

# Structural and Phase Changes of Products of the Oxidation and Ageing of Nanodispersed Aluminium upon the Interaction with Water

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## Abstract

Ultradispersed oxyhydroxides of aluminium have been obtained upon the interaction of electroexplosive nanodispersed aluminium with water at 55 °C. Initial samples were subjected to ageing under the alkaline condition (pH 10) at 20 and 50 °C. It has been demonstrated that the content of structural water in resultants of the reaction increases during the course of ageing; the specific surface and the limiting adsorption volume decrease. An increase in the intensity of reflexes of bayerite and a decrease in the intensity of pseudoboehmite lines with time have been noted. The sorption of saturated benzene vapour at 20 °C drops during the ageing of samples. The observed processes occur more intensively at 50 °C. An inference about the transformation pseudoboehmite → bayerite → boehmite that passes in the reaction medium has been made from the results of thermal and X-ray diffraction analysis.

## INTRODUCTION

In spite of numerous investigations, interest in studying the interaction of aluminium with water continues unabated [1, 2]. Meanwhile, researchers do not have the definite point of view on the nature of phase and thermal conversions of various polymorphic forms of aluminium oxyhydroxides (AOH). The nature of the arising transition phases of AOH and the sequence of their formation depend on mother substance, on its dispersity, its defective structure, etc.

The interaction of powdered aluminium with water at the temperatures of 20–80 °C, as a rule, gives rise to the following consecutive processes: an induction period, a stage of the acceleration of chemical interaction, and a stage of the retardation of the reaction [2]. Ultradispersed powders of aluminium with an average size of particles of no more than 100 nm show a thin oxide layer (1.6–2.0 nm) and a considerably higher reaction surface,

which provides for a short induction period, fast development of the reaction, and the maximum reaction rate and fractional conversion that are almost an order higher when compared to micrometer-sized powders [3]. Oxidation rate for ultradispersed aluminium powders is controlled by the ratio of the breakdown rate of the initial oxide layer, the rate of the formation and growth of oxyhydroxide, and the rate of water diffusion through the formed bed of reaction products. As the temperature of the oxidation rises, fast nucleation is observed, the crystallization degree of pseudoboehmite layer increases.

As of now, electric explosion of conductors is widely applied to produce nanodispersed powders (including aluminium too). Investigations have shown [4] that these nanodispersed powders differ in their specific surface, their sizes, and the character of their distribution in the particle sizes. Therefore, it is quite natural that the nanodispersed aluminium that has been obtained in various

explosion conditions (the input energy, the gas medium, *etc.*) shows a variable reactivity. The authors [5–12] have found that electroexplosive aluminium interacts with water upon a slight preheating, and the rate of hydrogen formation drastically increases at  $T > 50^\circ\text{C}$ . Reaction of these powders with water proceeds in one stage, and the influence of specific surface and particle size manifests only in a change in the duration of the induction period and the reaction rate that is controlled by the evolving of hydrogen. Irrespective of the physicochemical characteristics of the nanodispersed powder, the mass fraction of the reacted metal ranges up to 95 % in 2–3 h after the reaction begins.

Oxidation of aluminium in water is followed by ageing processes. The majority of researchers register the formation of amorphous oxyhydroxide during the first min of the reaction, which is typical of the processes of AOH obtaining both through precipitation [5, 13, 14, *etc.*] and by oxidation in hydrothermal conditions [2]. Fresh deposits of aluminium oxyhydroxide are amorphous and they feature a low specific surface ( $<1\text{ m}^2/\text{g}$ ) [13]. Pseudoboehmite is formed from the aggregates of amorphous oxyhydroxide, and, as opposed to well-crystallized boehmite, pseudoboehmite is typified by high specific surface (about  $300\text{ m}^2/\text{g}$  and over) and by a greater water content ( $>1.3\text{ mol of H}_2\text{O/mol of Al}_2\text{O}_3$ ) than that is requisite according to the stoichiometry of  $\text{AlOOH}$  formula [1, 15]. The roentgenogram of pseudoboehmite shows strongly broadened diffraction lines; an intensity maximum of the line that corresponds to the 0.611 nm interplane distance is shifted [1]. Similarity of boehmite and pseudoboehmite structures proves is supported by data of radial distribution of atoms [16]. Dehydration of pseudoboehmite and boehmite is characterized by endoeffects at 440 and  $510^\circ\text{C}$ , respectively [17].

