

USE OF THERMAL ANALYSIS TO FOLLOW THE MODIFICATION OF THE SKELETON STRUCTURES OF SILICA GELS WITH ALCOHOLS AND WATER VAPOUR

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Derivatograph was used to follow the modification of the skeleton structures of silica gels with alcohols and water vapour. Analogous investigations were carried out by other independent methods. Agreement between the results is good.

The derivatograph is widely used at present in studies on adsorbents [1–5] and packings of chromatographic columns [6, 7]. Simon [1] described the applicability of the derivatograph for determination of the adsorption capacity of industrial adsorbents. Das et al. [3] recently used the complex method for studies on the change of amorphous silica into cristobalite.

Utsugi et al. [4, 5] have investigated the surface groups of silica gels chemically modified with alcohols by means of differential thermal analysis and thermogravimetry. Silica gels esterified with alcohols are used in chromatography and in industry. Esterification reactions of hydroxylated silica gels with alcohols $R-OH$ can be presented in a simplified way [9]:



The degree of esterification of the silica gel surface depends on the temperature and time of the reaction, the pressure of alcohol vapour, the water content of the reaction system, and the porosity of the modified xerogel [8–10]. Studies have shown that during reaction (1), in addition to changes in the adsorption properties of the silica gel [4, 11], its texture and skeleton structure may also undergo modification [9, 12].

In the present paper the derivatograph has been used to follow the modification of the skeleton structure of hydroxylated silica gel with alcohols and water vapour.

Experimental

For the experiments we used adsorbents obtained by autoclave modification of the hydroxylated silica gel surface with *n*-alcohols and water vapour. Hydroxylated silica gel was produced by POCh Gliwice (Poland) and additionally purified with HCl. The reactions of the alcohols and water vapour with this silica gel were carried out in an autoclave. The following substances were used as modifying

reagents: distilled water, *n*-propanol, *n*-butanol, *n*-pentanol, *n*-hexanol, *n*-nonanol and *n*-decanol. The conditions of the modification process were as follows: time 6 hr, vapour pressure of modifying reagents 25 atm, temperature 250°. After modification in the autoclave the adsorbents were dried in a nitrogen stream for 6 hr at 140°. The xerogel samples were washed with acetone and then with carbon tetrachloride prior to further measurements, and dried in a vacuum desiccator for 4 hr at 140°. The specific surface area *S* of the adsorbents was determined by thermal desorption of nitrogen [13]. Elemental analysis of the esterified silica gels was carried out by using the Hewlett–Packard CHN analyzer model *F* and *M* 185. The surface properties of the adsorbents investigated here were discussed previously [14–16].

The characteristics of the silica gels studied are summarized in Table 1. The esterification degrees *D.E.* were calculated from the content of carbon in the samples studied and their specific surfaces, using the equation of Ballard et al. [8]:

$$D.E. = \frac{6.02 \cdot 10^{23} \cdot \%C}{12 n_C \cdot S \cdot 10^{20}} \quad (2)$$

Table 1

Characterization of surface properties of silica gels hydroxylated and esterified with aliphatic alcohols

Silica gel	Surface area, <i>S</i> , m ² /g	Elemental analysis		Degree of esterification <i>D.E.</i>	Specific density <i>d</i> , g/cm ³	Diameter of globules <i>D</i> , Å	Concentration of the OH groups in the bulk of the globule <i>K</i> , mg/Å ³ · 10 ⁻⁷
		%C	%H				
Hydroxylated (non-modified)	597	—	—	—	2.11	48	1123
Modified with water vapour	35	—	—	—	2.25	762	4103
Modified with <i>n</i> -propanol	393	0.68	0.32	0.3	2.07	74	266
Modified with <i>n</i> -butanol	186	0.25	0.26	0.2	2.05	157	42
Modified with <i>n</i> -pentanol	118	0.37	0.28	0.3	2.08	248	14
Modified with <i>n</i> -hexanol	378	0.92	0.41	0.2	2.08	76	87
Modified with <i>n</i> -nonanol	131	1.04	0.37	0.44	2.19	209	13
Modified with <i>n</i> -decanol	493	2.39	0.56	0.24	2.11	58	661

where %C is the carbon weight percentage in the esterified silica gel sample, S is the specific surface area, and n_C is the number of carbon atoms in the molecule of alcohol used for esterification.

