Glycothermal synthesis of metal oxides

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Abstract
The author has been exploring the synthesis of inorganic materials in
organic solvents at temperatures (200–300 °C) higher than their boiling points
(solvothermal reaction), and has developed various reaction methods for the
synthesis of ultrafine particles of metal oxides. In this paper, the reactions of
aluminium compounds (aluminium hydroxide ($Al(OH)_3$; gibbsite), aluminium
alkoxides, and aluminium salts) in various organic solvents (alcohols, glycols,
aminoalcohols, and inert organic solvents) are first reviewed, and reaction
mechanisms and effects of the starting materials and solvents on the products are
discussed. Then, the specificity of the use of glycols, especially 1,4-butanediol
(glycothermal reaction), is clarified, and glycothermal synthesis of crystalline
mixed oxides such as yttrium aluminium garnet is described. Finally, the use
of the solvothermally prepared products as the catalyst materials is described.

1. Introduction

Recently, use of organic media for inorganic synthesis has attracted much attention. Since
1984, we have been exploring the synthesis of inorganic materials in organic media at elevated
temperatures (200–300 °C) under autogenous pressure for the organics [1]. We showed that
some oxides such as α-alumina can be crystallized in glycols at temperatures lower than that
required by the hydrothermal conversion [2]. This method was termed 'glycothermal reaction'
because of the use of glycol in place of water for the hydrothermal reaction [2, 3]. We also
found that various mixed oxides were directly crystallized when two suitable starting materials
such as alkoxide, acetylacetonate, and acetate were allowed to react in 1,4-butanediol (1,4-BG)
at 200–300 °C [3, 4].

In this paper, our works on the solvothermal reactions of aluminium compounds will be
reviewed first, and reaction mechanisms for the formation of metal oxides by the solvothermal
reaction will be discussed. Although the prefix, 'solvo-' means any kinds of solvent including
water, aqueous alkaline or acid solutions, and inorganic liquids such as ammonia as well

as organic solvents, in the present paper, the word, 'solvothermal', will be used to refer the reaction in organic solvents, and the differences between and similarity of the solvothermal and hydrothermal reactions are addressed. Then, our recent works on the use of the solvothermally obtained products for catalyst materials will be described.

2. Typical reaction procedure

Yttrium acetate (4.24 g, 12.5 mmol) and aluminium isopropoxide (AIP, 4.26 g, 20.8 mmol) were suspended in 88 ml of 1,4-butanediol (1,4-BG) in a test tube, serving as an autoclave liner, and the test tube was placed in a 200 ml autoclave. An additional 20 ml of 1,4-BG was placed in the gap between the autoclave wall and the test tube. The autoclave was completely purged with nitrogen and heated to the desired temperature (usually 300 °C) at a rate of 2.3 °C min^{-1} and kept at that temperature for 2 h. After the assembly was cooled to room temperature, the resulting product, yttrium aluminium garnet (YAG), was collected by centrifuging. When the product was not settled down, suspension was sedimented by the addition of a small amount of ammonia. The product was washed with methanol repeatedly by vigorous mixing and centrifuging, and then air-dried.

3. Reaction of aluminium hydroxide in organic solvents

In lower alcohols

Hydrothermal reaction of aluminium hydroxides (Al(OH)$_3$; gibbsite, bayerite, and nordstrandite) is well established and the reaction yields boehmite (AlOOH) [5]. When lower alcohols (methanol, ethanol, and 1-propanol) were used in place of water for the hydrothermal reaction of gibbsite, boehmite was also obtained [6]. The morphology of the starting material (agglomerates of hexagonal plates) was completely altered by the reaction (figure 1(a)), suggesting that a dissolution–crystallization mechanism took place. With the increase in the carbon number of the alcohol, the yield of boehmite decreased (figure 2). This result is attributed to the decrease in the dissolution rate because the dielectric constant of the medium decreases with increase in the carbon number of the alcohol. Since the reaction temperature is near the onset temperature for thermal dehydration of gibbsite, dissolution of the starting material competes with the thermal dehydration, and the yield of χ-alumina increased with increase in the carbon number of the alcohol. The yield of χ-alumina reached a maximum when pentanol was used (figure 2). The reaction in this solvent preserved the morphology of the starting materials (figure 1(c)), and boehmite yield increased with increase in the particle size of gibbsite. These results indicate that thermal dehydration takes place in pentanol.

