Comparative assessment of characteristics of industrial and laboratory highly-efficient samples of adsorbents-desiccants

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Abstract. The research results of the physicochemical characteristics, adsorption kinetics and the value of adsorptive capacity, with reference to water vapors, of industrial adsorbents-desiccants Alumac 2-5H, Alusorb 675 and experimental samples based on aluminum oxide, obtained by centrifugal thermal activation of hydrargillite with its subsequent hydration in mild conditions, are presented. It is demonstrated that modification by sodium cations during synthesis at the hydration stage or impregnation with hygroscopic salt (CaCl₂) of the granules of synthesized aluminum oxide adsorbent allows obtaining desiccants with a higher value of dynamic capacity with respect to water vapors as compared to industrial adsorbents. The most balanced set of characteristics belongs to the aluminum oxide sample containing 0.6 % mass. of sodium, for which static capacity by water is higher than 20 g/100 g; the dynamic capacity value is at a level of 6.9 g/100 cm³, and the mechanical strength is 8.4 MPa.

1. Introduction
Aluminum oxide possesses unique properties; therefore, it is applied in different areas of production, in particular, as an adsorbent of water vapors from moisture-containing gases [1]. Water resistance is an important positive property of aluminum oxide and it often determines the selection of aluminum oxide as an adsorbent for drying and treatment of media containing condensed moisture. The use of a more effective desiccant (Al₂O₃) as a protective layer will allow for not only the protection of a bottom layer from condensed moisture but also an enhancement of the effectiveness and operational life of the adsorber [2]. The peculiarity of the developed adsorbents-desiccants based on aluminum oxide is their different phase and chemical compositions [3,4]. This work presents the research of the physicochemical and adsorption properties of two laboratory samples of adsorbents based on aluminum oxide, one of which is modified by sodium cations (OA-Na) and the other one is covered with hygroscopic salt – CaCl₂ [4] as compared with the samples of industrial aluminum oxide adsorbents in the comparable conditions.

2. Materials and methods of research
Laboratory samples of aluminum oxide desiccants based on bayerite and pseudoboehmite, synthesized by the technology of centrifugal and thermal activation of hydrargillite (CTA HG) with its subsequent hydration in mild conditions were used in the work [5,6]. Modification by sodium cations (sample OA-Na) was implemented at the stage of hydration of products of thermal activation of hydrargillite during synthesis of the bayerite-containing adsorbent. The pseudoboehmite-based (OA-CaCl₂) adsorbent sample impregnated with hygroscopic salt CaCl₂ was obtained by impregnating the matrix from the excess solution (equilibrium deposition filtration) [7]. A γ-Al₂O₃ sample in the form of granules of cylinder shape (5.0÷6.0 mm in length, 3.5÷3.6 mm in diameter) was used as a matrix (OA). The
laboratory samples were compared with the industrial samples based on activated alumina of Alumac 2-5H (AXENS Company, France) and Alusorb 675 (Salavat Catalyst Plant, Russia) grades, which were used for gas dewatering and cleaning from foreign and chemical impurities.

The mass fraction of Ca or Na in synthesized sorbents was determined by atomic emission spectroscopy of microwave plasma using the atomic emission spectrometer of microwave plasma “Agilent 4100” (Agilent -Technologies, USA) with preliminary “disclosure” of acids in the mixture in the system of microwave sample preparation “Speedwave four SW-4” (Berghof, USA). The content of the CaCl$_2$ salt in the adsorbent was calculated proceeding from the metal content. The textural characteristics of the adsorbents were determined by isotherms of nitrogen adsorption-desorption at 77 K using the 3Flex sorptometer (Micromeritics, USA). The mechanical strength of granules was assessed on the device “IPG -100” (Federal State Unitary Enterprise “UNIHIM with OZ”, Russia). The measurements were taken for 30 granules and the average value was found. The dynamic adsorption capacity (DC) of adsorbents with reference to water vapors was determined by means of measuring the amount of water vapors adsorbed from their mixture with the air, passing through the layer of adsorbent granules in the adsorber, at the moment of reaching the dew point temperature of the gas flow on exit from the adsorber (minus 40.0 °C). The resulting value was related to 100.0 cm$^3$ of the test sample. The layer height of the test sample (with the granule sizes of 2.0-4.0 mm in diameter and 2.0-4.0 mm in length) was 28.0-29.0 cm. The static adsorption capacity of the adsorbents with respect to water vapors was measured using the gravimetric method in the exsiccator. The static adsorption capacity (SC) of the samples was determined by the mass fraction of water absorbed by a mass unit of the adsorbent by the time of reaching adsorption equilibrium at a temperature of 25.0 °C in the atmosphere with relative humidity of 60.0 %. Experiments on the study of adsorption kinetics of water vapors on the modified samples were conducted using the adsorption plant and the quartz balance at a temperature of 25.0 °C and relative humidity of 100 % according to the procedure, described in work [8].

