ALCOHOTHERMAL TREATMENTS OF GIBBSITE: MECHANISMS FOR THE FORMATION OF BOEHMITE

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Abstract—Gibbsite samples of various particle sizes (0.2–80 μm) were heated at 250°C in a series of straight-chain primary alcohols under the autogenous vapor pressure of the alcohol (alcohothermal treatment of gibbsite). The treatment in ethanol yielded pure boehmite, the morphology of which was similar to that of the boehmite obtained by hydrothermal treatment of gibbsite. In middle-range alcohols, the boehmite yields were low (50% if 80 μm gibbsite was used), and the products were contaminated by a poorly crystallized phase, having a χ-alumina-like structure. The products preserved the morphology of the originating gibbsite, this feature being similar to the thermal dehydration of gibbsite. Complete conversion to boehmite was also attained in mineral oil (a hydrocarbon mixture, which was used as a limit of higher alcohol. The morphology of the boehmite formed in this medium was identical to that of the product prepared by thermal dehydration of gibbsite in a sealed bomb without a medium. If fine particle-size gibbsite was used, the yield of boehmite decreased and the yield of the poorly crystallized phase increased in all the media.

The reaction mechanisms may be discussed in terms of the reported mechanisms for the thermal and hydrothermal formations of boehmite from gibbsite. Thus, in lower alcohols boehmite formed by a dissolution-recrystallization mechanism, whereas in middle-range or higher alcohols it formed by intra-particle hydrothermal reaction mechanism proposed by de Boer and coworkers for the thermal dehydration of gibbsite. The difference in behavior in middle-range and higher alcohols can be explained in terms of the solubility of water in the medium: In the middle-range alcohols, water molecules formed by partial dehydration of gibbsite were removed from the gibbsite particles into the medium so that dehydration proceeded in a manner similar to that of thermal dehydration, whereas in the higher alcohols, the low solubility of water in the medium allowed the water molecules to remain on the surface of the particles, thereby promoting the complete hydrothermal formation of boehmite.

Key Words—Alcohol, χ-Alumina, Boehmite, Crystallization, Gibbsite, Thermal treatment.

INTRODUCTION

Boehmite can be synthesized by aging aluminum hydroxide gel (Shimizu *et al.,* 1964; Violante and Huang, 1985), by rehydration of transition aluminas (Day and Hill, 1953; Yamaguchi and Chiu, 1968), by oxidation of aluminum metal (Torkar *et al.,* 1960), and, most commonly, by hydrothermal treatment of aluminum hydroxide (gibbsite or bayerite) (Ginsberg and Koester, 1952). Some boehmite also forms if coarse-grained samples of crystalline aluminum hydroxides are calcined at about 250°C (Stumpf *et al.,* 1950).

During studies on controlling the pore texture of alumina used as a catalyst support (Inui *et al.,* 1982, 1983), a thermal treatment of gibbsite in ethylene glycol under autogenous pressure was found to yield an organic derivative of boehmite in which ethylene glycol moiety was incorporated between the layer structure of boehmite (Inoue *et al.,* 1986, 1988). Interestingly, the product had a honeycomb-like texture; the transition alumina obtained by calcination of the product preserved this unique texture and is of potential use as a catalyst support.

As an extension of this work, gibbsite has been heat-ed under pressure in a series of alcohols (this process is herein termed "alcohothermal" treatment, a phrase derived from "hydrothermal," but in which alcohols are used in place of water) to form boehmite. The present paper describes the morphology of such products and discusses the possible mechanisms of the reaction.

BACKGROUND

Mechanism for hydrothermal transformation of gibbsite to boehmite

Bauermeister and Fulda (1943) and Yamaguchi and Sakamoto (1959a) proposed a dissolution-recrystallization mechanism for the formation of boehmite by hydrothermal treatment of gibbsite. This mechanism is supported by the following results: (1) The formation of boehmite is accelerated by the alkalinity of the medium (Ginsberg and Koester, 1952; Russell *et al.,* 1955; Yamaguchi and Sakamoto, 1959a). (2) The presence of foreign ions in the medium affects the reaction rate (Inui *et al.,* 1983). (3) The presence of boehmite seed crystals shortens the induction period and lowers the temperature required by the reaction (Yamaguchi and

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Table 1. Properties of the starting gibbsite samples.

Gibbsite sample	Average particle size (μm)	Surface area[1] (m^2/g)	Impurity[2] (wt. %)	
			Na_2O	Fe_2O_3
I	80[3]	0.17	0.25	0.007
II	25[2]	1.1	0.21	0.007
III	8[2]	2.4	0.21	0.007
IV	0.2[2]	11	0.4	0.01
V	<0.2[3]	20	0.4	0.01

[1] Calculated by BET one point method based on the nitrogen adsorption determined at liquid nitrogen temperature using a gas chromatograph.
[2] Taken from producer's technical data sheet.
[3] Determined by scanning electron microscopy.

Sakamoto, 1959a). (4) Crystal and crystallite sizes grow by hydrothermal treatment of microcrystalline boehmite (de Boer and Linsen, 1964; Tettenhorst and Hofmann, 1980).

