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Effect of Mechanical Activation of $Al(OH)_3$ on Its Reaction with Li_2CO_3

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Abstract—The effect of preliminary mechanical activation of $Al(OH)_3$ on its solid-state reaction with Li_2CO_3 at temperatures above 800°C has been studied by thermogravimetry, X-ray diffraction, in situ X-ray diffraction, electron microscopy, and specific surface area and particle size measurements. The results demonstrate that preliminary mechanical activation of $Al(OH)_3$ in an AGO-2 planetary mill at 40*g* for 1 min allows phase-pure γ-$LiAlO_2$ to be obtained. The composition of the lithium aluminates resulting from mechanical activation and heat treatment depends on the phase composition of the aluminum oxides resulting from the thermal decomposition of $Al(OH)_3$. The particle size and specific surface area of the forming γ-$LiAlO_2$ have been determined.

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INTRODUCTION

γ-$LiAlO_2$ with a large specific surface area is used in tritium production in nuclear power engineering [1], in molten carbonate fuel cell electrolyte matrix support materials [2], as a separator material for lithium thermal batteries, and to modify the conductivity of lithium polymer electrolytes [3]. The most widespread approaches to the synthesis of fine-particle γ-$LiAlO_2$ are ceramic processing route [4, 5] and sol–gel processes [6–9].

The conventional ceramic processing route is easy to implement, but the forming γ-$LiAlO_2$ typically has a small specific surface area, insufficient for application in electrolyte matrix supports. Because of this, the lithium aluminate thus prepared has to be subsequently ground into fine-particle material, which leads to contamination of the product.

Sol–gel processing enables the preparation of γ-$LiAlO_2$ with a sufficiently large specific surface area, $S = 5–10$ m^2/g, but this approach requires expensive organic precursors of aluminum and lithium. Moreover, sol–gel processes are rather difficult to implement and present an environmental threat. In this context, there is currently great interest in novel, environmentally safe processes for the synthesis of fine-particle γ-$LiAlO_2$ from relatively inexpensive, readily available chemicals.

Among new synthetic approaches, mechanical activation (MA), widely used to synthesize mixed oxides [10], is of considerable interest. In particular, as shown by Kharlamova et al. [11, 12] the MA of a mixture of aluminum hydroxide and lithium carbonate in an AGO-2 planetary mill, followed by heat treatment of the activation products in air at temperatures from 800 to 850°C allows one to produce finely dispersed γ-$LiAlO_2$, which can be used in molten carbonate fuel cell electrolyte matrix supports and lithium thermal batteries [13]. As pointed out earlier [12], the heat treatment of a mixture containing lithium carbonate and mechanically activated aluminum hydroxide leads to the formation of phase-pure γ-$LiAlO_2$ at a lower temperature in comparison with unactivated aluminum hydroxide. This suggests that the initial state of aluminum hydroxide has a strong effect on its reaction with lithium carbonate.

The purpose of this work was to investigate the effect of the MA of $Al(OH)_3$ on its reaction with Li_2CO_3.

EXPERIMENTAL

The starting materials used were crystalline $Al(OH)_3$ (analytical grade, RF State Standard GOST 11841-76) and Li_2CO_3 (pure grade, Purity Standard TU 6-09-3728-83).

The aluminum hydroxide was first mechanically activated in an AGO-2 centrifugal planetary mill (200-ml steel vials) at 40*g* in air for 1, 5, and 10 min. At milling times of 5 and 10 min, the process was run discretely, with breaks after every 2.5 min of milling. We used 5-mm-diameter steel balls. The powder-to-ball weight ratio was 1 : 20. Mechanically activated or unactivated $Al(OH)_3$ was mixed with Li_2CO_3 in an agate mortar to give a stoichiometric mixture of $LiAlO_2$. The starting mixtures thus prepared were reacted in an SNOL 7.2/1100 laboratory muffle furnace at a heating rate of 10°C/min and then at 800°C for 4 h.

