FORMATION OF ORGANIC DERIVATIVES OF BOEHMITE BY THE REACTION OF GIBBSITE WITH GLYCOLS AND AMINOALCOHOLS

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Abstract—The reaction of gibbsite in various organic solvents at 250°–300°C under spontaneous vapor pressure of the solvents was examined. Glycols and aminoalcohols afforded the organic derivatives of boehmite in which one of the oxygen atoms of the glycol molecule or the alcoholic oxygen atom of aminoalcohol was incorporated into the boehmite layers. By increasing the molecular size of the solvent, the yield of the boehmite derivative decreased, and, at the same time, the basal spacing of the boehmite derivative increased. The product had a honeycomb texture on the surface of the particle, which suggests a dissolution-recrystallization mechanism for the formation of the boehmite derivatives. A hydroxyl group and a functional group, such as hydroxyl, methoxyl, or amino group having the ability to donate its lone pair electrons, were apparently necessary for the organic solvent molecules to form the boehmite derivative by this mechanism.

Key Words—Amino alcohol, Boehmite, Gibbsite, Glycol, Infrared spectroscopy, Organic derivative, X-ray powder diffraction.

INTRODUCTION

Recently, Inoue *et al.* (1986, 1988) found that the reaction of gibbsite in ethylene glycol (EG) at 250°–300°C under the vapor pressure of EG yielded a compound having an empirical formula of $AlO(OCH_2CH_2OH)_{0.31}(OH)_{0.69}$. From X-ray powder diffraction (XRD) patterns, infrared (IR) spectra, and the thermal decomposition behavior of the compound, they concluded that the compound was an EG derivative of boehmite, in which one of oxygen atoms of the EG molecule is incorporated into the layer structure of boehmite.

Kubo and Uchida (1970) also reported the formation of a methyl derivative of boehmite by the reaction of gibbsite with methanol at high temperatures. Inoue *et al.* (1989), however, examined the reaction of gibbsite in a series of straight-chain primary alcohols (higher than ethanol) at 250°C and found that boehmite was the predominant product and that a transition alumina was also formed if alcohols having carbon numbers 5–8 were used. Organic derivation of boehmite was not formed in these experiments. The present study was therefore conducted to determine the prime factor controlling the formation of the organic derivative of boehmite. In this work, the reaction of gibbsite in polyols, aminoalcohols, and some other organic solvents was examined.

EXPERIMENTAL

The following compounds were examined as the media in place of EG; 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, diethylene glycol, triethylene glycol, 1,2-propanediol, glycerin, monoethanolamine (2-aminoethanol), 2-(methylamino)ethanol, 2-(dimethyl-amino)ethanol, diethanolamine, triethanolamine, 2-methoxyethanol, 1,2-dimethoxyethane, xylene, dioctyl phthalate, N,N-dimethylformamide, and ethylene diamine.

Commercial gibbsite produced by the Bayer process was provided by Nippon Light Metal Company, Ltd. A gibbsite sample having a small particle size (<0.2 μm, 18 m^2/g surface area) was prepared by dry-grinding a commercial gibbsite for a week in a mechanically driven alumina mortar, 45 cm in diameter. Thirteen milliliters of one of the media mentioned above was placed in a Pyrex test tube, which served as an autoclave liner, and 3 g of the gibbsite was suspended in it. The test tube was set in an autoclave, and the atmosphere in the autoclave was replaced with nitrogen. The mixture was then heated to the desired temperature (usually 250°C) and held at that temperature for 2 hr under the autogenous pressure of the organic media. After cooling to the room temperature, the resulting white precipitates were washed with methanol repeatedly and air-dried. If polyols, such as 1,2-propanediol and glycerin, that have secondary hydroxyl groups were used, such polyols decomposed into brown, viscous, tarry matter under the reaction conditions. If the polyols were deoxygenated by bubbling the nitrogen gas through the polyols for 2 hr prior to the reaction, no tarry matter formed.

