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Solvothermal oxidation of gallium metal

Sung-Wook Kim, Shinji Iwamoto, Masashi Inoue *

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

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Abstract

Solvothermal oxidation of gallium metal in various organic solvents at 300 °C under the autogenous vapor pressure of the solvents was examined. The reaction of gallium metal in 1-butanol or 2-methoxy-ethanol at 300 °C did not proceed and unreacted gallium metal was recovered even with prolonged reaction time. On the other hand, gallium metal reacted in aminoalcohols such as 2-aminoethanol, 2-methylaminoethanol, 2,2′-iminodiethanol and 2,2′,2″-nitrilotriethanol yielding γ-Ga_2O_3. The product obtained by this reaction has a relatively large crystallite size as compared with γ-Ga_2O_3 prepared by the conventional method.

Keywords: A. Powders: chemical preparation; B. Porosity; Ga_2O_3; Solvothermal reaction

1. Introduction

Gallium oxide-based catalysts are known to be active for dehydrogenation of light hydrocarbons, aromatization of light alkanes and selective catalytic reduction of NO_x by hydrocarbons in the presence of oxygen [1,2]. Enhanced catalytic activities of zeolites containing gallium species as both framework gallium atoms and extra-framework gallium oxide have been reported [3–5], and mixed Ga_2O_3–Al_2O_3 oxides are known as promising catalysts for selective catalytic reduction of nitrogen oxides in exhaust gases from power stations [6–9]. Recently, researchers also focused on the synthesis of Ga_2O_3 with various morphologies. Yada et al. reported the homogeneous–precipitation synthesis of mesostructured gallium oxide templated by a surfactant [10]. Cheng and Samulski prepared Ga_2O_3 nanotubes by immersing a porous alumina membrane template in an amorphous $Ga_2O_3{\cdot}nH_2O$ sol [11]. Synthesis of Ga_2O_3 nanowires by evaporation of GaN in oxygen atmosphere [12,13] or by laser ablation of Ga_2O_3 [14] has been reported.

Gallium oxide has been reported to have five polymorphs: α, β, γ, δ and ε [15]. The β-modification is the only thermodynamically stable phase and all of the other modifications transform into β-form at high temperatures [15]. Although Roy reported that γ-Ga_2O_3 has no obvious relationship to γ-Al_2O_3, it is now generally believed that the γ-form has a defect spinel structure similar to that of γ-Al_2O_3 because Ga_2O_3–Al_2O_3 solid solutions were prepared [16,17]. In the solid solutions, Ga^{3+} ions preferentially occupy the tetrahedral sites of the defect spinel structure [16,17]. This polymorph is of particular interest because of its high surface area suitable for catalyst uses. Böhm first reported the synthesis of this phase by calcination of “gallium hydroxide gel” [18], but synthesis of this phase is not an easy task; the most important point is that the gel must be quickly dried [15,18,19]. Presumably, prolonged contact of the hydroxide gel particles with water causes the formation of GaOOH-like phase having a diaspore-type structure, which is a precursor of α-Ga_2O_3. This point is completely different from alumina chemistry where prolonged contact of aluminum hydroxide gel particles with water would give a boehmite-like structure, which yields γ-Al_2O_3 on calcination.

The most reliable method for the synthesis of the gallium hydroxide gel as the precursor of γ-Ga_2O_3 is the addition of an ethanolic solution (50 vol.%) of concentrated aqueous ammonia to a solution of gallium nitrate in ethanol at room temperature [19] and this procedure is followed by most of the recent papers [20–24] for the synthesis of γ-Ga_2O_3. Only few preparation methods other than that mentioned above have been reported: hydrothermal oxidation of gallium metal [25,26], glycothermal reaction of gallium acetylacetonate [27], and solvothermal reaction of $GaCl_3$ in DMF in the presence of an

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* Corresponding author. Tel.: +81 75 383 2478; fax: +81 75 383 2479.
E-mail address: inoue@scl.kyoto-u.ac.jp (M. Inoue).

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amine base [28]. However, physicals properties such as surface area, surface activity and pore texture depend on the preparation method. Therefore, development of a variety of synthetic procedures is highly desired.

