Hydrothermal modification of carbon adsorbents

J. Skubiszewska-Zięba · V.V. Sydorchuk · V.M. Gun'ko · R. Leboda

Abstract The effects of high-pressure autoclave treatments on porous structure and surface properties were studied for a variety of activated carbons (AC, synthetic and produced from plum stones) treated with water vapour, hydrogen peroxide (10–50%) or 10% aqueous ammonia solution at relatively low temperatures (250, 350, 400°C). Surface and structural *parameters* of modified ACs were determined using nitrogen, water, ammonia and benzene adsorption isotherms. It was found that the effects of AC modification resulting in changes in their porous structure and surface chemistry depend on the kind of initial ACs, modifier type and concentration of modifier and treatment temperature. At the same conditions synthetic ACs are modified to a larger extent than ACs prepared using natural raw materials. Repeated treatment of a given carbon intensifies changes in its porous structure.

Keywords Activated carbon · Hydrothermal treatment · Hydrogen peroxide · Porous structure · Slitshaped pores · Primary adsorption centres · Ammonia adsorption

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1 Introduction

Carbon adsorbents due to their structural characteristics and physicochemical properties are widely used in many adsorption, catalytic, liquid and air purification processes (Jankowska et al. 1991a; Fenelonov 1995). These materials are inert, exhibit a high specific surface area and a large pore volume and possess high chemical and mechanical stability. However, activated carbons (ACs) are characterized by certain surface heterogeneity (Jankowska et al. 1991a; Fenelonov 1995; Tarkovskaya 1981) because of the presence of such heteroatoms as oxygen, nitrogen, hydrogen and others whose amounts vary depending on the nature of the AC precursors, and reaction, activation and modification conditions (Jankowska et al. 1991a; Tarkovskaya 1981; Marsh et al. 1997). These heteroatoms are fixed in the carbon matrix in the form of carboxyls, carbonyls, phenols, ketones, amine, amide and other functionalities (Jankowska et al. 1991a; Fenelonov 1995; Marsh et al. 1997). Their presence affects acidity/basicity of the AC surfaces (Jankowska et al. 1991b). AC interaction with adsorbates, especially selectivity of the adsorption, strongly depends on the content and type of the mentioned functionalities (Tarkovskaya 1981; Salame and Bandosz 1999; Salame et al. 1999). Oxidation of carbons is the most frequently applied method of AC surface properties modification (Jankowska et al. 1991a; Fenelonov 1995; Marsh et al. 1997). This process can be carried out in gaseous media using oxygen, ozone and nitrogen oxides or in a liquid phase using hydrogen peroxide, nitric acid, perchloric acid, potassium permanganate, and other oxidizing agents (Jankowska et al. 1991a; Fenelonov 1995).

The degree of AC oxidation and the type of created surface functionalities depends on chemical properties of oxidizing agent, oxidation temperature and time, as well as

the chemical composition of the initial carbon materials (Jankowska et al. 1991a; Marsh et al. 1997; Gun'ko 2005; Choma et al. 1999; Moreno-Castilla et al. 1995). Small or large changes in the structural *parameters* of ACs depend on oxidation conditions (Jankowska et al. 1991a; Marsh et al. 1997; Gun'ko 2005; Choma et al. 1999; Moreno-Castilla et al. 1995; Gil et al. 1997). There are many methods to enhance the surface functionality of ACs (Choma et al. 1999). *Despite numerous papers published on AC oxidation or other modifications, the using of new techniques can be perspective for these purposes.*

This paper presents a simple way of modification of AC surface using hydrothermal high-pressure autoclave treatments (HTT). The effects of treatment conditions, kinds of modifiers and initial ACs on the surface properties and porous structure of modified ACs samples were studied. Water vapour, hydrogen peroxide of different concentration (10–50%) and 10% ammonia solutions were used as modifiers. The effects of modification of *commercial* and synthetic (prepared from organic polymers) ACs are compared. It should be noted that only few works, published earlier, were devoted to HTT of carbon materials (under sub- and supercritical conditions) with the purpose of modification of their porous and surface structure (Nieh and Grow 1987; Matsumura et al. 1997; Turov et al. 2002). Authors of these investigations were found the changes of porous structure parameters in hydrothermal conditions and suggested that observed changes are caused by gasification of carbon. However, indicated studies are not systematic. *Particularly, it is difficult to draw general conclusions about the effect of this treatment on carbon porous structure.*

