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Synthesis, Structure, Properties, and Application of Aluminium Hydroxide Intercalation Compounds

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Abstract

The possibility to use intercalation processes to modify physicochemical properties of gibbsite, a crystal modification of aluminium hydroxide, is considered. The structure and the mechanism of formation of aluminium hydroxide intercalation compounds with lithium salts $[LiAl_2(OH)_6]_nX \cdot pH_2O$ are investigated. The possibility to apply these compounds and intercalation processes to develop low-waste methods of the preparation of sorbents, fine aluminium hydroxide and corundum, lithium aluminates and aluminosilicates, nanophase and low-dimensional systems is demonstrated.

INTRODUCTION

Intercalation processes are reversible topotaxial chemical reactions involving the insertion of guest molecules into the host matrix of a solid which remains unbroken during the synthesis [1]. These processes are interesting for researchers in connection with the possibilities to synthesize, under soft conditions, novel compounds with a set of valuable physicochemical properties. So, the investigation of possibilities to use intercalation processes to modify physicochemical properties of matrices with layered structures is surely of interest for practice. A typical example of a layered matrix, aluminium hydroxide $\{Al(OH)_3\}$, exists as three crystal modifications, gibbsite, bayerite, and nordstrandite. The most important among these modifications is gibbsite which is produced on industrial scale and used for the preparation of metal aluminium and its compounds. All these compounds are widely used to produce catalysts, supports, ceramics, materials for electronics and medicine. The use of intercalation processes to modify the properties of aluminium hydroxide has been described in literature poorly.

THE SYNTHESIS AND STRUCTURE OF THE INTERCALATION COMPOUNDS OF ALUMINIUM HYDROXIDE

The structure of all the crystal modifications of aluminium hydroxide including gibbsite is formed by two-dimensional layers linked to each other by hydrogen bonds [2–4]. In turn, the layers are composed of two nets of tightly packed hydroxide ions. Aluminium ions occupy two thirds of octahedral voids in this packing, therefore one third of voids is empty (Fig. 1). The radius of octahedral voids is close to 0.6 Å which is sufficient to hold small cations (lithium, magnesium, transition metals). Interlayer space also contains rather large voids with the radius of 0.7–0.8 Å. They are connected with each other by channels [5, 6]. Such a structure allows aluminium hydroxide modifications to exhibit the properties of a host matrix in the intercalation of metal salts. For example, the formation of intercalation compounds in the interaction of well soluble lithium salts with gibbsite follows the equation

$$Li_nX + 2nAl(OH)_3 + pH_2O = [LiAl_2(OH)_6]_nX \cdot pH_2O \text{ (LADH-X)} \quad (1)$$

where $X = Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-$.

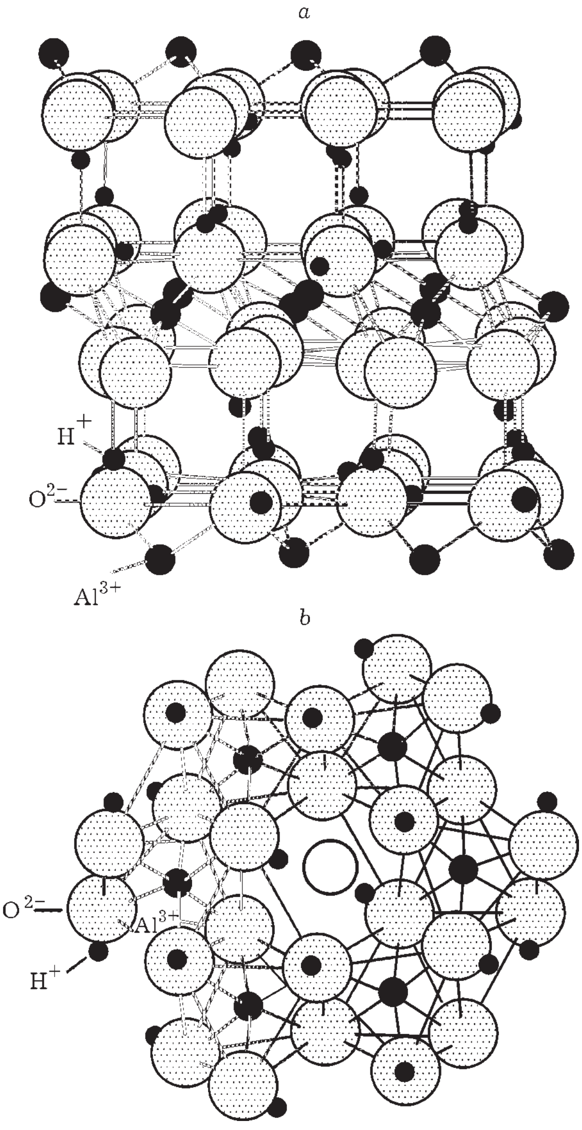

Fig. 1. Gibbsite structure: *a* – projection to the (100) plane; *b* – projection to the (001) plane. The position of octahedral voids is shown schematically.