The $D.E.$ is a measure of the number of esterified OH groups per μm^2 of silica gel surface.

The diameters D of the globules of the skeleton were calculated from the values of the specific surface areas S of the samples and their specific density d according to the equation [17]:

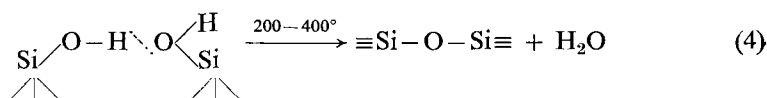
$$D = \frac{6 \cdot 10^4}{d \cdot S} \quad (3)$$

The specific density of the samples was measured pycnometrically, using carbon tetrachloride for this purpose. The adsorbents were analyzed on a Paulik, Paulik and Erdey type OD 112 derivatograph. The analysis was carried out in corundum crucibles. The bulk of the analyzed sample was 500 mg. The rate of temperature increase was $10^\circ/\text{min}$. The atmosphere was air.

Results and discussion

In Fig. 1A thermal curves of a silica gel sample esterified with n -decanol are presented. In the DTA curve two distinct exothermic peaks can be observed in the temperature ranges $200-470^\circ$ (I) and $470-640^\circ$ (II), with their maxima at 280 and 520° . These peaks correspond to an almost continuous decrease in sample mass (TG curve). The character of the DTA curve accounts for two types of transformations in the sample analyzed. The first transformation type is connected with silica gel itself and has a continuous character in the whole temperature range, i.e. from 20 to 1000° . For comparison, in Figs 1B and C curves for hydroxylated silica gels are presented. The second transformation type is connected with the mode of modification of the hydroxylated silica gel. The thermal curves for the other xerogels studied are presented in Fig. 2. Their course is on the whole similar.

According to the results of many authors [18–20] it is assumed that the concentration of surface hydroxy groups, α_{OH} , for silica gels is $4.5-4.8$ OH groups per 100 \AA^2 , i.e. about $7-8 \mu\text{moles}/\text{m}^2$. From a comparison of these values with the $D.E.$ values of the particular silica gels (Table 1) esterified with alcohols, it appears that these adsorbents are not completely esterified. Therefore, on their surfaces there exist silanol groups and alkoxy radicals chemically combined with the silica skeleton. The surface OH groups can have different characters [18]: from free to strongly combined with hydrogen bonds (bound and reactive OH groups). Alcohols react above all with free OH groups. At $200-400^\circ$ bound OH groups undergo condensation, forming surface siloxane groups:



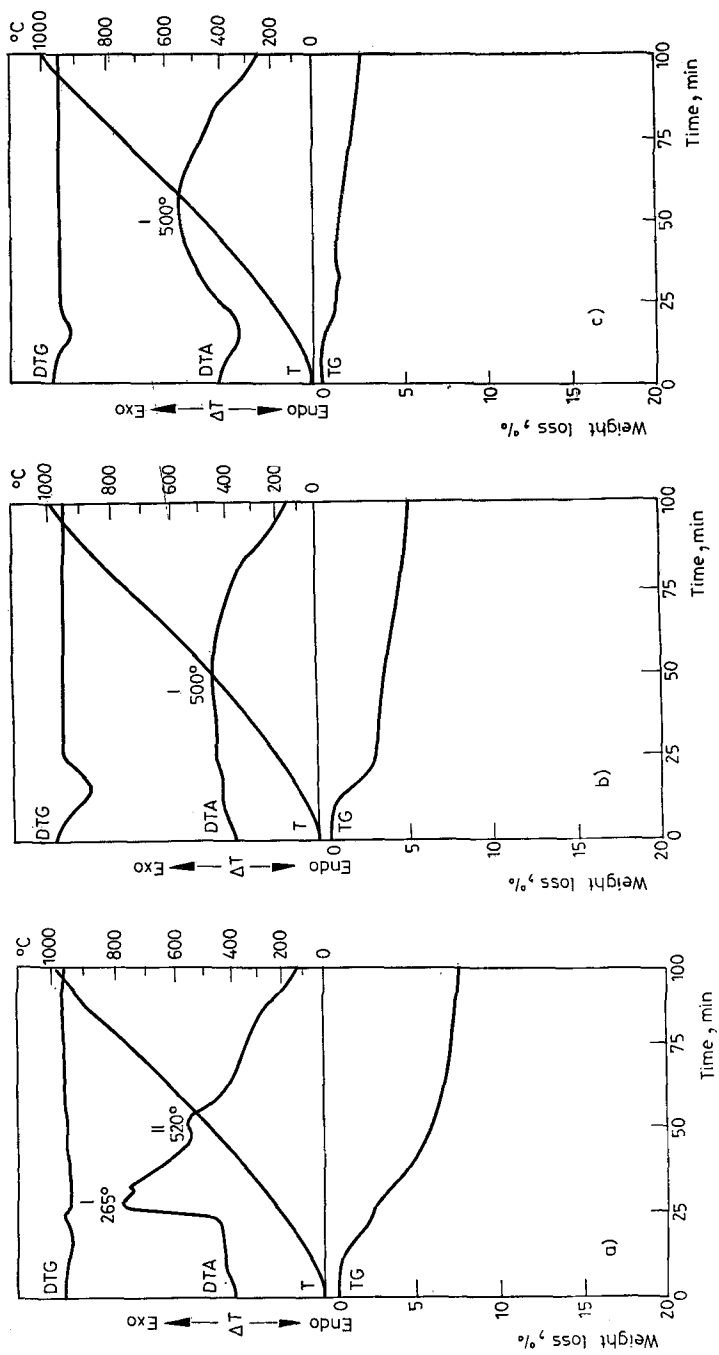


Fig. 1. Thermal curves of samples of silica gels: a — modified with *n*-decanole, b — nonmodified (hydroxylated), c — modified with water vapours (hydroxylated)

However, under these conditions free OH groups migrate on the surface, forming transitional active complexes (OH groups combined) which, on disintegration, give siloxane groups. In an air atmosphere alkoxy radicals also undergo destruction at about 200°, which the DTA curves account for in Figs 1 and 2. Thus, the mechanism of thermal analysis of the adsorbents studied here is complex because

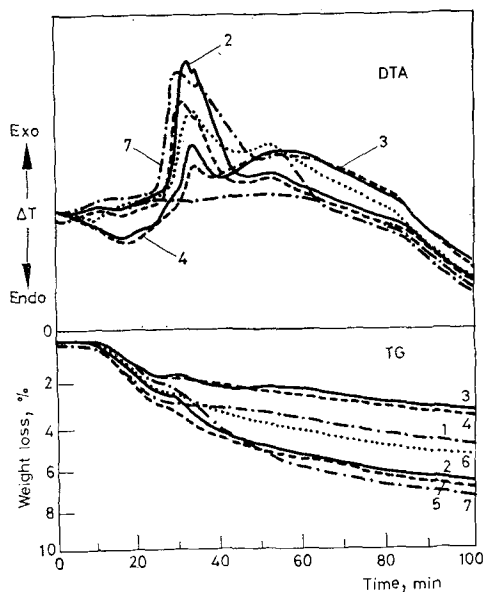


Fig. 2. DTA and TG curves of samples of silica gels; 1 — non-modified (hydroxylated) — · - · - ·, 2 — modified with *n*-propanole — — — — —, 3 — modified with *n*-butanole — — — — —, 4 — modified with *n*-pentanole — — — — —, 5 — modified with *n*-hexanole — — — — —, 6 — modified with *n*-nonanole . . . and 7 — modified with *n*-decanole — · - · - ·.

