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Effect of hydrothermal modification on the porous structure and thermal properties of carbon–silica adsorbents (carbosils)

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Abstract

Characterisation of porous structure and thermal properties of unmodified and hydrothermally modified (using H_2O_2, under high pressure conditions) carbon–silica adsorbents (carbosils) prepared by dichloromethane pyrolysis (under dynamic conditions) on the surface of narrow pore silica were discussed. The analysis was made based on the data of low-temperature nitrogen adsorption/desorption isotherms, transmission electron microscopy (TEM) and the results of differential thermal analysis. It was stated that both porous structure and thermal properties of tested samples are in correlation with the morphology and topography of the carbon deposit. This deposit forms globules and aggregates whose size and position on the inner and outer surface of silica depends on the time of its carbonisation. It was stated that hydrothermal treatment (HTT) of the carbosils changes both the porous structure and thermal properties of the tested samples. As a result of HTT of silica, decondensation and recondensation of orthosilic acid on large particles of silica takes place. Then a decrease in the specific surface area and increase in the radius of pores are observed. In the case of carbosils these changes are smaller and depend on the accessibility of the silica surface, which is connected with topography of carbon deposit.

Keywords: Carbosils; Hydrothermal modification; Transmission electron microscopy; Differential thermal analysis

1. Introduction

Carbon-mineral adsorbents have become more and more widely applied. This results not only from the possibility of preparation of new materials using these adsorbents, but mainly from their original surface properties. Such adsorbents may combine all features of nonpolar carbon and polar mineral adsorbents (e.g. the nature of adsorption sites such as Bröensted and Lewis acid sites, surface heterogeneity, pore structure) desired for different adsorption processes. Owing to these features, the adsorbents may simultaneously adsorb organic [1–8] (including enzymes [9,10]) and inorganic [6,9] substances, which is very important with respect to their utilisation in the processes of water and waste purification [6]. These materials can be used in analytical chemistry for isolation and concentration of trace amounts of the substances contained in water and other media [8,11].

The characteristics of carbon deposits and adsorbent as a whole can be changed due to variations in pyrolysis conditions, precursor origin, or pretreatment techniques (chemical modification, hydrothermal and thermal treatments [4,12–15]). In the paper [16] vast studies on the effect of various parameters of dichloromethane pyrolysis (among others, temperature and pyrolysis duration time, rate of pyrolyzate feeding and partial pressure of its vapours in the carrier gas) on the surface of wide, medium and narrow pores of silica gels were presented.

The object of our investigations are carbon–silica adsorbents (carbosils) formed in the pyrolysis of dichloromethane

$$CH_2Cl_2 \rightarrow C + 2HCl$$

This type of adsorbents is interesting from both cognitive [7] and practical points of view [8]. In this reaction carried out on the silica gel surface, carbosils of very interesting properties are obtained [7]. The carbon deposit is characterised here by exceptionally large hardness and perfect adhesion to the silica base. It was stated that heterogeneity and

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the way of distribution (topography) of the carbon deposit on the porous surfaces of silica gels exert a significant effect on the rate of their gasification [16,17].

It is known that besides the physicochemical processes taking place in the silica skeleton (recondensation and decondensation) there can also take place reactions in the carbon deposit, i.e. its gasification and oxidation with the oxygen evolved during the thermal decomposition of H_2O_2 [18] as well as with water vapour [19]. The hydrothermal treatment (HTT) of carbon sample causes partial degradation of the macro- and micropore structures, thus affecting the surface area and pore volume. This was accompanied by the change of modified sample surface chemistry.

It is also known that the carbosils show relatively high thermal resistance both in the atmosphere of air and nitrogen and in the atmosphere of hydrogen [20–22]. However, thermal properties of carbosils significantly depend on the nature of the carbonised substance. The process of gasification of carbon deposit is complex and depends on many factors, among others, on the chemical structure of carbon deposit, its distribution on the surface and on the porous structure of the adsorbent. Aliphatic compounds cause a decrease of thermal stability of carbon deposit.

The aim of the paper is the analyse of the porous structure and thermal properties of the carbon–silica adsorbents and those after HTT. Knowledge of these parameters makes these adsorbents possible to use as a carbonaceous materials in many practical yields. The results subsequent from the presented data were contributed by transmission electron microscopy (TEM) analysis of carbon deposits. The informations about thermal properties of adsorbents can be of great importance, because these adsorbents often work at high temperatures and in atmospheres of different gases which are often aggressive. In such conditions the adsorbents can undergo destruction, or in less dramatic conditions can gradually change their surface properties.

2. Experimental

2.1. Preparation of adsorbents

As an initial materials there were used porous silica gel and carbosils prepared on its base, differing in the content of carbon deposit. The preparation of the adsorbents was described in [17]. The initial series of carbosils was named CS-1, ..., CS-6.

2.2. Hydrothermal treatment

Hydrothermal modification of the tested carbosils and silica gel was carried out according to the procedure described in [23]. After modification, the samples, called CS-1-HTT, CS-2-HTT, ..., CS-6-HTT, respectively, were obtained.

