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Synthesis of Superfine Carbonate Form of Li–Al Double Hydroxide from Sodium Hydroaluminocarbonate

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Abstract

The interaction of $NaAl(OH)_2CO_3 \cdot 0.2H_2O$ (SHAC) with the aqueous solution of 5 M LiCl is investigated. It is shown that a complete transformation of SHAC and the formation of the carbonate form of the double lithium-aluminium hydroxide $[LiAl_2(OH)_6]_2CO_3 \cdot nH_2O$ occur at a temperature of 90 °C and interaction time 6 h. The morphological and structural characteristics of the synthesized compound were investigated by means of XPA, high-resolution electron microscopy, and measurements of the specific surface. A scheme of the formation of double Li–Al hydroxide is proposed on the basis of the data of the physicochemical and chemical analyses of the products of SHAC interaction with the aqueous solutions of LiCl.

INTRODUCTION

The carbonate form of lithium-aluminium layered double hydroxides (Li–Al LDH) is a compound of the composition $[LiAl_2(OH)_6]_2CO_3 \cdot nH_2O$. The structure of this compound consists of the positively charged metal hydroxide layers of the composition $[LiAl_2(OH)_6]^+$ alternating with the layers containing carbonate ions and water molecules. The $[LiAl_2(OH)_6]^+$ layers are formed by the tight two-layer packing of hydroxide ions; the octahedral cavities of this packing are completely filled with lithium and aluminium cations [1]. This compound is of interest as a precursor to obtain lithium monoaluminates [2] for use in the production of the matrix electrolyte of carbonate molten fuel elements [3], composite electrolytes with lithium conductivity [4] and breeders for obtaining tritium [5]. In addition, the carbonate form can be used in pharmacology as a prolonged form of lithium carbonate [6]. Lithium monoaluminates used in fuel elements and especially in obtaining composite electrolytes should have rather large specific surface (20 m^2/g and more) and sub micrometer particle size. In order to obtain such a material, one can use the carbonate form of Li–Al LDH with high specific surface and submicron particle size. These characteristics of the carbonate sort, along with definite texture and morphology, create prerequisites for the possibility of obtaining superfine lithium gamma-monoaluminate composed of the submicron-sized particles.

Several methods of obtaining superfine carbonate form of the Li–Al double hydroxide have been described in literature. Thus, in [7] the carbonate form was obtained by bubbling carbon dioxide through an alkaline aluminate solution containing lithium. The aluminate solution was prepared by dissolving metal aluminium in lithium hydroxide solution, or by adding the aqueous solution of lithium hydroxide to sodium aluminate solution. Carbon dioxide bubbling leads to the formation of the double hydroxide with the ratio Al : Li = 2.3–2.5 which differs from the ideal ratio equal to 2. In the opinion of the authors of [7], the deviation of the composition from the ideal one is connected with the formation of some amount of X-ray amorphous aluminium hydroxide precipitating together with the double hydroxide. The authors do not report any data on the specific surface of the synthesized compounds but point to the fact that the size of the resulting crystals is 4 to 8 mm. A disadvantage of this method is that the carbonate form with the variable aluminium to lithium ratio depending on process conditions is formed.

N. P. Tomilov with co-workers [8] synthesized the carbonate form of the double Al–Li hydroxide by means of long-term (tens of hours) interaction of carbon dioxide with the Al–Li double hydroxide obtained by dissolving metal aluminium in a concentrated aqueous solution of lithium hydroxide. The formed product is close in composition to $[LiAl_2(OH)_6]_2CO_3 \cdot 3H_2O$. No data on the specific surface and particle size for the product are reported in that work. A disadvantage of this method is long time necessary for the target product to be obtained.

C. J. Serna *et al.* [9, 10] synthesized the carbonate form of DHAL with submicron particle size by adding the solution of aluminium tri(*sec*-butoxide) in benzene to the aqueous solution of Li_2CO_3, followed by ageing of the formed double hydroxide at different temperatures. As a result, the samples of the carbonate form with rather high specific surface varying from 12 to 95 m^2/g depending on ageing temperature were obtained. A disadvantage of the method is the necessity to use expensive organic aluminium-containing reagents and the formation of a large amount of organic wastes. To obtain the carbonate form of Li–Al LDH, intercalation of lithium chloride into aluminium trihydroxides (gibbsite) can be used; this process results in the formation of the chloride form of double Li–Al hydroxide. Then the anion exchange of chloride ions for the carbonate ions is carried out [11]. The proposed method is based on the use of rather cheap and available reagents (gibbsite, LiCl and Na_2CO_3) and does not require complicated apparatus arrangement. However, the formed carbonate form of the double hydroxide is composed of rather large aggregates of particles sized from 1 to 10 μm and has relatively small specific surface (2–3 m^2/g).

