Reaction of Aluminium Alkoxides with Various Glycols and the Layer Structure of Their Products

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The reaction of $Al(OR)_3$ ($R = Pr^i$ or Bu^s) with glycols was examined. The XRD patterns and IR spectra of the products suggest that they have the layer structure of boehmite with the glycol moiety incorporated between its layers through covalent bonding. The crystallite size of the product increased in the following order (carbon number of glycol): $2 < 3 < 6 < 4$. When butane-1,4-diol was used the crystallite size of the product was the largest. This order suggests that heterolytic cleavage of C–O bonds is the prime factor controlling the growth of the boehmite structure.

Hydrothermal methods have been widely studied for the synthesis of a variety of minerals and inorganic materials. However, the use of organic solvents instead of water for hydrothermal synthesis has been scarcely examined. Using ethylene glycol as solvent, Bibby and Dale[1] synthesised silica sodalite, a novel compound which has not been so far synthesized in the aqueous system. Cruickshank and Classer[2] prepared a new barium aluminate glycolate ($BaAlO_8C_{6.76}H_{14.75}$) in aqueous ethylene glycol at 200 °C and found that the Al atoms were five-co-ordinated. Fanelli and Burlew[3] synthesized ultrafine alumina particles by thermal treatment of aluminium alkoxide in butan-2-ol. In their work, the alcohol was used as a precursor of water which is formed homogeneously in the system by thermal dehydration of the alcohol. Figlarz *et al.*[4] have developed a technique for the synthesis of Group 8 metal powders of micronic and submicronic size by treatment of metal hydroxides in glycol which acted as a reducing agent. The work mentioned elegantly made use of the specificities of organic media.

Treatment of inorganic materials in organic solvents such as alcohols has been studied as a technique to improve the surface affinity of pigments toward organic media.[5] For example, Bugosh[6] claimed modification of the surface properties of boehmite [AlO(OH)] particles with alcohol. In a slightly different category of the use of organic solvents in the synthesis of inorganic materials, Armor and Carlson[7] prepared a highly porous alumina aerogel by the removal of a hypercritical solvent (methanol–water) from the alkoxide-derived gel, avoiding shrinkage or compaction due to the surface tension of the residual liquid within the fragile gel structure.

During the course of our long-term work on controlling the pore texture of alumina for use as a catalyst support,[8] we found that thermal treatment of a crystalline aluminium hydroxide (gibbsite) in ethylene glycol (eg) yielded a novel derivative of boehmite in which the eg moiety was incorporated into the boehmite layers, and that the products had a unique honeycomb-like texture which was preserved even after calcination.[9] Subsequently, we found that organic derivatives of boehmite were also obtained by the reaction of gibbsite with alcohols such as aminoalcohols and 2-methoxyethanol which had a functional group having the ability to donate a lone pair of electrons.[10]

In the present work, the reaction of aluminium alkoxide with various glycols at 250–300 °C under the spontaneous vapour pressure of glycol has been examined. The structure and property of the products will be reported and the reaction paths will be discussed.[11]

Experimental

Reaction of Aluminium Isopropoxide with Glycols.—A suspension of aluminium isopropoxide (12.5 or 50 g) in butane-1,4-diol (bd) (130 or 500 cm^3) was placed in a test-tube, which was then set in an autoclave (300 cm^3 or 1 l). In the gap between the autoclave wall and the test-tube was placed glycol (30 cm^3). After the atmosphere inside the autoclave had been thoroughly replaced with nitrogen, the mixture was heated to a desired temperature (250–300 °C) at a rate of 2.3 °C min^{-1} and held at that temperature for 2 h under the spontaneous vapour pressure of the glycol. When the 1 l autoclave was used the mixture was stirred during the reaction, whereas the reaction in the 300 cm^3 autoclave was carried out without agitation. After the mixture was cooled, the resulting precipitates were washed repeatedly with methanol and air-dried. The product was a white fine powder which was stable in a moist atmosphere. This product will be designated by $Al(OPr^i)_3$–bd. Similarly, other products will be designated by abbreviations for the starting material [gibbsite and $Al(OBu^s)_3$ for aluminium *sec*-butoxide] and for the medium (pd for propane-1,3-diol and hd for hexane-1,6-diol) followed by the reaction temperature in °C where necessary.

