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# Structural and energetic properties of carbosils hydrothermally treated in the classical autoclave or the microwave reactor

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**Abstract** Carbon/silica adsorbents (carbosils) prepared by pyrolysis of $CH_2Cl_2$ at 823 K and the reaction time from 0.5 to 6 h on the mesoporous silica gel surface (Si-60, Merck, granule size 0.2–0.5 mm) and then hydrothermally treated at 473 K with steam or liquid water by using the classical autoclave with traditional heating way or in the microwave reactor were studied by means of TG, adsorption and Q-TG methods. Changes in the structural characteristics of hybrid adsorbents before and after hydrothermal treatment were analyzed on the basis of nitrogen adsorption. Thermal properties of initial and modified samples as well as concentration of carbon deposit were studied using thermogravimetry (TG) in the range of 293–1273 K. The adsorbed water layers were investigated by means of thermodesorption of water under the quasi-isothermal conditions (Q-TG) in the range of 293–573 K. Concentration of weakly and strongly adsorbed water and the surface free energy on the interphase of adsorbent/water were calculated. It was stated that hydrothermal treatment in the microwave reactor, contrary to that in the classical autoclave, allows to obtain adsorbents with noticeably higher values of total pore volume in relation to the initial adsorbents and in majority with a higher specific surface area. Application of microwave energy allows to obtain adsorbents with lower values of surface free energy in relation to the initial adsorbents and those modified in the autoclave.

**Keywords** Carbon-silica adsorbents · Hydrothermal treatment · Porous structure · Quasi-isothermal method · Adsorbed water layers · Gibbs free energy · Free surface energy

## 1 Introduction

Composite (hybrid) materials such as carbon-mineral adsorbents have become more and more widely applied (Gun'ko and Leboda 2002). It results from their original surface properties because they may combine the features of both nonpolar carbon and polar mineral adsorbents (Skubiszewska-Zięba et al. 2006a, 2006b). Owing to these features, the adsorbents may simultaneously adsorb organic (Kamegawa and Yoshida 1990, 1993, 1995; Leboda 1992, 1993; Mel'gunov et al. 2001; Tarasevich 1989; Rudziński et al. 1995; Seledets et al. 2005), including enzymes (Sokolovski and Kovalenko 1988) and inorganic (Seledets et al. 2006; Kovalenko and Kuznetsova 1996) substances, which is a very important factor with respect to their utilisation in the processes of water and waste purification (Leboda and Dąbrowski 1996). These materials can be also used for isolation and concentration of trace amounts of the substances contained in water, e.g. p-nitrophenol (Leboda et al. 2000a), phenol (Leboda et al. 2003), heavy metal ions (Seledets et al. 2005, 2006) and in other media (air pollutions) (Ansari et al. 2005). Additionally they are the potential polymer fillers and condensation agents (Krysztafkiewicz et al. 2005). These adsorbents are also used as intermediates in the preparation of carbons (Bandosz et al. 1996; Holstein 1995) of desirable and original properties of final materials. Carbon-mineral composites may also find application in electrochemistry as the electrodes for electrochemical capacitors (Kosmulski et al. 2007). Adsorption features of such hybrid adsorbents depend on the nature of a support and a kind of carbonized precursor (Gun'ko

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et al. 2001, 2004a) as well as on the conditions of pyrolysis (Skubiszewska-Zięba et al. 2003). In many technological applications when used as catalyst or catalyst carriers these hybrid adsorbents can work under such drastic conditions as high temperature and pressure in the presence of water vapour or other aggressive substances. Under such conditions certain changes in the structural and adsorption properties of these materials can occur.

The textural and adsorptive characteristics of carbon/silica (carbosils, CS) surfaces have been studied using a variety of methods, e.g. adsorption (Leboda et al. 2000a; Yanishpolski et al. 2000), electric (Leboda et al. 1995a) electrochemical (Gun'ko et al. 2000), SEM, TEM (Tracz et al. 1984; Leboda and Łodyga 1988; Gun'ko et al. 2001), $^1$H NMR (Turov et al. 1995; Turov and Leboda 1999), etc. Despite these investigations, the relationships between the structural characteristics of different phases of hybrid adsorbents and their influence on adsorption of polar and nonpolar compounds are still important. This is because of a variety of pyrocarbon deposits, the complexity of their morphology, and the availability of different active surface sites on both pyrocarbon and support phases.

Hydrothermal treatment (HTT) is one of the most effective methods of porous structure adsorbents modification. The results of HTT depend on many factors such as the initial structure of adsorbent (Leboda et al. 1995b, 1998), the temperature and time of the process (Leboda et al. 1995c, 1995d), gas or liquid phase (Leboda et al. 2000b) and pH of medium (Leboda et al. 1995e).

During the hydrothermal modification of silica gel, simple mathematical relations allowing to determine the extent of hydrothermal treatment effect on structural parameters (sizes and volumes of pores and specific surface areas (Leboda et al. 1995d)) can be obtained. In the case of composite materials the presence of carbon on the silica surface diminishes the effect of HTT and as a result, the change of both porous structure and character of adsorbent surface groups takes place (Leboda et al. 1994; Gun'ko et al. 2004b).

The structure of water layers adsorbed on the surface is very important in application of mesoporous materials as adsorbents in aqueous media. Due to hydrophilicity of adsorbents surface, the layer thickness can be from several to several scores of water molecule radii (Turov et al. 1997). In such a case the competition between the molecules of adsorbate and water exerts a significant effect on adsorption of substances from aqueous solutions (Turov and Leboda 1999). Usually, such HTT processes are performed by using high pressure autoclaves heated in traditional furnaces. However, a very interesting and useful source of thermal energy are microwaves. This technology makes it possible to carry out the chemical reactions which couldn't be performed in traditional conditions in so short time or with so high yield (Cha et al. 1993; Cha and Kim 2001; Ania et al. 2004). Therefore, the aim of this work is to study the influence of hydrothermal modification with steam or liquid water by using the classical autoclave or the microwave reactor on the changes in structural and energetic characteristics of carbon-silica adsorbents (carbosils) by means of nitrogen adsorption, thermogravimetry (TG) and thermodesorption of water under the quasi-isothermal conditions (Q-TG) methods.

## 2 Experimental

### 2.1 Materials

Carbon-silica adsorbents were prepared by pyrolysis of $CH_2Cl_2$ (purity 99%, Polish Chemical Reagent Factory) at Si-60 (Merck, grain fraction 0.2–0.5 mm, 10 g) under dynamic conditions in a flow rotary quartz reactor with the deoxidized nitrogen stream (100 $cm^3$/min) at 823 K for 0.5, 1, 2, 3, 4, and 6 h (labelled CS-$i$ at $i = 1$–6). The rate of liquid $CH_2Cl_2$ feeding to the reactor (through a glass evaporator heated at 373 K) was 0.6 $cm^3\ min^{-1}$ using a Masterflex (Cole Parmer) pump. Hydrothermal treatment of the samples was performed in the saturated water steam or liquid water at 473 K. 5 g of an adsorbent was placed in a quartz vessel in a classical stainless steel autoclave (0.3 L) with 20 ml of water being under or inside the quartz vessel (samples labelled as CS-$i_{\text{a-vap}}$ or CS-$i_{\text{a-liq}}$ accordingly) and next heated for 6 hours in the oven. The pressure of saturated water steam in all cases was 15.3 atm. In the case of modification in the microwave reactor (300 W, NaNo 2000, Plazmatronika, Poland) 1 g of adsorbent sample was placed into the quartz vessel which next was put in a special Teflon cuvette (100 ml). Then 40 ml of water was added on the bottom of the Teflon cuvette or into quartz vessel. Next the reactor was closed and then the sample was subjected to the action of microwaves for 1 h using 85% of the reactor power (samples labelled as CS-$i_{\text{m-vap}}$ or CS-$i_{\text{m-liq}}$). During the process the generated parameters of temperature and pressure were collected by computer. In all cases the temperature of systems attained about 473 K. During such a treatment the maximal pressure for the samples modified in the water steam achieved about 20 atm but in the case of modification under liquid water it was about 30 atm.

