Organic Derivatives of Layered Inorganics Having the Second Stage Structure

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The reaction of gibbsite (a modification of $Al(OH)_3$) in glycol at elevated temperatures yielded the glycol derivative of boehmite together with a small amount of well-crystallized boehmite and a residue of unreacted gibbsite. The addition of water to the medium increased the reactivity of gibbsite and yielded a novel phase having a large basal spacing. Pure product of this phase was obtained by the reaction of microcrystalline gibbsite (<0.2 μm) in 75 vol % ethylene glycol−water or in 95% 1,4-butanediol−water at 250 °C for 2 h. XRD analysis showed that the products had the boehmite layer structure and that the difference between the basal spacings of the present products and those of the corresponding glycol derivatives of boehmite obtained in pure glycols was about the same as the thickness of a boehmite layer. IR spectra of the present products exhibited a band due to hydrogen bonding between the boehmite layers. These results suggest that the products are the glycol derivatives of boehmite having the second stage structure. 2-Methoxyethyl and 2-(dimethylamino)ethyl derivatives of boehmite having the second stage structure were also formed by the similar reactions in 2-methoxyethanol and *N*,*N*-dimethylethanolamine, respectively.

Introduction

Substitution of surface hydroxyl groups of inorganics with alkoxyl groups can modify the surface properties of inorganic particles and therefore has been investigated in various fields such as pigments. When inorganic materials have lamellar structure, substitution of intralayer hydroxyl groups gives organic derivatives of layered inorganics. Recently, a number of layered metal organophosphates and organophosphonates were prepared,[1] but only few organic derivatives of layered inorganics other than metal−phosphorus oxides have been reported.[2,3] This class of compounds can be regarded as intercalation compounds in which guest molecules are bound to the host layers through the covalent bondings.

In the intercalation chemistry, staging is a common phenomenon, where certain interlayer regions are filled while others are totally vacant.[4] In the so-called second stage structure, guest molecules are located in every second interspace. In metal phosphate chemistry, it is known that when two different acids ($R-PO_3H$ and $R'-PO_3H$) are mixed in the synthesis of metal phosphate/phosphonate, segregation can occur yielding a compound consisting of layers of $M(O_3PR)_2$ alternating with layers of $M(O_3PR')_2$.[5,6] Thus, Wang et al.[7] reported the staged compound of zirconium phosphonate/phosphate, and this compound is a second stage compound if one assumes that the apparent substitution of the OH group of phosphate with the phenyl group would occur by intercalation. To our knowledge, however, organic derivatives of the layered inorganics other than metal−phosphorus oxides possessing the second (or higher) stage structure have never been reported.

Recently, we reported that the reaction of gibbsite (one of the polymorphs of aluminum hydroxide) in ethylene glycol (EG) at high temperatures (glycothermal reaction) yielded a glycol derivative of boehmite, $AlO(OH)_n(OCH_2CH_2OH)_m$ ($n + m = 1$). Thermal treatment of this product did not lead to recovery of the incorporated EG but yielded acetaldehyde as well as many other compounds derived by the condensation of the aldehyde. This result together with the consideration of the basal spacing suggested that one of the oxygen atoms of the glycol molecule was incorporated into the layer structure of boehmite.[8] Proposed structure of the glycol derivative of boehmite is given in Figure 1. The same product was also obtained by the reaction of

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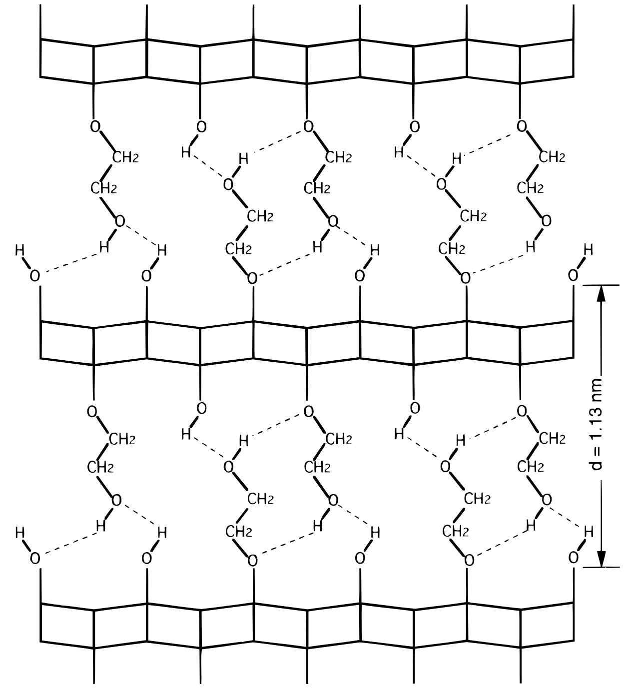