In higher alcohols and inert organic solvents

Further increase in the carbon number of the alcohol again increased the yield of boehmite (figure 2) [6]. As an extreme case, the reaction of gibbsite in mineral oil was examined. The reaction proceeded completely yielding well-crystallized boehmite, and the morphology of the product (figure 1(e)) was identical to that obtained by thermal dehydration of the same starting material in a sealed tube (figure 1(f)) [6]. Since the overall reaction is a dehydration reaction, water is formed. With increase in the carbon number of the alcohol, the affinity of the solvent for water decreases and the activity of water in the medium increases when the same amount of water is present in the system. If one assumes that the solubility of water in mineral oil is negligible even at higher temperatures, the activity of water becomes unity when
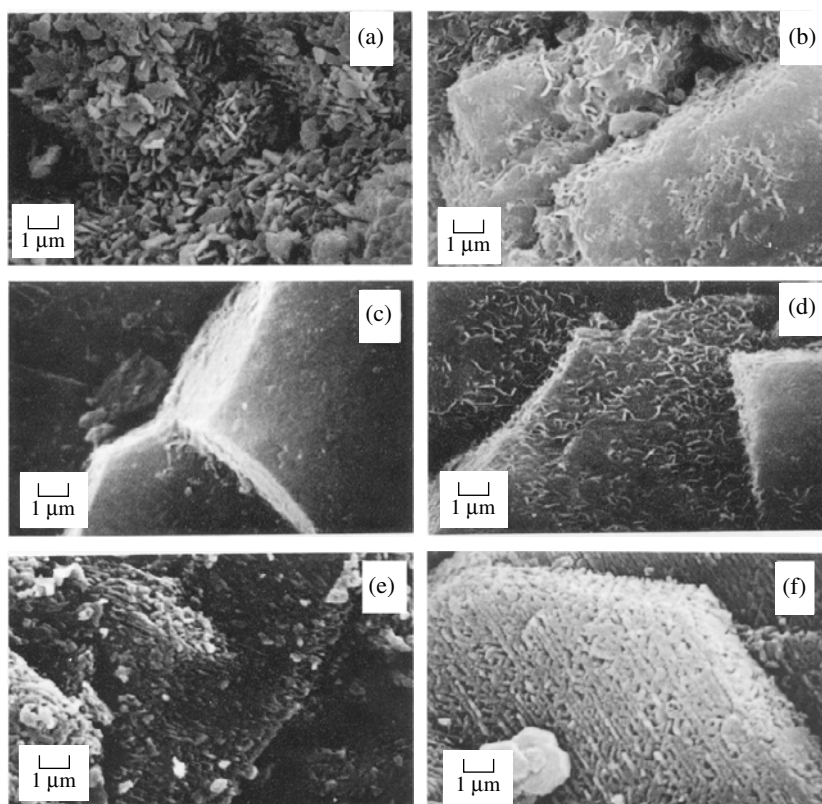
Figure 1. Scanning electron micrographs of the products obtained by treatment of a gibbsite sample with the average particle size of 80 μm in: (a) ethanol; (b) butanol; (c) pentanol; (d) octanol; (e) mineral oil; (f) a sealed tube; each at 250 °C for 2 h.

only a small amount of water is formed by partial dehydration of the starting materials. With increase in the activity of water, the proportion of water molecules adsorbed on the surface of the particle increases, and hydrothermal conditions are formed, thus yielding boehmite. Once hydrothermal reaction is started by a small amount of water adsorbed on the particle or by intraparticle hydrothermal reaction (see below), the reaction is completed with the aid of water molecules formed by the reaction.

In this regard, when the hydrogels, prepared by precipitation from aqueous salt solutions of metal salts, are suspended in inert organic solvents and solvothermally treated, oxides may be crystallized. However, the reaction here is not a 'solvothermal' reaction but a hydrothermal one. However, the reaction proceeds with a limited amount of water adsorbed on the particles and intermediate species cannot diffuse into the bulk of the solvent. Therefore, we can obtain products with unique morphologies, which reflect the shapes of particles or agglomerates in the suspension. For example, in the case of the reaction of gibbsite, a pseudomorph of the starting material was observed, whereas diamond-shaped boehmite particles are obtained by the usual hydrothermal reaction.

It must be noted that although the reaction was carried out in a closed system, the reaction in pentanol resembled the thermal dehydration in an open system where water molecules formed by dehydration are diffused out from the reaction system. This result suggests that the activity (fugacity) of water is lowered by the solvent molecules.
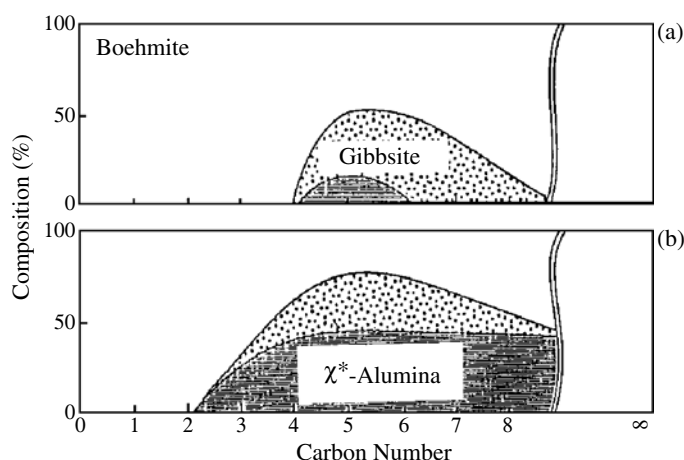
Figure 2. Compositions of the particles obtained by treatment of gibbsite with an average particle size of: (a) 80 μm; (b) 0.2 μm; each in straight-chain primary alcohols and in mineral oil (as an infinity for higher alcohol where the effect of the hydroxyl group is assumed to be negligible) at 250 °C for 2 h.

