V. S. VASIL’ EVA, I. V. DROGALEVA, A. V. KISELEV,

A. Ya. KOROLEV, and K. D. SHCHERBAKOVA

1961

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. S. VASIL' EVA, I. V. DROGALEVA, A. V. KISELEV, A. Ya. KOROLEV, and K. D. SHCHERBAKOVA

GEOMETRIC AND CHEMICAL MODIFICATION OF SILICA GEL FOR GAS-CHROMATOGRAPHIC PURPOSES

(Presented by Academician D. I. Shcherbakov, 28 XII 1960)

In works ([1]-[5]) we showed that, by combining geometric modification of silica by hydrothermal treatment with chemical modification of its surface by reaction with trimethylchlorosilane, it is possible sharply to reduce the adsorption energy and the magnitude of adsorption of vapors of various substances, in particular hydrocarbons, and to make the surface considerably more homogeneous. We also noted that such modification may prove useful both for better matching of fillers with media ([1],[2]) and for introducing into the gas-adsorption variant of chromatography (gas—solid) the advantages of its gas-liquid variant (gas—liquid) ([2],[6]). The shortcomings of the gas-adsorption variant are associated with an excessively large and nonconstant adsorption energy on a solid inhomogeneous surface, which usually leads to long retention times and sharp asymmetry of peaks. Liquid films applied to a solid body that serves only as the column packing possess a homogeneous surface. However, they are destroyed at high temperatures and, during prolonged operation, are carried away by the flow of carrier gas. Thus the gas-liquid variant of chromatographic separation at high temperatures (i.e., when working with sufficiently large molecules) does not ensure high stability. In addition, diffusion into the bulk of the liquid film slows mass transfer. The liquid film also does not completely protect against possible reactions with the carrier. Therefore, in the present work an attempt was made at geometric and chemical modification of an adsorbent convenient for gas chromatography—wide-pore silica gel—with the aim of obtaining on its surface a sufficiently stable and homogeneous film chemically bound to it, in particular a film of an organosilicon compound.

Silica gel of the ShSK grade was chosen as the starting material. The industrial silica gel was washed with dilute hydrochloric acid (1 : 1) to remove impurities of iron ions and other metals (until a negative reaction with ammonium rhodanide) and then with distilled water to remove chloride ions (until a negative reaction with silver nitrate). In this way a sample SI (initial silica gel) with a very inhomogeneous surface was obtained. Part of this silica gel was subjected to further treatment for the purpose of geometric and chemical modification.

Geometric modification of the silica gel was carried out by treatment with water in an autoclave at 275° for 19.5 hr. In this way sample SG was obtained. A third sample was prepared by chemical modification of the surface of sample SG, by treating it with liquid trimethylchlorosilane (sample SGM). The sample was analyzed for carbon content. At 1.22% carbon, calculated for the surface of hydrated silica gel, for every 100 Å^2 of the surface of the sample there are on average about 2.7 trimethylsilyl groups, which corresponds to coverage of the surface by an organosilicon film close to the densest possible. The geometric and chemical characteristics of the samples are given in Table 1.

Before the adsorption experiments the samples were heated for a long time in an adsorption vacuum apparatus on pans of quartz balances (^{7}) at 150° to a pressure of $1 \cdot 10^{-5}$ mm Hg.

Adsorption and desorption isotherms of benzene vapor were obtained in the range of relative pressures p/p_s from 0 to 1. From Fig. 1 it is seen that, as a result of hydrothermal treatment of the initial silica gel, the isotherm shifted strongly downward and to the right. The onset of capillary-condensation hysteresis shifted from $p/p_s = 0.2$ for sample SI to $p/p_s = 0.75$ for sample SG. All this indicates a sharp change in the geometric structure.

