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Investigation of adsorption of water vapor on porous aluminium oxide material

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Abstract. This paper deals with theoretical investigation and experimental verification of adsorption dynamics (kinetics) of water vapor on aluminium oxide material. Influence of vapor flow rate and grain size of the adsorbent on adsorption dynamics was carried out on a laboratory equipment using McBain-Bakr quartz balance. The flow rate at which there is no influence of external diffusion limitations was determined. The material was characterized by the BET method and X-ray phase analysis (XRD). The theoretical effective diffusion coefficient was predicted from the known structure of the adsorbent. Mathematical modeling of the mass transfer rates are based on a quasi-homogeneous model was performed. A comparison between theory and experiments for the various grain size adsorbent samples allows to determinate of the effective diffusion coefficient D_{eff} .

1. Introduction

Adsorbents based on aluminium oxide are widely used in chemical process as catalysts in cracking and hydrocracking processes of petroleum products, alcohol dehydration etc. [1-3], as well as adsorbents for industrial gases purification, to extract water vapors during drying of natural and associated petroleum gases [4-7]. Gas transportation makes special demands on its degree of drying and cleaning so far as the presence of water at low temperature leads to formation of hydrocarbon hydrates, which, partial or complete can blockage a gas pipeline. Advantages of aluminium oxide (high activity, thermodynamic stability, relative ease of production and significant mechanical strength) provide its wide application along with such adsorbents as zeolites and silica gels. In this regard, the search for new more effective adsorbents is still actually. Nowadays, effective adsorbents, based on low-temperature forms of aluminium oxide (η -, γ - and χ -), obtained by calcination of alkaline hydration products of thermally-activated aluminium hydroxide with a bayerite phase are actively studied [8].

One of the main parameters of adsorbents is maximum adsorption capacity, which depends on equilibrium process. The adsorption equilibrium of water vapor has been studied widely on different materials, such as activated carbon [9], silica gel [10], zeolite and activated alumina [11-13]. As well as the equilibrium characteristics of the adsorbent, an important role belongs to adsorption kinetics, which considers the dynamics of adsorption and diffusion in individual adsorbent's granules and the rate of filling the capacity of these granules. Since the adsorbent granules, used in industrial conditions, have as a rule a shape of cylinders and spheres of various sizes, an investigation on the influence of the grain size and water diffusion on the adsorption kinetics is important.



The aim of this paper is theoretical and experimental investigation of adsorption kinetics of water vapor on aluminium oxide material and the theoretical determination of the effective diffusion coefficient D_{eff} on the base a quasi-homogeneous model and experiments for the various grain size adsorbent samples.

2. Experimental part

2.1 Adsorbent characterization and testing

A high effective aluminium porous material, which was a product of centrifugal thermal activation of hydrargillite, was chosen as an object of research [8, 15]. The experiments on the study of kinetics on the different aluminium oxide samples (0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule) were carried out on a laboratory installation using McBain-Bakr quartz balance [14]. The amount of adsorbent is $0.02 \div 0.03$ g. To carry out the process of water vapor adsorption with 100 % moisture, argon, infiltrated through two Drexel bottles filled with distilled water, was supplied to the sample.

X-ray phase analysis (XRD) was performed on a Rigaku Miniflex 600 diffractometer with the following shooting parameters: the measurement range is $2\theta=10-90$ with Cu K α radiation; voltage is 40 kV; current is 15 mA; shooting rate is 2 deg./min. Diffraction pattern deciphering was carried out using the ICDD database, version PDF2.

The textural characteristics were determined by nitrogen adsorption isotherms at 77 K. The mesopore volume was calculated by analyzing the integral curve of pore volume distribution depending on their radius (along the adsorption branch).

3. Results and discussion

3.1. Material characterization

The adsorbent sample was characterized by physicochemical research techniques [15, 16]. According to the XRD results, the porous material under study represented a mixture of low-temperature modifications of aluminium oxide i.e. $(\gamma+\gamma')$ -Al₂O₃.