X-ray powder diffraction (XRD) analyses were made on a Rigaku Geigerflex-2013 diffractometer employing Ni-filtered CuKα radiation. Infrared (IR) spectra were obtained on a Shimadzu IR-435 spectrometer using the usual KBr-pellet technique. 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 nitrogen until
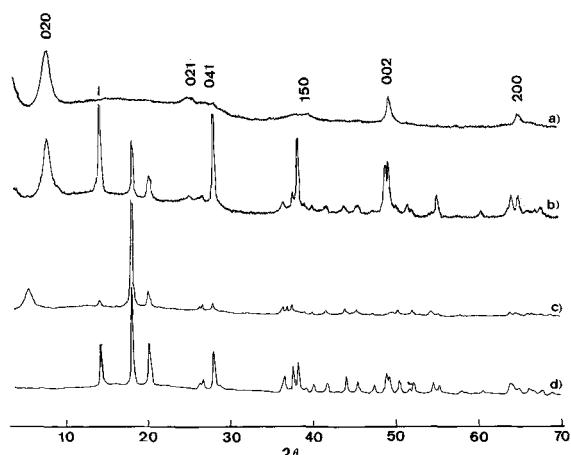
Figure 1. Typical X-ray powder diffraction pattern of products obtained by reaction of gibbsite in organic solvents ($C\nu K\alpha$ radiation). Reaction condition: (a) and (b), in 1,3-propanediol at 300°C; (c) and (d), in 2-(methylamino)ethanol at 250°C. Particle size of gibbsite: (a) and (c), <0.2 μm; (b) and (d), 80 μm.
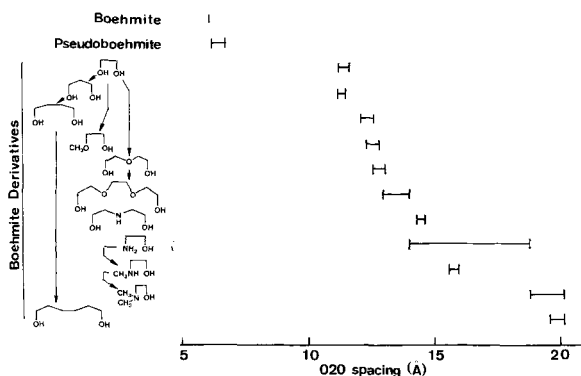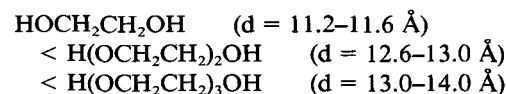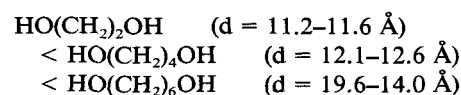

Figure 2. Basal spacings of organic derivatives of boehmite obtained by the reaction of gibbsite in various organic solvents. Structures of the organic solvents depicted are ethylene glycol, 1,3-propanediol, 1,4-butanediol, 2-methoxyethanol, diethylene glycol, triethylene glycol, diethanolamine, monoethanolamine, 2-(methylamino)ethanol, 2-(dimethylamino)ethanol, and 1,6-hexanediol in order from the top to the bottom. Homogeneous series of compounds are indicated by arrows. Ranges of the values observed for products obtained using gibbsite samples having various particle sizes are given by error bar.

no further weight decrease was detected, and then heated at a rate of 10°C/min in the same gas flow. Morphologies of the particles were observed with a scanning electron microscope (SEM), Hitachi-Akashi MSM4C-102.

RESULTS AND DISCUSSION

XRD profiles of the products

Typical XRD patterns of the products are shown in Figure 1. The XRD pattern of the product obtained by the reaction of gibbsite (<0.2-μm particle size) in 1,3-propanediol is similar to that of ethylene glycol derivative of boehmite (Inoue *et al.,* 1988) and can be indexed on the basis of boehmite structure (Reichertz and Yost, 1946; Christoph *et al.,* 1979). The 020 peak, however, appeared at a very low angle, whereas the 200 and 002 peaks occurred at the positions identical to boehmite. In other words, the *b*-dimension was largely expanded compared with boehmite. The 020 spacing varied slightly from experiment to experiment, due to the particle size of the gibbsite or the reaction conditions; however, no correlations was found between the 020 spacing and these factors. Grebille and Berar (1986) and Tettenhorst and Corbato (1988) calculated a theoretical XRD profile for microcrystalline boehmite (pseudoboehmite) and showed that the 020 peak shifted toward the low-angle side with decreasing crystallite size. This low-angle shift, however, was associated with an extensive broadening of the 020 peak. On the other hand, the 020 peak of the present product was much sharper than that of pseudoboehmite. Moreover, the 200 and 002 peaks were much sharper than the 020 peak, whereas the 021 and 041 peaks were shifted and broadened.