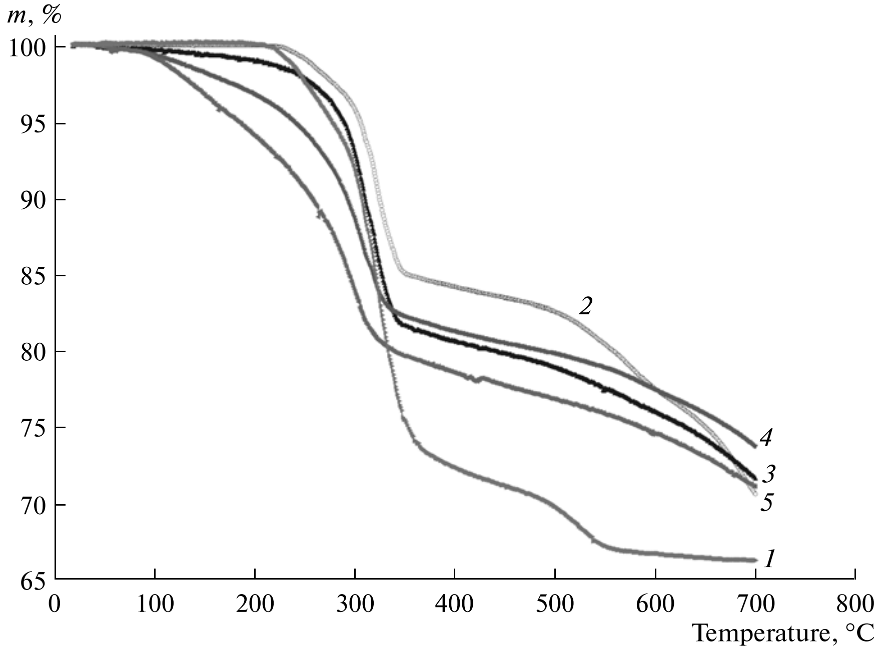

Fig. 1. Weight loss curves of (*1*) gibbsite, (*2*) a mixture of gibbsite and lithium carbonate, and (*3–5*) mixtures of lithium carbonate and mechanically activated aluminum hydroxide. Milling time of (*3*) 1, (*4*) 5, and (*5*) 10 min; sample weight, 200 mg; heating at a rate of 10°C/min in air.

The unactivated and mechanically activated aluminum hydroxides and the products of their reaction with lithium carbonate were characterized by thermogravimetry (TG), X-ray diffraction (XRD), in situ XRD, and specific surface area and particle size measurements.

XRD patterns were collected on a D8 Advance diffractometer (Bruker, Germany) (CuK_α radiation, air, $2\theta = 10°–50°$, heating rate of 2°C/min). In situ XRD measurements were performed on the D8 Advance diffractometer (Bruker, Germany), equipped with an NTK 1200 N high-temperature camera (Al_2O_3 holders, CuK_α radiation, air, $2\theta = 10°–50°$, heating rate of 10°C/min, temperatures from 25 to 900°C). One XRD scan took 8 min.

TG scans were performed with a Paulik–Paulik–Erdey thermoanalytical system in air at temperatures from 20 to 700°C and a heating rate of 10°C/min, using alpha-alumina crucibles.

The specific surface area of our samples was evaluated from argon adsorption/desorption isotherms. The particle size of the aluminum hydroxides and the products of their reaction with lithium carbonate was determined using a Microsizer-201A particle size laser analyzer, with ethanol as a dispersion medium. The morphology of the powders was examined by scanning electron microscopy (SEM) on a Hitachi TM-100.