Mechanism for the formation of boehmite by the thermal dehydration of gibbsite

De Boer *et al.* (1954a, 1954b) first proposed the idea that the boehmite formation requires hydrothermal conditions. This idea is now generally accepted (Papée and Tertian, 1955; Rouquerol *et al.,* 1975). De Boer *et al.* (1964) also presented some evidence for the formation of ink-bottle type pores by "intraparticle hydrothermal reaction" at the early stage of the dehydration and explained: "The development of water starts at the active spot in the gibbsite particle; water inside the particle cannot escape quickly enough and builds up a relatively high pressure, converting gibbsite into boehmite and water; on proceeding the reaction the water forces its way out; thus creating some ink-bottle type pores releasing the internal pressure, and inside the particle the conversion into boehmite has left some holes" (de Boer *et al.,* 1964).

Formation of transition alumina from gibbsite under thermal dehydration conditions

Brindley and Choe (1961) reported that when the dehydration of gibbsite was about 75% complete ($Al_2O_3 \cdot 0.75H_2O$), the reaction rate was reduced to almost zero in all the temperatures employed (250°–297°C). Rouquerol *et al.* (1975, 1979) and Paulik *et al.* (1983) reported that the thermal dehydration into such a transition alumina consists of two partial processes: The first process is a relatively rapid one, whose apparent order is zero toward the amount of unreacted gibbsite (Rouquerol *et al.,* 1975, 1979) and is affected by the water pressure of environment (Paulik *et al.,* 1983; Pokol *et al.,* 1984). The second process is a slow dehydration which requires progressively higher temperatures. Rouquerol *et al.* (1975, 1979) attributed the first process to the formation of ρ-alumina (Tertian and

Papée, 1958) and the second one to the dehydration of the ρ-alumina.

Relation of earlier studies to the present work

Dehydration of gibbsite in a mixture of alcohol (C_6–C_{10}) and hydrocarbon (C_{10}–C_{16}) at the reflux temperature under atmospheric pressure was examined by Suzuki *et al.* (1981), who found that the dehydration of gibbsite started at 200°C and was complete at about 250°, yielding a mixture of boehmite and ρ-alumina. Following the suggestion of Bugosh (1960), Kubo and Uchida (1970) examined a reaction of gibbsite with methanol and found that at high temperatures (>280°C) and pressures (>180 kg/cm^2) a "novel" transition alumina was formed, which was characterized by a sharp XRD peak at $2\theta = 42.5°$ (identical to the characteristic peak of χ-alumina).

Fanelli and Burlew (1986) autoclaved aluminum sec-butoxide in sec-butanol at 250°–300°C and found that a noncrystalline alumina having an apparent formula of $Al_2O_3 \cdot H_2O$ formed at short reaction times, which on prolonged reaction converted into χ-alumina.

Although not concerned with alumina *per se,* organic media have recently been used for the synthesis of "silica-sodalite", $Si_{12}O_{24} \cdot 2C_2H_4(OH)_2$ which cannot be formed under hydrothermal conditions (Bibby and Dale, 1985).
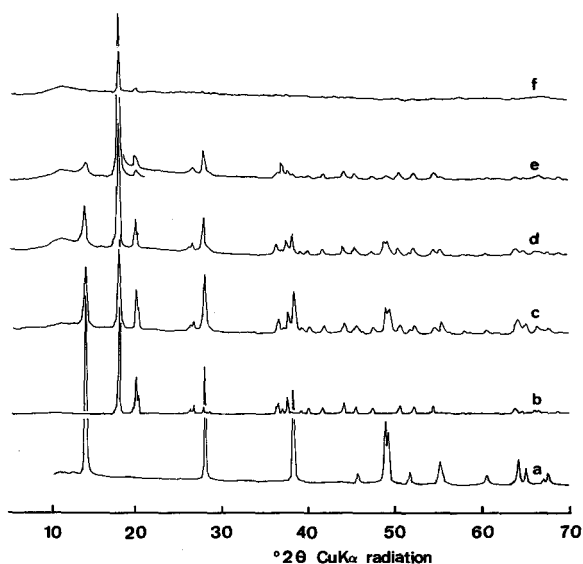

Figure 1. X-ray powder diffraction (XRD) patterns of the products obtained by pentanothermal treatment of gibbsite. (a) Boehmite obtained by hydrothermal treatment of gibbsite I, (b) gibbsite I, (c) product from gibbsite I, (d) product from gibbsite III, (e) product from gibbsite IV, (f) product from gibbsite V. The XRD patterns of gibbsite I, II, and III were identical, whereas the 002 peaks of gibbsite IV and V was much more intense than other peaks (see Yamaguchi and Sakamoto, 1959b). The broad peak at $11.5°2\theta$ is due to grease used to mount the sample. For gibbsite I–IV, see Table 1.

Table 2. Properties of the medium and the reaction pressure.[1]

Medium	Properties			Reaction pressure (kgG/cm²)
	Boiling point (°C)	Critical		
		Temp. (°C)	Pressure (atm)	
Water	100	374.2	218.3	49
Ethanol	78.3	243.1	62.96	118
1-propanol	97.2	263.6	51.02	50
1-butanol	111.7	289.8	43.55	35
1-pentanol	137.8	313	(36.7)²	19
1-hexanol	157.5	337	(32.3)²	12
1-octanol	195.2	385	(12.5)²	10
Mineral oil[3]	300–330	—	—	14

[1] Pressures attained by the thermal treatment of gibbsite in these media at 250°C for 2 hr.
[2] Estimated value.
[3] Mixture of the saturated hydrocarbons of the C_{17}–C_{19} fraction.

