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Abstract

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Adsorption of Ammonia on Methoxylated Surfaces of Silica Gel

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It is known that the specific adsorption properties of adsorbents depend substantially on their chemical and crystallochemical structure. For silica gels, quartz, quartz glasses, and silica-alumina gels, surface hydroxyl groups, capable of entering into hydrogen or donor–acceptor bonds with a number of substances, are of decisive importance (1–3). The degree of hydration or dehydration of the surface, the crystallochemical features of the substance (packing density and orientation of silicon–oxygen tetrahedra), as well as the magnitude of the specific surface area directly affect adsorption (4–7).

The results of studying all these factors can be interpreted on the basis of the assumption that it is precisely hydroxyls that are the specific adsorption centers. Their replacement by other, inactive groups leads to a decrease in the subsequent adsorption of vapors of methanol, water, benzene, and substances having the character of bases (2,8,9). Thus, for example, a number of authors indicate that upon methoxylation of a hydrated surface (by direct action of methanol vapor, by interaction with diazomethane, or, finally, by reaction of the alcohol with chlorinated silica gel) a portion of the methanol is bound irreversibly, entering into chemical interaction with the formation of ether bonds (10–12,17,18). Most authors, however, do not take into account the state of the surface or the degree of its hydration, and therefore the studies are qualitative or semiquantitative in character.

In our previous study of the adsorption of ammonia on a partially methylated surface of silica gel, an attempt was made to interpret the phenomenon quantitatively (13). In the present work these measurements have been extended to a series of silica gels methoxylated to different degrees. Samples with different numbers of methoxyl groups per unit surface area were obtained by a comparatively simple method. Previously activated silica gel, after preliminary 12-hour evacuation in a high vacuum with heating at 200°, was subjected to direct action of saturated methanol vapors at room temperature, and was then held for 2–4 hours in the same atmosphere, but already at 200°. The products formed as a result of the methoxylation reaction were removed during subsequent conditioning with heating of the surface under standard conditions. The operation was

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

repeated until the desired degree of replacement of OH groups was obtained. The objects of study were samples containing 1.02, 1.45, and 1.98 mg-equiv of methoxyl groups per 1 g of adsorbent. The specific surface areas of the samples, determined by the BET method from nitrogen vapor adsorption isotherms (615 m^2/g), did not change substantially after methoxylation. The amount of structural water was calculated from data on weight loss upon ignition in the temperature interval 200–1000° and proved to be 5.3 mmol/g. Adsorption was measured by a simple and convenient gravimetric method developed by MacBain (16). The extension of the spiral was read with a cathetometer (absolute error $\pm 1\mu$, accuracy of weight determination $\pm 10^{-5}$ g).

As an indicator making it possible to follow the change in the adsorption properties of the surface as a result of "poisoning," ammonia vapors were used. Their adsorption by the surface of silica gel, thermally dehydrated to varying degrees, was studied in detail by Bastick ([14,15]). On the basis of the differential heats of adsorption found, he came to the conclusion that adsorption of ammonia in amounts smaller than the corresponding equivalent amount of hydroxyl groups on the surface of silica gel is chemical in character. This is also consistent with our observation that desorption of ammonia does not proceed completely at room temperature (for complete removal of the gas, at least 4–5 hours of heating in high vacuum is required).

Fig. 1. Isotherms of ammonia adsorption at 25° on the initial silica gel and on silica gels methylated to different degrees. 1—for the unmethylated sample; 2—4—for samples containing methoxyl groups (in mg-equiv per 1 g of adsorbent): 2—1.02; 3—1.45; 4—1.98

The experimental data presented in Fig. 1 show that replacement of hydroxyl groups by methoxyl groups suppresses the adsorption capacity of the surface with respect to ammonia. In Fig. 2 are shown the dependences of α on $\lg P$. As can be seen, the amount of adsorbed ammonia is a linear function of the logarithm of the pressure not only for the initial "pure" samples, but also for the modified ones. Analytically, the isotherms may be represented by the equation:

Fig. 2. Isotherms of ammonia adsorption in the coordinates $\alpha(\lg P)$. The designations are the same as in Fig. 1

$$\alpha = m \lg P + b. \tag{1}$$

Fig. 3. Adsorption isotherms of ammonia on unmethylated silica-gel samples at 25° (1), 35° (2), 50° (3), and 70° (4) in coordinates $\alpha(\lg P)$.

