Influence of alkaline modification on adsorption properties of alumina

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Abstract. The kinetics of water vapor adsorption on alumina adsorbents at a temperature of 25 °C was studied. It was shown that modification by cations of alkali metals (K, Na) of the adsorbent based on alumina allows increasing its efficiency in the process of water vapor adsorption. The mathematical treatment of the experimental data by the dependence of water vapor adsorption on the time with the help of the Linear Driving Force (LDF) model and the dependence of adsorbent's adsorption capacity on the water vapor concentration (adsorption isotherm) by Dubinin-Astakhov equation was carried out. Constants included in the equations were defined.

1. Introduction

In most technological cycles, compressed air is used as frequently as electric power. At the current stage of technical development, air has to be dried everywhere, which is associated with a significant raise of the requirements for air quality. Year by year, an increasing number of high-tech enterprises are appearing, for which air humidity must have a strictly fixed value. In current technology, deep gas dewatering by means of adsorbents has replaced almost all other possible methods [1]. Desiccants based on active alumina are still most in demand in the market of adsorbents-desiccants [2]. High activity of alumina when interacting with polar adsorbates (primarily water vapors) ensures deep gas dewatering to the dew point (- 60 °C) and below. Advantages of alumina, providing its wide application along with such adsorbents as zeolites and silica gels, are thermodynamic stability, relative ease of production, as well as availability of raw materials.

Optimization of conditions of desiccants preparation, based on alumina, by using precursors of different phase compositions and dispersions, heat treatment conditions, introduction of modifying additives allows increasing significantly their adsorption capacity with respect to water and efficiency of the dehydration system as a whole. There are studies on highly effective alumina desiccant adsorbents based on low-temperature forms of aluminium oxide (η-, γ- and χ-) received by means of incineration of alkaline hydration products of thermally activated alumina containing bayerite phases of 50% and more [3-5]. Chemical modification of surfaces with acids and bases has become a more widespread method used to increase adsorption capacity of active aluminium oxide. When sulphuric acid was introduced at the preparation stage of moulding sorbent mass, the samples received from pseudoboehmite-contained aluminium hydroxide were comparable in dynamic capacity rates to bayerite-based adsorbents, and even exceeded them in the static capacity rate [5]. This is related to the change in the phase composition, textural characteristics, and acid–base surface properties. Moreover,

a greater modifying effect was observed in desiccants based on γ-Al_2O_3 that had a greater quantity of Bronsted acid sites (BAS) and potent Lewis acid sites (LAS) after introduction of sulphate ions, and the average diameter of pores was reduced. With alkaline solutions of NaOH and KOH, used at the stage, which contain moldable pastes made from pseudoboehmite-containing hydroxides that are produced by the centrifugal thermal activation method, it is possible to prepare strong grains of desiccants with high static and dynamic capacity that compares well with the best values previously reached for desiccants based on η-Al_2O_3 [2].

The main parameters of the equilibrium process are assumed to be the maximum adsorption capacity of sorbent, which serves as a basis for determining its optimum mass in the adsorber and the adsorption rate [6, 7].

In the paper, studies on the kinetics of water vapor adsorption on alumina adsorbents at a temperature of 250 °C, their characterization by physicochemical methods, as well as mathematical treatment of experimental kinetic curves of water vapor adsorption and adsorption isotherms, were undertaken.