A degree and direction of the crystallization of initial amorphous aluminium oxyhydroxide depend on the pH, on the temperature and duration of ageing. Accordingly, amorphous aluminium oxyhydroxide quickly converts to pseudoboehmite at  $\text{pH} \approx 9$  and ambient temperature, and at long-term ageing, bayerite lines appear on the roentgenograms with the simultaneous decrease of the intensity of

pseudoboehmite lines. The duration of the induction period for the formation of bayerite also depends on the media pH: the duration of the induction period decreases with an increase in its values.

In spite of a high activity of the nanodispersed aluminium, a certain part of agglomerates of the powder slowly reacts with water. Fractional conversion of aluminium can be raised by way of increasing the temperature, the reaction time, or the pH of the initial reaction mixture; however, this may result in structural and textural changes in resultants of the reaction [17–19].

From the practical point of view, oxidates of aluminium nanopowder, namely, ultra-dispersed oxyhydroxides, are of particular interest to be used as catalysts of petrochemical processing and effective adsorbents, which also involves solving a problem of oily sewage treatment [9–12, 20]. Herein, the efficiency of adsorbents depends on the oxyhydroxides structure and texture that may vary over a wide range [6–9].

The purpose of this work is to determine structural and textural characteristics of AOH that are formed during the interaction of nanodispersed aluminium with water and their subsequent ageing in order to reveal the optimum conditions for obtaining effective adsorbents of petroleum derivatives and other contaminants of the aqueous and air environment.

## EXPERIMENTAL

This work used nanodispersed aluminium that has been produced by electric explosion of a wire in argon environment. Aluminium powder is represented by particles with a rather wide size distribution. The distribution maximum falls on 50 nm, but the availability of agglomerates of particles is registered that are more than 1000 nm in size (5–7 mass %). Specific surface of the powder comprises  $19\text{ m}^2/\text{g}$ .

To produce AOH samples, a nanopowder of aluminium was held in water (the powder content of 50 g/l) at a temperature of  $55^\circ\text{C}$ . The suspension was vigorously stirred to prevent local warms and foaming. The alkalinity of the medium rises during the reaction and

reaches the pH values that are equal to 9.5 3 h later. After 3 h the reaction mixture was rendered alkaline to pH 10 with ammonia solution and the suspension was let to stand in an alkaline solution at the temperatures of 50 (series 1) and 20 °C (series 2). The reaction of the medium was maintained at a level  $\text{pH} \gg 10$  throughout the ageing period. After certain time intervals elapsed, part of the reaction product was withdrawn, washed with distilled water to reach the neutral medium, processed with acetone, and dried in a drying chamber (110 °C). As a consequence of the interaction of aluminium with water, oxyhydroxy phases of aluminium were produced with a maximum of the particle size distribution at 0.1 nm.

Specific surface ( $S_{sp}$ ) of samples was determined by the method of argon thermal desorption with a Sorptometer instrument [21]. Thermal analysis of samples of 0.2 g in mass was conducted in Q-1500 D Paulik–Paulik–Erdei derivatograph in a dynamic regime in a range of temperatures 20–1000 °C at the heating rate of 10 °C /min in the air atmosphere. X-ray diffraction analysis of samples was conducted in a DRON-3 diffractometer in the range of medium and large angles ( $\text{CuK}_\alpha$  radiation) with the continuous scanning at a rate of 1 deg/min. Determination of interplane parameters was performed from reference data with the use of ASTM standard. An integral intensity of peaks was evaluated with a planimeter.

Sorption of benzene was conducted in an exsiccator at ambient temperature over the course of 1 day [22]. A calculation of the limiting adsorption volume of oxyhydroxides was conducted with the use of a limiting sorptive capacity for benzene [23].

The ratio of molar content of water and aluminium oxide ( $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ ) has been used as a criterion to estimate chemical composition of aluminium hydroxides.