2 Experimental

ACs produced from fruit stones A2PS (Gryskaf, Poland) and KAU (Russia) and spherical carbon with nitrogen (SCN) prepared at the Institute of Sorption and Endoecology Problems (Kiev, Ukraine) were used as carbon adsorbents. Their modification was carried out in the steam phase at autogeneous pressure of modifier. Meantime, 1 g AC was loaded in quartz insert that was placed into stainless-steel autoclave with volume of 45 ml. 15 ml of modifier was poured on the bottom of autoclave. Distilled water, 10–50% w/w aqueous solutions of hydrogen peroxide and 10% aqueous solution of ammonia were used as modifiers. Temperature of HTT was 250, 350°C, its duration was 3 h. Activated carbon KAU was also subjected to more severe HTT, namely by pure water at 400°C, 50% w/w aqueous solutions of hydrogen peroxide at 350°C, and twice repeated HTT by 30% w/w H_2O_2 at 350°C. The latter variant of HTT was performed as follows: the reaction products were removed from the autoclave after the first treatment, a fresh solution of hydrogen peroxide

was added to the autoclave and then AC was subjected to repeated treatment.

Nitrogen adsorption–desorption isotherms were recorded at 77.4 K using a Micromeritics ASAP 2405N (V.1.01) adsorption analyser. Adsorption of water vapour, benzene and ammonia was measured at 20°C using a McBain apparatus with a quartz spiral.

The specific surface area S_{BET} was calculated according to the standard BET method (Gregg and Sing 1982) at $p/p_0 = 0.05 - 0.23$ (where p and p_0 denote the equilibrium and saturation pressures of nitrogen respectively). Sorption pore volume V_p was determined from nitrogen adsorption isotherms at $p/p_0 = 1$.

Pore size distributions (PSD, $f_V(x)$ and $f_S(x)$ with respect to the pore volume and the specific surface area, respectively) were calculated using overall equation within the framework of Density Functional Theory (DFT) (Do et al. 2001; Platzer and Maurer 1989) The differential PSDs $f_V(x)$ were converted to incremental PSDs (IPSD). The $f_V(x)$ and $f_S(x)$ functions were used to calculate contributions of micropores (S^*_{mic}, V_{mic}) at the pore half-width $x < 1$ nm, mesopores (S^*_{mes}, V_{mes}) at $1 < x < 25$ nm, and macropores (S^*_{mac}, V_{mac}) at $25 < x < 100$ nm to the specific surface area and the total porosity. Additionally, $f_S(x)$ was used to estimate deviation of the pore shape from the model of slitshaped pores (Platzer and Maurer 1993)

$$\Delta w = \frac{S_{BET}}{\int_{x_{min}}^{x_{max}} f_S(x)dx} - 1 \qquad (1)$$

where x_{max} and x_{min} are the maximal and minimal pore half-widths respectively. The S^*_{mic}, S^*_{mes} and S^*_{mac} values were corrected by multiplication by $(\Delta w + 1)$ that gives $S^*(\Delta w + 1) = S_{sum} = S_{mic} + S_{mes} + S_{mac} = S_{BET}$.