We have been exploring the synthesis of inorganic materials in organic media at elevated temperatures under autogenous pressure of the organic media (solvothermal reaction) [27,29–33], and showed that some oxides can be crystallized in organic media at the temperatures lower than that required by hydrothermal reaction [30]. Solvothermal oxidation of metals has been examined: aluminum metal is oxidized by straight-chain primary alcohols with a carbon number as high as 12, yielding the alkyl derivatives of boehmite, and the basal spacing of the product linearly increases with the increase in the carbon number of the alcohol used as the reaction medium [31,32]. When cerium metal tips with the superficial layers of oxide are allowed to react in 2-methoxyethanol at 250–300 °C, a colloidal solution containing 2–3-nm-sized CeO_2 particles is obtained after the removal of coarse ceria particles originating from the superficial layers [33].

In the present work, solvothermal oxidation of gallium metal with various aminoalcohols at 300 °C has been examined. The structure and property of the products will be discussed.

2. Experimental

2.1. Synthesis method

Commercially available gallium metal (Kanto Chemical) was used without further purification. In a Pyrex test tube serving as autoclave liner, 130 ml of an aminoalcohol and a piece of gallium metal were placed, and the test tube was then placed in a 300 ml autoclave. In the gap between the autoclave wall and the test tube was placed an additional 30 ml of the solvent. The autoclave was thoroughly purged with nitrogen, heated to the desired temperature (300 °C) at a rate of 2.5 °C/min and held at that temperature for a desired period (2–10 h). After the assembly was cooled to room temperature, the resulting precipitates were washed by repeated cycles of agitation with methanol, centrifuging and decantation, and then air-dried.

2.2. Characterization

Powder X-ray diffraction (XRD) was measured on a Shimadzu XD-D1 diffractometer using CuKα radiation and a carbon monochromator. Crystallite size was calculated from the peak at $2\theta = 64^\circ$ by Scherrer equation. Simultaneous thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a Shimadzu DTG-50 analyzer: a weighed amount (ca. 20 mg) of the sample was placed in the analyzer, dried in a 40 ml/min flow of dried air until no further weight decrease was observed, and then heated at the rate of 10 °C/min in the same gas flow. Morphologies of the products were observed with a scanning electron microscope (SEM), Hitachi S-2500X. The nitrogen adsorption isotherms were measured at liquid-nitrogen temperature by the usual constant volume method on Quantachrome Autosorb-1. The products obtained by the solvothermal method were previously outgassed at 300 °C for 30 min. Surface areas were calculated by the BET single point method, on the basis of the nitrogen uptake measured at 77 K using a Micromeritics Flowsorb II 2300. The average area occupied by a nitrogen molecule was assumed to be 0.162 nm^2.

3. Results and discussion

The reaction of gallium metal in 1-butanol or 2-methoxyethanol at 300 °C for 2 h did not proceed and unreacted gallium metal was recovered even with prolonged reaction time. Whereas the reaction of aluminum metal in primary alcohols yielded the alkyl derivatives of boehmite [30], gallium metal did not react in these solvents. This difference can be explained by the fact that aluminum metal is easier to be oxidized than gallium metal: standard reduction potential of aluminum ion (−1.676 V) is lower than gallium ion (−0.53 V). However, when aminoalcohols such as 2-aminoethanol (ethanolamine; MEA) and 2,2′-iminodiethanol (diethanol-amine; DEA) were used as the reaction media, the reaction proceeded, indicating that the reaction requires alcohols with a functional group (other than the hydroxyl group) having a strong ability to donate its lone pair electrons.

The XRD patterns of the products are shown in Fig. 1, which shows that γ-Ga_2O_3 was formed by the reaction of gallium metal in these organic solvents. For the reaction in MEA for 4 h (Fig. 1), only agglomerated particles were obtained but increased reaction time afforded mixtures of agglomerates and powders: agglomerated particles were settled down in the bottom of the test tube, while powder particles were floated in the solution, which were collected by centrifugation. Crystallite size of the powders was bigger than that of agglomerates and both increased with the reaction time (Table 1). The latter result shows a clear contrast against those for the reaction in DEA and 2,2′,2″-nitrilotriethanol (triethanolamine; TEA), where crystallite size of products was not changed by increasing the reaction time. These results indicate that dissolution and recrystallization of γ-Ga_2O_3 took place in highly polar MEA ($\varepsilon = 37.72$ at 25 °C [34]), while this process did not occur in less polar solvents (DEA, $\varepsilon = 24.69$; TEA, $\varepsilon = 28.11$ [35]). It is rather surprising to know that γ-Ga_2O_3 was fairly well crystallized, since this phase is usually only poorly crystallized having the crystallite size less than 5 nm.

