THERMAL BEHAVIOUR OF COMPLEX CARBON-SILICA ADSORBENTS (CARBOSILS)

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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 α-phenylethyl alcohol, *n*-octanol, *p*-chlorotoluene and mixtures of these substances on silica gel surfaces, and they were treated with hydrogen. Thermal analysis was carried out in air atmosphere. The following parameters characterizing the properties of the adsorbents were determined: carbon and hydrogen contents, specific surface area, nitrogen adsorption isotherms, differential distribution of pore volumes according to their radii, carbon layer thickness, conversion degree of the substance pyrolysed, and surface micrographs. The effects of the nature of the carbonized substance and pyrolysis intermediates on the thermal properties of the complex adsorbent are discussed.

Studies of the thermal properties of adsorbents are of great importance for their practical use. For example, in gas chromatography adsorbents or supports of stationary phases operate at high temperatures in atmospheres of various gases (H_2, N_2, CO_2, etc.), which often contain moisture or oxygen. A derivatograph provides great possibilities for studies of the properties of adsorbents and chromatographic supports [1–3].

Studies of the thermal properties of carbosils appear to be particularly interesting, because they comprise a new type of adsorbents. The surface of the carrier (silica) is covered with a mechanically stable carbon layer. Carbosils are prepared through high-temperature (700–900°) benzene conversion on a silica surface [4], or through the pyrolysis of alcohols [5, 6], CH_2Cl_2 [7] or other substances [8] at lower temperatures (>350°). The properties of a complex adsorbent depend, among other things, on the nature of the substance pyrolysed and on the applied method of carbonization (static–dynamic) [9].

In the present paper, the effects of the nature of the carbonized substance and the structure of the porous silica on the thermal properties of carbon-silica adsorbents (carbosils) were studied in atmospheres of air and hydrogen.

Experimental

Preparation of adsorbents

Two kinds of adsorbents were used for the preparation of the carbosils: a) silica gel for column chromatography (Macherey Nagel, FRG), grain size 0.15–0.30 mm (silica I); b) silica gel (POCh Gliwice, Poland), grain size 0.15–0.30 mm (silica II). Both commercial adsorbents were purified from surface metal ion impurities with concentrated HCl and were then heated at 800° for 6 h (silica I) or at 700° for 7 h (silica II).

Various substances or their mixtures were carbonized on separate silica gel portions (15 g) in a 0.2 l steel autoclave at 500° for 6 h. After the reaction, all complex adsorbents were washed free of pitch substances not bonded to the silica surface. This process was carried out in a Soxhlet apparatus, using N,N'-dimethylformamide and acetone as solvents. In this way a number of adsorbents were obtained, which were determined as follows:

carbosil A – pyrolysis of 2 ml of α-phenylethyl alcohol (FEA),

carbosil B – pyrolysis of 5 ml of p-chlorotoluene (p-chT),

carbosil C – pyrolysis of 2 ml of FEA + 5 ml of p-chT,

carbosil D – pyrolysis of 5 ml of p-chT + 2.64 ml of n-octyl alcohol (OA),

carbosil E – pyrolysis of 2 ml of FEA + 5 ml of p-chT.

For the preparation of carbosils A, B, C and D, silica I was used, whereas for carbosil E silica II was used.

Testing of adsorbents

Adsorption and desorption isotherms of nitrogen were investigated as previously [10]. The contents of carbon (%C) and hydrogen (%H) in the adsorbent samples were determined with the help of a Combi 55 apparatus (VEB Glaswerke Stutzerbach, Thüringen, GDR). Samples of adsorbents A, B and C (Table 1) were subjected to the action of hydrogen at high temperatures in a gradient-free stirred reactor constructed by Barcicki et al. [11]. Nitrogen was first conducted through the reactor heated to about 200°. After this temperature was reached, the gas flow was changed to hydrogen at 350 ml/min. (Both nitrogen and hydrogen were deoxygenated and dried.) The reactor temperature was then gradually increased to 700°. Under these conditions, chemical reaction occurred on the surface of the adsorbents, resulting in the formation of light hydrocarbons. The reactor was coupled to a gas chromatograph, permitting analysis of the volatile reaction products.

All adsorbents were analysed on a Paulik, Paulik, Erdey derivatograph. The

atmosphere was air. The analysis was carried out in corundum crucibles. The rate of temperature increase was 10 deg/min.