In glycols and aminoalcohols

When an alcohol having another hydroxyl group, an alkoxyl group or an amino group was used as the solvent, a completely different reaction occurred. The product was the alkyl (glycol) derivative of boehmite (AlO(OH)$_x$(O(CH$_2$)$_n$OH)$_y$; $x + y = 1$), in which solvent molecules are incorporated between the boehmite layers through the covalent bondings (figure 3); i.e., the product has Al–O–C bonds [7, 8]. This result indicates that equilibrium occurs between aluminium hydroxide and alkoxide and that alkoxide can be formed from hydroxide at high temperatures. The difference between the reactions in simple alcohols and in glycols can be attributed to the chelating effects of the lone-pair electrons of oxygen and nitrogen atoms upon the glycoxide and to the decrease in the activity of water due to the solvation by the highly hydrophilic solvent molecules.

The reaction is greatly affected by the particle size of the starting materials (table 1) [8, 9]. When coarse gibbsite was used, well-crystallized boehmite was formed together with the glycol derivatives of boehmite and unreacted gibbsite. Randomly oriented thin plates are formed on the surface of the particles (figure 4). An important point here is that the product is not formed in the bulk of the solvent. Two explanations are possible: the gibbsite surface acts as the nucleation sites of the product, and the gradient of the concentration of water, which declines from the surface of the particle to the bulk solvent, causes precipitation of the product near the surface of the staring particles. Formation of well-crystallized boehmite can be explained by intraparticle hydrothermal reaction mechanism. This mechanism was originally proposed by de Boer [10, 11] for the formation of boehmite by thermal dehydration of gibbsite. It is well known that when coarse gibbsite is thermally dehydrated, boehmite is formed, and that formation of boehmite stops when formation of χ-alumina starts. According to the mechanism, thermal dehydration starts at the 'hot spot' of the particle and water molecules formed by dehydration cannot diffuse out from the particles. Therefore, hydrothermal condition is achieved inside the particle and boehmite is formed. When thermal dehydration yielding χ-alumina starts, pore systems are formed inside the originating particle and water that facilitates the hydrothermal conversion into boehmite is diffused out from the particles;
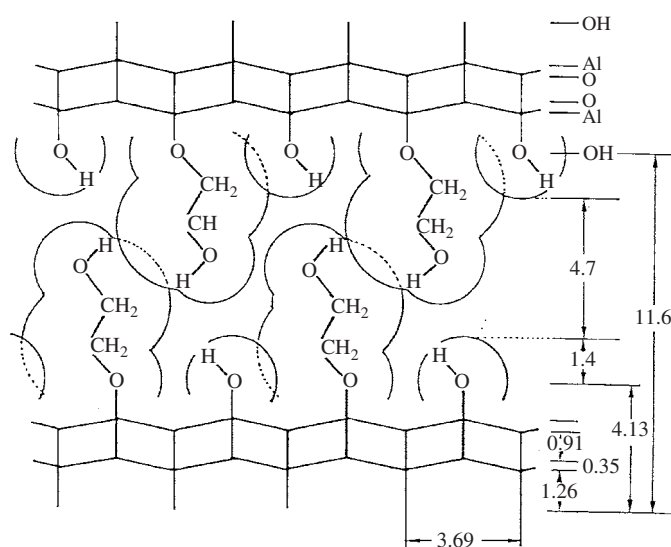
**Figure 3.** The structure of a glycol derivative of boehmite.

Table 1. The effect of the particle size of gibbsite on the glycothermal reaction (Note: reaction conditions: 30 g of gibbsite in 130 ml of ethylene glycol (+30 ml of additional ethylene glycol to the gap between the test tube and the autoclave wall) at 250 °C for 2 h.)

Average particle size of gibbsite (μm)	Recovered gibbsite (%)	Boehmite (%)	Glycol derivative of boehmite (%)
80	41	11	48
25	18	9.5	72
8	4.6	11	85
0.2	0.3	1.9	98
<0.2	0	0	100

therefore, formation of boehmite ceases. Formation of well-crystallized boehmite under the solvothermal conditions can be explained similarly. A chimney-like structure was observed when coarse gibbsite was used as the starting material (figure 5), which seems to be formed when water molecules are released from the particle [9].