Table 1 summarized the results for the reaction of gallium metal in various media. When the reaction in *N*-methylaminoethanols are compared, the conversion of gallium metal decreased with the increase in number of the methyl substituent of the amino group, indicating that methyl substitution of hydrogen atom of the amino group reduces the reactivity of the solvent because of the increase in the steric hindrance.

When the reaction in MEA was quenched at the reaction time of 2 h, 60.6% of gallium metal was converted, but no solid product was obtained. When the reaction system (gallium metal tip–MEA) was slightly warmed to melt gallium metal (mp = 29.75 °C) followed by ultrasonic irradiation to disperse

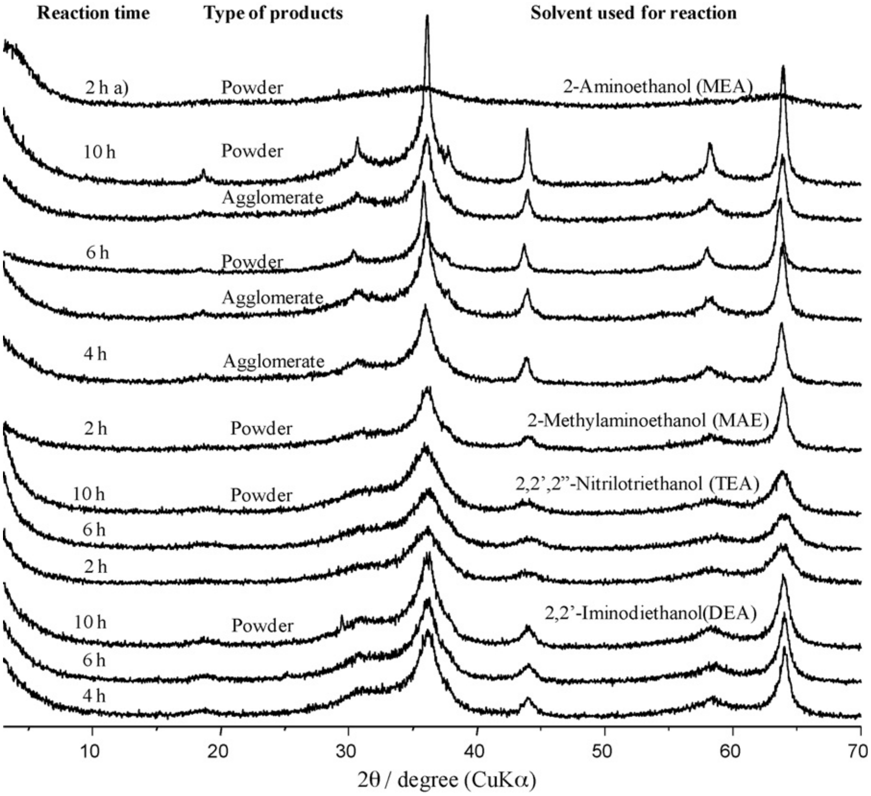

Fig. 1. X-ray diffraction patterns of the products obtained by solvothermal oxidation of gallium metal in aminoalcohols specified in the figure: (a) solid product precipitated from the solution after the colloidal solution was left standing for 1 month.

metal particles prior to the reaction; the conversion of gallium metal slightly increased (69%) (Table 2). When the reaction was carried out with stirring after the dispersion of gallium metal as mentioned above, the conversion of gallium metal further increased (88%). However, gray solid particles remained at the bottom of the vessel after the reaction.

When the solution obtained by the reaction in MEA for 2 h was diluted five times with water and irradiated by laser beam, Tyndall phenomenon was observed (Fig. 2a and b); therefore, colloidal particles seem to be present in the solution. To obtain solid products, ammonia or saturated NaCl solution was added, but precipitate was not formed. Since the solution was highly

Table 1

Preparation of gallium oxide by the solvothermal oxidation of gallium metal at 300 °C.