The microscopic pictures of the carbosil surface and films (layers) of carbon deposits were taken as described in [12].

The adsorption heats of hexane, benzene and chloroform were measured chromatographically as previously [7].

Results

Figure 1 presents TG and DTA curves of the selected carbosil samples. Moreover, for comparison, it shows DTA curves for the complex adsorbent obtained through the thermal decomposition of methylene chloride [7]:
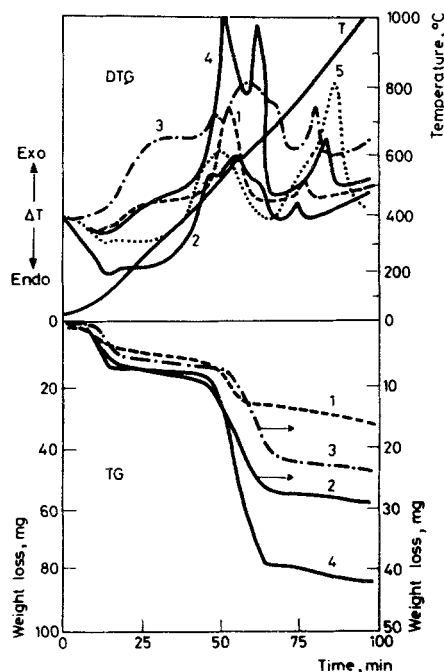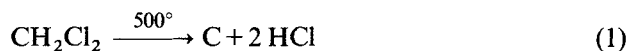
$$CH_2Cl_2 \xrightarrow{500°} C + 2\,HCl \tag{1}$$

Fig. 1 Thermal curves of samples of adsorbents: 1) carbosil A modified with H_2 at 692°; 2) carbosil C; 3) carbosil C modified with H_2 at 687°; 4) carbosil E; 5) carbosil prepared by pyrolysis of CH_2Cl_2

on the silica surface previously calcinated at 900°. The carbon content in this
adsorbent is 30% w/w. From the above reaction, as well as from IR spectroscopic
examinations, it follows [13] that the chemical structure of the carbon deposit here is
fairly homogeneous. The quantitative data relating to the thermal studies on the
carbosils are listed in Table 1. Appropriate characteristics are also given for the
selected adsorbents which were submitted to the action of hydrogen at elevated
temperatures. The temperature values which are underlined refer to crystal changes
occurring in the silica skeleton. From the data in Table 1 and Fig. 1, it appears that
the adsorbents studied are characterized by relatively high thermal stability in an
atmosphere of air. This is accounted for by the high temperatures at which the
maxima of the exothermic effects T_{exo} occur. The presence of one or more maxima
in the DTA curves suggests that the process of gasification of the carbon deposits
depends on the nature of the substance used for pyrolysis. For example, although
carbosils A, B and D contain similar amounts of carbon (Table 1), DTA curves with
different shapes were obtained for them (Fig. 1, Table 1). Thus, it can be concluded
that the different courses of the DTA curves for these carbosils result from the
differences in the chemical structures of their carbon deposits. For the carbosils
discussed, different values of adsorption heat were obtained (Table 1), which may
partially confirm the above suggestion.

The chemical structures of the carbon deposits of the adsorbents discussed can be
concluded from the data presented in Fig. 2. These data were obtained through
chromatographic analysis of post-reaction gases formed as a result of hydrogen
action on the carbosils. In these gases we found: methane (C_1), ethane (C_2),
ethylene (C_2^x), propene (C_3) and butane (C_4). The C_x/C_y ratios are shown in Fig. 2
(where $C_x = C_1, C_2, C_3$ and C_2^x; $C_y = C_2, C_3$ and C_4), depending on the time and
temperature of the reaction on the selected adsorbent. The individual curves in the
Figure depict the C_x/C_y changes at constant temperature (shown in the Figure) in a
given time interval of the reaction.

A decrease in C_x/C_y (Fig. 2) with increase of the reaction time and temperature
indicates that the concentration of component C_y increases in the products of
gasification of the carbon deposit, whereas that of C_x decreases, and vice versa.
However, a constant C_x/C_y ratio points to a regular chemical structure of the
carbon deposit on the carbosil surface. The values of these ratios can provide
information on the chemical structure of the carbon deposit. For example, on
carbosil D at 680° a value $C_2^x/C_2 = 1$ was obtained, which may suggest that there is
one C—C bond for each C = C bond. As regards the other carbosils near 670–690°,
this ratio approaches a value of 1.

