

UDC 546.623.34 + 66.040.2 + 549.669.712.7

Investigation of the Effect of Mixture Composition and Humidity on the Specific Surface Area and Phase Composition of Lithium γ -Monoaluminate Formed During the Mechanochemical Synthesis from Lithium Carbonate and Aluminium Hydroxide*

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Abstract

Lithium γ -monoaluminate was obtained as a result of mechanochemical activation of the mixture of lithium carbonate and aluminium hydroxide in AGO-2 planetary activator, followed by the thermal treatment. The effect of mixture composition and humidity on the phase composition and specific surface of lithium γ -monoaluminate was studied. It was shown that in the variation of the composition and humidity of the mixture the specific surface area of the final product decreases significantly (from 13 to 0.2 m²/g).

Key words: mechanical activation, aluminium hydroxide, lithium carbonate, lithium γ -monoaluminate

INTRODUCTION

Lithium γ -monoaluminate with a high specific surface is used in nuclear power engineering to manufacture tritium [1], is a part of matrix electrolyte of the fuel element with carbonate molten electrolyte [2], it is used as the material of the separator in thermal lithium batteries and as an additive modifying the conductivity of lithium-polymer electrolytes [3].

Traditional ceramic [4, 5] and sol-gel [6, 7] methods of obtaining highly-dispersed lithium γ -monoaluminate have a number of substantial disadvantages. In particular, the ceramic method is involved with high (900–1000 °C) temperatures of aluminate synthesis, at which sinters with a low specific surface (less than

1 m²/g) are formed. To obtain fine γ -monoaluminate with a specific surface more than 10 m²/g, it is necessary to grind the cakes for a long time (several ten hours) in ball mills; the final material gets contaminated during grinding. The sol-gel procedure allows obtaining pure lithium γ -monoaluminate with a quite high specific surface (5–10 m²/g). However, expensive reagents are necessary for the synthesis of the final product (lithium and aluminium alkoxides), the method itself is complicated in implementation, and a large amount of liquid organic wastes is formed during the synthesis. All these disadvantages stimulated the development of new methods to synthesize this material on the basis of other approaches: combustion [8–11], mechanochemistry [12] and some other methods [13–15].

Among the methods under development for the synthesis of lithium γ -monoaluminate, the mechanochemical method attracts attention due

* Materials of the IV Int. Meeting “Fundamentals of Mechanochemical Technologies”, June 25–28, 2013, Novosibirsk, Russia.

to its simplicity, ecological safety, the possibility to use available and relatively cheap reagents. The method is based on the mechanical activation of a mixture of crystal aluminium trihydroxide (gibbsite) with lithium carbonate in the planetary centrifugal mill AGO-2 and subsequent thermal treatment of activation products in the air at a temperature of 800–850 °C for several hours [16]. As a result of the process, highly-dispersed lithium γ -monoaluminate with the specific surface more than 10 m²/g is formed. The effect of the activator type, activation modes and thermal treatment on the composition of products and on the specific surface was studied [12, 16, 17]. The possibility to use the activators of not only the laboratory type (AGO-2) but also more productive devices of the planetary type (APF, AGO-3) was demonstrated. However, the effect of characteristics of initial reagents, in particular mixture composition and its humidity, on the phase composition and specific surface of lithium γ -monoaluminate was not studied in the listed publications. The present work was carried out for the purpose of filling in this gap. The data obtained may be interesting for the development of the technology of the mechanochemical synthesis of highly-dispersed lithium γ -monoaluminate.

EXPERIMENTAL

Crystalline aluminium hydroxide (gibbsite) of ch. reagent grade (GOST 11-841-76) with the specific surface of 0.2 m²/g and lithium carbonate of ch. reagent grade (TU 6-09-3728-83) with the specific surface of 0.7 m²/g were used in the work. To study the effect of the mixture composition, gibbsite and lithium carbonate were dried in the air at 105 °C. The effect of humidity of the mixture was studied by adding the necessary amount of water under mixing into the reagent mixture after preliminary drying.

The mechanical activation of the mixture containing aluminium hydroxide and lithium carbonate at a ratio necessary for obtaining lithium monoaluminate was carried out in the planetary centrifugal mill AGO-2 in the air in steel cylinders 130 mL in volume, with the acceleration of 40g for 10 min. Steel balls 5 mm in di-

ameter were used for activation; the ratio of substance mass to the total ball mass was 1 : 20. The thermal treatment of the mechanically activated mixture was carried out in the air in a laboratory muffle furnace PVK-1,4-8 at the heating rate of 10 °C/min and exposure at the temperature of 850 °C for 4 h.

The resulting substances were studied by means of TG, XPA, the specific surface was measured. The thermogravimetric analysis was carried out using the derivatograph of Paulik-Paulik-Erdey system in the air within temperature range 20–700 °C and corundum crucibles. The heating rate was 10 °C/min. The X-ray phase analysis was carried out with a Bruker D8 Advance diffractometer (Germany) involving CuK α radiation in the air within the range $2\theta = 10\text{--}50^\circ$ at a rate of 2°/min. The crystallite size was calculated using the Topas 4.2 software both taking into account microstresses and without taking into account microstresses. The specific surface was estimated by means of chromatography on the basis of argon desorption using a standard sample from the Institute of Catalysis of the SB RAS (Novosibirsk) according to the procedure described in [18].