### 2.2 Adsorption

Nitrogen adsorption-desorption isotherms were recorded at 77.4 K by means of a Micromeritics ASAP 2405N adsorption analyzer. The specific surface area (Table 1, $S_{BET}$) was computed using the standard *BET* equation (Gregg and Sing

**Table 1** Structural parameters of initial and hydrothermal treated samples

| Adsorbent | $C_C$ (wt.%) | $S_{BET}$ (m$^2$/g) | $\Delta S/S_{BET}$ % | $V_p$ (cm$^3$/g) | $\Delta V/V$ % | $R_p$ (nm) | $R_{\text{dom}}$ (nm) | $V_{\text{mic}}$ (cm$^3$/g) |
|---|---|---|---|---|---|---|---|---|
| Si-60 | – | 447 | – | 0.82 | – | 3.67 | 3.14 | – |
| Si-60$_{\text{a-vap}}$ | – | 61 | −86.4 | 0.26 | −68.3 | 8.62 | 20.81 | 0.003 |
| Si-60$_{\text{a-liq}}$ | – | 87 | −80.5 | 0.36 | −56.1 | 8.40 | 27.22 | 0.003 |
| Si-60$_{\text{m-vap}}$ | – | 231 | −48.3 | 1.06 | 29.3 | 9.16 | 12.29 | 0.002 |
| Si-60$_{\text{m-liq}}$ | – | 145 | −67.8 | 0.98 | 19.3 | 13.55 | 12.11 | – |
| CS-1 | 1.8 | 431 | – | 0.78 | – | 3.64 | 3.25 | – |
| CS-1$_{\text{a-vap}}$ | 1.9 | 403 | −6.50 | 0.83 | 6.4 | 4.13 | 3.24 | 0.007 |
| CS-1$_{\text{a-liq}}$ | 1.8 | 162 | −62.4 | 0.86 | 9.0 | 10.50 | 12.45 | 0.005 |
| CS-1$_{\text{m-vap}}$ | 2.0 | 444 | 3.0 | 0.85 | 10.3 | 3.86 | 3.16 | 0.006 |
| CS-1$_{\text{m-liq}}$ | 1.8 | 359 | −16.7 | 0.98 | 25.6 | 5.46 | 4.20 | 0.017 |
| CS-2 | 2.5 | 458 | – | 0.81 | – | 3.54 | 3.24 | – |
| CS-2$_{\text{a-vap}}$ | 2.8 | 370 | −19.2 | 0.80 | −1.2 | 4.37 | 4.41 | 0.006 |
| CS-2$_{\text{a-liq}}$ | 2.6 | 234 | −48.9 | 0.86 | 6.2 | 7.40 | 7.04 | 0.014 |
| CS-2$_{\text{m-vap}}$ | 3.3 | 497 | 8.5 | 0.91 | 12.4 | 3.66 | 3.20 | 0.003 |
| CS-2 $_{\text{m-liq}}$ | 3.0 | 430 | −6.1 | 1.02 | 25.9 | 4.73 | 4.42 | 0.013 |
| CS-3 | 6.0 | 445 | – | 0.78 | – | 3.50 | 3.15 | 0.004 |
| CS-3$_{\text{a-vap}}$ | 6.3 | 361 | −18.9 | 0.73 | −6.4 | 4.06 | 3.11 | 0.007 |
| CS-3$_{\text{a-liq}}$ | 6.3 | 311 | −30.1 | 0.79 | 1.3 | 5.06 | 5.77 | 0.017 |
| CS-3$_{\text{m-vap}}$ | 6.5 | 410 | −7.9 | 0.76 | −2.6 | 3.69 | 3.13 | 0.006 |
| CS-3$_{\text{m-liq}}$ | 6.6 | 454 | 2.02 | 0.97 | 24.4 | 4.27 | 3.22 | 0.015 |
| CS-4 | 8.3 | 427 | – | 0.74 | – | 3.46 | 3.23 | – |
| CS-4$_{\text{a-vap}}$ | 8.8 | 360 | −15.7 | 0.68 | −8.1 | 3.75 | 3.07 | 0.004 |
| CS-4$_{\text{a-liq}}$ | 8.4 | 355 | −16.9 | 0.93 | 25.7 | 5.20 | 5.79 | 0.016 |
| CS-4$_{\text{m-vap}}$ | 8.9 | 410 | −4.0 | 0.71 | −4.1 | 3.48 | 3.21 | – |
| CS-4$_{\text{m-liq}}$ | 9.2 | 439 | 2.8 | 0.85 | 14.9 | 3.88 | 3.22 | 0.014 |
| CS-5 | 13.1 | 399 | – | 0.68 | – | 3.89 | 3.21 | – |
| CS-5$_{\text{a-vap}}$ | 13.3 | 324 | −18.8 | 0.62 | −8.8 | 3.84 | 3.26 | 0.008 |
| CS-5$_{\text{a-liq}}$ | 13.3 | 329 | −17.5 | 0.75 | 10.3 | 4.60 | 5.73 | 0.016 |
| CS-5$_{\text{m-vap}}$ | 13.6 | 428 | 7.3 | 0.73 | 7.4 | 3.42 | 3.20 | 0.005 |
| CS-5$_{\text{m-liq}}$ | 13.9 | 429 | 7.5 | 0.82 | 20.6 | 3.84 | 2.93 | 0.012 |
| CS-6 | 18.9 | 354 | – | 0.59 | – | 3.31 | 3.25 | – |
| CS-6$_{\text{a-vap}}$ | 19.4 | 292 | −17.5 | 0.54 | −8.5 | 3.66 | 3.12 | 0.008 |
| CS-6$_{\text{a-liq}}$ | 20.0 | 340 | −4.0 | 0.71 | 20.3 | 4.17 | 4.12 | 0.014 |
| CS-6$_{\text{m-vap}}$ | 19.3 | 407 | 15.0 | 0.73 | 23.7 | 3.57 | 3.17 | – |
| CS-6$_{\text{m-liq}}$ | 21.5 | 401 | 13.3 | 0.72 | 22.0 | 3.61 | 3.21 | 0.011 |

Note. $C_C$ is the carbon deposit content calculated on the basis of TG mass losses under positive DTA peak; $S_{BET}$ is the specific surface area; $V_p$ is the pore volume; $V_{\text{mic}}$ is the micropore volume; $R_p$ (mean pore radius) $= 2V_p/S_{BET}$; $R_{\text{dom}}$ dominant pore radius; $\Delta S/S_{BET} = (S_{BET}^{\text{mod}} - S_{BET}^{ini})/S_{BET}^{ini}$ relative change of specific surface area; $\Delta V/V_p = (V_p^{\text{mod}} - V_p^{ini})/V_p^{ini}$ relative change of total pore volume

1982; Adamson and Gast 1997) at $p/p_0$ between 0.06 and 0.2 (where $p$ and $p_0$ denote the equilibrium and saturation pressures of nitrogen, respectively). The pore volume $V_p$ was estimated at $p/p_0 \approx 0.98$ converting the volume of adsorbed nitrogen to the volume of bulk fluid. $V_{\text{mic}}$ was determined on the basis of $t$-plot method. The average pore radius ($R_p$) was calculated for a model of cylindrical pores $R_p = 2V_p/S_{BET}$. Pore volume distributions in the function of their radius were calculated by using the Barrett-Joyner-Halenda (BJH) method (Barrett et al. 1951). On the basis of these dependences the values of dominant pore radius ($R_{\text{dom}}$) were determined.

### 2.3 TG and Q-TG investigations

The carbon content ($C_C$) in CS-*i* was determined by using the thermogravimetry (TG) and differential thermal (DTA) analyse on heating the samples in air from 293 K to 1273 K using a Derivatograph C (Paulik, Paulik and Erdey, MOM, Budapest) at the heating rate of 10 K/min. The carbon content was estimated from the mass loss of dry samples (pretreated at 473 K) under the positive DTA peak.

Thermodesorption of water from the surface of studied initial and HTT samples was performed under the quasi-isothermal conditions (Q-TG) in the range of 293–573 K. The method consists of heating the sample placed in the special construction covered platinum crucible at some heating rate (in the experiment 0.5 K/min) until the "temperature of conversion" is reached, i.e. when sharp evaporation of liquid takes place at the boiling point of the liquid out of pores or at the temperature for which the pressure of the saturated vapours above the liquid meniscus in the pore becomes equal to atmospheric pressure. Then isothermal conditions by means of control device are maintained. After completion of this conversion (i.e. after evaporation of the water portion being at a defined energetic state), the temperature is increased again until the temperature corresponding to the next conversion is reached. By using the special construction covered platinum crucible and the quasi-isothermal heating technique (quasi-static mode of measurement and a constant pressure of 100 kPa), the reactions leading to equilibrium can be studied under nearly ideal, quasi-isothermal, quasi-isobaric, and consequently quasi-equilibrium conditions.

