Influence of concentration modifier on the structure and functional properties of aluminum oxyhydroxide modified

L N Shiyan[1], E N Gryaznova[2*], S I Galanov[3] and O I Sidorova[3]

[1]Institute of High Technology Physics, Tomsk Polytechnic University, Tomsk, 634050, Russia
[2]Institute of Water, Tomsk Polytechnic University, Tomsk, 634050, Russia
[3]Faculty of Chemistry, Tomsk State University, Tomsk, 634050, Russia

*E-mail: t_elena@mail2000.ru

Abstract. Studying the properties of nanomaterials is an important task, but nanomaterials with desired properties is a promising direction. The aim of this work is to investigate the influence of the value of the concentration of the modifier (ions Mn^{2+}) on the structural and functional properties of modified aluminum oxyhydroxide. In this paper, using methods such as the X-ray diffraction studies, differential thermal analysis, electron microscopy, chromatography. The paper found that increasing the concentration of the modifier result in significant changes in the morphology, the appearance of metallic aluminum, which is well seen on X-ray data samples. The influence of thermal effects on a modified aluminum oxyhydroxide argon. Set the phase transition temperatures in the synthesized samples. It is shown that with increasing sodeozhaniya manganese in the composition of the synthesized samples decreases the value of specific surface area. Study of the functional properties showed that the synthesized material has catalytic properties in the oxidation of methane. It is shown that the effective sample is a sample with a manganese content of 2.7 wt. %. By XRD results calcined in air samples modified aluminum oxyhydroxide was shown that only in the sample with a manganese content of 2.7 wt. % $MnAl_2O_4$ phase is formed, which is catalytically active phase.

1. Introduction

Nanoparticles are increasingly being used in medicine, electronics, tribotechnology, catalysis [1, 2]. For example, multi-component nanoparticles serve as the basis for the creation of next-generation drugs, built on new principles, performing the role of the media not only drugs but also the functional part of the drug. Nanofibers aluminum oxyhydroxide (AlOOH) are used for the manufacture of dressings which have a high efficiency in the treatment of wounds and burns. On the basis of these fibers were developed adsorbents for water purification from microorganisms and viruses [3–7]. It is known that the scope of the nanoparticles is determined by their properties, so the preparation of nanoparticles with new properties is the actual direction of science and technology. Giving new properties of aluminum oxyhydroxides can be due to its modification [8, 9]. Due to the very small size of the material surface modification can not be accomplished, however, the volume in the modification process of direct synthesis of the material can be realized. In [10] described in detail the method of modifying aluminum oxyhydroxide manganese ions (II). As manganese modifier was selected as this is an active metal component in the catalysts of the oxidation of organic substances [11–14], which will bring the catalytic properties of aluminum oxyhydroxide.

The purpose of this paper is to establish the dependence of the change of the structural and functional properties of modified aluminum oxyhydroxide on the concentration of modifier in its composition.

At present, many research teams are studying the properties and field of application of aluminum oxyhydroxide [3–7]. Thus, this study is significant.

The objective of the work is to study the dependence of the phase constitution and functional properties of modified aluminum oxyhydroxide on the concentration of modifier in its composition.

2. Materials and methods

In this work electro explosive aluminum nanopowder was used, which was produced by electric wire explosion in an argon environment. The Fig. 1 is the microphotography of the electro explosive aluminum nanopowder.

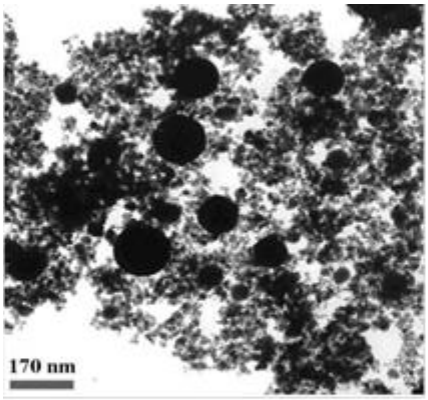

Figure 1. TEM image of the electroexplosive aluminum nanopowder.

Modifying agent was $MnSO_4 \times 5H_2O$. Manganese ions are used as catalysts for many chemical reactions such as decomposition of hydrogen peroxide, oxidation of iron (II) and others. In the experiments the different concentration of manganese ions were used, which are represented in table 1.

Table 1. Characteristics of modified nanofibers of aluminum oxyhydroxide.