Characterization.—X-ray diffraction (XRD) was measured on a Rigaku Geigerflex-2013 diffractometer employing Cu-$K\alpha$ radiation and a nickel filter. Infrared (IR) spectra were obtained on a Shimadzu IR-435 spectrometer with the usual KBr-pellet technique. Thermal analysis in air was performed on a Shimadzu DT-30 thermal analyser. The NMR spectra were obtained on a JEOL GSX-270 spectrometer. About 4.5 kHz sample spinning at the magic angle was used. The ^{27}Al NMR spectra were recorded at 70.3 MHz, the ^{13}C NMR spectra at 67.8 MHz using the cross-polarization (CP) technique.

Surface areas were calculated by applying the usual Brunauer–Emmett–Teller (BET) procedure to the nitrogen adsorption data measured on a Micrometric Accusorb 2100E instrument at 77.4 K, taking the average area occupied by a nitrogen molecule as 0.162 nm^2. Samples were predried at 130 °C for 2 h and then outgassed *in situ* at room temperature for 9 h. Ignition losses were determined by calcination at 1300 °C for 1 h. Elemental analyses were performed at the Laboratory of Organic Elemental Microanalysis, Kyoto University. For determination of ignition loss and elemental analysis, samples were previously dried at 110 °C for 24 h *in vacuo*.

Results

The Product Obtained in Butane-1,4-diol.—The XRD patterns

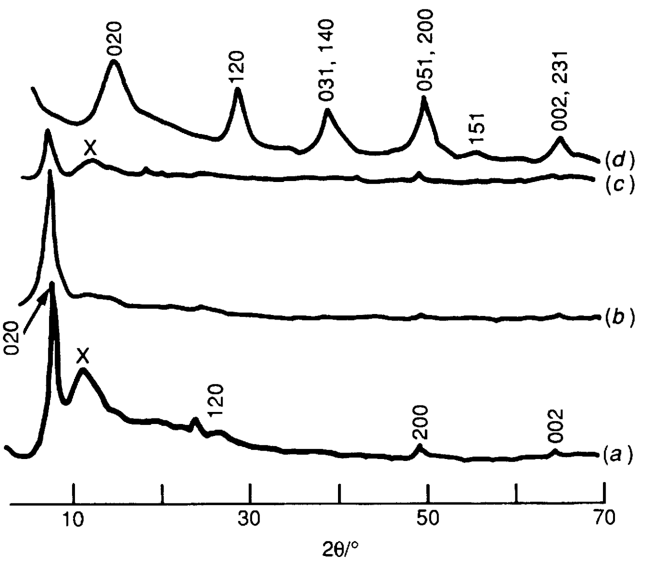


Fig. 1 X-Ray diffraction patterns of (*a*) the product obtained by the reaction of aluminium isopropoxide in butane-1,4-diol (bd) at 300 °C, (*b*) the product obtained by the reaction of aluminium *sec*-butoxide in bd at 300 °C, (*c*) the product obtained by the reaction of gibbsite in bd at 250 °C, and (*d*) pseudoboehmite: the broad peak at 2θ = 11.5°, indicated by X, is due to grease used to mount the sample