2. Experimental part

2.1. Materials

The objects of the study were 3 samples based on pseudoboehmite synthesized by centrifugal thermal activation of hydrargillite with its subsequent hydration under mild conditions (A-2-9C - an initial sample; A-2-Na-9C and A-2-K-9C are modified by Na and K ions accordingly) at the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences. Samples of alumina desiccants were represented by mixed phases of alumina $(\gamma+\chi)$-Al_2O_3 with an insignificant content of pseudoboehmite [8]. These samples were previously subjected to 9 cycles of adsorption-regeneration when studying their water vapor absorption at a pressure of 30 atm on a pilot 2-reactor adsorption plant (PAP) at the NIOST LLC - R and D center of CJSC SIBUR Holding, Russia [8]. Prior to cyclic tests, all samples had similar values of the specific surface area lying in the range of 280-310 m^2/g. After the tests, the specific surface area of the samples decreased, which was especially noticeable in the case of sample A-2-9C (from 308 to 201 m^2/g), and the crush strength of the samples (within the error of determination) did not change. As a result of the tests on the pilot plant, the surface condition of the samples under study stabilized. These samples of adsorbents were used for subsequent study of the adsorption characteristics at a pressure close to atmospheric pressure on laboratory adsorption plant (Tomsk State University, Russia) using quartz weights Mac-Ben-Bakr described in the work [9]. The content of modifying agents in the samples, their textural characteristics, crushing strength values are given in table 1.

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

Sample	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	Content of modif. additives, wt. %	Crushing strength, MPa
A-2-9C*	201	0.27	4.9	170	0.078	0.11 Na; 0.01 K	24
A-2-Na-9C	230	0.39	6.3	166	0.076	2.0 Na; 0.02 K	14
A-2-K-9C	233	0.39	6.2	178	0.082	0.13 Na; 2.1 K	13

*9C - samples subject to nine cycles of adsorption-desorption of water vapor on PAP

2.2. Research methods

The phase composition of sorbents was determined using X-ray diffraction (XRD) on a Rigaku Miniflex 600 diffractometer (Rigaku corp., Japan). Sodium and potassium contents in samples were determined with inductively coupled plasma mass spectrometry using the Agilent 7500cx (Agilent Technologies, USA). 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 $d_{ave} = 4000V_{pore}/A$, where d_{ave} – average pore diameter; V_{pore} – volume pore; A was the pellet surface area [10]. The surface area occupied by micropores was evaluated by treating isotherms of nitrogen adsorption using Dubinin-Astakhov equation (D-A).

The dynamic method was used in this study to observe adsorption of water vapours. The adsorption value had been determined by the weight method using a Mac-Ben-Bakr spring scale. The scale's sensitiveness was $2.9 \cdot 10^3$ g/mm. The elongation of the spiral was fixed with a V-630 cathetometer. Prior to the performance of adsorption measurements, each sample was regenerated at 200 °C in argon flow supplied during an hour at 5 l/hour. Wet argon was supplied to the sample to perform water vapour adsorption. Experiments were carried out under similar conditions: temperature – 25 °C, humidity – 100 %, the sample's grains were arranged in one layer. To exclude an impact of substance's advance speed on the outer granule surface, a series of experiments on water vapour adsorption at different gradually increasing flow rates up to 36 l/hour had been conducted before. It was established experimentally that when the speed of the gas was 27 l/h and above, the kinetics of water vapor adsorption did not depend on the flow rate of gas. On this basis, it was selected as the optimum feed rate of the wet gas amounting to 30 l/h. Adsorption equilibria of water vapor on these adsorbents were determined at 298 K, covering the entire humidity range to saturation. To construct isotherms of water vapor adsorption, equilibrium values of adsorption values obtained when reading the kinetic curves of water vapor adsorption with different contents of water vapor in the supplied gaseous mixture were used. The change in the water vapor concentration in the gas flow was achieved by mixing dry and wet argon (100 % of humidity) in the calculated ratios.

Samples' crush strength was determined using catalysts' hardness tester Lintel PC-21(BSKB Neftekhimavtomatika, Russia). For the study, 24 uniformly-sized adsorbent granules, shaped as cylinders, were selected. To avoid adsorption of water vapors from the air, the measurements were conducted over the shortest period of time. To reduce the influence of granules' surface roughness (parallelism of granule ends), the measurement was carried out using a thin paper insert between a device's rod and a sample granule.

