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Abstract

Full Text

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ADSORPTION AND CHEMISORPTION OF VAPORS OF OXYGEN-CONTAINING ORGANIC SUBSTANCES

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The study of the adsorption of oxygen-containing substances is of definite interest for the study of the processes of chemisorption and catalysis, as well as for the purification of mineral oils, the preparation and "aging" of bitumen–mineral mixtures, etc. The choice of oxygen-containing organic substances for studying adsorption processes was also connected with the works of L. G. Gurvich (^{1}), who noted very strong adsorption of resinous, asphaltene-like, etc., substances and discovered the phenomenon of low-temperature heterogeneous catalysis of unsaturated hydrocarbons in the presence of porous bodies. In studying the adsorption of several individual oxygen-containing compounds on silica gels and alumina (^{2}–^{10}), chemisorption phenomena were observed in a number of cases (^{2}–^{7}).

Fig. 1. Adsorption isotherms of benzene vapors on KSK silica gel (*a*) and alumina gel (*b*) at 25°.

We studied the adsorption of vapors of methanol, ethanol, diethyl ether, acetone, acetaldehyde, and acetic acid on KSK silica gel and alumina gel. Adsorption was carried out at a temperature of $25 \pm 0.05°$ in an adsorption apparatus with detachable ampoules, placed in an air thermostat with automatic heating and air stirring. Sorbent samples were taken in amounts of 1–8 g. Changes in pressure in the system were observed with a V-shaped manometer using a KM-6 cathetometer. Its readings were taken, depending on the task at hand, every

Fig. 2. Adsorption on alumina at 25° of methanol (a), ethanol (b), diethyl ether (c), acetone (d), acetic acid (e), and acetaldehyde (f) at 20.1°. (Points with strokes –secondary adsorption-desorption; with two strokes –tertiary adsorption-desorption)

Figure 2: Fig. 2. Adsorption on alumina at 25° of methanol (a), ethanol (b), diethyl ether (c), acetone (d), acetic acid (e), and acetaldehyde (f) at 20.1°. (Points with strokes –secondary adsorption-desorption; with two strokes –tertiary adsorption-desorption)

1, 2, 3, 5, etc., minutes. The pressure was considered to be at equilibrium if the last 3-4 five-minute measurements remained practically constant.

Desorption was also carried out at a temperature of $25 \pm 0.05°$.

The initial samples were preliminarily dried at 200° for 2 hours, then evacuated at the experimental temperature to $1 \cdot 10^{-4}$ mm Hg. The structural characterization of the samples was determined from the adsorption isotherms of benzene vapors (Fig. 1), obtained by the indicated method. Equilibrium pressure was reached, as a rule, within 20-40 min.

For KSK silica gel, the value of the specific surface area determined by the Brunauer-Emmett-Teller method proved to be 313 m^2/g; the value of the specific surface area of the adsorption film, determined by the method of A. V. Kiselev, was 295 m^2/g, and on the curve of the distribution of pore volume by diameter there is a clearly expressed maximum corresponding to pores with a diameter of about 100 Å. For alumina, $S_{\text{BET}} = 248$ m^2/g, $S' = 220$ m^2/g, $d_{\text{eff}} = 105$ Å. The area per benzene molecule in a dense monolayer was taken as 48 Å^2 (11).

Below is a comparison of the data obtained on the adsorption of vapors of oxygen-containing substances on alumina (Fig. 2) and silica gel

Fig. 2. Adsorption on alumina at 25° of methanol (*a*), ethanol (*b*), diethyl ether (*c*), acetone (*d*), acetic acid (*e*), and acetaldehyde (*f*) at 20.1°. (Points with one stroke–secondary adsorption-desorption; with two strokes–tertiary adsorption-desorption)

(Fig. 3). In doing so, we assumed that identical conditions of preliminary treatment of a fresh portion of alumina in each case lead to practically the same chemical state of its surface. In addition, the similar lengths of the hydrocarbon radicals of the adsorbate molecules ensure, in our opinion, equal accessibility of them to the surface of the sorbent. What has been said about alumina applies equally to silica gel.