EXPERIMENTAL

Materials

Four commercial gibbsite samples (gibbsite I–IV) produced by the Bayer process were kindly provided by Nippon Light Metal Company, Ltd. A fifth gibbsite sample having the finest particle size (gibbsite V) was prepared by dry-grinding a commercial gibbsite for a week in a mechanically driven alumina mortar, 45 cm in diameter. The properties of the five gibbsite samples are summarized in Table 1. Guaranteed grade alcohols were used without further purification.

Alcohothermal treatment of gibbsite

To a Pyrex test tube serving as an autoclave liner, 3 g of a gibbsite sample was added and suspended with 13 ml of an alcohol. The alcohol was also placed in the gap between the test tube and the autoclave wall to fill the space of the autoclave with alcohol vapor. The autoclave was sealed and purged completely with nitrogen. The sample was heated to the desired temperature (usually 250°C) at a rate of 2°C/min and then held at that temperature for 2 hr under the spontaneous vapor pressure of alcohol. Reaction pressure increased gradually during the course of the reaction, presumably because of the formation of water. The pressures at the end of the reaction period (2 hr) are shown in Table 2. After the assembly was cooled to room temperature, the resulting precipitates were washed with methanol and air dried. The products were loose powders of apparent particle sizes similar to the starting materials, except if gibbsite V was used. Here, the product consisted of tightly packed agglomerates having various particle sizes.

Analyses

Thermal analyses were performed on a Shimadzu DT-30 thermal analyzer. A weighed amount (~30 mg) of sample was placed in the analyzer, dried in a 40 ml/min flow of dried air until no further weight decrease was detected, and then heated at a rate of 10°C/min in the same gas flow. X-ray powder diffraction (XRD) analyses were made on a Rigaku Geigerflex-2013 diffractometer employing Ni-filtered CuKα radiation. For quantitative analysis, weighed amounts of each sample and α-alumina were mixed thoroughly in an agate mortar, and three diffraction peaks (2θ = 25.5° for α-alumina, 18.3° for gibbsite, and 14.5° for boehmite) were recorded at a scanning rate of 0.25°2θ/min. The gibbsite and boehmite contents of the samples were calculated by comparing the peak area ratios with calibration curves determined by using corresponding originating gibbsite samples and a hydrothermal boehmite. Morphologies of the particles were observed with a scanning electron microscope, Hitachi-Akashi MSM-102.

RESULTS

X-ray powder diffraction

The XRD patterns of the precipitates from the pentanothermal treatment of gibbsite samples of various particle sizes are shown in Figure 1 as representative of all results. For comparison, the XRD patterns of gibbsite and boehmite are also shown. From the XRD data, it is clear that well-crystallized phases other than boehmite and unreacted gibbsite are not present in the product.

The results of quantitative XRD analyses are summarized in Table 3. Although the results are slightly scattered, the yield of boehmite appears to have decreased with decreasing particle size of the starting material. In some runs, the gibbsite + boehmite contents totaled <100%, especially in the products obtained from gibbsite V. Close examination of the XRD patterns of these products reveals additional peaks at ~65° and ~42.5°2θ. The latter peak was more pronounced if a higher alcohol or reaction temperature of 300°C was used or if the product was calcined at 350°C in air. The former peak has been commonly observed for transition aluminas, and the latter peak is characteristic of χ-alumina (Stumpf et al., 1950). Therefore, these products contained a poorly crystallized phase, presumably having a χ-alumina-like structure (hereafter called "χ*-alumina"; the term "χ-alumina" will be restricted to the phase obtained by thermal dehydration of gibbsite).

The effect of the particle size of the starting gibbsite is illustrated in Figure 2. With increasing the particle size of gibbsite, the yield of boehmite increased and the yield of χ*-alumina decreased. The content of unreacted gibbsite was sensitive to the reaction conditions, but was clearly less if the finest particle-size gibbsite was used.

In Figure 3, the effect of carbon number of the al-

cohol is illustrated. Carbon number zero represents runs made in water (i.e., hydrothermal treatment), in which gibbsite converted completely into boehmite, irrespective of the particle size of the gibbsite. With an increase in the carbon number of the alcohol, the boehmite yield decreased and reached a minimum at carbon number 5 (pentanol). Further increase in the carbon number increased the boehmite yield. In Figure 3, the compositions of the products formed by treatment in mineral oil are also shown. Mineral oil is not an alcohol, but a hydrocarbon mixture; it was used as the limit for higher alcohol, assuming that the effect of the hydroxyl group can be neglected as compared with the effect of the alkyl group. Here, the product was boehmite, except for gibbsite V, which gave a significant amount of χ^*-alumina (not shown in Figure 3; see Table 3).

Thermal gravimetric analysis

Differential thermal gravimetric (DTGA) profiles for the samples, whose XRD patterns are shown in Figure 1, are shown in Figure 4. A relatively sharp peak was observed at 280°C for samples containing gibbsite; this peak is due to the dehydration of gibbsite to χ-alumina (Lodding, 1969; Paulik *et al.*, 1983). A rather broad weight-loss peak at $\sim$500°C is due to the dehydration of boehmite to γ-alumina. From the intensities of these two weight-loss peaks boehmite and gibbsite contents were estimated on the basis of the following reactions:

$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O$$
$$2\,AlOOH \rightarrow Al_2O_3 + H_2O.$$
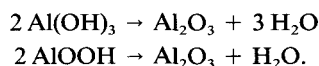
These values are 80–98% of those estimated from the XRD data, probably because the transition aluminas obtained by the thermal dehydration of boehmite or gibbsite may have contained significant amounts of hydroxyl ions in the structure (Wefers and Bell, 1972).

