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Abstract

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CARBON ADSORBENTS WITH MOLECULAR-SIEVE PROPERTIES

The effect of the inaccessibility of part of the micropores of active carbons corresponding to the initial region of activation has long been known. In our earlier studies, the relative adsorbability from aqueous solutions of substances with different molecular sizes was investigated on active carbons from sucrose, activated with gaseous substances to various degrees of burn-off ([1,2]). As the burn-off of the carbon increased, an inversion was observed in adsorption series of substances arranged according to increasing molecular weights or molecular sizes. The interpretation of this phenomenon was based on the idea that an ever larger part of the volume of the micropores of the active carbon becomes inaccessible as the size of the molecules of the adsorbed substances increases. Later this effect was given the name molecular-sieve action of adsorbents.

In work ([3]), using as an example the adsorption of benzene and cyclohexane vapors on an active carbon from polyvinylidene chloride subjected to heat treatment at 1750°, clearly expressed molecular-sieve properties of the active carbon were demonstrated. In the studies of T. G. Plachenov, methods were systematically investigated for obtaining active carbons with molecular-sieve properties by thermal decomposition of organic materials in the functional groups of which hydrogen ions had been preliminarily replaced by metal ions ([4]). In work ([5]), previously obtained experimental data on the development of micropore volume in the process of progressive activation of carbons were analyzed. It was shown that if benzene is used as the adsorbed substance for estimating the parameters of the microporous structure of active carbons, then at the initial stages of activation the micropore volume of the carbon develops predominantly through the opening of micropores initially inaccessible to benzene molecules. The total volume of such micropores reached 0.2 cm^3/g.

In light of the results presented above, carbon adsorbents with molecular-sieve properties can be obtained either by thermal decomposition of organic materials containing small additions of inorganic activating substances, or by carrying out very mild additional activation of a carbonized product with gaseous sub-

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Fig. 2. Sorption isotherms on coal of vapors at 20°. 1 —water, 2 —benzene. Black points —desorption

Figure 2: Fig. 2. Sorption isotherms on coal of vapors at 20°. 1 —water, 2 —benzene. Black points —desorption

stances to small burn-offs. In particular cases, the natural components of the ash elements of the carbon may play the role of activating additives.

In the present study, the adsorbent used was a shaped carbon based on wood, subjected to heat treatment up to 970–980° in an atmosphere of gases not containing substances with oxidizing functions. The gravimetric density of the carbon was 0.690 g/cm^3, and the ash content 3.46%. For the experiments, carbon was used that had been thoroughly washed with distilled water at a temperature of about 100° to remove the water-soluble part of the ash.

To determine adsorption isotherms of water and benzene vapors at 20°, and of nitrogen and oxygen at $-78°$ and $-196°$, a vacuum adsorption apparatus with quartz sorption balances having a sensitivity of 4.63 mg/mm. The elongations of the quartz spiral were read with a cathetometer with an accuracy of up to 0.01 mm. The experiments were carried out with a single coal sample weighing 522 mg. Preliminary evacuation of the coal was performed at 450° to a residual pressure of about $1 \cdot 10^{-6}$ mm. In carrying out adsorption measurements, special attention was paid to attaining constancy of the readings of the elongations of the quartz spiral. As a rule, the duration of experiments for determining each point of the adsorption isotherm was not less than one day, and for control desorption points of the water isotherm, up to one week. In experiments with water, constancy of the readings for the sorption balances was practically attained in 1–2 hours, and in experiments with oxygen at $-196°$ and nitrogen at $-78°$, over 6–12 hours.

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The study of the distribution of the volumes of macropores and part of the transitional pores of the coal by effective radii was carried out by the method of mercury intrusion on a PA-5 porosimeter ([6]). Fig. 1 gives the differential curve of the distribution of the pore volume of the coal. The principal volume of the coal macropores corresponds to effective pore radii from 3200 to 40000 Å; macropores with radii of about 13000 Å are most represented in the coal. The volume of the macropores of the coal is 0.270 cm^3/g, and their specific surface does not exceed 0.9 m^2/g. An idea of the volume and surface of the transitional

Fig. 3. Adsorption isotherms on carbon. 1 –O_2 at –196°, 2 –O_2 at –78°, 3 –N_2 at –78°, 4 –N_2 at –196°

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pores of the coal can be obtained from experiments on mercury intrusion and sorption of benzene vapors. The differential curve of Fig. 1, in addition to macropores, expresses part of the volume of transitional pores, 0.020 cm^3/g, in the interval of effective radii r from 230 to 34 Å. Pores with $r = 34$ Å correspond to $p/p_s = 0.54$ during capillary condensation of benzene vapors. In the interval of effective pore radii from 15* to 34 Å (p/p_s from 0.17 to 0.54), filling of the smaller transitional pores of the coal by capillary-condensed benzene may occur (^{7}). The volume of these pores, estimated from the benzene sorption isotherm, is 0.009 cm^3/g, and their specific surface is close to 9 m^2/g. As a result, the total volume of transitional pores is 0.029 cm^3/g, and the surface corresponding to them of an equivalent model sorbent with cylindrical pores (^{8}) is approximately equal to 17 m^2/g.

