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Abstract

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SYNTHESIS OF SPECIFIC SILICA GELS BY MODIFYING THEIR SURFACE

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Chemical modification of the surface of hydrated silica gels and highly dispersed nonporous silica by replacing hydroxyl groups with various radicals does not impart selectivity properties to them. In such modified samples, although to different degrees, the adsorption of both polar and nonpolar substances is reduced ([1–7]). Meanwhile, imparting to silica gel a pronounced selectivity with respect to the adsorption of particular substances could considerably broaden the possibilities for its use.

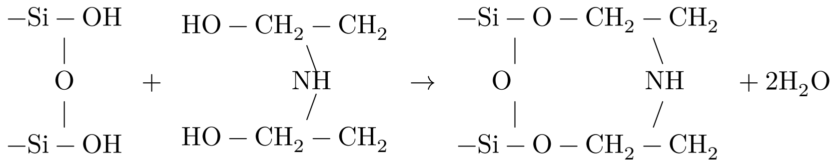
In the present study we set ourselves the task of carrying out chemical modification of silica gel with the aim of imparting basic properties to it. Such modification should lead to selective adsorption of acidic substances, which are weakly adsorbed on silica gel. Sorbents with basic properties may also find application as catalysts for dehydration reactions, etc.

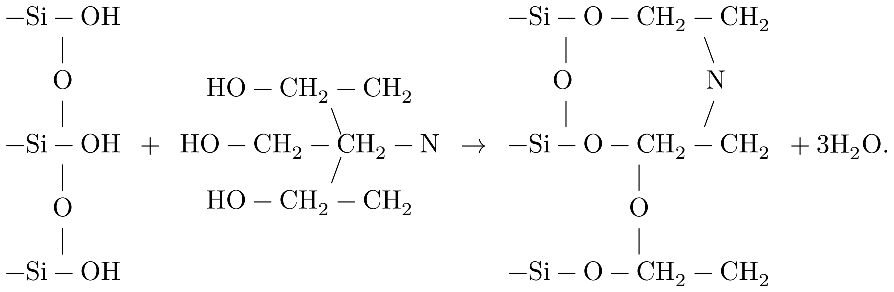
In ([8,9]), selectivity of the action of silica gel was achieved by saturating the latter with aqueous solutions of ammonia and ethylenediamine. Such silica gel, containing amino groups on its surface, possessed the ability to coordinatively bind elements forming ammoniates (Cu, Zn, Co, etc.). Work ([10–13]), as well as that of our laboratory, showed the possibility of introducing organic residues into silica gel by means of an esterification reaction. We supposed that, by using alcohols containing an amino group ([14]) for esterification, it would be possible to impart basic properties to silica gel. In the present study, for this purpose a series of amino alcohols with different degrees of basicity was used (mono-, di-, and triethanolamines). In all cases, as we conceived it, the interaction of silica gel with amino alcohols should proceed according to the reactions:

$$-\mathrm{Si}\overset{|}{\underset{|}{-}}\mathrm{OH} + \mathrm{HO}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{NH_2} \rightarrow -\mathrm{Si}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{CH_2}}}-\mathrm{CH_2}-\mathrm{NH_2} + \mathrm{H_2O}$$

Fig. 1

Figure 1: Fig. 1





However, in this connection possible steric hindrances should be taken into account, as a result of which, probably, not all the hydroxyls of di-, and especially triethanolamine, are involved in esterification. Therefore the reactions presented may be only a schematic representation of the process.

For chemical modification, hydrated samples of macroporous silica gel were used. Amination was carried out in two ways: in a flask with a reflux condenser at a temperature of 100-160° C, and in an autoclave at 160-250° for 2-5 h. The silica gel subjected to such treatment was evacuated in a vacuum oven at 100-180° and a pressure of 10^{-3} mm for 2-6 h.

The modified silica gels were analyzed for their content of aminospirit groups. For this purpose, a weighed sample was treated with an excess of a titrated hydrochloric acid solution. After shaking, the solution was separated from the sample and back-titrated with alkali using methyl red. For the initial and aminated samples, adsorption isotherms were obtained for vapors of methyl alcohol, diethylamine, carbon dioxide, and acetic acid from solutions in carbon tetrachloride. All isotherms were measured at 20°.

