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Abstract

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ADSORPTION AND ION-EXCHANGE PROPERTIES OF SILICAS MODIFIED BY A RADICAL WITH ACIDIC FUNCTIONS

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Imparting specificity to silica gel with respect to the adsorption of particular substances, for example those with acidic or basic properties, can considerably broaden the range of its application. In this connection, the chemical modification of silica gels by organic radicals with various functional groups appears promising. Replacement of the hydroxyls of silica gel by radicals with acidic or basic properties may lead to the creation of new types of nonswelling ion exchangers and catalysts for acid–base reactions. In this direction we had previously synthesized silica gels with basic properties ([1]).

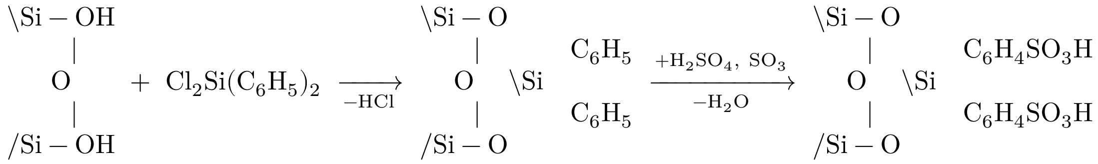
In the present work the aim was to obtain silica gels modified by a radical with acidic functions, which was to impart to it specificity with respect to the adsorption of substances with basic properties. As such a radical with clearly pronounced acidic properties, the sulfo group was chosen. For modification we used a homogeneous macroporous silica gel prepared in the laboratory, as well as a highly dispersed preparation of nonporous silica—Aerosil; their principal characteristics are given in Table 1. The value of the specific surface area was determined from methanol adsorption isotherms, and the content of structural water by the thermal method.

Table 1

Principal characteristics of silica gel and Aerosil

Sample	V_s, cm^3/g	S, m^2/g	r, Å	OH, meq/g
Silica gel	1.0	276	56	3.7
Aerosil	–	120	–	1.27

Sulfonation of the silica gel and Aerosil was carried out in two stages. First, the samples, dried in vacuum for 2 hr at 200°, were phenylated; for this they were treated with diphenyldichlorosilane. In this process the hydroxyl groups of the adsorbents interacted with diphenyldichlorosilane, as a result of which phenyl groups became covalently bound to the surface of the sample. In the second stage of the modification the phenyl groups located on the surface were subjected to sulfonation with sulfuric acid. After sulfonation the samples were thoroughly washed with distilled water to remove acid and were dried at 180-200°. The processes taking place during modification may be represented by the following scheme*:



$$\begin{array}{l}\backslash Si-OH\\ \quad|\\ \quad O\\ \quad|\\ /Si-OH\end{array} + Cl_2Si(C_6H_5)_2 \xrightarrow[-HCl]{} \begin{array}{l}\backslash Si-O\\ \quad|\\ \quad O \quad \backslash Si\\ \quad|\\ /Si-O\end{array}\begin{array}{l}C_6H_5\\ \\ C_6H_5\end{array} \xrightarrow[-H_2O]{+H_2SO_4,\ SO_3} \begin{array}{l}\backslash Si-O\\ \quad|\\ \quad O \quad \backslash Si\\ \quad|\\ /Si-O\end{array}\begin{array}{l}C_6H_4SO_3H\\ \\ C_6H_4SO_3H\end{array}$$

As a result, on the surface of the silica gel and Aerosil a portion of the hydroxyl groups proved to be replaced by a complex surface compound containing a sulfo group. The amount of attached phenylsilyl groups was de— was determined from the weight gain, and the sulfo groups from the results of ion exchange and chemical analysis. The ion-exchange properties of the sulfonated samples were characterized by the value of the static exchange capacity, according to exchange data from a 1 N aqueous NaCl solution (^3). At the same time, the pH of the equilibrium solution established as a result of exchange of H^+ sulfo groups for Na^+ of the solution was recorded; the pH was determined with an indicator glass electrode.

Table 2

Ion exchange on the initial and sulfonated silica gel and aerosil from a 1 N NaCl solution
(pH of the initial solution 6.6)

Sample	Exchange value, μeq/g	pH of equilibrium solution
Silica gel	11.2	4.0
Sulfosilica gel	510	1.8
Aerosil	6.3	4.3
Sulfoaerosil	250	2.1

Table 2 gives data on ion exchange on the initial and sulfonated samples of silica gel and aerosil. As is evident from the table, the ion-exchange properties of the sulfonated samples differ greatly from those of the initial ones. For them the pH value of the equilibrium solution is 1.8-2.1, i.e., exchange occurred in strongly acidic media. On unmodified, silanol silica gel, as is known (^4), at such pH

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* Other schemes of interaction of diphenyldichlorosilane with the surface are also possible (see, for example, (2)).