Light hydrocarbons are formed due to hydrogenation and thermal destruction of
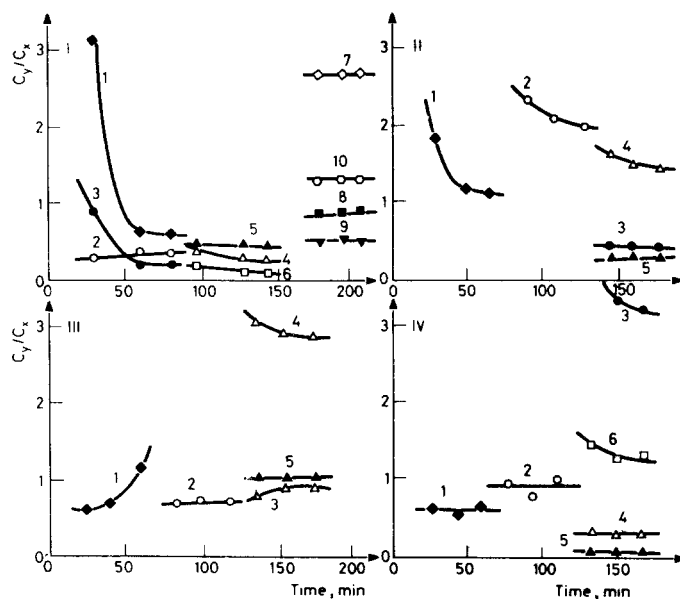the components of the carbon deposit that are less strongly bonded to the surface of

Fig. 2 Variation of C_x/C_y with the reaction time with hydrogen for carbosils A (I), B (II), D (III) and E (IV) at different temperatures:

I) 343°: 1 C_1/C_3, 2 C_3/C_4, 3 C_1/C_4;
512°: 4 C_1/C_4, 5 C_3/C_4, 6 C_1/C_4;
692°: 7 C_1/C_2, 8 C_2^x/C_2, 9 C_2/C_3, 10 C_1/C_3.

II) 334°: 1 C_3/C_4; 682°: 3 C_1/C_3, 4 C_1/C_2, 5 C_2/C_3;
511°: 2 C_1/C_3.

III) 333°: 1 C_3/C_4; 502°: 2 C_3/C_4;
680°: 3 C_1/C_3, 4 C_1/C_2, 5 C_2^x/C_2.

IV) 341°: 1 C_3/C_4; 493°: 2 C_3/C_4;
674°: 3 C_1/C_2, 4 C_1/C_3, 5 C_2/C_3, 6 C_2^x/C_2.

the support. Unsaturated elements of the carbon deposit interact most strongly with the silica surface.

An analysis of the data in Fig. 2 leads to the conclusion that the carbosils studied partially differ in the chemical structure of the carbon deposit. This is indicated, among other things, by the values of the C_x/C_y ratios. The absence of C_2^x ethylene in the products of the carbosil B reaction with hydrogen does not indicate the absence of unsaturated elements from the carbon deposit of this adsorbent, since it is rather unlikely that such elements are hydrogenated to C—C. They are rather strongly bonded to the silica surface and a higher temperature is needed for their gasification.

The discussed reactions, occurring in a gradient-free reactor, can be determined

as an additional pyrolysis of the carbon deposit with its partial hydrogenation. However, this additional pyrolysis of the carbosils studied did not cause unification of the structure of their carbon deposits, for, as appears from Fig. 1 and the data in Table 2, the adsorbents modified with hydrogen still possess different T_{exo} values (the data in brackets). Nevertheless, the discussed process caused an increase in thermal stability of the carbosils. This results from a comparison of the mass losses in the temperature interval 120–400° before and after carbosil modification in an atmosphere of hydrogen (Table 2).

The data presented above undoubtedly indicate that the chemical structure of the carbon deposit affects the thermal properties of the carbosils. However, in the DTA curve for the adsorbent obtained in reaction (1) two maxima are found, at 470 and 545°, although the carbon deposit was suggested to be chemically homogeneous here. Therefore, it should be assumed that there are still other factors determining the gasification of carbosils, such as the effects of the porous structure of the adsorbent, and the morphology and topography of the carbon deposit. It is evident that it is more difficult to oxidize the carbon deposit in narrow pores than that located in wide ones, i.e. on a more accessible surface. Moreover, the kinetics of the gasification or hydrogenation of the carbon deposit will depend on the development of the adsorbent surface (magnitude S).