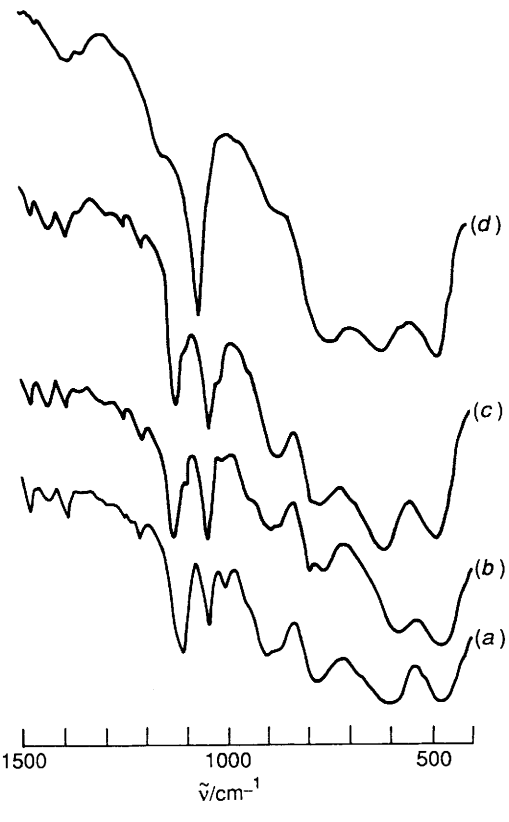


Fig. 2 Infrared spectra of the products obtained as in Fig. 1

of the products obtained by the reaction of $Al(OPr^i)_3$, $Al(OBu^s)_3$ and gibbsite with butane-1,4-diol (bd) [*i.e.*, $Al(OPr^i)_3$–bd, $Al(OBu^s)_3$–bd and gibbsite–bd] are shown in Fig. 1 and IR spectra of these products are given in Fig. 2. Both the XRD patterns and the IR spectra of the three products are identical, suggesting that the three different starting materials gave products having identical structure.

The most significant feature of the XRD pattern of the product is that it exhibited a low-angle diffraction peak with high intensity. This pattern is similar to that of 'pseudoboehmite-c' reported by Bye and Robinson[12] who prepared it by hydrolysis of $Al(OBu^s)_3$ in 98% ethanol–water. However, they did not fully elucidate the structure. The IR spectra of the products exhibited bands at 1070, 760, 615 and 480 cm⁻¹ together with those whose positions are in good agreement with those of liquid bd. The four peaks cited are characteristic of the boehmite structure.[13]

Table 1 Some properties of the product obtained by the reaction of aluminium isopropoxide in glycol at 300 °C for 2 h[a]

Glycol	eg	pd	bd	hd
Basal spacing (nm)	1.16	1.13	1.16	1.40
Crystallite size (nm)[b]	5	11	29	13
BET surface area ($m^2\,g^{-1}$)	516	223	150	—
Bulk density	0.28	0.19	0.14	0.42
Ignition loss (%)	39.5	31.7	37.8	36.7
C found (%)	16.25	17.95	15.55	19.90
H found (%)	3.40	3.50	3.55	4.35
Glycol/Al	0.57	0.37	0.26	0.22:1

[a] Samples were previously dried at 110 °C for 24 h *in vacuo*. [b] Calculated by the Scherrer equation. The shape factor, *K*, was taken as 1.84.

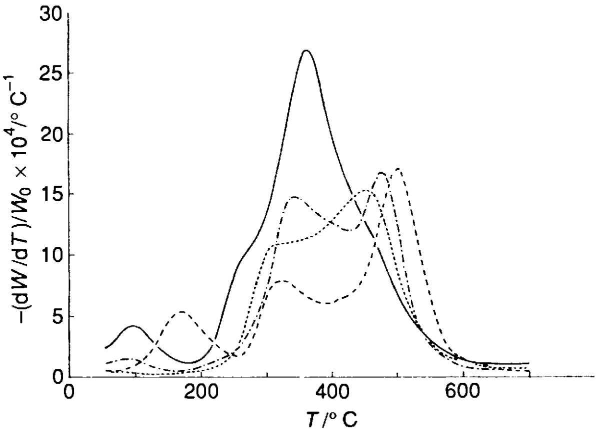


Fig. 3 DTG profiles of the products obtained by the reaction of aluminium isopropoxide in ethylene glycol (——), propane-1,3-diol (-----), butane-1,4-diol (– – – –), and hexane-1,6-diol (—•—•—•—) at 300 °C for 2 h

Effect of the Carbon Number of the Glycol.—All the products obtained by the reaction of $Al(OPr^i)_3$ in various glycols at 300 °C exhibited the low-angle diffraction peak and characteristic bands due to the boehmite structure in the IR spectra. However, the low-angle peak with eg was completely broadened and the IR bands due to the boehmite layer structure were also broad and accompanied by a shoulder at around 430 cm⁻¹. These findings suggest that the layer structure of boehmite was only poorly developed in $Al(OPr^i)_3$–eg.

As is summarized in Table 1, the spacing of the low-angle diffraction and the crystallite sizes increased with increasing carbon number; however, $Al(OPr^i)_3$–bd had a much larger crystallite size than that expected from this tendency.

