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Influence of the composition of the adsorbent “hygroscopic salt/aluminum oxide” on its physicochemical 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 composite adsorbent “CaCl₂ – aluminum oxide”. Sorbent synthesized by centrifugal thermal activation of hydrargillite and its subsequent hydration in mild conditions was used as a carrier. It was shown that, in the studied range of change in the CaCl₂ content of the adsorbent (8.6-15.5% mass.), a sample containing 13.8% mass. of CaCl₂ was the most promising when used as a desiccant. This sample was characterized by static capacitance that was higher than 20 g/100 g, by quite high dynamic capacitance of 5.8 g/100 cm³ and good mechanical strength of 4.9 MPa.

1. Introduction

It is common knowledge that classic adsorbents (activated carbon, silica gel, aluminum oxide, zeolite) can act as a matrix for different hygroscopic inorganic salts [1]. Dehumidifying effect of such composite materials, known as sorbents of the “salt in the porous matrix” type, is based on a combination of adsorption principles owing to developed specific surface and volume absorption of water by the solution of hygroscopic salt. During gas dewatering, these sorbents have advantages over traditional desiccants since they possess higher sorption capacity and lower (150-200 °C) regeneration temperature [2]. The porous matrix is not only able to absorb adsorbate, but also acts as a dispersion medium, forming the required particle size of salt and its surface, can change the salt state and its properties and provides heat input through the solid phase and gas transport through the system of pores. Development of energy saving and environmentally safe technology of obtaining effective sorbent based on aluminum oxide applying centrifugal thermal activation (CTA) of hydrargillite and its subsequent hydration in mild conditions has allowed obtaining aluminum oxide which has a more developed surface and is characterized by the presence of meso- and micropores, as well as high strength [3-7]. In this connection, the study of a possibility of using this aluminum oxide adsorbent as a matrix is of interest. For instance, CaCl₂ can act as hygroscopic salt. Calcium chloride is a strongly hygroscopic salt; it absorbs energetically water vapors, thus forming a number of crystalline hydrates. Transitions of crystalline hydrates into each other are characterized by different temperatures: CaCl₂ · 6H₂O at 30.1 °C melts and



transforms into $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, then into $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (at 45.1 °C) and into $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ (at 175.5 °C). Calcium chloride is completely dehydrated only at temperatures above 250 °C [8]. However, practical application of massive salt is limited by the fact that at low relative pressure of water vapors (about 0.2), the solution possessing corrosion properties starts to form, which can be dangerous for reactors (adsorbers). To eliminate this effect, the salt is introduced into the adsorbent matrix pores [9]. In this paper, a series of adsorbents $\text{CaCl}_2/\text{Al}_2\text{O}_3$, differing by the content of hygroscopic salt in the samples, has been obtained and considered. Their physicochemical and adsorption characteristics have been studied in detail.

2. Materials and methods of research

A γ - Al_2O_3 sample in the form of granules of cylinder shape (5.0÷6.0 mm in length, 3.5÷3.6 mm in diameter), synthesized by centrifugal thermal activation of hydrargillite with its subsequent hydration in mild conditions, was used as a matrix. Conditions of synthesis of this sample were described in paper [10]. The mass fraction of Ca 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). Then, proceeding from the metal content, the salt content in the adsorbent was recalculated. Textural characteristics of the adsorbents were determined by isotherms of nitrogen adsorption-desorption at 77 K using the 3Flex sorptometer (Micromeritics, USA). The specific surface area was measured using the BET method. The mesopore volume was determined by analyzing the integral pore volume distribution curve depending on the radius (along the desorption branch); the average pore diameter (in nm) was determined by equation $d_{\text{ave}} = 4000V_{\text{pore}}/A$, where d_{ave} – average pore diameter; V_{pore} – volume pore; A was the pellet surface area [11]. The surface area occupied by micropores was evaluated by treating isotherms of nitrogen adsorption using Dubinin-Astakhov equation. To perform thermal analysis of aluminum oxides in argon atmosphere, the synchronous thermal analysis instrument “STA 449 F3, Jupiter”, made by NETZSCH (Germany), was used. The device simultaneously captured the differential scanning calorimetry (DSC) curves and the weight loss (WL). The temperature measurement range was 30-350 °C; the heating rate of the samples was 10 deg/min.

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 cm³ 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.