The number of samples	Initial concentration of manganese ions in suspension, (mg/L)
0	-
1	1.0
2	30.0
3	60.0

The synthesis process of nanofibers in salt solutions was carried out under the same conditions as the synthesis in distilled water [5]. The volume of solution was 200 ml and the weight of aluminum nanopowder was 0.075. The synthesis of AlOOH nanofibers consists in three state. The first one was the preparation of aluminum nanopowder suspension and the salt solution, dispersing of the suspension using an ultrasonic bath for 5 min. The second stage involved the synthesis of nanofibers in a solution of $MnSO_4$ at constant temperature 60 °C during 6 hours. The third stage was the drying of the finished product at 60 °C.

The quantitative content of manganese ions in the modified nanofibers was determined by chemical analysis, according to GOST 4974-72. Morphological structure of the initial and modified nanofibers were studied on transmission electron microscope - JEM-2100F, Japan. The changes of specific surface areas were determined by the analyzer, "Air heater-M" by the BET method (low temperature adsorption of nitrogen-helium mixture). Quality of the products of synthesis was determined by X-ray diffraction on Shimadzu XRD-7000 diffractometer. The range of scanning angles was from 0 to 1000 with step 0.50 and scanning speed 1 degree per minute. The thermal stability of the modified aluminum oxyhydroxide and aluminum oxyhydroxide samples for the thermal oxidation in air and in argon were controlled with using thermal analyzer SDT Q-600.

3. Results and Discussion

In this work was prepare 4 samples of the modified aluminum oxyhydroxide. The value of specific surface area was a quantity of the effectiveness of the modification of AlOOH nanofibers. The table 2 shows the results of measurement of specific surface area of samples synthesized in solutions with different concentrations of salt.

Table 2. Characteristics of modified nanofibers of aluminum oxyhydroxide.

The number of samples	Initial concentration of manganese ions in suspension, (mg/L)	The concentration of manganese ions in samples, (mas %)	The specific surface area, (m^2/g)
0	-	-	196.16
1	1.0	0.4	219.48
2	30.0	1.4	211.76
3	60.0	2.7	110.10

The results in the table 2 are shown that the value of concentration of manganese ions is influenced on the value of specific surface area of the synthesis products. The increasing of specific surface area can be associated with an low concentrations of manganese ions in solution was adsorbed on the faces of the slow-growing nanowires, thereby blocking their growth, and fast-growing end face manganese ions can be incorporated into the crystal, without hindering its growth. However, if the manganese concentration in the solution the amount of active growth centers aluminum oxyhydroxide is reduced by blocking their manganese ions, which leads to a decrease in specific surface area. The increasing of the proportion of the amorphous AlOOH phase in the presence of Mn (II) was confirmed by X-ray diffraction of the obtained samples. Figure 2 presents the X-ray diffraction patterns of the initial (sample no. 0) and modified sample nos. 1, 2, and 3.

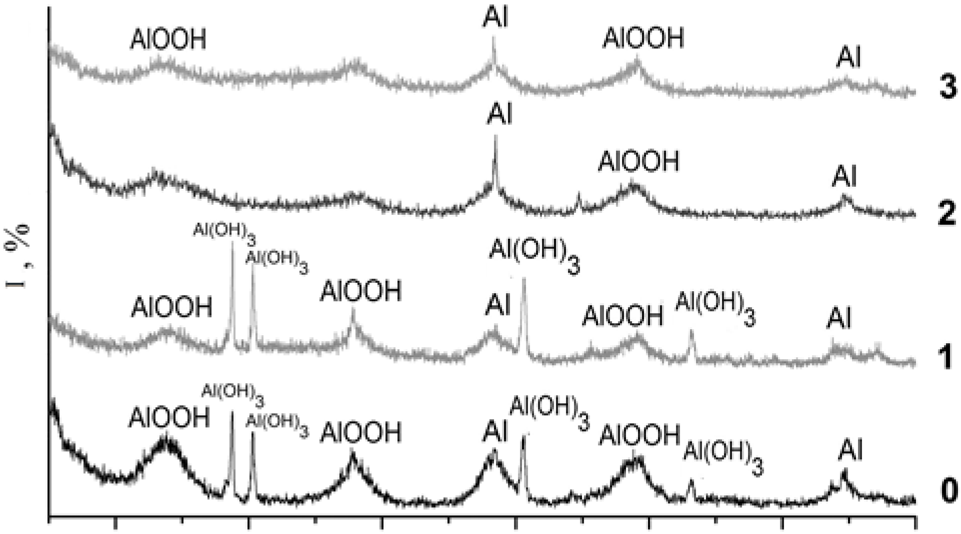

Figure 2. X-ray diffraction patterns of the nanofibers: (0) Initial and (1–3) manganese-modified samples.