So, these examples provide evidence that the reported methods of obtaining monophase superfine carbonate form only in a few cases [9, 10] allow one to obtain the substance with submicron-sized particles. Because of this, it was necessary to develop a new method of synthesis of the superfine monophase carbonate sort of Li–Al LDH with submicron particle size devoid of the above-listed disadvantages and based on the use of available and rather cheap reagents.

In this connection, it was interesting to investigate the synthesis of the carbonate form by the interaction of $NaAl(OH)_2CO_3$ (SHAC) with aqueous solutions of lithium salts. The attractiveness of this method is due to the availability of sodium hydroaluminocarbonate (SHAC) which can easily be synthesized under laboratory conditions from relatively simple and chap reactants (sodium aluminate, aluminium hydroxide, soda). It should also be noted that this compound is manufactured on an industrial scale because SHAC is the major phase of the precipitates at the second stage of carbonisation of aluminate solutions when manufacturing alumina from aluminium ores by means of agglomeration [12].

It is stressed in [13] that the interaction of SHAC with the aqueous solutions of lithium salts results in the formation of the carbonate form of double lithium-aluminium hydroxide with the overall composition $Li_2O \cdot 2.3Al_2O_3 \cdot 1.1CO_2 \cdot 11H_2O$. Unfortunately, no data on process conditions, morphology of the formed product, its particle size (dispersed state) and physicochemical properties are reported in that work. Judging from the chemical composition reported in that paper, the aluminium to lithium ratio differs from 2, which means that the substance is not monophase. Later in [14] it was shown that the interaction of SHAC with the diluted aqueous solution of lithium chloride (0.01 M) in the presence of a 2 M NaCl solution at pH 12 leads to the dissolution of SHAC in NaOH solution with the formation of soda aluminate solution. The interaction of this solution with lithium chloride results in the formation of the carbonate form of the double hydroxide of aluminium and lithium. Unfortunately, no data on the specific surface of the formed product is reported. The formed carbonate form of the double hydroxide contains a substantial amount of poorly crystallized aluminium hydroxide as an admixture, which causes the formation of the carbonate form with aluminium to lithium ratio differing substantially from the ideal composition.

So, the data available from literature provide evidence of the principal possibility of SHAC application to synthesize the carbonate form of Li–Al LDH; however, the conditions of obtaining monophase samples of this compound with high specific surface and submicron particle size have not been revealed yet. The main goal of the present work is to remedy the existing situation.

EXPERIMENTAL

To obtain the monophase samples of the carbonate form of Li–Al double hydroxide, we used the interaction of SHAC with concentrated aqueous solutions of lithium chloride. The initial SHAC was synthesized by carbonisation of the aqueous solution of sodium aluminate (caustic module 40, aluminium content of solution 0.05–0.06 g/l calculated for Al_2O_3) at room temperature, followed by ageing at a temperature of 70–75 °C. During carbonisation, the solution pH decreases from 14 to 12. The analysis of the synthesized compound gives the following values for the major components (mass %): Na 15.5, Al 18.1, C 8.2, H 1.63. The composition of the synthesized compound, calculated from the data of chemical analysis, is close to the composition $NaAl(OH)_2CO_3 \cdot 0.2H_2O$. The X-ray phase analysis of SHAC provides evidence of its monophase character (Fig. 1, *a*). All the basic reflections of the synthesized compound coincide with the literature data (ASTM 12-499). The interaction of the concentrated (5 M) aqueous solution of LiCl with SHAC was investigated within the temperature range 70 to 90 °C. The liquid to solid ratio (l : s) was 20 : 1. A weighed portion of SHAC was introduced into the preliminarily heated concentrated 5 M aqueous solution of LiCl and kept at the given temperature for a definite interval of time under mixing. The accuracy of temperature maintenance was ±0.5 °C. After the experiment, the solid phase was filtered and washed with distilled water on the filter to remove lithium salts. In some cases, the aluminium content of filtrates was determined. The solid samples were dried in the air till the air-dry state, then at a temperature of 50–60 °C for 2 h. In the dried samples, the content of Li, Na, Al, C, Cl was analysed. Lithium and sodium were determined by means of flame photometry, aluminium by means of atomic absorption. Carbon was determined with a C : N : H analyser, chlorine was measured using mercurimetry. In some cases the carbon content was determined using the manometric method by dissolving the solid

