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THERMAL MODIFICATION OF SILICA GELS WITH TEMPERATURE PROGRAMMING

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A derivatograph was used for the thermal modification of the surface properties of different silica gels. Analogous investigations were carried out with an isothermal method. The possibility of using the thermal method of temperature programming to modify adsorbents is discussed.

One of the simplest ways of modifying the surface properties of silica gels is partial or complete dehydroxylation of their surface [1, 2]. This process is usually carried out by means of heat treatment of the adsorbent and is often accompanied by modification of the silica gel texture. The adsorbent properties depend on the temperature and duration of the modification process, on the primary structure of the silica gel pores, and on the nature of the other substances it contains. An increase in the temperature of heat treatment is followed by a decrease in the rate of hydroxylation of the silica gel surface. Industrial silica gels mainly contain narrow pores and are contaminated with metal ions. Moreover, silica gels containing metal ions are used as catalysts of chemical reactions. For example, silica gels modified with sodium ions are used to decompose cumene [3]; other ions are used in the preparation of silica-carbon adsorbents [4]. The activities of such adsorbents depend on the amount and nature of the ions deposited on the silica surface and on the surface area. The processes of heat treatment of silica gels containing metal ions are on the whole difficult to control, especially in the case of alkali metal ions, which considerably accelerate the process of modification of the porous structure. Silica gel undergoes calcination, due to which considerable decreases occur in its surface area and hence in the number of catalytically active centres. It should be added that narrow-pore silica gels are calcined to a greater extent than large-pore ones.

It follows from the authors' investigations that thermal modification with temperature programming offers better possibilities of controlling and regulating the properies of silica gels in comparison with the traditional method, i.e. under isothermal conditions [5]. The present paper reports some results obtained using this method and discusses the possibilities of the thermal method of modifying adsorbents with temperature programming.

Experimental

Adsorbents. The following kinds of adsorbents were modified thermally.

1. Adsorbent A: hydroxylated silica gel produced by POCH Gliwice (Poland); grain fraction 0.1 – 0.2 mm. This adsorbent was washed with HCl to remove surface metal ions.
2. Adsorbent B: obtained by modifying adsorbent A with Na^+ ions in the way described previously.
3. Adsorbent C: hydroxylated silica gel manufactured by Macherey Nagel (FRG) for column chromatography; grain fraction 0.15 – 0.30 mm in diameter.
4. Adsorbent D: adsorbent C modified in an autoclave with water vapour; 1 mole of water was used for 50 g of silica gel; conditions of the reaction: temp. 250°, time 6 hr, a steel autoclave with a capacity of 1 l. After the hydrothermal treatment the silica gel was dried at 120° for 24 hr.
5. Adsorbent E: adsorbent C modified with Na^+ ions.
6. Adsorbent F: adsorbent C modified with Cs^+ ions.

Separate portions of adsorbent C (10 g each) were covered with an aqueous solution of 1.45 g $CsNO_3$ or 6.689 g $NaNO_3$. The water was then removed in a rotary evaporator during approximately 12 hr, and the adsorbent was dried at 120°.

Thermal modification

All adsorbents were modified thermally with temperature programming using the following heating rates: 2.5, 5, 10 or 20°/min. The temperature was programmed from 20° to 1000° (adsorbents A, C and D), 700° (Adsorbents B, E and F) or 600° (Adsorbents E and F). Modification was carried out in an air atmosphere using a Paulik – Paulik – Erdey OD 112 derivatograph. For comparison, the chosen adsorbents (A and B) were modified under isothermal conditions at 700°. Adsorbent A was modified for 50, 100, 200, 400 or 600 min, and adsorbent B for 35, 70, 140 or 280 min.