## RESULTS AND DISCUSSION

Figure 1 displays roentgenograms of three samples of the series 1 that were drawn from a reaction mixture after 1, 3, and 94 h (AOH-1, AOH-3, AOH-7, respectively). It is evident that the AOH-1 sample contains pseudoboehmite that

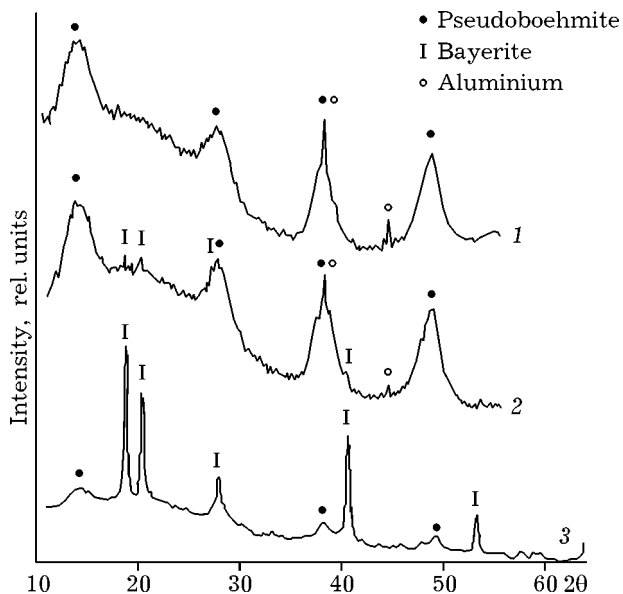


Fig. 1. Diffractograms of aluminium oxyhydroxide samples that were synthesized over the course of 1 (1), 3 (2), and 94 h (3).

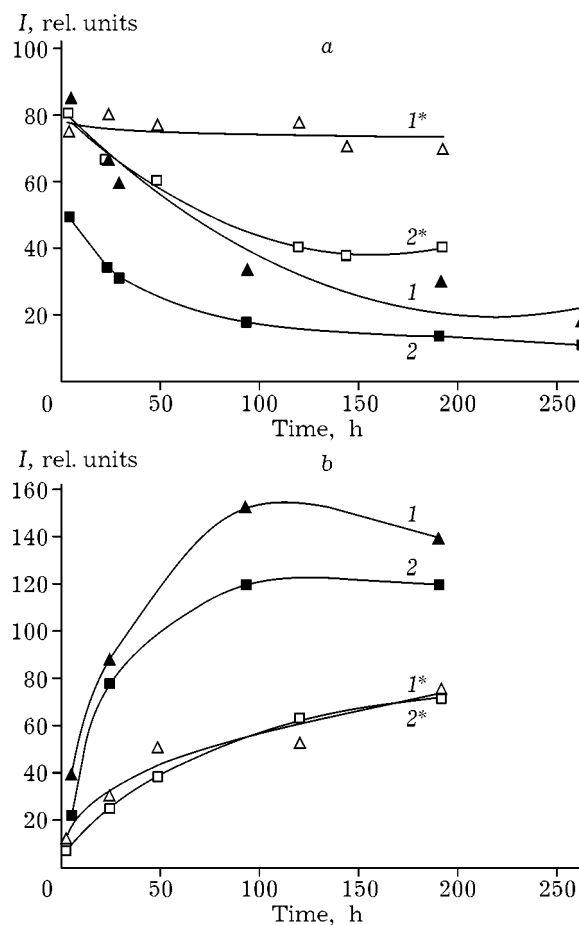


Fig. 2. Dependence of relative intensity of diffraction peaks of pseudoboehmite (a) and bayerite (b) on the time for ageing of samples AOH at 20 ( $1^*$ ,  $2^*$ ) and 50 °C (1, 2): a – 0.62 (1,  $1^*$ ), 0.234 nm (2,  $2^*$ ); b – 0.474 (1,  $1^*$ ), 0.437 nm (2,  $2^*$ ).

produces wide lines, amorphous aluminium oxyhydroxide, the availability of which is evidenced by a halo in the region of  $20^\circ$  and by unreacted aluminium (curve 1). The presence of pseudoboehmite, amorphous aluminium oxyhydroxide, and residual aluminium is recorded for AOH-3 sample. In addition, AOH-3 contains bayerite, as demonstrated by the emerging characteristic peaks of the substance that correspond to the interplane distances 0.474 ( $19^\circ$ ), 0.437 ( $20^\circ$ ), 0.222 nm ( $41^\circ$ ) (see Fig. 1, curve 2). Long-term ageing of AOH samples leads to a decreased intensity of pseudoboehmite characteristic lines and to a gain in bayerite peaks (see Fig. 1, curve 3). The variation of the intensity of lines of bayerite and pseudoboehmite occurs much more quickly in the case of samples ageing at  $50^\circ\text{C}$  (Fig. 2).