Table 1

Characteristics of the silica-gel samples used

Sample	Method of modification	Pore volume v_s, cm^3/g	Specific surface area S, m^2/g	Average diameter of silica globules D, Å	Average diameter of pore necks d, Å	Carbon content, %
SI	Not treated	0.89	310	100	90	–
SG	Treated in an autoclave with water vapor at 275° for 19.5 h	0.78	80	400	340	–

Sample	Method of modification	Pore volume v_s, cm^3/g	Specific surface area S, m^2/g	Average diameter of silica globules D, Å	Average diameter of pore necks d, Å	Carbon content, %
SGM	SG treated with liquid trimethylchlorosilane at 20–57°, then evacuated	0.60	(80)	(400)	(380)	1.21
SGM	SG treated with liquid trimethylchlorosilane at 20–57°, then evacuated	0.60	(80)	(400)	(380)	1.23
SGM	SG treated with liquid trimethylchlorosilane at 20–57°, then evacuated	0.60	(80)	(400)	Average	1.22

The sharp decrease in surface area was the result of a strong increase in the size of the globules composing the silica-gel skeleton (8). The average diameter of the silica-gel globules after hydrothermal treatment increased almost fourfold (Table 1). The number of small pores decreased.

Thus, as a result of hydrothermal treatment of the silica gel, coarsening and smoothing of the particles forming its skeleton occurred, with complete hydration of its surface. This made it possible, by subsequent treatment of sample SG with trimethylchlorosilane, to obtain a silica gel with a surface covered by

Figure 1

Figure 1: Figure 1

a fairly dense layer of trimethylsilyl groups. This chemical modification of the silica-gel surface, as in the case of aerosil (^{2,5}), led to a sharp decrease in adsorption with respect to benzene up to the onset of capillary condensation. In the upper left part of Fig. 1 are given the initial portions of the benzene adsorption isotherms, calculated per unit surface area for all three silica-gel samples. The adsorption of benzene per unit surface area of sample SGM decreased significantly in comparison with the two samples having a hydrated surface. Thus, at $p/p_s = 0.1$, the absolute value of benzene adsorption on samples SI and SG is $a \simeq 2$ μmol/m^2, while on sample SGM $a \simeq 0.1$ μmol/m^2, i.e., chemical modification led to a 20-fold decrease in benzene adsorption. The adsorption of benzene on the chemically modified sample remains very insignificant up to $p/p_s \simeq 0.8$. Capillary condensation, beginning near the points of contact of the silica-gel skeletal globules at high p/p_s, plays the main role, similarly to weak adsorption and significant capillary condensation of water in the pores of activated carbon that does not contain surface oxides (^{9}).

These data made it possible to suppose that silica gel modified in this or a similar manner can be used for chromatographic separation, for example, of hydrocarbon mixtures by the gas-adsorption method, even if the mixture contains components that are strongly adsorbed on the initial silica gel. Measurements of the heats of adsorption of *n*-hexane and benzene (^{5}) on the surface of aerosil strongly modified with trimethylchlorosilane showed that these substances are adsorbed extremely weakly,

Moreover, the shapes of the adsorption isotherms at small p/p_s approach linear ones.

Next, exploratory experiments were carried out to determine the possibility of using an SGM* silica-gel sample in chromatography. The experiments were performed on a Griffin and George chromatograph with a column 4 mm in diameter and 1 m long. Two samples of silica gels treated by the same method as the SG and SGM samples were taken for packing the column (fraction 0.25-0.5 mm).

Fig. 1. Adsorption isotherms of benzene vapor on silica-gel samples: 1 —original silica gel SG; 2 —hydrated in an autoclave, SG; modified after hydration, SGM. Black points —desorption

In the case of hydrated silica gel of the SG type, at ordinary temperature benzene did not leave the column even after half an hour. At 82°, peaks of benzene and hexane were obtained; however, the retention time of benzene was still large: $12'40''$ (for hexane it was $1'50''$). At the same time, the benzene peak was strongly broadened (Fig. 2 A, 1). Under the same conditions, a modified silica gel of the SGM type was tested. The retention time of both hexane and benzene decreased sharply. In addition, the benzene peak differed from the peak on the SG sample: the "tail" of the peak almost disappeared (Fig. 2 A, 2).

The same experiment was carried out at lower temperatures. At 35°, on hydrated silica gel of the SG type, benzene did not give a distinct peak at all, whereas on the modified silica gel the retention time of benzene proved to be only $2'20''$. Accordingly, a mixture of benzene and hexane on the modified silica gel at 35° was separated satisfactorily. The chromatogram obtained is shown in Fig. 2 B.

The gas-adsorption chromatograms obtained were compared with the chromatogram of a mixture of benzene with hexane recorded by the gas-liquid method, where celite impregnated with silicone E-301 was used as the column packing. Thus, the nature of the liquid layer in this case was rather close to the nature of the chemically modifying film on the surface of the silica gel. The chromatogram of the benzene-hexane mixture obtained in this case at 74° (the other conditions were the same as in the case of the silica gels) is shown in Fig. 2 C. At 35°, separation does not occur.