In addition to these two dehydration peaks, all samples containing significant amounts of χ^*-alumina
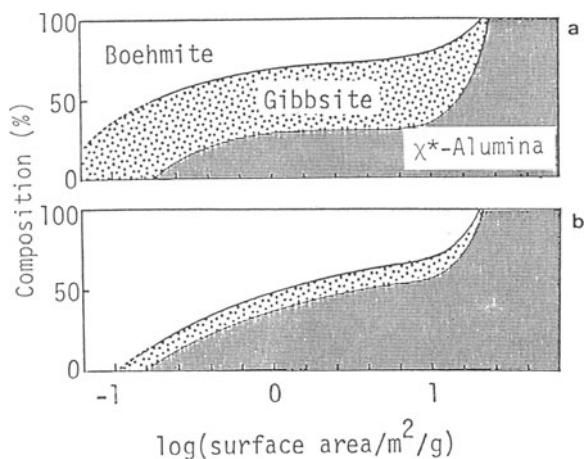

Figure 2. Effects of the particle size (surface area) of gibbsite on the product composition of alcohothermal treatments: (a) in hexanol and (b) in octanol.

showed a broad peak centered at 300°C. Therefore, this peak is assumed to have been due to the dehydration of this phase. The water content of χ^*-alumina was calculated from the intensity of this peak, yielding about one mole per mole of Al_2O_3, which is much larger than that for the ordinary transition aluminas.

Figure 5 shows the DTGA profiles for the originating gibbsite samples. The coarse gibbsite samples showed two additional peaks, in addition to the 280°C peak, for the dehydration of gibbsite into χ-alumina. This behavior is explained by a dual dehydration sequence (Brown *et al.*, 1953), and the 250°C (shoulder) and 520°C peaks probably represent the formation of boehmite from gibbsite and the dehydration of boehmite to γ-alumina, respectively (Brown *et al.*, 1953; Tertian and Papée, 1958; Paulik *et al.*, 1983). TGA analysis of the gibbsite samples was also performed using the heating profile similar to the alcohothermal treatment (Figure 6).

Table 3. Composition of the product obtained by thermal treatment of gibbsite in various media.[1,2]

Gibbsite	Component	Solvent							
		H_2O	C_2OH	C_3OH	C_4OH	C_5OH	C_6OH	C_8OH	Mineral oil
I	Boehmite	100	100	99	98	51	51	86	100
	Gibbsite	0	0	1.0	2.0	33	49	11	0
II	Boehmite	100	100	69	88	61	33	60	100
	Gibbsite	0	0	2.1	3.1	21	37	11	0
III	Boehmite	100	100	70	56	21	27	41	100
	Gibbsite	0	0	5.7	5.5	38	43	5.6	0
IV	Boehmite	100	74	85	80	12	23	31	100
	Gibbsite	0	2.4	4.3	0.9	43	48	13	0
V	Boehmite	100	20	0[3]	1.5	0.9	1.4	0	12
	Gibbsite	0	1.3	4.3	3.8	15	10	6.8	0

[1] As determined by an X-ray powder diffraction technique using α-alumina as an internal standard.
[2] Reaction conditions of the treatment: 250°C for 2 hr.
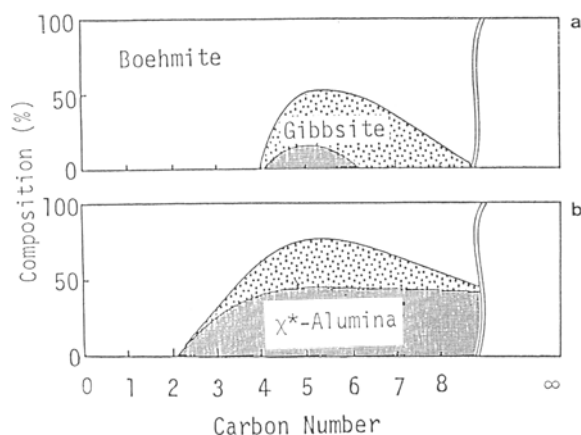[3] An organic derivative of boehmite was obtained.

Figure 3. Effects of the carbon number of the alcohols used as medium for alcohothermal treatment of: (a) gibbsite I and (b) gibbsite IV. Origin and infinity of abscissa represent runs made in water and in mineral oil, respectively. See text, for detail.

Figure 5. Differential thermal gravimetric profiles of original gibbsite samples. Heating rate 10°C/min in 40 ml/min air flow.

Scanning electron microscopy

If water or a lower alcohol (C_1–C_4) was used as the reaction medium, the product was composed of aggregates of randomly oriented, diamond-shaped boehmite crystals (Figure 7). If C_5 or C_6 alcohol was used, the product was morphologically similar to the starting material (gibbsite), although crystal surfaces seemed to be slightly rough (Figure 8a). If higher alcohols or mineral oil was used, the product showed a strict pseudomorphosis to the starting material, and an apparent orientation of the boehmite crystals was observed (Figures 8b and 8c). The particle size of the products of all reactions was similar to that of the starting materials.