The XRD patterns of the products obtained in ami-

noalcohols, 2-methoxyethanol, and higher homologues of 1,3-propanediol at 250°C also contained a peak in the region 3°–7.5°2θ. The spacing of this low-angle peak varied with the solvent used; the results are summarized in Figure 2. For comparison, d-values of boehmite (6.107 Å; Christoph *et al.,* 1979) and pseudoboehmite (prepared by the hydrolysis of aluminum isopropoxide) are also given in the same Figure. A comparison at a homogeneous series of compounds shows that the spacing increased with the increase in the molecular size of the solvent:

$$HO(CH_2)_2OH \quad (d = 11.2\text{–}11.6 \text{ Å})$$
$$< HO(CH_2)_4OH \quad (d = 12.1\text{–}12.6 \text{ Å})$$
$$< HO(CH_2)_6OH \quad (d = 19.6\text{–}14.0 \text{ Å})$$

$$HOCH_2CH_2OH \quad (d = 11.2\text{–}11.6 \text{ Å})$$
$$< H(OCH_2CH_2)_2OH \quad (d = 12.6\text{–}13.0 \text{ Å})$$
$$< H(OCH_2CH_2)_3OH \quad (d = 13.0\text{–}14.0 \text{ Å})$$

These results suggest that the peak was due to the basal spacing of the organic derivative of boehmite. On the basis of the structure proposed by Inoue *et al.* (1988) for the EG derivative of boehmite, the structure of the present product is proposed as depicted in Figure 3. One of the oxygen atoms of glycol molecule or the alcoholic oxygen atom of the aminoalcohol or methoxyethanol is taken inot the layer structure of boehmite. In other words, hydroxyalkyl, aminoalkyl, or methoxyethyl groups were incorporated covalently between the beohmite layers. These incorporated, substituted alkyl groups will be referred as organic moiety, hereafter.

As shown in Figure 1, XRD patterns of the most products also contained the peaks of boehmite and
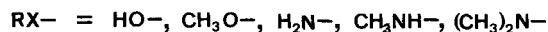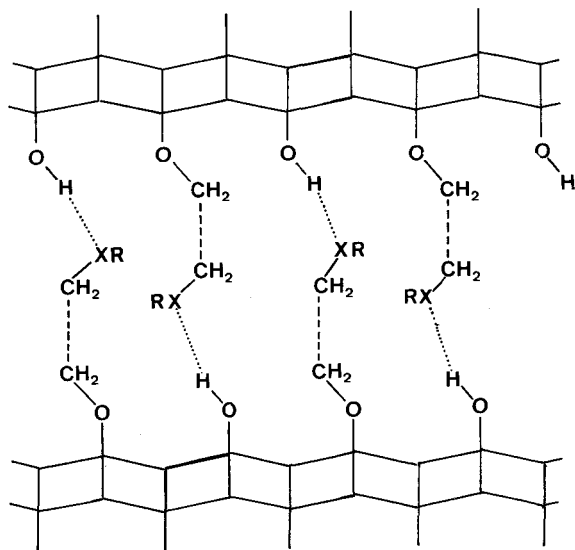
RX— = HO—, CH₃O—, H₂N—, CH₃NH—, (CH₃)₂N—

Figure 3. Proposed structure of organic derivatives of boehmite.