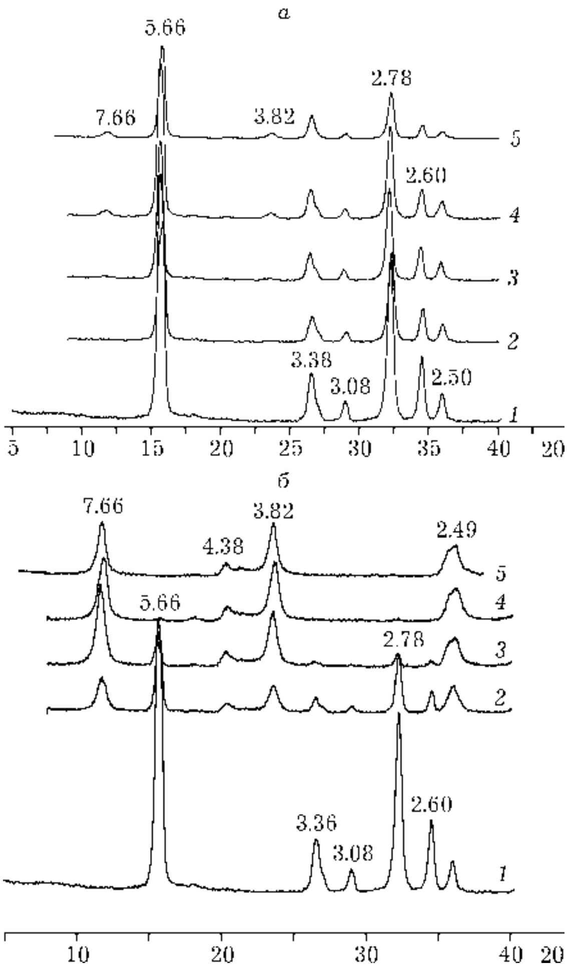

Fig. 1. X-ray diffraction patterns of the initial SHAC (*1*) and the products of its interaction with the aqueous solution of 5 M LiCl (*2*, *3*) at a temperature of 70 (*a*) and 90 °C (*b*). Time, h: 1 (*2*), 2 (*3*), 4 (*4*), and 6 (*5*).

phase in hydrochloric acid. To investigate the phase composition, X-ray phase analysis was used. The examination was carried out with a DRON-4 diffractometer (CuK_α radiation). The accuracy of 2θ angle measurement was ±0.02°. We used α-quartz and silicon as the external standard. The electron microscopic images of the samples were taken with a JEM-2000FXII microscope. Measurements of the specific surface were carried out using BET procedure with argon adsorption-desorption.