For comparison, two samples were prepared: (1) Gibbsite I was heated at 250°C in an air flow (55% boehmite and 32% gibbsite as determined by XRD); (2) The same gibbsite was heated at 250°C in the au-
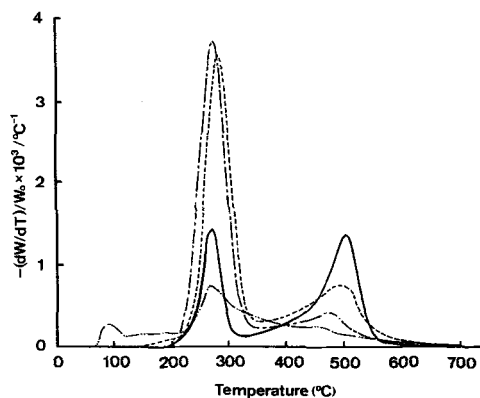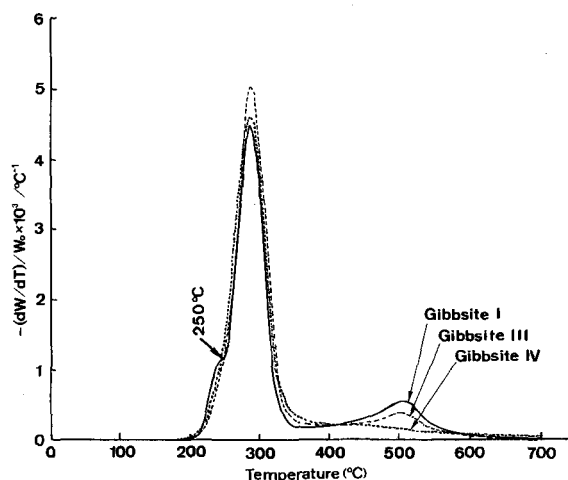
toclave without a medium (100% boehmite as determined by XRD). The SEM photographs of these two products are shown in Figure 9. The outline of the product of the treatment (1) strictly preserved that of the original gibbsite, just as was observed for the products of pentano- and hexano-thermal treatments. The morphology of sample (2) was the same as what was seen in the product of the treatment in mineral oil.

Effect of reaction period on the product composition

To obtain kinetic information, the reactions were quenched at various times; typical results are shown in Figure 10. Because of the initial heating period, gibbsite was partially converted at 0 hr (the reaction was quenched immediately after the temperature
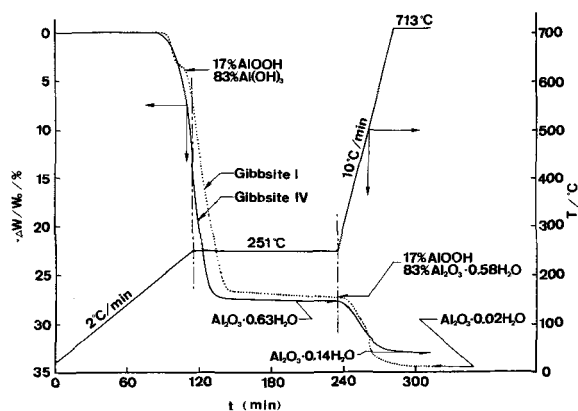

Figure 4. Differential thermal gravimetric profiles of products obtained by the pentanothermal treatment of : ——, gibbsite I; – – –, gibbsite III; –·–·–, gibbsite IV; –··–··–, gibbsite V. Heating rate, 10°C/min in 40 ml/min air flow.

Figure 6. Thermal gravimetric profiles of the originating gibbsite samples determined using the heating process similar to the alcohothermal treatment (2°C/min). Product compositions shown in the illustration were calculated from weight loss.

reached 250°C). In butanol, the reaction followed ordinary kinetics. In hexanol, boehmite formation stopped at a certain point in the reaction and the boehmite yield then increased after prolonged reaction time.

DISCUSSION

Boehmite formation by treatment in lower alcohols

Although physical properties of the medium change gradually from water to mineral oil, the product distribution did not change monotonously, suggesting that the change of the product distribution cannot be explained on the basis of only one mechanism, i.e., solid phase transformation proposed by Ginsberg and Koester (1952) and Sato (1960) for thermal and hydrothermal formation of boehmite. Two different mechanisms seem to be operative in the formation of boehmite; one in lower alcohols and the other in higher alcohols. The products formed in lower alcohols contain randomly oriented boehmite crystals; this feature is similar to the product of hydrothermal treatment, suggesting that the reaction in lower alcohol proceeded via the dissolution-recrystallization mechanism as proposed for hydrothermal treatment (Bauermeister and Fulda, 1943; Yamaguchi and Sakamoto, 1959a).

According to the dissolution-recrystallization mechanism, polyaluminate species (Yamaguchi and Sakamoto, 1959a) are dissolved from the gibbsite crystals into the medium, nucleation takes place in the supersaturated solution, and then boehmite crystals grow. In alcohothermal treatment, the nucleation of boehmite seems to take place near the crystal surface of the gibbsite, because apparent particle sizes of the products were similar to those of the starting material (gibbsite). With the increase in the carbon number of the alcohol, the possibility that dissolved polyaluminate species diffused away from the gibbsite crystal surface is less, and, therefore, the apparent shape of the product aggregate of boehmite crystals more closely resembled that of the original gibbsite (Figure 7). At the same time, the solubility of the polyaluminate species decreased and the rate for the conversion into boehmite decreased. If the carbon number > 5 (pentanol), boehmite formation via the dissolution-recrystallization mechanism is impossible, and a different mechanism must have been operative.