Figure 4. Composition of products obtained by reaction of gibbsite (80 μm) in various solvents. Because peak intensities of pure boehmite derivatives are not known, relative intensities of the main peaks are plotted.

unreacted gibbsite. The apparent crystallite size of boehmite was much larger than that of the boehmite derivative, and boehmite formed in the present reaction will be referred as well-crystallized boehmite to avoid the confusion between boehmite and the boehmite derivative. With decreasing particle size of the gibbsite, the yield of the boehmite derivative increased, and both the yield of well-crystallized boehmite and the amount of unreacted gibbsite decreased. The relative intensities of the XRD peaks of the boehmite derivative ($3°$–$7.5°2\theta$), well-crystallized boehmite ($14.4°2\theta$) and gibbsite ($18.1°2\theta$) for the product obtained from a gibbsite sample having a particle size of 80 μm are plotted in Figure 4. As shown in Figure 4, the yield of the boehmite derivative tended to decrease with an increase in molecular size of the solvent. Ethylene diamine, 1,2-dimethoxyethane, 1,2-propanediol, mono-alcohols, and hydrocarbons did not yield boehmite derivatives. These results suggest that a hydroxyl group and a functional group, such as hydroxyl, methoxyl, or amino group having the ability to donate lone pair electrons, were necessary for the formation of the boehmite derivatives; however, steric hindrance around the electron-donating group seems also to have been important, because 1,2-propanediol did not yield the boehmite derivative.

Bye and Robinson (1961, 1974) prepared a compound having a XRD pattern identical to that of the present products by hydrolysis of aluminum sec-butoxide in 98% benzene-2% water. Although they did not fully elucidate the structure of their compound, the compound was possibly an alkyl derivative of boehmite, i.e., sec-butyl groups were bound covalently to the
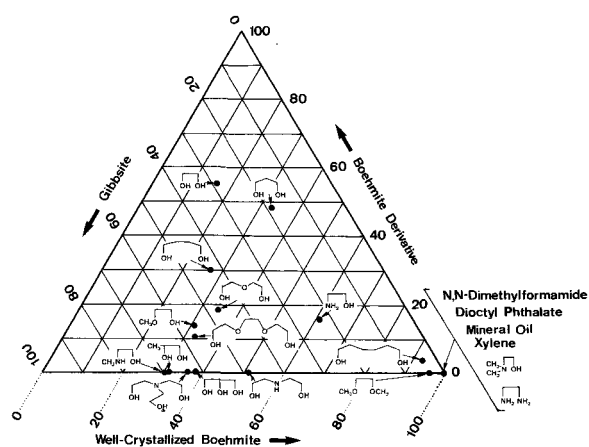
oxygen atoms of boehmite layers. Kubo and Uchida (1970) also reported the formation of a methyl derivative of boehmite. Although these alkyl derivatives of boehmite seem to have formed via mechanisms different from that of the present reaction, the existence of alkyl derivatives of boehmite having no electron-donating group in alkyl moiety suggests that possible stabilizing effect of hydrogen bonding between the electron donating group and the adjacent boehmite layer as depicted in Figure 3 cannot be the principal reason for the necessity of the electron-donating group in the present reaction. In the present reaction, the electron-donating group was required for kinetic reasons to stabilize the intermediate species in solution, rather than for thermodynamic reasons, i.e., for the stabilization of the boehmite derivative structure.

The ratio of the content of well-crystallized boehmite to the content of unreacted gibbsite in the product also depended on the nature of solvent used. In aprotic solvents gibbsite transformed completely into boehmite, whereas in protic solvents, unreacted gibbsite remained. Inoue *et al.* (1989) examined the boehmite formation from gibbsite in alcoholic media and found that in an alcohol having a carbon number >5 (higher alcohols), the boehmite yield increased with an increase in the carbon number of the alcohol. They attributed this increase in the boehmite yield to the increase in fugacity of water formed by partial dehydration of gibbsite and concluded that in these higher alcohols, boehmite formed by means of an intraparticle *hydrothermal* reaction mechanism, originally proposed by de Boer *et al.* (1954a, 1954b, 1964) for the formation of boehmite during the thermal dehydration of gibbsite. Similarly, in the present system, the ratio of unreacted gibbsite to well-crystallized boehmite in the product can be explained by the fugacity of water, as follows. Water molecules were formed by the partial
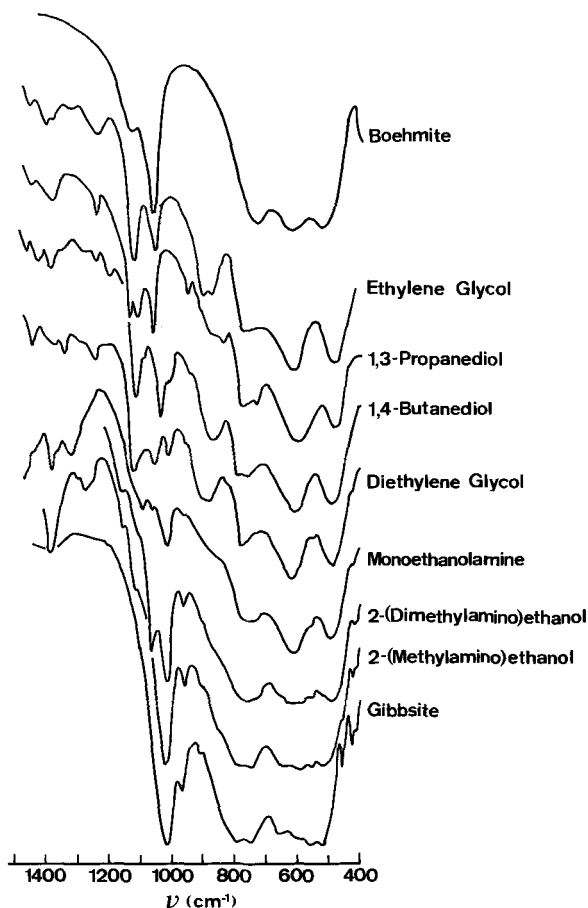
Figure 5. Infrared spectra of products obtained by reaction of gibbsite having the finest particle size (<0.2 μm) in various solvents at 250°C for 2 hr.