The derivative thermogravimetric (DTG) profiles of the products are shown in Fig. 3. Three weight losses were observed. For $Al(OPr^i)_3$–eg, the last peak was merged with the second large peak and was seen at the shoulder of the second weight loss. The first weight loss is due to desorption of water and/or methanol (below 100 °C), or desorption of adsorbed bd (170 °C). The second weight loss was exothermic. The peak temperature (the temperature at which the maximum rate of weight decrease was observed) of the weight loss became higher with increasing carbon number of the glycol. For the third

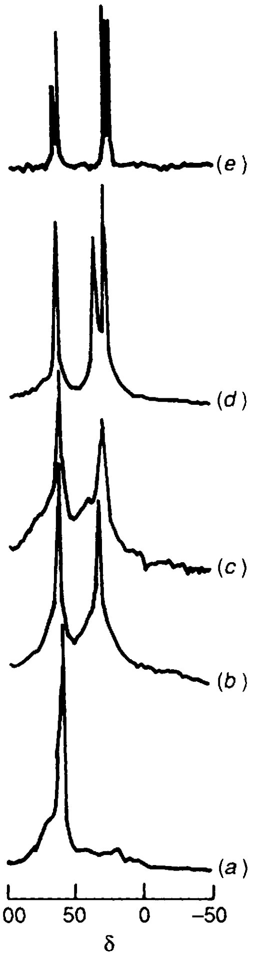


Fig. 4 Cross-polarization magic angle spinning ^{13}C NMR spectra of the products obtained by the reaction of $\mathrm{Al(OPr^i)_3}$ in (*a*) ethylene glycol, (*b*) propane-1,3-diol, (*c*) butane-1,4-diol and (*d*) hexane-1,6-diol, each at 300 °C for 2 h (*e*) Spectrum of $\mathrm{Al(OPr^i)_3}$

weight-loss process the peak temperature rose in the order: $\mathrm{Al(OPr^i)_3}$–eg < -pd < -hd < -bd.

The cross-polarization magic angle spinning (CP MAS) ^{13}C NMR spectra of the products are shown in Fig. 4. For comparison, the spectrum of $\mathrm{Al(OPr^i)_3}$ is also given, which is essentially identical to that in solution.[14] It should be noted that the anisotropic effect caused by substitution of the OH group by the OAl< group is relatively small, because the chemical shifts of the methyl and methine carbons of $\mathrm{Al(OPr^i)_3}$ are quite similar to those of propan-2-ol (δ 25.1 and 63.4 for methyl and methine carbons, respectively). All the ^{13}C spectra of the products exhibited a peak at around δ 60 and one or two peaks at higher field. These spectra are explained by the glycol moieties incorporated into the products.

The MAS ^{27}Al NMR spectra of the products are shown in Fig. 5 together with that of $\mathrm{Al(OPr^i)_3}$. It is well known that octahedrally and tetrahedrally co-ordinated Al atoms exhibit peaks at around δ 0 and 55–80, respectively,[15] while five-co-ordinated Al atoms exhibit a peak at around δ 35.[16] The spectra of the products indicate that the Al atoms in the products are predominantly octahedrally co-ordinated; however tetrahedrally co-ordinated Al atoms are apparently present in all the products.

Scanning electron microscopy (SEM) photographs of the products are shown in Fig. 6. The $\mathrm{Al(OPr^i)_3}$–eg was comprised of fine particles. On the other hand, $\mathrm{Al(OPr^i)_3}$–bd had a honeycomb-like texture, similar to that observed on the surface of gibbsite–eg.[9]

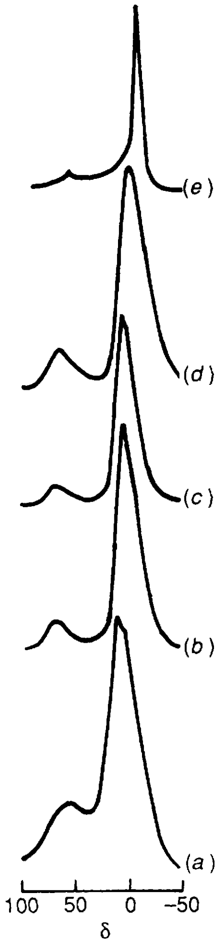


Fig. 5 Magic angle spinning ^{27}Al NMR spectra of the products obtained as in Fig. 4