The distribution functions $f(\Delta G)$ of Gibbs free energy (ΔG) of adsorption of water and benzene were calculated using the Langmuir equation (Gregg and Sing 1982)

$$\Theta = \frac{bc}{1 + bc}, \qquad (2)$$

(where $b = e^{-\frac{\Delta G + z}{R_g T}}$, $c = p/p_0$ is the relative pressure; and R_g is the gas constant, having regard to lateral interactions (z) between adsorbed molecules assuming $z = 3/2R_g T$) as the kernel in the overall adsorption equation in the form of Fredholm integral equation of the first kind

$$\Theta(T, C_{eq}) = \int_{\Delta G_{min}}^{\Delta G_{max}} \Theta_l(T, C_{eq}, \Delta G) f(\Delta G) d(\Delta G). \qquad (3)$$

Equation (3) was solved using a regularization procedure under the nonnegativity condition ($f(\Delta G) > 0$ at any ΔG values) and the fixed regularization parameter $\alpha = 0.01$. Equation (3) was also used to calculate the distribution

Table 1 Structural characteristics of A2PS samples

Sample	Treatment condition	S_{BET} m²/g	S_{mic} m²/g	S_{mes} m²/g	S_{mac} m²/g	V_p cm³/g	V_{mic} cm³/g	V_{mes} cm³/g	V_{mac} cm³/g	Δw_{slit}
A2PS-0		1054	930	121	3	0.940	0.468	0.258	0.213	0.239
A2PS-1	Water, 250°C	1080	975	101	4	0.969	0.508	0.246	0.215	0.128
A2PS-2	Water, 350°C	1019	927	90	3	0.837	0.465	0.185	0.187	0.184
A2PS-3	10% H_2O_2, 250°C	1021	905	113	3	0.831	0.441	0.203	0.187	0.261
A2PS-4	10% NH_3, 250°C	960	874	83	3	0.791	0.462	0.178	0.151	0.128
A2PS-5	20% H_2O_2, 250°C	994	873	116	6	0.961	0.443	0.246	0.272	0.108
A2PS-6	30% H_2O_2, 250°C	933	843	86	4	0.767	0.418	0.209	0.141	0.131
A2PS-7	30% H_2O_2, 350°C	1042	953	86	3	0.742	0.430	0.153	0.159	0.274

functions of nitrogen adsorption energy using the Fowler–Guggenheim equation (describing localized monolayer adsorption with lateral interaction) (Gun'ko and Mikhalovsky 2004) as the kernel.

Concentration of primary adsorption centres (PAC) was calculated from the water vapour adsorption data using Dubinin–Sierpinsky equation (Dubinin and Sierpinsky 1981). Geometrical surface S_g (Dubinin's term) of activated carbon SCN was also determined from isotherms of water vapour (Dubinin and Sierpinsky 1981).

3 Results and discussion

There are not clear relationships between conditions of carbon A2PS treatment and changes in the structural characteristics of the samples (Table 1); however, certain tendencies can be found. For instance, the treatment of A2PS with water vapour at 250°C results in slight increase of the specific surface area due to development of microporosity, since a small *raise* in the S_{mic}, V_{mic}, and V_p values but insignificant changes in other structural characteristics is observed. It should be noted that increase both of specific surface area and microporosity as a result of treatment by supercritical water (600°C, 34.5 MPa) was earlier observed (Matsumura et al. 1997). Elevation of temperature to 350°C, on contrary, leads to some reduction of S_{BET} and V_p which, obviously, occurs owing to partial destruction of mesopores (S_{mes} decreases from 121 to 90 m²/g and V_{mes} lowers from 0.26 to 0.19 cm³/g).

At the same time, hydrothermal modification of A2PS with H_2O_2 causes a decrease in all structural characteristics. Meantime, the *higher* concentration of H_2O_2 is, the greater effect HTT at 250°C causes. Thus, S_{BET} and V_p reduce in 11.5 and 18.0%, respectively, when concentration of H_2O_2 grows to 30%. Observed lowering of S_{BET} and V_p can be explained by changes both in micro- and mesoporous structure of carbon, namely breaking (*through* burning *of carbon*) of pores walls. The treatment with the ammonia solution leads

to a reduction of the porosity, and it is *bigger* than that after the treatment with 10% H_2O_2 solution. This unexpected result may be due to the fact that carbon dioxide, released during the oxidation of carbon, is bonded with ammonia. Therefore, the equilibrium of process shifts toward the reaction products, i.e. oxidation occurs *more deeply. However, nitrogen is not incorporated in the structure of carbon. The latter is confirmed by elemental analysis (Hereaus CNH analyzer).*