Glycothermal reaction of aluminium salts

The glycothermal reaction of aluminium salts such as nitrate, sulfate, and chloride also yielded the glycol derivatives of boehmite [9]. However, nitrate ions have a strong oxidizing ability and therefore glycol molecules are oxidized and condensation reactions of the thus-formed carbonyl compounds proceed further, yielding highly viscous liquid (caramel). Therefore, it is quite difficult to isolate the inorganic product from the reaction mixture. Sulfate ions also act as oxidizing agents at higher temperatures yielding sulfur dioxide as the reduced product [12]. On the other hand, reaction of the halides in glycol liberates hydrogen halides and, therefore, the autoclave may be severely damaged. Addition of alkaline hydroxide or amine base to the reaction mixture can avoid damage of the autoclave. However, it must be noted that anions (and alkaline ions if alkaline hydroxide is used to neutralize the liberated acid) may be occluded in
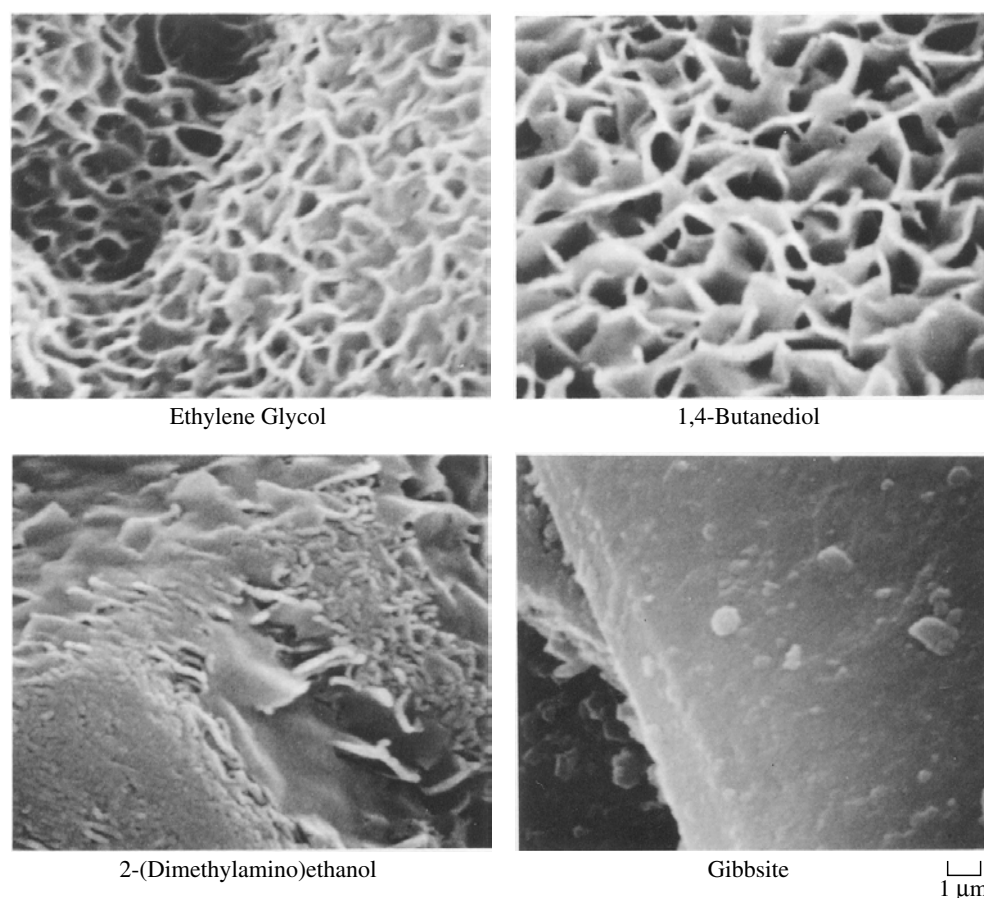
Figure 4. Scanning electron micrographs of the samples obtained by treatment of gibbsite with an average particle size of 80 μm in the solvents specified in the figure at 250 °C for 2 h.

or adsorbed on the product particles, and these ions may severely affect the properties of the products, especially when the product is used as the catalyst.

Formation of α-alumina

Since the dissolution of gibbsite is the most important process for the formation of the glycol derivatives of boehmite, the increase in carbon number of the 1,ω-glycol increased the recovery of the unreacted gibbsite, and we examined the reaction at higher temperature (300 °C) and found the formation of α-alumina [2]. α-alumina is formed via the glycol derivative of boehmite (figure 6), and the product has hexagonal plate morphology. Since the intermediate, the glycol derivative of boehmite, has a honeycomb-like morphology, a dissolution–crystallization mechanism took place during this transformation.

