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Solvothermal oxidation of gallium metal

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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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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