of their only partial esterification. The more so since calcination of silica gels at high temperatures causes changes in the primary structure of the silica skeleton [18, 21]. Moreover, besides the surface OH groups, hydroxylated silica gels possess interglobular hydroxyl groups. These groups are removed from silica at temperatures above 500°. The total calcination losses of the samples studied (%*W*) will therefore be the total loss resulting from removal of surface hydroxy groups, %*W*_{OH}, intraglobular OH groups, %*W*_g, and alkoxy groups, %*W*_C:

$$\%W = \%W_{\text{OH}} + \%W_{\text{g}} + \%W_{\text{C}} \quad (5)$$

The exothermic peaks I in Figs 1A and 2 are connected primarily with the removal of alkoxy radicals from the surface. Identification of the peaks II is a little more difficult. The temperatures at which the maxima of peaks I and II occur are listed in Table 2. Generally speaking, with the increase in the specific

surface of the esterified silica gel the temperature at which the maximum of peak II appears decreases. A similar regularity, but to a lesser degree, can be observed for the temperature of peak II.

Tchertov et al. [21] have found that the maximum discharge of structural surface water and interglobular OH groups from samples of hydroxylated silica gels occurs in the temperature interval 450–550°. Davydov et al. [19] and Fripiat and Uytterhoeven [22], however, have observed that hydroxy groups begin to leave the sample from the depths of the silica skeleton at 500–600°; a consider-

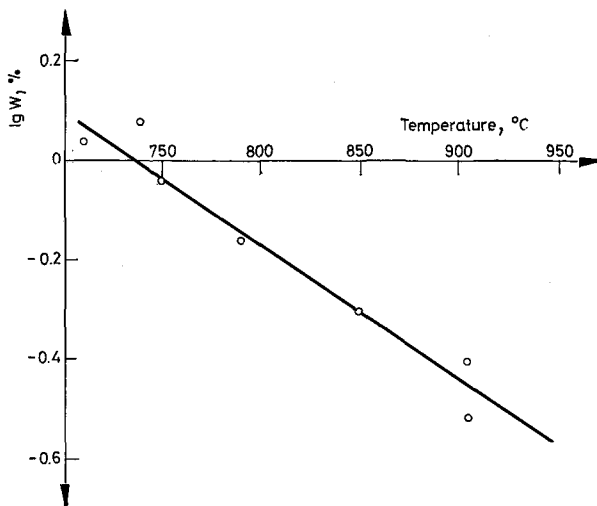


Fig. 3. The dependence of the logarithm of % W_{endo} on the temperature t_{endo}

able proportion of the hydroxy groups can be removed from the depths at 700–800°. It can be expected that under these conditions amorphous silica will be transformed into a crystalline form (cristobalite). The transformation rate, as may be expected, will depend on the temperature and time of heating and the primary structure of the thermally modified xerogel, i.e. on the specific surface, porosity and interglobular water content. Snyder and Ward [23] and Guillemin et al. [24] have found that large-porous silica gels are more “crystalline” than narrow-porous xerogels. Thus, the exothermic peaks II in Figs 1 and 2 come mainly from discharge of water formed by condensation of combined and free OH groups and partially from interglobular water.