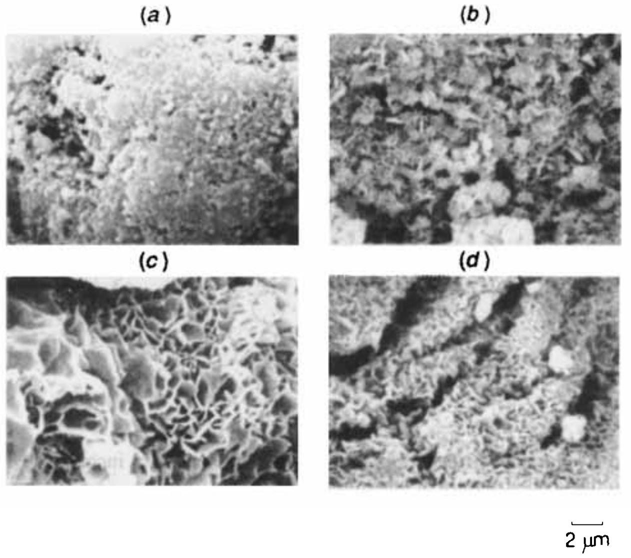


Fig. 6 Scanning electron micrographs of the products obtained by the reaction of $\mathrm{Al(OPr^i)_3}$ in (*a*) ethylene glycol, (*b*) propane-1,3-diol, (*c*) butane-1,4-diol and (*d*) hexane-1,6-diol, each at 300 °C for 2 h

The BET surface areas, bulk densities, ignition losses and analytical results for these products are summarized in Table 1. The glycol to Al molar ratios, calculated from ignition loss and elemental analysis, decreased with increasing carbon number of glycol.

Effect of Water Added.—Water was added to the glycol and reactions were carried out. The products exhibited a new diffraction peak due to pseudoboehmite at 2θ = 14.5 (*d* = 0.61

Table 2 Some properties of the product obtained by the reaction of aluminium isopropoxide in glycol at various temperatures for 2 h[a]

Autoclave	1 l			300 cm^3		
Stirring	Yes			No		
Glycol	eg	eg	eg	eg	pd	bd
Temperature/°C	250	265	300		250	
Crystallite size (nm)[b]	—	*ca.* 9	*ca.* 9	—	7.5	8.6
BET surface area (m^2 g^{-1})	339	482	391	304	312	308
Bulk density	0.53	0.40	0.31	0.27	0.19	0.26
Ignition loss (%)	49.3	42.1	36.7	55.2	39.0	37.3
C found (%)	18.65	20.40	14.25	21.55	18.85	19.85
H found (%)	5.50	4.10	3.35	5.25	3.60	4.05
Glycol/Al	0.78	0.75	0.48	1.02	0.44	0.34:1

[a] Samples were previously dried at 110 °C for 24 h *in vacuo*. [b] Calculated by the Scherrer equation. The shape factor, *K*, was taken as 1.84.

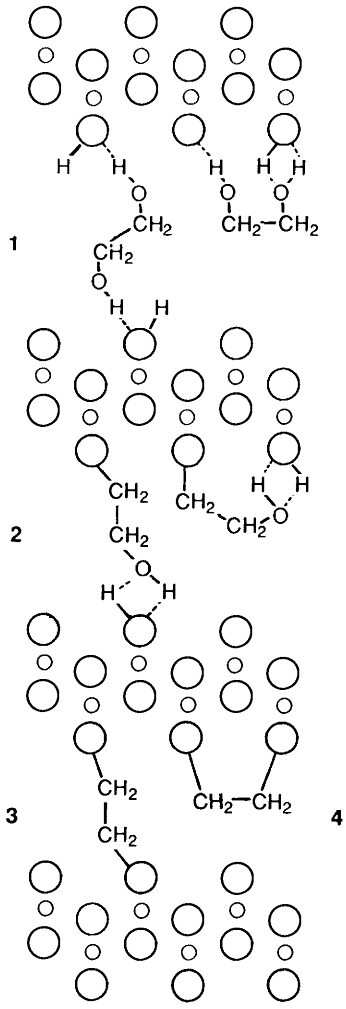


Fig. 7 Possible structures in which glycol moieties are incorporated into the layer structure of boehmite

nm) which is known to be formed by hydrolysis of aluminium alkoxides.[17,18] With increasing amount of water the peak intensity for pseudoboehmite increased, while the intensity of the low-angle diffraction peak for the glycol derivative of boehmite decreased. However, the crystallite size of the glycol derivative of boehmite was not altered by the addition of water.