Medium[a]	Type of products	Reaction time (h)	Conversion of gallium metal (wt%)	Surface area[b] (m^2/g)	Crystallite size (nm)	Crystal phase of products[c]
MEA	Solution	2	60.6	No solid product		
	Aggromerate	4	53	7.8	17.6	γ
	Aggromerate	6	52	33.5	19.1	γ
	Powder			8.6	25.9	γ
	Aggromerate	10	66.7	16.5	28.3	γ
	Powder			7.2	30.2	γ
DEA	Solution	2	100	No solid product		
	Powder	4	100	6	14	γ
	Powder	6	100	3.8	12.5	γ
	Powder	10	100	7.1	11.6	γ
TEA	Powder	2	97.5	71.1	4.5	γ
	Powder	6	96.4	83.2	4.7	γ
	Powder	10	96.8	76.3	5.9	γ
MAE	Powder	2	57.5	9.5	17.3	γ
DMAE	Solution	2	4.2	No solid product		

[a] MEA, 2-aminoethanol; DEA, 2,2′-iminodiethanol; TEA, 2,2′,2″-nitrilotriethanol; MAE, 2-methylaminoethanol; DMAE, 2-(*N*,*N*-dimethylamino)ethanol.

[b] Pre-treated at 300 °C for 30 min.

[c] γ, γ-Ga_2O_3.

Table 2
Effect of pre-treatment of gallium metal on the solvothermal oxidation of gallium metal in 2-aminoethanol.

Pre-treatment condition of gallium metal	Precursor gallium metal (g)	Recovered gallium metal (g)	Reacted gallium metal (g)	Conversion of gallium metal (wt%)
Without pre-treatment	0.249	0.098	0.151	60.6
Ultrasonic treatment	0.286	0.089	0.196	68.5
Ultrasonic treatment +stirring	0.181	0.0215	0.16	88.4

Reaction condition: temperature; 300 °C, time; 2 h.

basic because of the presence of aminoethanol used as the reaction medium, it was neutralized by addition of HNO_3 and then a NaCl or $Al(NO_3)_3$ solution was added. However, precipitation did not occur. At this stage, therefore, no evidence other than Tyndall phenomenon was obtained for the presence of colloidal particles, and further work is in progress using small-angle X-ray scattering. Note that when this solution was left standing for 1 month, a solid product was precipitated out from the solution. The XRD patterns of the product indicated that the product was poorly crystallized γ-Ga_2O_3 (Fig. 1, top). A transparent solution was obtained by adding the precipitate to methanol. When a NaCl solution was added to this transparent solution, precipitate was not formed but Tyndall phenomenon was observed by irradiation of laser beam to this transparent solution (Fig. 2c).

Scanning electron micrographs (SEMs) of the products are shown in Fig. 3. The agglomerated product obtained by the reaction in MEA was composed of irregularly shaped plate-like particles having numerous voids with various sizes (Fig. 3a). On the other hand, the powder product was composed of spherical particles formed by aggregation of thin platelet particles (Fig. 3b) and the platelet particles were developed by prolonged reaction time (Fig. 3c). Similar morphology was also observed for the products obtained in MAE, although spherical secondary particles were much smaller than those observed in the products obtained in MEA (Fig. 3f).

These morphologies are rather unexpected because γ-Ga_2O_3 has a defect spinel structure having no anisotropy in the crystal structure. Presumably, thin platelets were formed through an intermediate having anisotropic crystal structure. However, quenching the reaction with shorter reaction time resulted in formation of a colloidal solution, as mentioned above. On the other hand, the products obtained in TEA and DEA were composed of spherical particles with a smooth surface (Fig. 3d and e).

Nitrogen adsorption isotherms of the products obtained in MEA and TEA are shown in Fig. 4. The product obtained by the reaction in MEA for 10 h exhibited a very low nitrogen uptake and no hysteresis loop, indicating that the products has no mesopores; however, an increase in nitrogen uptake at the high relative pressure region (Fig. 4a) indicates the presence of macro-pores formed between plate-like particles shown in the SEM image (Fig. 3c). In the *t*-plot (Fig. 4b) derived from the isotherm, the plot exhibits a straight line going through the origin at region lower than 12 Å, indicating the absence of micro- or meso-pore in the sample. The larger increase in the slope of the *t*-plot indicates the presence of macro-pores in the sample.