Testing adsorbents

The samples obtained from adsorbents A and B were used to investigate nitrogen adsorption and desorption. The measurements were made on a Sorptomat 1800 apparatus, manufactured by Carlo Erba (Italy). From the obtained data, and using the BET method, we calculated the values of the specific surface areas S and the differential distributions of the pore volume V with respect to the radius R in the manner described previously [7]. The specific surface areas of the remaining adsorbents were measured via the thermal desorption of nitrogen [8]. Moreover, the diameters D of the globules were calculated for the adsorbents from the formula [9]:

$$D = 6 \cdot 10^4 / S \cdot d. \qquad (1)$$

In the above equation d denotes the specific density of the adsorbent. It was assumed after Karnauchov [9] that $d = 2.2$ g/cm^3 for all silica gels. This value may increase slightly with the increase in temperature of the silica gel treatment, i.e. to about 2.3 g/cm^3 (crystalline type of silica [10]). Consequently, the assumption that the value d is constant for the adsorbent studied does not introduce significant errors into the calculations of the D value.

Modification under isothermal conditions

From a practical aspect it is important to find the correlation between the conditions (temperature and duration) of silica gel modification and its properties (degree of surface hydroxylation, porous and globular structures), since such information allows prediction of the adsorption, mechanical, catalytic and other silica gel properties. It appears from the work of other authors [11] that thermal modification of silica gels up to about 700° does not cause considerable changes in the specific surface area S and, consequently, in the diameter of the globules. The rapid decrease of these parameters occurs only above this temperature. An increase in the duration of silica gel modification at an appropriate temperature should be followed by a decrease in S and by an increase in D. Corresponding data for the adsorbents A and B are summarized in Table 1. The $S = f$(time) dependences for both adsorbents are linear, which allows prediction of the modified silica gel properties. The addition of Na$^+$ ions to silica gel (adsorbent A) considerably reduces the calcination temperature of the pores. The specific surface areas S of silica gel adsorbents modified with such ions (absorbent B) are therefore much smaller than the S values of adsorbents obtained by thermal treatment of hydroxylated silica gel (adsorbent A). The Na$^+$ ions introduced onto the silica react with it, forming surface silicates. These ions or their compounds may diffuse into the depths of the modified silica skeleton [12]. Thus, silica gels obtained from adsorbent B consist of larger globules (Table 1) than silica gels obtained from the adsorbent which does not contain Na$^+$ ions (adsorbent A).

Table 1

Properties of adsorbents A and B modified thermally under isothermal conditions

Adsorbent A			Adsorbent B		
Duration of modification, min	Surface area S, m^2/g	Diameter of globule D, Å	Duration of modification, min	Surface area S, m^2/g	Diameter of globule D, Å
50	348	78	35	102	267
100	342	80	70	93	295
200	346	79	140	91	301
400	318	86	280	78	350
600	286	95			

Figure 1 compares the courses of adsorption and desorption of nitrogen on the modified adsorbent A. The shapes of the isotherms shown in Fig. 1 are similar,

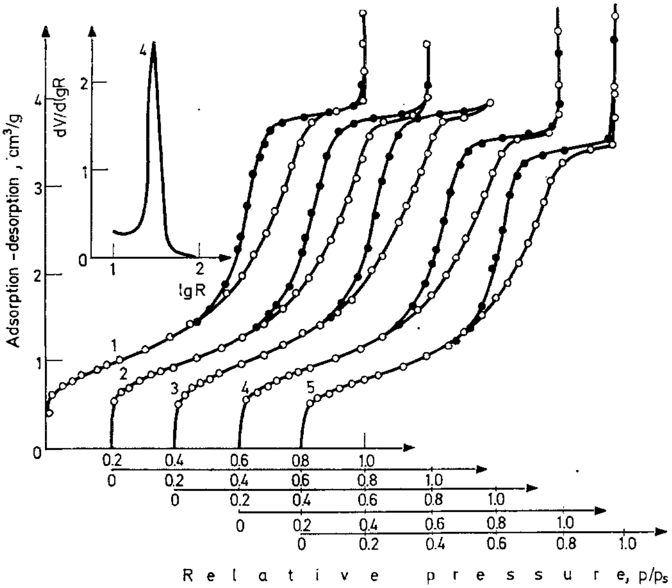

Fig. 1. Adsorption o and desorption ● isotherms of nitrogen on non-modified adsorbent A (1) and on thermally modified adsorbent at 700°. Duration of modification: 50 (2), 100 (3), 200 (4) and 600 (5) min. Upper graph: differential pore volume (V) as a function of the pore radius (R) for adsorbent A modified for 200 min

