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The Reaction of Crystalline Aluminum Hydroxide in Ethylene Glycol

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Thermal treatment of crystalline aluminum hydroxide in ethylene glycol yields a compound having a boehmite structure with ethylene glycol incorporated between the boehmite layers. The grain size of the starting material was the predominant factor governing the formation of the product. The product had a unique honeycomb-like texture.

Boehmite, one of the modifications of aluminum hydroxide oxide AlO(OH), has a layer structure in which AlO_6 octahedra are joined by sharing of edges such that they form zig-zagged layers.[1)] As the hydrogen bonding between layers is strong, intercalation of guest molecules into this structure is not possible. The compound known as pseudoboehmite (sometimes also called gelatinous boehmite or boehmite gel) may be regarded as an intercalation compound of boehmite because the extra water molecules in pseudoboehmite is believed to be bound with the hydrogen bridges between the layers of boehmite.[2)] This compound, however, cannot be synthesized through a reaction of boehmite with water, but rather is usually prepared by aging amorphous alumina gel.[3)] Besides water, organic moiety can also be incorporated between boehmite layers. Only two examples have been reported thus far: One is "pseudoboehmite-c", reported by Bye and Robinson.[4)] They prepared this compound through the hydrolysis of aluminum *sec*-butoxide in 98% ethanol-water and concluded that "some ethanol or alkoxide groups" were incorporated into the layer of boehmite. The second example is a compound having an approximate formula of $AlO(OH)_{0.5}(OCH_3)_{0.5}$. It was prepared by autoclaving gibbsite in methanol at high pressure.[5,6)] Kubo and Uchida concluded that methoxide groups were located between the boehmite layers.[6)]

During the course of our study on controlling the pore texture of alumina used as a catalyst support,[7)] we found that the thermal treatment of crystalline aluminum hydroxides (i.e., gibbsite, bayerite or nordstrandite) in ethylene glycol (EG) yields a new intercalated compound (hereafter designated as PBEG) in which ethylene glycol moiety is incorporated in the boehmite layers. The experimental results will be reported here.

Aluminum hydroxide (30 g) suspended in 130 ml of EG was placed in an autoclave. The atmosphere in the space of the autoclave was replaced with nitrogen and then the content was heated to 250 °C for 2 h. Upon cooling, the resulting precipitates were washed with methanol and air dried.

Treatment of a commercial gibbsite (Nippon Light Metal) made by the Bayer process in EG produced PBEG together with a small amount of well crystallized boehmite and a residue of unreacted gibbsite. The yield of PBEG was not improved by either prolonged reaction times or increased temperatures. Higher reaction pressure as well had essentially no effect on yield. The reaction was not affected by varying the alkali content of gibbsite nor by impregnating the gibbsite with sodium carbonate (0.2% as Na_2O). The addition of small amounts of water (up to 10%) to EG slightly improved the conversion, but further addition of water resulted in the formation of ordinary pseudoboehmite. The dominant factor influencing the formation of the product was found to be the grain size of gibbsite; essentially pure PBEG uncontaminated by well crystallized boehmite or gibbsite could be obtained by using a gibbsite sample ground to less than 0.2 µm.

The infrared (IR) spectrum of the PBEG thus obtained (Fig. 1) showed bands at 773, 615, and 478 cm^{-1} which can be attributed to the torsion of OH, ν_3 and ν_4 modes of AlO_6 octahedra of boehmite structure.[8] Bands due to the incorporated EG moiety were seen at 3440s, 2490m, 2880m, 1460w, 1400m, 1250w, 1128m, 1062m, 900m and 868m cm^{-1}. Elemental analysis showed that 0.6 mol EG per mol of Al_2O_3 was incorpo-

Table 1. Effects of Particle Size of Gibbsite

Gibbsite				
Particle diameter	Alkali content	Product composition/%		
µm	%	PBEG	Boehmite	Gibbsite
80	0.25	48	11	41
20-25	0.21	72	9.5	18
6-10	0.21	85	11	4.6
∿0.2	0.4	98	1.9	0.3
<0.2	0.21	100	0	0

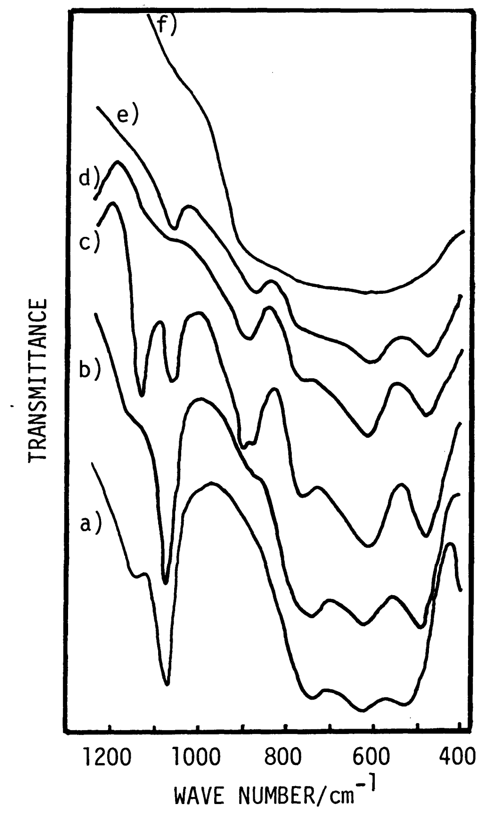

Fig. 1. IR spectra (KBr) of; a) boehmite, b) pseudoboehmite, c) PBEG, and products obtained by calcination of PBEG at d) 284 °C, e) 391 °C, and f) 500 °C.

