THE THERMAL PROPERTIES OF CARBON-SILICA ADSORBENTS (CARBOSILS) PREPARED BY METHYLENE CHLORIDE PYROLYSIS

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The thermal properties of complex carbon-silica adsorbents (carbosils) were investigated using differential thermal analysis. The adsorbents were prepared by pyrolysis of methylene chloride. Pyrolysis reaction on silica surface was carried out at different temperatures (400–700 °C) and at different pressures of CH_2Cl_2 vapours. Thermal analysis was carried out in air atmosphere. The following parameters characterizing the properties of the adsorbents were determined: carbon content, specific surface area, carbon layer thickness, pore volume, mean pore radius, differential of heats of adsorption of *n*-hexane and benzene, and micrographs. The correlation between topography and morphology of carbon deposits (dependent on the parameters of the pyrolysis process) and the courses of DTA and TG curves corresponding to individual carbosils have been determined.

In a previous paper [1] the effect of the nature of the carbonized substances and the structure of porous silica on the thermal properties of carbon-silica adsorbents (carbosils) has been investigated. Carbosils formed in the pyrolysis of methylene chloride [2–6]:

$$CH_2Cl_2 \xrightarrow{\text{temp}} C + 2HCl \tag{1}$$

are interesting both from the cognitive and practical point of view. In this reaction conducted on silica gel surface carbosil of relatively new properties are obtained. The carbon deposit is characterized here by exceptionally big hardness and perfect adhesion to the silica base (silica is not etched by HF due to the perfect coverage of its surface). Furthermore this deposit has a homogeneous chemical structure [2]. However, despite the simple reaction course of CH_2Cl_2 pyrolysis, complex dependences of the properties of carbosils on the parameters of their preparation have been found [5, 6]. It is to be noted that in the pyrolysis of other substances (alcohols [7], polyaromatic hydrocarbons [8]) there occur simple relationships between the amount of the carbonized substances and the surface characteristics of

the complex adsorbent. Therefore the purpose of this paper is to study the effect of the conditions of the preparation of the carbosil (temperature of CH_2Cl_2 pyrolysis and vapour pressure of this substance over the silica gel surface) on its thermal properties.

Experimental

Preparation of adsorbents

The initial adsorbent for obtaining carbosils was silica gel of type Si 100 Merck (FRG), of grain fraction 0.20–0.25 mm. This commercial adsorbent was initially treated with 2N hydrochloric acid to remove admixtures of metal ions from it, then with distilled water, and dried at 120° for 6 hrs and calcined at 600° for 5 hrs.

Carbonization was conducted in the dynamic reactor designed and constructed by Leboda [2]. This apparatus permits regulation of both pyrolysis temperature and the amount of the carbonizing agent, its concentration in the carrier gas and its rate of flow into the reactor.

Carbosils 1–4 (Table 1) were obtained at different temperatures ranging from 400 to 700° at constant working parameters of the reactor (the saturator temperature determining the pressure of CH_2Cl_2 vapour was 24°, the flow rate of carrier gas—argon feeding vapours into the reactor—20 ml/min and the constant amount of carbonized CH_2Cl_2—100 ml).

Table 1 Effect of reaction temperature on the surface properties of carbosils

Ads. No.	Temp. of pyro- lysis, °C	Carbon content, %C w/w	Surface area (S), m²/g	Pore volume (v_p), cm³/g	Mean pore radius, $\bar{R}$ Å	L_c, Å	Heat of adsorption, kJ/mol	
							n-hexane	benzene
1	400	5.1	293	1.245	85	0.7	37.2	43.5
2	500	12.4	280	0.860	62	1.8	52.7	57.6
3	600	25.0	279	0.849	61	3.7	64.4	54.7
4	700	25.5	271	1.409	104	3.7	48.5	60.6
5	500 autoclav	13.1	385	1.182	84	1.9	—	—
0	Initial	SiO_2	380	0.806	43	—	35.9	35.9

Adsorbents 6–8 (Table 2) were prepared at constant temperature (500°) at variable concentrations of the pyrolysate in the carrier gas. The feed rate of CH_2Cl_2 vapours was also constant (20 ml/min). The amount of the substance carbonized was 100 ml.