Individual character of the synthesized compounds was proved by means of chemical, X-ray, and crystal optical analyses [6–11]. The synthesis of these compounds can be performed using nonaqueous solvents [6, 12, 13], as well as low-temperature melts of lithium salts. The investigation of intercalation kinetics dependence on temperature, lithium salt concentrations, solvent type, dispersity, and defect content of the initial gibbsite was reported in [6, 14]. It was discovered that rather high concentration of lithium salt (more than 20 %) and temperature above 90 °C are required to achieve high degree (more than 90 %) of gibbsite transformation into intercalation compounds within reasonable time (several hours).

The structure of the compounds $[LiAl_2(OH)_6]X$ ($X = Cl^-$, Br^-, NO_3^-) and $[LiAl_2(OH)_6]Cl \cdot H_2O$ was studied using powder X-ray and neutron diffraction analyses (Rietweld method), as well as NMR on aluminium, lithium and hydrogen nuclei. It was demonstrated that, similarly to the initial hydroxide, the structure of the formed intercalation compounds involved hydroxide layers. However, unlike gibbsite, octahedral voids in these layers are occupied by lithium cations. To conserve zero charge, anions intercalate into the solid matrix. Together with water molecules they occupy positions in the interlayer space (Fig. 2). The intercalation of lithium cations into the voids leads to some changes in the positions of oxygen atoms of hydroxide ions that form these voids; they are also reoriented. The intercalation of anions and water molecules into the interlayer space leads to a sharp increase of the distance between the layers depending on the anion. More complicated inorganic and organic anions can also act as intercalating ions. It is convenient to use a two-stage process to synthesize intercalates comprising these anions [6, 18]. At the first stage, the intercalate containing a single-charged anion, most often chloride, is synthesized according to the reaction (1). At the second stage, the synthesized intercalate is treated with aqueous solutions of salts containing the necessary anion Y^{n-}; the process follows the equation

$$n[LiAl_2(OH)_6]Cl \cdot pH_2O + Na_nX + aq = [LiAl_2(OH)_6]_nX \cdot pH_2O + nNaCl \qquad (2)$$

Organic anions in the intercalates are oriented in a manner providing direct contact between oxygen atoms of the acid groups (carboxylic, *etc.*) and the surface of $[LiAl_2(OH)_6]^+$ layer. The change of the charge and geometry

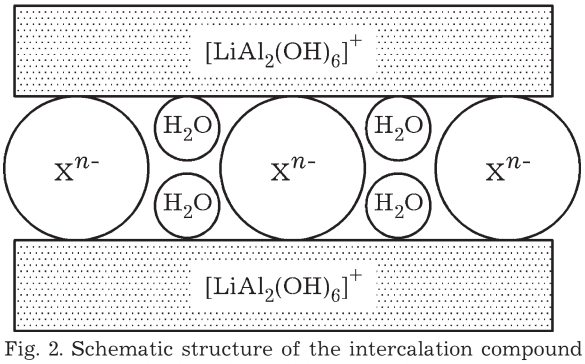

Fig. 2. Schematic structure of the intercalation compound of aluminium hydroxide with lithium salts.

of the anion allows to vary in a wide range the distance not only between the layers but also between the nearest anions in the layer starting from molecular contact till the distance of about 5–6 Å.

INTERCALATION OF LITHIUM SALTS INTO GIBBSITE

The *in situ* investigation of the interaction of gibbsite single crystals with lithium salts by means of polarization microscopy is the evidence of anisotropy of the intercalation process. The boundary between the initial gibbsite and intercalation compound moves in the direction parallel to basal planes of the initial compound [6, 8, 9, 14, 19]. The interaction of gibbsite single crystals with lithium salts leads to the formation of block intercalate crystals that conserve the morphology of the initial gibbsite single crystals. The investigation of orientation relations between the initial gibbsite and reaction products containing lithium chloride, bromide, iodide and sulphate showed that the interaction of gibbsite with lithium salts is characterized by the following orientation relations:

$[010]_g \parallel [010]_{\text{LADH-X}}$ $(a_g \approx a_{\text{LADH-X}})$;

$[100]_g \parallel [100]_{\text{LADH-X}}$ $(b_g \approx b_{\text{LADH-X}})$

This means that the (001) planes of LADH-X are parallel to the (001) planes of gibbsite.