which suggests only slight changes in the geometrical structure of adsorbent A modified at 700° and for different periods. A typical pore distribution curve for the discussed adsorbents is shown in the upper part of Fig. 1. Generally speaking, an increase in the duration of modification of adsorbent A at 700° does not cause a change in the predominant pore radius R_{dom}. However, a change does occur in the area under the pore distribution curve. This becomes proportional to the volume of pores of a given size. These changes are also proportional to the changes in the S value of the modified adsorbent. The obtained S values are listed in Table 1. The R_{dom} values for these adsorbents are nearly 30 Å. It follows from an analysis of Fig. 2 that the presence of Na^+ ions in silica gel causes considerable changes in the structure of its pores. This observation is confirmed by the differences in the shapes of the adsorption and desorption isotherms. The shape of the desorption hysteresis loop depends on the geometrical structure of the adsorbent pores [13]. One can therefore assume that the adsorbents obtained from adsorbents A and B posses different pore shapes. Figure 2 also shows typical shapes of the pore distribution curves for the two chosen adsorbents. After a longer calcination of adsorbent B, there is a decrease in the area under the curve $\mathrm{d}V/\mathrm{d}\log R = f(\log R)$, accompanied by a simultaneous change in the radius of the predominant pores. The R_{dom} values for the adsorbents whose isotherms are presented in Fig. 2 are: 77 Å (35 min), 89 Å (70 min), 92 Å (140 min) and 90 Å (280 min). The duration of thermal treatment of

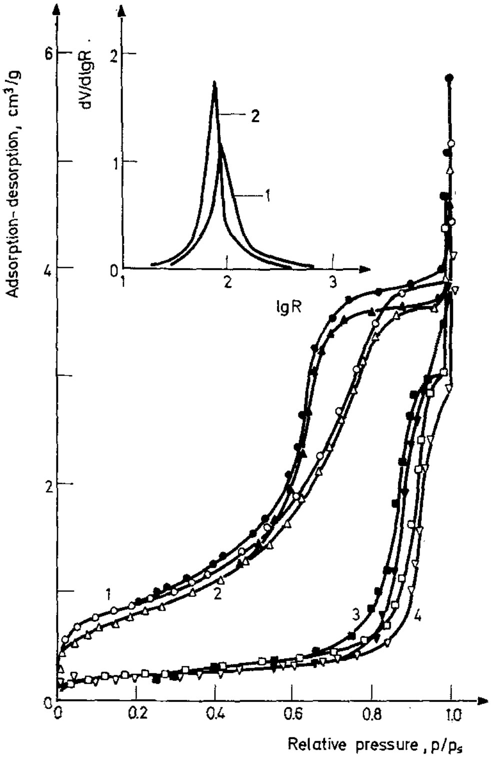

Fig. 2. Adsorption and desorption isotherms of nitrogen on adsorbent B modified at 700°C Duration of modification: 35 (1), 70 (2), 140 (3) and 280 (4) min. Upper graph: differential pore volume as a function of the pore radius

adsorbent B is given in brackets. The above data indicate that only the dependences of the magnitude of the specific surface area *S* on the duration of thermal modification of the silica gel can be described by means of a simple mathematical equation. The relation of *S* to the temperature of silica gel treatment however, has a more complex character. It should also be noted that, although thermal treatment of silica gels has long been used as a method of modifying their surface properties no systematic, thorough studies concerning the influence of the above-mentioned factors on the texture and structure of the skeleton of silica gels having different initial parameters have been carried out so far.