On the other hand, the product obtained in TEA suggests that the product had micro-pores, which is shown by abrupt decrease in the slope of the *t*-plot at $t = 8$ Å. The presence of micro-pores suggests that each spherical particle (Fig. 3d) is composed of much smaller primary particles between which the pore-system is formed. Relatively small crystallite size of this product also supports this argument. The hysteresis loop suggests that slit-shaped pores were formed. The micro-pores may have been formed between the plate-like crystals. This product also has the macro-pores formed between small spherical particles (Fig. 3d) because an abrupt increase of nitrogen uptake at high relative pressure region, which is also

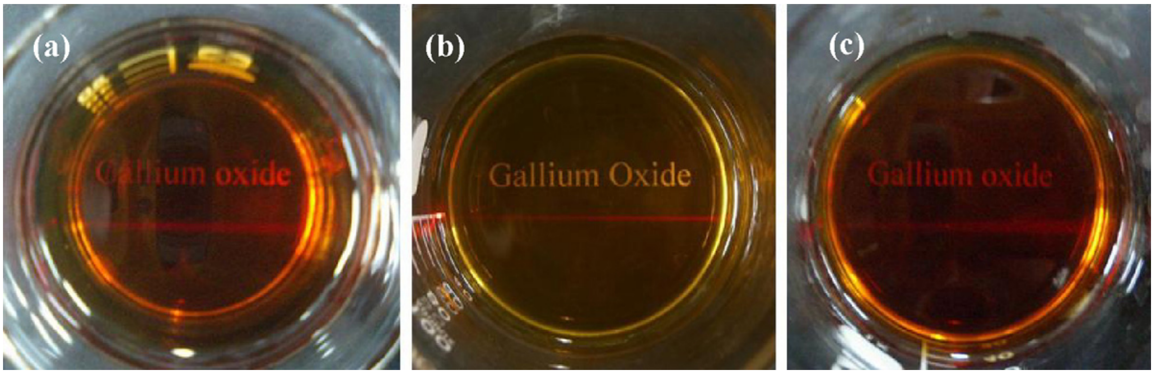

Fig. 2. Photographs showing the Tyndall phenomena of the solution obtained by the reaction of gallium metal in 2-aminoethanol: (a) solution as obtained by reaction for 2 h; (b) solution diluted five times with water; (c) solution obtained by addition the precipitates to methanol: the precipitate was obtained by keeping the colloidal solution for 1 month.