An example of isotherms of nitrogen adsorption and desorption, as well as pore-size distribution according to their radii on the selected adsorbents, is shown in Fig. 3. From the curves $dV/d \log R = f(\log R)$, it appears that the pyrolysis products of the gasified substance fill some of the narrowest pores of the modified silica. As follows from Table 1, the value of the predominating radius $R_{dom} = 34$ Å is virtually constant. The volume of pores with $R \approx 27$ Å changes. Accordingly, the magnitude S for the initial silica decreases. The changes in the porous structure of silica gel depend on the nature of the gasified substance (Table 1). For example, carbosil B has a larger specific surface S than carbosil A (Table 1), although these carbosils are characterized by equal carbon content (%C) and medial thickness L_C (Table 1). This indicates that in the case of carbosil B less carbon is in narrow pores than in carbosil A. As a result, T_{exo} for the first peak in the DTA curve is lower for carbosil C. Hence, the different T_{exo} values for carbosils C and E (Table 1) must result from the considerable differences in the specific surfaces of these adsorbents (Table 1), because they were prepared through pyrolysis of the same substances.

From previous work [14], it appears that the shape of the DTA curves for the carbosils obtained through CH_2Cl_2 decomposition (Eq. 1) depends on the amount of carbon deposited on the silica surface. It has been found that for small amounts of carbon (up to several per cent) one distinct maximum occurs in the DTA curves. (At larger amounts a point of inflection occurs, as at $T_{exo} = 470°$ in curve 5 in Fig. 1.) The value of T_{exo} increased from 445 to 525° along with the carbon content.

Table 1 Characterization of surface properties of complex carbon-silica adsorbents

Adsorbent	Elemental analysis		Surface area, S, m²/g	Pore radius, R_{dom}, Å	Degree of conversion D.C.	$\%C/S$ $\times 10^{-3}$	Layer thickness of carbon L_c, Å	Heats of adsorption kJ/mol		
	$\%C$	$\%H$						hexane	benzene	chloroform
Silica gel	—	—	382	27; 34	—			33.1	36.4	30.6
Carbosil A	5.24	0.43	281	35	0.54	13.72	0.8	48.1	48.8	43.1
Carbosil B	5.31	0.26	320	35	0.28	13.90	0.8	47.7	61.5	47.0
Carbosil C	13.23	0.76	274	34	0.46	34.63	1.9	49.4	53.2	46.8
Carbosil D	5.81	0.44	306	35	0.20	15.21	0.8	38.5	47.3	39.3
Carbosil E	6.50	0.5	170	72	0.22	33.16	2.0	48.9	53.2	48.0

Table 2 Results of analysis of thermal curves of complex carbon-silica adsorbents modified and non-modified thermally with hydrogen (the data in brackets)

| Adsorbent	Mass losses, % w/w			Exothermic peak temperature, °C	Elemental analysis	
	20–120 °C	120–400 °C	400–1000 °C		%C, w/w	%H, w/w
Carbosil A	2 (0.65)	0.5 (0.45)	3.5 (2.15)	540, 585, 765 (455, 555, 555, 790)	5.24	0.43
Carbosil B	2.25 (1.0)	1.0 (0.45)	6.7 (5.75)	475, 555, 580, 755 (575, 625, 870)	5.31	0.26
Carbosil C	2 (2)	1.85 (1.0)	10.5 (8.5)	505, 585, 670, 780 (475, 575, 575, 685, 805)	13.23	0.76
Carbosil D	0.9	0.5	6.05	460, 575, 765	5.81	0.44
Carbosil E	1	0.25	6.9	545, 655, 855	6.50	0.50
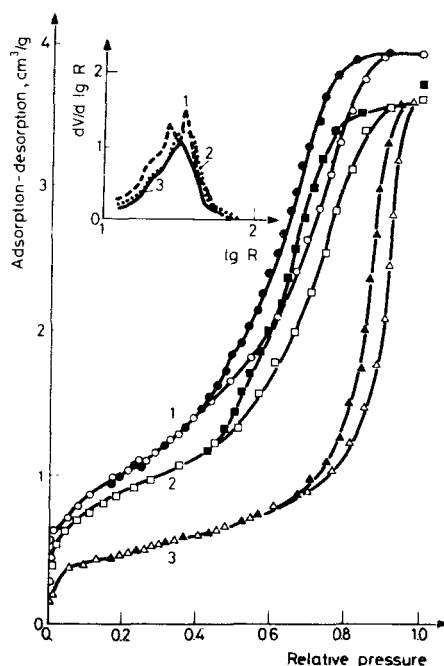
Fig. 3 Adsorption and desorption isotherms of nitrogen on initial silica gel (1) and on carbosils D (2) and C (3). Upper graph: differential pore volume (V) as a function of the pore radius (R)