Modification under dynamic conditions

(a) Hydroxylated silica gels

The data in Table 2 indicate a clear influence of the rate of heating of the silica gel on the *D* and *S* values. They also depend on the maximum temperature at which the silica gel undergoes calcination. The higher the maximum temperature and the

Table 2

Structural characteristics of adsorbent A ($S = 375$ m²/g, $D = 73$ Å) thermally modified with programmed temperature. Programme from 20° to t_{max} equal to 700 or 1000°

Heating rate, deg/min	Surface area S, m²/g		Diameter of globule D, Å	
	$t_{max} = 700°$	$t_{max} = 1000°$	$t_{max} = 700°$	$t_{max} = 1000°$
2.5	244	222	112	123
5.0	297	229	92	119
10.0	324	254	84	107
20.0	308	308	88	88

lower the rate at which the adsorbent is heated, the smaller the S value and the larger the D value. The dependence of log S on the rate of heating is linear and can be described by the following equation:

$$\log S = \log S_0 + a \cdot F \tag{2}$$

where S denotes the specific surface area of the thermally modified silica gel, S_0 the specific surface area of the initial gel, and F the rate of temperature increase. Coefficient a depends on the maximum heating temperature. It may also depend on the nature of the modified silica. Similarly to the case when modification is carried out under isothermal conditions, in the course of silica gel treatment with temperature programming changes also occur in its globular and porous structure (Table 2, Figs 3 and 4). In the process of adsorbent A modification with temperature programming up to 700°, no significant changes occur in the diameter of the predominant narrow pores; only their capacity undergoes a change. This is reflected in the S values of particular adsorbents (Table 2). A typical $\mathrm{d}V/\mathrm{d} \log R = f(\log R)$ curve for the discussed adsorbents is shown in the upper Fig. 3. The value of the predominant radius R_{dom} is 31 Å. Slightly larger changes in the porous structure of adsorbent A can be observed on heating to 1000°. This can be seen from the data presented in Table 2 and Fig. 4. Such a modification causes a change in the capacity of

Table 3

Structural characteristics of adsorbent B thermally modified with programmed temperature. Programme from 20° to t_{max} equal to 700°

Heating rate, deg/min	Surface area S, m²/g	Diameter of globule D, Å
2.5	sintered very strongly	
5.0	100	273
10.0	95	287
20.0	101	270

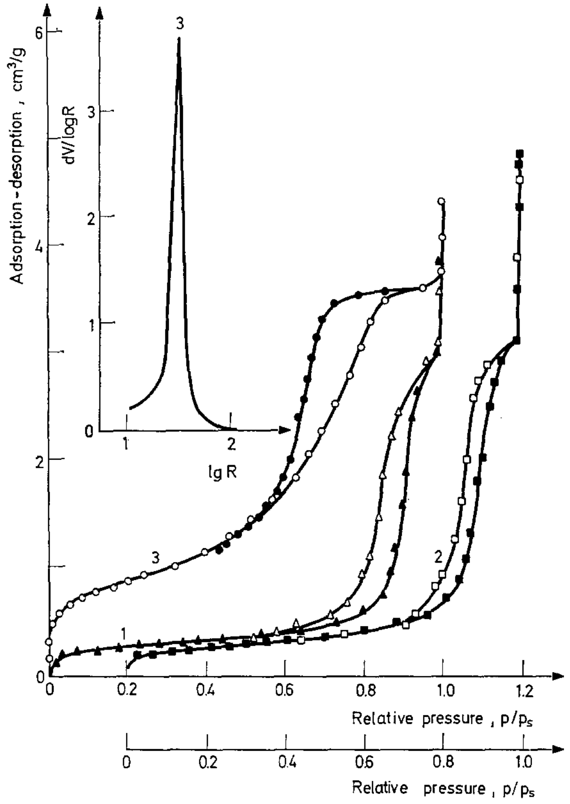

Fig. 3. Adsorption and desorption isotherms of nitrogen on adsorbent A thermally modified with programmed temperature in the range 20–700°. Heating rate: 5°/min (1), 10°/min (2), 20°/min (3). Upper graph: differential pore volume as a function of the pore radius for adsorbent modified at a heating rate of 20°/min