Before the Q-TG experiments the water vapour was adsorbed on the silica gel and carbosils surface at room temperature (293 K). The portion (ca. 1 g) of the adsorbent was placed for 72 h in the desiccator containing liquid double distilled water. Then the weighed portions (ca. 50 mg) of so treated adsorbents were placed in the spherical spiral platinum crucible of the thermogravimetric analyser. The measurements of programmed water thermodesorption were made by means of Derivatograph C (Paulik, Paulik and Erdey, Hungary).

The experimental data obtained by Q-TG correspond to mass loss with temperature. When measurements are performed over a temperature range without any chemical reactions leading to changes in the adsorbent mass that $\Delta m = f(T)$ dependence reflects changes in concentration of substance on the adsorbent surface under equilibrium. These data were used as the initial ones for evaluation of energetic characteristics of the studied adsorbents. This method was described precisely in (Turov et al. 2001).

There exists two boundary phases when water is present on the adsorbent surface, i.e., adsorbent/water and water/air interfaces. So, three main responsible reasons of decrease in Gibbs free energy of water on the interface of adsorbent/water can be distinguished. This change is caused by strong adsorption of water molecules on the adsorbent surface centres ($\Delta G^S$), capillary condensation in the pores ($\Delta G^{por}$) and the presence of water/air interface ($\Delta G^{air}$).

A necessary condition which must be fulfilled for evaporation of adsorbed water under the equilibrium conditions is the equality of the Gibbs free energy of adsorbed water and that of water in the gas phase. Water begins to desorb from the surface when its Gibbs free energy becomes equal to that of water vapour at a given temperature (considering the changes in free energy due to the phase transition). Because the thermodynamic functions of the water vapour are tabulated over a wide temperature range (Glushko 1978), changes in the Gibbs free energy of water can be calculated using the equation:

$$\Delta G = G - G_0 = 0.197(T - T_0) \tag{1}$$

where $T_0$ is the temperature chosen as the standard. In the case of derivatographic measurements, this can be the initial temperature from which the examination begins or any other temperature characteristics for the studied process. Generally, this temperature is close to 293 K. So, on the basis of $\Delta m_{\text{H}_2\text{O}} = f(T)$ experimental data (Q-TG) the dependences of changes in the Gibbs free energy on the concentration of adsorbed water were calculated, $\Delta G = f(C_{\text{H}_2\text{O}})$.

## 3 Results and discussion

Comparing the data presented in Table 1 one can see that structural parameters of silica gel change during its hydrothermal treatment depending both on the state of modifier (vapour or liquid water) and the kind of heating source (classical autoclave or microwave reactor). This is due to mass transfer of silica through its dissolution and recondensation (Leboda et al. 1995c, 1995d). The smallest silica particles which possess maximum surface energy, due to having the highest chemical potential, are the first to be dissolved. As a result of this dissolution the silica is transferred and deposited onto bigger particles, whose surface energy and chemical potential are smaller.

$$\text{SiO}_2 + 2\text{H}_2\text{O} \longleftrightarrow \text{Si}(OH)_4 \tag{2}$$

In all cases we observe the decrease of specific surface area ($S_{BET}$) and increase of the mean pore radius ($R_p$) from 3.67 (sample Si-60) up to 13.55 nm for the silica modified

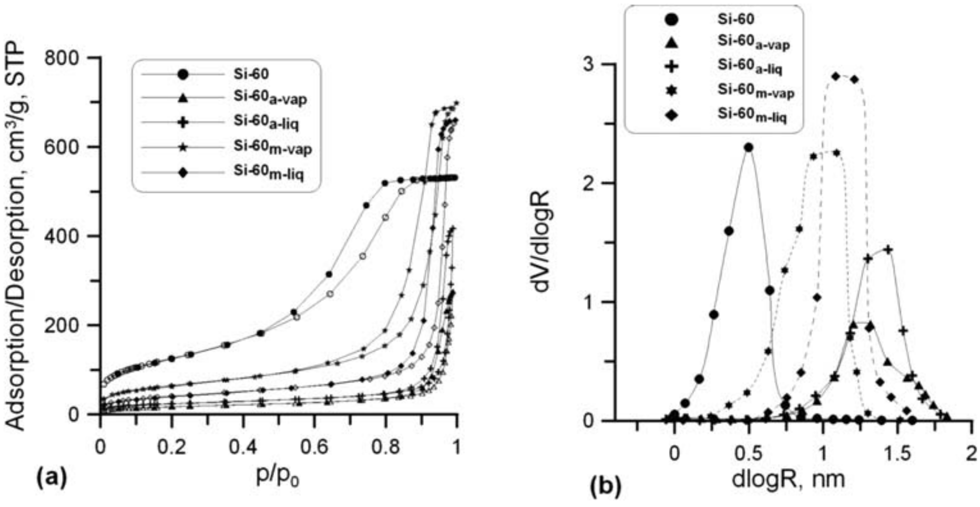
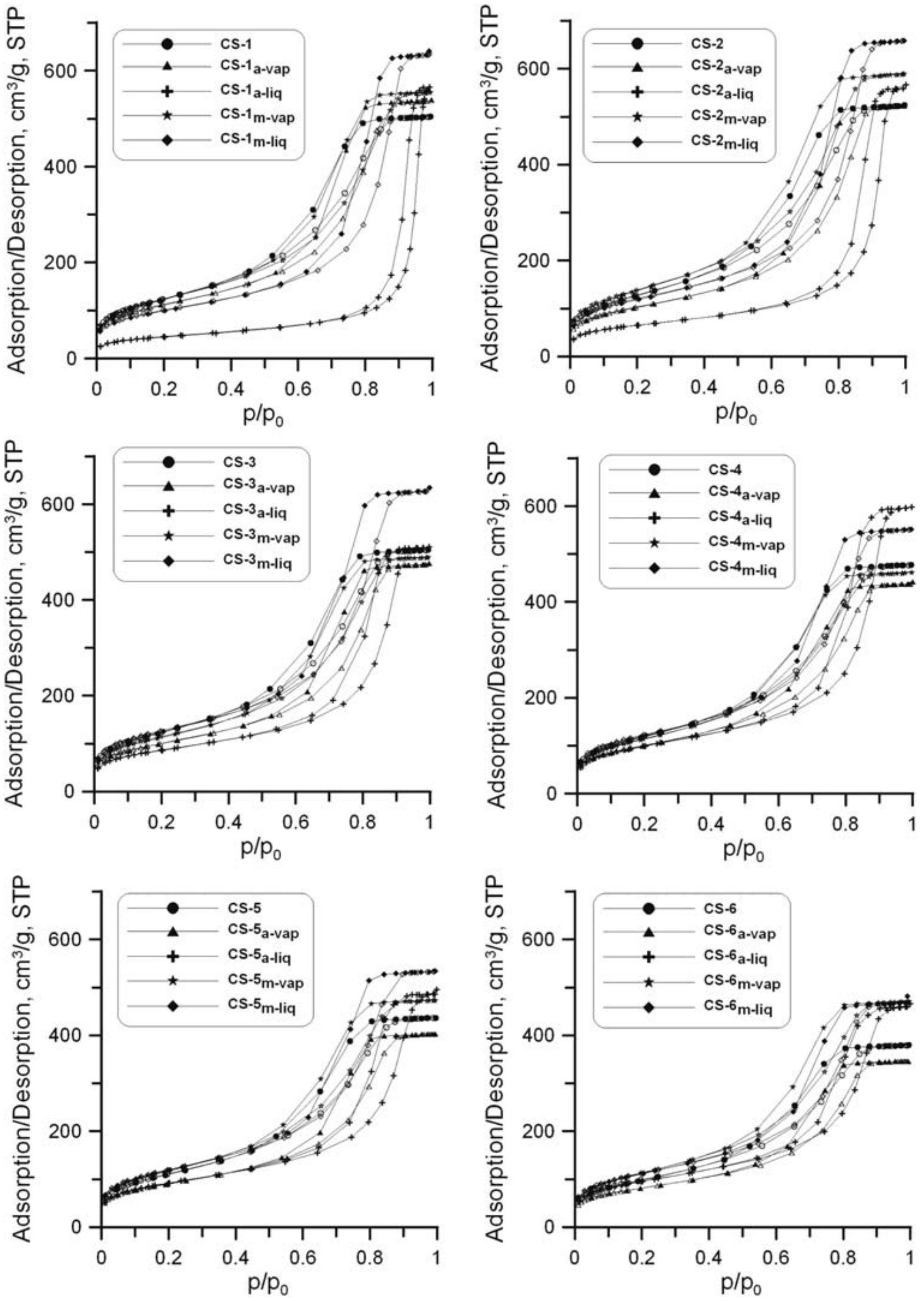