Figure 1. Proposed structure of the ethylene glycol derivative of boehmite having the first stage structure.[8]

aluminum alkoxide in glycols.[9] Apblett et al.[10,11] prepared triethylsiloxy-substituted alumoxane, $AlO(OH)_n(OSiEt_3)_m$ ($n + m = 1$), by the hydrolysis of $[Al(OSiEt_3)_3]_2$ and concluded that their product has a core structure analogous to that of boehmite. Therefore, the alumoxane with a high degree of polymerization may have the similar structure of the glycol derivative of boehmite. The glycol derivative of boehmite prepared from aluminum hydroxide or alkoxide had a unique honeycomblike texture made of thin wrinkled sheets of the layered structure of boehmite, and calcination of the product preserved the texture yielding an alumina having a large pore diameter and a large pore size.[13] In this paper, we examine the effects of addition of water to the reaction medium upon the formation of the glycol derivatives of boehmite and will report the formation of the organic derivatives of boehmite having the second stage structure.

Experimental Section

Commercial gibbsite samples produced by the Bayer process were kindly provided by Nippon Light Metal Co. A gibbsite sample having a mean particle size of 25 μm was used as received and is designated as gibbsite I. Another gibbsite sample (mean particle size, 0.2 μm) was previously sieved by elutriation under 0.2 μm, discarding the coarse particles. This sample is called gibbsite II. An additional gibbsite sample of <0.2 μm particle size (gibbsite III) was prepared by dry grinding of gibbsite I for a week on an automortar of alumina. A gibbsite sample (15 g) was suspended in 130 mL of an aqueous glycol, and the suspension was poured into a Pyrex test tube that was then placed in a 300 mL autoclave. In the gap between the autoclave wall and the test tube was place an additional 30 mL of the medium. The autoclave was thoroughly purged with nitrogen and the assembly was heated to the desired temperature (250−300 °C) at a rate of 2 °C/min and held at that temperature for 2 h. After cooling, the resulting precipitates were washed with methanol repeatedly and air-dried.

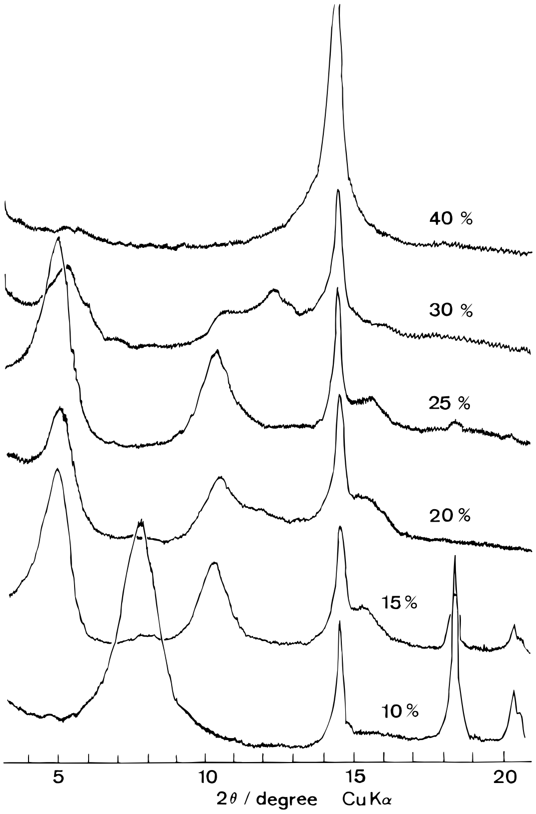

Figure 2. XRD patterns of the products obtained by the treatments of coarse gibbsite (gibbsite I) in aqueous ethylene glycol at 250 °C for 2 h. Volume percentage of water in the medium is specified in the figure. The peaks at $2\theta = 18.4$, 20.3, and 20.8° are due to unreacted gibbsite while the peak at $2\theta = 14.6°$ is attributed to well-crystallized boehmite.