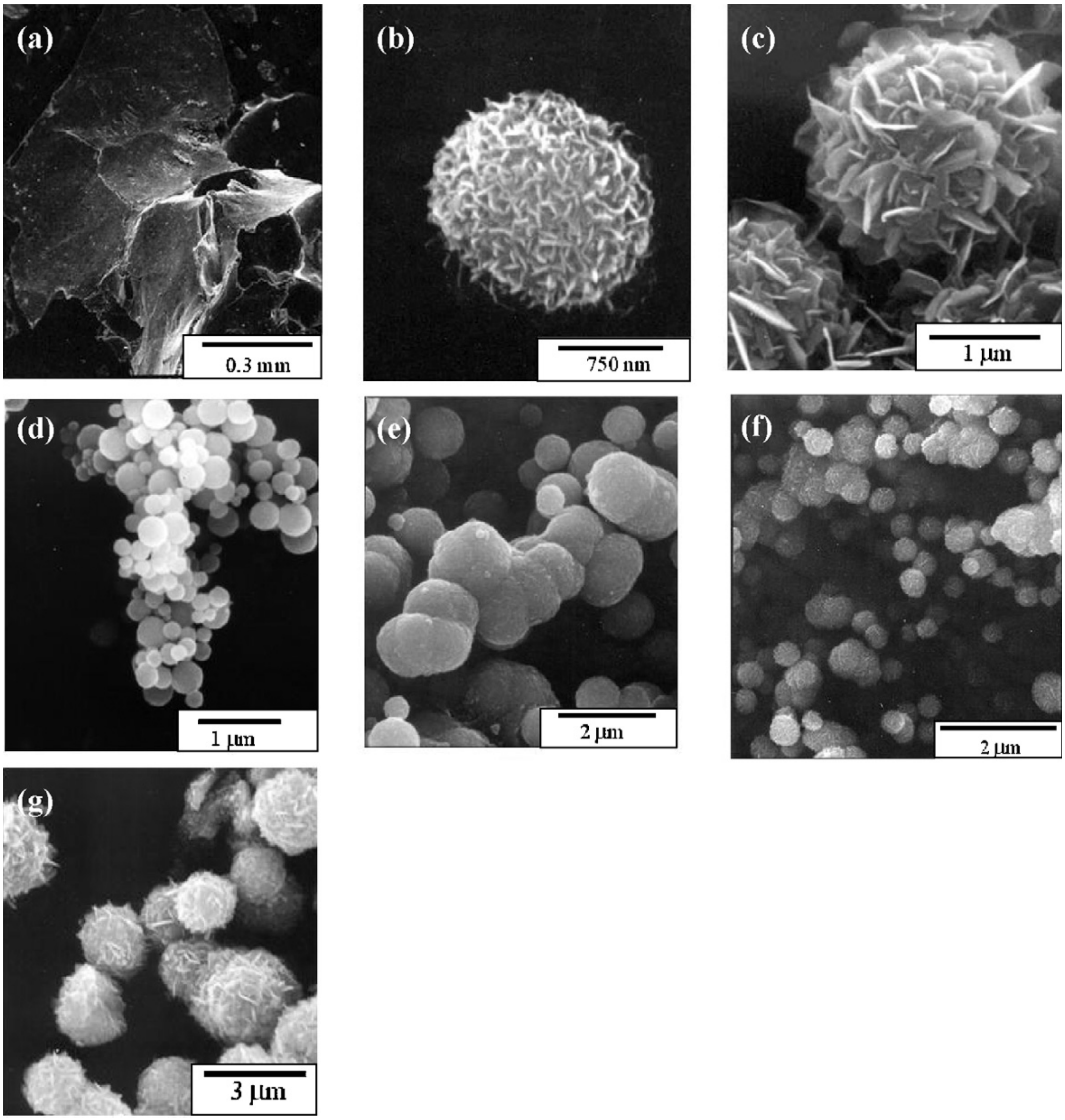

Fig. 3. Scanning electron micrographs of: (a–f), the products obtained by the reaction of gallium metal: (a–c) in 2-aminoethanol for: (a) 4 h (agglomerate); (b) 6 h (powder); (c) 10 h (powder); (d) in 2,2′,2″-nitoriloethanol for 2 h; (e) in 2,2′-iminoethanol for 4 h; (f) in 2-methylaminoethanol for 2 h: (g), the sample obtained by calcination of product (c) in air at 1000 °C for 30 min.

shown by the *t*-plot of this product (increase of the slope at high *t* region).

The results for the thermal analysis of the products are shown in Fig. 5. The TG–DTA profile showed a weight decrease processes at 300–400 °C, which was associated with exothermic response in DTA, suggesting that the weight decrease is due to combustion of the organic moieties remaining on the surface of the product particles. The peak temperature for the exothermic response depended on the solvent used in the reaction and had a tendency to increase with the increase in basicity of the solvent (p*K*a values of MEA, DEA, and TEA are 9.50, 8.88, and 7.76, respectively). This result suggests the nitrogen atom of the solvent molecule firmly coordinates to the surface acid site of the products particles.

The XRD patterns of the calcined samples are shown in Fig. 6. The γ-phase transformed into β-phase after calcination at 600–800 °C. Although it is generally accepted that $\gamma \rightarrow \beta$ transformation temperature is 650 °C, the present products required a slightly high temperature for this transformation (see Fig. 6d), which may be due to higher crystallinity of the present products. It is interesting to note that the $\gamma \rightarrow \beta$ transformation was not accompanied by enlargement of the crystallite size. This result shows a sharp contrast against those for the ordinary γ-Ga_2O_3 samples, where β-Ga_2O_3 with quite a large crystallite size is formed from poorly crystallized γ-Ga_2O_3 phase.