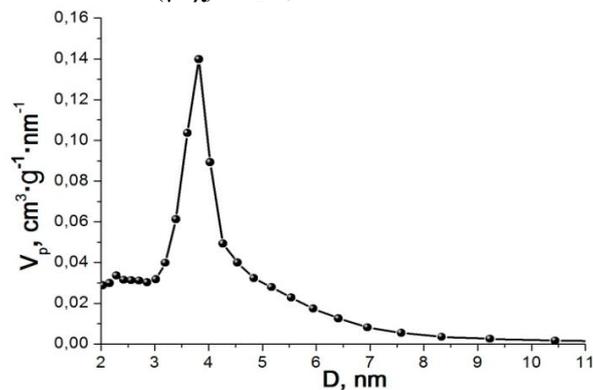


Figure 1. Pore size (D) distribution for the adsorbent (V_p -pore volume).

Based on the isotherms of low-temperature adsorption and desorption of nitrogen, the specific surface area, porosity and pore size distribution were determined. Adsorption isotherms at relative pressures of 0.05-0.3 were described by the BET equation, which allowed calculating the specific surface size, which was $\sim 305 \pm 30$ m²/g. Fig.1 shows the pore size distribution. The presence of fine mesopores (3÷7 nm) with a diameter of ~ 4 nm indicates that the adsorption process can be influenced by internal diffusion of water vapors in the adsorbent. Therefore, it is important to determine the influence of the grain size of adsorbent particles on adsorption kinetics.

3.2. Theoretical estimation of effective diffusion coefficient

The mass transfer in the adsorbent pores, depending on the pore size, can obey the laws of either molecular or Knudsen diffusion. The total diffusion coefficient of water in air is defined as [3]

$$D^* = \left(\frac{1}{D_M} + \frac{1}{D_K} \right)^{-1} \quad (1)$$

In addition, the diffusion path in the catalyst pores is tortuous rather than straight, and pores have irregular shape with a variable cross-section. As a result, the gas flow passing through a porous adsorbent depends on its porosity χ and tortuosity ξ of the pores. Therefore the effective coefficient of diffusion is expressed as $D_{eff} = \Pi \cdot D^*$. Here, the permeability coefficient $\Pi = \chi/\xi$. Considering that values of porosity are within 0.3-0.7, tortuosity ranges from 2 to 7, and their ratio is 0.04-0.35. The molecular diffusion coefficient D_m for binary gas diffusivities for water and air under the reaction conditions ($T = 25^\circ\text{C}$, $P = 1$ bar) is calculated, according to the following equation [17]:

$$D_M = D_{H_2O-Air} = \frac{10^{-7} \cdot T^{1.75} \cdot \sqrt{\frac{1}{M_{H_2O}} + \frac{1}{M_{Air}}}}{P \cdot (V_{H_2O}^{0.333} + V_{Air}^{0.333})^2} = 0.252 \cdot 10^{-4} \text{ m}^2 / \text{c} \quad (2)$$

The Knudsen diffusivity D_K ($\text{m}^2 \text{s}^{-1}$) was calculated by:

$$D_K = 9700 \cdot r_p \cdot \sqrt{\frac{T}{M_{H_2O}}} \quad (3)$$

The pore radius of catalyst was estimated from the Figure 1, $r_p \approx 2$ nm. The Knudsen diffusion coefficient and the total ones has the following values, $D_K = 0.79 \cdot 10^{-6} \text{ m}^2/\text{s}$ and $D^* = 0.77 \cdot 10^{-6} \text{ m}^2/\text{s}$, $D_{eff} = \Pi \cdot D^*$, where $\Pi = 0.04-0.35$.

3.3. Effect of flow rate

Figure 2 shows the effect of the flow rate on water adsorption in the wide range of 3.6-36 l/h at the different time. The experiments were carried out to exclude the influence of the external diffusion.