EXPERIMENTAL RESULTS

Reaction of crystalline aluminum hydroxide with lithium carbonate studied by TG and XRD. TG data demonstrate that, when crystalline aluminum hydroxide is reacted with lithium carbonate, weight losses begin at 220°C and are observed throughout the temperature range studied, up to 700°C (Fig. 1). Since the TG curve of individual aluminum hydroxide is similar in shape to that of the mixture at temperatures of up to 500–550°C, it is reasonable to assume that, below these temperatures, the weight loss is predominantly due to $Al(OH)_3$ dehydration. This assumption is qualitatively supported by in situ XRD data (Fig. 2), which demonstrate that, when the mixture is heated to 200°C, the reflections from $Al(OH)_3$ almost completely disappear and reflections from boehmite emerge. Their intensity decreases with increasing temperature, and they almost completely disappear at 500°C. The intensity of the reflections from lithium carbonate remains essentially unchanged throughout the temperature range 25–400°C. At 500°C, there is a slight decrease in intensity. The XRD pattern taken at 600°C shows rather strong reflections from the α-phase of lithium aluminate. After heating to 700°C, there are reflections from both the α-phase and γ-$LiAlO_2$. At higher temperatures, the percentage of the γ-phase increases, while that of α-$LiAlO_2$ decreases. Nevertheless, even at 900°C the γ-phase coexists with α-$LiAlO_2$ as an impurity phase.

Reaction of mechanically activated aluminum hydroxide with lithium carbonate studied by TG and XRD. TG data demonstrate that, during heating of a mixture of Li_2CO_3 and mechanically activated $Al(OH)_3$, a weight loss begins at a lower temperature in comparison with the mixture containing unactivated

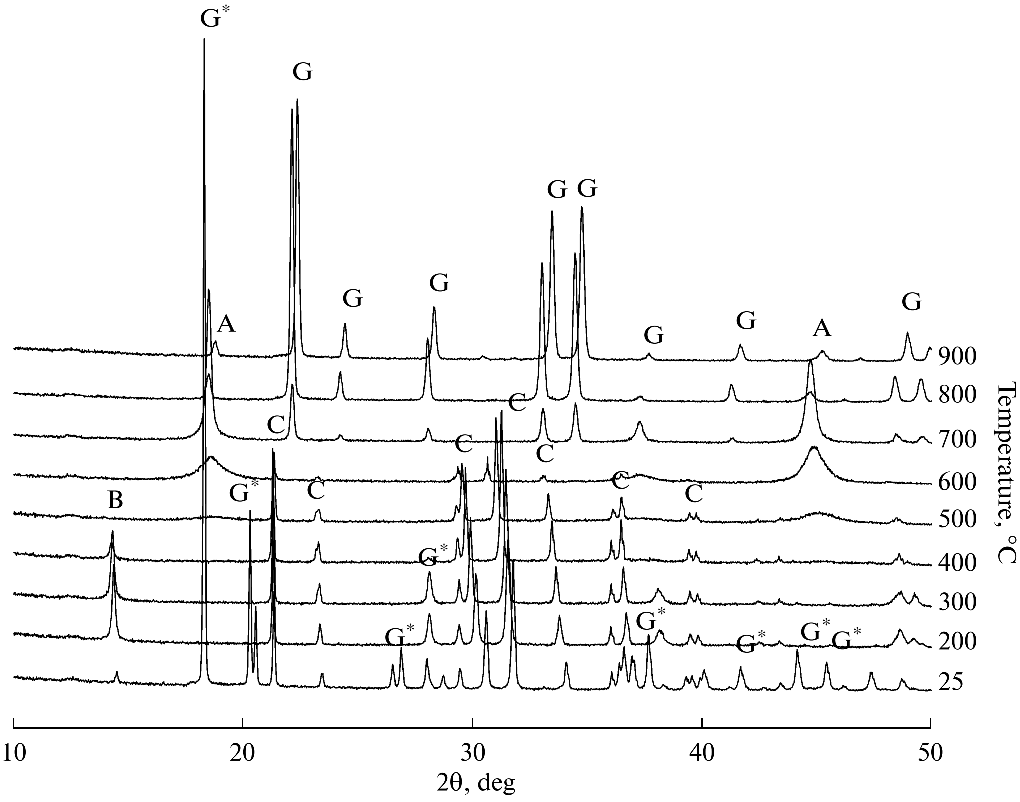

Fig. 2. In situ XRD patterns of a mixture of lithium carbonate and unactivated aluminum hydroxide. A = α-$LiAlO_2$, G = γ-$LiAlO_2$, B = boehmite, G* = $Al(OH)_3$, C = Li_2CO_3.

gibbsite (Fig. 1). Nevertheless, in this case as well aluminum hydroxide dehydration prevails in the initial stages of the reaction. This assumption is supported by in situ XRD results (Fig. 3). In particular, in the case of a mixture containing $Al(OH)_3$ mechanically activated for 5 min, heating to 200°C causes its reflections to disappear, without boehmite formation. The intensity of the reflections from Li_2CO_3 remains essentially unchanged up to 400°C. The reflections from γ-$LiAlO_2$ emerge at a temperature as low as 600°C. Heating to 800°C leads to the formation of almost phase-pure γ-$LiAlO_2$.

