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Figure 1

Figure 1: Figure 1

Abstract

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ADSORPTION PROPERTIES OF ALUMINOSILICATE CATALYSTS AND THEIR DEPENDENCE ON COMPOSITION

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It was shown earlier ([1]-[4]) that the adsorption properties of a unit surface of silica gel with respect to water and methyl alcohol molecules depend substantially on the degree of hydration of the surface. The latter is not a single-valued function of the temperature at which the sample is treated, but depends on a number of factors, including the crystallochemical features of its structure and the magnitude of its specific surface. It seemed of interest to extend these studies to a series of aluminosilicates of different composition, whose surface, like the surface of silica gel, contains hydroxyl groups ([5]), i.e., to determine to what extent the replacement of silicon atoms by aluminum atoms in the structure of aluminosilicates ([6]) affects the degree of hydration of the surface and its adsorption properties.

Fig. 1. Heats of wetting by water as a function of the content of structural water for silica gel K-2 (1) and aluminosilicates containing Al_2O_3 15% (2), 30% (3), and 50% (4). Crosses mark the data for samples treated at 300°.

As the first stage of these investigations, we studied the adsorption of water vapor and methyl alcohol vapor, as well as the heats of wetting by water, of synthetic aluminosilicate catalysts containing Al_2O_3 15% (Houdry catalyst), 30%, and 50%. Before the experiments, the samples were washed with bidistilled water and then treated at each of the specified temperatures for 24 hours in air. The specific surfaces of all the investigated samples were determined by the BET method from nitrogen-vapor adsorption isotherms. The procedure for preparing samples for determining heats of wetting, adsorption measurements, and specific surface was the same as in works ([1]-[4], [7]). Adsorption measurements were carried out on an adsorption apparatus with quartz spring balances; measurements of the heats of wetting were made in a calorimeter with constant

Fig. 2

Figure 2: Fig. 2

heat exchange, having a temperature sensitivity of $5 \cdot 10^{-5}$ °C. Structural water was determined from the magnitude of the loss on ignition (^{1}) (Table 1).

Figure 1 presents the heats of wetting by water as a function of the structural-water content for all the aluminosilicates investigated. The curves obtained, as in the case of silica gels (curve 1), have maxima corresponding to preliminary thermal treatment of the samples at 200–300°. However, in contrast to silica gels (^{1}), the heats of wetting by water per unit surface of aluminosilicates prove to be higher.

Also noteworthy is the considerable amount of structural water, especially for samples with a high content of Al_2O_3. It is possible that, in this case, part of the water, in addition to the surface hydrate, may also enter into a bulk compound. Comparing points obtained for samples treated under identical conditions, for example at 300°, it can be seen that for silica gel and an aluminosilicate with a low Al_2O_3 content (15%), even with nearly the same surface hydration, the heats of wetting differ by approximately a factor of two. On these same samples, adsorption isotherms of water vapor and methyl alcohol were studied. The initial portions of the isotherms obtained are shown in Figs. 2 and 3. In accordance with the data on the heats of wetting, the isotherms of primary adsorption and desorption* of water vapor are arranged in such a way that higher adsorption values correspond to aluminosilicates with a higher Al_2O_3 content. From comparison of the isotherms shown in Fig. 2, it is evident that, in contrast to silica gel ($3'$), the desorption isotherms on each of the samples lie noticeably below the adsorption isotherms. This is apparently connected with the fact that, in the case of aluminosilicates, the values of irreversible sorption of water are large (Table 1), and desorption proceeds from a surface whose energy is lower than that of the initial surface, as follows from Fig. 1. For silica gel, no such phenomenon is observed, since irreversible adsorption of water on samples treated at 300° is very small (3). The adsorption isotherms of methanol vapor were obtained on samples hydrated at $p/p_s = 1$ and then evacuated at 250°. The data presented in Fig. 3 show that the difference in adsorption values is smaller than for water vapor, but the sequence of arrangement of the isotherms is preserved. In any case, the adsorption isotherm of methanol vapor even on the sample with a low Al_2O_3 content (15%) differs from that for silica gel.

Fig. 2. Adsorption isotherms (light points) and desorption isotherms (black points) of water vapor on aluminosilicates with Al_2O_3 contents of 50% (1), 30% (2), and 15% (3). The corresponding isotherms on silica gel ($3'$) are shown by the dashed line.