AOH samples that were obtained during the interaction of nanodispersed aluminium with water and the subsequent ageing of resultants of the reaction were exposed to dehydration in the thermo-programmed heating mode. Dehydration curves of the AOH-1 sample are presented in Fig. 3, *a* (curve 1). Wide minima in the DTA and DTG curves at the temperatures of 130, 170, and  $400^\circ\text{C}$  are caused probably by the respective removal of sorbed, "bound", and crystal water of pseudoboehmite [16]. It is characteristic that no endothermic melting peak is observed in the DTA curve for residual nanodispersed aluminium at  $660^\circ\text{C}$ , because the last-mentioned starts oxidizing in the air at  $420^\circ\text{C}$  [8]. After 2 h of the interaction of aluminium with water, a product is formed, the decomposition of which occurs with a shift of the minimum in the DTG curve at  $170^\circ\text{C}$  in the region of lower temperatures ( $150^\circ\text{C}$ ) and with the emergence of a weak minimum at  $280^\circ\text{C}$  (Fig. 3, *a*, curve 2). An additional peak at  $230^\circ\text{C}$  in the DTA and DTG curves is evidenced 3 h later from the beginning of the reaction (see Fig. 3, *a*, curve 3). It is evident from Fig. 3, *a* that the intensity of the minima at 230 and  $280^\circ\text{C}$  increases with an increase in the AOH ageing time. In addition, peaks for the samples AOH-6–AOH-9 and AOH-6\* (see Fig. 3, *a*, *b*) are observed in the DTA and DTG curves at a temperature of about  $510^\circ\text{C}$  that correspond to the decomposition of crystalline boehmite [16]. The intensity of these peaks