the narrowest pores, i.e. those for which $R = 100-200$ Å, and a slight change in R_{dom}. The latter approximates to the value of R_{dom} characteristic of the xerogel modified to 1000°. It follows from analysis of the data presented in Table 4 that the

Table 4

Structural characteristics of silica gel modified with water vapour ($S = 18$ m²/g), and next modified thermally with programmed temperature

Heating rate, deg/min	Surface area S, m²/g	Diameter of globule D, Å
2.5	16.5	1652
5.0	17.7	1540
10.0	18.0	1515
20.0	22.0	1239

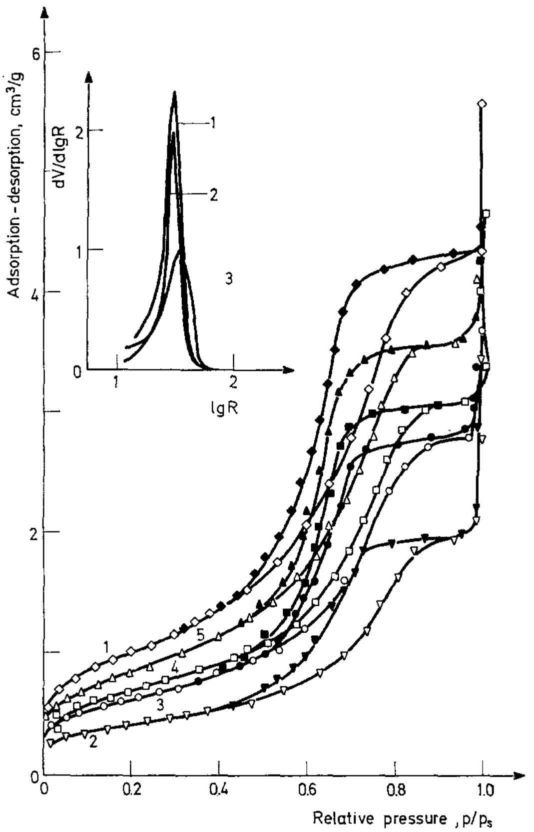

Fig. 4. Adsorption and desorption isotherms of nitrogen on adsorbent A modified with programmed temperature from 20 to 1000°. Heating rate: 2.5°/min (2), 5°/min (3), 10°/min (4), 20°/min (5), (1) initial silica gel. Upper graph: differential pore volume as a function of the pore radius

dependences of *S* and *D* on the rate of heating the modified silica gel with water vapour are approximately linear. This is useful, since such a dependence allows the prediction of the silica gel properties.

(b) Influence of metal ions

Table 3 shows a comparison between the specific surface areas *S* and the diameters of the globules *D* obtained for adsorbent B modified in the temperature range 20–700°. At the lowest heating rate adsorbent B underwent very strong calcination and hence the *S* value for the adsorbent obtained in this way was within the limit of error for the applied methods. A higher rate of temperature increase leads to adsorbents with relatively large specific surface areas. No clear influence of the heating rate on the *S* and *D* values can be observed. It follows from analysis of

Table 5

Structural characteristics of silica gel containing Na^+ and Cs^+ ions and thermally modified with programmed temperature to 500° or 700°