The equilibrium point between diaspore and α-alumina under the hydrothermal conditions was reported to be 360 °C [13]. Since boehmite, which is obtained from aluminium compounds by hydrothermal reaction at lower temperatures, is slightly less stable than diaspore, the 'equilibrium' point between boehmite and α-alumina must be lower than the above-mentioned temperature. However, the conversion rate near the equilibrium point is quite low. Practical
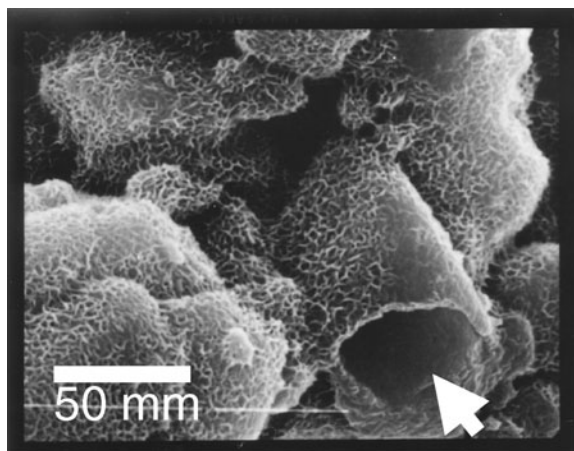
Figure 5. Chimney-like structure found in the product of the reaction of gibbsite with 80 μm particle size in ethylene glycol at 250 °C.
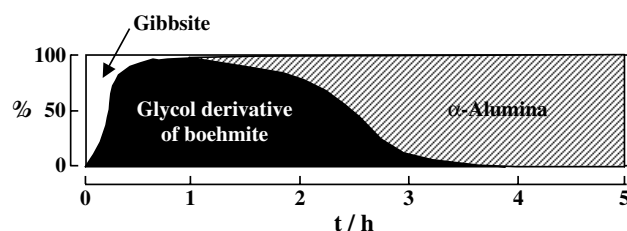

Figure 6. The reaction of microcrystalline gibbsite (<2 μm) in 1,4-butanediol at 285 °C.

synthesis of α-alumina under hydrothermal conditions has been examined by many researchers. For example, Yamaguchi *et al* [14] reported that 445 °C and 10 h are required for complete conversion of boehmite into α-alumina even though the reaction was carried out in a 0.1N NaOH solution in the presence of α-alumina seed crystals. On the other hand, under glycothermal conditions, complete conversion into α-alumina was attained at 285 °C for 4 h. The difference between glycothermal and hydrothermal reaction can be attributed to the stability of the intermediate phases, that is, the glycol derivative of boehmite is thermodynamically much less stable than well-crystallized boehmite and therefore the former compound has a larger driving force for conversion into α-alumina. The lower activity (fugacity) of water in the glycothermal media also contributes to the conversion into α-alumina because the overall reaction is dehydration.

Since the formation of the intermediate, the glycol derivative of boehmite, is severely affected by the particle size of the starting material, formation of α-alumina is also affected by the particle size of the starting material, and gibbsite with particle size less than 0.2 μm gave α-alumina, while gibbsite with particle size larger than 0.2 μm gave χ-alumina. As discussed above, dissolution of gibbsite into the medium is the important factor, and the crystals of the glycol derivative of boehmite are formed near the surface of the originating gibbsite particles. If particle size is large, the thus-formed crystals of the intermediate prevent the dissolution of the remaining part of the staring material and thermal dehydration takes place, yielding χ-alumina. χ-alumina is fairly stable under the reaction conditions and essentially insoluble in the glycol media. Once χ-alumina was formed, conversion of the glycol derivative of boehmite into χ-alumina took place with the aid of the underlying χ-alumina crystals.
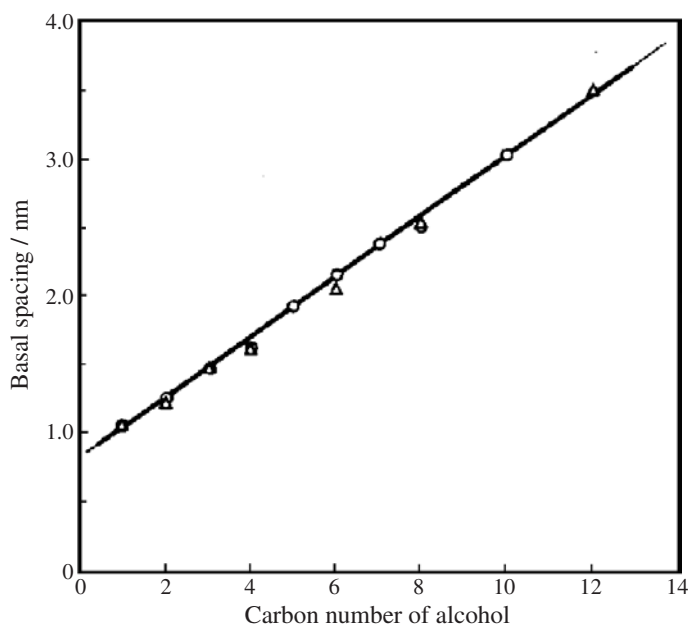
Figure 7. Interlayer spacings of the alkyl derivative of boehmite obtained by the reaction of: ○, aluminium metal: △, aluminium isopropoxide in straight-chain primary alcohols.
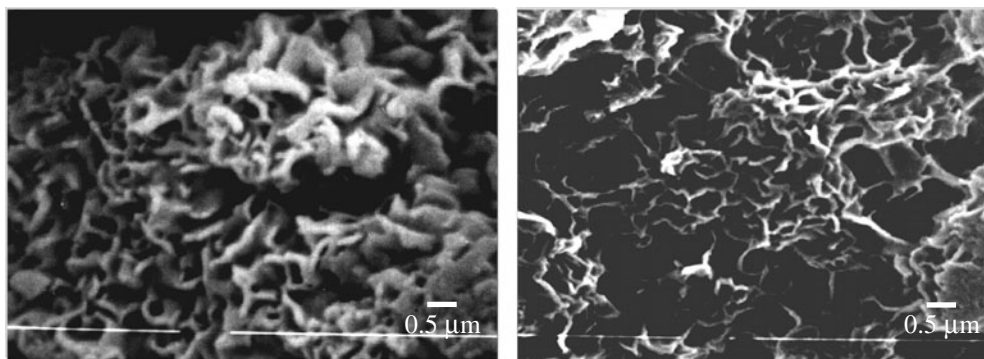
4. The reaction of aluminium alkoxide

