PREPARATION NANOCRYSTALLS OF ALUMINIUM OXIDE BY DECOMPOSITION OF SUPRAMOLECULAR STRUCTURE: TEREPHTHALIC ACID - ALUMINIUM HYDROXIDE IN A SUPERCRITICAL WATER FLUID

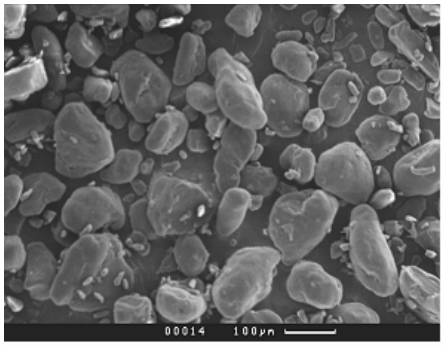
G.P. Panasyuk*, L.A. Azarova, I.L. Voroshilov., Savost'yanov A.P.
N. S. Kurnakov Institute of General and Inorganic Chemistry
Russian Academy of Sciences (IONH RAN)
Leninsky Prospect 31, Moscow, GSP-1, 117907, Russia
Panasyuk@igic.ras.ru Fax +7 (095) 954 1279

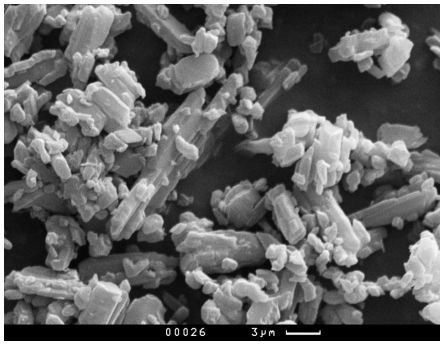
Creation and research of new supramolecular structures is a cardinal problem of advanced area of a modern science - supramolecular chemistry. Among numerous supramolecular structures significant interest is represented by system: terephthalic acid - aluminium hydroxide. Terephthalic acid is one of organic compounds possessing layered structure and strong hydrogen bonds. Presence of loosely connected layers defines their lability and an opportunity of migration with formation large supramolecular particles in wich interlayer space, are capable to be placed molecular clusters or nanocrystals with similar structure.

It is possible to expect, that on the basis of two compounds: terephthalic acid-aluminium hydroxide can be created new supramolecular structures. Such structures represents independent interest, and also can be used for preparation important technically material: nanosize or submicronic crystaline aluminium hydroxide, which after thermal or thermovaporous treatment will pass into aluminium oxide with the same size of particles.

The purpose of the present work was creation supramolecular structures on the base of terephthalic acid - aluminium hydroxide and preparation nanocrystalline aluminium oxide at their decomposition at thermal and thermovaporous treatment.

The selling terephthalic acid manufacture of the company "Acros Organics" and company "Chimreaktiv" and solution of sodium aluminate obtained at dissolution of hydrargillite (mark "MDGA", manufacture of company "Pikalevo") in solution of sodium hydroxide ("pro analysis" purity) was used. The concentration of aluminium in a solution was 0,2 – 2.0 mass %.
Electronic microphotos initial terephthalic acid are submitted in Fig.1.

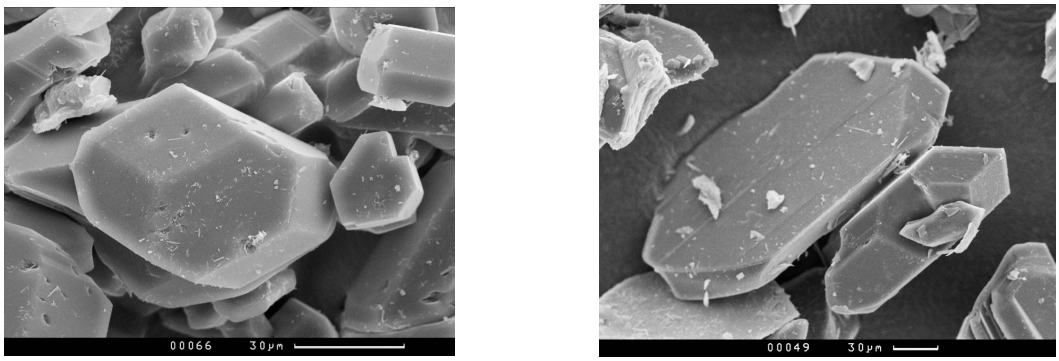




a b

Fig. 1. Terephthalic acid manufacture of company "Acros Organics " (a) and companies "Chimreaktiv" (b)

Electronic microphotos of initial terephthalic acid are represented at Fig.1. As indicated in the picture the used terephthalic acid substantially differ in size of its particles. Particles of the both used samples have irregular form and comprise polycrystals peculiar to layered structures. Monocrystals of terephthalic acid may be synthesized during autoclave treatment (Fig. 2).



a b

Fig 2 Terephthalic acid of manufacture companies "Chimreaktiv" after treatment in an autoclave at 200°C for 4 days (a) and at 300°C within 16 hours (b)

Treatment of terephthlic acid in the solution of sodium aluminate at room temperature during 10 - 30 minutes lead to substantial increasing of flocules size.