Mechanism of boehmite formation in higher alcohols

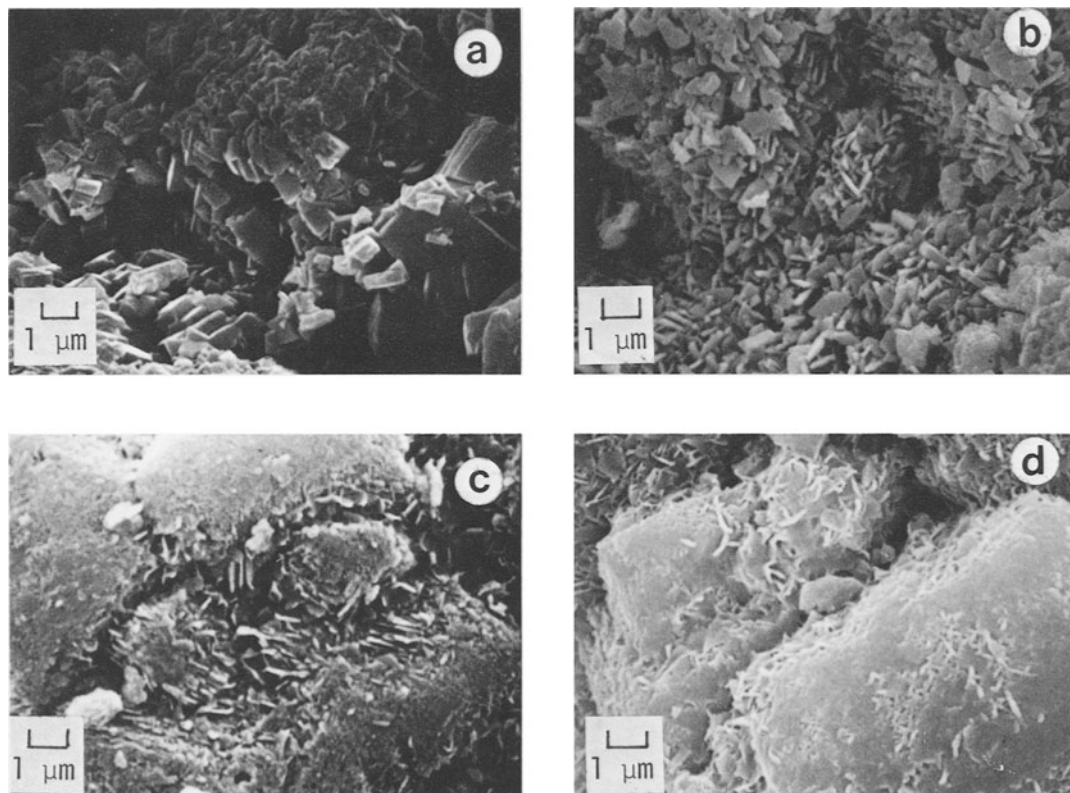The product from the treatment in alcohols higher than C_5 contained a significant amount of the transition al-

Figure 7. Scanning electron micrographs of products obtained by alcohothermal treatment of gibbsite I: (a) hydrothermal treatment, (b) ethanothermal treatment, (c) propanothermal treatment, (d) butanothermal treatment.
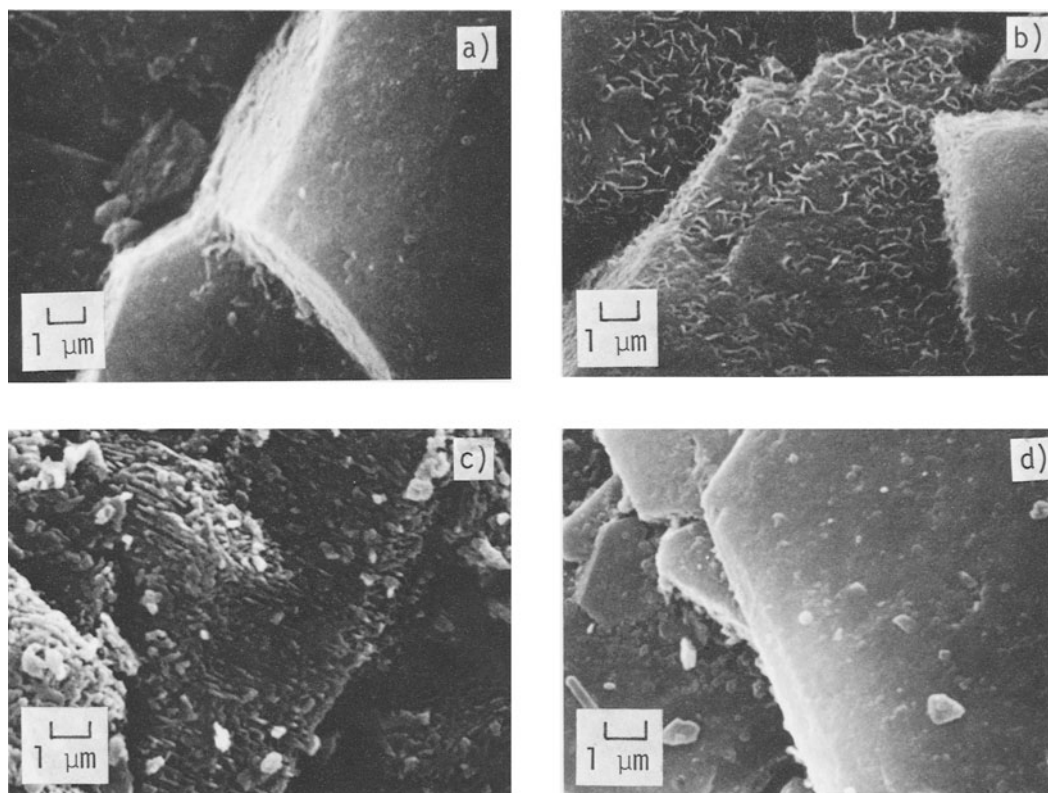
Figure 8. Scanning electron micrographs of products obtained by treatment of gibbsite I in: (a) pentanol, (b) octanol, and (c) mineral oil, and (d) the original gibbsite.

