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ADSORPTION STUDY OF COMPOSITE AND GRANULAR ADSORBENTS

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The paper presents an adsorption study of granular and composite adsorbents together with an analysis of the obtained images of the adsorbent surfaces. Based on the desiccator method of studying adsorbents, adsorption isotherms were plotted. According to these isotherms, active aluminum oxide was established as optimum for the manufacture of composite adsorption materials. However, the adsorption capacity of composite materials is less than that of granular adsorbents by 10–15%, which is compensated by higher density values.

Keywords: adsorption, compressed air, dryer, gas drying, adsorbent, monolith, composite

Introduction

For an industrial adsorption purification and gas drying, adsorbents with a developed inner surface (activated carbon, silica gels, aluminogels) are traditionally used in a granulated, crushed or powdered form. In addition, composite adsorption materials (CAMs) [1, 2] are used, including matrix-type materials [2], consisting of a plastic base (binder) and a filler (initial adsorbent). In this case, materials with a controlled composition and adapted to different requirements can be created. The properties of CAM components, as well as the parameters of their molding and thermal treatment, directly affect the properties of the obtained composite adsorption materials. In this regard, along with comparisons of the characteristics of CAMs and initial materials, studies of the relationship between the technological parameters of the internal structure formation and characteristics of composite adsorption materials (such as packing density, adsorption capacity, surface structure) adsorbents appear to be relevant, [3].

The main source of information for assessing the physicochemical and technological characteristics of adsorbents, as well as for the comparative analysis of adsorption materials, involves the adsorption isotherm, which represents the dependence of the adsorbed substance quantity on the partial pressure of this substance in the gas phase at a constant temperature [4–6]. Another important characteristic of the adsorption material is the type (size) of pores: according to the accepted classification, macro-, meso-, and micropores are distinguished [5–7].

Industrial adsorbents may have pores of various sizes. If the pore fractions of different types in the adsorbent are commensurate, then the adsorbent is classified as mixed. A correlation between the types of isotherms and pores can be noted [4].

The present work sets out to experimentally study the adsorption characteristics of both granular and molded adsorbents by the construction of adsorption isotherms to select the best material for compressed gas drying up to low dew point values in short-cycle non-heating adsorption (SCA) units [8].

The advantages of SCA over high-heating regeneration drying include a significant reduction in energy (due to the absence of the energy consumption for gas heating) and time costs (heating and cooling of the adsorber

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are inertial long-term processes). In addition, SCA units are characterized by the simplicity of their design and process automation scheme [1, 8, 9].

In order to analyze the surface condition, commercially available adsorbents, based on zeolites and active aluminum oxide (AAO), as well as the prototypes of AAO-based CAMs were selected.

AAO is superior in characteristics to silica gels (at a low humidity) and zeolites (at a high humidity). An additional peculiarity of aluminum oxide is its water resistance, which often determines the selection of AAO in terms of an adsorbent for drying and processing media that contain drip moisture.

Six CAM samples (KM-1 – KM-6) were prepared using AAO-1 adsorbent (manufactured by Sorbis Grupp LLC, Russia) under various molding conditions: $x_1 < x_2 < x_3$, $p_1 < p_2 < p_3$, $t_1 < t_2$ (x – mass ratio of the polymer binder and the adsorbent; p – molding pressure; t – molding duration). The conditions were selected taking into account the minimum values of the binder quantity, pressure, and molding duration (i.e., taking into account the lowest costs).

Among the six prepared CAM samples, two retained their shape: KM-1 (x_3, p_2, t_1) and KM-5 (x_1, p_3, t_1).

Static and dynamic methods are traditionally used to study the adsorption of gases and vapors by solids. When using static methods, the adsorbent is placed in a gas or vapor atmosphere to allow the equilibrium pressures, temperature, and quantity of an absorbate to be measured following the establishment of equilibrium. The adsorption capacity is determined either by increasing the mass of the adsorbent (gravimetric method), or by the difference in the quantity of the adsorbate, which is injected into the measuring cell and remained in the equilibrium gas phase following contact with the adsorbent (volumetric method). *With dynamic methods,* the concentrations of the adsorbate in the flow at the inlet and outlet of the adsorber are measured [4, 5].

In the present work, adsorption materials were studied using the static gravimetric desiccator method. This approach is commonly used in engineering practice to control the quality of adsorbents due to its simplicity. The essence of the method consists in the saturation of the regenerated adsorbent sample, which is placed in weighing bottles with adsorbent vapors; here, the adsorption capacity is determined by the mass difference of the weighing bottle with the adsorbent both before and after posthunmsaturation [4]. The adsorbate consists of water; the specified water vapor pressure in the volume of the desiccator is provided by sulfuric acid solutions of various concentrations [10].

Various adsorbents were experimentally studied by the desiccator method [3]:

– granular mesoporous adsorbents – active aluminum oxides AAO-1 (Sorbis Grupp LLC, Russia) and AAO-2 (Real Sorb LLC, Russia);

– granular microporous adsorbents – SaA-1 and SaA-2 zeolites (Real Sorb LLC, Russia) with granular diameters of 0.4–0.8 and 1.6–2.0 mm, respectively;

– composite adsorption materials (based on an AAO-1 adsorbent) KM-1 and KM-5, obtained under various molding conditions.

Samples of adsorbents with a mass of 0.05 g (Fig. 1) were pre-dried at 105°C for 2 h to a constant mass.

The samples were then placed in desiccators together with sulfuric acid solutions corresponding to certain humidity values φ (see Table 1) and weighed every 30 min until reaching a constant mass. The error of the results (not more than 15%) was determined by the method of estimating the error of an indirectly measured value at single measurements [8].