2.3. Testing of adsorbents

2.3.1. Nitrogen adsorption

Nitrogen adsorption/desorption isotherms were recorded at −195 °C using a Micromeritics model ASAP 2010 (V-2.00) adsorption analyser. The specific surface area (S_{BET}) values were calculated according to the standard Brunauer–Emmet–Teller (BET) method [24] at p/p_s between 0.06 and 0.2, where p and p_s denote the equilibrium pressure and the saturation pressure of nitrogen at −195 °C, respectively. The pore parameters (volume V_p, radius R_p) were evaluated from the adsorption data at $p/p_s \approx 1$. The pore size distribution was evaluated from the desorption branch of isotherm using the Barret–Joyner–Halenda (BJH) method [25].

2.3.2. Thermal analysis

Differential thermal analysis was carried out in a Paulik, Paulik and Erdey (MOM, Budapest) derivatograph, model C. The temperature range was 20–1000 °C, atmosphere–air. The rate of temperature increase was 10 °C min^{-1}. The mass of weighted sample was 20 mg. The platinum crucibles were used.

2.3.3. Transmission electron microscopy

TEM micrographs of CS-*i* samples were made using a BS 540 (T) apparatus (accelerating voltage 80 kV, resolution 0.8 nm, magnification 24000×). Microscope samples were prepared using the platinum–carbon replication method with evaporation of carbon and platinum onto the adsorbent surface, then treated in hydrofluoric acid to dissolve silica.

3. Results

3.1. Porous structure

The structural characteristics of all tested samples are presented in Table 1. Figs. 1 and 2 present adsorption/desorption isotherms of nitrogen determined for the starting silica gel (Si-60) and the carbosils obtained by pyrolysis of different quantities of dichloromethane (CS-1, ..., CS-6). According to the common classification of adsorption isotherms [26], the isotherms obtained for unmodified (starting) silica gel and carbosils can be considered as isotherms of type IV. The hysteresis loops observed during desorption are typical for mesoporous materials and closely resemble the loops of H1 type according to the IUPAC classification [27]. Hysteresis loops of H1 type were obtained, among others, for adsorbents having a uniform globular structure, in which pores are represented by interglobular spaces. Similarly, the adsorption/desorption isotherms for the carbosils after HTT can be classified into IV and H1 types, respectively. This indicates that modification of the initial silica does not disrupt its globular structure.

Table 1
Structural characteristics of the investigated adsorbents (adsorption of nitrogen)

Adsorbents	S_{BET} ($m^2\ g^{-1}$)		ΔS_{BET} (%)	V_p ($cm^3\ g^{-1}$)		ΔV_p (%)	R_p (nm)	
	Before HTT	After HTT		Before HTT	After HTT		Before HTT	After HTT
Si-60	408.2	49.9	87.8	0.957	0.123	87.1	4.7	4.9
CS-1	418.6	356.8	14.8	0.843	0.803	4.7	4.0	4.5
CS-2	450.4	347.3	22.9	0.916	0.755	17.6	4.1	4.3
CS-3	308.7	276.9	11.5	0.620	0.579	6.6	4.0	4.2
CS-4	290.4	246.5	15.1	0.549	0.516	6.0	3.8	4.1
CS-5	266.2	221.8	16.7	0.494	0.443	10.3	3.7	4.0
CS-6	175.4	163.6	6.7	0.302	0.315	−4.3	3.4	3.8

Fig. 3 presents dependencies of the specific surface area on the carbon deposit contents (curves a and b) and the carbon deposit contents as a function of coating time (curves c and d) for samples before (curves a and c) and after (curves b and d) HTT. As follows from Fig. 3, the dependence of the carbon deposit content versus the carbonisation time can be well approximated with a straight line, both for samples before and after HTT (Fig. 3, curves c and d). Commonly the increase in the amount of carbon (%C) deposited on the silica surface results in the regular decrease of specific surface area of the adsorbent being carbonised [28]. As follows from the data included in Tables 1 and 2 the carbosils CS-1 and CS-2 containing 5 and 7.8% (w/w) C, respectively, possess a larger specific surface area than that of the initial silica (SG) (Fig. 3, curve a).

As known [29], two extreme systems of carbon deposition on porous materials, i.e. diffusion and kinetic ones can be distinguished under dynamic conditions. The diffusion system occurs when the pyrolysis reaction rate is larger than the reagent diffusion one. As a result, the total process is limited by diffusion and the carbon deposition takes place in the zone adjacent to the outer surface of the adsorbent grain (which is promoted by high temperature of pyrolysis, large reaction efficiency of initial reagents, small sizes of carbon deposit support pores) (in the kinetic system diffusion can contribute to uniform distribution of carbon deposit on the