Thus, when a mixture containing lithium carbonate and unactivated or mechanically activated aluminum hydroxide is heated to 400°C or lower temperatures, the predominant process is the decomposition of the aluminum hydroxide.

Preliminary milling of $Al(OH)_3$ considerably increases the percentage of γ-$LiAlO_2$ in the reaction products in comparison with unactivated aluminum hydroxide under comparable heat-treatment conditions. This conclusion is supported by the phase composition of the products obtained under identical heat-treatment conditions after the milling of $Al(OH)_3$ for different lengths of time (Fig. 4). It can be seen that, under identical heat-treatment conditions (800°C, 4 h), preliminary milling of $Al(OH)_3$ for just 1 min allows phase-pure γ-$LiAlO_2$ to be obtained.

Effect of the MA of $Al(OH)_3$ on the morphology, specific surface area, and particle size of the solid phase. The unactivated $Al(OH)_3$ had $S = 0.15$ m^2/g (Fig. 5) and consisted predominantly of spherulite-like intergrowths of prismatic crystals (Fig. 6). Most of the intergrowths were 40 to 120 μm in size (Fig. 7). The MA of the $Al(OH)_3$ increased the S of the powder by two orders of magnitude. Moreover, MA increased the percentage of the X-ray amorphous phase (Fig. 5). The average particle size (D) evaluated from S as

$$D = 6/(\rho S),$$

where ρ is the density of aluminum hydroxide (2.4 g/cm^3) and S is the specific surface area of the powder (cm^2/g), is on the order of 0.15 μm (milling time of 5 min).

Milling for 1 min substantially decreased the percentage of large particles (40–120 μm) and increased the percentage of smaller particles (less than 40 μm in size). Increasing the milling time to 5 min gave rise to aggregation processes, which showed up as a reduction in the percentage of small particles (less than 6 μm in size) and an increase in the percentage of particles greater than 40 μm in size. Finally, milling for 10 min had little effect on the particle size composition of the solid phase.