Figure 6. Thermal analysis of some products obtained by reaction of gibbsite (<0.2 μm) in various solvents. Products obtained in ethylene glycol, 1,3-propanediol, and 1,4-butanediol were pure by X-ray powder diffraction, while the product obtained in monoethanolamine contained ~3% unreacted gibbsite. Relatively sharp peak at 252°C observed for this product is probably due to the dehydration of gibbsite.

molecules, thereby preventing the formation of boehmite.

IR spectra

IR spectra of the products from the gibbsite sample of <0.2-μm particle size are given in Figure 5, in which the spectra are arranged from top to bottom in order of decreasing intensity of the 020 diffraction peak of the boehmite derivative relative to sum of the intensities of boehmite and gibbsite peaks. The IR spectra of boehmite (top) and gibbsite (bottom) are also shown in the figure. The IR spectrum of boehmite shows characteristic bands at 1070, 760, 615, and 480 cm^{-1}. The first two bands are assigned to the hydrogenic mode and the second two have been reported to be due to the structural vibrations of boehmite layers (Fripiat *et al.,* 1967; Stegmann *et al.,* 1973; Kiss *et al.,* 1980). In the spectra of the products shown in upper part of Figure 5, these four bands are clearly seen, although these products were essentially free from well-crystallized boehmite. The first two bands are slightly shifted and weakened, whereas the second two bands are at frequencies identical with those of boehmite. With decreasing relative intensity of the low-angle peak (going from top to bottom in Figure 5), the intensity of absorption band characteristic of the layer structure of boehmite progressively decreases, and bands due to the unreacted gibbsite become significant. These results further confirm that the low-angle XRD peak at 3°–7.5°2θ was due to the organic derivative of boehmite. Bands due to the incorporated organic moieties were