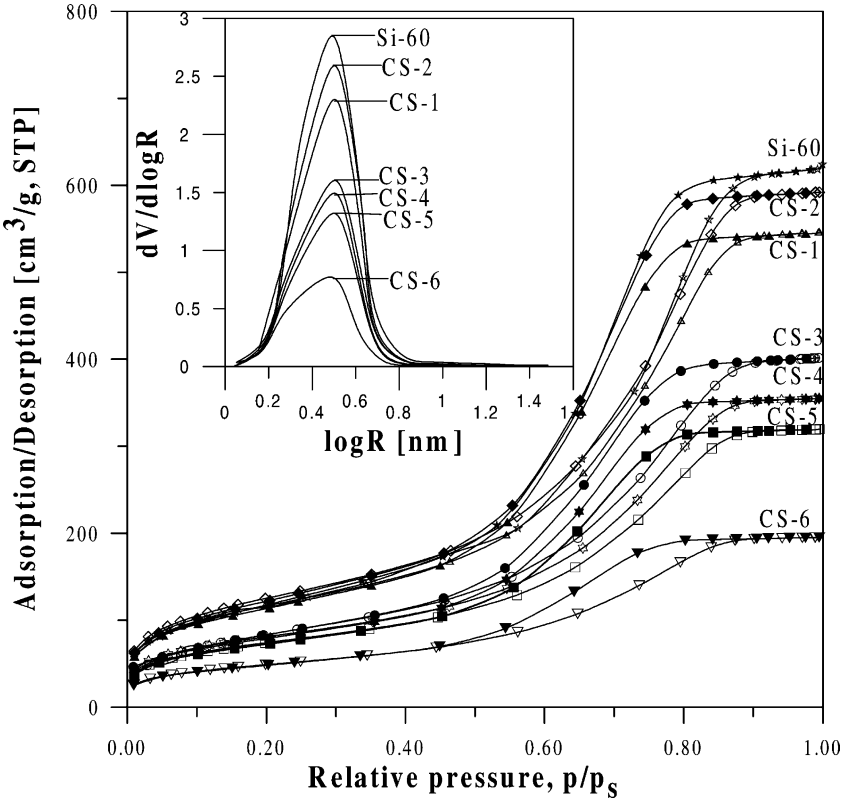

Fig. 1. Nitrogen adsorption/desorption isotherms as well as pore volume distribution as a function of the pore radius logarithm on the initial silica gel and series of carbosils.

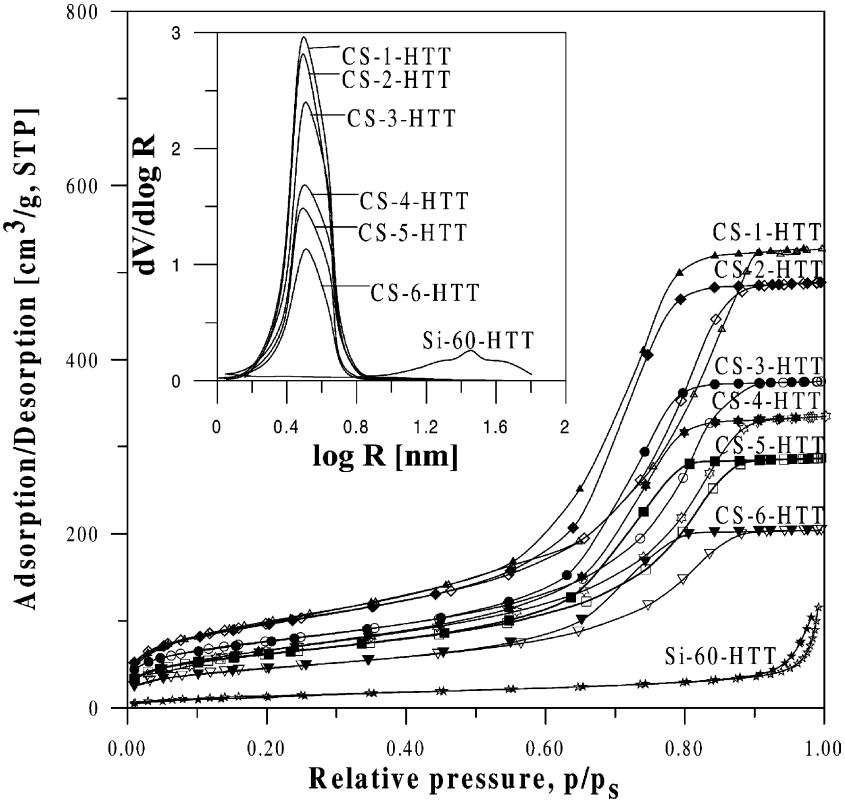

Fig. 2. Nitrogen adsorption/desorption isotherms as well as pore volume distribution as a function of the pore radius logarithm on the hydrothermal treated silica gel and carbosils.

modified adsorbent surface). Thus, a porous carbon layer is formed on the outer surface of grains on which carbon can still be deposited. After some time, when the amount of deposited carbon increases, it can fill (or mask) narrow pores of modified silica which causes a gradual decrease in specific surface area of the complex adsorbent (samples CS-3–CS-6, Table 1; Fig. 3, curve a).

It is known that the dependence of carbosil specific surface area size on carbon deposit amount (decreasing or in the form of the extremum as in the results presented here: Fig. 3, curve a) results largely from carbonisation conditions and the primary structure of the modified adsorbent. It is worth noting that the complex dependences observed here $S_{BET} = f(\%C)$ (Fig. 3, curve a) can have definite practical meaning. They indicate that in the conditions of outer diffusion carbon deposition, it is possible to obtain complex adsorbents possessing a larger specific surface area than the modified support owing to porous carbon deposition on its surface.