In Figs. 2*a*, *b* the initial portions of the adsorption isotherms of methanol and ethanol vapors on alumina are presented. In the character of the arrangement of the adsorption and desorption branches they are analogous to the adsorption isotherms of methanol vapors on aluminum oxide obtained in (2), and indicate

Fig. 3

Figure 3: Fig. 3

the presence of chemisorption hysteresis, whereas the adsorption isotherm of diethyl ether vapors (Fig. 2*c*) has a reversible initial portion.

We observed an interesting picture in studying the adsorption of acetone vapors on alumina (Fig. 2*d*). From the arrangement of the curves it may be said that in this case we are dealing with low-temperature heterogeneous

catalysis, similar to that observed earlier for vapors of diallyl and cyclohexene on certain Volga opokas (^{11}). It was noticed that by the end of the first adsorption cycle the alumogel had acquired a straw-yellow color and had an odor different from that of acetone. In addition, in studying the adsorption of acetone vapors on alumogel it was necessary to depart from the measurement procedure adopted by us, since equilibrium was not reached for a long time (more than 6 h). In this connection, measurements in the initial region of P/P_s were taken after one hour, and at $P/P_s \sim 0.19$, after two hours.

In the case of adsorption of acetaldehyde vapors (Fig. 2d), a change in the color of the alumogel to lemon-yellow was observed already in the initial region of the curve. The arrangement of the adsorption and desorption curves here differs somewhat from that for acetone, but the absence of constancy in vapor pressure (the measurement was made after 3 h) when practically all points were taken also indicates a catalytic process on the surface of the alumogel.

Fig. 3. Adsorption on KSK silica gel at 25° of ethanol (a), diethyl ether (b), acetone (c), acetic acid (d), and acetaldehyde (e) at 20.1°

The nature of the arrangement of the adsorption-isotherm curves for acetic acid vapors on alumogel (Fig. 2e) is similar to that of the adsorption curves for acetone on alumogel; however, in our opinion, one should speak here only of chemisorption on the surface, since for all points constancy in the equilibrium pressure was reached. Such an arrangement of the branches of the isotherm is in good agreement with the supposition that the surface OH groups of the sorbent enter most completely into chemical reaction only when the isotherm is taken up to $P/P_s = 1$ (^{3}).

As for the adsorption of vapors of oxygen-containing substances on KSK silica gel (Fig. 3), it should be noted that in almost all cases chemisorption hysteresis is observed (with constancy of pressure present upon attainment of the equilibrium state). The reversible character of the adsorption isotherm of diethyl ether vapors on silica gel is consistent with the work (^{12}), where the absence of chemical interaction of ether molecules with the surface OH groups of silica gel is noted. Evidently, the same conclusion should also be drawn for the adsorption of diethyl ether vapors on alumogel (Fig. 2b).

It is interesting to note that the absolute amount of adsorption of diethyl ether vapors by silica gel at completion of the monolayer, $\alpha_m \cong 3.6$ μmol/m^2 (at $P/P_s \sim 0.044$), agrees fairly well with the literature data [10], where $\alpha_m \cong 3.2$ μmol/m^2 at $P/P_s \sim 0.04$; for benzene, $\alpha \cong 2.2$ μmol/m^2 at $P/P_s = 0.1$, whereas the authors [13] have, at this P/P_s, the value $\alpha \cong 2.1$ μmol/m^2.

As is evident from a comparison of Figs. 2 and 3, chemical processes on the surface of silica gel are less pronounced than on the surface of alumina under the same conditions, especially for acetone, acetaldehyde, and acetic acid. The explanation for this should evidently be sought in the different chemical nature of the chemisorption-active sites on the surface of the sorbents.

Thus, the data presented on the adsorption of vapors of a number of oxygen-containing organic compounds indicate the presence of various physical and chemical processes on the surface of the sorbents studied. These data are of interest for the study of chemisorption processes on the surfaces of porous bodies. They suggest further investigation of these interesting phenomena.

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