3. Results

According to the results of X-ray diffraction analysis, shown in Figure 1, the major phase of the samples under study is $\gamma$-Al$_2$O$_3$. The boehmite phase is present in the X-ray patterns of the industrial samples Alumac 2-5H and Alusorb 675. For the OA-CaCl$_2$ sample, the calcium chloride phase is not identified probably because of its X-ray amorphousness. The assumed interval of peaks of the calcium chloride phase is 15-40 $2\theta$.

![Figure 1. XRD-analysis of aluminium oxide materials (* $\gamma$-Al$_2$O$_3$, x - boehmite).](image)

As a result of studying the adsorption process, it was established that isotherms of nitrogen adsorption at relative pressures of 0.05-0.2 on all the samples were described by the BET equation. These isotherms belonged to isotherms of the IV type according to the IUPAC classification with an initially sudden rise at a low relative pressure, which was conditioned by the presence of micropores and a gradual increase
in the adsorption value with a pressure increase. In the range of relative pressures over 40%, adsorption-desorption isotherms exhibited pronounced hysteresis. This type of the isotherm pointed to the presence of mesopores on the surface of the samples under study, as well as the presence of reversible capillary condensation in adsorbent mesopores. The isotherms of low-temperature nitrogen sorption of industrial and modified laboratory samples of adsorbents are presented in Figure 2. It is established that the larger adsorption capacity by nitrogen belongs to the industrial samples of aluminum oxide adsorbents.

The composition, textural characteristics and values of the mechanical strength of the examined samples of the aluminum oxide adsorbents are given in Table 1.

| Sample  | Composition of the sample | Shape and sizes of granule, \( \text{mm} \) | \( \text{S}_{\text{BET}} \) (m\(^2\)/g) | \( V \) (cm\(^3\)/g) | \( d \) (nm) | Micropore surface area (m\(^2\)/g) | Limiting micropore volume (cm\(^3\)/g) | Crushing strength (MPa) |
|---------|---------------------------|------------------------------------------|-------------------------------|-----------------|----------------|-------------------------------|-------------------|-----------------|
| Alumac 2-5H | aluminum oxide, boehmite | Sphere \( \Omega = 2.0 \div 5.0 \) | 350 | 0.40 | 5.2 | 2 | 0.050 | 2.3 |
| Alusorb 675 | Al\(_2\)O\(_3\), boehmite | Sphere \( \Omega = 4.0 \div 4.3 \) | 373 | 0.45 | 4.9 | 77 | 0.037 | 14.5 |
| OA | Al\(_2\)O\(_3\) | Cylinder 3.6x5.2 | 290 | 0.36 | 4.8 | 226 | 0.104 | 7.1 |
| OA-Na | Al\(_2\)O\(_3\)+0.6 mass. % Na | Cylinder 3.6x5.2 | 315 | 0.30 | 3.8 | 97 | 0.047 | 8.4 |
| OA-CaCl\(_2\) | Al\(_2\)O\(_3\)+13.8 mass. % CaCl\(_2\) | Cylinder 3.6x5.2 | 144 | 0.21 | 5.9 | 119 | 0.055 | 4.9 |

The textural characteristics of the samples of the aluminum oxide were compared. It was established that the industrial samples of the adsorbents, initial sample and OA-Na sample have similar values of the specific surface, ranging from 290 to 380 m\(^2\)/g. At the same time, the surface area, occupied by the micropores, and the micropore volume for the industrial adsorbents are
lower. The value of the total volume and the average pore size for the industrial adsorbents is slightly higher than that of the initial sample of the aluminum oxide adsorbent and sample, modified by sodium cations. The introduction of hygroscopic salt into aluminum oxide makes major changes in the properties of hygroscopic salts and the initial adsorbent used as a matrix. This is manifested through the change in textural, adsorption and strength characteristics. When the salt content in aluminum oxide increases, the nitrogen adsorption capacity, volume of meso- and micropores, specific surface area decrease along with the increase in the diameter of mesopores. The pore-size distribution for all the examined samples of the desiccants is given in Figure 3. The samples under study are characterized by the presence in the structure of fine mesopores, being in the distribution interval of 3-8 nm. Samples OA-CaCl$_2$ and Alumac 2-5H have one maximum on the curve of pore-size distribution in a range of 3.5-4.3 nm. As regards Alusorb 675 and OA-Na samples, there is a bimodal distribution with the first maximum in the range of 3.5-4.3 nm and the second one in a range of 4.5-8.0 nm. The mechanical strength of the Alusorb 675 sample is the highest amongst all the analyzed adsorbents, and that of the foreign sample Alumac 2-5H is the lowest. The introduction of sodium cations into the adsorbent allowed increasing the mechanical strength of the OA-Na sample, and impregnation of the matrix with hygroscopic salt decreased the strength of the OA-CaCl$_2$ sample as compared to the initial sample.