RESULTS AND DISCUSSION

The treatment of SHAC with the aqueous solution of 5 M LiCl at 70 °C for 2 h does not cause substantial changes in the appearance of X-ray diffraction patterns; only after the interaction for 4 h we observe the appearance of new multiple reflections of weak intensity with d/n = 7.6, 3.74 Å, which are characteristic of the carbonate form of Li–Al double hydroxides (see Fig. 1, *a*). Temperature rise to 90 °C allows one to accelerate the interaction process substantially: as early as after 1 h, we observe rather intensive basal (7.66, 3.82, 2.49 Å) and non-basal (4.38 Å) reflections of the carbonate form of Li–Al LDH (see Fig. 1, *b*). In addition to the reflections of SHAC and Li–Al LDH, a weak reflection of bayerite with d/n = 4.72 Å appears in the diffraction patterns after the interaction for 1–4 h. The interaction for 6 h leads to almost complete disappearance of SHAC reflections and to the appearance of the reflections related only to the carbonate form of Li–Al LDH; the reflections of bayerite are absent. The XPA data are confirmed by the chemical analysis of solid products: lithium appears in the solid phase, and its relative content with respect to aluminium increases with an increase in the time of interaction (Table 1). Chemical analysis of the solid products formed after the interaction for 6 h (%): Al 23.6, Li 2.9, C 2.51, Al/Li 2.1, C/Li 0.50 – provides evidence of the appearance of the carbonate form of double Li–Al hydroxide with the composition close to the ideal one: $[LiAl_2(OH)_6]_2CO_3 \cdot nH_2O$. Sodium and chlorine content of this compound is at the limit of detection by the methods used for analysis. A small excess of the experimentally detected Li/Al ratio (0.53) over the theoretically expected value (0.5) can be explained by the error of lithium determination by means of flame photometry (5–6 %). The X-ray diffraction patterns of the synthesized carbonate form of Li–Al LDH do not contain intensive reflections with d/n equal to 2.92 and 2.82 Å which are characteristic of lithium carbonate and appear in the angle region 2θ = 30–32°.

TABLE 1

Chemical composition of the products of interaction of $NaAl(OH)_2CO_3 \cdot 0.2H_2O$ with the aqueous solution of 5 M LiCl at 90 °C

Time, h	Concentration, mass %		Li/Al atomic ratio
	Al	Li	
0	14.5	0	0
1	22.2	1.4	0.25
2	24.1	2.5	0.40
4	23.3	2.8	0.46
6	21.1	2.9	0.53

A comparison of the X-ray diffraction patterns of the carbonate form of Li–Al synthesized from SHAC with the diffraction patterns of the carbonate forms obtained using other methods is presented in Fig. 2. The patterns of the carbonate form synthesized from SHAC is almost identical with the patterns of the form obtained from the aluminate solution. The po-

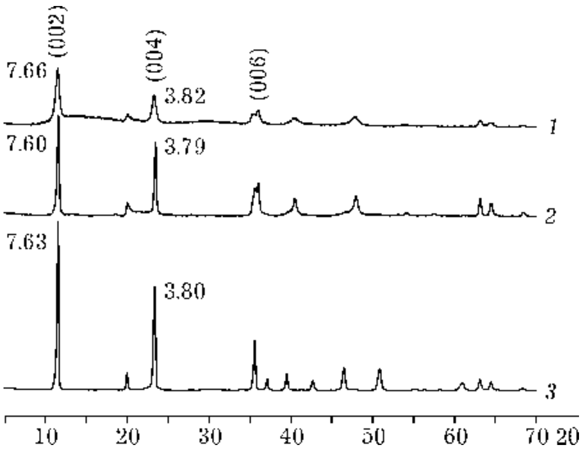

Fig. 2. X-ray diffraction patterns of the carbonate form of Li–Al LDH: *1* – synthesized by the interaction of SHAC with the aqueous solution of LiCl; *2* – by carbonisation of the Al–Li double hydroxide obtained from the aqueous solution of aluminate; *3* – by the anion-exchange substitution of chloride ions for carbonate ions in the chloride form of Li–Al LDH obtained by LiCl intercalation into gibbsite.

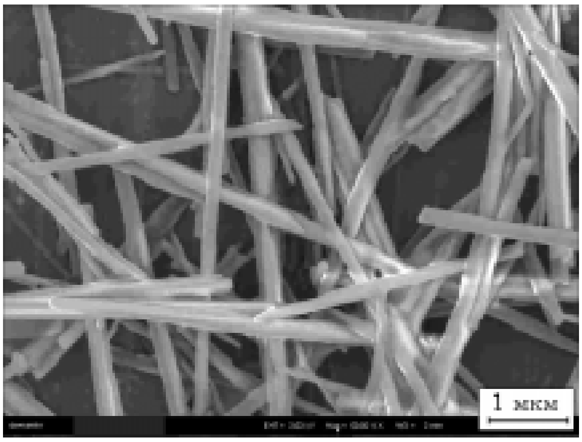

Fig. 3. Electron microscope image of SHAC.

sitions of the basal reflections for all the shown carbonate forms almost coincide, which is an evidence of approximately the same thickness (7.6 Å) of the layer packages of these compounds. Such a coincidence in the diffraction patterns and the same thickness of layer packages allow us to assume that the structure of the carbonate form synthesized from SHAC can be described on the basis of a model proposed previously for the carbonate form obtained using other methods [13, 14].