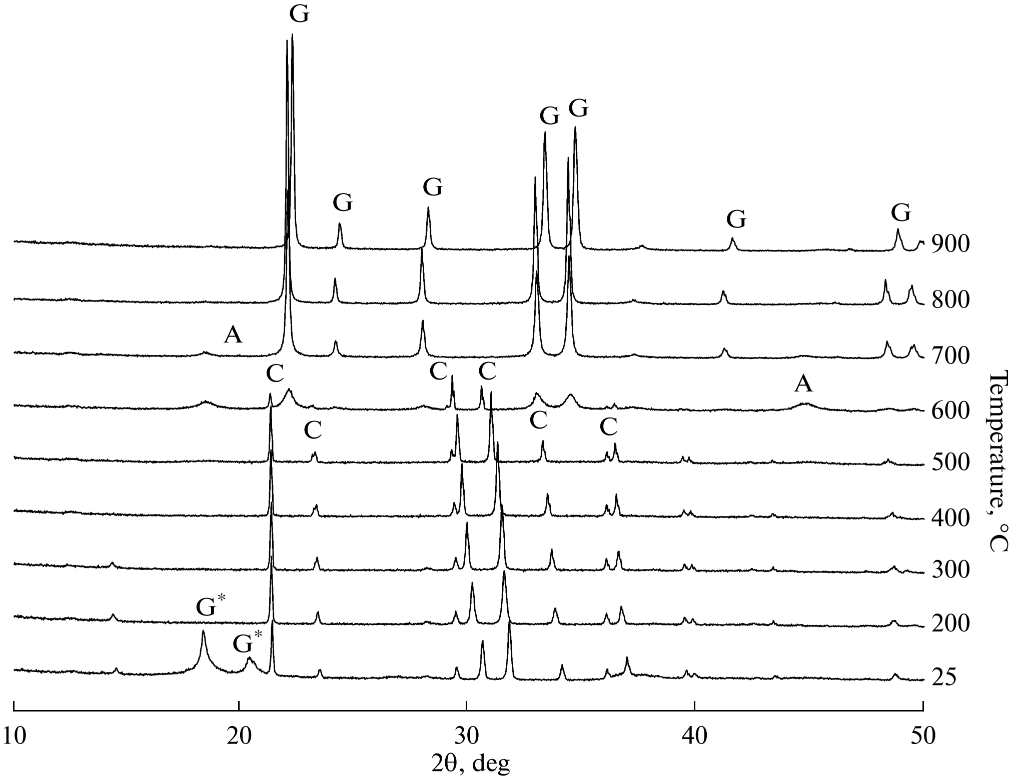

Fig. 3. In situ XRD patterns of a mixture of aluminum hydroxide mechanically activated for 5 min and lithium carbonate. A = α-$LiAlO_2$, G = γ-$LiAlO_2$, B = boehmite, G* = $Al(OH)_3$, C = Li_2CO_3.

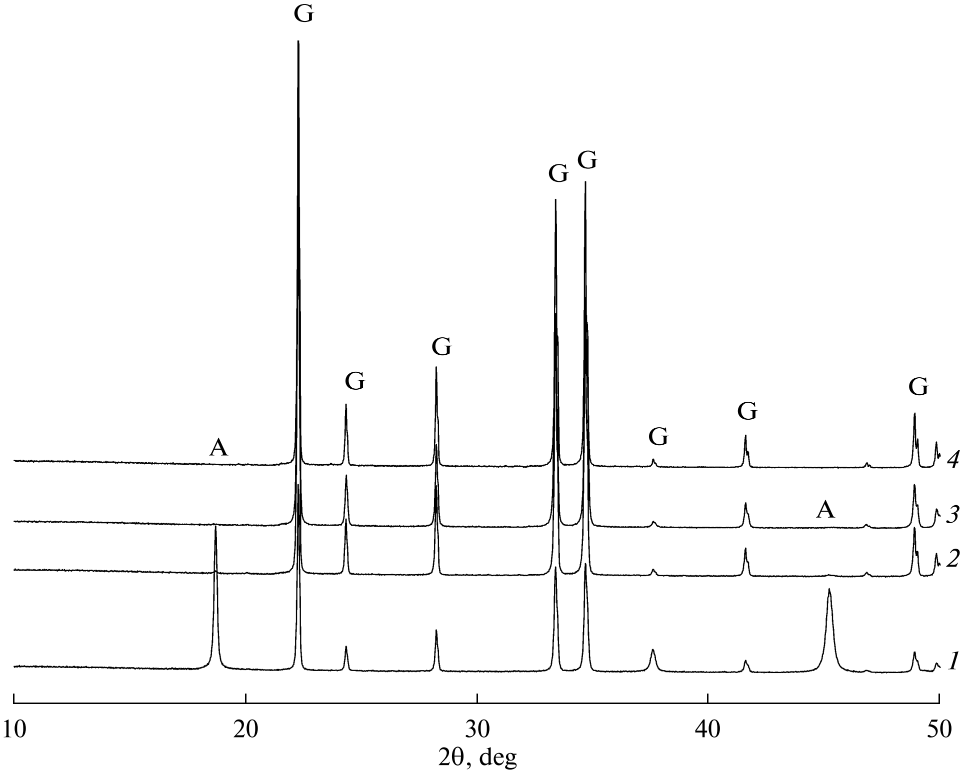

Fig. 4. XRD patterns taken after heat treatment (800°C, 4 h) of a mixture of $Al(OH)_3$ mechanically activated for (*2*) 1, (*3*) 5, and (*4*) 10 min and Li_2CO_3; (*1*) without MA. A = α-$LiAlO_2$, G = γ-$LiAlO_2$.