In Fig. 3 electronic microphotos of terephthalic acid of company "Chimreaktiv" after treatment by an alkaline solution within 10 minutes are submitted. Distinctly are fixated initial orientation of polycrystalline formations merging further in a uniform large particle.

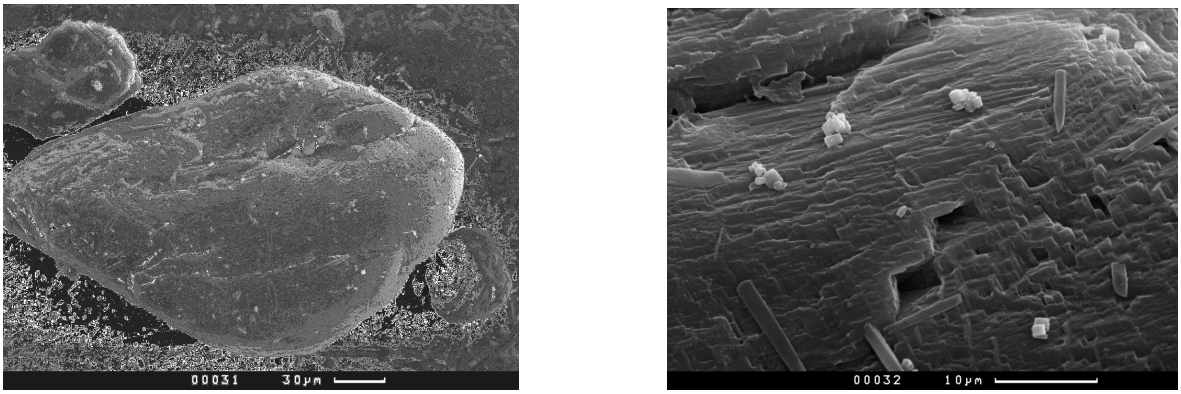
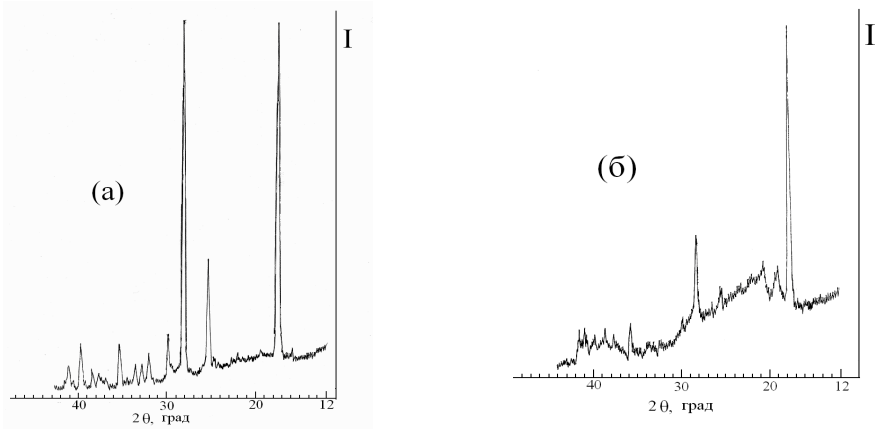


Fig 3. Terephthalic acid of company "Chimreaktiv" after treatment by an alkaline solution within 10 minutes.

Obtained supramolecular structures were investigated by methods: X-ray diffraction (XRD), thermal analysis (DTA, TG), optical and electronic microscopy.