3. Results and discussion

As a result of studying the adsorption process, it was established that isotherms of nitrogen adsorption at relative pressures of 0.05-0.3 on the samples is described by the BET equation. These isotherms belong to isotherms of the IV type according to the IUPAC classification with an initially sudden rise at a low relative pressure, which is conditioned by the presence of micropores and a gradual increase of the adsorption value with a pressure increase (figure 1).
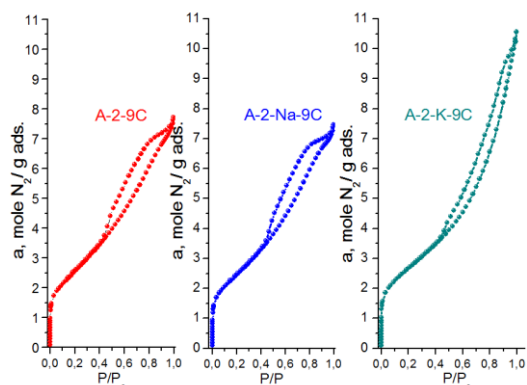
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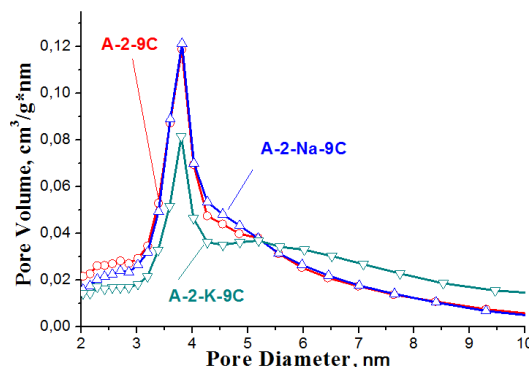**Figure 1.** Isotherms of nitrogen adsorption on test samples.

Figure 2. Pore size distribution of samples A-2-9C, A-2-Na-9C, A-2-K-9C.

In the range of relative pressures over 40 %, adsorption-desorption isotherms exhibited pronounced hysteresis. This type of the isotherm points 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. Nitrogen adsorption capacity, i.e. the pore volume, was the largest in the sample containing potassium – A-2-K-9C. For the initial sample - A-2-9C and a sample containing sodium – A-2-Na-9C, adsorption capacities were comparable.

The data on the distribution of pores by the sizes of the investigated samples (figure 2) are evidence of the presence of small mesopores in the adsorbents under study (3 ÷ 8 nm) with a maximum volume of pores ~ 4 nm in diameter. As follows from the data in table 1, using alkalis for plastification of pseudoboehmite-containing aluminum hydroxide (reference sample A-2-9C, table 1) results in that desiccants with larger average pore diameter and mesopore volume are formed, which confirms the data given in [2].

Figure 3 and table 1 show the data on measurement of the kinetics of water vapor adsorption on the test samples. It turned out that alkaline modification of the alumina adsorbents' surface led to an increase in the adsorption capacity (a). The modification by potassium led to an increase in adsorption capacity a^* (by ~ 19 %) as compared to the unmodified adsorbent.

The experimental kinetic curves shown in figure 3 were analyzed using the mathematical model "Linear Driving Force" (LDF) proposed by Glueckauf [11] for processes of water vapor absorption by the surface of hydrophilic adsorbents [12].
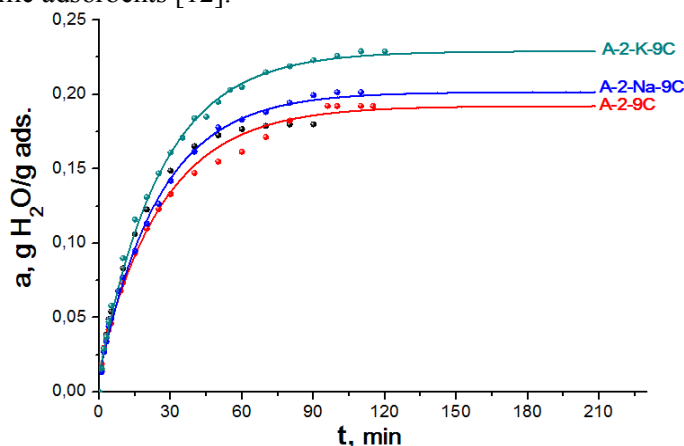

Figure 3. Kinetic curves of adsorption and desorption of water vapor on the samples for a fraction of 0.5–1.0 mm: A-2-9C, A-2-Na-9C, A-2-K-9C. Points are experimental data; lines are calculated according to the Glueckauf equation; (conditions: carrier gas adsorption rate – at 30 l/h, desorption – at 10 l/h).