These data, as well as the comparison of the structure of initial gibbsite with reaction products allow us to propose a scheme to describe the intercalation of lithium salts into gibbsite [5, 6]. According to this scheme, at the first stage lithium cations, anions, and water molecules get into the interlayer space. Then lithium cations move from the interlayer space inside the octahedral voids of the aluminium hydroxide layer. The intercalation of anions and water molecules causes the increase of the distance between aluminium hydroxide packings by 2.8 Å and more. As a result, substantial elastic strain appears at the boundary gibbsite – intercalation compound. The relaxation of this strain leads both to the dispersion of initial gibbsite and to plastic deformation of the initial gibbsite before the reaction front. As it was shown in [14], plastic deformation is connected with the formation of partial dislocations. Their movement leads to the formation of packing defects in gibbsite prior to the reaction front.

Not only gibbsite but also another crystal modification, bayerite, is able to act as intercalation matrix [6].

POSSIBLE APPLICATION AREAS FOR INTERCALATION PROCESSES AND INTERCALATION COMPOUNDS

Selective recovery of lithium from highly mineralized solutions

The size of octahedral voids in the hydroxide layer is sufficient to place small cations (lithium, magnesium, transition metals). To place larger cations (sodium, calcium, barium, strontium) inside the layer means to deform it substantially. So, the salts of these metals do not intercalate into crystal aluminium hydroxide. This not only explains a well known fact that amorphous aluminium hydroxides are highly selective to lithium salts [20, 21] but also allows to propose new ways to synthesize selective sorbents of lithium on the basis of structurally disordered aluminium hydroxide forms obtained from technical gibbsite. One of the possible synthesis routes is connected with the preliminary mechanical activation of gibbsite in high energy planetary activators. The activation of gibbsite leads not only to disordering of hydrogen bonds between hydroxide layers but also to their partial dehydroxylation with the formation of X-ray amorphous phase [6, 21–27]. The rate of lithium salt intercalation into such a defect-containing structure increases sharply [6, 21, 28, 29]. This allows to use X-ray amorphous hydroxide both directly to recover lithium from liquors and to synthesize selective adsorbents of lithium [30–34].

Preparation of fine aluminium hydroxide and corundum

Intercalation of lithium salts into aluminium hydroxide is reversible [6, 35–37]. The treatment of intercalation compounds with water leads to the release of lithium salts into the liquid phase and to the appearance of aluminium trihydroxide in the solid phase according to the equation

$$[LiAl_2(OH)_6]_nX \cdot pH_2O + aq \rightarrow 2nAl(OH)_3 + Li_nX \quad (3)$$

Under definite conditions (temperature, time, liquid to solid ratio) it is possible to achieve practically complete removal of lithium salts from the intercalation compound. Aluminium hydroxide formed after deintercalation possesses a different, layered morphology (Fig. 3), higher specific surface and dispersity than the initial gibbsite (Table 1). After the cycle is over, a sharp decrease (by two orders of magnitude) of sodium content in the solid phase is observed. X-ray diffraction patterns of the formed fine hydroxide suggest that packing defects are formed [35]. Diluted aqueous solutions of lithium salts (with concentration of 5–10 g/l) formed after deintercalation can be concentrated and used repeatedly for the synthesis of intercalation compound. This provides the possibility to use intercalation-deintercalation reaction in a waste-free procedure of the preparation of fine aluminium hydroxide with a low alkali content [38]. In order to concentrate diluted aqueous solutions, one can use both the traditional evaporation method and energetically more profitable elecrodialysis. Moreover, electrodialysis can be combined with deintercalation which allows to speed up the recovery of lithium salts and to decrease energy consumption [39, 40].

Fine hydroxide can be used directly as a flame retardant material. Besides, a low sodium and lithium content allows to use it for the preparation of low-alkaline fine corundum. Thermal treatment of fine hydroxide at temperatures of 1453–1473 K for 2–3 h allows to obtain practically pure, well crystallized corundum with specific surface of about 10 m^2/g without using any fluorinating agents (HF, NH_4F). The obtained corundum is composed of