**Fig. 1** The low-temperature adsorption-desorption of nitrogen (**a**) and pore volume distribution functions in respect of their radius (**b**) for initial silica gel Si-60 and hydrothermally treated in autoclave or in microwave reactor

in liquid water by using of the microwave reactor (sample Si-$60_{\text{m-liq}}$). However, the parameters of dominant pores radius ($R_{\text{dom}}$) are the highest for the silica samples modified in the autoclave, up to about 27 nm for the sample Si-$60_{\text{a-liq}}$ (Table 1). The modification performed in the classical autoclave results in a large decrease of $S_{BET}$ in comparison to the microwave reactor. For the silica samples relative changes of the specific surface area ($\Delta S/S_{BET} = (S_{BET}^{\text{mod}} - S_{BET}^{ini})/S_{BET}^{ini}$) due to the HTT modification in the autoclave are about $-80\%$ in comparison to the microwave reactor ($-48$ and $-67\%$ for Si-$60_{\text{m-vap}}$ and Si-$60_{\text{m-liq}}$ respectively). This fact can be explained by longer time (6 h) of the HTT modification performed in the autoclave than in the microwave reactor (1 h). However, for the samples modified in the microwaves the total pore volume $V_p$ noticeably increases. It is clearly seen comparing the $\Delta V/V_p$ values (Table 1). In the case of silica samples, relative changes of the total pore volume ($\Delta V/V_p = (V_p^{\text{mod}} - V_p^{ini})/V_p^{ini}$) due to HTT modification in microwaves noticeably increase up to 29% for Si-$60_{\text{m-vap}}$ in relation to the initial silica Si-60. Whereas for the silica modified in the classical autoclave this parameter decreases in a significant extent up to $-68\%$ for the sample Si-$60_{\text{a-vap}}$ (Table 1). It is also confirmed by the courses of adsorption-desorption isotherms presented in Fig. 1a and pore volume distributions shown in Fig. 1b. As one can see the shapes of isotherms depend both on the state of water (vapour or liquid) and type of reactor. The hysteresis loop for the initial silica gel belongs to H2 type according to the IUPAC classification (Gregg and Sing 1982). Such a kind of loop suggests the presence of globular mesoporous structure with wide distribution of pores (Fig. 1b). Hydrothermal modification of pure silica gel leads to formation of more homogeneous structure of pores giving hysteresis loops of H1 type. Moreover, it is clearly seen that in the case of hydrothermally modified silica samples their adsorption/desorption branches are shifted both along the axis of relative pressures and that of adsorption. This is in good agreement with the pore volume distribution functions presented in Fig. 1b where large differences for the samples modified in a different manner are visible. The samples modified in the autoclave possess a wider dominant pore radius, $R_{\text{dom}}$ up to 27 nm for the sample Si-$60_{\text{a-liq}}$ (Table 1) but lower pore volume in relation to that parameter for the samples modified in the microwaves (compare 0.26 and 1.06 $\text{cm}^3/\text{g}$ for the samples Si-$60_{\text{a-vap}}$ and Si-$60_{\text{m-vap}}$ accordingly). This may be the result of higher globular water content present in the silica samples modified in the microwaves (Skubiszewska-Zięba and Leboda 2006). Such water may effectively influence the formation of more regular silica globule structure. Moreover, during the action of microwave radiation the process of sample heating starts from its inner part which may be the additional factor allowing more homogeneous porous structure formation with high pore volumes.

For the hybrid carbon-silica samples at a low carbon deposit concentration up to 6% of $C_C$ (samples CS-1, CS-2 and CS-3) the specific surface area and the pore volume change to a small extent due to a thin layer of carbon loaded in the mesopores of silica gel. But in the case of the samples with a higher carbon deposit concentration due to a thicker carbon layer (samples CS-4, CS-5 and CS-6) these values decrease noticeably (Table 1). During the hydrothermal modification carbon deposits strongly shield the silica gel surfaces against pore wall disruption on HTT that results in significant differences in the shapes of the isotherms (Fig. 2). The hysteresis loops for almost all studied carbon-silica adsorbents belong to H2 type, instead of the samples CS-$1_{\text{a-liq}}$ and CS-$2_{\text{a-liq}}$ with the lowest carbon deposit concentration, after HTT performed in the autoclave with liquid water. These hysteresis loops belong to H1 type as in the case of hydrothermally treated pure silica gel samples (Fig. 1a). During the HTT modification in the autoclave independently on water state (vapour or liquid) the decrease of

**Fig. 2** The low-temperature adsorption-desorption of nitrogen for initial carbon-silica adsorbents and hydrothermally treated in autoclave or in microwave reactor



specific surface area is observed and this effect is greater for the samples modified in liquid water ($\Delta S/S_{BET}$, Table 1). Moreover, because of shielding effect of carbon deposit relative changes in the specific surface area due to HTT decrease with the increasing $C_C$. Analysing the structural parameters of the samples modified in the microwave reactor (both in steam and liquid water) an increase of $S_{BET}$ values after the HTT modification for the adsorbents at the highest $C_C$ (CS-$5_{\text{m-vap}}$, CS-$5_{\text{m-liq}}$, CS-$6_{\text{m-vap}}$ and CS-$6_{\text{m-liq}}$) is observed and in the case of the samples with lower carbon deposit concentration an increase of $S_{BET}$ for CS-$1_{\text{m-vap}}$ and CS-$2_{\text{m-vap}}$ is noticed (up to 444 and 497 m$^2$/g accordingly). This may be the result of carbon deposit activation leading to formation of new porous structure in the carbon layer. Because char is a good receptor of microwave energy (Cha et al. 1993; Menendez et al. 1999) during the HTT modification, when the hybrid carbon-silica samples are subjected to action of microwaves, creation of high temperature in the carbon phase is most likely. Such conditions, in the presence of the oxidizing agent such as water makes the activation more effective than during modification in the autoclave.

Comparing the total pore volumes ($V_p$) for the carbosils before and after HTT (Table 1) in general, an increase of this parameter for the samples HTT modified in the microwave reactor up to about 25% of $\Delta V/V$ ($\Delta V/V_p = (V_p^{\text{mod}} - V_p^{ini})/V_p^{ini}$) is observed (especially for the samples modified in liquid water). This is in agreement with the observations made for the silica samples modified by using microwaves. Moreover, in the case of carbosils, the additional factor is of importance, i.e. the formation of high temperature in the carbon layer as well as high concentration of globular water (Skubiszewska-Zięba and Leboda 2006) in the silica matrix.

The above discussed changes in the structural parameters of the carbon-silica samples before and after hydrothermal treatment are also confirmed by the courses of pore volume distribution functions shown in Fig. 3. Here we can see that for the samples with a higher carbon deposit concentration the presented curves run close between themselves and they lie in the narrower range in the pore radius ($1 < R < 10$ nm) than in the case of the samples with low $C_C$, where these curves are more spread ($1 < R < 32$ and $1 < R < 18$ nm for CS-1 and CS-2 respectively). This is also well visible when the values of mean ($R_p$) and dominant ($R_{\text{dom}}$) pore radius (Table 1) are compared. Moreover, as it could be expected the hydrothermal modification causes the creation of micropores, especially in the case of carbon-silica samples modified under liquid water, where $V_{\text{mic}}$ are about twice as large as the samples modified with steam (Table 1). But in the case of adsorbents before HTT the absence of micropores was stated.

A very good illustration of the above discussed problems is given in Fig. 4 where relative changes of the specific surface area $\Delta S/S_{BET}$ and the pore volumes $\Delta V/V_p$ of the studied samples under HTT modification are presented. As we can see, for pure silica gel and carbosils at low carbon deposit concentration these parameters are high but following higher $C_C$ the slope of curves becomes smaller and in consequence, they become almost parallel to the abscissa axis.