On the other hand, modification with 30% hydrogen peroxide solution at 350°C causes certain development of microporosity (S_{mic}, V_{mic}) and macroporosity (V_{mac}), but decrease in the S_{BET} value and contribution of mesopores (V_{mes}) in comparison those for A2PS treated with 30% H_2O_2 at 250°C. At the same time, comparison of porous structure parameters for these modified samples with those for initial A2PS indicates that effect of HTT is minimal. The latter can be associated with inhibition of modification (oxidation) process by gaseous reaction products.

Activated carbon KAU, which *is similar to A2PS,* has stone fruit origin, was subjected to *the same* HTT. Besides, other procedures of modification were used, namely double HTT with 30% H_2O_2 and HTT with 50% H_2O_2. Table 2 presents some of obtained results. As can be seen, double HTT causes *greater* decrease of all porous structure parameters, except V_{mes}, compared with single HTT. Even more significant reduction in porosity is observed as a result of HTT with 50% hydrogen peroxide solution, although the volume of mesopores increases in this case. Obviously, part of micropores transforms into mesopores using *HTT by* high-concentrated H_2O_2.

The KAU treatment with pure water at 400°C increases contribution of micropores to the surface area (Table 2, S_{mic}); however, the V_p and S_{BET} values decrease.

The third studied carbon SCN *has* poorly developed porosity determined from adsorption of nitrogen (Table 3, SCN-0); therefore, one can expect that HTT modification of SCN can give rather positive structural changes. The treatment of SCN with water vapour at 250°C does

Table 2 Structural characteristic of KAU samples

Sample	Treatment condition	S_{BET}, m²/g	S_{mic}, m²/g	V_p, cm³/g	V_{mic}, cm³/g	V_{mes}, cm³/g	Δw_{slit}
KAU-0	Initial	952	796	0.51	0.33	0.15	0.053
KAU-1	HTT H_2O, 400°C	944	803	0.48	0.33	0.12	0.041
KAU-2	Single HTT 30% H_2O_2, 350°C	973	662	0.54	0.28	0.16	0.125
KAU-3	Double HTT 30% H_2O_2, 350°C	725	436	0.46	0.21	0.16	0.213
KAU-4	Single HTT 50% H_2O_2, 350°C	706	336	0.39	0.15	0.24	0.022

Table 3 Structural characteristics of SCN samples

Sample	Treatment condition	S_g, m²/g	S_{BET} m²/g	S_{mic} m²/g	S_{mes} m²/g	S_{mac} m²/g	V_p cm³/g	V_{mic} cm³/g	V_{mes} cm³/g	V_{mac} cm³/g	Δw_{slit}
1	2	3	4	5	6	7	8	9	10	11	12
SCN-0		422	192	175	14	3	0.305	0.099	0.108	0.098	0.014
SCN-1	Water, 250°C	435	191	171	16	5	0.407	0.111	0.124	0.173	0.064
SCN-2	10% H_2O_2, 250°C	569	461	437	20	5	0.626	0.222	0.129	0.275	−0.055
SCN-3	10% NH_3, 250°C	425	173	152	17	4	0.423	0.096	0.156	0.170	−0.063
SCN-4	Water, 350ºC	455	295	280	12	4	0.461	0.157	0.110	0.194	−0.110
SCN-5	20% H_2O_2, 250°C	523	345	322	17	6	0.659	0.185	0.160	0.313	0.008
SCN-6	30% H_2O_2, 250°C	494	186	161	23	7	0.572	0.087	0.145	0.340	0.276
SCN-7	30% H_2O_2, 350°C	481	297	279	15	3	0.459	0.153	0.147	0.159	−0.071