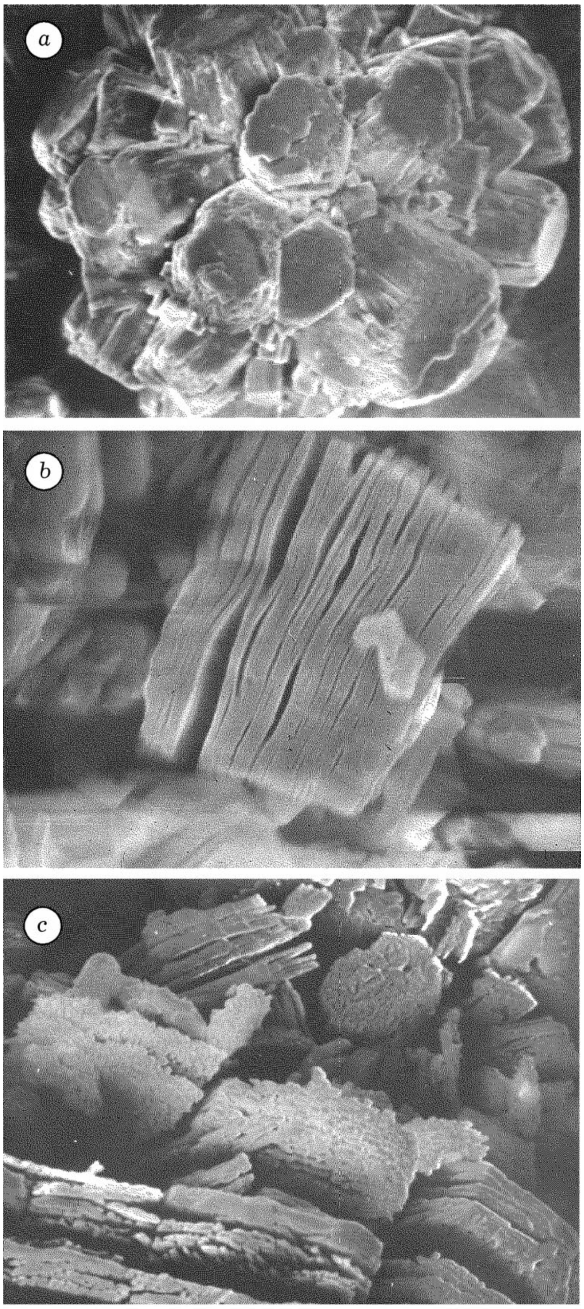

Fig. 3. Electron micrographs of: *a* – initial gibbsite (magnification 500), *b* – fine hydroxide (magnification 5000), *c* – corundum (magnification 5000).

TABLE 1

Comparison of some characteristics of the initial gibbsite and the product formed after the intercalation-deintercalation of lithium chloride

Characteristic	Initial gibbsite	Fine gibbsite
Morphology	Spherolyte-type concretions of prism-like crystals	Aggregates of thin plates
Specific surface, m^2/g	0.1–0.2	6–8
Mean particle size, μm	50–60	8–10 (mean diameter), 0.1–0.15 (thickness)
Sodium content, %	0.2–0.3	< 0.002–0.003
Lithium content, %	0	0.01–0.015

primary particles with the size of about 0.1 μm that form porous plates of the same thickness. The diameter of these plates varies within a wide range from 1 to 20–30 μm. In turn, the plates form packs. So, the morphology of the formed corundum is close to the morphology of the initial fine aluminium hydroxide (see Fig. 3). At rather small mechanical action, these aggregates are decomposed to form particles of the size of 1–3 μm. This corundum is important as an initial material to prepare supports for catalysts. The studies conducted at the Laboratory of Profound Oxidation Catalysts (Boreskov Institute of Catalysis, SB RAS) demonstrated a principal possibility to manufacture the microblocks with wall thickness of 0.25 mm made of fine corundum. Preliminary experiments performed at the same laboratory have demonstrated that the catalysts prepared using these microblocks are promising for ethylene oxidation into ethylene oxide, selective catalytic oxidation (SCO) of methane into synthesis gas, purification of tail gases from nitrous acid production by means of selective reduction of nitrogen oxides.

It should be noted that the traditional methods of the synthesis of fine corundum from technical gibbsite with a low alkali content involve much higher annealing temperatures (1400–1450 °C) and long (20 h) grinding of the resulting agglomerates in ball mills.

Preparation of lithium aluminates and aluminosilicates

Various lithium aluminates ($LiAl_5O_8$, α-$LiAlO_2$, β-$LiAlO_2$, γ-$LiAlO_2$, α-Li_5AlO_4, β-Li_5AlO_4) and aluminosilicates, both pure and doped, are used as catalysts, materials for the production of tritium and solid electrolytes with lithium conductivity. Ceramic methods of the synthesis of these compounds are connected with long high-temperature treatment of aluminium oxide mixtures with lithium salts (mostly lithium carbonate). In order to obtain single-phase compounds, a repeated intermediate attrition of the formed agglomerates is required. Sol-gel methods allow to decrease time and temperature of thermal treatment and to improve the purity of products. However, this is connected with the use of large amounts of solvents and leads to the formation of large amounts of liquid wastes that are to be utilized.