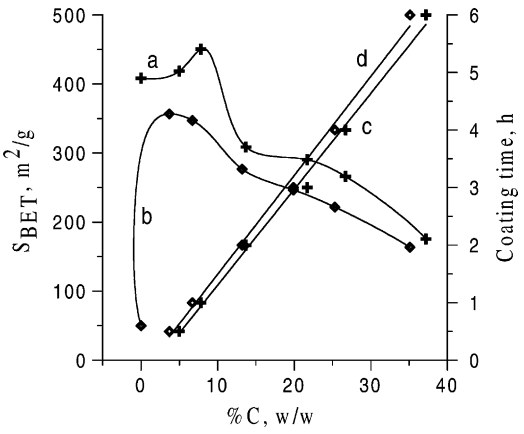

Fig. 3. The dependences $S_{BET} = f(\%C)$ and $\%C = f(\text{coating time})$ for the initial (curves a and c) and modified (curves b and d) samples, respectively.

As follows from the data in Table 1 HTT of the carbosils under consideration causes drastic changes in S_{BET} size of individual samples. The extent of these changes (ΔS) depends not only on the amount of carbon contained in a given carbosil, but also on its distribution (topography) on the modified silica surface.

During the HTT of silica, depolimerisation (decondensation) of small particles of orthosilic acid and deposition of this acid (recondensation) on large particles of silica take place. In our case water taking part in the above reaction forms through thermal decomposition of molecules of the modifier, H_2O_2. As a result, a decrease in the specific surface area and total volume of modified silica pores as well as an increase in the mean radius of pores and primary globule sizes are observed. The specific surface area S_{BET} and the pore volume V_p of the initial silica gel (Si-60) after its HTT decrease by over 87% (Table 1). In the case of carbosils

Table 2
The results of thermal analysis of initial silica gel and carbon–silica adsorbents before and after HTT

Adsorbents	Loss of the mass (%) (w/w)				Range of positive DTA peak (°C)	ΔT_{exo} (°C)	T_{exo}^{max} (°C)	%C (w/w)
	20–200 °C	200–400 °C	400–800 °C	800–1000 °C				
Si-60	4.05	1.85	1.95	0.75	–	–	–	–
CS-1	2.6	1.4	6.15	0.14	463–625	162	560	5
CS-2	2.0	1.45	8.3	0.2	449–636	187	579	7.8
CS-3	1.65	1.45	14.05	0.15	441–652	211	592	13.7
CS-4	1.75	1.1	22.05	0.8	423–663	240	605	21.7
CS-5	3.2	1.15	26.15	0.2	420–681	261	616	26.7
CS-6	2.45	1.7	36.75	0.05	405–740	325	609	37.2
Si-60-HTT	5.15	3.1	6.95	1.4	–	–	–	–
CS-1-HTT	4.25	1.25	4.6	0.2	446–606	160	549	3.7
CS-2-HTT	4.05	1.7	9.6	0.55	460–630	170	573	6.7
CS-3-HTT	3.0	1.6	14.1	0.52	450–639	189	588	13.2
CS-4-HTT	3.25	0.5	20.1	0.3	433–663	230	610	19.9
CS-5-HTT	4.81	2.42	25.8	0.35	440–681	241	628	25.3
CS-6-HTT	2.9	2.45	34.1	0.2	416–714	298	625	35.1

these changes are much smaller which is connected with screening of the initial silica surface by the carbon deposit. Hence the reaction of decondensation of the particles of orthosilic acid in the HTT process is smaller here. It depends on the accessibility of this surface for water molecules which, in turn, is connected with topography of carbon deposit on the modified silica surface.

As follows from the analysis of the data included in Table 1, the changes of the S_{BET} and V_p sizes of the carbosils subjected to HTT are not complementary. The ΔS sizes for a given carbosil are larger than their ΔV_p values. The exception is the carbosil CS-6 for which a small increase in porosity ($\Delta V_p = -4.3\%$) is observed after HTT, though the largest carbon deposit (37.2% (w/w)) in this case should screen most of all the initial silica surface.

It is worth nothing that contrary to the initial silica gel, the HTT of carbosil causes homogenising of mesopore structure of these adsorbents. This can be seen while comparing corresponding curves of carbosil mesopore volume distribution (Fig. 1) and after their HTT (Fig. 2). These curves are narrower for the carbosils CS-*i*-HTT ($i = 1, 2, \ldots, 6$) than for the initial ones (CS-*i*). Radii of the pores dominating R_{dom} for the unmodified carbosils CS-1–CS-4 and CS-5 and CS-6 are 3.1 ± 0.1 and 2.3 nm, respectively. However, after the HTT process, the sizes R_{dom} are homogenised for all carbosils. They are 3.1 ± 0.1 nm. For the initial silica (Si-60) $R_{dom} = 3.1$ nm, but after its HTT the size R_{dom} is 28.8 nm. The above data are different from the corresponding sizes R_p (Table 1) which follows from the asymmetry of the curves $dV/d \log R$ (Figs. 1 and 2) as well as from the possibility of some microporosity in the studied adsorbents. This indicates that the HTT mechanism of carbon–silica adsorbents (carbosils) is quite complex. In our case the HTT process causes some changes in the amount of carbon deposit of modified carbosils as evidenced by the suitable data (%C) included in the last column in Table 2. Generally speaking, the percentage of these changes is lower for the carbosils containing large amounts of carbon deposit (samples CS-4–CS-6).