X-ray powder diffraction (XRD) was measured on a Shimadzu XD-D1 diffractometer using Cu Kα radiation and a carbon monochromator. Infrared (IR) spectra were recorded on a Shimadzu IR-430 spectrometer using the usual KBr technique. Thermal analyses were performed on a Shimadzu TG-30 thermal analyzer at a heating rate of 10 °C/min in a 40 mL/min flow of dried air.

Results and Discussion

The reactions of gibbsite I in mixtures of EG and water were carried out, and the XRD patterns of the products are shown in Figure 2. As reported in the previous paper, the reaction of coarse gibbsite in EG yielded the glycol derivative of boehmite together with a small amount of well-crystallized boehmite and a residue of unreacted gibbsite, and addition of a small amount (10 vol %) of water did not alter the essential nature of the reaction. With the increase in the content of water in the medium, the reactivity of gibbsite increased and intensities of the peaks due to unreacted gibbsite decreased. When the contents of water in the medium were 15−25 vol %, the peak due to the glycol derivative of boehmite ($d = 1.16$ nm) disappeared and a new peak appeared at 1.77 nm. However, further increase in the water content resulted in the formation of well-crystallized boehmite by the hydrothermal reaction.

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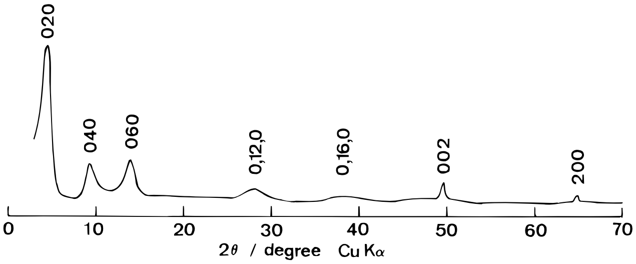

Figure 3. XRD pattern of the product obtained by the treatment of microcrystalline gibbsite (gibbsite II) in 75 vol % ethylene glycol−water at 250 °C for 2 h. Miller indices are based on the boehmite structure.

As reported previously,[14] formation of a small amount of well-crystallized boehmite by the glycothermal reaction of coarse gibbsite samples proceeds by the intraparticle hydrothermal reaction mechanism originally proposed by de Boer et al.[15] to account for the particle size effect of gibbsite on its thermal decomposition into χ-alumina and well-crystallized boehmite, and the yield of well-crystallized boehmite decreased with the decrease in particle size of gibbsite.[14] To obtain phase-pure samples of the new phase, therefore, gibbsite II or gibbsite III was treated, and the XRD pattern of the product obtained in 75% aqueous EG is given in Figure 3.

This pattern resembled the typical pattern of the EG derivative of boehmite and can be indexed on the basis of the boehmite structure, the low-angle peak being attributed to the 020 diffraction. The 0*k*0 peaks were broad, which suggests the presence of statistical distribution of the basal spacing of the product. On the other hand, diffraction peaks from the *ac* plane were sharp, and the lattice parameters *a* and *c* of the product are essentially identical with those of well-crystallized boehmite. As the *ac* plane of boehmite is parallel to the boehmite layer, the product has the boehmite layer structure.

The most significant feature of the XRD pattern of the present product is that the basal spacing (1.77 nm) was much larger than that of the ordinary (the first stage) EG derivative of boehmite (1.16 nm). The basal spacing of the product slightly varied with the reaction conditions, but in no cases were products with the basal spacing of 1.2−1.7 nm formed, suggesting that the large basal spacing of the present product is not due to the incorporation of extra water or EG molecules in the interspaces of the boehmite layers. The difference between the basal spacings of the first stage derivative and the present product corresponds to the thickness of the boehmite layer (0.611 nm).[16] This fact strongly suggests that the present product has the second stage structure of the glycol derivative of boehmite, and the proposed structure for the present product is depicted in Figure 4.