When adsorbing water vapor under isothermal conditions at constant partial pressure (P_0), the kinetics of water vapor absorption on aluminium oxide (figure 3) is well described by the equation given in [13]:

$$\frac{a}{a_m} = 1 - e^{-KT} \quad (1)$$

where a is the amount of water adsorbed at time t on an initially clean adsorbent; a_m is the equilibrium adsorption capacity of water at P_0 and temperature T; K is the rate constant, min^{-1}; t - time, min. As table 2 shows, for the studied samples the constant of the adsorption rate changes symbatically relatively the value of their adsorption capacity.

Table 2. Characteristics of the kinetic curves of the water vapor adsorption on the alumina samples and Dubinin-Astakhov equation.

Sample	a_m, g/g $_{ads}$	K, min^{-1}	q_s, mmol/g	βE, kJ/mole
A-2-9C	0.192	0.0320	11.7	1.91
A-2-Na-9C	0.204	0.0397	9.7	2.17
A-2-K-9C	0.229	0.0399	10.8	1.72

The equilibrium in the adsorption system depends on the nature of the adsorbent-adsorbate interaction and is determined by the adsorbent texture. Many studies have been undertaken to research the water adsorption isotherms and models on activated alumina. Numerous studies of water vapor adsorption on different activated aluminas can be found in the literature, and various adsorption isotherm equations for water vapor adsorption on aluminas have been also established by researchers. The isotherms for pure water vapour adsorption on activated aluminas are typically Type I (microporous) or Type IV (mesoporous) in the shape according to the Brunauer classification. Empirical adsorption equilibrium models like Langmuir and Freundlich can generally be used to describe type I pure water vapour adsorption isotherms on aluminas. The Toth equation can be used when the alumina is energetically heterogeneous and the isotherm shape is Type I [13].

In the case of the water vapor/alumina system, as it presents a type II isotherm, the n-layer BET equation (eq 2), frequently employed in the correlation of this type of isotherm [7], was used:

$$\frac{q}{q_m} = \frac{C_{BET} \cdot x [1 - (1 - (n+1)x^n + n \cdot x^{n+1}]}{(1-x) \cdot [1 + (C_{BET} - 1) \cdot x - C_{BET} \cdot x^{n+1}]} \, . \qquad (2)$$

In this equation, x = P/P_0 and P, Po are the water vapor equilibrium and saturation pressures respectively and C_{BET}, q_m, and *n* are the isotherm fitting parameters. Parameter q_m is related to the monolayer coverage and C_{BET} – to the convexity of the isotherm at the low partial pressures. As for parameter *n*, when it is equal to 1, the n-layer BET equation reduces to the Langmuir equation, while as it approaches the infinite, the classical BET equation is obtained.

Equation D-A is the most widely used equation for describing vapor adsorption on porous adsorbents [14]:

$$q = q_s \exp \left\{ -\left[\frac{RT}{\beta E} ln(Po/P)\right]^m \right\}. \qquad (3)$$

In equation (3), q is the equilibrium molar loading; q_s is the maximum molar loading; E is the characteristic energy of adsorption; P and Po(T) are the equilibrium and saturation pressures respectively; R is the ideal gas law constant; T is the absolute temperature and m is a heterogeneity parameter related to the pore size distribution of the adsorbent. Parameter β is a constant which is a function of the adsorption only. It has been found by Dubinin and Timofeev (1946) that this parameter is proportional to the liquid molar volume [15].

Previously D-A equation was used to describe isotherms of water vapor adsorption on commercial samples of active alumina in works [16 - 18]. Value m in equation D-A for the industrial adsorbents, studied in these works, varied from 0.332 to 0.67, and E – from 0.7 to 1.99 kJ/mole.