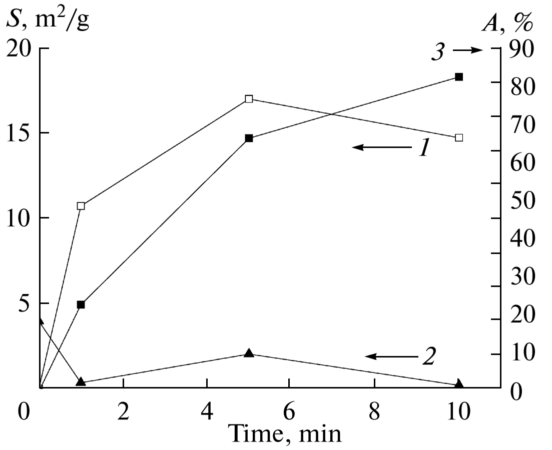

Fig. 5. (*1*) Specific surface of aluminum hydroxide, (*2*) specific surface of lithium aluminate, and (*3*) amorphous phase content of mechanically activated aluminum hydroxide as functions of milling time (the percentage of the X-ray amorphous phase was evaluated from the integrated intensity of the reflection at $d/n = 4.82$ Å).

Thus, the milling of gibbsite produces aggregates of submicron-sized particles, with the aggregate size ranging widely: from a few to hundreds of microns. It is worth pointing out that a considerable increase in the specific surface area of aluminum hydroxide upon activation in planetary mills was reported by Zolotovskii [14] and Menzheres et al. [15]. Isupov et al. [16] observed aggregation of submicron-sized particles.

Effect of MA on the particle size and morphology of the products of the reaction between aluminum hydroxide and lithium carbonate. The reaction between crystalline $Al(OH)_3$ and Li_2CO_3 under the experimental conditions of this study (800°C, 4 h) leads to an increase in the specific surface area of the solid phase by a factor of ~30 (Fig. 5). The reaction product, a mixture of α- and γ-$LiAlO_2$, is similar in morphology and particle size to the parent gibbsite (Figs. 6, 7).

Milling for 1 min increases the *S* of the aluminum hydroxide and sharply reduces the *S* of the reaction product: phase-pure γ-$LiAlO_2$. The subsequent variation in the specific surface area of the γ-$LiAlO_2$ is sim-