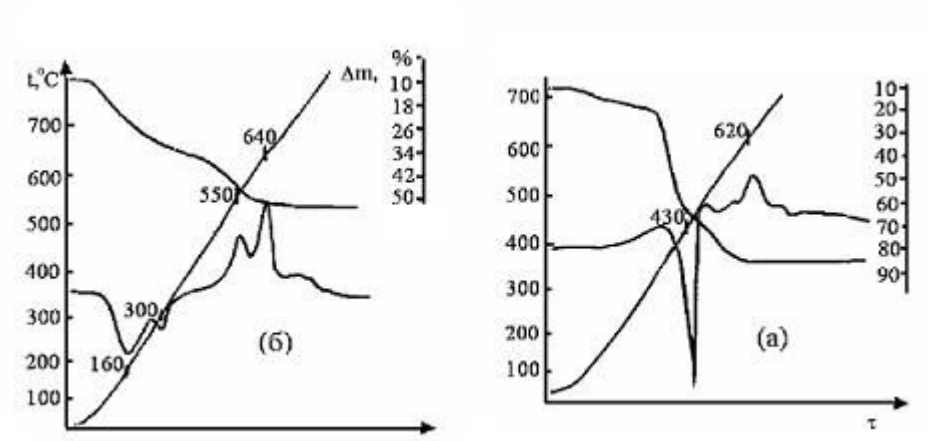


a b

Fig. 4. XRD pattern of the solid phase containing 7.57 mass % A1 (a) and 26.15масс. % (b).

As apparently from figure in both cases X-ray diffraction patterns correspond to terephthalic acid. Crystal phases corresponding to aluminium hydroxide practically do not fixed up to the content 26 %. Increase of concentration of aluminium in a solution lead to disorder structure of terephthalic acid.

Heating curves of these supramolecular structures are submitted in Fig.5.



b a

Fig 5. Heating curves of supramolecular structures obtained at interaction of terephthalic acid ("Chimreaktiv") with a solution of sodium aluminate concentration 0.55 mass % (a) and 1.98 mass % (b)

On a curve (a) the endothermic effect at 430°C with 80 % loss of mass corresponds to disintegration of terephthalic acid, exothermic effect at 620°C is not accompanied by loss of mass and defined by crystallization of aluminium oxide.

On a curve (b) endothermic effects at 160°C and 300°C are responsible for the loss of water from alumina (about 20 mass %), exothermic effect at 640°C is responsible for the aluminium oxide crystallization beginning.

The characteristic of supramolecular structures received at interaction terephthalic acid with a solutions of sodium aluminate of various concentration are submitted in Table.

% Al in solution	XRD
0.24	Terephthalic
0.30	Terephthalic
0.30	Terephthalic acid
0.30	Terephthalic acid
0.43	Terephthalic acid
0.55	Terephthalic acid
0.66	Terephthalic acid
0.78	Terephthalic acid
1.20	Terephthalic acid
1.98	Terephthalic acid + aluminium hydroxide

The maximum content of aluminium included in structure at concentration of a solution of 1,98 % is equal to 26 %. Thus the crystal modification of aluminium hydroxide - bayerite is fixed. At lower concentration on XRD patterns fixed only of terephthalic acid.

At autoclave treatment of the supramolecular structure obtained from terephthalic acid and sodium aluminate with concentration of aluminium of 1,98 % forms boehmite with the size of crystals 300-700 nanometers. Electronic microphotos of the received boehmite are submitted in Fig. 6.
Calcination of these samples on air at 800°C within 2 hours lead to formation of gamma aluminium oxide as spherical formations with length of fibres about 300 nanometers and thickness 50 - 100 nanometers

Calcination at higher temperatures lead to sintering and increase in the size of obtained crystals.

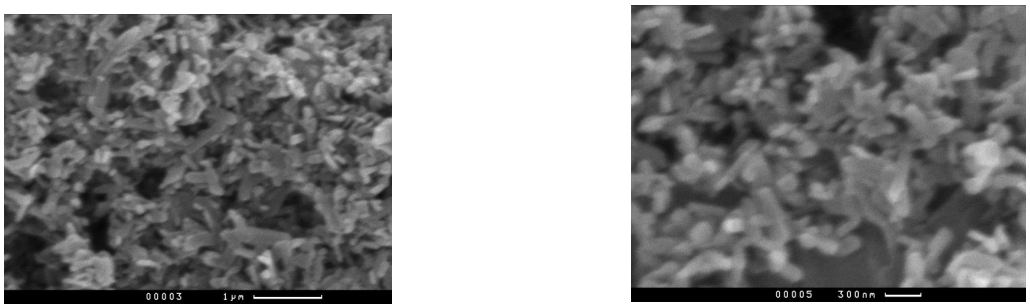


Fig. 6. Electronic microphotos of supramolecular structures obtained at interaction of terephthalic acid with a solution of sodium aluminate with concentration 1.98 mass % after autoclave treatment in water vapour at 420°C during 16 hours.

Conclusions: the method of preparation of supramolecular structures in sistem: terephthalic acid - aluminium hydroxide is developed. The way consists in treatment of terephthalic acid in solutions of aluminates of alkaline metals.
It is shown that at thermovaporous treatment of such structures is formed boehmite with the size of crystals 300 - 500 nanometers.
Calcinated on air at 800°C allows to obtain fiber of aluminium oxides with thickness about 50 - 100 nanometers.