Effects of the Reaction Temperature.—The product of the reaction of $Al(OPr^i)_3$ in eg at 250 °C, *i.e.* $Al(OPr^i)_3$–eg(250), was almost amorphous, while $Al(OPr^i)_3$–pd(250) and –bd(250) had the layer structure of boehmite. By using a 1 l autoclave, $Al(OPr^i)_3$ was allowed to react with eg with mild stirring at various temperatures. Some properties of the products are summarized in Table 2. As the reaction temperature was raised, the half-height width of the (020) diffraction peak became narrow, suggesting that the layer structure developed well at higher temperature. The amount of organic residue decreased with increasing temperature.

Discussion

Structure of the Product.—In a previous paper[9] the structure of gibbsite–eg was investigated and it was concluded that it is an ethylene glycol derivative of boehmite in which one of the oxygen atoms of the glycol moiety is incorporated in the boehmite layer through covalent bonding. The shift of the (020) diffraction peak to lower angles was attributed to the enlargement of the basal spacing.

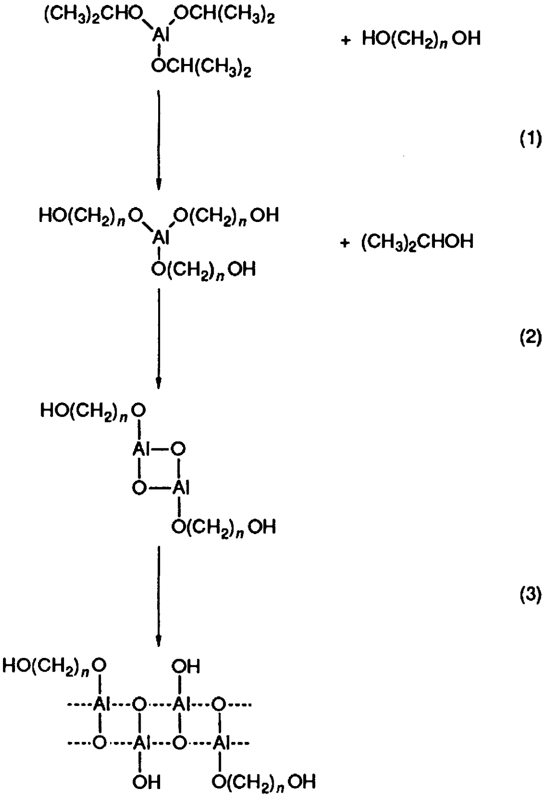
Because the present products had XRD patterns and IR spectra similar to those of gibbsite–eg and –bd, they also have similar structures to those of the products obtained from gibbsite. However, as such a structure will not be familiar to most readers, we will re-examine it, ignoring the discussion already presented in the previous paper.

It was reported that the (020) diffraction peak of pseudoboehmite shifted toward lower angles with decreasing crystallite size of boehmite.[19] However, this idea cannot be applied to the present case because the product having fairly large crystallite size, $Al(OPr^i)_3$–bd, also exhibited the low-angle peak. The XRD peaks of the product can be indexed based on the boehmite structure, the low-angle peak being attributed to the (020) diffraction. The lattice parameters *a* and *c* of the product are essentially identical to those of well crystallized boehmite, while the *b* is largely expanded. As the *ac* plane of boehmite is parallel to the boehmite layers, the present product has the boehmite layer structure. This argument is further supported by the presence of bands characteristic of the boehmite layers in the IR spectra of the products.

It is known that, on calcination, well crystallized boehmite decomposes into γ-alumina at around 550 °C and that with decreasing crystallite size of boehmite the decomposition takes place at lower temperatures.[20,21] In accordance with this, the present product exhibited a weight-loss peak at 400–510 °C and the peak temperature decreased with decreasing crystallite size of the product. Therefore, this weight loss is due to the collapse of the boehmite layer structure.

The IR and ^{13}C NMR spectra suggested the presence of glycol moieties, the isopropyl (or isopropoxyl) groups being completely expelled from the product. Therefore, we concluded that the glycol moieties were incorporated between the layers of boehmite resulting in enlargement of the basal spacings. This conclusion is supported by the fact that the basal spacing of the product increased with increasing carbon number of the glycol.