The kinetic curves of adsorption of water vapors on the obtained samples of modified adsorbents are presented in Figure 4. The adsorption equilibrium for the OA-Na sample was reached in 90 minutes after the beginning of the experiment, and for the industrial samples – in 200-250 minutes. As for the sample, modified by calcium chloride, the water vapor adsorption capacity did not reach the equilibrium value after 5 hours since the beginning of the experiment.

![Figure 4. Kinetic curves of adsorption of water vapors on the samples for a fraction of 0.5–1.0 mm (conditions: carrier gas adsorption rate – 30 l/h).](image)

![Figure 5. Approximation of experimental data by equation $a=A \tau^{1/2}$.](image)

Approximation of the experimental data by different kinetic equations showed that the adsorption rate on all the samples was best described by the equation $a=A \tau^{1/2}$ (Figure 5), where $a$ - the amount of water adsorbed at time $\tau$; $A$ - the rate constant, g/min$^{1/2}$; $\tau$ - time, min. The values of rate constants $A$, determined in this equation for the samples under study, are given in Table 2. The equation of linear dependence of the adsorption value on $\sqrt{\tau}$ was earlier used specifically in the description of the kinetics of water vapor adsorption on aluminum oxide [9] and the composite material “calcium chloride/silica gel” [10]. The equation was evidence of the fact that the limiting stage of the process is water diffusion in the adsorbent pores.

![Table 2. Characteristics of the kinetic curves of water vapor adsorption on aluminum oxide samples and the values of static and dynamic capacity.](image)
Sample | \( a_{\text{max}} \) | \( a = A \times t^{1/2} \) | SC (g/100g ads) with 60% humidity | DC (g/100 cm³)
--- | --- | --- | --- | ---
Alumac 2-5H | 0.27 | 0.0208 | 0.99 | 21.1 | 4.4
Alusorb 675 | 0.25 | 0.018 | 0.98 | 21.0 | 5.0
OA-Na | 0.22 | 0.025 | 0.99 | 20.3 | 6.9
OA-CaCl₂ | 0.34 | 0.022 | 1.00 | 23.2 | 5.8
OA | 0.25 | 0.020 | 0.99 | 23.4 | 4.6

\( a \) value of the adsorption capacity in 280 minutes after the beginning of the experiment;
\( b \) R – linear correlation coefficient.

The values of the ultimate adsorption capacity by water, determined in the kinetic experiments, decrease amongst Alumac 2-5H, Alusorb 675, OA-Na. The values of static capacity change symbatically for these samples as well. Dynamic capacity in passing from Alumac 2-5H to OA-Na increases. As to the sample impregnated with calcium chloride, in a time of conducting the experiment (280 minutes), the value of the ultimate adsorption capacity was not obtained (Figure 4). A large value of static capacity (Table 2) and higher as compared to the industrial adsorbents dynamic capacity turned out to be typical of this sample. However, the largest dynamic capacity and adsorption rate among all the studied samples belong to the laboratory sample modified by sodium cations (OA-Na).

4. Conclusions
The introduction of modifying additives into aluminum oxide changes significantly the adsorbent properties. This is manifested in the change of textural, adsorption and strength characteristics. When aluminum oxide is impregnated with hygroscopic salt, the value of the specific surface decreases, the volume of meso- and micropores reduces. In this case the primary contribution into the adsorption process is made by the absorption of water vapors by hygroscopic salt [4]. As a result of the alkaline modification, the specific surface increases, but the average diameter and pore volume decrease. The most probable reasons for increasing the sorption indicators of this adsorbent, as compared to the initial sample (OA), can be a higher specific surface (Table 2), as well as formation of optimal acid-base properties of the surface, determined by the chemical modification. The kinetic curves of water vapors adsorption for all the adsorbents are best described by the equation applied for the processes the rate of which is limited by diffusion in the adsorbents pores. Adsorption rate constant A for the modified samples is higher than that of the initial sample and samples of industrial adsorbents.

All the examined samples of the adsorbents are characterized by the presence in the structure of small mesopores, pertaining to a narrow distribution range of 3.5-8.0 nm. The value of the specific surface for the industrial samples of adsorbents is slightly larger than that for the laboratory samples; however, the surface area, occupied by micropores, is less. In the micropores (with a diameter of less than 2 nm), there is the volume filling of the adsorption space. On the one hand, mesopores transport water vapors to micropores; on the other hand, mesopores adsorb water by means of the capillary condensation. When dewatering different gases in industry, dynamic sorption is most often applied. Therefore, the value of dynamic capacity of the desiccant, depending on the value of its specific surface, the volume of capacity and transport pores and their ratios, is of paramount importance when selecting an adsorbent. The conducted research demonstrates that the obtained experimental samples surpass the samples of the industrial adsorbents by this parameter. Besides, they have quite high static capacity and mechanical strength. The aluminum oxide sample, modified by sodium cations, turns out to be the most promising for using as a desiccant throughout the entire set of characteristics. For this sample, static capacity by
water is higher than 20g/100g, the value of dynamic capacity is at a level of 6.9 g/100 cm³, and the mechanical strength is 8.4 MPa.

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