From other papers [7, 9] it is known that carbon in reaction (1) may form energetically and geometrically relatively complex structures on the silica surface. The value of T_{exo} will undoubtedly be affected by the energy of interaction of the carbon deposit with the medium (silica) and by the nature of its distribution on the surface (agglomerates–homogeneous layer).

Photographs of the surface of carbosil C at various magnifications are presented in Figs 4 and 5. At small magnifications, of the order of 6000 × (Fig. 4), differences in topography of the non-modified carbon deposit and that modified with hydrogen at 678° can already be noticed. At a magnification of 2000 ×, details of the carbosil texture and topography and the carbon deposit morphology are visible (Fig. 5). It appears that the deposit is located rather in pores and various irregularities of the silica surface (dark patches). Furthermore, it does not form a uniform film, although the value $L_C = 2$ Å for this adsorbent (Table 1) might suggest the formation of a carbon monolayer on the silica surface [15]. Treating carbosil with hydrogen does not remove the carbon deposit from its pores (Fig. 5b). Therefore, high T_{exo} values remain for adsorbents modified with hydrogen (Table 2). The photographs in Figs 6 and 7 show that the films of the carbon deposits of the carbosils studied do have not a homogeneous structure. Besides the thin layers
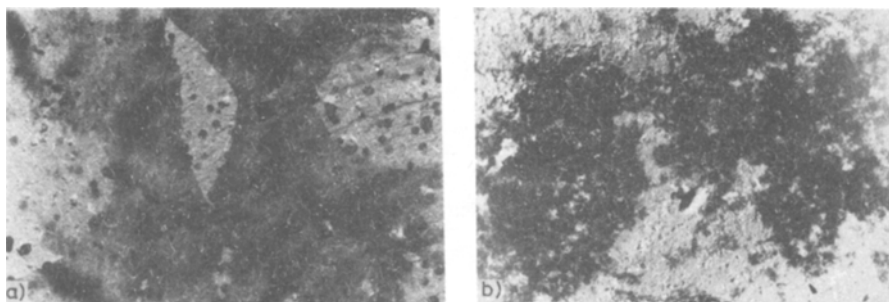
Fig. 4 Surface of non-modified carbosil C (a) and carbosil C modified with hydrogen at 687° (b), by transmission electron microscopy (TEM). Magnification 6000 ×
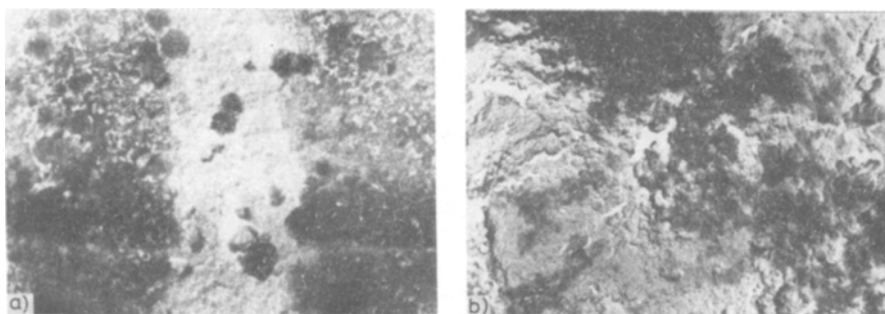