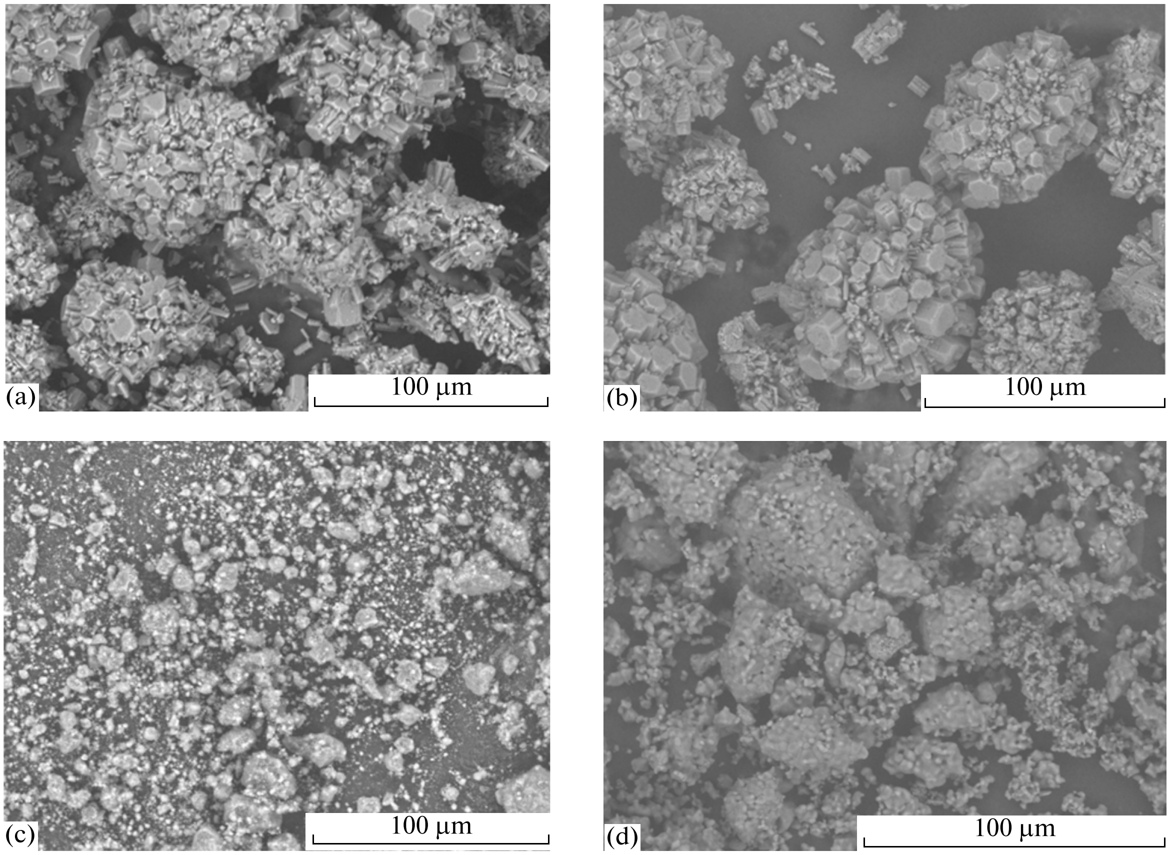

Fig. 6. Electron microscopic micrographs of the (a) unactivated aluminum hydroxide, (b) the product of its reaction with lithium carbonate, (c) aluminum hydroxide mechanically activated for 10 min, and (d) the product of the reaction of the mechanically activated aluminum hydroxide with lithium carbonate.