A SEM photograph of the calcined sample is shown Fig. 3g. Formation of β-Ga_2O_3 did not alter the essential the feature of the morphology of the products. This result also

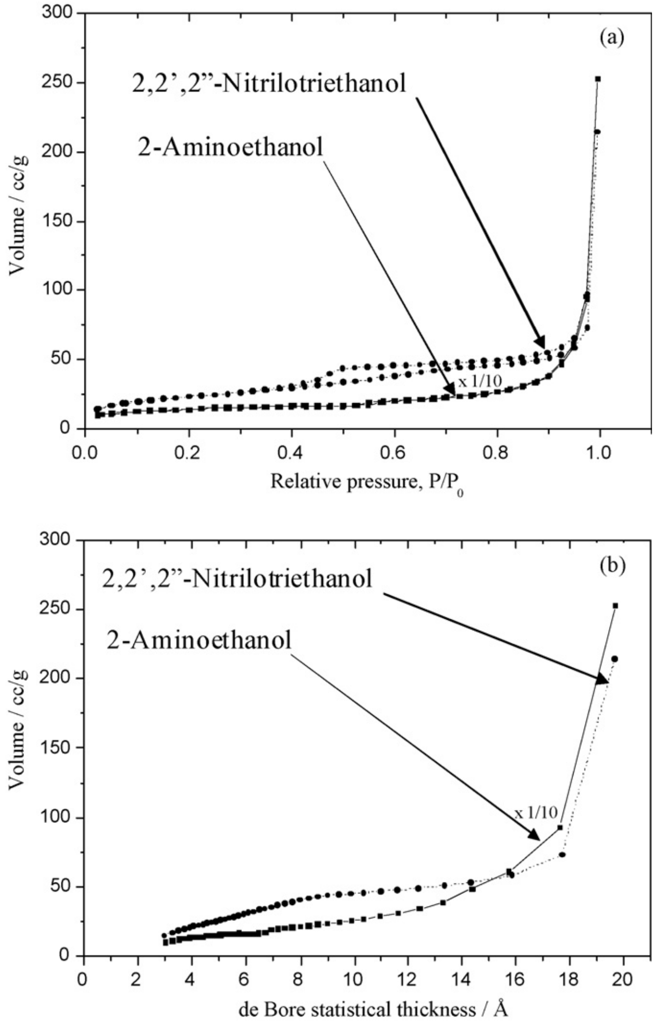

Fig. 4. Nitrogen adsorption isotherms (a) and *t*-plot (b) of the powder obtained by solvothermal oxidation of gallium metal.

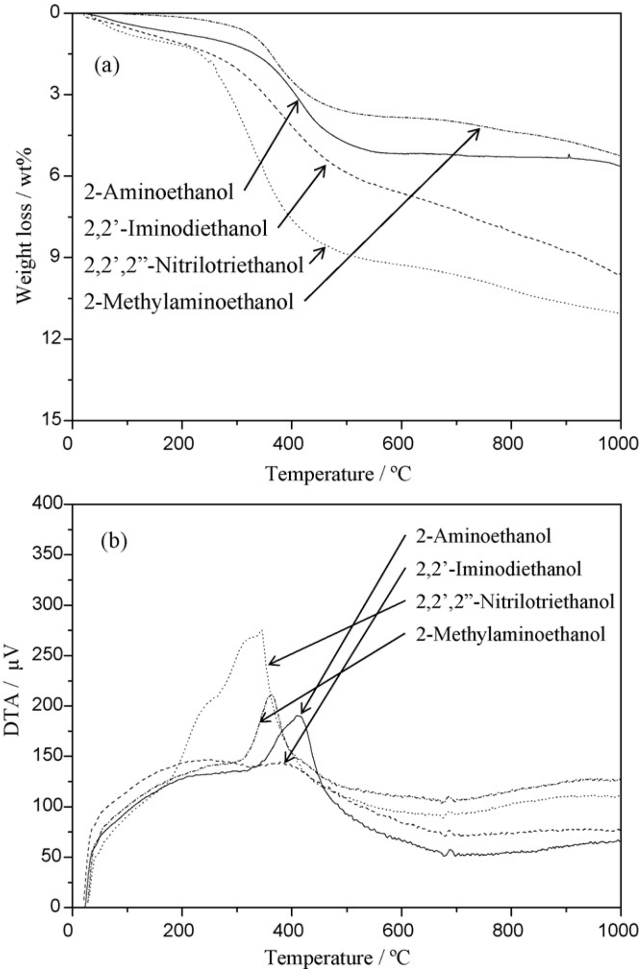

Fig. 5. Thermal analysis of the products obtained by the reaction of gallium metal in various solvents in a 40 ml/min flow of dried air at the heating rate of 10 °C/min: (a) TG and (b) DTA.