As depicted in Fig. 7, there are four possible structures in which glycol moieties are incorporated into the layer structure



Scheme 1

of boehmite. Structure **1** represents an intercalation compound, while the remaining three are not true intercalation compounds but glycol derivatives of a layer compound (boehmite). Structure **1** is ruled out because glycol molecules were not desorbed from the layers; the organic residue was stable beyond the boiling points of the glycols and decomposed at 300–350 °C; **3** is also eliminated because the distance between two oxygen atoms in two different boehmite layers is far greater than the distance between the two oxygen atoms in a glycol molecule. In structure **4** layers are stacked by van der Waals forces between methylene groups of two different layers. This possibility may also be ruled out because the product did not show any swelling properties. Structure **2** should give ^{13}C NMR peaks corresponding in number to the carbon number of the glycol. In fact the two high-field peaks of $Al(OPr^i)_3$–hd split into doublets, suggesting that the methylene carbons at the β (or γ) positions with respect to the two oxygen atoms are in different chemical environments. Unfortunately, only one peak was observed for $Al(OPr^i)_3$–eg and two for $Al(OPr^i)_3$–pd and –bd. This seems to be due to the fact that the peaks are broad and that the anisotropic effect of the Al atoms is small. The similarity of the IR spectra of liquid bd and $Al(OPr^i)_3$–bd also suggests that the conformation of the glycol moiety is not fixed, and that free rotation around C–C bonds can occur. Therefore, structure **2** is the most probable for the present products.

In a previous study[9] we carried out gas chromatographic analysis of the gases evolved upon thermal decomposition of the organic moiety in gibbsite–eg and detected acetaldehyde, ethyl acetate, ethanol, *etc*., but eg or acetylene was not detected. Subsequent work[10] showed that the reaction of gibbsite with alcohols such as 2-methoxyethanol and aminoalcohols which have an electron-donating group also gave the boehmite derivatives. These findings are also consistent with structure **2**.[22]

Maleki and Schwing-Weill[23] reported that the reaction of $Al(OBu^s)_3$ with eg in benzene solution at 90–100 °C yielded a highly hygroscopic and easily hydrolysable product, which released excess of glycol molecules at 150 °C and gave a compound having the molar ratio OCH_2CH_2O/Al of 7:4. On the basis of the well established structure of $Al(OPr^i)_3$, they[23] proposed a tetrameric structure for this compound. On the other hand, the present products were not hygroscopic and had much lower glycol/Al ratios. Under the present reaction conditions, the compound prepared by Maleki and Schwing-Weill may be formed as an intermediate. However, since the reaction temperature is much higher than that used by Maleki and Schwing-Weill, subsequent partial decomposition reactions would take place.

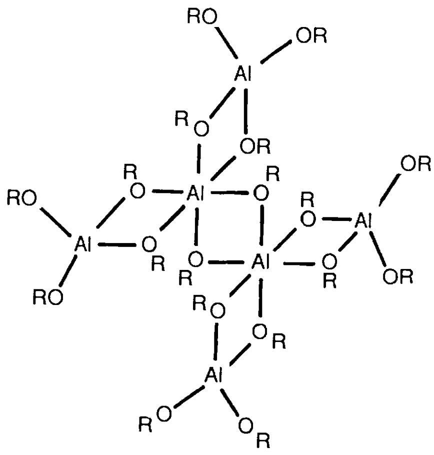
Reaction Mechanisms and Effect of the Carbon Number of the Glycol.—The formation of a glycol derivative of boehmite from $Al(OPr^i)_3$ seems to involve three primary reactions depicted in Scheme 1. Reaction (1) is the transesterification between $Al(OPr^i)_3$ and glycol forming an aluminium glycoxide as an intermediate. Reaction (2) is the formation of a primary framework of boehmite and (3) is the growth of the boehmite layer.

Reaction (1) is reversible, and therefore the equilibrium composition is determined by the activities of glycol and propan-2-ol. The total amount of glycol charged in the autoclave was 1.47 mol (for bd) and the theoretical amount of propan-2-ol liberated from $Al(OPr^i)_3$ was 0.183 mol; a much larger amount of glycol was present in the system. Moreover, since the reaction temperature was much higher than the critical point of propan-2-ol (235 °C), most of the propan-2-ol escaped from the condensed phase into the gas phase. Therefore, reaction (1) would proceed completely to the intermediate.