In simple alcohols

The reaction of aluminium alkoxide in straight-chain primary alcohols yields the alkyl derivative of boehmite [15]. The interlayer spacing of the product was linearly increased with increase in the carbon number of the alcohol (figure 7). The alkyl groups derived from the solvent alcohols are incorporated between the layers of boehmite and the alkyl groups originating from aluminium alkoxide are expelled from the products. This is due to the fact that a large excess of the solvent molecules is present in the system and alkoxyl groups are easily exchanged under the reaction conditions:

$$Al(OR)_3 + 3R'OH \rightleftarrows Al(OR')_3 + 3ROH.$$
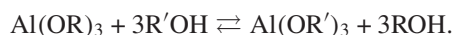
Aluminium metal can be used for this reaction. Aluminium metal is oxidized by alcohol yielding alkoxide and hydrogen, and the alkoxide decomposes into the alkyl derivative of boehmite. Similar reaction of metallic zinc and magnesium yields the corresponding oxides. The reaction of cerium metal tips having oxide superficial layers in 2-methoxyethanol is interesting; it yields a transparent colloidal solution of ceria with 2 nm particle size after separation of coarse ceria particles derived from the superficial layer [16].

The reaction of aluminium alkoxides in secondary alcohols belongs to another category. Since dehydration of the solvent alcohols occurs at relatively low temperatures, hydrolysis of the alkoxides takes place via the water molecules formed in the reaction system. This method, originally proposed by Fanelli and Burlew for the synthesis of ultrafine alumina particles [17], can avoid the heterogeneity caused by the addition of water to hydrolyse the metal alkoxide, and therefore can be considered as the alkoxide method version of the homogeneous precipitation method.

Figure 8. Morphologies of the glycol derivative of boehmite obtained from aluminium isopropoxide (left) and gibbsite with particle size less than 0.2 μm (right).

In glycols

The reaction of aluminium alkoxides in glycol yields the glycol derivative of boehmite [18, 19]. The crystallite size of the product increased in the following order: $HO(CH_2)_2OH <$ $HO(CH_2)_3OH < HO(CH_2)_6OH < HO(CH_2)_4OH$. Physical properties of the products and the aluminas derived by calcination thereof varied according to this order. This result suggests that the development of the product structure is controlled by the heterolytic cleavage of O–C bonds of the glycoxide intermediate, $>Al–O–(CH_2)_nOH$, formed by alkoxyl exchange between aluminium alkoxide and the glycol used as the medium. The presence of an electron withdrawing group, i.e., the hydroxyl group, near the O–C bond retards the formation of carbocations; thus only poorly crystallized product was obtained in ethylene glycol. On the other hand, the largest crystallite size, obtained by the use of 1,4-butanediol (1,4-BG), is interpreted in terms of the ease of the cleavage of the O–C bond due to the participation of the intramolecular hydroxyl group [20], which yields an aluminate ion ($>Al–O^-$) and protonated tetrahydrofuran. A similar medium effect was also observed for the glycothermal treatment of other alkoxides.

It must be noted that the reactions of both aluminium *hydroxide* and *alkoxide* in glycol yielded glycol derivatives of boehmite with identical morphology (figure 8) [7, 9, 19]. As is indicated by this example, it is known that hydroxide and alcohol are in equilibrium with alkoxide and water ($M(OH)_n + nROH \rightleftarrows M(OR)_n + nH_2O$) [21]. Because of this equilibrium, glycoxide (a kind of alkoxide) is generated from the hydroxide under glycothermal conditions, and therefore partially hydrolysed alkoxide can be used for the reaction. (Hydrolysis of aluminium alkoxides yields pseudoboehmite (microcrystalline boehmite), the structure of which is fairly stable, and therefore fully hydrolysed alkoxide does not give the desired product by glycothermal reaction.) Actually, the glycothermal reaction does not require any precaution for handling alkoxides, and reproducible results are obtained even without the purification of the starting alkoxides [22]. (As far as I know, zirconium alkoxide is the only exception; polycondensation reaction of Zr–OH group proceeds rapidly as compared with the alkoxyl exchange reaction; as a result, partial hydrolysis of zirconium alkoxide severely affects the physical properties of the glycothermal products [22–24].)