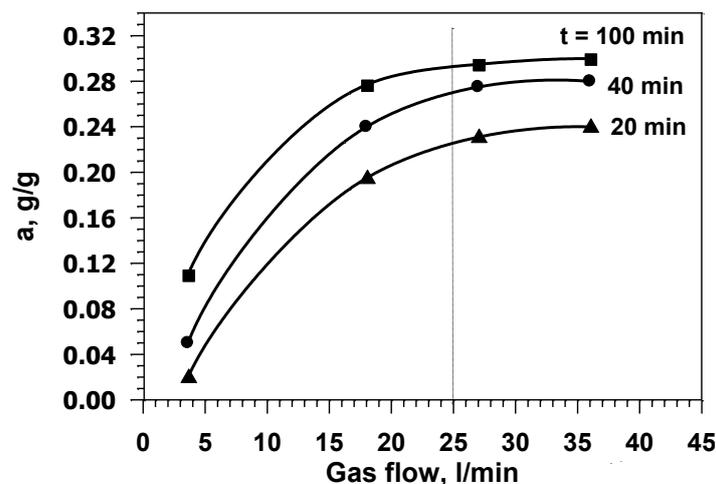


Figure 2. Influence of gas flow rate at different time on adsorption dynamics.

It was shown that at the water vapor flow rates less than 25 l/min the sample weight grows with an increase in the gas velocity for the each adsorption time. In these conditions, the external diffusion seems to be the rate-determining step of the water adsorption process. In the range of 25-35 l/min, the sample weight did not depend on the flow rate, and it can be concluded that the adsorption occurs in the kinetic regime. Therefore, all the experiments, presented on figure 3, were carried out at a flow rate of 30 l/h.

3.4. Effect of granules size on adsorption kinetics

At the same time with the capacities of the adsorbents, an important role play the adsorption kinetics. Adsorbent granules that are used in industrial conditions are shaped as cylinders and spheres of various sizes. To study the influence of the granule size on the dynamics (kinetics) of water vapor adsorption, the following fractions of the investigated aluminium oxide sample were taken: 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule.

Mathematical modeling allows to obtain the quantitative estimation of parameters, such as adsorption rate constants and effective diffusion coefficient of the substance inside the grain. A quasi-homogeneous model is used most commonly. The mathematical model considering the adsorbent as a homogeneous absorbing medium includes the following equations:

- change in the concentration of the water (C_{H_2O}) in the adsorbent grain:

$$\varepsilon_c \frac{\partial C_A}{\partial t} = D_{eff} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C_A}{\partial r} \right) - f_a R(C_{H_2O}, \theta), \quad (4)$$

- change in the concentration of adsorption sites on the adsorbent surface occupied by the water molecules:

$$\frac{\partial \theta_{H_2O}}{\partial t} = R(C_A, \theta). \quad (5)$$

Initial and boundary conditions:

$$t=0: C_{H_2O}(0, r) = C_A^0, \theta_{H_2O}=0. \quad (6)$$

$$r=0: \frac{\partial C_{H_2O}(t, r)}{\partial r} = 0, \quad r=R: C_{H_2O}(t, r) = C^0.$$

Here the adsorption-desorption process of water vapor on the surface of the aluminium oxide adsorbent can be represented by a scheme of Langmuir type

$$R = k_1 \cdot C_{H_2O} \cdot (1 - \theta_{H_2O}) - k_2 \cdot \theta_{H_2O} \quad (7)$$

In this case, C_{H_2O} is molar fraction of the water; t is time, s; D_{eff} is effective diffusion coefficient of the adsorbate in the adsorbent granule, m^2/s ; ε_c is grain porosity; r is grain radius coordinate, m; θ_{H_2O} is concentration of sites on the adsorbent surface occupied by the adsorbate; k_1, k_2 are constants of adsorption/desorption rate of water vapors; C^0 ($=3.06$ % vol.) is molar concentration of water vapors in the gas flow corresponded to 100% moisture at 25 °C.