3.2. TEM investigations

Fig. 4 shows microphotographs of the surface of unmodified initial silica gel (a) and the carbosil CS-2 (b) possessing the largest size S_{BET} of the adsorbents (Table 1). The Si-60 surface seems rough and granular and globules forming large particles of silica gel are formed (Fig. 4a) as well as large transport pores (dark areas in micrographs); however, main mesopores of silica gel at $R_p < 10$ nm are invisible due to relatively low TEM magnification (24000×). In turn, strongly dispersed, small molecules (globules) of carbon deposit of the sizes below 10 nm can be observed on the surface of carbosil CS-2 (Fig. 4b). At the same time such globules form aggregates of linear sizes form several hundred to several thousand nanometer in some sites. Further increase of silica surface carbonisation causes formation of a greater and greater number of large aggregates of carbon deposit which can be seen in the microphotography of CS-4 (Fig. 5a) and CS-6 (Fig. 5b) carbosils surface. Despite a relatively large amount of carbon deposit in these samples, i.e. 21.7 and 37.2%, respectively, their surface is a mosaic one. It enables access of water molecules to the silica skeleton and the course of reaction decondensation [30] during the HTT of these carbosils. The reaction yield and, in consequence, the changes of structural parameter sizes (Table 1) depend on the extent of initial silica surface screening by the carbon deposit. The extent diminishes with the increase of carbon deposit content in a given carbosil which can be seen in the microphotographs in Figs. 4b and 5a, b for the samples CS-2, CS-4 and CS-6, respectively.

The microphotographs and the complex course of the dependence $S_{BET} = f(\%C)$ (Fig. 3, curve a) indicate that both size and distribution of carbon deposit molecules (globules) in the prepared samples are heterogeneous in the range at

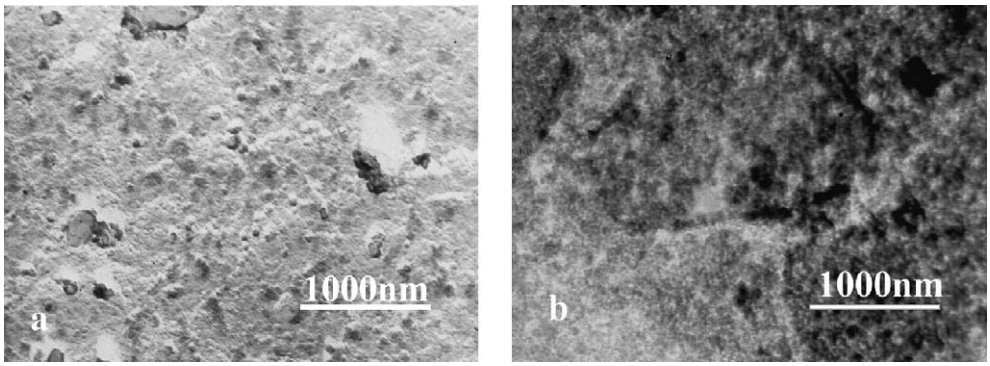

Fig. 4. TEM micrographs of Si-60 (a) and CS-2 (b) samples (prepared by carbon–platinum replica, magnification 24000×).

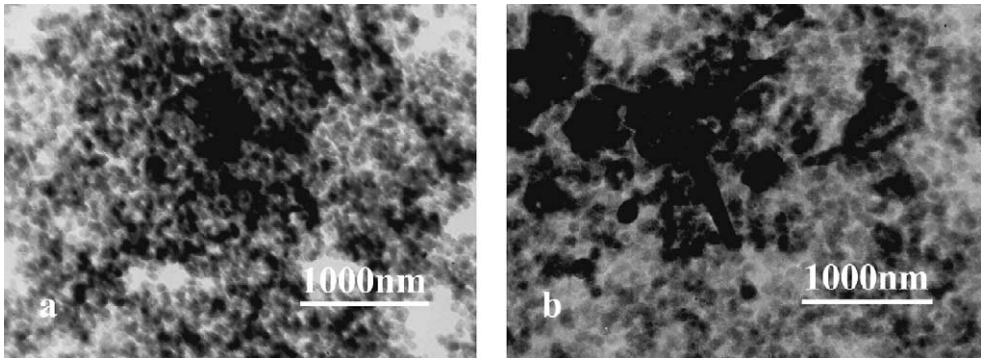

Fig. 5. TEM micrographs of CS-4 (a) and CS-6 (b) samples (prepared by carbon–platinum replica, magnification 24000×).

least to 13.7% (w/w) C. In the preliminary period of initial silica gel carbonisation, carbon deposit globules do not fill the initial pores of the modified adsorbent gradually and uniformly which can be observed also on the curves $S_{BET} = f(\%C)$ (Fig. 3, curve a). With the large content of carbon deposit (>13.7% (w/w)), the above mentioned dependence has a character close to the linear one which would indicate homogenisation of initial silica surface carbonisation. Similar correlation are observed for the modified samples (Fig. 3, curve b).