Fig. 3. Adsorption isotherms of methanol vapor on aluminosilicates with Al_2O_3 contents of 50% (1), 30% (2), and 15% (3). The isotherm on silica gel ($3'$) is

Fig. 3

Figure 3: Fig. 3

shown by the dashed line.

Aluminosilicates, in their structure, are close to silica, since the SiO_4 tetrahedra in the lattices of these compounds can be isomorphously replaced by AlO_4 (^{6}), forming disordered or, in the case of many natural aluminosilicates, layered structures. Hydroxyl groups on the surface are bonded both to Si atoms and to Al atoms (^{8,9}). The chemical properties of these groups differ from those for silica. Containing water in aluminosilicates may have more "acidic" properties in comparison with the initial oxides SiO_2 and Al_2O_3 (^{6}), which is confirmed by studies of the ion-exchange properties of aluminosilicates. There are also indications that OH groups are included in the surface structure of aluminosilicates, the chemical functions of which have a "basic" character (^{10}). Thus, the surface of aluminosilicates is more heterogeneous than the surface of silica gel. The composition of the surface of aluminosilicates and, in particular, the degree of its hydration depend on the previous history of the samples and on the method of their treatment; this, probably, explains the different hydration of our samples and those studied in (^{10}). As the data obtained by us show, the energetic and adsorption properties of the surfaces of silica gel and aluminosilicates under completely identical conditions of their preparation are different. This difference apparently applies both to the hydrated and to the dehydrated part of the surface of the indicated adsorbents.

On the basis of the coincidence of the "absolute" adsorption isotherms of methanol vapor on silica gel, on aluminosilicates with an Al_2O_3 content of 10-20% (^{11}, ^{12}), and of benzene vapor on natural samples close to them in composition (^{14}), as well as on the basis of the coincidence of the "absolute" heats of wetting for these adsorbents, the authors of (^{11}, ^{13}, ^{14}) conclude that "physical adsorption of methanol vapor is little sensitive to whether silicon atoms or aluminum atoms lie beneath the surface hydroxyl groups and oxygen atoms" (^{11}), since it is determined by the interaction of alcohol molecules with OH groups or oxygen atoms of the surface. Such conclusions, from our point of view, are unfounded*. Consideration of the mechanism of adsorption cannot be reduced only to local interactions of the adsorbed molecules with active centers, without taking into account their topography and concentration on the surface, and also the influence on the energetic properties of the surface of the stoichiometric composition and structure of the bulk phase. In those cases where the interaction of molecules with adsorption centers is due not

* For convenience of comparison, the desorption isotherms have been reduced to zero, i.e., the values of irreversible sorption of water have been subtracted from all ordinates.

only to forces of physical adsorption but also to chemical adsorption, including hydrogen bonding, the adsorbent and adsorbed molecules should be considered ([16]) as a single quantum-mechanical system, the adsorption properties of which are very sensitive to various defects in the structure of the adsorbent, including changes in the concentration and nature of accidentally present or specially introduced impurities.

Table 1

Adsorption characteristics of aluminosilicate catalysts

Al_2O_3 content, %	Calcination temp., °C	Specific surface, m^2/g	Heat of wetting, erg/cm^2	Structural-water content, $\mu M/m^2$	Irreversible sorption of water after evacuation, $\mu M/m^2$ at 20°	Irreversible sorption of water after evacuation, $\mu M/m^2$ at 250°
15	300	257	330	3.62	7.92	0.61
30	300	496	310	7.3	8.31	0.56
50	300	357	518	12.6	14.5	1.34

* The authors of ([11]), determining the specific surface area of the samples from experimental isotherms, did not take into account the influence on adsorption and, consequently, on the magnitude of the landing area of the alcohol molecule, of the nature of the adsorbent surface ([2], [4], [15]), which, naturally, should have affected the calculated value of the specific surface area. From the coincidence of the "absolute" isotherms calculated in this way, it is not yet possible to conclude that the adsorption properties per unit surface of these adsorbents are identical. It also follows from this that the recommended methods for determining the specific surface area of silica gels and aluminosilicates from one point of the isotherm ([11], [13]) and from the "absolute" heats of wetting ([12], [13]) may lead to significant errors.

mixtures. The latter should also include the chemisorbed molecules themselves.

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