not practically change the specific surface area of different pores (Table 3, *S*) but causes increase in the porosity (V_p, V_{mes}, V_{mac}). However, *elevation of HTT temperature by 100°C* results in significant increase in both types of structural *parameters* (specific surface area and *pore volume*). Hydrogen peroxide solution more strongly affects the structural *parameters* of SCN. The 10% H_2O_2 solution at 250°C gives significant increase in the S_{BET} and S_{mic} as well as V_p, V_{mic}, V_{mac} values (Table 3). Meantime S_{BET} increases by almost two and a half times, and V_p grows more than twice. With increasing H_2O_2 concentration the porosity, especially macroporosity, rises but the surface area drops down. Changes in the porous structure of SCN treated with 10% ammonia *resemble that obtained for A2PS treated in the same conditions.*

It should be noted that *actual* increase both of specific surface area S_{BET} and *sorption pore volume* V_p observed during HTT of SCN *may be not so.* Indeed, comparison of S_{BET} with the corresponding values of S_g, calculated from the adsorption isotherms of water vapor (columns 3 and 4 of Table 3), confirms this assumption. This can be explained by the fact that the lowered S_{BET} and V_p values were obtained for samples with the smallest pores (including initial) using low-temperature measurements of nitrogen adsorption. Obviously, the smallest pores are inaccessible for nitrogen molecules in these conditions. At the same time, smaller molecules of water penetrate into these pores at 20°C. Therefore, S_g is greater than S_{BET} for all samples and

ratio S_g/S_{BET} can indicate fraction of the smallest pores in sample. However, general trend of changes in specific surface area with increasing of HTT temperature and hydrogen peroxide concentration is preserved when the value S_g is used. Thus, S_g grows in 1.4 times as a result of HTT of SCN at 250°C with 10% H_2O_2 solution while S_{BET} of this sample exceeds that for initial SCN in 2.4 times. In our opinion, value of S_g/S_{BET} indicate fraction of the smallest pores in SCN samples.

Analysis of the PSDs for three series of treated carbons calculated from adsorption-desorption of nitrogen (Figs. 1–3) shows that changes are *much more significant* for treated SCN samples (Fig. 3) than those for A2PS (Fig. 1) or KAU (Fig. 2). Initial A2PS (A2PS-0) as a carbon produced from a natural raw material (plum stones) *has a relatively large Δw value. This reveals that the shape of pores does not exactly correspond to ideally slitshaped pores. Treatment with water at 250°C (A2PS-1) leads to *structure of pores which is more close to slitshaped* because of the removal of ash nanoparticles and other defective fragments which are more hydrophilic than ideal basal planes responsible for the slit-shaped porosity of the material; however, the PSD changes are insignificantly (Fig. 1). An increase in the HTT temperature to 350°C slightly enhances nonideality of the pore shape and changes in the PSD *become more significant.*

Modification of A2PS with H_2O_2 or NH_3, leads to certain decomposition of the pore walls because the *pore volume* and the specific surface area decrease in comparison