Fig. 2 shows the sorption isotherms of water and benzene vapors on the coal. The water sorption isotherm has the S-shaped form typical of active carbons and is characterized by a clearly expressed hysteresis region. The limiting sorption volume of the coal with respect to water is 0.145 cm^3/g, if the density of a normal liquid is taken for the sorbed water. Adsorption

* With correction for the thickness of the monomolecular adsorption layer.

benzene on the carbon is very small, and the limiting sorption value at $p/p_s = 0.99$ reaches only 0.200 mM/g (limiting sorption volume 0.018 cm^3/g). Adsorption of benzene on the carbon may occur either in part of the larger micropores of the carbon or on the surface of transition pores and macropores. The experimental points of the adsorption isotherm of benzene on the carbon satisfactorily obey the BET equation in the p/p_s interval from 0.03 to 0.25. The adsorption value a_m for a complete monolayer is 0.0725 mM/g, and the constant $c = 92$. In that case, the specific surface area of the carbon on which polymolecular adsorption of benzene occurs would be about 18 m^2/g, taking the molecular area of benzene as 41 Å^2.

Fig. 3. Adsorption isotherms on carbon.
1 –O_2 at –196°, 2 –O_2 at –78°,
3 –N_2 at –78°, 4 –N_2 at –196°.

Figure 3 gives the adsorption isotherms on the carbon for oxygen and nitrogen at various temperatures. The oxygen isotherm at –196° clearly indicates the accessibility of the microporous structure of the carbon to oxygen molecules. The limiting adsorption volume for oxygen is about 0.15 cm^3/g. Adsorption of nitrogen at –196° is very small, and in the interval p/p_s from 0.016 to 0.167 the adsorption values vary from 0.174 to 0.178 mM/g. The almost constant mean adsorption value in this pressure interval, with the molecular area of nitrogen 16.2 $Å^2$, corresponds to a specific surface area of about 17 m^2/g, practically coinciding with the specific surface area estimated from the experiments with benzene. Consequently, benzene and nitrogen are adsorbed mainly on the surface of the larger varieties of pores in the carbon, while its microporous structure is inaccessible both to benzene molecules and to nitrogen molecules.

When the temperature is raised to −78°, nitrogen adsorption increases substantially. This effect is entirely analogous to that observed in the adsorption of nitrogen on zeolite NaA ([9]) and is due to the presence of a large activation energy for the process of penetration of nitrogen molecules through the entrances into the micropores of the carbon. The observed slow attainment of equilibrium states for oxygen also indicates a noticeable activation energy for oxygen as well.

Thus, the carbon studied possesses pronounced molecular-sieve properties. Its microporous structure is accessible to water and oxygen molecules and inaccessible to benzene and nitrogen molecules. Adsorption of benzene and nitrogen occurs mainly on the surface of transition pores and macropores of the carbon. From the experimental data presented, an important fundamental conclusion also follows concerning the mechanism of sorption of water vapor. The shape of the water sorption isotherm typical of active carbons and the presence of a hysteresis region (Fig. 2) cannot be due to capillary condensation of water, since the entrances into the micropores of the carbon are so small that they are inaccessible even to nitrogen molecules at −196°.

In the general case, the molecular-sieve properties of a carbon may be due either to the smallness of the actual dimensions of the micropores or to the narrowness of the entrances into the micropores. Experimentally, this question can be resolved by additional activation of the carbon with gaseous substances to a burn-off of 5–10%. Such a small burn-off cannot lead to a substantial increase in the dimensions of the micropores themselves, but it can cause widening of the entrances into the micropores. Such experiments were carried out for the active carbon made from polyvinylidene chloride V-1750, described in work ([3]). Table 1 gives values, interpolated from the plots of the experimental adsorption isotherms $(a - \lg p/p_s)$

adsorption values of benzene and cyclohexane vapors at 20° for various equilibrium relative pressures. According to the data of Table 1, carbon B-1750 exhibits typical molecular-sieve properties in the adsorption of benzene and cyclohexane. A portion of carbon B-1750 was subjected to additional activation with carbon dioxide at 950° to a burn-off of 11.0% in the apparatus described earlier ([1,2]). For the resulting carbon sample B-1750-A, the adsorption isotherms of benzene and cyclohexane vapors at 20° were determined.

Table 1

Carbon	Vapor	a, mM/g at $p/p_s = 1 \cdot 10^{-4}$	a, mM/g at $p/p_s = 1 \cdot 10^{-3}$	a, mM/g at $p/p_s = 1 \cdot 10^{-2}$	a, mM/g at $p/p_s = 1 \cdot 10^{-1}$	a, mM/g at $p/p_s = 1$
B-1750	C_6H_6	1.49	2.51	3.19	3.40	3.79
B-1750	C_6H_{12}	0.05	0.11	0.17	0.21	0.28
B-1750-A	C_6H_6	1.89	2.92	4.36	5.53	6.36
B-1750-A	C_6H_{12}	1.51	2.30	3.04	3.93	4.80

Additional activation of carbon B-1750 makes its microporous structure accessible to cyclohexane molecules; moreover, as a result of the activation, the entrances to the micropores of carbon B-1750, which previously were inaccessible to benzene molecules, also become widened. This may be judged from the substantial increase in the adsorption values for carbon B-1750-A in comparison with carbon B-1750 over the entire studied range of equilibrium relative pressures. Consequently, the molecular-sieve properties of the carbons studied are determined by the presence of narrower entrances to the micropores.

In light of the results obtained, the concept of closed micropores (5) may have a relative character. In the general case they may be pores inaccessible to the chosen adsorbed substance, for example benzene in work (5), used to determine the parameters of the microporous structure of carbon. More complete information on the nature of "closed micropores" may be obtained by investigating the adsorption of substances with different molecular sizes.

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