Fig. 5 Topography of carbosil C as in Fig. 4. Magnification 20,000 ×
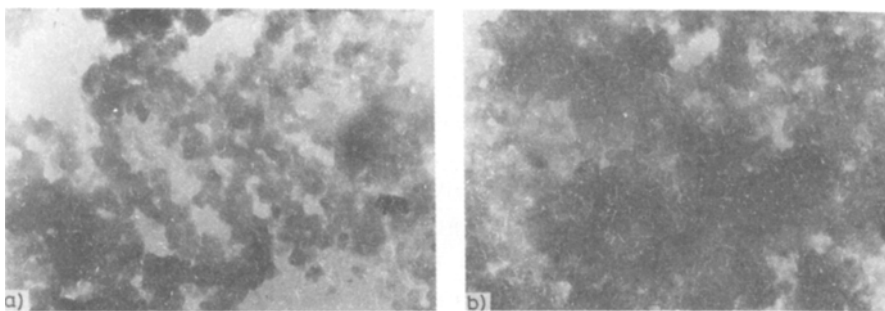

Fig. 6 Morphology of carbon layer in carbosil C as in Fig. 4. Magnification 6000 ×

(brighter patches in the photographs), there occur layers with a considerable thickness (dark patches). These are presumed to be large agglomerates (micro-crystals) of carbon with another chemical structure than that of the deposit forming the thinner layers. It can be assumed that gasification of the carbon present in the two different layers visible in the photographs will proceed quite differently.
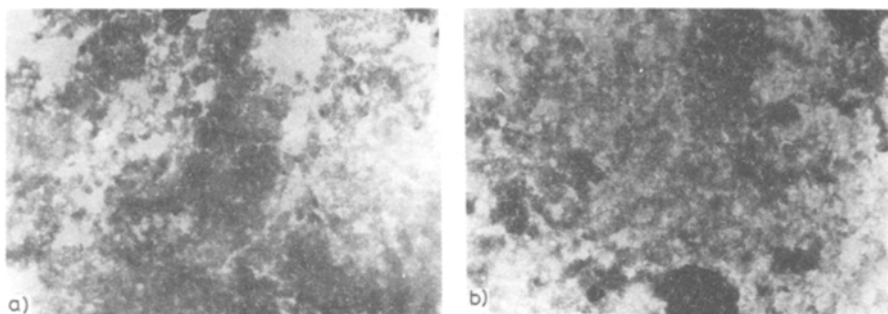
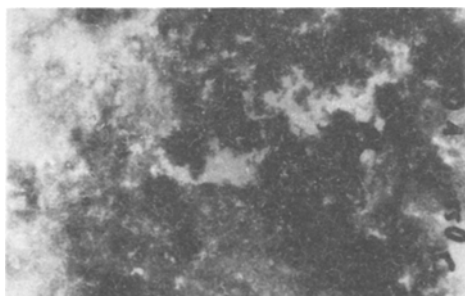**Fig. 7** As in Fig. 6. Magnification 20,000 ×

Fig. 8 Morphology of carbon layer in carbosil prepared by pyrolysis of α-phenylethyl alcohol on surface of silica gel. Magnification 6000 ×

Appropriate photographs of the carbosil prepared through the pyrolysis of FEA are shown in Fig. 8. It can also be seen here that the carbon deposit is heterogeneous. A mosaic structure of the topography of the adsorption centres of the carbosils studied indicates that the adsorption heats presented in Table 1 reflect the approximate differences in the chemical structures of the carbon deposits of the particular adsorbents.

Discussion

From an analysis of the data in Table 2, it follows that a significant role is played in the creation of the properties of the carbosils by intermediate products formed through pyrolysis of the substances studied. The following can be mentioned here: a) the chemisorption of FEA on the silica surface (carbosil A) and to a lesser extent of p-chT (carbosil B); b) the formation of 4,4′-chloromethyldiphenylmethane and possibly 4,4′-chloromethylpolydiphenyl in the reaction between p-chT molecules (carbosil E); c) the formation of p-alkoxytoluene through the bonding of alcohols

with p-chT (carbosils C, D and E). As a result of the above reactions, intermediates are formed which are bonded much more strongly than the initial substrates to the silica surface (chemisorption, formation of substances with higher molecular weight). Accordingly, carbosils were obtained which had a relatively high carbon content (Table 2) in comparison with the complex adsorbents described in other publications [6–9].

From Table 2, it follows that the degree of pyrolysed substance conversion (D.C.) for p-chT (carbosil B) is almost half that for FEA (carbosil A). This results from the fact that alcohols can react at elevated temperature both with the surface OH groups of silica and with siloxane bridges [3], while p-chT molecules react with hydroxyl groups only. Such groups are few on the silica surface, because they were removed from the primary surface during its initial treatment at 800°. Furthermore, the surface OH groups make first a surface in narrow pores. The $\equiv$Si—O—Si$\equiv$ bridges formed there react with alcohols, but not with p-chT. Therefore, FEA pyrolysis causes greater changes than p-chT carbonization in the structure of porous silica (Table 2, Fig. 2).