Table 2 Effect of CH_2Cl_2 vapour pressure on the surface properties of carbosils

Ads. No	Temp. of thermost. °C	Carbon content, %C w/w	Surface area (S), m²/g	Pore volume (v_p), cm³/g	Mean pore radius, $\bar{R}$ Å	L_c, Å	Heat of adsorption, kJ/mol	
							n-hexane	benzene
6	24	14.0	286	0.956	67	2.0	52.7	57.3
7	32	21.4	271	0.899	66	3.1	52.7	47.2
8	40	11.6	285	0.744	52	1.7	57.7	54.4

Carbosil No. 5 in Table 1 was obtained under static conditions, i.e. in a steel autoclave of 0.3 l capacity. The amount of the carbonized CH_2Cl_2 was 2 ml. The initial adsorbent was Lichrosorb Si 100, Merck (FRG).

Testing of adsorbents

Differential thermal analysis was carried out in a Paulik–Paulik derivatograph, model 1000/1500. The temperature range was 20–1005°, atmosphere—air. The analysis was carried out in corundum crucibles, with a sample size of 100 mg. The rate of temperature increase was 10 deg/min.

The surface area and adsorption capacity of pores were determined by the BET method, using the data from low-temperature nitrogen adsorption measurements using a Sorptomat 1800 apparatus (Carbo Erba, Italy). The isosteric heats of adsorption of n-hexane and benzene were determined from the temperature dependences of the retention volume. These measurements were carried out on a Giede, model 18.3 (GDR) gas chromatograph at 150–200° on 1000 × 4 mm i.d. columns with a thermal conductivity detector.

For testing adsorbents by electron microscopy a Tesla BS 540 transmission electron microscope (TEM) was used. Microscope samples were prepared by the method described elsewhere [9].

Results

Surface properties

The chemical reaction studied here proceeded in heterogeneous solid-gas system. The rate of such reactions depends on many factors, among others on the adsorption properties and porous structure of the solid.

The effect of the parameters of methylene chloride carbonization on silica gel surface on the properties of carbosil surface were discussed in detail in papers [2–6]. Therefore, attention has been drawn only to some aspects of this problem. The data

in Table 1 represent the surface properties of the carbosils prepared at different temperatures. With the temperature increase of CH_2Cl_2 pyrolysis the amount of the carbon deposited on the surface of modified silica increased. At 700° this increase was small in relation to that at 600°, because at this temperature the reaction proceeded very rapidly in the whole volume of the reactor, due to which a part of carbon precipitated on its walls. Carbon deposition on silica surface caused a considerable decrease in the size of its specific surface. This means that the carbon deposited blocks a part of the narrow pores of modified silica. The mean radius of silica gel pores increased after being carburized. In spite of this the total volume v_p of the adsorbent pores decreased, which suggests that the carbon deposit develops its own pore structure. Another situation was observed for Adsorbent 4 (obtained at 700°) for which the total pore volume v_p increased. This is connected with the fact that carburization process does not occur on the surface of silica only, but violently in the entire volume of the reactor. At this temperature pyrolysis proceeds largely beyond the surface of silica gel. Part of the carbon formed is deposited on the reactor walls and is also formed in the form of independent particles. In this way we obtained enlarged structure of surface carbosil.

Generally speaking, with the increased amount of carbon deposited on the silica gel surface the heats of adsorption of the substances tested increased. However, this dependence is not as clear as in the case of the carbon deposits obtained by pyrolysing of the substances [7, 8]. Adsorbents 3 and 4 binding practically the same amount of carbon, differ considerably in their adsorption heats and volume of pores. The heat of adsorption depends on the nature of the energetic centres present on the surface of the adsorbent and on the geometrical structure of the pores.

The differences in the v_p magnitude of the individual carbosils, particularly Nos. 3 and 4, indicate that the inner structure of narrow pores present in the carbon deposit is also a fact affecting the magnitude of adsorption heat of the substances tested. As it is known narrow pores are strong adsorption centres, because an increased potential of non-specific interaction occurs in them [10].