After HTT of Si-60 at 200 °C for 6 h, the silica surface becomes spongy (Fig. 6a) which is accompanied, as pointed out earlier (Table 1), by a significant decrease of primary parameters of modified silica porous structure, due to enlargement of pores and reduction of their number, because of disruption of the pore walls on the intensive hydrolysis of Si–O–Si bonds. The other microphotographs show replicas of surface of some carbosils modified hydrothermally, i.e. CS-2-HTT (Fig. 6b), CS-4-HTT (Fig. 7a) and CS-6-HTT (Fig. 7b). Unfortunately, it is no use comparing these pictures with corresponding photographs for unmodified carbosils (i.e. in Figs. 4b and 5a, b), because these replica refer to quite random parts of surface of the studied carbosils. However, the microphotographs in Figs. 6b and 7a, b allow for

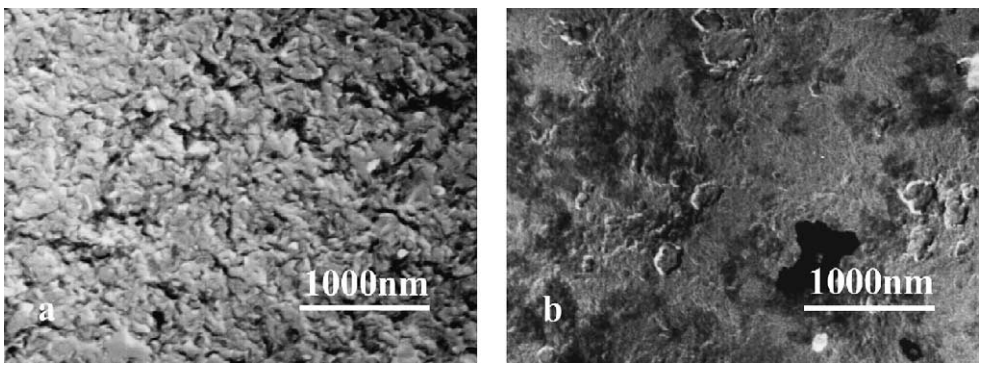

Fig. 6. TEM micrographs of Si-60-HTT (a) and CS-2-HTT (b) samples (prepared by carbon–platinum replica, magnification 24000×).

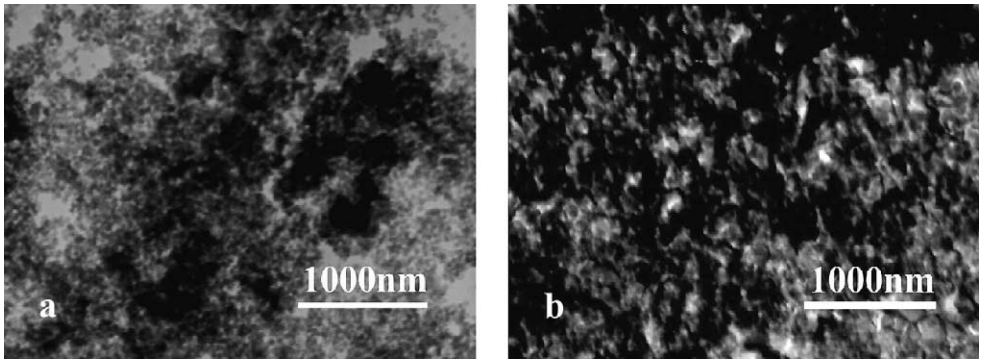

Fig. 7. TEM micrographs of CS-4-HTT (a) and CS-6-HTT (b) samples (prepared by carbon–platinum replica, magnification 24000×).

estimation of changes in the carbosil surface structure after their HTT. Thus comparing the pictures of carbosils surface after HTT in the above figures, one can state that such treatment causes smaller changes in the texture of silica surface not covered by the carbon deposit. They are less spongy than the silica surface both before and after its hydrothermal modification. Screening a part of silica surface, the carbon deposit makes its hydrothermal modification impossible through decondensation and recondensation processes.

Large dispersion and small sizes of carbon globules in the sample CS-2 (Fig. 4b) and the enlarged specific surface area of this adsorbent compared with that of the initial silica gel (Table 1) suggest that the deposited carbon masks primary narrow pores of modified silica to a small extent. Such pores are the most reactive in the HTT process. Hence the greatest values of ΔS_{BET} and ΔV_p (Table 1) were obtained for the sample CS-2.

Generally speaking, the microphotographs presented in Figs. 6b and 7a, b indicate that carbon deposit becomes more compact due to HTT of carbosils than in the case of untreated samples (Figs. 4b and 5a, b). The silica surface not covered with pyrolysis products is "smoother" compared with those of the initial silica gel (Fig. 4a) and of the adsorbent subjected to HTT (Fig. 6a). The exception is the carbosil CS-6-HTT whose surface texture is more complex (Fig. 7b) than that of the other samples which indicates a great effect of silica skeleton restructuring during carbosils HTT on the global texture of the complex carbon–silica adsorbents.