Heating rate, deg/min	Surface area S, m^2/g				Diameter of globule D, Å			
	t_{max} = 500°		t_{max} = 700		t_{max} = 500		t_{max} = 700	
	Na^+	Cs^+	Na^+	Cs^+	Na^+	Cs^+	Na^+	Cs^+
2.5	269	279	77	49	101	91	350	557
5.0	292	305	85	48	93	89	321	568
10.0	271	316	68	50	100	86	400	545
20.0	256	320	80	41	106	85	341	665

Figs 5 and 6 and of data in Table 5 that the weight losses of the analyzed samples E and F depend on the rate of temperature increase, as well as on the nature of the metal ion deposited on their surface. The temperature at which sodium nitrate undergoes decomposition is 380°. This value may be changed under the influence of the support (silica). It appears from the course of curve 1 in Fig. 5 that a rapid loss of sample mass occurs at 427°. At a rate of 5°/min the corresponding temperature is approximately 460°, and the temperature value increases together with the increase in the rate of heating of the samples.

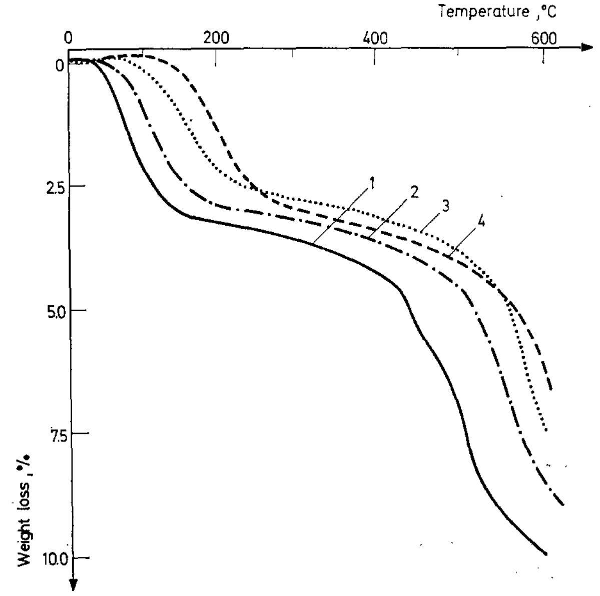

Fig. 5. Weight loss as a function of heating temperature of adsorbent E. Heating rate: (*1*) 2.5°/min, (*2*) 5°/min, (*3*) 10°/min, (*4*) 20°/min

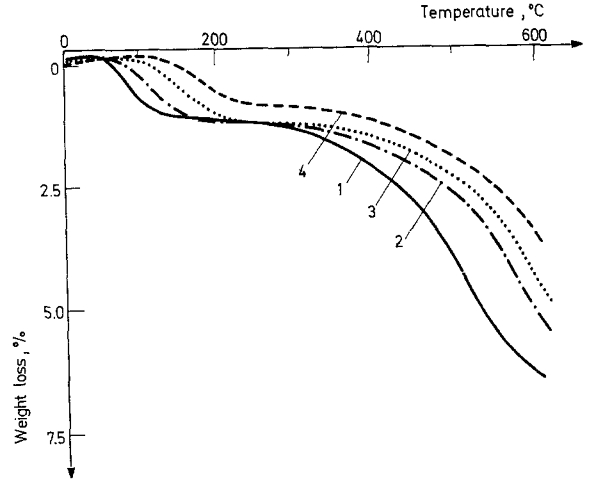

Fig. 6. Dependence of weight loss of adsorbent F on the heating rate: (*1*) 2.5°/min, (*2*) 5°/min, (*3*) 10°/min, (*4*) 20°/min

Decomposition of cesium nitrate occurs at the boiling temperature of this compound. The melting point of $CsNO_3$ is 414°. The total decomposition of cesium nitrate deposited on silica probably occurs above 500°. One can assume the presence of sodium nitrate or cesium nitrate as well as Na_2O or Cs_2O on the surface of the modified adsorbents. These substances may react with silica. The amount of the reaction products depends on the rate of temperature increase. The above reactions cause changes in the primary structure (the S and D values) of the adsorbents E and F, as is illustrated by the data in Table 5.