The data in Table 2 concern the experiments in which the temperature of the reactor, the flow rate of the carrier gas feeding the pyrolysate and the amount of the substance carbonized were constant. The reaction time and CH_2Cl_2 concentration changed in the reaction space. As can be seen the latter factor exerts an evident effect on the surface properties of the carbosil. In reality the process of carburizing the silica gel surface with the product of CH_2Cl_2 pyrolysis is relatively complex. HCl released in reaction (1) is adsorbed on the silica surface, blocking its active centres on which, at least for some time, carbon does not precipitate. The deposited carbon particles become active centres for some time which develop their spatial structure. This means that although the mean thickness L_c of the carbon layers in carbosils 2–8 (Tables 1 and 2) is theoretically sufficient for the total coverage of the

silica base, these adsorbents may possess intermediate properties between those of silica gel and carbons due to incomplete coverage of the carrier surface with a carbon deposit. Hence among other things, direct relationships are not obtained between the parameters of the preparation process of carbosils in reaction (1) and their surface properties.

Thermal properties

DTA and TG curves for samples of the adsorbents summarized in Tables 1 and 2 are shown in Figs 1 and 2. In Table 3 the data obtained from these thermal curves are presented. From an analysis of these data it appears that with temperature increase of CH_2Cl_2 pyrolysis deposits are formed, whose temperature range of exothermic processes is broadening. Thus, for example, for carbosil 1 containing the smallest amounts of carbon the main exothermic process connected with mass decrement occurs in the interval of 500–620°, whereas for carbosil 4 in the interval of 500–880°. The shape of DTA curves becomes more complicated as the carbon content of the carbosil increases. This is clear if we take into consideration the fact that the time of thermal analysis is the same for all carbosils differing in their
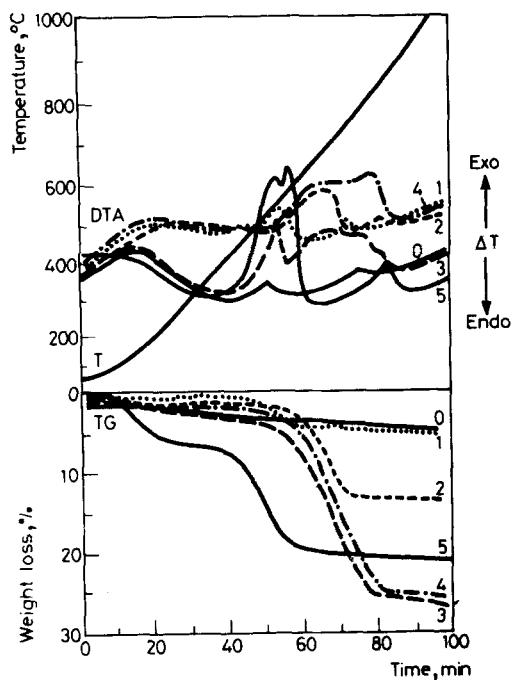

Fig. 1 Thermal curves of samples of adsorbents 0–5 (Table 1) prepared by pyrolysis of CH_2Cl_2 at different temperatures (400–700 °C)
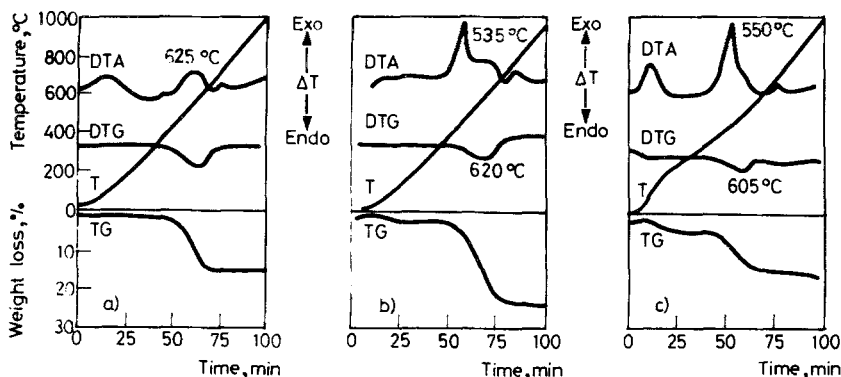
Fig. 2 Thermal curves of samples of carbosils 6–8 (Table 2) prepared by pyrolysis of CH_2Cl_2 with different vapour pressures of modifying agent