The fact that $[LiAl_2(OH)_6]^+$ layers in the intercalation compounds of aluminium hydroxide contain lithium and aluminium cations mixed at the molecular level opens a principal possibility to use these compounds as precursors for the synthesis of lithium aluminates and aluminosilicates. Taking into account the fact that other metals can be present in intercalation compounds as anions ($[Fe(CN)_6]^{n-}$, $[Medta]^{2-}$, CrO_4^{2-}, *etc.*), one can foresee a principal possibility to synthesize lithium aluminates and aluminosilicates doped with these metals. Really, as it was demonstrated in [41–47], the use of intercalation compounds allows to substantially decrease temperature and time of the synthesis of lithium aluminates and aluminosilicates compared to the ceramic method. The amount of solvents used and the wastes formed is decreased several times, compared to the coprecipitation and sol-gel methods.

Synthesis of nanophase and low-dimensional systems

The intercalation compounds of aluminium hydroxide incorporate two-dimensional structural fragments of nanometre thickness that are sharply different in composition and properties. They are: the hydroxide layer of the composition $[LiAl_2(OH)_6]^+$ and interlayer particles (anions and water molecules). This allows to perform chemical reactions involving both separate fragments and the entire structure of the compound. This provides the possibility to use intercalation compounds to synthesize nanophase and low-dimensional systems.

The reactions of interlayer molecules. Several types of chemical transformations involving interlayer molecules were studied. One of these processes is connected with chemical transformations of the anions of organic acids located in the interlayer space. Thus, it was demonstrated that keeping of the intercalate containing the anions of *meta*-aminobenzoic acid in the air leads to the polycondensation of anions and to the formation of polyconjugated system at the conservation of the layered character of the solid matrix [48]. This feature of the intercalation matrix is important for the creation of hybrid organic-inorganic materials combining the properties of both organic and inorganic compounds.

Another example of chemical reactions of organic molecules in the interlayer space can be the oxidation of the anions of polyconjugated organic acids by aqueous potassium permanganate solution [49]. This leads to manganese fixing as the Mn^{2+} cation in the interlayer space of the intercalation compound. Thus obtained solid product allows to prepare, after heating in the air, Li – Al – Mn oxides that can be used as selective sorbents of lithium [50].

Chemical transformations of $[LiAl_2(OH)_6]^+$ layers. A vivid example of a chemical reaction in which mainly the transformation of hydroxide layer occurs is thermal decomposition of intercalation compounds containing thermally stable anions (Cl^-, Br^-, SO_4^{2-}) [51, 52]. As a result, the composite is formed that contains nanometre-sized (5–10 nm) aluminium oxide particles with a thin layer of lithium salts spread over the surface of the oxide. This material possesses much higher conductivity than individual lithium salts do. It can be used in chemical current sources as solid electrolyte with lithium conductivity.

Chemical reactions involving the entire structure of intercalation compounds. Thermal decomposition, in vacuum or in inert atmosphere, of intercalates $[LiAl_2(OH)_6]_nY \cdot qH_2O]$ containing the anions of organic acids leads to the destruction of both the hydroxide layer and the anions; nanocomposites containing carbon clusters are formed along with X-ray amorphous lithium aluminate [53]. The size of the formed carbon clusters varies from several carbon atoms to 50 and more. Both the size and the structure of clusters depend on the type of the organic acid anions. This allows to vary the nature of the formed nanocomposite by varying the composition of intercalation compound and temperature of its decomposition.

Another example is the formation of nanocomposites during thermal decomposition of the intercalation compounds $[LiAl_2(OH)_6]_2[Medta] \cdot 4H_2O$ (M – Co, Cu, Ni) [54–58]. Thermal decomposition of these compounds leads to the formation of nano-sized particles of transition metals with the size of 2 to 100 nm. It is interesting that for the case of nickel the formed round particles exhibit very narrow size distribution with the mean diameter close to 5 nm. Mean distance between the particles determined according to the small angle scattering data is about 20 nm. For the case of cobalt and copper, mean particle size and size scattering are larger. These nanocomposites can be used as catalysts, materials for magnetic liquids, absorbing screens.

CONCLUSION

Thus, crystal modifications of aluminium hydroxide are able to act as an intercalation matrix. Intercalation processes can be used to modify physicochemical properties of intercalation compounds. This allows to obtain new compounds with interesting and practically important properties, and to create new, low-waste technologies of the preparation of the known materials.

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