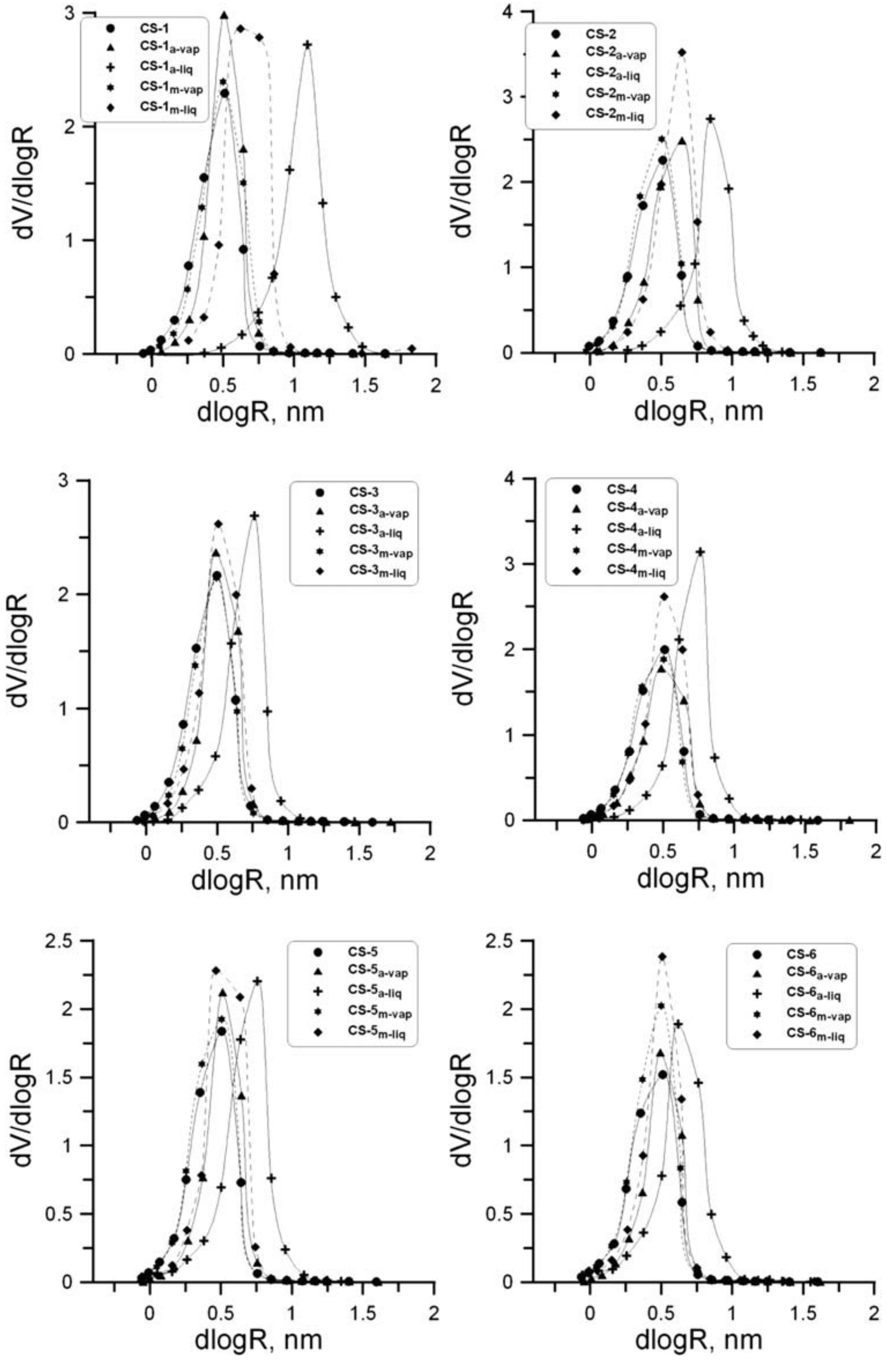
During the hydrothermal modification of composite carbon-silica adsorbents a double role of water should be taken into consideration. In such processes water acts as a modifying agent of silica gel causing changes in its globular structure and in that its initial centres from the partial hydrolysis of Si–O–Si bonds. Moreover, it acts as an oxidizing agent by creation of additional pores in the carbon deposit as well as the formation of carbon-oxygen groups on its surface. As a result, changes in the structure of adsorbed water layers can occur.

Figure 5 shows the exemplary curves of $\Delta m_{\text{H}_2\text{O}} = f(T)$ and $\Delta G = f(C_{\text{H}_2\text{O}})$ dependences. For high hydration degrees of the surface, all adsorbent pores are filled with water, and with the increasing temperature the process of evaporation of water runs practically without any changes in the pore filling degree. In our measurements first losses in water mass started to appear at 65 °C ($\Delta G^{65} = 8.7$ kJ/mol) and slightly increased up to the temperature corresponding to the boiling point of water (at $T_b = 100\,^\circ\text{C}$, $\Delta G^{100} = 15$ kJ/mol). At this stage, the water is evaporated from the water/air interface, and the water surface is separated from the adsorbent surface by a thick layer of water filling the pores. This process is presented as the initial portion of $\Delta m_{\text{H}_2\text{O}} = f(T)$ dependence (Fig. 5a) and the final portion of $\Delta G = f(C_{\text{H}_2\text{O}})$ in Fig. 5b. Changes in water concentration corresponding to this portion of water are small and do not exceed 10–15% of the initial concentration of water contained in the whole sample, denoted as $C_{\text{H}_2\text{O}}^{\text{max}}$. Then the area limited by the $\Delta G = f(C_{\text{H}_2\text{O}})$ curve over the concentration range between $C_{\text{H}_2\text{O}}^{\text{max}}$ and $C_{\text{H}_2\text{O}}^{b}$ (water concentration in filled pores, as abscissa corresponding to the initial boiling point $T_b$) is equal to the change in the free energy of the system due to evaporation of water, when pores are filled ($\Delta G_{\Sigma}^{i}$). After attainment of the temperature corresponding to the boiling point of the water contained in the pores, desorption of the majority of adsorbed water occurs. Removal of such bulk water takes place in a relatively broad temperature range. This is connected with the fact that the boiling temperature of water in pores increases with the decreasing pore diameter, and in the case of mesoporous carbosils prepared on the basis of silica gel, the pore size distribution corresponds to the Gaussian type (Fig. 1b). Bulk water evaporation from pores is connected with the central portion of $\Delta m_{\text{H}_2\text{O}}(T)$ and $\Delta G(C_{\text{H}_2\text{O}})$ curves shown in Fig. 5a and 5b (vertical and parallel sections of these dependences accordingly). This part of desorbed water is connected with the change of Gibbs free energy of the system caused by capillary condensation in the pores $\Delta G_{\Sigma}^{por}$. As the temperature of tested sample increases, the adsorbed water remains only in the thin layer whose thickness does not exceed one molecular diameter, and then there occurs the thermodesorption of water bonded directly to the adsorbent surface This portion corresponds to water molecules strongly bound with the surface, $C_{\text{H}_2\text{O}}^{S}$. As follows from Fig. 5b, the initial part of $\Delta G(C_{\text{H}_2\text{O}})$ dependence can be approximated by a straight line and the intersection point of this straight line with the ordinate axis determines the maximal decrease in the energy of water adsorbed at room temperature ($\Delta G^t$). Then the maximal value of changes in the Gibbs free energy for the strongly bound water can be obtained

$$\Delta G^S = \Delta G^t - \Delta G^b \tag{3}$$

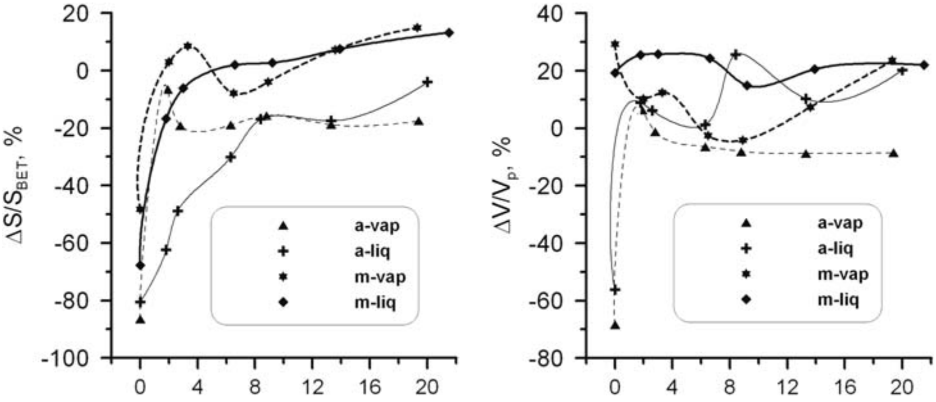
where $\Delta G^b = 15$ kJ/mol (at 100 °C), $\Delta G^t = 54$ kJ/mol (at 300 °C).