**Table 3** Results of analysis of the thermal curves of complex carbon-silica adsorbents (carbosils)

Ads.	Mass losses, % (w/w)			Exothermic peak temperature, °C	Range of exoth. reaction, °C
	20–120 °C	120–400 °C	400–1000 °C		
1	0.05	0.75	5.0	200, 440, 540, *740*	500–620
2	0.25	0.5	12.25	145, 440, 625, 760	500–690
3	0.75	2.25	25.25	85, 160, 515, 665, 665, *790*	400–775
4	0.75	0.75	25.25	180, 440, 675, 730, *810*	500–880
Silica gel	1.0	0.9	2.2	470, *710*	—
5	0.5	0.25	13.9	200, 420, 625, *765*	470–690
6	0.5	1.0	21.25	140, 550, 605, *765*	100–200, 440–640
7	0.75	1.75	11.75	120, 580, 665, *790*	40–220, 440–700
8	5.0	3.0	15.25	100, 510, 540, 565, *830*	60–180, 400–625

carbon content. Accordingly, the kinetics of calcination of the carbon deposit may be different for individual adsorbents.

However, for carbosils 3 and 4 having practically the same amounts of carbon (25%) various shapes of DTA curves are obtained, which means that calcination of both deposits may be affected by other factors connected with the structure characteristics of carbon deposits of the complex adsorbents studied. These characteristics are manifested by the differences in the heat of adsorption of *n*-hexane and benzene, as test substances, and by the differences in v_p size of the carbosils studied.

To elucidate more closely the effect of the structure of carbon deposit on their thermal properties in air atmosphere, the photomicrographs of several adsorbents were examined. In Fig. 3 photomicrographs are compared with the TEM of the
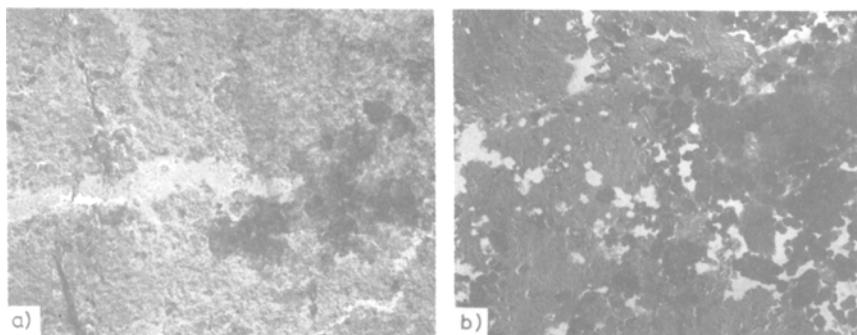
Fig. 3 Surface topography of carbosils obtained at 400 °C (Ads. 1) (a) and at 700 °C (Ads. 4) (b) (Table 1, TEM ×6000)

surface of the carbosils obtained at 400° (a) and 700° (b). In both cases despite considerable differences in the content of carbon and in the mean thickness L_c of its associated layer, a mosaic surface could be observed. Dark areas represented "patches" of the carbon deposit. In the first case this deposit was more degenerated than on carbosil 4 (Fig. 3b). Other photographs (Figs 4–6) present the morphology of carbon deposits. They were obtained by the technique described in paper [11].