To investigate the morphological changes that occur during the synthesis of Li–Al LDH, we carried out the electron microscopic investigations of SHAC and the products of its interaction with LiCl. The initial SHAC is composed of ribbon-shaped crystals the length of which varies from 2 to 10 μm, the width from 0.1 to 0.3 μm (Fig. 3). The specific surface of the compound is 14 m^2/g. Such a morphology of the compound is connected with the features of its structure: it is composed of linear chains formed by aluminium cations situated at a distance of 2.8 Å from each other. The aluminium cations are connected with each other through the hydroxide and carbonate ions (Fig. 4). Sodium cations link these chains with each other. The interaction of SHAC with LiCl causes the appearance of hexagonal lamellar crystals located on the surface of the ribbon-like SHAC crystals. With an increase in the time of interaction, the number of the hexagonal crystals increases. The product $[LiAl_2(OH)_6]_2CO_3 \cdot nH_2O$ synthesized from SHAC is composed completely of the junctions of clearly expressed thin hexagonal plates with submicron dimensions and the specific surface of 28–30 m^2/g (Fig. 5). The thickness D of the plates is substantially smaller than their size in the plane. The average D value can be estimated using equation $D = 2/(\rho S)$ where ρ is the density of the substance, S is specific surface. This equation can be used to estimate the mean thickness of monodisperse lamellar particles with the thickness substantially smaller than their cross size. Substituting the density of the carbonate form (2 g/cm^3) and specific surface (28 m^2/g) into this equation, we obtain D value equal to 0.04 μm.

As we have already mentioned, for high pH of solution (>12) the interaction of SHAC with lithium salts occurs due to the formation of the soda aluminate solution from which the crystallization of the carbonate form of double hydroxide occurs. However, in our experiments the initial pH of LiCl solution is close to neutral,

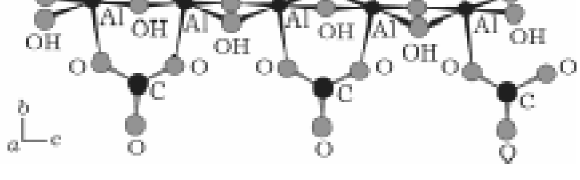

Fig. 4. Fragment of SHAC structure. The nearest aluminium cations are connected with each other through two hydroxide groups and one carbonate group, the distance between the two nearest aluminium cations in the chain is 2.8 Å.

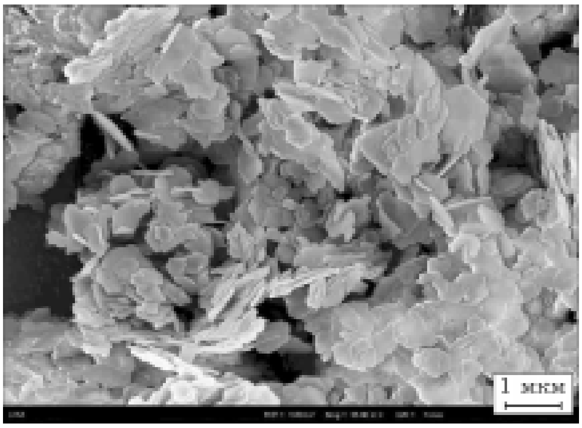

Fig. 5. Electron microscope image of the carbonate form of Li–Al double hydroxide synthesized by the interaction of SHAC with the aqueous solution of 5 M LiCl.

it does not exceed 8–9 during the experiment. Analysis of the solutions formed after the interaction of SHAC with LiCl provides evidence that the concentration of aluminium in them does not exceed 1 μg/ml (3.7 10^{-5} mol/l). Since the amount of aluminium in solution is small, we may assume that the carbonate form of Li–Al LDH is formed mainly not as a result of SHAC dissolution with the formation of the soda aluminate solution but according to another mechanism. From our point of view, in this case the interaction of aqueous solutions of lithium salts with solid products formed during the hydrolytic decomposition of SHAC occurs. It was concluded in [15] on the basis of the analysis of XPA data and the results obtained by means of scanning electron microscopy that at $T \le 100$ °C the interaction of dowsonite with water results in the formation of bayerite according to equation