shows a clear contrast against the alumina chemistry where formation of thermodynamically stable α-alumina from transition aluminas completely alters the morphology. This seems to be due to the fact that stacking of oxygen sublattice for γ- and β-Ga_2O_3 are essentially identical, while γ- to α-alumina transformation requires rearrangement of oxygen stacking from the cubic closest packing to the hexagonal one.

Change of surface area by calcination in air was investigated and the results are shown in Table 3. In the case of the product obtained in TEA, surface area decreased with the increase of calcination temperature, while surface area of the product obtained in MEA increased by calcination at 600 °C. However, the surface area of the latter product is much smaller than that expected from the SEM image and voids between the plate-like particles in the core of the spherical aggregate seems to be filled with MEA. Since the desorption temperature of MEA is quite high (Fig. 5), MEA is not desorbed from the product particles by the pre-treatment prior to the nitrogen adsorption.

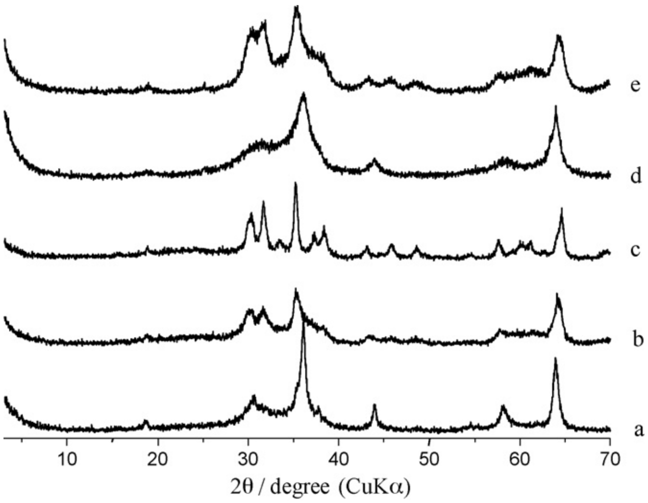

Fig. 6. X-ray diffraction patterns of the samples obtained by calcination of the products at: (a) 600 °C; (b) 800 °C; (c) 1000 °C; (d) 750 °C; (e) 900 °C; each in air for 30 min. The products were obtained by solvothermal oxidation of gallium metal: (a)–(c) in 2-aminoethanol at 300 °C for 10 h; (d) and (e) in 2,2′-iminodiethanol at 300 °C for 6 h.

Table 3
Surface areas and phases of calcined products.

Medium[a]	Reaction time (h)	Product[b]	Calcination temperature (°C)	Surface area (m^2/g)	Crystal phase[c]
MEA	10	A	As syn	16.5	γ
			600	20.6	γ
			800	3.9	γ, β
			1000	4.5	β
		P	As syn	7.2	γ
			600	24.7	γ
			800	20.4	γ, β
			1000	4.6	β
TEA	6	p	As syn	83.2	γ
			600	74.7	γ
			800	56.3	γ, β
			1000	19.2	β
	10	p	As syn	76.3	γ
			600	71.2	γ
			800	60.8	γ, β
			1000	28.1	β

[a] MEA, 2-aminoethanol; TEA, 2,2′,2″-nitrilotriethanol.

[b] A, agglomerate; P, powder.

[c] γ, γ-Ga_2O_3; β, β-Ga_2O_3.

4. Conclusion

Phase-pure γ-Ga_2O_3 was formed by solvothermal oxidation of gallium metal in aminoalcohols such as MEA, MAE and TEA. For the reaction in 2-aminoethaol, crystallite size of the product increased with prolonged reaction time. The products had unique morphologies.

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