dehydration of gibbsite. In protic solvents, such water molecules were stabilized by hydrogen bonding with solvent molecules; as a result, the fugacity of water was lowered and boehmite formation was hampered. On the other hand, water molecules were not stabilized in aprotic solvents (hydrocarbons and related compounds) and the high fugacity (activity) of water facilitated the hydrothermal reaction of gibbsite resulting in complete formation of boehmite. Note that if gibbsite alone was heated in an autoclave at 250°C, it transformed completely to boehmite (Inoue *et al.,* 1989). Apparently (ostensibly), the gibbsite structure was stabilized by the presence of glycolic media; however, this stabilization effect was not due to the direct interaction between glycol molecules and gibbsite, but was due to lowering the fugacity (activity) of water by the glycol
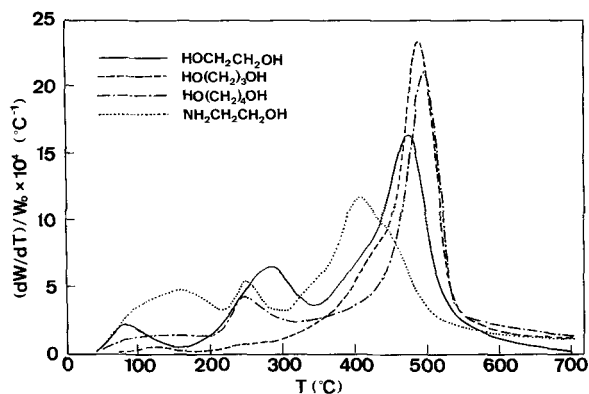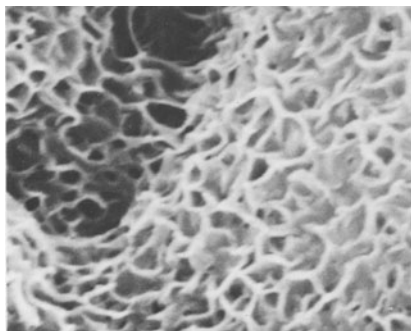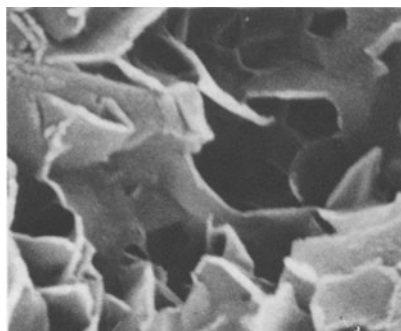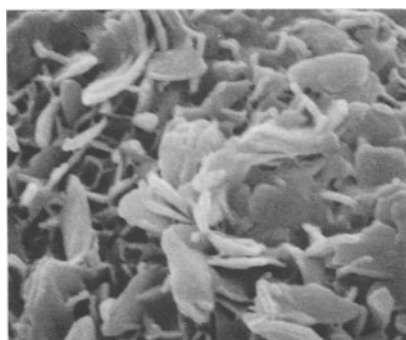
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Figure 7. Scanning electron micrographs of products obtained by reaction of gibbsite having the largest particle size (80 μm) in various solvents at 250°C for 2 hr.
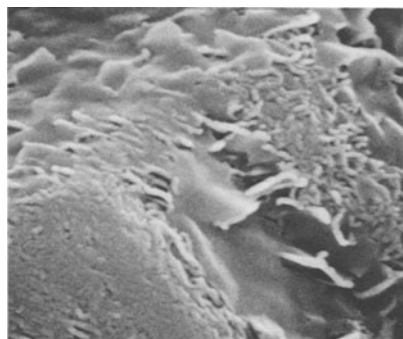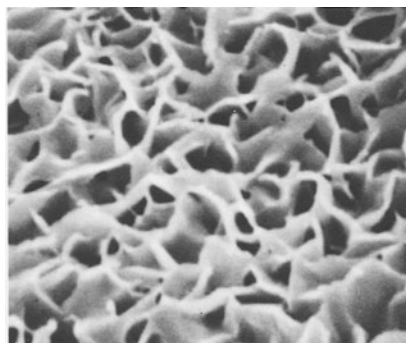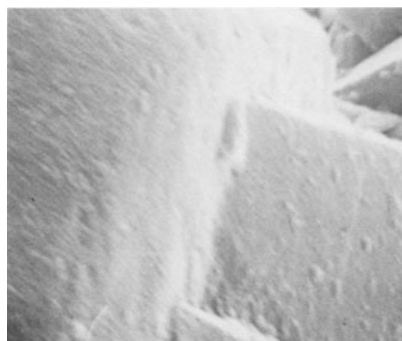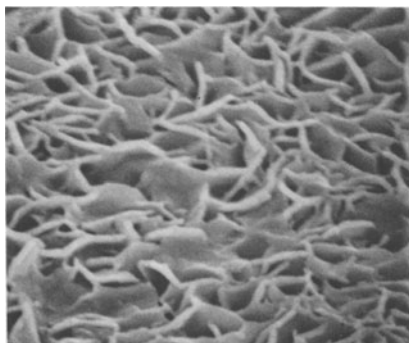
Ethylene Glycol