On the whole the carbon deposits presented in Figs 4–6 have a globular structure, however, depending on the conditions of the preparation of the particular carbosils, the globules are more or less homogeneous in respect of their dimensions. Thus carbosil 1 obtained at 400° has a deposit of irregular globules 200–800 Å in diameter (Fig. 4a). On carbosil 2 obtained at 500°, globules of similar diameters of the order 800–1200 Å can be distinguished, whereas carbosil 3 (600°, Table 1) is characterized by a less homogeneous globular structure. In the latter case the diameter of the globules is of the order of 300 Å.
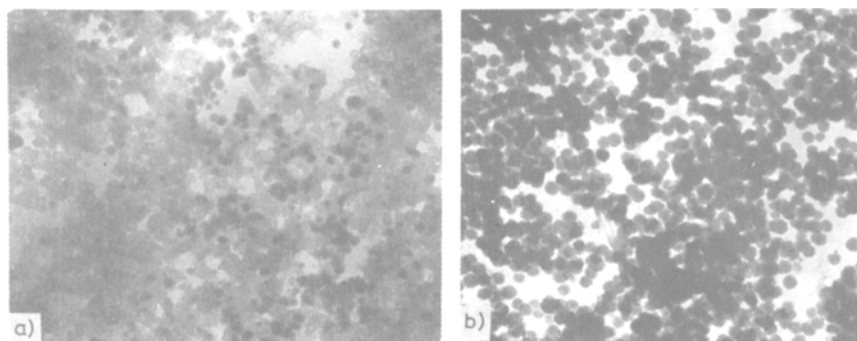
Fig. 4 TEM of a thin liyer of carbon deposit from surface of Ads. 1 (a) and 2 (b) (Table 1, ×40000)
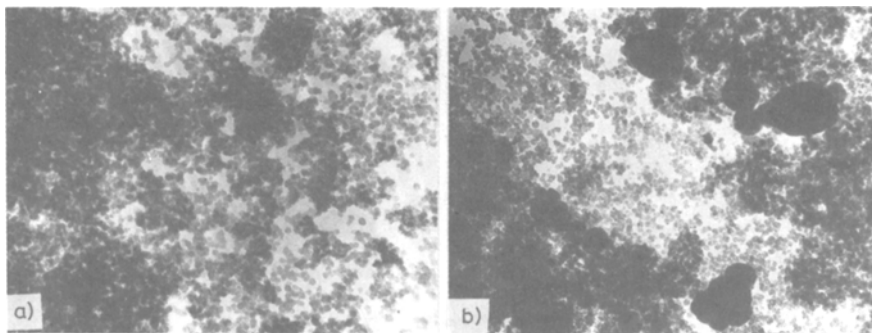
Fig. 5 TEM of a thin layer of carbon deposit from surface of Ads. 3 (a) and 4 (b) (Table 1, × 40000)
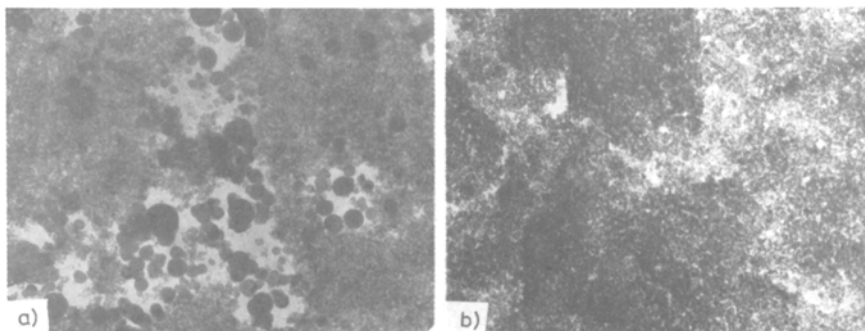
Fig. 6 TEM of a thin layer of carbon deposit from surface of Ads. 4 (a) (× 10000) and Ads. 5 (b) (× 40000) prepared in autoclave

It is interesting to compare the morphology of carbosil 3 and 4. In Fig. 5 at least two kinds of globules can be distinguished, i.e. small ones, 200–300 Å in diameter and big aggregates of globules 2500–7500 Å in diameter. From a direct comparison of photographs a and b in Fig. 5 it can be seen that the carbon deposits of carbosil 3 and 4 contain comparable amount of carbon in their morphology. In all photographs the presence of carbon membranes of "darker" globules against "lighter" ones results from the spatial distribution of globules and aggregates in the carbon deposit.

In Fig. 6a the morphology of the carbon deposit of carbosil 4 (Table 1) is additionally shown at another site of the carbosil surface than in Fig. 5b. Also in this photograph there can be found a three-dimensional structure of the carbon deposit of carbosil 4, and besides a fairly homogeneous "membrane" of globules of small dimensions, i.e. about 200–300 Å larger globules-aggregates can be distinguished which frequently lie on the membrane surface and form a three-

dimensional structure. The dimensions of these aggregates are several to dozens of times larger than the smallest globules.

