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Synthesis of aluminum-oxide adsorbents using alkalis at the hydration stage and study of their physicochemical and adsorptive properties

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Abstract. The paper presents the research results of physicochemical characteristics, adsorption kinetics and value of adsorption capacity with respect to water vapors of the aluminum-oxide adsorbent modified with potassium and sodium cations. It was shown that modification of desiccants by potassium and sodium cations at the hydration stage of products of hydrargillite thermal activation during synthesis allowed obtaining adsorbents-desiccants with high values of static (more than 20 g/100g) and dynamic capacitance (more than 5.0 g/cm^3) by water vapors.

1. Introduction

One of the key priorities in perfection of the process of sorption air drying is the right choice of commercially produced adsorbents depending on the required degree of air drying [1], dynamic capacitance and regeneration conditions, mechanical strength, resistance to condensed moisture [2], abrasion and etc. or development of new sorbing materials possessing high sorptive and strength characteristics [3]. Generally, silica gels, zeolites, active aluminum oxide are used in the systems of air drying. It is common knowledge that aluminum oxide in its characteristics surpasses silica gels at low humidity and zeolites at high humidity. Besides, an important positive feature of aluminum oxide is its water resistance. This is an indicator that often predetermines the choice of aluminum oxide as an adsorbent for drying and reprocessing of media, which contain condensed moisture [1]. In addition, aluminum-oxide adsorbents have such advantages over other desiccants as high mechanical strength, stability of adsorption capacity during multicycle work, completeness and simplicity of regeneration, resistance to wear, resource availability [4, 5]. The purpose of the work is to obtain samples of aluminum-oxide adsorbents – desiccants – modified by potassium and sodium cations at the hydration stage during synthesis and to study their physicochemical characteristics.

2. Materials and methods of research

To obtain adsorbents based on aluminum oxide, a method of centrifugal thermal activation (CTA) of hydrargillite (HG) with subsequent hydration of the obtained product in mild conditions was used, which

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allowed synthesizing adsorbents-desiccants with a high specific surface [6, 7].

Hydration of the product by CTA of HG was carried out in the temperature range of 97-98 °C at atmospheric pressure during 6 hours in the alkaline medium in the reactor during constant stirring. A ratio of solid and liquid phases was =1:4; pH of the medium at the moment of loading the CTA powder was equal to 10-12. An alkaline module (alkaline mole / Al₂O₃ moleKOH medium), and during synthesis of samples 5A, 8A – 0.06 (in the NaOH medium). Hydration products, for the purpose of cost-cutting of the technological process, were not washed free from admixtures; they were discharged into a stainless steel container and placed in the drying cabinet with forced convection at temperature of 120 °C during 24 hours. After drying, the sample was discharged and ground in the ball mill for 8 hours. As a result of it, fine-dispersed aluminum hydrate with the powder particle size of 5-25 µm was obtained. Later ground aluminum hydrate in the amount of 250 g was poured into the mixer with Z-shaped blades. Then the aqueous solution of electrolyte-peptizer was added. In case of necessity, an additional amount of water was added drop-wise to obtain plastic mixture suitable for forming by extrusion. During peptization, nitric acid was used to synthesize all the samples. An acid module (acid mole/Al₂O₃ mole) for samples 1A, 2A, 5A was 0.05, and for sample 8A - 0.08. The finished plastic mixture was pressed through the die obtaining granules of cylinder shape (diameter $-3.5 \div 3.6$ mm, length $-5.0 \div 6.0$ mm). The obtained extrudates were dried in the air during 24 hours, whereupon they were exposed to baking in the flow of dry air in the pipe furnace with a volume of 5 litres at 450 °C for 4 hours with an air flow rate of 5000 h¹. The duration of the baking after acceleration was 4 hours. The baking rate was no more than 50 °C/hour. After the baking, the samples were cooled and tested by measuring static and dynamic capacitance by water vapors, and other characteristics were studied, and other characteristics were studied, and other characteristics were studied.