Analysis of the X-ray diffraction patterns showed that sample no. 0 actually contains crystalline $Al(OH)_3$ and amorphous AlOOH phases, as well as metallic Al phase. The X-ray diffraction pattern of sample no. 1 is virtually identical to that of the initial sample, except for the occurrence of significantly broadened peaks of AlOOH and metallic Al phases. Sample nos. 2 and 3 exhibit virtually identical patterns which differ from those of sample nos. 0 and 1 by the lack of the $Al(OH)_3$ phase and occurrence of a high background level. Although manganese was not detected by the X-ray diffraction technique, its participation in synthesis is indicated by the change in the phase composition of the products with increasing manganese ions concentration in solution. The difference in the phase compositions of the products for the reactions of aluminum with liquid water and salt solutions was confirmed by the DTA data. Figure 3 shows the thermograms of the initial and modifyed samples.

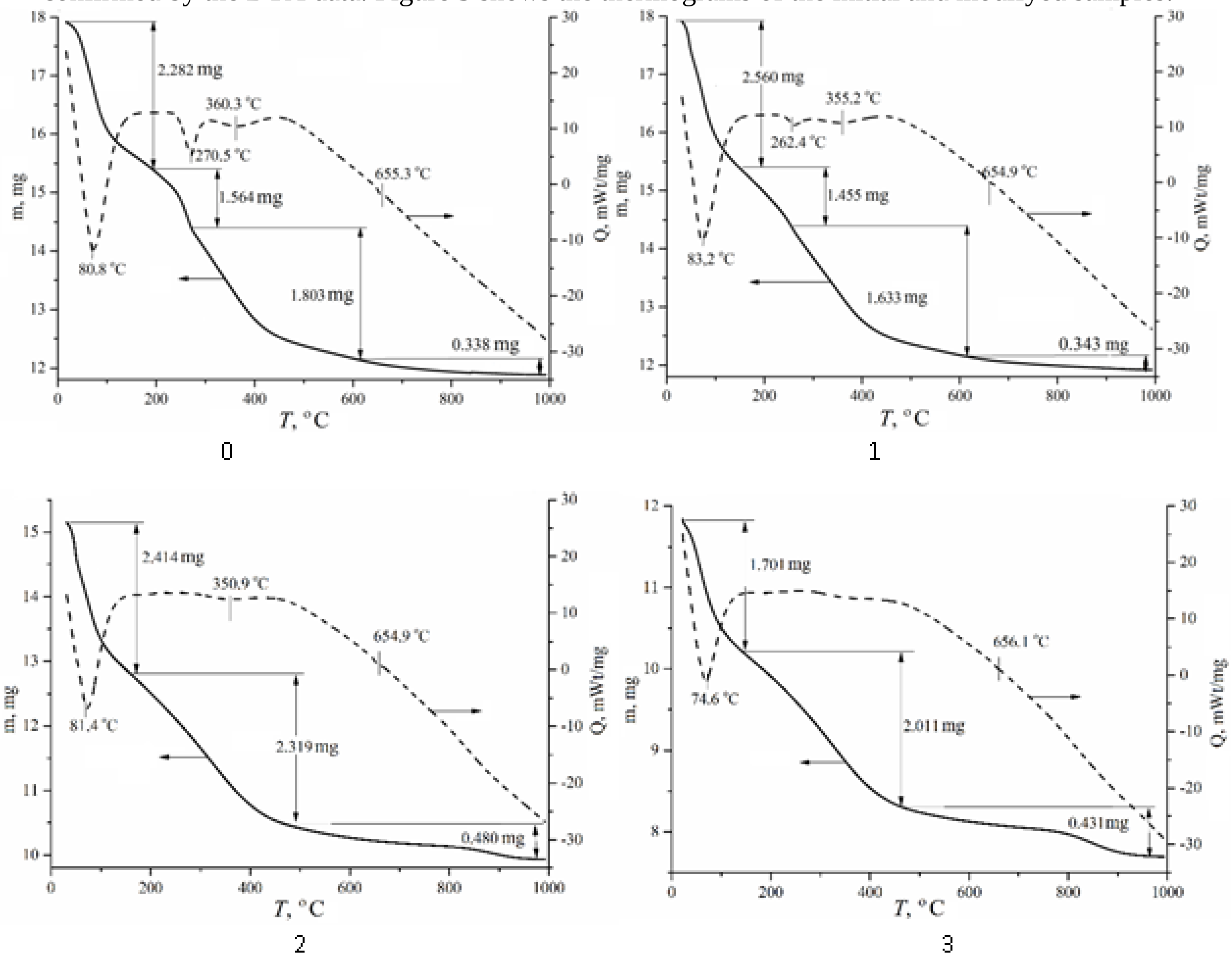

Figure 3. Thermograms of the nanofibers: (0) Initial and (1–3) manganese-modified samples.