In inert organic solvents

Thermal decomposition of aluminium isopropoxide at 300 °C in inert organic solvents such as toluene yields χ-alumina [25]. Since the decomposition in the gas phase affords an amorphous

Table 2. Preparation of yttrium aluminium garnet (YAG) by the glycothermal reactions.

Aluminium compound	Yttrium source	Medium	Reaction temperature (°C)	Product
Isopropoxide	Acetate	1,4-BG	300	YAG
Isopropoxide	Acetate	1,4-BG	280	YAG
Isopropoxide	Acetate	1,4-BG	250	YAG, YO(OAc)
Isopropoxide	Acetate	EG	300	Amorphous
Isopropoxide	Oxide	1,4-BG	300	Y_2O_3 glycol derivative of boehmite
Gibbsite	Acetate	1,4-BG	300	YO(OAc), gibbsite
Pseudoboehmite	Acetate	Water	300	Boehmite > YAG
Gibbsite	Acetate	Water	300	YAG > boehmite

product, the presence of the organic solvent facilitates the crystallization of the product. It was generally believed that χ-alumina was only formed by dehydration of gibbsite. The product directly transformed into α-alumina without formation of high temperature transition aluminas. Aluminium *n*-alkoxide was not decomposed at this reaction temperature, while aluminium *tert*-butoxide decomposed at much lower temperature, yielding an amorphous product. These results suggest heterolytic cleavage of O–C bonds yielding a carbocation and the aluminate ion is a key step for the reaction.

This method can be applied for the synthesis of other oxides such as titania [26] and zirconia [23, 24]. However, one drawback of this reaction method is that care must be taken to prevent the hydrolysis of the staring materials. Unlike the glycothermal reaction, this reaction does not allow regeneration of the alkoxide from hydroxide.

5. Synthesis of mixed oxides

Since aluminium glycoxide decomposes into $>$Al–O$^-$ ions under the glycothermal conditions, Al–O–M bonds may be formed when suitable cations are present in the reaction system. This working hypothesis was proved by the glycothermal reaction of a stoichiometric mixture of aluminium alkoxide and yttrium acetate, which affords single-phase crystalline YAG [3, 27].

The reaction of the same starting materials in ethylene glycol afforded a gelatinous amorphous product [28, 29]. This result can be explained by the difficulty of cleavage of the C–O bond in ethylene glycoxide. However, when the gelatinous product was calcined in air, YAG was crystallized at 920 °C, suggesting that yttrium and aluminium atoms were homogeneously mixed in the product.

For comparison, the hydrothermal reaction of pseudoboehmite (hydrolysed product of AIP) with yttrium acetate at 300 °C was examined. A small amount of YAG was obtained, but the major product was well-crystallized boehmite (table 2). Single-phase YAG was not obtained even with prolonged reaction time [3]. Under the hydrothermal conditions, aluminium compounds are easily converted to boehmite, which is much more stable than the glycol derivative of boehmite, formed as an intermediate in the glycothermal reaction. Therefore, the former intermediate has a smaller driving force for the formation of final product, YAG. Similarly, when either of the starting materials is easily converted into stable hydroxide or oxide under the hydrothermal conditions, hydrothermal synthesis of mixed oxide requires severe conditions or prolonged reaction times as compared with those required by the glycothermal reaction.

All the thermodynamically stable rare earth aluminium garnet can be prepared glycothermally [27]. Moreover, europium and dysprosium aluminium garnets, that have never
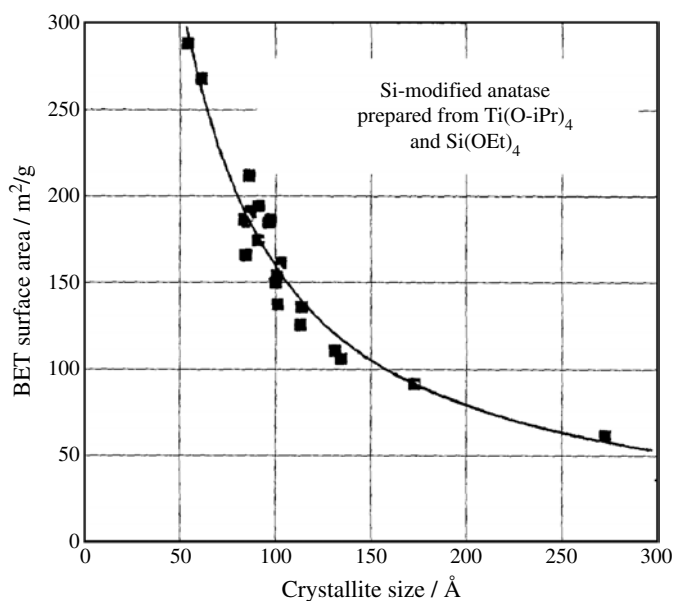
Figure 9. The relation between the surface area and crystallite size of titania and silica-modified titania prepared by the glycothermal reaction of titanium isopropoxide with/without tetraethyl silicate.