If we take parameter m = 1, then the linear form of equation (3) takes the form:

$$\ln q = \ln q_s + \frac{RT}{\beta E} \ln(P/P_0). \qquad (4)$$

The experimentally obtained isotherms are rectified in the coordinates: $\ln q - \ln(P/P_0)$ with a linear correlation coefficient of 0.99; this suggests that the equation describes quite well the experimental data and can be used in the calculation of the characteristic energy of adsorption and the maximum molar loading. Calculated parameters q_s and βE of the equation are given in table 2. Comparison of the results of the calculation by equation (4) in case of parameter m = 1 with the experimental data shown in figure 4 also demonstrates that this equation describes the experimental results quite well. The values of parameter m for different adsorbents usually vary within 1-3, rising with an increase of energy uniformity. The lowest value of parameter q_s was fixed for sample A-2-Na-9C, which probably can be related to the lower value of the surface area occupied by micropores for this sample.
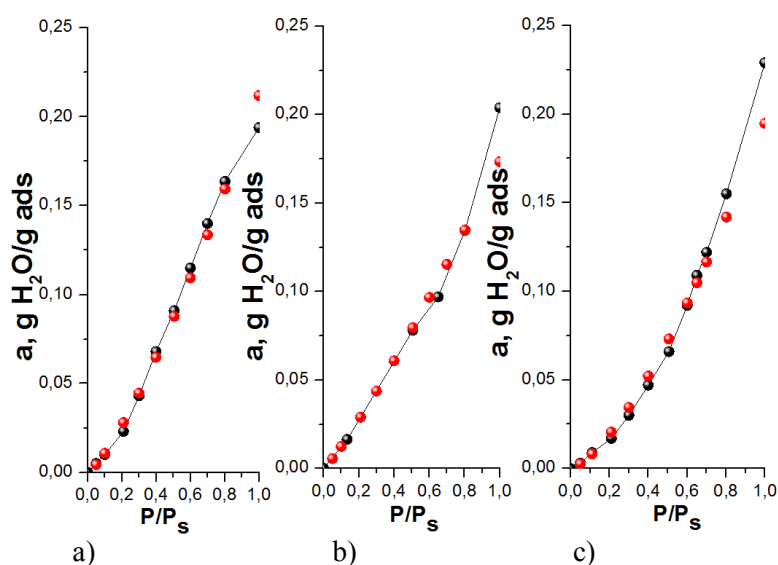

Figure 4. Adsorption isotherms of water vapor on a) A-2-9C, b) A-2-Na-9C and c) A-2-K-9C at 298 K (lines [—■—] - experimental; points [▲] - Dubinin-Astakhov fitting).

4. Conclusion

According to the results of the work, the following conclusions can be drawn:

Modification of the surface of alumina adsorbents with alkali metal cations (K, Na) allowed increasing their efficiency during water vapor adsorption. The modification by potassium led to an increase in adsorption capacity a^* (by ~ 19%) as compared to the unmodified adsorbent. However, during modification the crush strength of the adsorbent decreased.

Textural characteristics of the samples were studied using the BET method. It was shown that the obtained samples of alumina adsorbents have a surface with small mesopores of $3 \div 8$ nm in size. It was established that the samples modified by K and Na cations have a large volume (by 44%) and an average size of fine mesopores (by 29 %) as compared to the original sample ($V_{mesopores} = 0.27 cm^3/g$, $d_{mezopores} = 4.9$ nm). They also contain micropores ($S_{microporous} \approx 170$ m^2/ g).

It was demonstrated that the kinetics of water vapor adsorption on the test samples of fine fraction ($0.5 \div 1.0$ mm) of alumina adsorbents can be described quite well by the Linear Driving Force (LDF) model. The values of constants of the water vapor diffusion rate (K) and equilibrium values of the adsorption capacity (a_m) were determined.

It was established that experimental data of the dependence of the adsorbent's adsorption capacity on the water vapor concentration (adsorption isotherm) were a good fit with Dubinin-Astakhov equation. The parameters of the equation for the considered samples of the adsorbents were determined.