The present products had empirical formulas of $AlO(OH)_{0.43}[O(CH_2)_2OH]_{0.57}$, $AlO(OH)_{0.63}[O(CH_2)_3OH]_{0.37}$, $AlO(OH)_{0.74}[O(CH_2)_4OH]_{0.26}$, and $AlO(OH)_{0.78}[O(CH_2)_6OH]_{0.22}$, for $Al(OPr^i)_3$–eg, –pd, –bd and –hd, respectively, which means more than two of the three $HO(CH_2)_n$–O–Al< bonds must be broken at either C–O or O–Al. The cleavage of the O–Al bond leaving an alkoxide anion can proceed by hydrolysis. Although the present reaction was carried out without addition of water, a small amount of water may be present in the glycol sample and is possibly formed by the thermal decomposition of glycol. However, the addition of water to the present system resulted in formation of pseudoboehmite. Moreover, based on the inductive effect of the intramolecular hydroxy group, one would expect that the reactivity of the intermediate decreases with increasing carbon number of the glycol and amounts of glycol moieties remaining in the product increase. Opposite was actually observed. Therefore, we conclude that, in the present system, hydrolysis of O–Al bonds did not take place but cleavage of C–O bond occurred.

Since reaction (1) proceeds at much lower temperature than the present reaction temperature, the cleavage of the C–O bonds [reactions (2) and (3)] seems to control the development of the boehmite layer structure. When the development of the boehmite layer structure is assessed by the crystallite size of the product, it increases in the order (carbon number of glycol): $2 < 3 < 6 < 4$. Since the solvolysis rate of ω-methoxyalkyl *p*-bromobenzenesulphonates increases with the length of the alkyl chain in exactly the same order,[24] the development of the layer structure of boehmite is closely associated with the heterolytic cleavage of the C–O bond of $HO(CH_2)_nO$–Al< [reactions (2) and (3)]. In the solvolytic reaction of $HO(CH_2)_2O$–Al<, the O^-–Al< group is considered to be a leaving groups and because of the inductive effect of the hydroxy group the cleavage of the C–O bond is expected to proceed more easily with increasing carbon number of the glycol. When the carbon number is 4 the cleavage of the C–O bond is accelerated by the participation of the intramolecular hydroxyl group forming tetrahydrofuran, which was actually detected in the supernatant of the reaction mixture.

As the heterolytic cleavage of C–O bond in reactions (2) and (3) is the key factor in the development of the layer structure of boehmite a high reaction temperature was required; when the reaction was carried out at 250 °C the products had only small



$R = (CH_2)_nOH$

Fig. 8 A possible structure for the primary framework of boehmite during the formation of a glycol derivative of boehmite

crystallite sizes and $Al(OPr^i)_3$–eg(250) no longer had the layer structure of boehmite.

The appearance of the peak due to tetrahedrally co-ordinated Al in the ^{27}Al NMR spectra of the products needs comment because Al atoms in boehmite layers are octahedrally co-ordinated. In the tetrameric structure of aluminium alkoxide the formal negative charge of the central octahedrally co-ordinated Al atom is cancelled by bonding to tetrahedrally co-ordinated Al through bridging alkoxide groups. Similarly, the negative charge of the boehmite primary framework may be cancelled by tetrahedrally co-ordinated Al atoms. A possible structure is depicted in Fig. 8. With development of the boehmite layer the tetrahedral : octahedral ratio decreased. If co-ordination sites of Al atoms at the surface (except 010) of the product particle are occupied by glycoxide anions, the particle would be negatively charged. To neutralize the negative charge, tetrahedral Al atoms seem to be required.

As shown in Fig. 6, with increasing crystallite size of the product, a honeycomb-like texture developed. This suggests that the honeycomb-like texture involves a random orientation of plate-like crystals of glycol derivatives of boehmite. An identical texture was observed on the surface of particles of gibbsite–eg.[9] In other words, two different materials, $Al(OPr^i)_3$ and gibbsite, gave products having not only an identical structure but also an identical morphology. This suggests that the two reactions proceed through an identical intermediate soluble in glycol.

The bulk density of powder materials usually increases with decreasing surface area. Nevertheless, the bulk densities of the present products show a tendency contrary to the general rule. This is explained as follows: the surface area of the product decreased with increasing crystallite size while the honeycomb-like texture developed with increasing crystallite size. The honeycomb-like texture possesses macro pores and thus, the product having a large crystallite size (low surface area) has a low bulk density.

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