$$NaAl(OH)_2CO_3 + H_2O \Leftrightarrow Al(OH)_3 + HCO_3^- + Na^+ \quad (1)$$

On the basis of these data, we may assume that in our case, too, the interaction of SHAC with LiCl at the early stages involves the hydrolytic decomposition of the initial compound with the formation of bayerite in the solid phase. This may be confirmed by the fact that at the early stages of the reaction we almost in all the cases observe the appearance of bayerite reflections of small intensity ($d/n = 4.72$ Å) which disappear completely when the interaction process is over. Bayerite may interact with the aqueous solutions of lithium salts according to reaction [16]:

$$2nAl(OH)_3 + Li_nX + aq = [LiAl_2(OH)_6]_nX \cdot mH_2O \quad (2)$$

The degree of bayerite interaction with the solutions of lithium salts is strongly dependent on their concentrations. For instance, with LiCl concentration below 1.0 mol/l (interaction temperature: 90 °C, time: 6 h) the degree of transformation is not high and does not exceed several per cent. An increase in LiCl concentration to 4–5 mol/l leads to almost complete transformation of bayerite into the double hydroxide. A strong dependence of the reaction rate on the concentration of lithium salts is the reason why the degree of $Al(OH)_3$ interaction with the saturated aqueous solution of poorly soluble Li_2CO_3 is small under the experimental conditions and does not exceed 1–2 %.

Since a concentrated (5 M) solution of LiCl was used for the synthesis of the carbonate form in the amounts much exceeding the stoichiometrically necessary value, the liquid phase formed during the experiment consisted mainly of the concentrated aqueous solution of LiCl containing a small amount of the products of reaction (NaCl and Li_2CO_3). Due to the substantially higher concentration of LiCl in solution in comparison with Li_2CO_3, it may be assumed that mainly the interaction of bayerite with LiCl resulting in the formation of the chloride form of the double hydroxide of aluminium and lithium occurs at the first stage of the process. Bicarbonate ions formed in solution during the hydrolysis of SHAC are unstable and decompose at elevated temperatures according to reaction

$$2HCO_3^- \Rightarrow H_2O + CO_3^{2-} + CO_2^{\Uparrow} \quad (3)$$

At the second stage, the anion exchange of chloride ions in the formed chloride form for carbonate ions occurs according to equation

$$2[LiAl_2(OH)_6]Cl \cdot mH_2O + CO_3^{2-} + aq = [LiAl_2(OH)_6]_2CO_3 \cdot nH_2O + 2Cl^- \quad (4)$$

The possibility of the anion exchange substitution of chloride ions for carbonate ions was demonstrated by us when investigating the interaction of the chloride form of Li–Al double hydroxide with the aqueous solutions of alkaline metal carbonates [9, 14]. We found that the anion exchange proceeds almost completely at relatively low concentrations of carbonate ions (0.1 M) even at 60 °C and interaction time 4 h.

So, taking into account all the abovementioned considerations, the overall reaction of the formation of the target product can be described by equation

$$4NaAl(OH)_2CO_3 \cdot 0.2H_2O + 2LiCl + (n - 0.8)H_2O = [LiAl_2(OH)_6]_2CO_3 \cdot nH_2O + 2NaCl + 2Na_2CO_3 + CO_2^{\Uparrow} \quad (5)$$

An excess of LiCl in the system can interact with sodium carbonate with the formation of poorly soluble lithium carbonate:

$$2LiCl + Na_2CO_3 = Li_2CO_3^{\Downarrow} + 2NaCl \quad (6)$$

The amount of precipitated solid lithium carbonate depends on the excess of LiCl over the stoichiometry, on its concentration, process temperature, initial l : s ratio. Since solid samples are washed with water after the reaction, along with the removal of the formed sodium salts and unreacted LiCl, almost complete removal of Li_2CO_3 occurs. The solubility of the latter in water at the room temperature is rather high (about 1.3 g/100 g of water).

CONCLUSION

Thus, the monophase carbonate form of the double hydroxide of aluminium and lithium with high specific surface and submicron particle size can be obtained by the interaction of sodium hydroaluminocarbonate with the concentrated aqueous solution of LiCl.

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