Besides EG, 1,4-butanediol (1,4-butylene glycol, 1,4-BG), *N*,*N*-dimethylethanolamine, and 2-methoxyethanol also gave the boehmite derivatives having the second stage structure, although the reactions gave mixtures of the first and the second stage compounds in most cases. The basal spacings of the first stage and the second stage compounds are summarized in Table 1. The basal spacings of both the first stage compound and the second stage compound are well correlated with the molecular dimension of the guest moieties. It must be noted that the formation of the boehmite derivatives from 2-methoxyethanol and *N*,*N*-dimethylethanolamine supports our previous conclusion that only one of the two oxygen atoms of a glycol molecule is incorporated in the boehmite layer.[8,9,17]

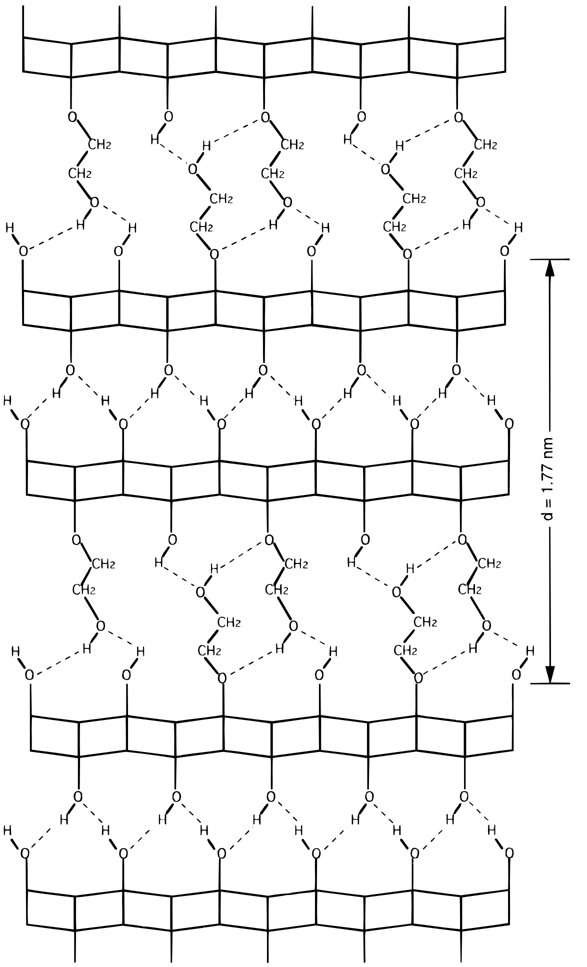

Figure 4. Proposed structure of the present product (the ethylene glycol derivative of boehmite having the second stage structure).

Table 1. Basal Spacings of the Boehmite Derivatives[a]

alkyl moiety attached to the boehmite layers	basal spacings/nm first stage	basal spacings/nm second stage	Δ*d*/nm
CH_2CH_2OH	1.13	1.77	0.64
$(CH_2)_4OH$	1.21	1.84	0.63
$CH_2CH_2OCH_3$	1.28	1.90	0.62
$CH_2CH_2N(CH_3)_2$	1.47	2.05	0.58

[a] Samples were previously dried at 130 °C for 2 h.

The second stage products were prepared under the narrow range of the reaction conditions: Low water contents favored the formation of the first stage compound, while higher water content facilitated the formation of well-crystallized boehmite. The reaction in 1,4-

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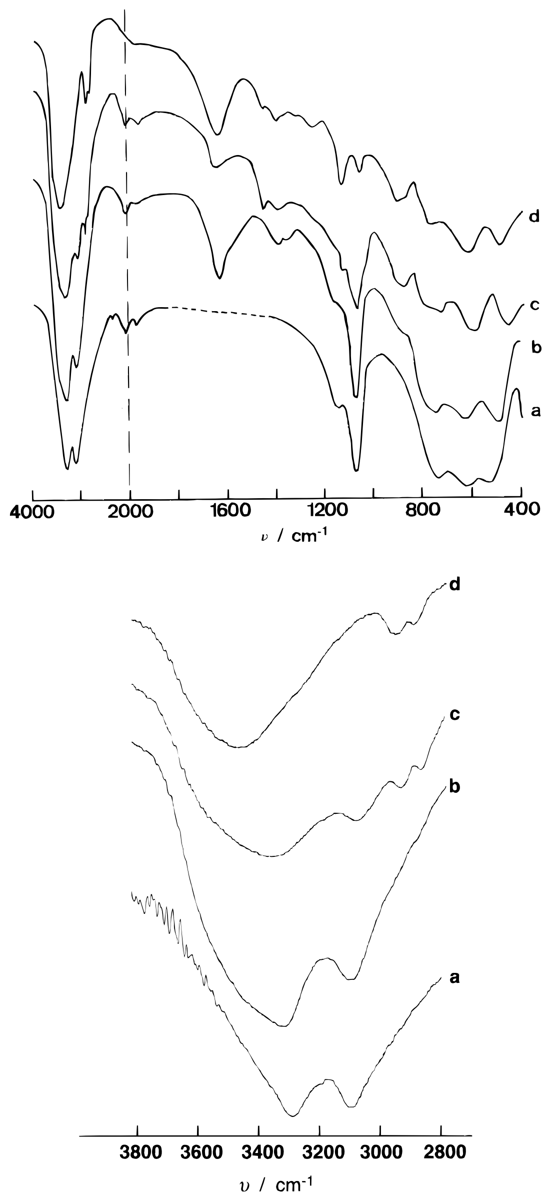