umina, and the yield of boehmite decreased with decreasing particle size of the gibbsite (Figure 2). This behavior is similar to the behavior of gibbsite during thermal dehydration (Thibon *et al.,* 1951; Yamaguchi and Sakamoto, 1959b; Naumann *et al.,* 1983; see also Figure 7), in which dual dehydration sequences occur: one via direct dehydration to a transition alumina and the other via formation of boehmite (Brown *et al.,* 1953; Ginsberg *et al.,* 1957a, 1957b; Funaki and Shimizu, 1959). In middle-range alcohols, the product particles preserved the outline of the original gibbsite aggregates (Figure 8a). This feature was also observed for the product of thermal dehydration of gibbsite at 250°C (Figure 9 upper). These results suggest that the transformation proceeded by a mechanism similar to that operating in thermal dehydration, namely, intraparticle hydrothermal reaction (de Boer *et al.,* 1954a, 1954b).

In the thermal dehydration of gibbsite, the formation of boehmite stops when the formation of χ-alumina starts, probably due to the release of internal water pressure through the pores or cracks developed by the formation of boehmite or χ-alumina (de Boer *et al.,* 1954a, 1954b, 1964). Similarly, the reason for the absence of the peak due to the formation of boehmite in

a TGA of the products, which contained a significant amount of unreacted gibbsite and whose apparent particle sizes were large (Figure 4), can be explained as follows: Because of the difference of specific volumes of gibbsite and boehmite or χ*-alumina, micropores or cracks must have been created by partial formation of boehmite or χ*-alumina during the alcohothermal treatment. These micropores and/or cracks prevented a build up sufficient internal water pressure for the intraparticle hydrothermal reaction during TGA analysis. The particle size effect observed in the present study (Figure 2) can be explained by the same assumption proposed for the thermal dehydration; i.e., that intraparticle hydrothermal conditions cannot exist with very small crystals due to ease of release of water pressure (de Boer *et al.,* 1954a, 1954b).

For prolonged reaction time, χ*-alumina converted into boehmite. In thermal dehydration, rehydration of transition aluminas has never been observed, probably because thermal dehydration is usually examined in an open system—water formed by the partial dehydration of gibbsite diffuses out of the reaction system. In contrast, alcohothermal treatment was carried out in a closed system, and water formed by partial dehydration of gibbsite remained in the system and
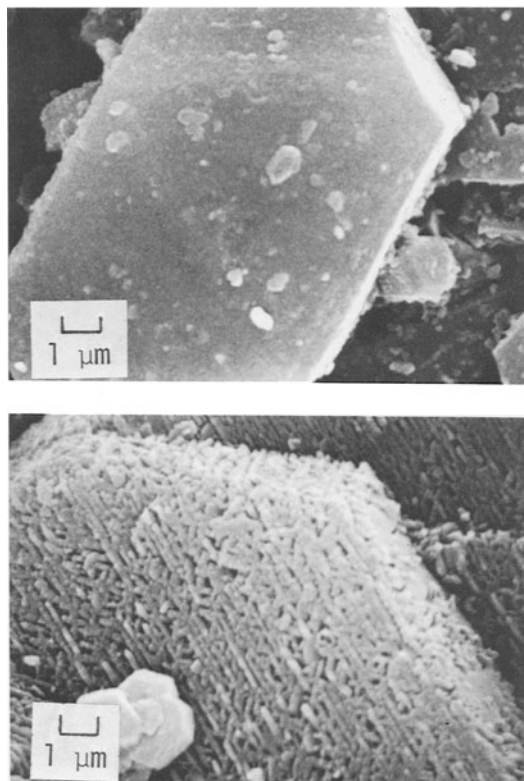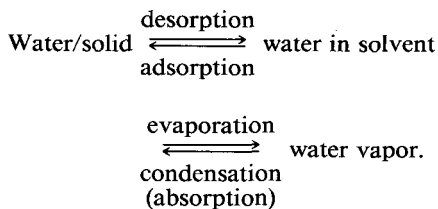
Figure 9. Scanning electron micrographs of products obtained by the thermal dehydration of gibbsite I at 250°C for 2 hr: in an air flow (upper) and in a sealed bomb without a medium (lower).
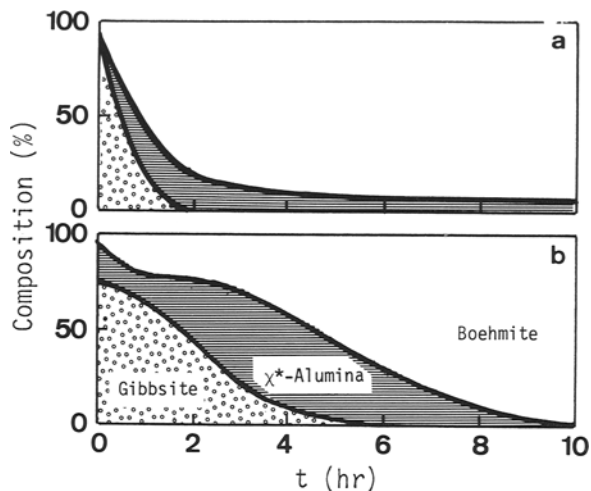