been prepared by any other method, are also formed although these phases were not obtained in a single phase [27]. Electron micrographs showed the presence of large spherical particles of these garnets, indicating that nucleation is difficult because of the difference in ionic size of the two metal ions. Note that when rare earth acetate alone was allowed to react under the solvothermal conditions (1,4-BG), crystalline rare earth acetate hydroxides, Re(OH)$_2$(OAc), REO(OAc) (two morphs) and Re(OH)(OAc)$_2$, were formed depending on the ionic size of the rare earth element [30, 31].

Our group have prepared various mixed oxides by glycothermal reactions. For detailed mechanisms for crystallization of the mixed oxides and specificity of the product, see [22, 27, 32].

6. Application of the solvothermal product for catalysis

Titania

Solvothermal reaction of titanium alkoxide was reported in 1991 [26]. The product was anatase and had quite large surface areas (table 3). However, the surface area was drastically decreased by calcination at 600 °C. Therefore, silica-modified titania having the anatase structure was prepared glycothermally. The product maintained surface area above 150 m^2 g^{-1} even after calcination at 600 °C [33, 34]. Because the product has a quite large surface area, the deNOx and hydrodesulfurization catalysts supported on the product show higher activity as compared with the conventional catalysts. The product also exhibits a quite high photocatalytic activity for mineralization of organic pollutants in water. Note that the large surface area is not due to the presence of amorphous silica particles, because the surface area was inversely correlated with the crystallite size of anatase determined by the XRD peak width, as shown in figure 9.

Table 3. Solvothermal synthesis of titania.

Ti source	Reaction medium	Temperature (°C)	Product phase	Surface area (m^2 g^{-1})
Isopropoxide	EG	300	Unknown	150
Isopropoxide	1,4-BG	300	Anatase	42[a]
Isopropoxide	2-butanol	250	Anatase	72
Isopropoxide	Toluene–2-butanol[b]	250	Anatase	120
TiO(acac)$_2$	EG	300	Rutile, Anatase	120
TiO(acac)$_2$	1,4-BG	300	Anatase	62
TiO(acac)$_2$	Toluene	300	Anatase	200
TiO(acac)$_2$	Toluene	250	Anatase	250
TiO(acac)$_2$	Toluene	200	Amorphous	

[a] By adjusting the product-drying conditions, products with surface area of ~90 m^2 g^{-1} are now obtained.
[b] 2-butanol/titanium isopropoxide = 9.

Zinc aluminate spinel (ZnAl$_2$O$_4$)

The reaction of a stoichiometric mixture of aluminium alkoxide (or gallium acetylacetonate) and zinc acetate in 1,4-BG at 300 °C yields zinc aluminate (or zinc gallate) having the spinel structure [4]. The copper catalyst supported on the glycothermally prepared zinc aluminate spinel (350 m^2 g^{-1}) had the highest activity for steam reforming of methanol among the supported copper catalysts [35].

Zirconia

Glycothermal reaction of zirconium propoxide yields tetragonal zirconia [23, 24]. Nickel catalyst supported on the product had a high activity for decomposition of methane yielding hydrogen and carbon nanotubes [36].

γ-Ga$_2$O$_3$–Al$_2$O$_3$

Glycothermal reaction of gallium acetylacetonate alone yields γ-Ga$_2$O$_3$ [37, 38], and the glycothermal reaction of mixtures of gallium acetylacetonate and aluminium alkoxide yields Ga$_2$O$_3$–Al$_2$O$_3$ binary oxides having the gamma-type defect spinel structure, although the presence of large excess aluminium alkoxide resulted in contamination of the binary oxide with the glycol derivative of boehmite. Gallium ions preferentially occupy the tetrahedral sites and aluminium ions occupy the octahedral sites. This binary oxide has quite high activity for selective catalytic reduction of NOx with methane.

7. Conclusion

For the solvothermal reaction of metal hydroxide and hydrogels formed by precipitation from aqueous solutions, water formed by dehydration of the starting material has a significant effect on the reaction. On the other hand, glycothermal reaction of metal alkoxide, acetylacetonate, or acetate is a convenient route for the synthesis of crystalline oxides, avoiding the effect of water. Because of instability of the intermediates, crystal growth proceeds quite rapidly, although the nucleation step is always kinetically prohibited [32]. Crystal defects may be formed during the rapid crystal growth, and because of the low solubility of the oxide crystals in organic solvents, defects formed on the surface of the products cannot be eliminated. This point

shows a sharp contrast to the hydrothermal reaction where dissolution–deposition equilibrium eliminates surface defects. Because of the large surface area and presumably defects on the surface of the products, the products show high and unique performances for various catalyses.

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