Figure 5. Top: Infrared spectra of (a) well-crystallized boehmite (obtained by the hydrothermal treatment of gibbsite I at 200 °C); (b) pseudoboehmite (microcrystalline boehmite, Pural SB, Condea Chemie); (c) the product obtained by the treatment of microcrystalline gibbsite (gibbsite II) in 75 vol % ethylene glycol−water at 250 °C for 2 h (ethylene glycol derivative of boehmite having the second stage structure); (d) the product obtained by the treatment of microcrystalline gibbsite (gibbsite III) in ethylene glycol at 250 °C for 2 h (the ethylene glycol derivative of boehmite having the first stage structure). Bottom: Infrared spectra of the same samples at the OH stretching region recorded by expanded scale.

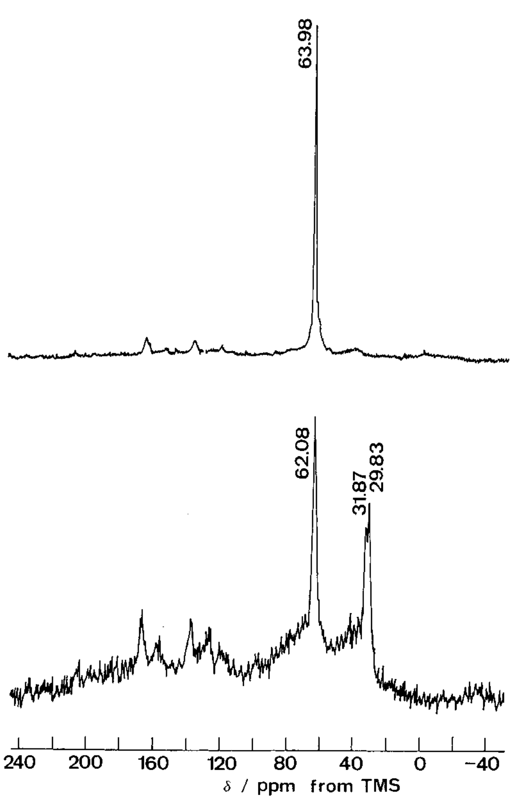

Figure 6. Cross-polarization magic angle spinning ^{13}CNMR spectra: (top) the product obtained by the treatment of microcrystalline gibbsite (gibbsite II) in 75 vol % ethylene glycol−water at 250 °C for 2 h (ethylene glycol derivative of boehmite having the second stage structure); (bottom) the product obtained by the treatment of microcrystalline gibbsite (gibbsite II) in 95 vol % 1,4-butanediol−water at 250 °C for 2 h (the butylene glycol derivative of boehmite having the second stage structure).

BG was further complicated by the formation of α-alumina at high temperatures,[18] and the XRD pure 1,4-BG derivative of boehmite with the second stage structure was obtained by the reaction in 95 vol % 1,4-BG−water at 250 °C for 4 h.

The IR spectra of the products are shown in Figure 5. The spectra were similar to those of the first stage products and bands due to the boehmite layer structure were observed at 1065, 720, 600, and 460 cm^{-1}.[19] The bands at 2920, 2870, 1460, 1410, 1130, and 880 cm^{-1} are attributed to the glycol moieties and the peak positions are in good agreement with those of liquid glycols, suggesting that the conformations of the glycol moieties are not fixed and that free rotation around C−C bonds can occur.