It follows from a comparison of the corresponding data in Table 5 that Na^+ ions modify the silica gel structure to a greater extent than do cesium ions under the same conditions. Similarly to the previous case (Table 3) temperature programming prevents the strong calcination of the adsorbents. Moreover, it allows differentiation between the properties of the modified adsorbents.

Discussion

It follows from the works of other authors [6, 12, 14] that the thermal modification of silica gels results mainly in the binding of the globules of their skeleton and in the increase of their contact until the smallest particles decay. The course of these processes is accelerated and facilitated by the presence of sodium or other substances on the silica gel surface. There is a fundamental difference between the mechanisms of the processes of geometrical modification of adsorbent B and adsorbents E and F. In the first case silica gel was wetted with an aqueous solution of soda. Since such a solution has an alkaline reaction, the smallest particles (silica globules) are dissolved, and sodium silicate is formed in the first stage. Then, during evaporation of the solution, the dissolved silicates and silicic acid are deposited by diffusion on larger globules. A further increase in the diameter of the globules occurs during the thermal treatment of the dried xerogel. As shown in Table 5, the result of these processes is that the thermally modified silica gels consist of globules four times larger than the initial ones. The silicates deposited on the surface of the globules reduce the thermal and chemical stabilities of the silica gel, which may consequently undergo strong calcination at an adequately high temperature. In our case, this can be observed at a low rate (2.5°/min) of silica gel heating. This fact testifies to a considerable influence of the time for which the thermal treatment is carried out on the surface properties of the adsorbent obtained. It also testifies to the slowness of the diffusive process of transferring the silicates from small globules to large ones and into their depths. While programming the temperature, one should take into account the temperature gradient in the particles of the modified adsorbent. Such a gradient may grow, following the rate of temperature increase. The productivity of the processes of diffusion and calcination taking place inside a crystalline silica gel will therefore be greater at a small rate of temperature increase. In the case of a large increase of temperature, the processes of modification of the structure of the silica gel skeleton may occur mainly on the surface of the particles.

Since aqueous solutions of cesium and sodium nitrate are neutral, silica should not undergo dissolution in the course of impregnating silica gel with these compounds. The processes of geometrical modification may then occur not earlier than in the course of calcination of the adsorbents E and F. In the reactions occurring on solid bodies it is primarily the cation that is active, the activity of the anion being lower. Moreover, the cations may pass from the surface of a solid body into its depths and back. The diffusion of ions occurs under the influence either of an electric field or of the changes (decrease) in the chemical potential. These changes take place due to the concentration gradient in the system. It can be assumed then that Na^+ and Cs^+ ions deposited on the silica gel surface will diffuse into the depths of its globules. The rate of the reaction will depend on the temperature and energy of the activation. Such reactions as those that occur in the course of the discussed modifications depend on at least two factors:

1. formation of silicates;
2. diffusion of the silicates formed.

The second of these processes is the slower one. The rate of diffusion will also depend on the physicochemical properties of the metal ions, e.g. their size. The diameter of the cesium ion is far larger than that of the Na^+ ions, and thus the activity of the former and consequently the extents of the two above processes, should be smaller. It follows from the data in Table 5 that in this way one can obtain a smaller change in the specific surface area and in the diameter of globules of adsorbent F than in the case of adsorbent E.