Static adsorption capacity of the adsorbents with respect to water vapors was measured using the gravimetric method in the exsiccator. The static adsorption capacitance (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 temperature of 25.0 °C in the atmosphere with a 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 temperature of 25.0 °C and relative humidity of 100 % according to the procedure, described in work [10].

3. Results

Before impregnation of the aluminum oxide, the salt used for impregnation was baked at temperature of 200 °C for 4 hours in the muffle electric furnace “EKPS 10” (Smolenskoe SKTB-SPU, Russia). The impregnated CaCl₂ samples of aluminum oxide adsorbents were obtained by impregnation from the solution excess (equilibrium deposition filtration) [12]. The composition and textural characteristics of the initial sample of aluminum oxide (sample No. 1) and samples of modified adsorbents synthesized on its basis (samples 2-5) are given in Table 1.

Table 1. Textural characteristics, crushing strength and modifying additives content in the alumina samples.

Sample	Composition of the sample	Content of hygroscopic salt (wt. %)	S _{BET} (m ² /g)	V _{mesopores} (cm ³ /g)	d _{mesopores} (nm)	Micropore surface area (m ² /g)	Limiting micropore volume (cm ³ /g)	Crushing strength (MPa)
1	Al ₂ O ₃	0	290	0.358	4.8	226	0.104	7.1
2	Al ₂ O ₃ +	8.6	225	0.314	5.2	177	0.080	4.1
3	CaCl ₂	12.7	182	0.301	6.0	143	0.065	4.1
4		13.8	144	0.245	6.1	119	0.055	4.9
5		15.5	96	0.180	6.6	79	0.036	6.8

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. Isotherms for the initial sample and sample No. 5 are shown in Figure 1 as an example.

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 initial sample of aluminum oxide possesses maximum nitrogen adsorption capacity, specific surface area, volume of micro- and mesopores, mechanical strength. 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 (Table 1, Figure 2). The mechanical strength of adsorbent granules containing 8.6 % mass. of the salt is significantly lower than that of the initial sample granules of aluminum oxide. However, when the salt content in the aluminum oxide rises, the strength of the modified sample granules increases (Table 1).

According to literature data [13], the process of water precipitation from Al₂O₃ was stepwise. At the first stage (up to 100 °C) there was precipitation of physically adsorbed water. At the second (100-350 °C) and third (350-550 °C) stages there was precipitation of chemically combined water. According to the data of work [14], the water from the sample, similar in composition to sample No 1, started to exude already at 52 °C, and the maximum of exudation fell to 136-153 °C. Peaks in the high-temperature region on the thermogram were absent for this sample.

The results of the study of the samples by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are given in Figure 3 and in Table 2.

As it turned out, there were two peaks in the temperature region up to 350 °C for the obtained samples on the DSC curves (Table 2). It is possible to note that when the salt content in the sample grew, there was a tendency towards an increase in the peak maximum temperature being in a higher temperature region (100-300 °C). At the same time, sample mass losses in the temperature range of 30 - 350 °C, determined by the TG-curve (Table 2), increased naturally as the content of hygroscopic salt in the

sample grew from 4.46 % mass. for sample No. 2 to 7.19 % mass. for sample No. 5. The water was removed from the samples more intensively in the temperature region of 100-350 °C.

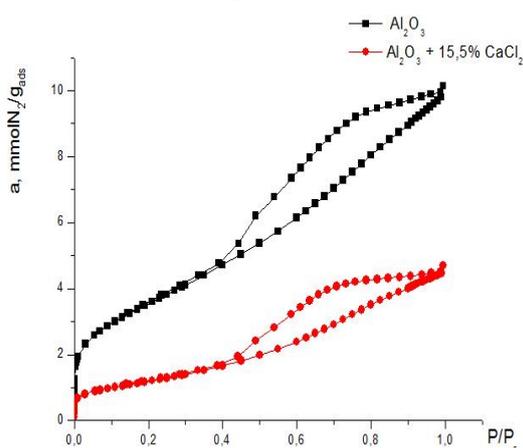


Figure 1. Isotherms of nitrogen adsorption-desorption on the initial Al₂O₃ sample and the sample containing 15% mass. of salt.