The most important difference between the IR spectra of the first stage and the second stage compounds is that a broad band was observed at 3080 cm^{-1} for the second stage compounds, while the first stage compounds did not exhibit this band. Well-crystallized boehmite exhibits two OH stretching modes at 3090 and 3295 cm^{-1} due to the hydrogen bonding between the boehmite layers.[19] The appearance of the 3080 cm^{-1} band indicates the presence of the empty interspace of the boehmite layers and supports the proposed structure depicted in Figure 4. A broad band at 3360 cm^{-1} can be explained by overlapping the absorption peak (ca. 3450 cm^{-1}) due to the hydrogen-bonded hydroxyl groups of the glycol moieties with the 3295 cm^{-1} band of hydrogen bonds between two boehmite layers.

The cross-polarization magic angle spinning (CP MAS) ^{13}CNMR spectra of the second stage products are shown in Figure 6. The EG derivative of boehmite gave a peak at 63.98 ppm, while the first stage compound showed the peak at 64.37 ppm. This peak is attributed

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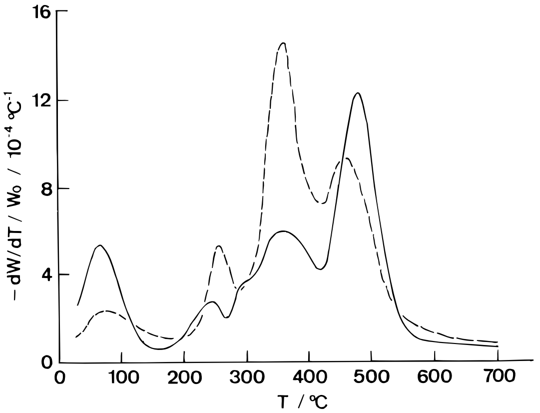

Figure 7. Thermogravimetric analyses: solid line, the ethylene glycol derivative of boehmite having the second stage structure (obtained by the treatment of microcrystalline gibbsite (gibbsite III) in 80 vol % ethylene glycol−water at 275 °C for 2 h); broken line, the ethylene glycol derivative of boehmite having the first stage structure (obtained by the treatment of microcrystalline gibbsite (gibbsite III) in ethylene glycol at 275 °C for 2 h). Analysis conditions: heating rate, 10 °C/min; in a 40 mL/min flow of dried air.

to the methylene carbons at the α positions with respect to the two oxygen atoms of the glycol. On the other hand, the NMR spectrum of the 1,4-BG derivative of boehmite with the second stage structure exhibited three peaks at 62.08, 31.87, and 29.83 ppm. The two peaks at higher frequencies are due to the two central methylene carbons of the 1,4-BG moiety, which confirms that two methylene carbon atoms at the β positions are in different chemical environments. Unfortunately, both the EG and the 1,4-BG derivatives of boehmite gave only one peak for two terminal methylene carbons. This seems to be due to the facts that the peak is broad and that the anisotropic effect caused by substitution of the OH group by the OAl< group is relatively small.[9]

A result of thermogravimetric analysis of the EG derivative of boehmite with the second stage structure is shown in Figure 7. In air flow the product decomposed through four successive processes at 70, 250, 360, and 485 °C. The first process was associated with an endothermic response in DTA and is attributed to the desorption of physisorbed water molecules. The next two processes were highly exothermic, suggesting oxidative degradation of the glycol moiety took place at these temperatures.

On heating, the basal spacing of the products gradually decreased together with the broadening of the XRD peaks. After the thermal treatment at 225 °C, the basal spacing of the EG derivative of boehmite with the second stage structure shrunk to 1.67 nm. A slight decrease in the basal spacing suggests that some of the glycol moieties were decomposed, and the angle between the boehmite layer and the chain axis of the glycol moiety became small.

In the cases where both the first stage and the second stage products were present, the diffraction peak due to the first stage structure broadened at lower temperature, and the shrinkage of the basal spacing took place more easily as compared with the second stage product. These results suggest that in the present system the second stage product has higher thermal stability than the first stage product due to the strong hydrogen bondings in the vacant interspaces.