Figure 3: Fig. 3. Adsorption isotherms of ammonia on unmethylated silica-gel samples at 25° (1), 35° (2), 50° (3), and 70° (4) in coordinates $\alpha(\lg P)$.

It may be assumed that in this case we are dealing with the Temkin adsorption isotherm, especially since, as Bastick showed, in the pressure and temperature range studied the differential heat of adsorption is an almost linear function of pressure with a very slight negative slope. It should, however, be noted that the coefficients of the straight lines characterizing adsorption on unmodified samples at different temperatures are not in directly proportional dependence on absolute temperatures (Fig. 3), and remain almost constant. However, regardless of the type of equation to which adsorption conforms, in all cases it would be possible to introduce a passivation factor P, taking into account the number of adsorption centers (i.e., OH groups) that are deactivated and rendered inactive as a result of adsorption of one modifier molecule.

Denoting by x the number of initial adsorption centers per unit surface area and by μ the number of millimoles of methyl alcohol irreversibly bound to the surface, we can write that, as a result of the act of adsorption, the active surface decreases by a factor of $(1 - P\frac{\mu}{x})$.

Fig. 3. Adsorption isotherms of ammonia on unmethylated silica-gel samples at 25° (1), 35° (2), 50° (3), and 70° (4) in coordinates $\alpha(\lg P)$.

For a surface free of modifier, the amount of adsorbed substance is

$$\alpha = \alpha_0 \theta, \tag{2}$$

where α_0 is the maximum amount of substance adsorbed when a monolayer is formed, and θ is the degree of coverage.

Then adsorption in the presence of a modifier will be expressed by the relation

$$\alpha_\mu = \alpha_0 \left(1 - P\frac{\mu}{x}\right) \theta_\mu, \tag{3}$$

whence

$$P = \left(1 - \frac{\alpha_\mu}{\alpha}\frac{\theta}{\theta_\mu}\right)\frac{x}{\mu}. \tag{4}$$

It is obvious that, in the case of the Langmuir isotherm (the process does not depend on the prior history of the adsorbent), θ does not depend on the presence of "poison" molecules. Then, for the same pressures, $\theta/\theta_\mu = 1$, and

$$P = \left(1 - \frac{\alpha_\mu}{\alpha}\right)\frac{x}{\mu} = \text{const.}$$

In all other cases, when P is determined only on the basis of α_μ and α, it must be an apparent function of pressure, tending to a limit when $\theta/\theta_\mu \to 1$. The values of P given in Table 1 were calculated by formula (4) on the basis of the most probable straight lines (Fig. 2) at the corresponding pressures and under the assumption that $\theta/\theta_\mu = 1$.

Table 1

$\lg P$	$\mu =$ 0.00	-1.0	-0.5	0	0.5	1.0	1.5	2.0	2.5
P	$\mu =$ 1.02	2.628	1.873	1.605	1.468	1.385	1.342	1.289	1.259
P	$\mu =$ 1.45	2.875	2.046	1.752	1.602	1.510	1.449	1.405	1.372
P	$\mu =$ 1.98	1.893	1.549	1.428	1.365	1.328	1.302	1.284	1.159

From the data in Table 1 it is seen that Π decreases monotonically with increasing pressure, approaching values close to unity. Deviations of the quantity Π from the mean value indicate the degree of reproducibility of the results. If in the region of lower pressures $\theta_\mu < \theta$ and adsorption obeys the Temkin equation, then $\Pi_{\text{calc}} > \Pi_{\text{true}}$. As the pressure increases, θ_μ tends to θ, and Π_{calc} to Π_{true}. The fact that θ_μ is indeed smaller than θ follows from the physical picture of adsorption on pure and modified silica-gel surfaces. On being adsorbed, like-charged positive ammonium ions begin to repel one another, which is the cause of the observed decrease in the heat of adsorption.

Upon modification, hydroxyl groups are partially replaced by methoxyl groups, and the repulsion arising between the positive methyl radicals manifests itself already at the first portions of absorbed gas. Therefore, one and the same amount of ammonia on pure and methoxylated surfaces corresponds to greater adsorption on the pure surface, i.e., to a more substantial decrease in the differential heat of adsorption. This, in essence, also explains why, at identical temperatures and pressures, the degree of coverage of the pure surface exceeds the degree of coverage of the methoxylated surface.

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