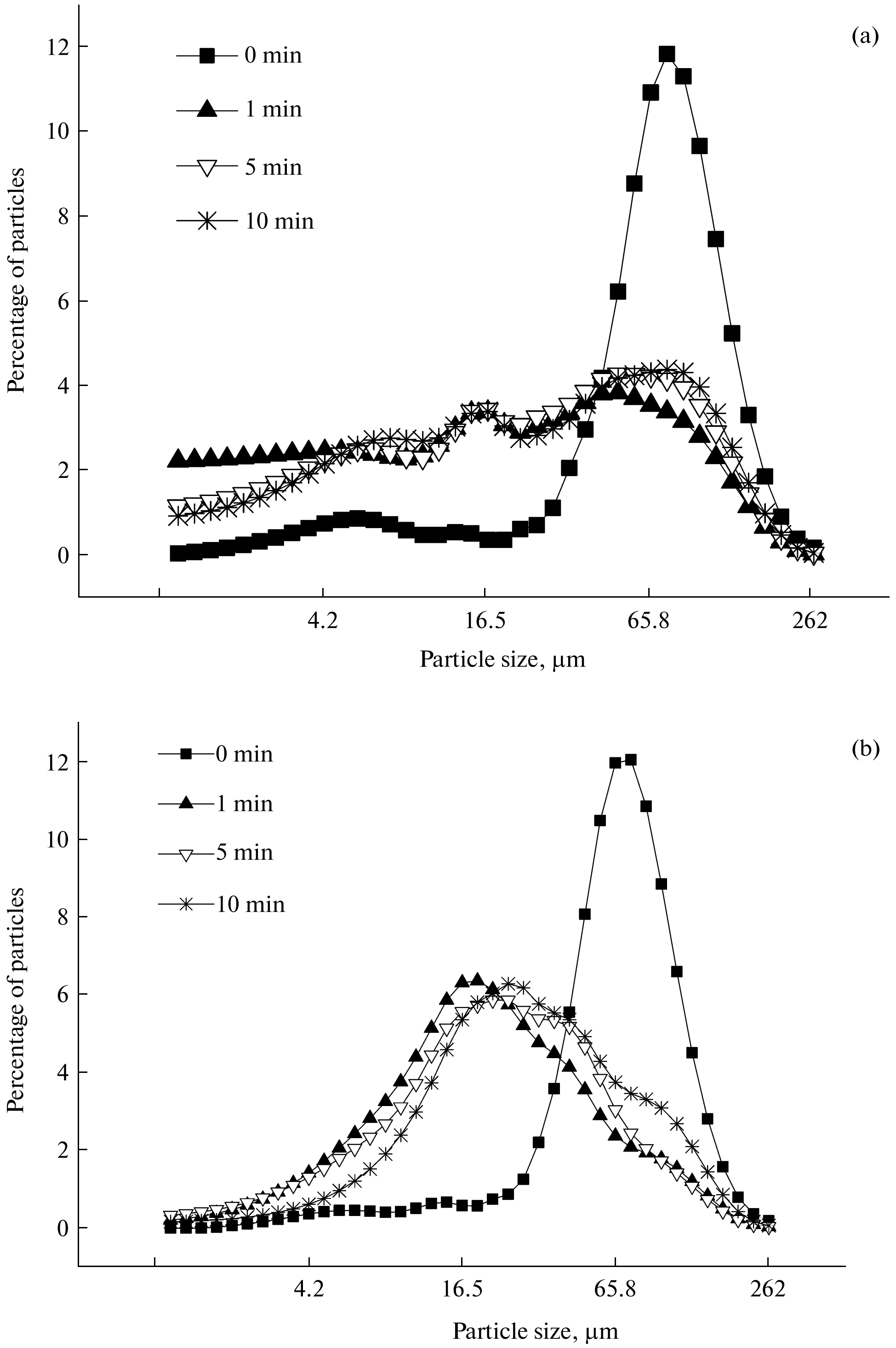

Fig. 7. Particle size distributions of the (a) unactivated and mechanically activated aluminum hydroxide and (b) lithium aluminate synthesized from the aluminum hydroxide.

ilar to the variation in the specific surface area of the mechanically activated Al(OH)$_3$ used in the synthesis of the lithium aluminate. The average particle size of the γ-LiAlO$_2$ (D) evaluated from the S data ranges from 1 μm after milling for 5 min to 6–7 μm after milling for 10 min. The particles form aggregates which range widely in size, from a few to hundreds of microns, as determined from laser light scattering and electron microscopy data.

Comparison of the particle sizes of the mechanically activated aluminum hydroxide and the products of its reaction with lithium carbonate (Fig. 7) demonstrates that the peak in the particle size distributions of the aluminates is shifted to smaller particle sizes in comparison with the parent hydroxide.

DISCUSSION

The present results demonstrate that the initial stages of the reaction between crystalline $Al(OH)_3$ and Li_2CO_3 are dominated by aluminum hydroxide dehydration, which follows a scheme described in sufficient detail in Ref. [17]. According to that scheme, in the first step of the dehydration process some of the aluminum hydroxide decomposes to form boehmite, AlOOH, which was detected by in situ XRD. Next, the residual aluminum hydroxide decomposes to form χ-Al_2O_3. Heating to higher temperatures (above 450°C) leads to boehmite dehydration and γ-Al_2O_3 formation. The oxide phases in question are difficult to detect by in situ XRD because the strongest reflections from these phases coincide with reflections from lithium carbonate and the forming α-$LiAlO_2$. Reactions of these aluminum oxides with lithium carbonate lead to predominant formation of the α-phase of lithium aluminate in the initial stage of the process.

Preliminary milling of $Al(OH)_3$ leads to amorphization of the material, and the amorphous phase content increases with increasing milling time (Fig. 5). The thermal decomposition of the X-ray amorphous phase in a wide temperature range, from 250 to 770°C, leads to the formation of X-ray amorphous π-aluminum oxide, which contains aluminum in four-, five-, and sixfold coordination [14].

CONCLUSIONS

The present results lead us to assume that the difference in phase composition between aluminum oxides resulting from the thermal decomposition of unactivated and mechanically activated $Al(OH)_3$ is one of the major causes why MA influences the phase composition of the products of the reaction between $Al(OH)_3$ and Li_2CO_3.

Despite the rather large difference in specific surface area between the parent aluminum hydroxide and the forming lithium aluminate, their particle size distributions differ rather little. This suggests that the lithium aluminate has the same aggregate size as the parent aluminum hydroxide.

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