The phase composition and structural parameters of the samples were researched using the diffractormeter XRD-6000 based on CuK_{α}-radiation. Analysis of the phase composition was conducted using data bases PDF 4+, as well as programs of full-profile analysis POWDER CELL 2.4. The content of the mass fraction of Na and K was determined by atomic emission spectrometry with inductivelycoupled plasma (AES-ICP). Analysis was conducted using the atomic emission spectrometer with inductively-coupled plasma OPTIMA 4300DV produced by PERKINELMER company with the wavelength operation range from 170 to 800 µm. The specific surface and porous structure of initial products of CTA and obtained adsorbents were determined using the apparatus produced by Quantachrome Corporation by adsorption and desorption of nitrogen. To calculate the values of the specific area of the BET surface, pore volume and pore size distribution, the program "Gas Sorpsion Report Autosob for Windows for AS-3 and AS-6" Version 1.23, was used. The differential thermal analysis (DTA) was conducted using the apparatus NETZSCH STA 449C in the temperature range from 20 to 1000 °C with a heating rate of 10 deg./min in the air; the sample weight was 0.2 g, the accuracy of determination of mass losses was ± 0.5 %. The static capacitance of adsorbents with regard to water vapors was determined by the gravimetric method by the mass fraction of water absorbed by the mass unit of the adsorbent by the time of reaching adsorption equilibrium at temperature of 25.0 °C in the atmosphere with relative humidity of 60.0%. Dynamic adsorption capacitance of adsorbents with regard to water vapors was determined by measuring the amount of water vapors adsorbed from their mixture with the air, passing through the layer of adsorbent granules from adsorber by the time of reaching the dewpoint temperature of gas flow on exit from the adsorber (minus 40.0 °C). The resulted value was referred to 100.0 cm³ of the tested sample. The kinetics of adsorption-desorption of water vapors at pressure close to atmospheric pressure was studied on the adsorption plant using the quartz balance described in work [8]. The experiments were made at room temperature (25 °C) and relative humidity of ~ 100 % using a fraction of 0.5-1.0 mm.

3. Results

According to the thermal analysis, the performed calculation of the content of hydroxides in the hydration products, proceeding from the temperatures of decomposition and weight losses accepted for them, showed that in the products of alkaline hydration there were up to 50 % of trihydroxides as well as pseudoboehmite and amorphous hydroxide. The content of the modifying admixtures and physicochemical characteristics of the synthesized samples after heat treatment are given in Table 1.

Sample	S _{sp} (m²/g)	V _{por} (cm ³ /g)	Content (mass. %)		D (Å)	Mechanical strength	Dynamic capacitance	Static capacitance (g/100g) with 60	
			Na^+	\mathbf{K}^+		(MPa)	$(g/100 \text{ cm}^3)$	% humidity	
1A	354	0.38	0.10	1.85	42.6	5.8	5.0	20.0	
2A	346	0.47	0.10	2.20	42.8	3.7	5.5	20.1	
5A	314	0.31	2.20	0.01	39	5.3	6.5	20.2	
8A	317	0.30	2.30	0.01	38	8.4	7.5	20.2	

Table 1. Physicochemical properties of adsorbent samples.

According to the results of the X-ray phase analysis, the major phase of the studied samples is a low-temperature modification η - of aluminum oxide. A degree of crystallinity of the samples varies within the range from 30 to 40 %.