Fig. 1. Adsorption isotherms of methyl alcohol vapor on initial (1) and modified with monoethanolamine (2) silica gels

Fig. 2. Adsorption isotherms of acetic acid from solutions in CCl_4 on initial (1) and modified silica gels: 2 –1.75 meq/g $C_2H_4NH_2$-groups; 3 –1.75 meq/g $(C_2H_4)_3N$-groups; 4 –3.3 meq/g $C_2H_4NH_2$-groups

Fig. 2

Figure 2: Fig. 2

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

When silica gel was treated with ethanolamines and subjected to prolonged evacuation in vacuum at 100-180°, 1.2-13.5 meq/g of ethanolamine was retained on the silica-gel surface. Special experiments on desorption of aminated silica gels by evacuating them in vacuum at 10^{-5} mm and 200° showed that 1.2-1.75 meq/g of ethanolamines are retained most strongly; these are undoubtedly bound to the silica-gel surface by chemical affinity forces. This may serve as confirmation of the amination mechanism proposed by us earlier.

Figure 1 presents the initial portions of the adsorption isotherms of methyl alcohol on aminated and initial silica-gel samples. As is seen from Fig. 1, amination of silica gel with aminospirit groups, as in the case of modification with any other organic radicals [1-7], leads to a substantial decrease in the adsorption value in the initial portions of the isotherms and to a shift of the relative-pressure region corresponding to the sharp rise of the middle parts of the isotherms toward higher relative pressures. Such a decrease in adsorption is associated with a weakening of the donor-acceptor interaction of methyl alcohol molecules with the modified silica-gel surface.

Figure 2 presents adsorption isotherms of acetic acid from solutions in CCl_4 on the initial and aminated silica gels. As can be seen from Fig. 2, the introduction into the silica gel of an organic radical bearing an amino group causes an increase in the adsorption of acetic acid. For the sample with the higher amine content this difference in adsorption properties is still more pronounced (curves 2 and 4). At the same degree of modification, the adsorption isotherm of acetic acid for the sample treated with triethanolamine lies above the isotherm obtained on the sample treated with monoethanolamine (curves 2 and 3). In going from the initial to the modified silica gel, an increase in the adsorption of carbon dioxide is also observed, as can be seen from Fig. 3.

It was of interest to determine how amination of silica gel would affect the adsorption of substances of a basic character. For this purpose, adsorption isotherms were obtained

Fig. 3. Adsorption isotherms of carbon dioxide on initial (1) and monoethanolamine-modified (2) silica gels.

Fig. 4. Adsorption isotherms of diethylamine vapor on initial (1) and modified silica gels: 2 —with monoethanolamine; 3 —with triethanolamine. Content of amino-alcohol groups: 1.75 meq/g.

for diethylamine on the initial and aminated samples. These isotherms are presented in Fig. 4, from which it is seen that, in going from the initial to the aminated silica gel, adsorption of diethylamine decreases sharply. The adsorption decreases especially sharply for the sample treated with triethanolamine.

Acetic acid, as is known, is adsorbed on silica gel with the formation of a hydrogen bond (15). In the case of aminated silica gels, the adsorption bond with acetic acid is considerably stronger. This accounts for the increase in the adsorption potential of aminated silica gel with respect to acetic acid and for the increase in its adsorption in going from the initial to the aminated silica gel. The increased adsorption of carbon dioxide is likewise due to the basic properties of the aminated sample. Thus, in both cases, chemisorption occurs on the modified silica gels. The strength of the latter increases with increasing alkaline properties of the surface. In going from primary to tertiary aliphatic amines, their basic properties increase (16). This explains the higher position of the adsorption isotherms of acidic substances on silica gel aminated with triethanolamine as compared with adsorption on samples modified with monoethanolamine.

For diethylamine, which has basic properties, amino groups are not active adsorption centers, as a result of which a decrease in its adsorption is observed on aminated silica gels.

media. The concave shape of the adsorption isotherm of diethylamine on the sample treated with triethanolamine indicates an extremely weak interaction between the adsorbate and the adsorbent. Thus, the data presented show that, by modifying the surface of silica gel with organic radicals containing particular functional groups, it is possible to impart to it specific adsorption properties. Replacement of the hydroxyl groups on the surface of silica gels by radicals with acidic residues will probably lead to the production of an adsorbent selective toward basic substances and to the creation of a non-swelling ion exchanger based on silica gel. In this way it will also be possible to create selective contacts for acid–base catalysis.

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