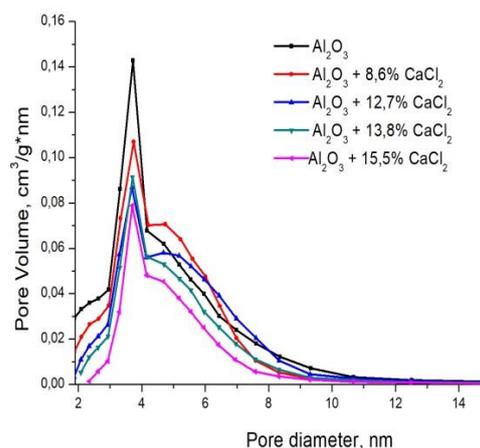
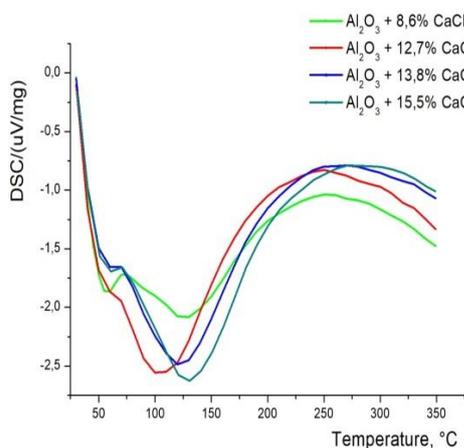
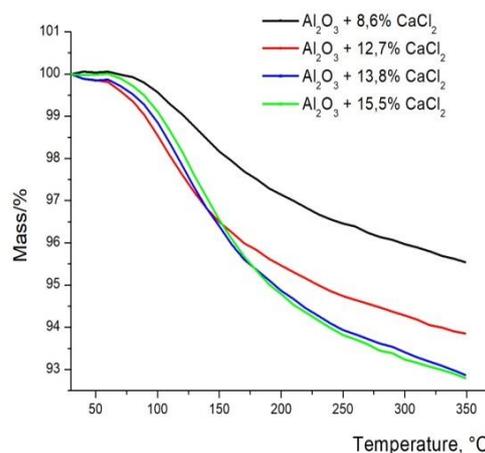


Figure 2. Pore size distribution of samples.



a)



b)

Figure 3. DSC (a) and TG (b) curves for modified samples.

Table 2. DTA and TGA data of the alumina samples.

Sample	The weight loss on the TG curve (%)
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	to 100°C (Δm_1^a)	from 100 °C to 350°C (Δm_2^b)	T_{max} (DSC) (°C)
1	0.20	3.30	140
2	0.42	4.04	58; 126
3	1.45	4.70	58; 103
4	1.15	5.95	60; 123
5	0.94	6.25	59; 129

^a Δm_1 – weight change determined by TGA at a heating rate of 10°/min to 100 C integration
^b Δm_2 – weight change determined by TGA at a heating rate of 10°/min to 350° C and holding for 1h

Kinetic curves of adsorption-desorption of water vapors on the obtained samples of modified adsorbents are presented in Figure 4. Adsorption equilibrium for the initial sample was reached 200 minutes later after the beginning of the experiment. In case of the samples modified by calcium chloride, the water vapor adsorption capacity did not reach the equilibrium value after 5 hours since the beginning of the experiment. Adsorption equilibrium for the initial sample was reached 200 minutes later after the beginning of the experiment. In case of the samples modified by calcium chloride, the water vapor adsorption capacity did not reach the equilibrium value after 5 hours since the beginning of the experiment.

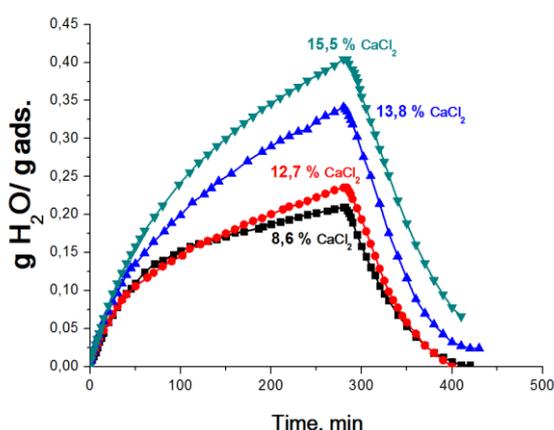


Figure 4. Kinetic curves of adsorption and desorption of water vapors on the samples for a fraction of 0.5–1.0 mm (conditions: carrier gas adsorption rate – at 30 l/h, desorption – at 10 l/h).