rated (Found: C, 10.11; H, 3.07%; ignition loss, 30.85%). The X-ray diffraction (XRD) patterns (Fig. 2) showed an increase in 020 spacing from ca. 6.5 Å for pseudoboehmite to 11.6 Å for PBEG, which suggests that EG is incorporated between the layers of boehmite.$^{9)}$

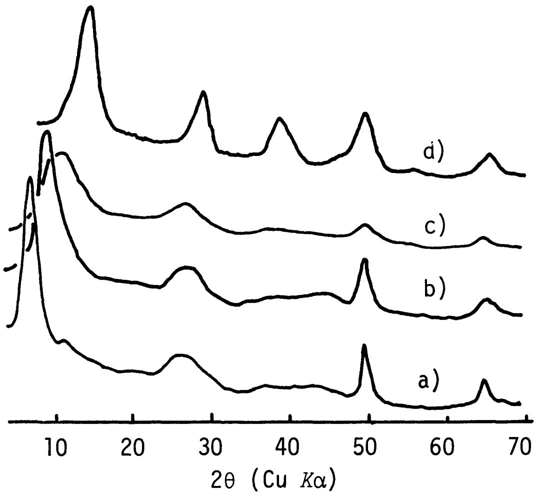

Fig. 2. XRD patterns of; a) PBEG b) and c) products obtained by calcination of PBEG at 284 and 391 °C, respectively, and d) pseudoboehmite.

Thermal analysis indicates that in air flow PBEG decomposes through four successive processes. The first weight loss (ca. 80 °C, endothermic) is caused by desorption of the physisorbed water. The second weight loss (271 °C), highly exothermic) is caused by the oxidative degradation of EG, leaving carbonyl compound(s) between the layers of boehmite as suggested by IR spectrum (ν_{max} 2920w, 2880w, 1680s, and 1250m cm^{-1}). The third weight loss (339 °C, exothermic) appeared to be due to the carbonization of the carbonyl compound(s). Although the IR spectrum of the resulting sample showed no characteristic peaks for organic moiety, elemental analysis revealed 1.90% carbon. The relatively large 020 spacing (Fig. 2) and boehmite skeletal vibration bands (Fig. 1) clearly show that carbonaceous material still remains between the boehmite layers. In the fourth weight loss (445 °C, endothermic) the boehmite structure is broken down into amorphous alumina. It must be noted that the peak temperature for the fourth loss is quite close to the dehydration temperature of well crystallized boehmite.

Bayerite and nordstrandite were also usable as the starting material for PBEG. Well crystallized boehmite and pseudoboehmite did not react with EG. Amorphous aluminum hydroxide gel gave conflicting results: One gel yielded PBEG as the sole product, another resulted in the formation of pseudoboehmite, but usual outcome was to obtain a mixture of the two products. These conflicting results seem to be connected with poor reproducibility in preparing gel and with the lack of means for full description of the gel properties.

The most interesting feature of the reaction presented in this paper is the morphology of the product. As can be seen in Fig. 3, PBEG has a honeycomb-like texture. When large grained gibbsite was used as the starting material, the honeycomb-like texture of PBEG developed on the surface of the hexagonal plate particles of the gibbsite. This result shows a sharp contrast to the reaction of gibbsite in methanol at high pressure where a topotactic reaction occurs yielding a product with hexagonal plate particles.[6)] This would indicate that the reaction in EG proceeds by a completely different mechanism than the one in methanol at high pressure and that the honeycomb-like texture of PBEG is formed by means of dissolution-recrystallization mechanism in the solvent cage in which concentration gradient of water, formed by dehydration of gibbsite, is provided by diffusion of water molecules from the gibbsite grain surface to the bulk solvent.

Finally, it must be noted that the honeycomb-like texture of PBEG is not destroyed by thermal treatment until the formation of α-alumina at ca. 1000 °C even though boehmite structure was broken down into a transitional alumina. Catalysis using this alumina are now under investigation.

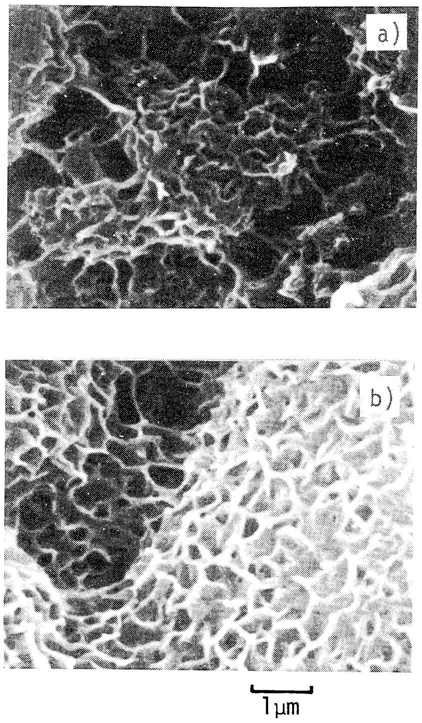

Fig. 3. SEM photograph of PBEG obtained from; a) gibbsite of 0.2 μm, and b) gibbsite of 70 μm. Note for b), inside of the obsrvable honeycomb-like texture, unreacted gibbsite core is present.

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9) Unit cell parameters of well crystallized boehmite are as follows: Orthorhombic, a=3.700, b=12.227, c=2.868; Joint Commitee of Powder Diffraction Patterns 21-1307.

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