The last photograph (Fig. 6b) shows the membrane of carbon deposited on the silica gel surface during CH_2Cl_2 pyrolysis in the autoclave (carbosil 5, Table 1). The characteristic feature of the carbon deposit obtained in this way is its relatively high homogeneity, which is seen in the photograph. A three-dimensional structure can also be observed here to a small extent. Carbon obtained in the autoclave usually forms agglomerates consisting of uniform globules of diameter smaller than 100 Å.

In the light of the facts the differences in the course of DTA curves of the carbosils analysed (Figs 1 and 2) become comprehensible. They result from differences between the topography and morphology of carbon deposits of the particular carbosils. Although the temperature increase of CH_2Cl_2 pyrolysis results in an increased rate of methylene chloride decomposition to give carbon, this does not cause the formation of uniform globular structures. At higher temperatures, carbon deposits can develop active centres for the deposition of carbon, and this feature depends on the temperature. This could explain the high pore volume value observed for adsorbent 4 (Table 1).

In the initial period of the thermal analysis of carbosils, removal of moisture traces from their surface and physical oxygen adsorption occur. Adsorption is an exothermic process therefore maxima on the DTA curves (Figs 1, 2, Table 3) are already observed at low temperatures (200°). With temperature increase physical adsorption decreases, whereas chemisorption of oxygen increases. It has been found that the optimum temperature for maximum chemisorption of oxygen lies close to 400° [12]. Below 500°, the rate of formation of surface oxides exceeds the rate of their decomposition but at higher temperature the complexes become less stable and the rate of their decomposition into carbon dioxide and carbon monoxide exceeds the rate of their formation. The formation of CO and CO_2 requires an appreciable concentration of oxygen complexes. The capacity of a carbon adsorbent depends on its surface area S and hydrogen content.

The data in Tables 1 and 2 show that the carbosils studied do not differ significantly in their S magnitudes. Moreover, the course of reaction (1) does not indicate the presence of hydrogen in their carbon deposit. They differ, as shown earlier, in the size of globules. An analysis of the data in Table 3 and of the photomicrographs (Figs 3 and 5) permits to assume that the more homogeneous the globular structure of carbon deposits, the less complex are the DTA curves. This can be seen on the example of carbosils Nos. 1 and 5, for which the photographs of "membranes" of carbon deposits point to their highest homogeneity, the smallest differentiation of the size of globule diameters. Thus, it is only natural that for these carbosils relatively narrow ranges have been obtained in which the main exothermic

reactions occur. On the basis of the shapes of the thermal curves in Fig. 2 it can be assumed that the carbosils studied were characterized by fairly homogeneous globular structure. They were obtained at 500° at various rates of carbonizing silica gel. Thus it can be concluded that the temperature plays a bigger role in the formation of various globular structures and agglomerates than the pressure of pyrolysate vapours over the silica modified, because the DTA curves in Fig. 2 have a relatively narrow temperature interval. However, the effect of the discussed factor on the properties of carbon deposits cannot be excluded. Thermal curves in Figs 2a and 2c concern two carbosils with similar amounts of carbon. Nevertheless, their DTA curves differ slightly. The DTA curves in Figs 2b and 2c, however, are similar, although the compared carbosils differ considerably in their carbon content. Accordingly, it can be concluded that at a temperature of 500° carbon globules with dominating diameters are formed. The temperature of calcination of such globules is similar for the particular carbosils as regards their maximal exothermic effects (Fig. 2, Table 3). Discrepancies of the order of 5–20° result among other things, from different total content of carbon in the particular deposits as well as from a different amount of globules with smaller or bigger diameters than those predominating in the given carbosil.

The DTA curve for Ads 8 (Table 2) has distinct peak in the temperature range of 40–120° for exothermic process. The presence of this peak is connected with the increase of the carbosil mass (Fig. 2c). The maximum temperature of this reaction is 140°. This phenomenon can be interpreted in terms of carbon surface oxidation by oxygen from air, accompanied by the formation of surface functional groups e.g. COOH, CO. This reaction should occur in the case of amorphous carbon, which is formed in a too fast carburization process. Similar phenomena (although in smaller degree) are observed for the adsorbent 7 (Table 2, Fig. 2b) carburized more slowly. This effect is not observed for carbon deposit of highly ordered structure, produced at higher temperature and more slowly accomplished carburization process.