**Fig. 3** The pore volume distribution functions in respect of their radius for initial carbosil samples and hydrothermally treated in autoclave or in microwave reactor

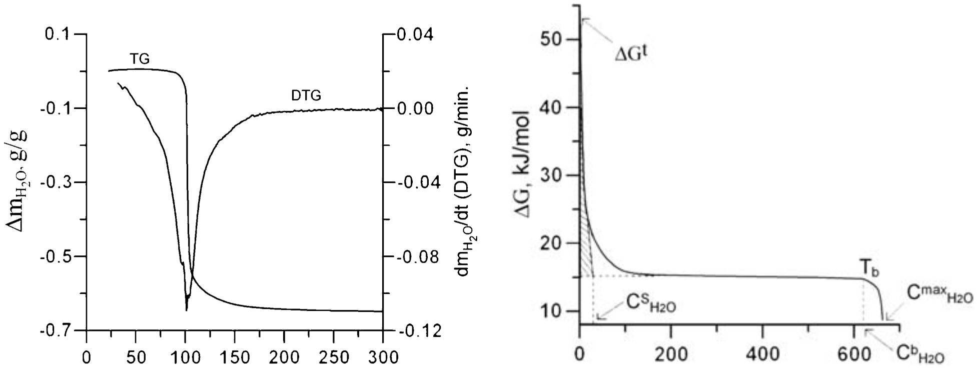


The thickness of strongly bound water layer $C^S_{\mathrm{H_2O}}$ can be determined by extrapolation of the $\Delta G(C_{\mathrm{H_2O}})$ curve, up to its intersection with the horizontal line drawn through the point corresponding to the initial boiling stage of water in the pores ($T_b$). At the same time the area of the right triangle determines the decrease in the Gibbs free energy of the system $\Delta G^S_\Sigma$ caused by adsorption of water vapour on the adsorbent surface under the conditions when pores are not filled with water. In such a way the value $\Delta G^S_\Sigma$ determines the free surface energy on the interface of adsorbent/strongly bound water.

**Fig. 4** The dependences of relative changes of the specific surface area (**a**) and the total pore volume (**b**) for silica gel and carbosil samples hydrothermally treated by different way



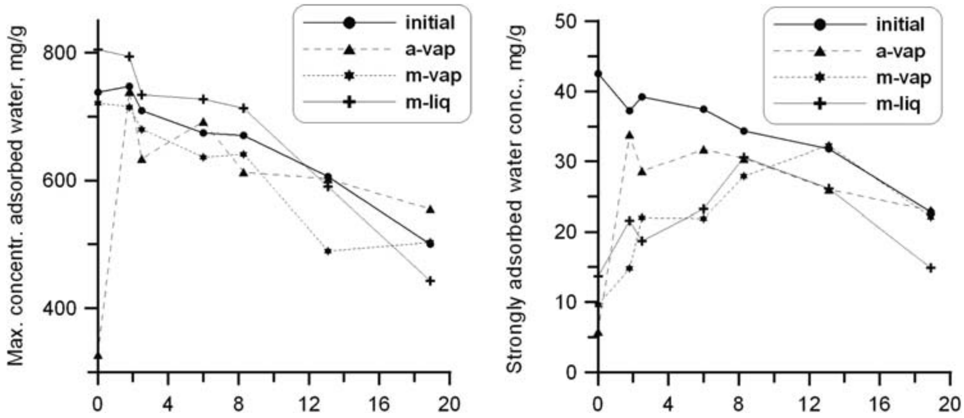
(a) Carbon deposit concentration, % w/w (b) Carbon deposit concentration, % w/w



(a) Temperature, °C (b) Adsorbed water concentration, mg/g

**Fig. 5** The dependences of Q-TG and Q-DTG curves of water thermodesorption from carbosil sample (**a**); The dependence of changes in free Gibbs energy of water $\Delta G$ on its concentration on carbosil sample (**b**)

**Fig. 6** The dependences of maximal concentration of adsorbed water $C^{\max}_{H_2O}$ (**a**) and strongly adsorbed water $C^{S}_{H_2O}$ (**b**) on carbon deposit concentration for initial silica and carbosil samples



(a) Carbon deposit concentration, % w/w (b) Carbon deposit concentration, % w/w

The area limited by $\Delta G(C_{H_2O})$ over all concentration of water gives the total decrease in the Gibbs free energy of water caused by adsorption from air ($\Delta G_\Sigma$). If we assume that concentration of water adsorbed on the adsorbent surface is maximal (pores are filled with water), then the $\Delta G_\Sigma$ value determines free surface energy on the adsorbent/water interface.

Table 2 presents the characteristics of adsorbed water layers on all tested silica gel and carbosil samples. Figure 6 shows the dependences of maximal and strongly adsorbed water concentration on initial and differently hydrothermally treated samples in relation to the carbon deposit content. As follows from these data the hydrophilic properties of the samples before HTT decrease with the increasing

**Table 2** Characteristics of adsorbed water layers on tested adsorbents

| Adsorbent | $C_{H_2O}^{max}$ mg/g | $n$ | $C_{H_2O}^{S}$ mg/g | $\Delta G^S$ kJ/mol | $\Delta G^b$ kJ/mol | $\Delta G_\Sigma^S$ mJ/m$^2$ | $\Delta G_\Sigma$ mJ/m$^2$ |
|---|---|---|---|---|---|---|---|
| Si-60 | 738 | 5.0 | 42.5 | 38.3 | 15.7 | 101.1 | 816 |
| Si-60$_{\text{a-vap}}$ | 327 | 16.0 | 5.8 | 38.7 | 15.3 | 102.4 | 2302 |
| Si-60$_{\text{m-vap}}$ | 721 | 9.4 | 9.6 | 38.9 | 15.1 | 44.9 | 1284 |
| Si-60$_{\text{m-liq}}$ | 805 | 16.7 | 13.7 | 38.6 | 15.4 | 101.4 | 2421 |
| CS-1 | 747 | 5.2 | 37.2 | 38.0 | 16.0 | 91.0 | 863 |
| CS-1$_{\text{a-vap}}$ | 739 | 5.5 | 33.8 | 38.2 | 15.8 | 89.0 | 897 |
| CS-1$_{\text{m-vap}}$ | 715 | 4.8 | 14.8 | 38.8 | 15.2 | 36.0 | 678 |
| CS-1$_{\text{m-liq}}$ | 794 | 6.7 | 21.6 | 38.5 | 15.5 | 64.2 | 971 |
| CS-2 | 709 | 4.7 | 39.2 | 38.2 | 15.8 | 90.8 | 765 |
| CS-2$_{\text{a-vap}}$ | 634 | 5.2 | 28.6 | 38.3 | 15.7 | 82.1 | 823 |
| CS-2$_{\text{m-vap}}$ | 680 | 4.1 | 22.0 | 38.2 | 15.8 | 46.9 | 644 |
| CS-2$_{\text{m-liq}}$ | 734 | 5.1 | 18.7 | 38.9 | 16.1 | 47.1 | 819 |
| CS-3 | 674 | 4.6 | 37.4 | 38.2 | 15.8 | 89.2 | 751 |
| CS-3$_{\text{a-vap}}$ | 692 | 5.8 | 31.7 | 38.3 | 15.7 | 93.3 | 919 |
| CS-3$_{\text{m-vap}}$ | 636 | 4.7 | 21.9 | 38.2 | 15.8 | 56.8 | 781 |
| CS-3$_{\text{m-liq}}$ | 727 | 4.8 | 23.2 | 38.2 | 15.8 | 54.3 | 724 |
| CS-4 | 670 | 4.7 | 34.3 | 38.2 | 15.8 | 85.2 | 774 |
| CS-4$_{\text{a-vap}}$ | 613 | 5.1 | 30.4 | 38.2 | 15.8 | 89.7 | 834 |
| CS-4$_{\text{m-vap}}$ | 641 | 4.7 | 27.9 | 38.2 | 15.8 | 72.2 | 721 |
| CS-4$_{\text{m-liq}}$ | 713 | 4.9 | 30.6 | 38.2 | 15.8 | 74.0 | 753 |
| CS-5 | 606 | 4.6 | 31.8 | 38.0 | 16.0 | 84.0 | 764 |
| CS-5$_{\text{a-vap}}$ | 602 | 5.6 | 26.0 | 38.3 | 15.7 | 85.4 | 885 |
| CS-5$_{\text{m-vap}}$ | 489 | 3.4 | 32.3 | 38.2 | 15.8 | 80.0 | 561 |
| CS-5$_{\text{m-liq}}$ | 590 | 4.1 | 26.1 | 38.2 | 15.8 | 64.5 | 623 |
| CS-6 | 500 | 4.3 | 22.8 | 38.0 | 16.0 | 68.0 | 691 |
| CS-6$_{\text{a-vap}}$ | 555 | 5.7 | 23.0 | 38.2 | 15.8 | 83.5 | 914 |
| CS-6$_{\text{m-vap}}$ | 503 | 3.7 | 22.1 | 38.3 | 15.7 | 57.7 | 589 |
| CS-6$_{\text{m-liq}}$ | 443 | 3.3 | 14.9 | 38.0 | 16.0 | 39.1 | 509 |