Fig. 1. Adsorption isotherms of heptane vapor (A) and benzene vapor (B) at 20° on initial (1), sulfonated (2), and phenylated (3) aerosil.

Figure 1: Fig. 1. Adsorption isotherms of heptane vapor (A) and benzene vapor (B) at 20° on initial (1), sulfonated (2), and phenylated (3) aerosil.

Fig. 2. Adsorption isotherms of methyl alcohol vapor (A) and diethylamine vapor (B) at 20° on initial (1), sulfonated (2), and phenylated (3) aerosil.

Figure 2: Fig. 2. Adsorption isotherms of methyl alcohol vapor (A) and diethylamine vapor (B) at 20° on initial (1), sulfonated (2), and phenylated (3) aerosil.

values no exchange is observed. Only at a pH of about 4 does exchange already become noticeable, but its magnitude is several orders lower than on sulfonated silica gel. Thus, for sulfosilica gel the value of the static exchange capacity was 510 μeq/g

Fig. 1. Adsorption isotherms of heptane vapor (**A**) and benzene vapor (**B**) at 20° on initial (**1**), sulfonated (**2**), and phenylated (**3**) aerosil.

Fig. 2. Adsorption isotherms of methyl alcohol vapor (**A**) and diethylamine vapor (**B**) at 20° on initial (**1**), sulfonated (**2**), and phenylated (**3**) aerosil.

at a pH of the equilibrium solution of 1.8, whereas for the initial silica gel the value of ion exchange at pH 4.0 was only 11.2 μeq/g.

Thus, the presence on the surface of silica gel and aerosil of a strongly acidic ionogenic sulfo group covalently bound to it causes ion exchange on such samples even in strongly acidic media, where the hydrogen of the outer sheath of the silica-gel double layer, owing to its considerably lower protonation compared with the hydrogen of the sulfo group, is incapable of dissociation and exchange.

The change in adsorption properties as a result of modification may be caused by changes both in the porosity of the sorbents and in the chemical nature of their surface. In order, in studying the adsorption properties of sulfonated samples, to separate the influence of porosity, there was used

An unporous preparation of silica—Aerosil—was studied. On the initial, phenylated, and sulfonated Aerosil samples, adsorption isotherms were measured for the vapors of benzene, heptane, methyl alcohol, and diethylamine. These data are presented in Figs. 1 and 2. As is evident from the figures, phenylation of Aerosil caused a substantial decrease in the adsorption of all the vapors used. A different picture is observed on sulfonated Aerosil. The adsorption isotherms of benzene and heptane lie only slightly above the isotherms on phenylated Aerosil (this is explained by partial destruction of the phenylsilyl coating during sulfonation), while the adsorption isotherms of methyl alcohol and diethylamine lie above not only those for phenylated Aerosil, but even those for the original Aerosil.

The decrease in the magnitude of adsorption of benzene and heptane on sulfonated and phenylated Aerosil is associated with a decrease in the dispersion component of the van der Waals interaction. This is due chiefly to the removal of adsorbing molecules from the adsorbent surface as a result of replacing hydroxyls by larger phenylsilyl or sulfophenylsilyl groups (5–10). For benzene this effect is intensified by a decrease in the energy of electrostatic interaction with hydroxyls. The increase in adsorption of methyl alcohol and diethylamine on sulfonated Aerosil, as compared with phenylated and original Aerosil, is associated with interaction of the molecules of these substances with sulfo groups present on the surface. It is known that oxygen-containing compounds, such as alcohols and ethers, as well as nitrogen-containing organic bases, can interact with strong mineral acids (11). Such interaction evidently also takes place on sulfonated Aerosil, since the sulfo group possesses the properties of a strong mineral acid. This is also indicated by the fact that, upon desorption from sulfonated samples, the amount of irreversibly bound diethylamine and methanol proves to be greater than for the phenylated and original samples. Consequently, the adsorption of CH_3OH and $(C_2H_5)_2NH$ on sulfonated Aerosil is chemisorptive in character. For these molecules the sulfo groups are active adsorption centers, as a result of which adsorption of methanol and diethylamine increases. For C_6H_6 and C_7H_{16} molecules, the sulfo groups are not such centers, and this leads to a decrease in the adsorption potential of the modified Aerosil toward the vapors of these substances.

Thus, by modifying silica gels with organic radicals bearing acidic or basic functions, one can obtain specific adsorbents and catalysts. Sulfosilica gels, in particular, may be used as nonswelling ion exchangers in strongly acidic media. Owing to the fact that the framework of such ion exchangers is a heat-resistant silica gel, they can operate at higher temperatures, at which the framework of ordinary synthetic ion-exchange resins undergoes destruction (12).

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Note: Figure translations are in progress. See original paper for figures.

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