A comparison of theoretical and experimental data of water vapor adsorption on a sample of aluminium oxide adsorbent of different fractions was performed. It was obtained that the time for achieving an equilibrium filling of adsorbent granules depends on size. Thus, for the granule, the time necessary for the equilibrium achieving filling of adsorbent pores it takes about 250 minutes, and for a fraction of 0.25-0.5 mm it takes about 30 min. Further reduction of the granule size to a fraction of 0.125-0.25 mm does not influence the time of adsorption [15].

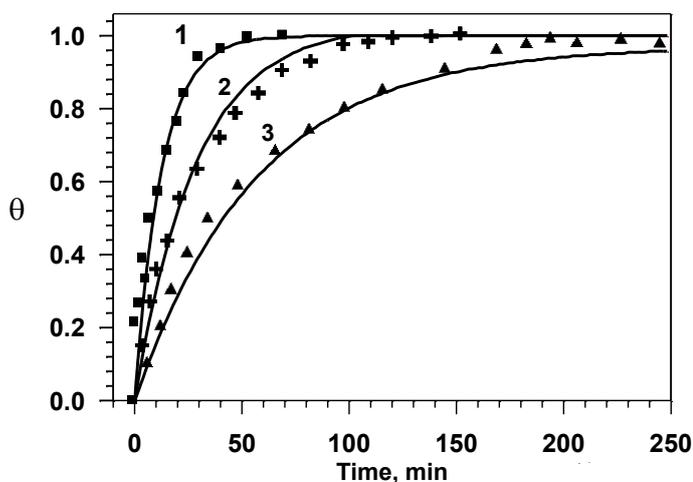


Figure 3. A comparison of theoretical and experimental data of water vapor adsorption on a sample of aluminium oxide adsorbent of different fractions: 0.25-0.5 mm (1), 0.5-1.0 mm (2) and a 3.7 x 6 mm granule (3). Symbols – Experiment; lines – calculated.

Mathematical model (4)-(7) describes quite well the experimental data (Figure 3) on the adsorption kinetics of water vapor on the aluminium oxide adsorbent. The theoretically effective diffusion coefficient was predicted from the known pore structure of the adsorbent. This led to the value of $(0.04-0.35) \cdot 10^{-6} \text{ m}^2/\text{s}$. The experimentally determined value is $1.2 \cdot 10^{-6} \text{ m}^2/\text{s}$. This value is correlated with effective diffusion coefficient ($3.6 \cdot 10^{-6} \text{ m}^2/\text{s}$) obtained during the study of the kinetics water adsorption on alumina [18]. It should be noted that according to the literature data, the experimentally determined diffusion coefficient obtained by various authors can differ by more than 10 times [18].

4. Conclusion

On the basis of a quasi-homogeneous mathematical model, a description of the dynamics of the adsorption of water vapor on a porous material was made. A high effective aluminium porous material, which was a product of centrifugal thermal activation of hydrargillite, was chosen as an object of research. The influence of the adsorbent granule size on the adsorption kinetics of water vapors on fractions of 0.25-0.5 mm and 0.5-1.0 mm and a 3.7 x 6 mm granule was studied. The experiments were carried out on the adsorption equipment using McBain-Bakr quartz balance. On the basis of the isotherms of low-temperature adsorption and desorption of nitrogen, the specific surface area, porosity and pore size distribution were determined. Adsorption isotherms were described by the BET equation, which allowed calculating the specific surface size, which was $\sim 305 \pm 30 \text{ m}^2/\text{g}$. The presence of fine mesopores with a diameter of $\sim 4 \text{ nm}$ indicates that the adsorption process can be influenced by internal diffusion of water vapors in the adsorbent. It was shown that when the fraction size is greater than 0.25-0.5 mm, the water vapor adsorption rate is controlled by internal diffusion. Mathematical modeling allowed obtaining the quantitative estimation of parameters, such as adsorption rate constants and effective diffusion coefficient of the water inside the grain. Mathematical model describes quite well the experimental data on the adsorption kinetics of water vapor on the high active aluminium oxide adsorbent and can be used for adsorbent modeling.

Acknowledgments

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