1,6-Hexanediol

1,3-Propanediol

2-(Dimethylamino)ethanol

1,4-Butanediol
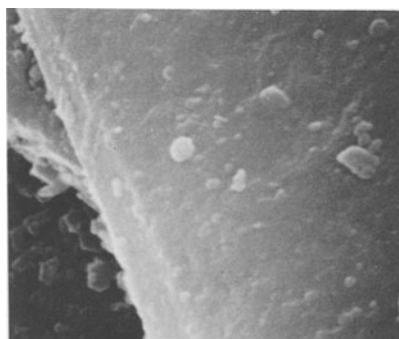
1,2-Propanediol

Diethylene Glycol

Gibbsite　　1μm

also noted at ~2930 and ~2850 cm^{-1} (νCH) and in the 1500–800-cm^{-1} region.

TGA patterns

The TGA patterns of the relatively pure organic derivatives of boehmite are shown in Figure 6. The organic moieties present between the boehmite layers were stable beyond the boiling points of the corresponding glycol or aminoalcohol. This result suggests that glycol or aminoalcohol molecules were not present as the adsorbed species; it is also consistent with the proposed structure of the boehmite derivatives (Figure 3) in which the organic moieties are covalently bound to the boehmite layers. With the increase in the carbon number of the glycol, the second decomposition peaks shifted toward higher temperatures. The final weight loss was accompanied by disappearance of both the 020 XRD peak and IR bands due to the boehmite layer structure and, therefore, was probably due to the collapse of the boehmite layers into noncrystalline alumina. This collapse took place at 450°–500°C, in good agreement with the decomposition temperature of well-crystallized boehmite into γ-alumina (Lippens and de Boer, 1964). If aminoalcohols were used, the final decomposition temperature occurred at ~400°C, significantly lower than that for the glycol derivative of boehmite; thus, the decomposition of the boehmite structure was probably facilitated by the presence of traces of amine bases.

SEM observation

The SEMs of the products obtained from gibbsite of 80-μm particle size are given in Figure 7. The original gibbsite sample was composed of aggregates of hexagonal prisms and plates. With the increase in the yield of the boehmite derivatives, a honeycomb texture composed of randomly oriented thin plates of the boehmite derivatives was developed on the surface of the product particles. Because of this texture, apparent particle size possibly increased by the reaction; however, SEM observation at lower magnification did not show a significant difference between the mean particle sizes before (80.6 μm) and after (81.6 μm) the reaction in EG. The product obtained in 2-(dimethylamino)ethanol is interesting because the initial stage of the formation of the honeycomb texture can be seen. A few thin plates of the boehmite derivative formed on hexagonal pseudomorphs of the original gibbsite crystal. The orientation of these crystals was random and did not correlate with the surface structure of the original gibbsite, suggesting that the boehmite derivative formed by a dissolution-recrystallization mechanism; the dissolution-recrystallization mechanism for the *hydrothermal* formation of boehmite from gibbsite has been well established (Bauermeister and Fulda, 1943; Ginsberg and Koester, 1952; Yamaguchi and Sakamoto, 1959). This result is in sharp contrast with that reported by

Kubo and Uchida (1970) for the reaction of gibbsite with methanol. Their product, having an approximate empirical formula of $AlO(OCH_3)_{0.5}(OH)_{0.5}$, was pseudomorphous after the original gibbsite particles (hexagonal plates). They concluded that the reaction took place by means of a solid state reaction with the aid of methanol molecules diffusing in the structure of gibbsite by Hedvall effects (Hedvall, 1956). Diffusion of the bulkier glycol or aminoalcohol molecules into the gibbsite structure is improbable and therefore, the solid state reaction did not take place in the present reaction.

SUMMARY

In summary, the reaction of gibbsite in various glycols and aminoalcohols at 250°C under spontaneous vapor pressure of the solvent yielded the organic derivatives of boehmite, the basal spacings of which increased with the increase in molecular size of the solvents. The yield of the organic derivatives of boehmite decreased with the increase in the molecular size of the solvents and with the increase in the particle size of gibbsite. The morphology of the products strongly suggests that the reaction proceeded by means of a dissolution-recrystallization mechanism. A hydroxyl group and a functional group having an ability to donate its lone pair electrons were apparently essential for the formation of the derivatives of boehmite by this mechanism.