In all samples studied, the endothermic effect occurs during calcination, which is probably connected with the onset of the formation of the crystalline silica form. The temperature, t_{endo} , at which this effect begins, depends on the kind of the adsorbent analyzed. These temperatures are given in Table 2. This Table also includes quantitative data concerning the losses due to calcination of the particular xerogel samples. From a comparison of the calcination losses in the temperature ranges $t_{\text{endo}} - 1000^\circ$ and $200^\circ - t_{\text{endo}}$, diminished by the losses resulting from the

esterification of the samples, W_R , it appears that the particular xerogels differ distinctly in structural water content. What is more, t_{endo} depends strictly on the water content of the sample. In Fig. 3 the dependence of t_{endo} on the logarithm of $\%W_{\text{endo}}$ for the samples studied is presented. This dependence is seen to be linear. This is important information from the point of view of the studied mechanism of autoclave modification of hydroxylated silica gels with alcohols. One of the reasons for the occurrence of differences in the percentage losses of the particular sample bulks during their calcination at as high as 1000° (W_g) and t_{endo} (W_E) (Table 2) are the differences in the values of their specific surface and small ones in esterification degrees. For hydroxylated silica gels the losses resulting from thermal removal of surface hydroxyl groups can be calculated from the following equation:

$$N_s = a_{\text{CH}}^s \cdot m = \alpha_{\text{OH}} \cdot S \cdot m \quad (6)$$

in which a_{OH}^s denotes the concentration of OH groups in moles/g, S is the value of the sample surface, and m its mass. It was found that for silica gels $a_{\text{OH}}^s/S = \alpha_{\text{OH}} = \text{constant}$. On this basis the specific surface of silica gels can be determined by not taking the adsorption methods into consideration [25]. There exist many methods for determination of α_{OH} . The simplest one is that proposed by de Boer [26]:

$$\alpha_{\text{OH}} = \left\{ \frac{2}{3} \cdot 10^3 \cdot W \cdot S^{-1} \right. \quad (7)$$

where W denotes the loss of silica mass (weight %) due to its calcination at 1200° (or at 1000° , after an appropriate calcination time) after its previous drying at 120° ; S is the specific surface determined by the method of nitrogen adsorption. However, it appears from the experimental data that this method gives high results in the case of adsorbents with small specific surfaces [21]. Recently Scott and Kucera [27] successfully used de Boer's equation for studying hydroxylated silica gel ($S = 496 \text{ m}^2/\text{g}$) as well as silica gels thermally modified at $200-900^\circ$. From these authors' studies it appears that, with a suitably chosen time of silica gel calcination, calcination losses obtained at temperatures lower than 1200° (1000°) can be utilized in Eq. (7).

If Eq. (7) is applied to calculations of α_{OH} values for hydroxylated silica gels, i.e. non-modified with water vapour, utilizing for this purpose the calcination losses of these adsorbent at 1000° , we obtain values of OH group concentrations on the surface of 5.7 and 45 OH groups/100 Å, respectively. The former value is higher by about 1 OH group than α_{OH} values generally attributed to silica gels. However, the α_{OH} for xerogel modified with water vapour is quite absurd, as it would mean that on the surface of this adsorbent each silica atom is combined with about 8 hydroxyl groups. This surplus in the concentration of silanol groups should be attributed to the presence of interglobular water in both samples, which also appears from the above analysis of the thermal curves (Figs 1b and c, Table 2).

Table 2
Results of quantitative analysis of thermal curves presented in Figs 1-2

Silica gel	Losses of weight												t_{endo} , °C	Temperature or maximum of peaks, °C	
	20-1000°		200-1000°		200°- t_{endo}		t_{endo} -1000°		200°- t_{endo} -D.E.		Interglobular groups OH			I	II
	mg	%W	mg	%	mg	%WR	mg	%WE	mg	%WR	mg	%Wg			
Hydroxylated (non-modified)	25.2	5.1	11.5	2.3	8	1.6	3.5	0.7	8	1.6	6.5	1.3	740	-	485
Modified with water vapour	12	2.4	8	1.6	6	1.2	2	0.4	6	1.2	9.5	1.9	855	-	510
Modified with <i>n</i> -propanol	34.5	6.9	22.5	4.5	18	3.6	4.5	0.9	13	2.6	5.65	1.13	700	290	505
Modified with <i>n</i> -butanol	17.5	3.5	9.5	1.9	8	1.6	1.5	0.3	5.05	1.01	8.5	1.7	855	300	510
Modified with <i>n</i> -pentanol	18.5	3.7	10.5	2.1	9	1.8	2	0.4	5.75	1.15	11	2.2	855	315	520
Modified with <i>n</i> -hexanol	35.5	7.1	21.5	4.3	16	3.2	6	1.2	9.35	1.87	6	1.2	690	285	500
Modified with <i>n</i> -nonanol	27.5	5.5	17	3.4	14.5	2.9	2.5	0.5	7.45	1.49	13	2.6	800	305	490
Modified with <i>n</i> -decanol	37	7.4	27.5	5.5	22	4.4	5.5	1.1	7.25	1.45	6.75	1.35	660	280	520