It is seen that the mass loss (TGA) and heat effect (DTA) curves for sample nos. 0–2 are similar though different from those of sample nos. 3. The first endothermic peak (80.8 °C) is to the removal of physisorbed water. The weight reduction at a high temperature (270.5 °C) associated with transformation of Al(OH)3 to AlOOH (boehmite) and the third dehydration endothermic peak associated with dehydroxylation of boehmite (removal of OH groups). Thermograms of the sample 3 are shown that the third endothermic peak is absent because of a decrease in the yield of fibrous boehmite.

Figure 4 shows the electron micrographs of the initial and modified samples. It is seen that the sample no. 0 has a fibrous structure which is similar in principle to that of sample nos. 1 and 2 with the lowest manganese content. Sample no. 3 does not exhibit a prominent fibrous structure and contains unreacted spherical metallic aluminum particles. This fact confirms the presence of metallic aluminum phase on the X-ray sample 3 diffraction patterns (Fig. 2).

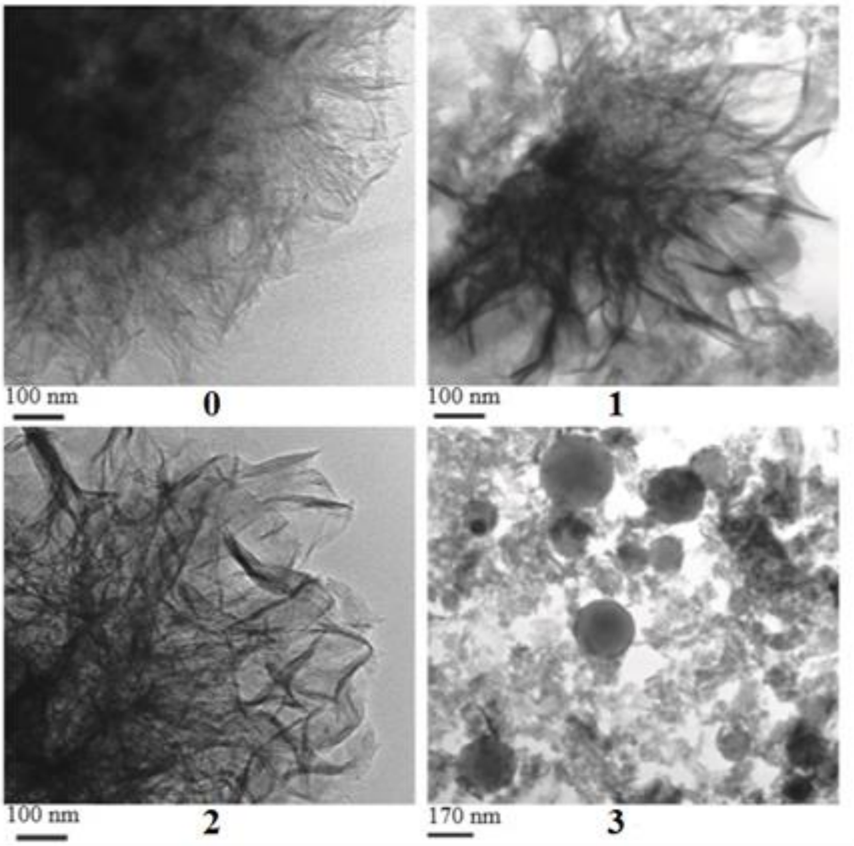

Figure 4. TEM image of the (0) initial and (1–3) modified samples.

The new functional properties of modified aluminum oxyhydroxide was studied on the reaction of the oxidation of methane, because the manganese are widely used as catalyst for oxidation reactions of organic substances. It was founded that heat treatment at 850 °C of modified aluminum oxyhydroxide leads to the formation of the combined structures of aluminum oxide with manganese and stable phases The results of investigation present on Figure 5 and table 3.