Note: $C_{H_2O}^{max}$ is maximal concentration of adsorbed water, $n$ number of statistical adsorbed water layers calculated on the base of maximal concentration of adsorbed water, $C_{H_2O}^{S}$ is the concentration of strongly adsorbed water calculated by extrapolation of the $\Delta G(C_{H_2O})$ curve until its intersection with the horizontal line drawn through the point corresponding to the initial boiling stage of water in pores, $\Delta G^b$ is the change in free energy of water during its evaporation from filled pores, $\Delta G^S$ is a maximal value of changes in the free energy for strongly adsorbed water (during it evaporation from the surface), $\Delta G_\Sigma$ is total free surface energy on the interface of adsorbent/water calculated as the area limited by $\Delta G(C_{H_2O})$ curve in the all range of water concentration, $\Delta G_\Sigma^S$ is surface free energy on the interface of adsorbent/strongly bound water calculated as the area of right triangle limited by $\Delta G(C_{H_2O})$ curve in the range of strongly bound water

$C_C$ (instead of small gain for the sample CS-1) (Fig. 6a). The drop of maximal water concentration when the carbon layer becomes thicker is observed. Such lowering of hydrophilic properties is in agreement with the values of immersion heats of water ($H_{im}$) presented in (Skubiszewska-Zięba et al. 2004). These values change from 162 mJ/m$^2$ for the initial Si-60 to 138 mJ/m$^2$ for the sample with the highest carbon deposit concentration (CS-6). Hydrothermal modification performed in saturated water steam, both in the autoclave and the microwave reactor (a-vap and m-vap series), generally decreases the maximal concentration of adsorbed water $C_{H_2O}^{max}$. In the case of modification in the autoclave this may be connected with lowering of surface active centres concentration together with the decrease of specific surface area and of total pore volume (Table 1). The immersion heats for such treated samples are lower in comparison to this parameter for the samples before HTT and their values are from 144 mJ/m$^2$ for Si-60$_{\text{a-vap}}$ to 100 mJ/m$^2$ for the CS-6$_{\text{a-vap}}$ sample (Skubiszewska-Zięba et al. 2004). In the case of the samples modified in microwaves in saturated water steam (m-vap series) such a result may be probably connected with effective blocking of active centres of silica by carbon particles and the reduction of surface oxide carbon groups in the carbon layer due to creation of high temperature during microwave radiation (Menendez et al. 1999; Carrott et al. 2001; Miura et al. 2004; Nabais et al. 2004).

The additional information can be obtained after the recalculation of $C_{\text{H}_2\text{O}}^{\max}$ into a number of statistical monolayers "$n$" by the formula $n = C_{\text{H}_2\text{O}}^{\max} \cdot N \cdot \omega / M_{\text{H}_2\text{O}} \cdot S_{BET}$, where $C_{\text{H}_2\text{O}}^{\max}$ maximal concentration of adsorbed water (mg/g), $N$ Avogadro number, $\omega$ surface occupied by one absorbed water molecule (assumed as 0.09 nm$^2$), $S_{BET}$ specific surface area (m$^2$/g), $M_{\text{H}_2\text{O}}$ molecular mass of water (18 g/mol).

Taking into account the thickness of adsorbed water given in the statistical monolayers "$n$" it is clearly seen that all studied samples after HTT in the autoclave in water steam (a-vap series) have thicker water layer ("$n$" up to 16 for the sample Si-60$_{\text{a-vap}}$) in relation to the non modified samples. For these samples a significant increase of surface free energy $\Delta G_\Sigma$ on the adsorbent/water interface is also noticed, e.g. from 816 to 2302 mJ/m$^2$ for Si-60$_{\text{a-vap}}$ and from 691 to 914 mJ/m$^2$ for carbosil with the highest carbon deposit content CS-6$_{\text{a-vap}}$. This is the evidence for the presence of long distance surface forces on such modified samples. But in the case of carbosils modified in the microwave reactor (m-vap series) the lowering of water monolayers number with the increasing $C_C$ is observed. It is also in agreement with the drop of surface free energies $\Delta G_\Sigma$ and $\Delta G_\Sigma^S$ on the interfaces of adsorbent/water where pores are filled with water and adsorbent/strongly bound water when pores are empty for these adsorbents in relation to the samples before HTT (Table 2).

Analysing dependences in Fig. 6a one can observe that the samples modified in microwaves under liquid water layer (m-liq series) show the highest maximal water concentration $C_{\text{H}_2\text{O}}^{\max}$ at lower $C_C$ (CS-1$_{\text{m-liq}}$, CS-2$_{\text{m-liq}}$, CS-3$_{\text{m-liq}}$ and CS-4$_{\text{m-liq}}$). However, this parameter is almost the lowest for the samples CS-5$_{\text{m-liq}}$ and CS-6$_{\text{m-liq}}$ (Fig. 6a, Table 2). Taking into account the number of statistical monolayers one can say that on the sample Si-60$_{\text{m-liq}}$ the adsorbed water is sufficiently thick (16.7 monolayers, Table 2) and for carbosils with lower $C_C$ (up to 9% C) an insignificant increase of thickness water layer in relation to the samples before HTT is observed. But for the carbosils CS-5$_{\text{m-liq}}$ and CS-6$_{\text{m-liq}}$ the adsorbed water layers are the thinnest (Table 2). This is in accordance with the values of free surface energy $\Delta G_\Sigma$ and $\Delta G_\Sigma^S$ for these samples. In the case of carbosils at low carbon deposit concentration this may be the result of relatively high values of pore volume and the specific surface area in relation to other studied samples, as discussed earlier (Table 1, Figs. 1–3). But with the higher carbon deposit content (samples CS-5$_{\text{m-liq}}$ and CS-6$_{\text{m-liq}}$) the reduction of oxide-carbon centres may take place. In such a situation the obtained lower values of free surface energy on the adsorbent/water interface $\Delta G_\Sigma$ and on the adsorbent/strongly bound water interface $\Delta G_\Sigma^S$ on these samples (in comparison with the initial samples) are understandable. This may be explained assuming that during the action of microwave radiation (HTT modification), the presence of liquid water in the modified sample influences the formation of porous structure and the kind of carbon-oxide surface centres. Such liquid water can take away the heat formed into the carbon layer more effectively than water steam.

Comparing the dependences presented in Fig. 6b concerning the strongly adsorbed water concentration $C_{\text{H}_2\text{O}}^S$, a consequent decrease of this parameter along all carbon deposit content in the series of initial samples is observed. However, for the hydrothermally treated carbosil samples a distinct increase up to 9% of $C_C$ is noticed. In the case of initial carbosil samples series this may be connected with effective blocking of the active centres for water adsorption. But in the case of HTT modified adsorbents this fact is most probably the result of adsorption on the most active centres formed during activation by water molecules and additionally the creation of carbon-oxide surface groups in the carbon deposit. For the samples with a thicker carbon deposit layer their surface seems to be more homogeneous as well as the accessibility of silica surface by water molecules is more difficult so the concentration of strongly bound water may be lower.

The complete illustration of the characteristics under discussion provides Fig. 7, in which the dependences of free Gibbs energy of adsorbed water in relation to its surface concentration for initial and HTT modified samples are presented. Here is well visible the significant influence of the carbon deposit concentration and applied way of modification on the hydrophilic properties of studied adsorbents.