Fig. 1 DFT pore size distributions with respect to (**a**) the pore volume and (**b**) the specific surface area for treated A2PS samples (carbon numbers are from Table 1)
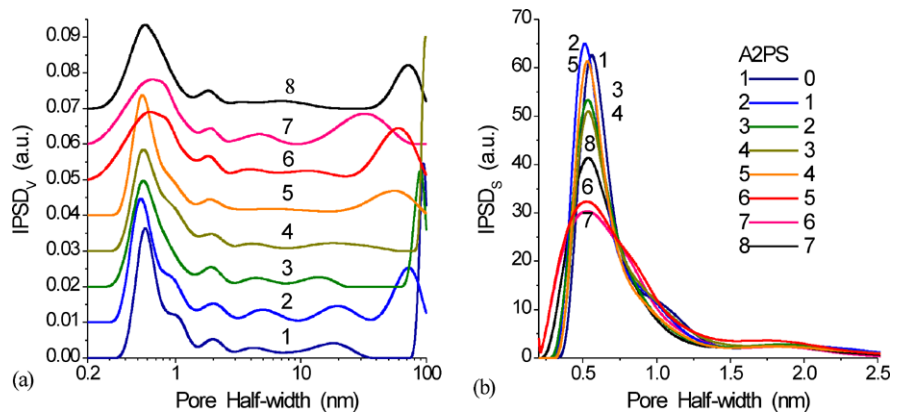
Fig. 2 IPSD for treated carbons KAU (**a**) calculated using Quantachrome DFT software and (**b**) another DFT approach (Platzer and Maurer 1993) (carbon numbers are from Table 2)
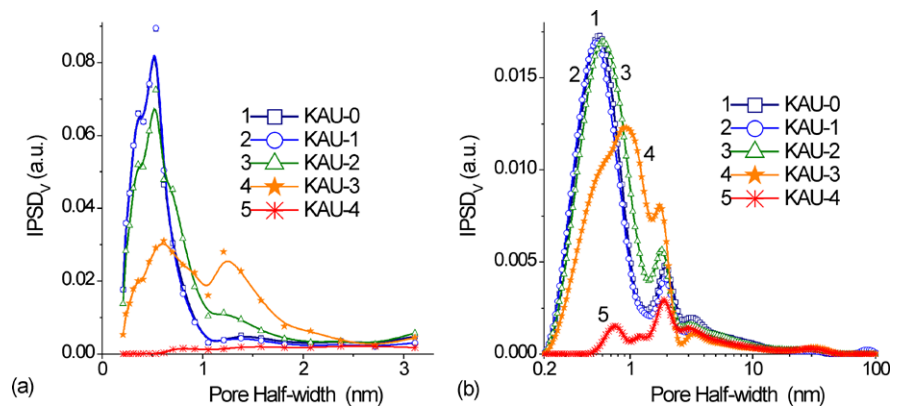
Fig. 3 PSDs calculated using DFT with the model of slitshaped pores for treated carbon SCN samples (carbon numbers are from Table 3)
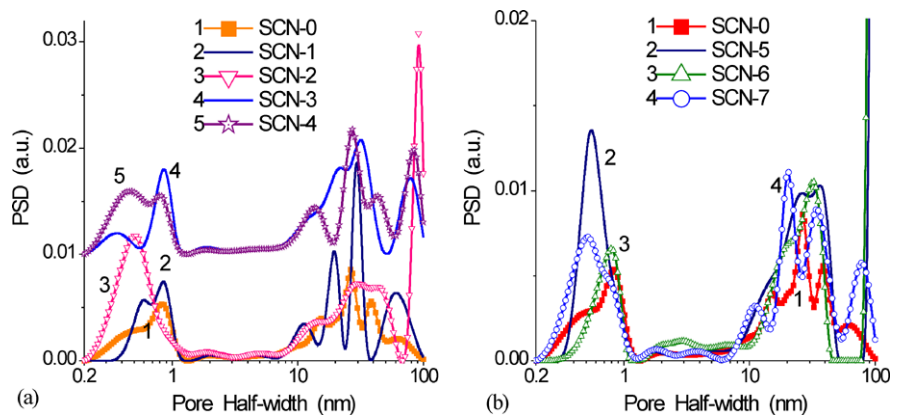
with the initial A2PS. *Some redistribution of different type of pores occurs, as a result.* The character and the *extent* of these structural changes depend on treatment conditions (temperature and concentration of H_2O_2 or NH_3). Clearly, the maximal changes in the structure of pore walls occur at the maximal temperature and the maximal H_2O_2 concentration (Fig. 1) that give the maximal Δw value. In other words, the treatment leads initially to the improved pore structure (Δw decreases) but than the nonideality of the pore shape grows (Δw increases) because partial decomposition of the pore walls occurs. Similar but *slightly more significant* (because of higher temperature or greater concentration of