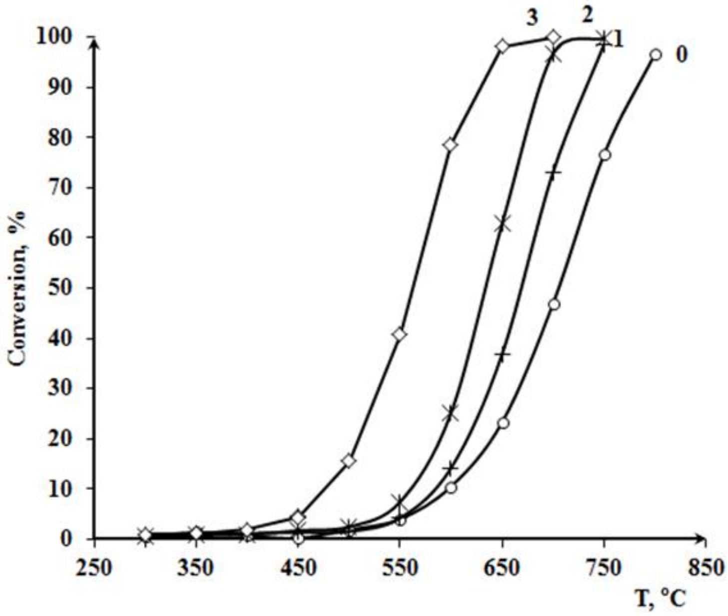

Figure 5. The conversion of the methane on the (0) initial and (1–3) modified samples.

Table 3. The phase constitution of samples after heat treatment at 850 °C

The number of samples	The concentration of manganese ions in samples, (mas %)	The phase constitution of samples after heat treatment at 850 °C
0	-	γ-Al_2O_3
1	0.4	γ-Al_2O_3
2	1.4	γ-Al_2O_3
3	2.7	δ-Al_2O_3, Al_2O_3, $MnAl_2O_4$

Figure 5 shows that the modification leads to the catalytic properties of the modified samples. It is shown that the amount of manganese in the modified samples affects the temperature methane. Figure 5 shows that the complete conversion of methane for sample 3 reached at 600 °C.

4. Conclusion

Thus it was shown that the modification process of manganese ions (II) of aluminum oxyhydroxide leads to a change in the phase composition, morphology and surface area. With the concentration of manganese increasing the contents of the hydroxide phases decreases and as a consequence of the specific surface area decreases.

Found that the most effective in the oxidation of methane is an industrial sample containing manganese ions (II) 2,7 wt. % Due to the formation of a spinel structure by calcination phase composition and unchanging during operation.

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References

[1] Irtegov Y, An V *Advanced Materials Research* 2014 **1040** 171-175
[2] Shiyan L, Yavorovskii N, Pustovalov A, Gryaznova E *Advanced Materials Research* 2014 **1040** 59-64
[3] Jaworowskii N, Shiyan L, Saveliev G, Galanov F *Nanotechnics* 2008 40-45
[4] Shutilov A, Zenkovets G, Tsybulya S, Gavrilov V *Kinetics and Catalysis* 2012 **53** 128–140
[5] Streletskii A, Kolbanev I, Borunova A, Butyagin P *Colloid Journal* 2005 631-637
[6] Alwitt R *Journal of The Electrochemical Society* 1974 1322-1328
[7] Fernando J, Chung D *Journal Por. Mater* 2002 211-219
[8] Paul B, Martens N, Frost R *Journal of Colloid and Interface Science* 2011 **360** 132-138
[9] Lojkowski W, Gedanken A, Grzanka E, Opalinska A, Strachowski T, Pielaszek R, Tomaszewska-Grzeda A, Yatsunenko S, Godlewski M, Matysiak H, Kurzydłowski K *J. Nanopart Res* 2009 **11** 1991–2002
[10] Gryaznova E, Shiyan L, Yavorovskii N, Korobochkin V *Rus. J. of Appl. Chem.* 2013 **86** 360-365
[11] Bulavchenko O, Tsybulya S, Afonasenko T, Tsyrulnikov P *Applied Catalysis A: General*. 2013 **459** 73–80
[12] Craciun R, Nentwick B, Hadjiivanov K, Knözinger H *Applied Catalysis A: General* 2003 **243** 67–79
[13] Frey K, Iablokov V, Safran G, Osan J, Sajo I, Szukiewicz R, Chenakin S, Kruse N *Journal of Catalysis* 2012 **278** 30–36
[14] Iablokov V, Frey K, Geszti O, Kruse N *Catalysis Letters* 2010 **134** 210–216