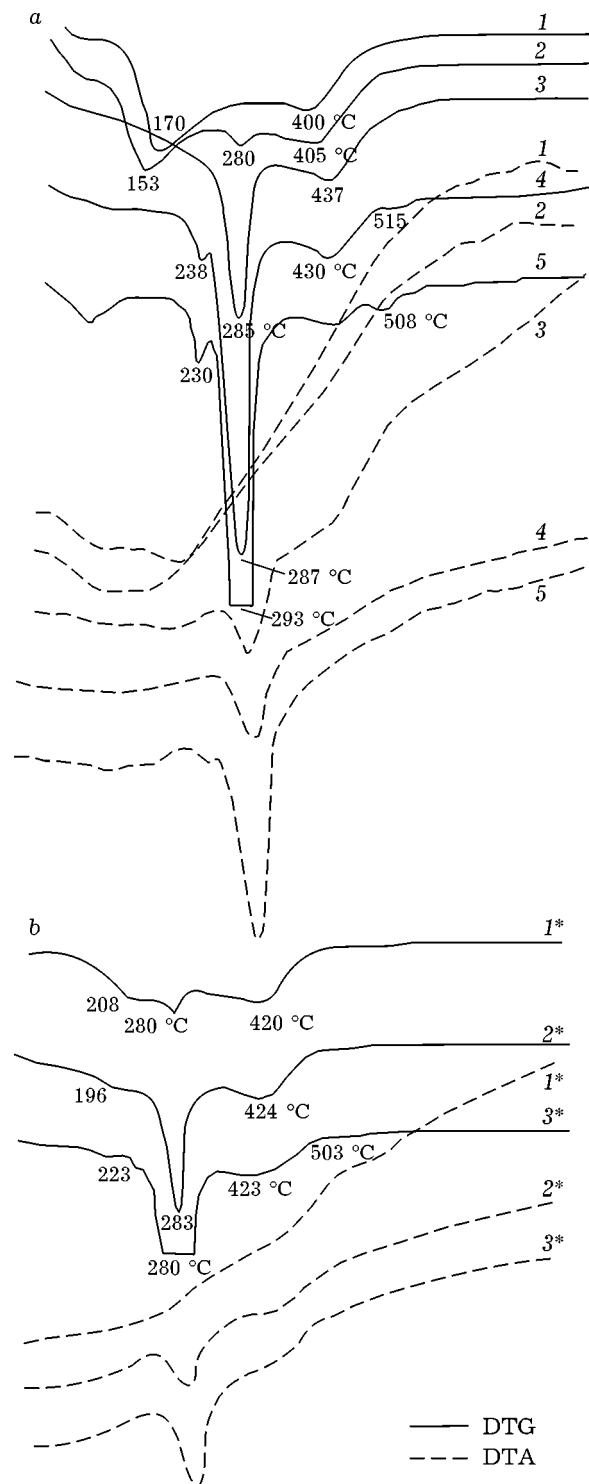


Fig. 3. Thermodecomposition curves for AOH samples of series 1 (*a*) and 2 (*b*) at the ageing temperatures of 50 and  $20^\circ\text{C}$ , respectively: *a* – AOH-1 (1), AOH-2 (2), AOH-3 (3), AOH-6 (4), AOH-9 (5); *b* – AOH-1\* (1\*), AOH-3\* (2\*), AOH-6\* (3\*).

TABLE 1

Temperature effect of heat treatment of aluminium oxyhydroxide (AOH) samples on the dehydration process

Sample	Temperature range of the thermodecomposition, °C					
	130–160	130–220	160–220	130–950	160–950	220–950
Water losses, mass %						
AOH-1	2.1	8.3	6.3	24.2	22.1	15.9
AOH-2	2.6	6.6	4.0	23.8	21.2	17.2
AOH-3	0.7	2.7	2.0	22.9	23.0	20.7
PB*	0.85	2.9	2.05	25.1	24.3	22.2

\*PB – pseudoboehmite.

increases, as bayerite accumulates in the samples. Bayerite transforms into  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and partially into boehmite during the dehydration at the temperatures of 220–350 °C and boehmite converts to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at a temperature of 510 °C [18].

Table 1 discloses an effect of the treatment temperature of AOH samples on the process of their dehydration. The sorbed and “bound” water of pseudoboehmite and the water that was excreted in the course of dehydration of amorphous oxyhydroxide excrete in the temperature range of 130–220 °C. The observed decrease of the water losses is related to a

decreased concentration of amorphous oxyhydroxide in the samples. Within 3 h after the reaction, the AOH-3 sample is analogous to the pure pseudoboehmite in its water content and the shape of the derivatographic curves (see Table 1). A gradual increase in the quantity of water that was excreted from the samples at higher temperatures (220–950 °C) is caused by the accumulation of bayerite in the samples, as evidenced by an increase in the intensity of peaks in the sample diffractograms (see Fig. 1).

For the samples of the series 2 that were aged at 20 °C, the intensity of peaks over the region of 280 °C grows significantly slower and

TABLE 2

Characteristics of samples of aluminium oxyhydroxides (AOH)

Sample	T, °C	Synthesis time, h	S <sub>sp</sub> , m <sup>2</sup> /g	H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub> , mol/mol <sup>a</sup>	Sorption of benzene, g/g	V <sub>s</sub> , cm <sup>3</sup> /g
AOH-1	55	1	319	1.19	0.46	0.52
AOH-2	55	2	364	1.29	0.45	0.51
AOH-3	55	3	297	1.48	0.44	0.50
AOH-4	50	5	275	1.59	0.45	0.51
AOH-5	50	24	249	1.74	0.60	0.68
AOH-6	50	29	199	1.89	0.45	0.51
AOH-7	50	94	108	2.26	0.20	0.23
AOH-8	50	191	102	2.48	0.15	0.17
AOH-9	50	264	65	2.42	0.12	0.14
AOH-1*	55	3	295	1.34	0.47	0.53
AOH-2*	20	24	294	1.42	0.41	0.47
AOH-3*	20	48	279	1.60	0.40	0.45
AOH-4*	20	120	216	1.71	0.37	0.42
AOH-5*	20	144	209	1.91	0.30	0.34
AOH-6*	20	192	205	1.95	0.32	0.36

Note. V<sub>s</sub> is the limiting adsorption volume of pores.