REFERENCES

Bauermeister, B. and Fulda, W. (1943) The Bayer process (for purification of bauxite): *Aluminium* **25**, 97–100.

Bye, G. C. and Robinson, J. G. (1961) Preparation of bayerite and a modified form of pseudoboehmite: *Chem. Ind. (London)*, 1363.

Bye, G. C. and Robinson, J. G. (1974) The nature of pseudoboehmite and its role in the crystallization of amorphous aluminium hydroxide: *J. Appl. Chem. Biotechnol.* **24**, 633–637.

Christoph, G. G., Corbato, C. E., Hofmann, D. A., and Tettenhorst, R. T. (1979) The crystal structure of boehmite: *Clays & Clay Minerals* **27**, 81–86.

de Boer, J. H., Fortuin, J. M. H., and Sterggerda, J. J. (1954a) The dehydration of aluminum hydrates: *Konkl. Ned. Acad. Wetenschap. Proc.* **57B**, 170–180.

de Boer, J. H., Fortuin, J. M. H., and Sterggerda, J. J. (1954b) The dehydration of aluminum hydrates. II: *Konkl. Ned. Acad. Wetenschap. Proc.* **57B**, 435–443.

de Boer, J. H., van den Heuval, A., and Linsen, B. G. (1964) Studies on pore systems in catalysts. IV. The two causes of reversible hysteresis: *J. Catal.* **3**, 268–273.

Fripiat, J. J., Bosmans, H., and Rouxhet, P. G. (1967) Proton mobility in solids. I. Hydrogenic vibration modes and proton delocalization in boehmite: *J. Phys. Chem.* **71**, 1097–1111.,

Ginsberg, H. and Koester, M. (1952) Note on the aluminum oxide monohydrate: *Z. Anorg. Allgem. Chem.* **271**, 41–48.

Grebille, D. and Berar, J. F. (1986) Calculation of diffraction line profiles in the case of coupled stacking fault and size effect broadening: Application to boehmite AlOOH: *J. Appl. Crystallogr.* **19**, 249–254.

Hedvall, J. A. (1956) Current problems of heterogeneous catalysis: *Adv. Catal.* **8,** 1–17.

Inoue, M., Kitamura, K., Tanino, H., Nakayama, H., and Inui, T. (1989) Alcohothermal treatments of gibbsite: Mechanisms for the formation of boehmite: *Clays & Clay Minerals* **37,** 71–80.

Inoue, M., Kondo, Y., and Inui, T. (1986) The reaction of crystalline aluminum hydroxide in ethylene glycol: *Chem. Lett.* 1421–1424.

Inoue, M., Kondo, Y., and Inui, T. (1988) An ethylene glycol derivative of boehmite: *Inorg. Chem.* **27,** 215–221.

Kiss, A. B., Keresztury, G., and Farkas, L. (1980) Raman and i.r. spectra and structure of boehmite (γ-AlOOH). Evidence for the recently discarded D_{2h}^{17} space group: *Spectrochim. Acta, Part A* **36A,** 653–658.

Kubo, T. and Uchida, K. (1970) Reaction between aluminum hydroxide and methanol: *Kogyo Kagaku Zasshi* **73,** 70–75 (in Japanese).

Lippens, B. C. and de Boer, J. H. (1964) Study of phase transformations during calcination of aluminum hydroxides by selected area electron diffraction: *Acta Crystallogr.* **17,** 1312–1321.

Reichertz, P. P. and Yost, W. J. (1946) The crystal structure of synthetic boehmite: *J. Chem. Phys.* **14,** 495–501.

Stegmann, M. C., Vivien, D., and Mazieres, C. (1973) Studies on the infrared vibration mode of aluminum oxyhydrates boehmite and diaspore: *Spectrochim. Acta, Part A* **29A,** 1653–1663.

Tettenhorst, R. T. and Corbato, C. E. (1988) Comparison of experimental and calculated X-ray powder diffraction data for boehmite: *Clays & Clay Minerals* **36,** 181–183.

Yamaguchi, G. and Sakamoto, K. (1959) Hydrothermal reaction of aluminumtrihydroxides: *Bull. Chem. Soc. Jpn.* **32,** 696–699.