As can be seen from a comparison of Figs. 2 B and 2 C, a mixture of benzene and hexane can be separated in the case of modified silica gel by the gas-adsorption method more rapidly than by the commonly used gas-liquid method, and even at a lower temperature: the retention times of benzene and hexane at 35° on the modified silica gel are almost 2 times shorter than their retention times at 74° on celite impregnated with silicone. The shape of the benzene peak in the case of gas-adsorption sep-

* Jointly with R. S. Petrova, with the assistance of N. Ya. Smirnova, V. I. Kalmanovskii, N. Balakhnina, and Ya. I. Yashin. The authors express their gratitude to them.

separation on silica gel of the SGM type is nevertheless less symmetrical than when the gas-liquid method is used. This is evidently explained by the still insufficient uniformity of the pores and of the surface of the modifying layer. It is therefore necessary to seek still deeper geometrical and chemical modification of the silica-gel skeleton and its surface*. Although this problem has not yet been solved in the present work, the experiments carried out on the separation of benzene and hexane on modified silica gel give grounds to suppose that chemical modification of the surface of silica gel, as well as of other adsorbents or of the walls of capillary columns, with the formation of heat-resistant films of grafted compounds, may be able to replace, in chromatography, impregnation with liquids, eliminating the difficulties and shortcomings associated with them in the gas-liquid variant of chromatography while retaining its advantages.

Fig. 2. Chromatograms of a mixture of benzene and *n*-hexane vapors. **A**—at 82° on silica gels: 1—SG, 2—SGM; **B**—at 35° on SGM; **C**—at 74° on celite impregnated with silicone E-301.

Thus, the combination of geometrical modification of the adsorbent skeleton

Fig. 2. Chromatograms of a mixture of benzene and n-hexane vapors. A—at 82° on silica gels: 1—SG, 2—SGM; B—at 35° on SGM; C—at 74° on celite impregnated with silicone E-301.

Figure 2: Fig. 2. Chromatograms of a mixture of benzene and n-hexane vapors. A—at 82° on silica gels: 1—SG, 2—SGM; B—at 35° on SGM; C—at 74° on celite impregnated with silicone E-301.

with chemical modification of its surface, in particular by reaction with trimethylchlorosilane, leads to the production of silica gel with very large pores, the surface of which is fairly uniform. Modified adsorbents, in particular those bearing chemically grafted functional groups on top of the organosilicon layer, will probably prove suitable for the purposes of gas chromatography, making it possible to combine the advantages of its gas-adsorption and gas-liquid variants.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Moscow State University
named after M. V. Lomonosov

Received
25 VII 1960

CITED LITERATURE

1. A. V. Kiselev, N. V. Kovaleva, A. Ya. Korolev, K. D. Shcherbakova, DAN, **124**, 617 (1959).
2. I. Yu. Babkin, V. S. Vasil' eva, I. V. Drogaleva, A. V. Kiselev, A. Ya. Korolev, K. D. Shcherbakova, DAN, **129**, 131 (1959).
3. I. Yu. Babkin, A. V. Kiselev, DAN, **129**, 357 (1959).
4. A. V. Kiselev, A. Ya. Korolev, R. S. Petrova, K. D. Shcherbakova, Kolloidn. zhurn., **22**, No. 6 (1960).
5. I. Yu. Babkin, A. V. Kiselev, A. Ya. Korolev, DAN, **136**, No. 2 (1961).
6. A. V. Kiselev, K. D. Shcherbakova, *Material zum 2. Symp. über Gas-Chromatogr. in Böhlen, Oktober 1959.* Berlin, 1959.
7. A. V. Kiselev, T. A. Pogosyan, Kolloidn. zhurn., **22**, No. 3 (1960).
8. A. V. Kiselev, E. A. Leont' ev et al., ZhFKh, **30**, 2149 (1956).

9. A. V. Kiselev, N. V. Kovaleva, ZhFKh, **30**, 2775 (1956).

* At p/p_s = 0.1, as a result of modification of aerosil (5), the adsorption of benzene vapor decreased by a factor of 35; on going from SG to SGM, however, it decreased only by a factor of 20.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.