RESULTS AND DISCUSSION

Effect of mixture composition on the specific surface of γ -LiAlO₂

As a result of thermal treatment of the mechanically activated mixture with the stoichiometric composition, powdered product is

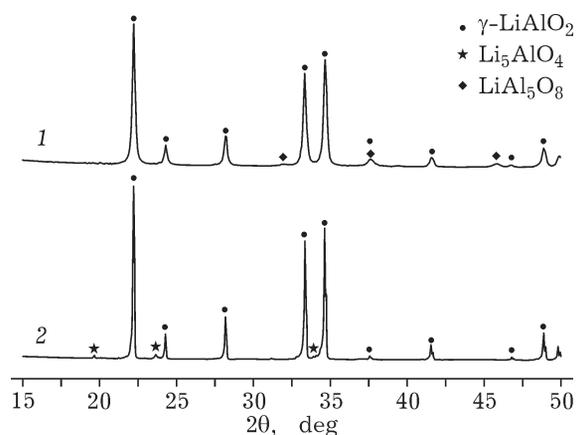


Fig. 1. X-ray diffraction patterns of γ -LiAlO₂ synthesized from mixtures with different Li/Al atomic ratios: 0.9 (1), 1.1 (2).

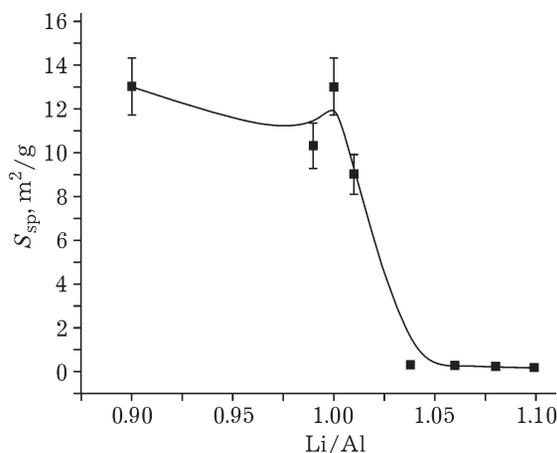


Fig. 2. Dependence of the specific surface of lithium γ -monoaluminate, synthesized by annealing of mechanically activated mixture, on the Li/Al atomic ratio in the mixture. Time of mixture activation: 10 min (AGO-2, 40g); annealing temperature 850 °C, annealing time 4 h.

formed, X-ray diffraction patterns of which are identical with that of lithium γ -aluminate. With a decrease in Li/Al atomic ratio in the mixture from 1 to 0.9, along with the reflections of γ -LiAlO₂ weak reflections of LiAl₅O₈ appear in the diffraction patterns. An increase in Li/Al atomic ratio from 1 to 1.1 is accompanied by the appearance of weak reflections of β -Li₅AlO₄ along with the reflections of γ -LiAlO₂ (Fig. 1). A decrease in the atomic ratio of Li/Al below the stoichiometric value has no substantial effect on the changes of the specific surface of lithium γ -monoaluminate (Fig. 2). Quite contrary, for the atomic ratio Li/Al higher than the stoichiometric value, the specific surface of the product decreases substantially, which is an evidence of agglomeration of the target product. The formation of cakes with a high mechanical strength points to sintering of lithium γ -monoaluminate.

The size of crystallites of lithium γ -monoaluminate synthesized from mixtures with different atomic ratios Li/Al was determined (Table 1). It was discovered that the account of microstrain for the calculation of crystallite size has almost no effect on the result. An increase in Li/Al atomic ratio in the mixture is accompanied by an increase in the size of lithium γ -monoaluminate crystallites, which is another evidence of the crystallization of the solid phase with an increase in lithium carbonate content in it.

TABLE 1

Microstructural characteristics of γ -LiAlO₂ samples synthesized from the mixture with different Li/Al atomic ratio

Li/Al	Size of γ -LiAlO ₂ crystallites (<i>D</i>), nm	
	Without taking microstrain into account	With microstrain taken into account
0.9	69±5	68±5
1.0	92±7	91±7
1.1	>150	>150

To explain sintering at the increased content of lithium carbonate, it is necessary to consider a thermogram of mechanically activated mixture with the stoichiometric component ratio (Fig. 3). One can see that at a temperature of 650–700 °C the curve of mass change for the mechanically activated mixture reaches a plateau corresponding to almost complete consumption of lithium carbonate. The specific surface of the solid phase formed at this temperature is 40–50 m²/g (see Fig. 3). At higher temperature (800–850 °C) corresponding to the crystallization of lithium gamma-monoaluminate, the specific surface of the solid phase decreases to 13–18 m²/g. It may be assumed that lithium carbonate present in the mixture in excess over the stoichiometry forms a melt when temperature exceeds its melting point (732 °C). The latter not only reacts with lithium γ -monoaluminate with the formation of β -Li₅AlO₄ but also promotes sintering of fine lithium γ -monoaluminate.