Using a Phenom Pro X electron microscope with the system of an integrated energy dispersion analysis (maximum magnification 150,000×, resolution 8 nm), the surface images of the studied adsorption materials were obtained.

Fig. 1. Weighing bottles with samples, placed in desiccators.

Table 1
Parameters of Sulfuric Acid Solutions for Desiccators at a Temperature of 25°C

Solution concentration, %	Solution density, g/mLiter	Relative humidity φ of air above the solution, %
5.0	1.0230	98
38.3	1.2845	60
50.0	1.2950	35
55.0	1.4412	25
64.5	1.5439	10
70.0	1.6059	4.5

The adsorption capacity of samples a (g/100 g) is determined by the formula [10]:

$$a = \frac{m_i - m_d}{m_d - m_b} \cdot 100\%, \quad (1)$$

where

m_i – mass of the weighing bottle with the adsorbent after the establishment of the adsorption equilibrium, g;

m_d – mass of the bottle with the dried adsorbent, g;

m_b – mass of the empty bottle, g;

100 – conversion coefficient.

Results and Discussion

According to the analysis of adsorbent surface images (Fig. 2), the structure of the presented adsorbents was characterized as micro-grained and chaotic.

Fig. 2. Surface images of the initial adsorption materials: (a) AAO-1 (magnification 710×); (b) AAO-1, fraction 1 mm (magnification 470x); (c) SaA (magnification 470×).

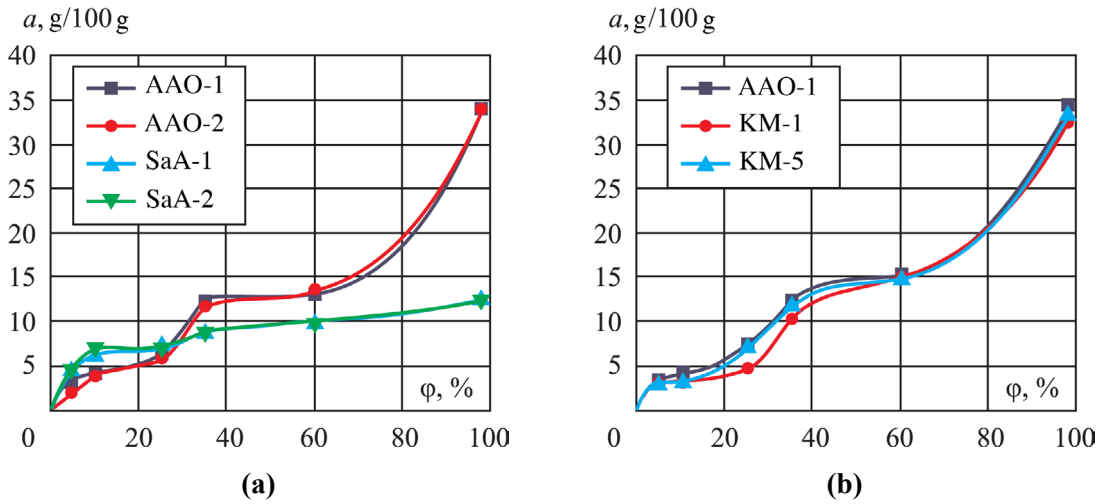

Fig. 3. Adsorption isotherms of (a) AAO-1, AAO-2, SaA-1, SaA-2 and (b) AAO-1, KM-1, KM-5 samples.

According to the generally accepted Brunauer classification, microporous SaA samples belong to Type 1 adsorption materials having a more ordered structure. AAO and KM samples, which are classed as mesoporous, contain both micropores and transition (transport) pores as characterized by the presence of a hysteresis loop on the adsorption/desorption isotherms.

Due to its small particle size (in emulsions, $d < 1$ μm), the CAM polymer binder does not block the surface of the adsorbent; here, the point contacts of binder particles with the surface of the adsorbent fix the granules of the adsorbent (filler) to form secondary transport pores.

According to the form of experimentally obtained adsorption isotherms (Fig. 3), SaA-1, SaA-2 and AAO-1, AAO-2 samples belong to type I and II of adsorption isotherms, respectively. At relative humidity φ values greater than 25%, the AAO samples have a higher adsorption capacity than zeolite-based adsorbents. Since the gas enters the drying unit in a saturated state (with a humidity of 100%), it can be concluded that mesoporous AAO adsorbents are the most suitable materials for CAM manufacture.

When comparing the experimental adsorption isotherms for CAM and AAO-1 (see Fig. 3), it is obvious that CAM isotherms repeat the shape of the isotherm for an AAO-1 granular adsorbent; at the same time, the CAM

adsorption capacity value is lower (for KM-1 and KM-5 samples, by an average of 16 and 9%, respectively) due to the binder filling the pores of the adsorbent to reduce the adsorption surface.

Despite the reduction in adsorption capacity, the application of CAMs may be appropriate when it is necessary to improve the operational characteristics of devices, as well as for regulating the kinetic and adsorption properties of adsorbents. For example, when using adsorbents in transport, CAM can be applied to ensure the horizontal location of the adsorber and reduce its overall adsorber dimensions without performance deterioration.

CONCLUSION

Adsorption isotherms were experimentally obtained to assess and compare the adsorption properties of granular and composite adsorbents used for drying air to low dew-point values.

Mesoporous materials are established as more suitable for the manufacture of CAMs (as compared to microporous materials), due to the condensation adsorption taking place in mesopores, which increases adsorption capacity. The values of the CAM adsorption capacity are lower (as compared to the initial granular adsorbent) due to the filling of adsorbent pores with a binder. Since the volume of the molded adsorbent will be less that of a granular adsorbent due to an increase in adsorbent density during CAM formation, a reduction in adsorption capacity by 10–15% is acceptable.

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