The processes occurring during the preparation of carbosils C, D and E differ slightly, because the formation of p-alkoxytoluenes eliminates active OH groups from alcohols before the reaction of pyrolysis. This is particularly significant for the pyrolysis of n-octyl alcohol in a mixture with p-chT. Aliphatic alcohols are carbonized through dehydration and then polymerization of the formed olefins, progressing towards the formation of polycyclic aromatic structures. The octyl radical in p-alkoxyltoluene (under appropriate conditions) probably does not undergo dehydrogenation and deep polymerization. Therefore, the degree of conversion (pyrolysis) D.C. is small for carbosil D. Thus, the carbon deposit of this carbosil contains many aliphatic elements. Such elements cause a decrease in the thermal stability of the carbon deposit (Table 2). From further analysis of the data in Table 1, it follows that the D.C. of the pyrolysed substance depends largely on the specific surface S of the modified silica. The D.C./S ratio is approximately constant for carbosils C and E, although two different silica gels were used for the preparation of these adsorbents. As a result, the %C/S values for these carbosils are similar (Table 1). Small differences in the values of these ratios may result from: i) differences in the porous structures of the initial silica gels, and ii) slightly different conditions of their initial thermal processing. Such processing determines the adsorptive and catalytic properties of silica.

Conclusions

1. The carbosils studied have relatively high thermal strength, both in an atmosphere of air and in hydrogen. Their properties distinctly depend on the nature of the substance carbonized.

2. The process of carbon deposit gasification is complex and depends on many factors, among other things on the chemical structure of the carbon deposit, its distribution on the support surface, and the porous structure of the medium. Aliphatic elements decrease the thermal stability of the carbon deposit.

3. The carbon deposit of carbosils exerts a distinct effect on the change of amorphous to crystalline silica. This is justified by the differences between the T_{exo} values of the particular carbosils both before and after their processing in an atmosphere of hydrogen (Table 2, data underlined). This effect depends on the topography and morphology of the carbon deposit.

4. The properties of carbosils largely depend on the nature of the intermediates formed before pyrolysis.

The data presented point to a relatively complex character of the problem dealt with in this paper. Therefore, they are considered as a reconnaissance. As recently shown by Reisz and Inczédy [16], the problem of the oxidation of organic substances must be approached carefully.

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Zusammenfassung — Thermische Eigenschaften von Kohlenstoff-Siliciumdioxid-Adsorbentien (Carbosil) wurden differentialthermoanalytisch untersucht. Die Adsorbentien wurden durch Pyrolyse von α-Phenylethylalkohol, n-Octanol, p-Chlortoluen und Mischungen dieser Verbindungen auf Silicagel-Oberflächen hergestellt und mit Wasserstoff behandelt. Die thermische Analyse wurde in Luftatmosphäre ausgeführt. Die Adsorbentien wurden durch Bestimmung folgender Parameter charakterisiert: Kohlenstoff- und Wasserstoffgehalt, spezifische Oberflächengröße, Stickstoffadsorptionisothermen, differentielle Porenvolumenverteilung, Dicke der Kohlenstoffschicht, Konversionsgrad der pyrolysierten Substanz, mikroskopische Abbildungen der Oberfläche. Zusammenhänge zwischen der Natur der carbonisierten Substanz und der Pyrolysezwischenprodukte einerseits und der thermischen Eigenschaften des komplexen Adsorbens andererseits werden diskutiert.

Резюме — Методом ДТА исследованы термические свойства сложных углерод — силикатных адсорбентов (Карбосилы), полученных пиролизом α-фенилэтилового спирта, н-октанола, п-хлортолуола и их смесей на поверхности силикагеля и затем обработанных водородом. Термический анализ адсорбентов проведен в атмосфере воздуха и для них были определены такие характерные параметры, содержание углерода и водорода, удельная площадь поверхности, изотермы адсорбции азота, дифференциальное распределение объёма пор, согласно их радиуса, толщина углеродного слоя, степень превращения вещества и поверхностная микрография. Обсуждено влияние природы обугленного вещества и промежуточных продуктов пиролиза на термические свойства адсорбентов.