Acknowledgments

References

[1]   Shumyatsky Yu 2005 Adsorption processes, available at: http://www.studmed.ru/download/e0d8980d234/

[2]   Danilevich V, Isupova L, Danilova I, Zotov R and Ushakov V 2016 Characteristics optimization of activated alumina desiccants based on product of a centrifugal thermal activation of gibbsite *Russian Journal of Applied Chemistry* **89/3** 343-353

[3]   Danilevich V; Isupova L; Kagyrmanova A; Kharina I; Zyuzin D; Noskov A 2012 Highly Effective Water Adsorbents Based on Aluminum Oxide *Kinet. Catal.* **53** 632–639

[4]   Zotov R; Glazyrin A; Danilevich V; Kharina I; Zyuzin D; Volodin A and Isupova L 2012 Influence of the Temperature of Calcination of Bayerite-Containing Aluminum Hydroxide Pellets on the Water Vapour Adsorption Capacity and Acid-Base Properties of Alumina *Kinet. Catal.* **53** 570–576

[5]   Danilevich V; Isupova L; Paukshtis E and Ushakov V 2014 Effect of modifying desiccants with sulfuric acid on their physiochemical properties *Kinet. Catal.* **55** 372–379

[6]   Zelentsov V and Datsko T 2012 Application of adsorption models for describing equilibrium in the system of aluminium oxyhydroxide – fluorine *Electronic material processing* **48 (6)** 65–73

[7]   Ribeiro A, Sauer T, Carlos A, Moreira R, Loureiro J and Alı´rio E 2008 Adsorption Equilibrium and Kinetics of Water Vapor on Different Adsorbents. *Ind. Eng. Chem. Res.* **47** 7019–7026

[8]   Zotov R, Isupova L, Danilevich V, Babina A, Sinelnikov A, Meshcheryakov E and Kurzina I 2016 Dynamic capacity at increased pressure of desiccants based on modified alumina // Catalysis in industry **16/5** 6–13

[9]   Livanova A, Meshcheryakov E, Reshetnikov S and Kurzina I 2017 Study of water vapour adsorption kinetics on aluminium oxide materials *AIP Conf. Proc.* **1899** 020018-1–020018-6. DOI: 10.1063/1.5009843

[10] Fenelonov V Introduction to Physical Chemistry of Adsorbents and Catalysts Supramolecular Structure (*Publ. House of the Siberian Branch of the Russian Academy of Science, Novosibirsk 2004*) 440

[11] Glueckauf E and Coates J 1947 *J. Chem. Soc.* 1315–1321

[12] Reshetnikov S, Livanova A, Meshcheryakov E, Kurzina I and Isupova L 2017 Kinetic regularities of adsorption on alumina desiccants doped with cations of alkali metals *J. Appl. Chem.* **90** 1451-1457

[13] Sircar S, Rao M and Golden T 1996 Drying of gases and liquids by activated alumina *Stud. Surf. Sci. Catal.* **96** 629–646

[14] Marcussen L and Vinding C 1982 Experimental Breakthrough Curves Determined under Carefully Controlled Conditions for the Adsorption of Water Vapor on Alumina in Adiabatic Fixed Bed *Chem. Eng. Sci.* **37/2** 311–317

[15] Duong D. 1998 Adsorption Analysis: Equilibrium and Kinetics *Imperial College Press* **2** 888

[16] Moore Joshua D and Serbezov A 2005 Correlation of Adsorption Equilibrium Data for Water Vapor on F-200 Activated Alumina *Adsorption* **11** 65–75

[17] Solomon I, Ribeiro A, Santos J, Loureiro J, Rodrigues A, Sandu I and Mămăligă I 2013 Adsorption equilibrium of water vapor on activated carbon and alumina and carbon and

alumina impregnated with hygroscopic salt *Turk. J. Chem.* **37** 358–365

[18]   Ambrożek B, Zwarycz-Makles K and Szaflik W 2012 Equilibrium fnd heat of adsorption for
          selected adsorbent-adsorbate pairs used in adsorption heat *Polska energetyka słoneczna*
          10(1-4) 4–11