It also appears from the works of other authors [15, 16] that the mechanism of the modification of silica gel with water vapour is similar to the reactions taking place in the presence of hydroxides of the alkali metals. It consists in decondensation and recondensation of silicic acid which is formed due to the dissolution (breaking of the siloxane bonds) of the smallest particles-globules of the modified silica gel. The silicic acid, which assumes a monomeric or polymeric form, is deposited on larger particles, especially in the area of their contact. Consequently, the primary globules of silica are enlarged. Further, it is probable that part of the surface of primary globules which are in the depths of the larger, enlarged molecules will turn out to be inaccessible to the large molecules of silicic acid. Due to this fact, narrow pores (ultrapores) accessible to small water molecules appear in the forming porous structure of the modified silica; such pores are inaccessible to larger molecules such as N_2, benzene, methanol and the like. The formation of ultrapores is facilitated by the uneven deposition of silicic acids on particular globules. This is a result of increases in the chains of polysilicic acid in certain places and inhibition of the chain growth in other areas of the modified silica. Recondensation of silicic acids occurs mainly in the areas characterized by the smallest negative surface curvature. These are primarily the areas between the skeletons of silica gels in contact with one another via the globules. It was found that, due to a partial polymerization (condensation) of silicic acids, there is some water left in the ultrapores which cannot be removed by drying the silica gel in vacuum at 150–200°. Hence, silica gels modified with water vapour have a high content of intraglobular water [17].

During calcination of large-pore silica gels obtained by the hydrothermal treatment of narrow-pore adsorbents, adsorbent D in our case, there should occur further bonding processes of the primary globules of their skeletons and decay of the smallest globules. This primarily concerns the large-pore silica gels which are heterogeneous as regards their globular structure. Interglobular water begins to be removed at 450–600°. The productivity of the silica gel dehydroxylation processes as well as the processes of the growth of its globules, especially inside the silica gel particles, should depend on the rate of heating of a sample of the modified adsorbent. The water found in the ultrapores or larger pores with narrow outlets, e.g. having a bottle shape, may play a special role here. The formation of such pores is quite possible in the process of hydrothermal modification of narrow-pore, heterogeneous silica gels, due to the steric obstacles for large molecules of silicic acid or its polymerization products. The water bound in the interglobular space, and exerting a high pressure in the course of heating of the silica gel, may explode, thus widening the narrow outlets of the pores that had previously been inaccessible to nitrogen molecules; consequently, an increase can also be observed in the specific surface area of the adsorbent as this occurs when adsorbent D (Table 4) is heated at 20°/min. When the temperature increase is slower, the process of thermal treatment lasts longer, and hence further processes of calcination of silica gel globules occur. In our case such processes take place in the course of the thermal modification of adsorbent D at rates of 2.5 and 5°/min (Table 4).

Conclusions

1. Thermal modification with temperature programming allows the avoidance of the strong calcination of silica gels and at the same time leads to changes in the chemical nature of the adsorption centres on the surface (partial or complete dehydroxylation) and in its geometrical structure at arbitrary high temperatures.
2. The silica gel properties depend on the rate of temperature increase and on the maximum temperature to which it is heated, as well as on the nature of the metal ions present on its surface. The described method allows the preparation of adsorbents with relatively high specific surface areas and containing large amounts of Na^+ ions and others, without exposing them to strong calcination.
3. The method permits wide research possibilities in the sense of both adsorbent and catalyst preparation and the study of the mechanism of their modification. It may be assumed that both the dispersion of the metallic and nonmetallic catalyst and the depth of its penetration into the support will depend on the rate of temperature increase.
4. The essence of the method consists in using temperature gradients to modify the adsorbent particles at different heating rates. These gradients, dependent on the rate of temperature increase, determine the extents of the reactions occurring on the surface of the crystal and in its depth.

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ZUSAMMENFASSUNG — Ein Derivatograph wurde zur thermischen Modifizierung der Oberflächeneigenschaften von verschiedenen Kieselgelen benutzt. Analoge Untersuchungen wurden unter isothermen Bedingungen ausgeführt. Möglichkeiten zur Modifizierung von Adsorbentien mit der temperaturprogrammierten thermischen Methode wurden diskutiert.

Резюме — Дериватограф был использован для термического изменения поверхностных свойств различных силикагелей. Аналогичные исследования проведены изотермическим методом. Обсуждена возможность видоизменения адсорбентов термическим методом, используя программирование температуры.