In the hydroxylated silica gels the total amount of hydroxy groups, G_{OH} , in one globule of radius R can be expressed as follows [20]:

$$G_{\text{OH}} = K \cdot V + \alpha_{\text{OH}} \cdot S \approx \frac{4}{3} \pi R^3 K + \frac{4}{3} \pi R^2 \alpha_{\text{OH}} \quad (8)$$

where V and S are the volume and the surface area of one globule, while K is the concentration of OH groups in the bulk of the globule. If the surface of the silica gel is esterified, Eq. (8) assumes the form:

$$G_{\text{OH}} = K \cdot V + \frac{\alpha_{\text{OH}} - D.E.}{S} \quad (9)$$

From the last two equations it can be seen that the value of $\%W_g$ depends on the radius R of the globules and on the concentration K of OH groups in the depths of the globule. Table 2 lists the values $\%W_g$ calculated from Eq. (5) for the silica gels studied. It appears from a comparison of these data that the xerogels studied differ considerably from one another in interglobular water content. This means that during modification of hydroxylated silica gel with water vapour and alcohol there occurred a change in the structure of the primary globules of this adsorbent. This conclusion is supported by the data contained in the last columns of Tables 1 and 2. These columns give the diameters D of the globules of the adsorbents studied and the coefficient values K , which are the concentration ratios of OH groups in these globules. As can be seen from a comparison of these data for the particular samples, modification of hydroxylated silica gel with water vapour and alcohols brings about changes not only in the D values of the primary globules, but in the concentration K of OH groups in their depths as well.

The values $\%W_g$ in Table 2 may in reality appear higher in calcination of the samples studied at 1200°. However, the relationship found between t_{endo} and $\lg \%W_{\text{endo}}$ (Fig. 3) and the data obtained by independent methods (Table 1) seem to account for the appropriate use of derivatograph in studies on the mechanism of autoclave modification of the skeleton structure of silica gels. It should be added that studies of this kind using other methods were the object of the author's earlier papers, and their results fully confirm the conclusions drawn from the results of the present studies concerning the influence of the kind of alcohol used for modification on the skeleton structure of the silica modified.

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RÉSUMÉ — Un Derivatograph a été utilisé pour suivre le processus de modification de la structure du squelette des gels de silice traités par des alcools et la vapeur d'eau. Une étude analogue a été mise en œuvre à l'aide d'autres méthodes indépendantes. Les résultats obtenus par ces divers procédés sont en bon accord.

ZUSAMMENFASSUNG — Der Derivatograph wurde zum Nachweis des Modifizierungsprozesses der Skelettstruktur von Silikagelen durch Alkohole und Wasserdampf eingesetzt. Analoge Prüfungen wurden durch andere, unabhängige Methoden ebenfalls durchgeführt. Es besteht eine gute Übereinstimmung der auf diese Weise erhaltenen Ergebnisse.

Резюме — Дериватограф был использован для того, чтобы проследить модификационный процесс скелетной структуры силикагеля со спиртами и парами воды. Аналогичные исследования были выполнены другими независимыми методами. Совпадение между результатами, полученными таким путем, хорошее.