The above discussed data concerning maximal and strongly adsorbed water concentration are in good agreement with the parameters of total surface free energy calculated on the adsorbent/water interface $\Delta G_\Sigma$ when pores are filled with water and on the adsorbent/strongly bound water interface $\Delta G_\Sigma^S$ when pores are empty and only strongly adsorbed molecules are present on the adsorbent surface (Table 2). Comparing these parameters it follows that the maximal $\Delta G_\Sigma$ values are obtained for the treated silica

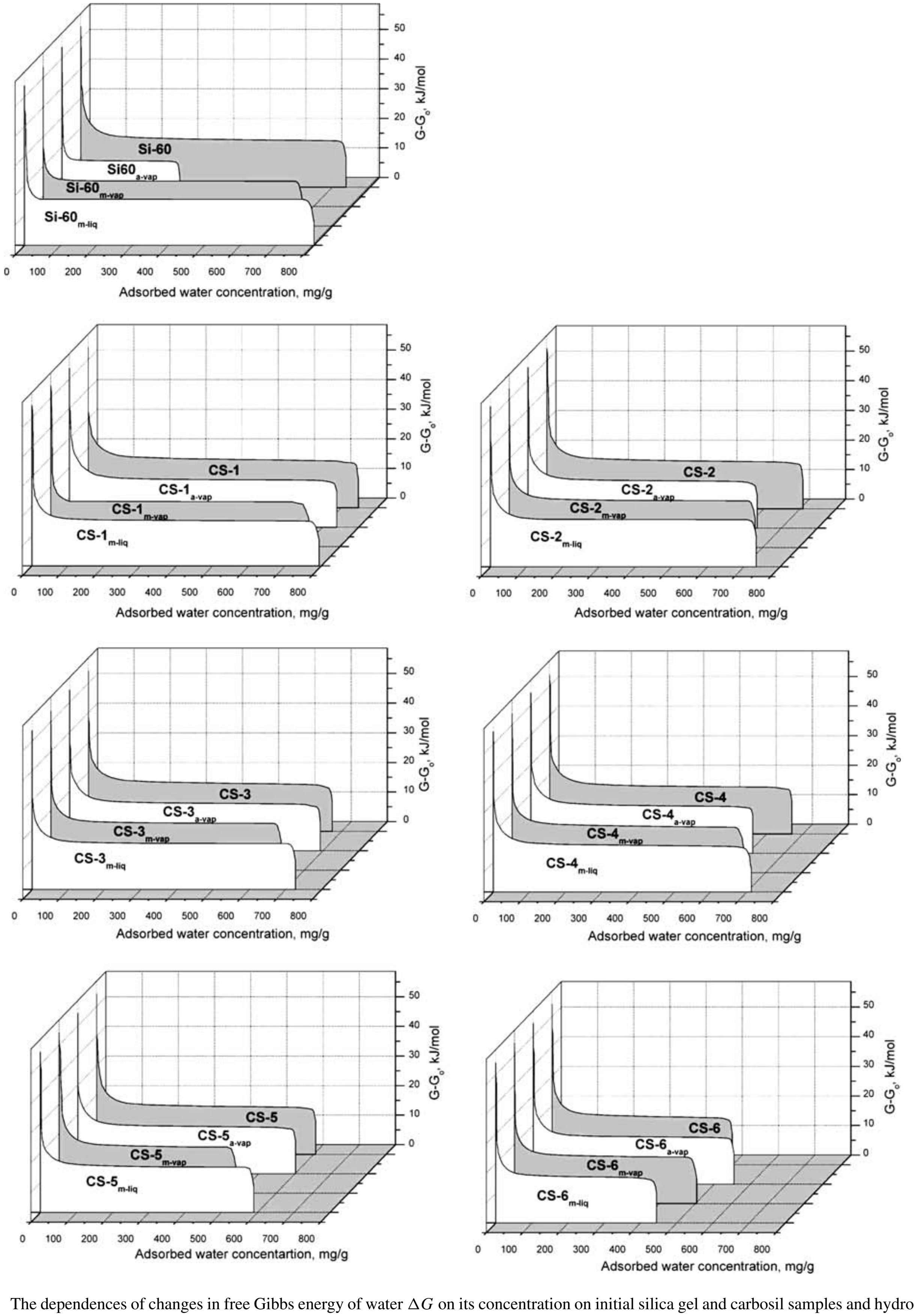


**Fig. 7** The dependences of changes in free Gibbs energy of water $\Delta G$ on its concentration on initial silica gel and carbosil samples and hydrothermally treated by different way

gel HTT, especially for that modified in microwave under liquid water (Si-60$_{\text{m-liq}}$). For this sample the highest maximal concentration of adsorbed water $C^{\max}_{H_2O}$ is also noticed. But by correlation of these parameters for the series of carbosils one can say that their hydrothermal modification performed in the autoclave in saturated water steam (samples CS-$i_{\text{a-vap}}$) generally causes a significant increase of both $\Delta G_\Sigma$ and $\Delta G^S_\Sigma$ parameters instead of two cases observed for CS-1$_{\text{a-vap}}$ and CS-2$_{\text{a-vap}}$ (for $\Delta G^S_\Sigma$). In the case of carbosils with higher carbon deposit concentrations after modification in the autoclave this may be the result of effective oxygen-carbon surface groups formation but for the samples with lower $C_C$ contents this may be connected with higher hydroxylation of silica after HTT. As mentioned earlier the HTT modification of carbosil samples by using microwaves causes a decrease of strongly bound water concentration $C^S_{H_2O}$ and consequently, the values of $\Delta G^S_\Sigma$ for the samples at higher $C_C$. This was explained earlier by the influence of microwave radiation on the reduction of carbon-oxide groups. As follows from the data for the analysed samples the maximal $\Delta G_\Sigma$ values are about one order larger than those obtained for similar samples by the $^1$H NMR method (Turov and Leboda 1999). Although a general trend of changes in $\Delta G_\Sigma$ is the same, the absolute values of the free surface energy determined by the Q-TG method are several times higher. This is connected with the significant contribution of the surface energy of the water-air interface to $\Delta G_\Sigma$ and this free energy is several times higher than that for the adsorbent in the aqueous medium.

## 4 Conclusion

Deposition of pyrocarbon on the silica gel surface reduces the porosity and the specific surface area of CS adsorbents with the increasing $C_C$ values, which also affects the pore sizes. The pyrocarbon layer can be non-continuous but it covers active surface sites and can inhibit adsorption of water that reduces the reaction rate of hydrolysis of the CS surfaces on hydrothermal treatment. Shielding of the silica gel surfaces by pyrocarbon deposits causes significantly smaller structural changes on HTT in comparison with that of pure silica gel. Hydrothermal modification by using microwaves causes an increase of specific surface area and total pore volume in relation to these parameters in the initial samples. Hydrothermal modification of carbosils performed in the autoclave in saturated water steam causes significant increase of total free surface energy on the adsorbent/water interface and free surface energy on the adsorbent/strongly adsorbed water interface.

## Nomenclature

| | | |
|---|---|---|
| $C_C$ | Carbon deposit concentration | wt.% |
| $C^b_{H_2O}$ | Water concentration in filled pores, corresponding to the initial boiling point $T_b$ | mg/g |
| $C^{\max}_{H_2O}$ | Maximal concentration of adsorbed water | mg/g |
| $C^S_{H_2O}$ | Concentration of strongly bound water | mg/g |
| $\Delta G$ | Changes in Gibbs free energy of the interfacial water | kJ/mol |
| $\Delta G^t$ | Maximal changes in Gibbs free energy of adsorbed water | kJ/mol |
| $\Delta G^S$ | Maximal changes in Gibbs free energy of the strongly bound water | kJ/mol |
| $\Delta G^b$ | Changes in Gibbs free energy of water during its evaporation from filled pores | kJ/mol |
| $\Delta G_\Sigma$ | Surface free energy on the interface adsorbent/water | mJ/m$^2$ |
| $\Delta G^S_\Sigma$ | Surface free energy on the interface adsorbent/strongly bound water | mJ/m$^2$ |
| $H_{\text{im}}$ | Immersion heat | mJ/m$^2$ |
| $n$ | Number of statistical monolayers | |
| $R_p$ | Pore radius | nm |
| $R_{\text{dom}}$ | Dominant pore radius | nm |
| $S_{BET}$ | *BET* specific surface area | m$^2$/g |
| $\Delta S/S_{BET}$ | Relative changes in the *BET* specific surface area | % |
| $T_b$ | Temperature of initial boiling point in pores | °C |
| $V_p$ | Pore volume | cm$^3$/g |
| $\Delta V/V_p$ | Relative changes in the pore volume | % |
| $V_{\text{mic}}$ | Micropore volume | cm$^3$/g |

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