Table 1 shows that for the samples, modified by potassium, the specific surface value of the adsorbent accompanied by the increase in potassium content in the sample (1A, 2A) practically did not change. However, there was a tendency to an increase in the volume and average diameter of pores during reduction of mechanical strength and static capacitance with respect to water vapors. At the same time, there was no dependence in the change of dynamic capacitance. When replacing KOH by NaOH at the hydration stage, the specific surface value, the volume and the average diameter of pores of the obtained adsorbents reduce with a commensurable value of static capacitance (samples 5A and 8A, Table 1). It is possible to note that with a similar content of the alkaline metal in the adsorbent, mechanical strength and dynamic capacitance increase during transition from sample 2A to sample 5A. An increase in the concentration of peptizer - HNO₃ during synthesis (sample 8A) allowed a greater growth in the value of mechanical strength and dynamic capacitance of the adsorbent-desiccant. Kinetic curves of adsorptiondesorption of water vapors on the samples are shown in figure 1. An irreversibility effect turned out to be typical of the adsorbents under study: after desorption of water vapors, curves did not regain their initial state (the difference was ~ 8 mass. %). This can be explained by the presence on the surface of adsorbents of Lewis sites capable to thoroughly adsorb water. At the initial stage of adsorption of water vapors, the fast growth of adsorption capacity (Figure 1) was conditioned by formation of a monomolecular layer on the adsorbent surface - chemisorption. Further multi-molecular adsorption was conditioned by means of molecular interaction. The energy of these two processes differs significantly: for chemisorption - 6-9 kcal/mole of the adsorbed substance, and for physical adsorption - ~0.5 kcal/mole. It is possible that ~ 8 mass. % of residual water is a result of chemical interaction of water vapors with the adsorbent surface.

An increase in the alkaline content at the hydration stage during synthesis of sample 2A as compared to sample 1A led to the decrease in the adsorption rate (Figure 1, a; Table 2). This could be explained by an increase in the amount of potassium admixture in the near-surface layer, which led to a slowdown of mass transfer and diffusion reduction [9]. Nevertheless, the value of the ultimate adsorption capacity for these samples coincided. As Figure 1 b) shows, kinetic curves for these samples practically coincide.

The data obtained during analysis of kinetic curves of water vapors adsorption on samples 1A, 2A, 5A, 8A, are given in Table 2. The kinetic curves for all samples are described by the following equations: $-\ln(a_m - a) = \beta t - \ln a_m$, $a = k^* \ln \tau$, $a = A^* \tau^{1/2}$.

Approximation of the experimental data by the above-mentioned mathematical functions shows that equation $a=A^*\tau^{1/2}$ is best suited to describe kinetic curves on all experimental samples, since in this case the linear correlation coefficient is closest to one. The adsorption rate of water vapors for the samples under study is similar.



a) samples 1A and 2A

b) samples 5A and 8A

Figure 1. Kinetics of water vapor adsorption on the fraction of 0.5-1.0 mm of adsorbent granulate based on aluminum oxide, modified by cations of alkaline metals (velocity of the gas – carrier during adsorption – 30 l/h, during desorption – 10 l/h at T = 25 °C).

It is common knowledge that [10] for conventional porous desiccants (silica gel, zeolite, aluminum oxide), a limiting adsorption stage is water vapor diffusion in the adsorbent pores. This process is usually realized by the volume, more rarely – by the surface. The analysis of the kinetic curves of water vapor adsorption on the experimental samples of aluminum-oxide adsorbents, conducted in this work, confirms the appropriateness of using diffusion models to describe the process of water absorption by adsorbents.

N⁰	a _{max} ,	$-\ln(a_{m}-a)=$	βt - In a _m	a=k*lnτ		$a = A^* \tau^{1/2}$	
Sample	$\mathbf{g}_{water}/\mathbf{g}_{ads}$	β, min ⁻¹	R ₀	k	\mathbf{R}_2	Α	R ₁
1A	0.25	0.0279	0.97	0.0619	0.97	0.0220	0.98
2A	0.25	0.0234	0.95	0.0524	0.91	0.0205	0.99
5A	0.23	0.0298	0.95	0.0517	0.95	0.0209	0.99
8A	0.23	0.0258	0.98	0.0517	0.93	0.0208	0.99

Table 2. Characteristics of experimental samples.

4. Conclusions

As a result of the undertaken studies it was shown that modification of desiccants by potassium and sodium cations at the hydration stage of products of hydrargillite thermal activation during synthesis allowed obtaining adsorbents-desiccants with high values of static (more than 20 g/100g) and dynamic capacitance (more than 5.0 g/cm^3) by water vapors. To obtain the adsorbent with a more optimal set of characteristics, it was preferable to use sodium cations as a modifier and maintain the acid module at the level of 0.06 at the peptization stage.

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