Table 2. Elemental Analysis of the Products

	reaction conditions			found		
glycol	H_2O (vol %)	temp (°C)	time (h)	C (%)	H (%)	ignition loss (%)
EG	25	250	2	8.55	3.41	33.9
EG	25	275	2	7.97	3.16	32.0
1,4-BG	10	250	4	5.15	2.62	23.9

Although the product thermally treated at 447 °C was XRD amorphous, the IR spectrum of the sample exhibited the bands due to the boehmite layer structure. The last weight decrease process at 485 °C was endothermic and is attributed to the collapse of boehmite structure into a transition alumina. The collapse of the boehmite structure of the present product took place at a slightly higher temperature than that of the first stage product but at a slightly lower temperature than that of well-crystallized boehmite.[20]

Elemental analyses of the products are summarized in Table 2. From the analyses, the empirical formulas of the second stage products were calculated to be $AlO(OH)_{0.80}(OCH_2CH_2OH)_{0.20} \sim AlO(OH)_{0.73}(OCH_2CH_2OH)_{0.27}$ and $AlO(OH)_{0.928}(O(CH_2)_4OH)_{0.072}$ for the EG and the 1,4-BG derivatives of boehmite, respectively, while the empirical formula of the EG derivative of boehmite with the first stage structure varied in the range of $AlO(OH)_{0.69}(OCH_2CH_2OH)_{0.31} \sim AlO(OH)_{0.43}(OCH_2CH_2OH)_{0.57}$, depending on the preparation conditions. The content of the EG moiety in the second stage product was approximately half of that in the first stage compound.

Formation of the boehmite derivatives from aluminum hydroxide must involve the displacement of one of the hydroxyl groups in the coordination sites of aluminum into the alkoxyl (i.e., ω-hydroxyalkyl) group. Although this is the reverse reaction of alkoxide hydrolysis, alkoxides and hydroxides are in equilibrium and it is known that some alkoxides can be prepared by continuous removal of water from the reaction system:[21]

$$>\mathrm{Al{-}OH} + \mathrm{ROH} \rightleftharpoons >\mathrm{Al{-}OR} + \mathrm{H_2O} \tag{1}$$

In the present reaction, addition of water shifts the equilibrium composition to the left-hand side of reaction 1. Because the formation of the second stage product requires only a low alkoxyl/hydroxyl ratio in the coordination sites of aluminum, relatively high water content was favored by the formation of the second stage products as compared with that of the first stage products, but further increase in the water content in the reaction system would shift the equilibrium completely to the hydroxide side, resulting in the formation of well-crystallized boehmite. Therefore, stringent control of water content was required for the formation of the second stage compounds.

The equilibrium 1 is maintained in solution, and dissolution of the starting material (hydroxide) is controlled by another equilibrium. The addition of water to the reaction system also affects the latter reaction. Water facilitates the dissolution of the starting material and thereby increases the reaction rate.[14] This effect

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can be seen in Figure 2, which shows that the amount of unreacted gibbsite decreased with the increase in water content in the medium.

In the previous paper,[9] we examined the reaction of aluminum alkoxide in glycol and found that the 1,4-BG moiety (i.e., 4-hydroxybutyl group) in the glycoxide formed by the alkoxyl-exchange reaction can be decomposed most easily as compared with other glycol moieties because of the intramolecular participation of the hydroxyl group.[22] Because of this reaction, the 1,4-BG moiety in the coordination site of aluminum is unstable, and therefore the formation of the 1,4-BG derivative of boehmite having the second stage structure required much less water content when compared with the suitable conditions for formation of the EG derivative of boehmite with the second stage structure. The instability of the 1,4-BG moiety also explains the results that the content of glycol moieties in the former compound was lower than that in the latter compound, although the former compound was prepared in a medium with lower water contents.

The origin of the staging is a controversial issue, but it is generally believed that the charge-transfer effect has an important role for the formation of a higher stage structure.[23] However, in the present system, the guest moieties are bound to the host layers by covalent bonds, and the host layers are insulators in nature. Therefore, the charge-transfer effect through the layers is not the sole reason for the origin of the staging phenomena.

In the present system, formation of nuclei of the crystals seems to determine the structure of the product. The presence of water in the reaction system maintains low alkoxyl/hydroxyl ratio in the coordination sites of aluminum, and only the nuclei for the second stage products are formed. The chemical formula of the nuclei may not precisely reflect the equilibrium compositions of alkoxide and hydroxide in solution, and therefore a range of water content in the reaction system was allowed for the formation of the second stage products.

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