3.3. Thermal properties

The results of thermal analysis, i.e. the TG and DTA curves for the studied samples are presented in Figs. 8–11, respectively.

Table 2 includes the quantitative data obtained from the analysis of the curves presented in Figs. 8–11. As follows from these figures essential changes in the studied carbosil samples occur during their heating at temperatures above 400 °C (Figs. 8 and 9). These changes are accompanied by strong exothermic effects (Figs. 10 and 11). In the case of the samples of initial silica gel and that hydrothermally modified

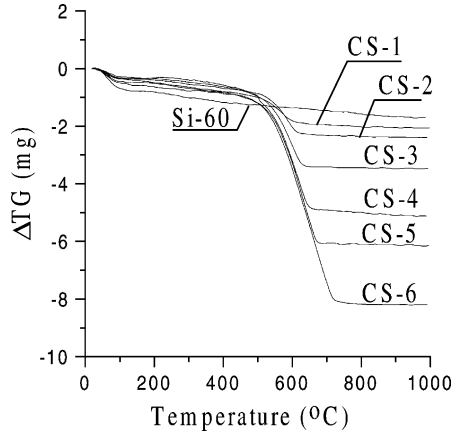

Fig. 8. Dependence of mass changes (ΔTG) as a function of increase of temperature obtained for the initial series of adsorbents (before HTT).

there is observed continuous change of mass during their heating which is connected with gradual removal from their surface of:

- physically adsorbed water (to about 200 °C);
- next water formed from surface condensation of bound OH groups (200–400 °C); and

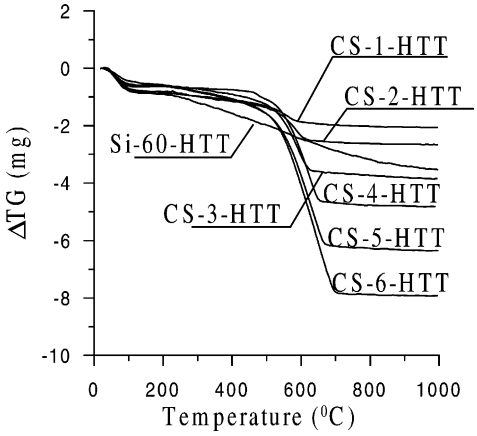

Fig. 9. Dependence of mass changes (ΔTG) as a function of increase of temperature obtained for the hydrothermally treated adsorbents.

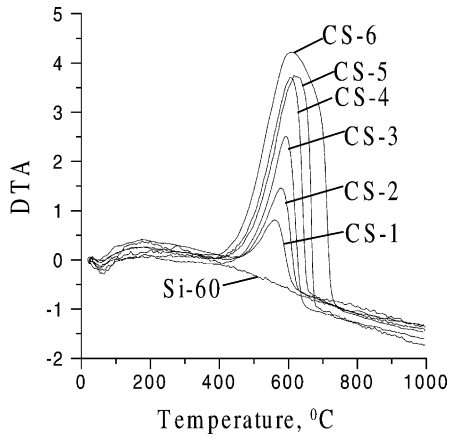

Fig. 10. DTA curves obtained for the initial silica gel and the carbon–silica adsorbents as a function of temperature increase.

- at higher temperatures of other surface OH groups and interglobular water [2].

During heating of individual carbosils their mass losses increase from the sample CS-1 to CS-6 which is accompanied by a simultaneous increase of the field below the DTA curve (Figs. 10 and 11) which can be clearly seen in the quantitative data in Table 2. The carbon deposit contents (%C (w/w)) in individual adsorbents given in the last column are taken as equal to the losses of the heated sample in the range of corresponding exothermic peak temperatures.

In the initial period of the thermal analysis of investigated carbosils, removal of moisture traces from their mosaic surface (20–200 °C) and physical oxygen adsorption occur on the surface of complex adsorbents. Adsorption is an exothermic process. Therefore small maxima on the DTA curves (Figs. 10 and 11) are already observed at low temperatures (≤200 °C). With the temperature increase physical adsorption decreases, whereas chemisorption of oxygen increases. The optimum temperature for maximum chemisorption of oxygen lies close to 400 °C. Below 500 °C, the rate of surface oxides formation exceeds that 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 that of their formation. The formation of CO and CO_2 requires an appreciable concentration of oxygen complexes. The capacity of carbon adsorbent depends on its surface area and morphology.

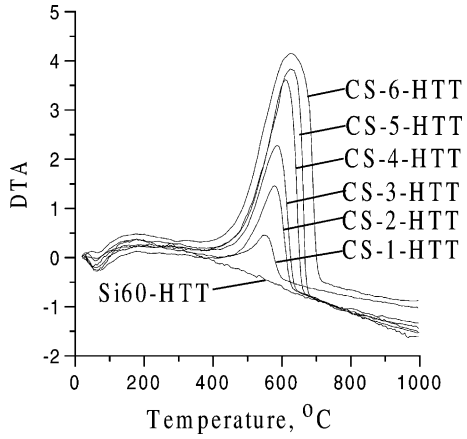

Fig. 11. DTA curves obtained for the hydrothermally treated silica gel and the carbon–silica adsorbents as a function of temperature increase.