The temperatures in Table 3, the values of which are underlined concern changes of amorphous silica into crystal forms. As in the previous paper [1], the effect of the present carbon deposit on the height of the temperature of such changes can be observed. This temperature can be thought to be determined by the topography and morphology of the carbon deposit.

Conclusion

The carbon deposit obtained by CH_2Cl_2 pyrolysis on the surface of the silica gels are of globular structure. The size of globules and the way of their spatial distribution depend largely on the temperature of pyrolysis. The higher the

temperature the more heterogeneous is the size of globules. This homogeneity is manifested by the shape of the DTA curves. The more homogeneous the globules the more distinct is the DTA curve, i.e., it is narrower with more distinctly marked maxima and minima. From TG and DTA curves (Fig. 1) and data listed in Table 1 results that temperature increase of CH_2Cl_2 pyrolysis on silica surface shift the burning process of carbon deposit towards higher temperatures (from 500–620° for Ads. 1 to 500–880° for Ads. 4). This phenomenon is connected with an increase in the sizes of carbon globules on SiO_2 surface as well as with an increase of the order of the microcrystalline structure of carbon.

The degree of order of the carbon deposit depends not only on the temperature of pyrolysis. The speed of the carburization process plays also here an important role (concentration of CH_2Cl_2 in carrier gas). An increase in CH_2Cl_2 concentration in the pyrolysing gas causes formation of parts characterized by less regular carbon deposit, which undergoes oxidation in air atmosphere at low temperature (140–200°), connected with the formation of surface functional groups e.g. COOH, CO, OH. This can be confirmed by the existence of an exothermic peak on DTA curves connected with an increase of adsorbent weight in this temperature range (Fig. 2). This means that the thermal analysis data may serve for determination of the morphology and to some extent the topography of carbon deposits. It also seems that the carbon deposits obtained in CH_2Cl_2 pyrolysis may serve as models in studies of other carbon adsorbents, particularly those with globular structure, because of their chemical homogeneity and also because of the possibility of the formation of globules of various sizes.

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Zusammenfassung — Mittels DTA wurden die thermischen Eigenschaften von komplexen Kohlenstoff-Silikaadsorptionsmitteln (Carbosil) untersucht. Die Adsorptionsmittel wurden durch Pyrolyse von Methylenchlorid gefertigt. Die Pyrolyse wurde an der Oberfläche von Silika bei verschiedenen Temperaturen (400–700 °C) und bei verschiedenen CH_2Cl_2-Drücken durchgeführt. Die Thermoanalyse geschah in Luftatmosphäre. Folgende Parameter zur Charakterisierung der Eigenschaften der Adsorbenten wurden ermittelt: Kohlenstoffgehalt, spezifische Oberfläche, Kohlenstoffschichtdicke, Porenvolumen, Porendurchmesser, Ableitung der Adsorptionswärme von n-Hexan und Benzol sowie Oberflächenmikrogramme. Es konnte der Zusammenhang zwischen Topografie und Morfologie der Kohlenstoffablagerungen (abhängig von den Parametern des Pyrolysevorganges) sowie dem Verlauf der DTA- und TG-Kurven der entsprechenden Carbosile festgestellt werden.

Резюме — Методом ДТА изучены термические свойства сложных угольно-кремнистых адсорбентов (карбосилов). Адсорбенты были получены пиролизом хлористого метилена. Реакция пиролиза проводилась на поверхности двуокиси кремния при различных температурах (400–700°) и при различном давлении паров хлористого метилена. Термический анализ проводился в атмосфере воздуха. Были определены следующие характерные параметры адсорбентов: содержание углерода, удельная площадь поверхности, толщина углеродного слоя, средний радиус пор, дифференциальная теплота адсорбции n-гексана и бензола, а также микроснимки поверхности. Установлена корреляция между топографией и морфологией углеродистых отложений, зависящих от параметров процесса пиролиза, и ходом кривых ДТА и ТГ для каждого отдельного карбосила.