Figure 10. Product composition change during the treatment of gibbsite V: (a) in butanol and (b) in hexanol at 250°C. Heating period: 110 min (2°C/min from room temperature to 250°C).

contributed to the conversion of the less-stable, poorly-crystallized phase (χ-alumina) into a stable, well-crystallized phase (boehmite).

Because of the low solubility of water into higher alcohols and the high hydrophilic nature of the crystal surface, water molecules cannot be removed from the crystal. Therefore, boehmite formed in these media. In other words, the water content in the particle was determined by the following equilibrium:

$$\text{Water/solid} \underset{\text{adsorption}}{\overset{\text{desorption}}{\rightleftharpoons}} \text{water in solvent}$$

$$\underset{\substack{\text{condensation}\\ \text{(absorption)}}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{water vapor.}$$

If the solubility of water in the solvent is negligible, the above equilibrium can be simplified as follows:

$$\text{Water/solid} \underset{\text{condensation}}{\overset{\text{evaporation}}{\rightleftharpoons}} \text{water vapor.}$$
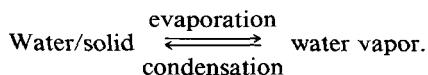
This situation is similar to the dehydration of gibbsite

in a sealed bomb without a medium. Under the latter conditions, complete conversion to boehmite was attained, which is consistent with the results reported by Huettig and van Wittgenstein (1928); moreover, the morphology of the product (Figure 9 lower) was the same as that of the product of the treatment in mineral oil (Figure 8c).

The reaction mechanisms proposed above are illustrated in Figure 11. Additional evidence to support the proposed mechanisms came from experiments on calcined products. The pore texture of the aluminas obtained by the calcination of the products from the treatment in higher alcohols was characterized by the presence of the micropores, the texture of which was identical to that of the alumina obtained by the calcination of the hydrothermal boehmite. On the contrary, this type of micropore was not detected in the alumina from the boehmite obtained by the treatment in propanol or butanol. These results are explained by
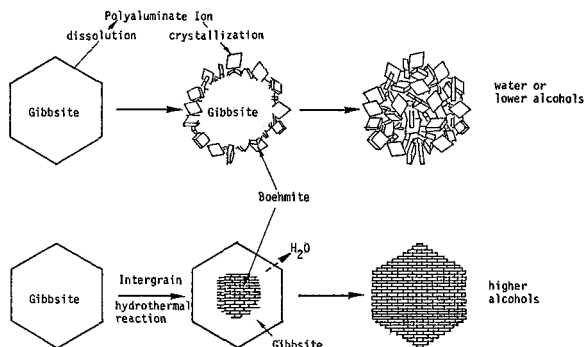

Figure 11. The mechanisms of formation of boehmite by the alcohothermal treatment of gibbsite.

the fact that the boehmites formed by the intraparticle hydrothermal reaction had properties similar to those of the hydrothermal boehmite, whereas the boehmites recrystallized from alcoholic media had different characteristics. A detailed discussion on the pore texture of the alumina will be reported elsewhere.

The formation and nature of χ^*-alumina

The χ^*-alumina may be regarded as a transition alumina formed by the thermal dehydration at the reaction temperature of 250°C. The water content in this alumina (one molecule/Al_2O_3), however, was much larger than that of the transition alumina obtained by the thermal dehydration of gibbsites using the heating profile similar to the alcohothermal treatment (0.6 molecule/Al_2O_3; see Figure 6).

Because the water pressure was low at the beginning of the dehydration by the alcohothermal treatment, noncrystalline (ρ-) alumina may have formed just as the dehydration of gibbsite under the reduced pressures. The water content of ρ-alumina is known to be relatively high and to be dependent on the reaction conditions (Tertian and Papée, 1958; Rouquerol et al., 1975, 1979). This phase can be transformed into χ-alumina by developing its crystal structure by the aid of the water pressure (Rouquerol et al., 1975, 1978). Therefore, the χ^*-alumina may be a borderline case for or a mixture of ρ- and χ-aluminas. The formation of similar ρ- or χ-aluminas having significant amounts of water from organic media has been reported (Suzuki et al., 1981; Kubo and Uchida, 1970; Fanelli and Burlew, 1986). Further studies, however, are desired for complete understanding of the structure of these phases.

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