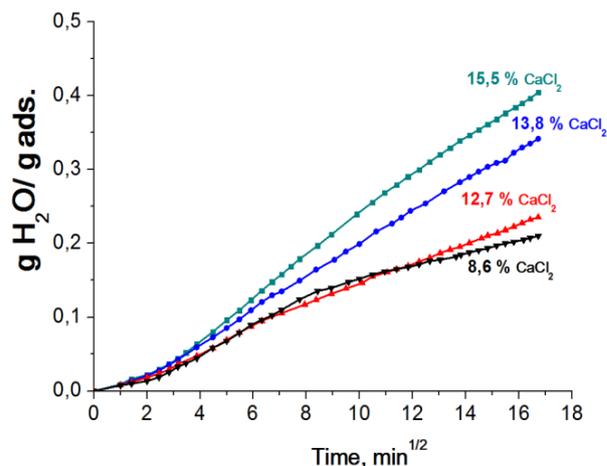


Figure 5. Approximation of experimental data by equation $a=A t^{1/2}$.

Approximation of the experimental data by different kinetic equations showed that the rate of the adsorption process was described best of all by equation $a=A t^{1/2}$ (Figure 5), where a - the amount of water adsorbed at time t ; A - the rate constant, $g/min^{-1/2}$; t - time, min. Values of rate constants A determined in this equation for the samples under study are given in Table 3. The equation of linear dependence of the adsorption value on $t^{1/2}$ was earlier used specifically in the description of water vapor adsorption kinetics on aluminum oxide [15] and the composite material – “calcium chloride/silica gel” [16]. The equation was evidence of the fact that the limiting stage of the process is water diffusion in the adsorbent pores.

Table 3. Characteristics of the kinetic curves of water vapor adsorption on alumina samples and the values of static and dynamic capacitance.

Sample	a, $t=280\text{min}$ (g/g _{ads})	A (g /min ^{-1/2})	SC (g/100g _{ads}) at 60% humidity	DC (g/100 cm ³)
1	0.246 ^a	0.0199	23.4	4.6
2	0.210	0.0134	21.4	7.0
3	0.235	0.0146	21.0	6.8
4	0.341	0.0217	23.2	5.8
5	0.404	0.0263	29.5	4.3

^afor the initial sample, reaching ultimate water adsorption capacity for 200 minutes was registered.

The adsorption capacity of the modified samples with respect to water vapors and rate constants (Table 3), determined from kinetic data, increase when the salt content grows. When the content of aluminum oxide is at the level of 13.8 mass. % of CaCl₂ and higher, these characteristics exceed the values determined for the initial sample. Values of static capacitance also change symbatically for these samples. Dynamic capacitance with respect to water vapors, when introduced into aluminum oxide, at first increases, but the salt content higher than 12.7% mass. gradually decreases.

4. Conclusions

Introduction of hygroscopic salt into aluminum oxide makes major changes in properties of hygroscopic salts and initial adsorbent used as a matrix. This is manifested through the change in textural, adsorption and strength characteristics, in the form of curves on thermograms. When the salt content increases, the value of specific surface decreases; the volume of meso- and micropores decreases. The porous matrix, in this case aluminum oxide, is primarily a medium facilitating dispersion of salt. It is noted in work [1] that on such carriers as γ -Al₂O₃, having 6-9 nm pores, there is stronger dispersion of salt, which significantly influences the sorption behavior of impregnated desiccant. In the pores of the mentioned systems, stoichiometric crystalline hydrates does not form at all. This fact can explain the absence of peaks on DSC curves, corresponding to their decomposition. The water vapor adsorption capacity of impregnated aluminum oxide desiccants, determined by kinetic curves, grows with the increase in the percentage content of salt in the samples. The same tendency is observed in case of static capacitance. This bears evidence of predominant contribution of hygroscopic salt in the adsorption process. Since just adsorption properties of hygroscopic salt determine the properties of the entire composite, a low value of specific surface of obtained adsorbents does not play a pivotal role. The kinetic curves of aluminum oxide adsorbents with addition of hygroscopic salts are best described by the equation used for description of processes the speed of which is limited by diffusion in adsorbents pores. Adsorption rate constant A increases along with the amount of the introduced modifier. Among the experimental samples impregnated by hygroscopic salts throughout the entire set of characteristics, sample No. 4 is the most promising for the use as a desiccant, of which the following is typical: the value of static capacitance is higher than 20 g/100g, the high value of dynamic water capacitance is at the level of 5.8 g/100 cm³, and good mechanical strength is 4.9 MPa.

Acknowledgments

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