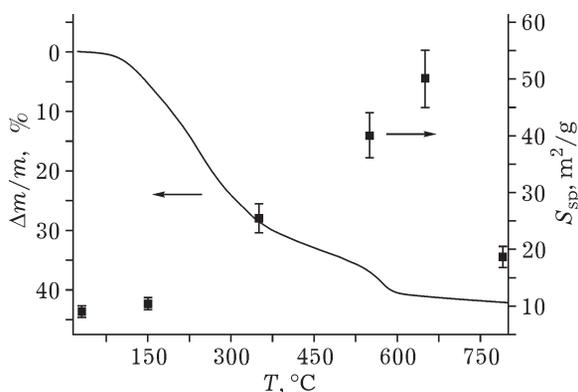


Fig. 3. Dependence of specific surface and mass loss by the mixture of Al(OH)₃ and Li₂CO₃ activated for 10 min, on the temperature of thermal treatment.

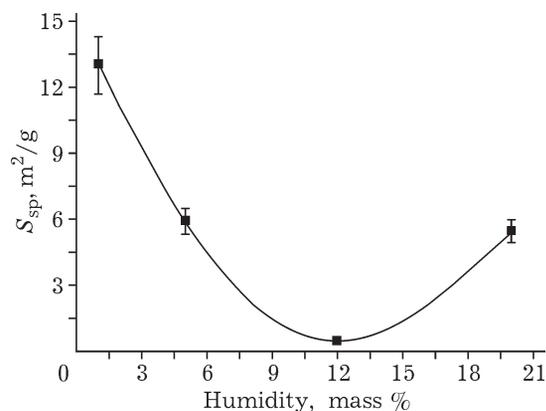


Fig. 4. Dependence of the specific surface of lithium γ -monoaluminate on the humidity of initial mixture.

Effect of the mixture humidity on the phase composition and specific surface of γ -LiAlO₂

Changes in the mixture humidity within the range 0–20 mass % do not affect the phase composition of the final product of mechanochemical synthesis; lithium γ -monoaluminate is formed in all cases. However, the specific surface of the lithium γ -monoaluminate formed depends substantially on the humidity of the initial mixture (Fig. 4). To reveal the reasons of this effect, we studied the phase composition of products formed at the stage of mechanical activation of the mixture at the low humidity of the mixture, only broadened reflections of lithium carbonate are observed in the X-ray diffraction patterns of activation products (Fig. 5). With an increase in the mixture humidity, reflections of crystal aluminium hydroxide ap-

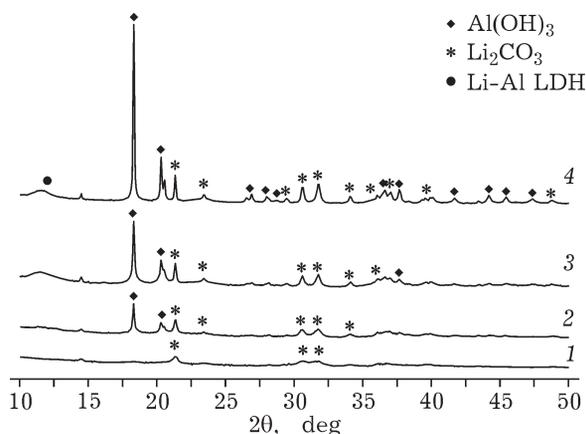


Fig. 5. XPA data on the products of mechanical activation of a mixture of $Al(OH)_3$ with Li_2CO_3 with different humidity (mass %): 0 (1), 5 (2), 12 (3), 20 (4).

pear in the diffraction patterns of activation products. The intensity of these reflections increases with humidity, and the crystallinity degree of lithium carbonate increases. In addition, with an increase in mixture humidity, broadened reflections are recorded within the region $2\theta = 11$ – 12° . These reflections relate to the layered double hydroxide of Li and Al. So, the increased humidity of the mixture leads to an increase in the crystallinity degree of aluminium hydroxide and lithium carbonate, and to the appearance of the product of their interaction – that is layered double aluminium-lithium hydroxide. It may be assumed that the change of the phase composition and crystallinity degree of activation products causes the change of the specific surface of lithium γ -monoaluminate formed during the subsequent thermal treatment. However, the specific mechanism of this influence is not clear yet and requires further investigation.

CONCLUSION

The investigation conducted showed that the composition and humidity of the mixture composed of lithium carbonate and aluminium hydroxide have a strong if not critical effect on the specific surface of lithium γ -monoaluminate formed during mechanical activation of the mixture in a planetary activator AGO-2 and subsequent thermal treatment of activation products in the air at $850^\circ C$. Depending on the mixture composition and humidity, the specific surface of lithium γ -monoaluminate may vary from 13 to $0.2 m^2/g$. To obtain highly-dispersed lithium γ -monoaluminate with specific surface of more than $10 m^2/g$, the atomic ratio of Li/Al in the initial mixture should vary within the range 0.98–1.02, and its humidity should not exceed 2 %.

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