<sup>a</sup>The crystal water was calculated from data of mass loss of the samples at a temperature above 220 °C.

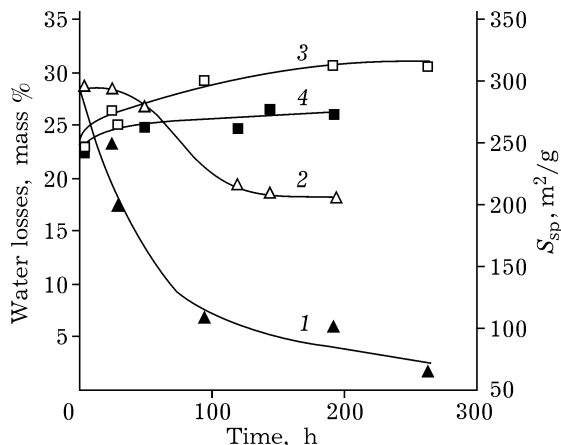


Fig. 4. Specific surface (1, 2) and losses of water (3, 4) versus the ageing time of samples at 50 (1, 3) and 20 °C (2, 4).

the peak at 230 °C appears only 192 h later (see Fig. 3, b).

From data of the Table 2 and Fig. 4 it will be obvious that specific surface, the content of structural water and pore space of a sample depend essentially on the duration of the reaction. Meanwhile, specific surface of samples reaches its maximal value within the first three hours (364 m<sup>2</sup>/g) and then decreases (see Table 2). The limiting adsorption volume typical is typified by a constancy of values during the first day (about 0.50 cm<sup>3</sup>/g) and by the subsequent decrease as the reaction time increases. Accordingly, for AOH-9 sample that was aged in an alkaline solution at 50 °C within 264 h, specific surface and the limiting adsorption volume comprise 65 m<sup>2</sup>/g and 0.14 cm<sup>3</sup>/g, respectively. From the data of the Table 2 it follows that maximal  $S_{sp}$  and  $V_s$  values are typical of aluminium oxidates that stay in the mother solution for no more than 1 day.

The content of structural water of AOH samples permanently grows during the reaction. In response to the thermo-programmed heating, the samples AOH-1–AOH-9 lose 1.19 to 2.48 mol H<sub>2</sub>O/mol Al<sub>2</sub>O<sub>3</sub> at 50 °C and the samples AOH-1\*–AOH-6\* lose 1.34 to 1.95 mol H<sub>2</sub>O/mol Al<sub>2</sub>O<sub>3</sub> at 20 °C.

The tendency to an increase in the intensity of bayerite lines, the content of structural water, and to a decrease of the intensity of pseudoboehmite lines and specific surface is more noticeable for the AOH samples that were obtained at 50 °C (see Figs. 1–4).

The results arrived at are in good agreement with data of the works [1, 4, 6–8, 14–18, *etc.*] and they testify that AOH of a variable phase composition are formed upon the oxidation of nanodispersed aluminium by water. At first, amorphous oxyhydroxide is formed that may transform to pseudoboehmite, boehmite, or bayerite depending on the conditions of the reaction. In this research, when the oxidation of nanodispersed aluminium by water begins in the neutral medium and comes to the end in the alkaline medium, the resultant of the reaction in 1 h constitutes pseudoboehmite for the most part, as well as amorphous oxyhydroxide and aluminium. Oxidation of aluminium and ageing of the resultants of the reaction proceed in parallel and they have the antibate influence on the variation of the specific surface. On the one hand, aluminium is oxidized by water with the formation of amorphous oxyhydroxide that turns into pseudoboehmite within several minutes [13, 17]. This process occurs with an increase of the specific surface. On the other hand, transformation of pseudoboehmite into bayerite is possible under the created conditions. These processes cause a decrease in the specific surface and in the limiting adsorption volume. As aluminium is exhausted, ageing becomes the limiting stage.