Rapid changes in mass of the carbosil samples connected with carbon deposit combustion begin at temperatures over 400 °C. The range of temperatures ΔT_{exo} (width of the DTA peak) in which there occur exothermic processes of carbon deposit gasification and the temperature in the maximum of the DTA peak (T_{exo}^{max}) depends on the amount of carbon in a given carbosil (Table 2). The more carbon deposit in a given carbosil, the wider temperature range it is gasified and the higher value of T_{exo}^{max} is. As follows from Fig. 12, the dependence ΔT_{exo} on %C can be approximated with a straight line which allows to predict the width of exothermic peaks (temperature range) in which a carbosil is gasified. Slight deviation of points from the corresponding lines in this figure can result from the differences in heterogeneity of sizes of carbon deposit globules and aggregates which are observed between individual carbosil samples.

It can be also thought that after the HTT process carbosils gasify more quickly. Hence the diagram $\Delta T_{exo} = f(\%C)$ for this series of carbosils (Fig. 12) lies below the line for unmodified carbosils. It means that unmodified and modified carbosils possessing the same amount of carbon deposit will be gasified at different time (in a different range of temperature) in the HTT process. A similar effect of HTT on the value T_{min} of carbosils (Table 2) is observed. This parameter indicates temperature in the minimum curve of DTG (differential thermogravimetric) (not shown here) at which the reaction rate has its maximum. These temperatures (as well as the widths of the DTG curves) increase with the increase of the carbon deposit amount in a given carbosil.

The samples of carbon deposit content over 20% show very strong “graphite” electric conduction [17]. This means that carbon deposits prepared by us are homogeneous with respect to the chemical structure as can be seen in the form of single DTA peaks for all studied carbosils (Fig. 10). In the HTT process these carbosils are surface-oxidised (part

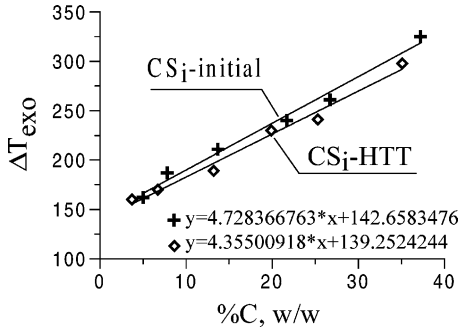

Fig. 12. Dependence of ΔT_{exo} as a function of carbon deposit concentration obtained for the initial and hydrothermally treated carbon–silica adsorbents.

of the deposit was most probably gasified like in the typical process of carbon activation as indicated by changed quantities %C, Table 2), however, the inner chemical structure of carbon deposit globules and aggregates should not change. At the same time, as pointed earlier, the carbon deposit after HTT becomes more compact. Therefore one can think that differences in behaviour of modified and unmodified carbosils in HTT results from both chemical (differences in the surface chemistry) and physical (size and topography of carbon deposit agglomerate) reasons.

As follows from the data in Table 2, like in the case of both silica gels (Si-60 and Si-60-HTT), a smaller loss of their mass takes place during heating (thermal analysis) of carbosils at the temperature above 800 °C. This may be connected with the presence of interglobular water in them and residual OH groups which, as mentioned earlier, are removed at high temperatures. As can be seen slightly larger mass losses were observed for the carbosils subjected to HTT than those for the initial carbosils. This is due to the fact that HTT of silica gel causes a significant increase in concentration of OH groups in the bulk of its globule [2]. This increase depends, among others, on the screening degree by carbon deposit of the silica matrix.

4. Conclusions

The presented experimental results show that during the pyrolysis of dichloromethane on the surface of silica gel we can obtain the carbon deposit which amount is in the correlation with the time of processes. The obtained carbon deposit has a globular structure and the globules combine in large aggregates forming spatial layers. Under the dynamic conditions of pyrolysis, in the initial period of carbonisation of porous silica structure there are formed small globules which are more susceptible to quick gasification during thermal analysis than large agglomerates. Topography of the porous surface also plays a significant role in the carbon deposit gasification. The globules on the outer surface are gasified more quickly, because diffusion of substrates (oxygen) and products (carbon oxides) to and from the surface of carbosils subjected to thermal analysis is facilitated. Owing to such topography of globules, carbosil is also susceptible to decondensation and recondensation during the hydrothermal modification.

With the increase of size of carbon deposit agglomerates there is observed the increase of temperature range in which its combustion takes place; this is accompanied by the increase of temperature in the maximum of exothermic peak and of that in which the reaction rate is the largest. However, the porous structure of the carbosil (both modified and unmodified) and the site of deposit localisation play a significant role. These factors affect diffusion processes and, consequently, kinetics of carbon deposit combustion.

Hydrothermal treatment of carbosils causes changes in their porous structure, topography and morphology of carbon deposit which affects their thermal properties. Surface oxidation of carbon deposit during such treatment facilitates its combustion. The HTT process causes some changes in the amount of carbon deposit of modified samples. It was stated also that carbon deposit becomes more compact due to HTT of carbosils than in the case of untreated samples.

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