; dashed line: heating temperature trajectory.

IV. Conclusions

Noncoagulated submicrometer boehmite needles can be prepared easily by hydrolysis at 150°C of a 1:1 molar mixture of $\text{Al}(\text{O-}i\text{-Pr})_3$ and $\text{Al}(\text{O-}i\text{-Am})_3$ acidified with an aqueous HCl solution. In general, hydrolysis of only $\text{Al}(\text{O-}i\text{-Pr})_3$ under the same conditions results in flat fibrils in the same size

range, while use of $\text{Al}(\text{O-}i\text{-Pr})_3$, $\text{Al}(\text{O-}i\text{-Am})_3$, or $\text{Al}(\text{O-}t\text{-Bu})_3$ yields shorter but fairly needlelike particles. The boehmite particles are polycrystalline and have about 40% polydispersity in their length.

A major advantage of the alkoxide route is the possibility of synthesizing particles with a particular average length between 100 and about 500 nm, by choosing the appropriate initial amounts of $\text{Al}(\text{OR})_3$ and HCl.

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