## CONCLUSION

It has been demonstrated that structural and textural characteristics of ultradispersed AOH that are formed during the reaction of nanodispersed aluminium with water, complicated by ageing, are subject to variation. Formation of bayerite from pseudoboehmite begins in the reaction mixture just in 2 h, which proves to be true by the appropriate peaks available in the diffractograms and derivatographic curves. As a consequence of AOH ageing under the alkaline condition for more than 24 h, especially at 50 °C, their specific surface and the limiting adsorption volume drop. Hence to increase fractional conversion of aluminium and to obtain products with a high sorption capacity it is sufficient to limit the time for the synthesis to three hours at 50 °C and to finish the reaction

at ambient temperature over the course of 1 day.

#### REFERENCES

- 1 The Structure and Properties of Adsorbents and Catalysts, in B. G. Linson (Ed.), Acad. Press, New York, 1970.
- 2 S. F. Tikhov, V. E. Romanenkov, V. A. Sadykov *et al.*, Poristye kompozity na osnove oksid-alyuminiyevykh kermetov (sintez i svoystva), Izd-vo SO RAN, Novosibirsk, 2004.
- 3 V. V. Zhilinskiy, A. K. Lokenbach, *Izv. AN LatvSSR. Ser. Khim.*, (1988) 622.
- 4 N. A. Yavorovskiy, *Izv. Vuzov. Fiz.*, 4 (1996) 114.
- 5 A. P. Lyashko, A. A. Medvinskiy, G. G. Saveliev, N. A. Yavorovskiy, *Kinetika i Kataliz*, 31 (1990) 967.
- 6 V. G. Ivanov, M. N. Safronov, O. V. Gavriilyuk, *Khim. Ust. Razv.*, 8 (2000) 705.
- 7 V. G. Ivanov, M. N. Safronov, O. V. Gavriilyuk, *Fiz. Gor. i Vzryva*, 37 (2001) 57.
- 8 V. G. Ivanov, O. V. Gavriilyuk, *Ibid.*, 35 (1999) 1.
- 9 G. I. Volkova, V. G. Ivanov, O. A. Kukharenko, *Chem. Sust. Dev.*, 13, 3 (2005) 425.  
<http://sibran.ru/English/csde.htm>
- 10 E. E. Sirotkina, V. G. Ivanov, O. V. Glazkov *et al.*, *Ibid.*, 5, 4 (1997) 403.
- 11 G. I. Volkova, T. A. Solodova, V. G. Ivanov, O. A. Kukharenko, Proc. 5 Mezhdunar. konf. "Khimiya nefi i gaza", Tomsk, 2003.
- 12 Pat. 2075345 RF, 1997.
- 13 B. C. Lippens, *Chem. Weekbl.*, 62 (1966) 336.
- 14 V. A. Dzisko, A. S. Ivanova, G. P. Vishnyakova, *Kinetika i Kataliz*, 17 (1976) 483.
- 15 A. S. Ivanova, M. M. Pugach, E. M. Moroz *et al.*, *Izv. AN SSSR. Ser. Khim.*, (1989) 2169.
- 16 S. V. Ketchik, L. M. Plyasova, *Neorg. Mat.*, 14 (1978) 1124.
- 17 A. S. Ivanova, G. S. Litvak, G. N. Kryukova *et al.*, *Kinetika i Kataliz*, 41 (2000) 137.
- 18 N. F. Ermolenko, M. D. Efros, Regulirovaniye poristoy struktury okisnykh adsorbentov i katalizatorov, Nauka i tekhnika, Moscow, 1971.
- 19 V. A. Dzisko, Osnovy metodov prigotovleniya katalizatorov, Nauka, Novosibirsk, 1983.
- 20 L. N. Vosmerikova, L. M. Velichkina, L. L. Korobitsyna, A. V. Vosmerikov, *Zh. Prikl. Khim.*, 73 (2000) 1477.
- 21 N. E. Buyanova, A. P. Karnaukhov, Yu. A. Alabuzhev, Opreddeniye poverkhnosti dispersnykh i poristykh materialov, Novosibirsk, 1978.
- 22 L. D. Gluzman, I. I. Edelman, Laboratorny kontrol' koksokhimicheskogo proizvodstva, Kharkov, 1957.
- 23 S. J. Gregg and K. S. W. Sing, Adsorption, Specific Area and Porosity, Academic Press, London, 1982.