H_2O_2) changes are characteristic for treated KAU (Fig. 2) than that for A2PS (Fig. 1). *Large* changes in the structural characteristics of treated KAU samples cause significant changes in the energetic characteristics of the nitrogen adsorption (Fig. 4). Maximum diminution of the adsorption potential and adsorption energy is observed for KAU treated with 50% H_2O_2 at 350°C (single HTT). *Therefore, negative changes, i.e. resulting in decrease of specific surface area and sorption pore volume, take place during of A2PS and KAU HTT.*

The *initial* SCN material produced from the polymer precursor *has* pore shape *which is more close* to ideal slitshaped

Fig. 4 The distribution functions of nitrogen adsorption (**a**) potential and (**b**) energy for treated KAU samples

(a)

(b)
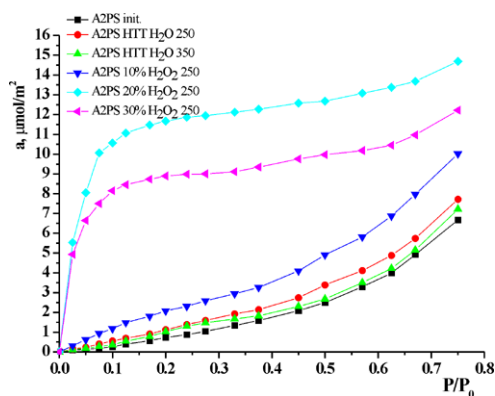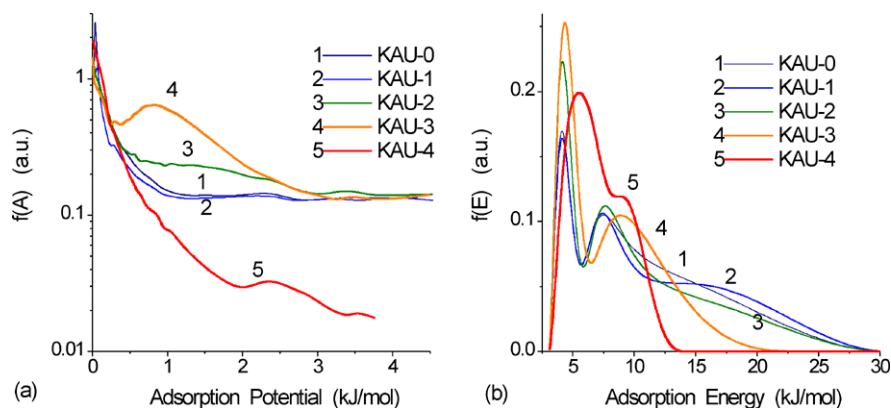
Fig. 5 The absolute adsorption isotherms of water vapour at 20°C on adsorbents prepared based on the carbon A2PS

Table 4 Influence of HTT on primary active centres concentration μ ($\mu mol/m^2$) for different ACs

Conditions of HTT	A2PS	SCN
Initial	0.60	0.37
250°C H_2O	0.69	0.38
250°C 10% H_2O_2	0.79	0.40
250°C 20% H_2O_2	2.02	1.70
250°C 30% H_2O_2	3.89	3.16
250°C 10% NH_3	0.56	0.42
350°C H_2O	0.79	0.64
350°C 30% H_2O_2	1.20	1.40

pores in comparison with fruit stone based A2PS or KAU because the deviation for the initial SCN corresponds to only 1.4% and the Δw values are typically smaller for the treated SCN samples (Table 3) than that for the treated A2PS (Table 1) and KAU (Table 2) samples. However, tendencies in changes in the pore shape of SCN differ from those for A2PS and KAU. For instance, for certain SCN samples the Δw values are negative in contrast to A2PS or KAU. This effect can be caused by enhanced contribution of the outer surface of treated carbon granules that is much *more significant* for SCN with low surface area than A2PS or KAU with much higher *specific* surface area.

The adsorption of nitrogen onto carbons is mainly due to nonspecific interactions; however, specific interactions on adsorption of polar, aromatic and other adsorbates can play a very important role on the practical applications of carbon adsorbents. Therefore, the adsorption of water, ammonia and benzene onto studied carbons can give useful information *about* the treatment effects on the adsorption properties of treated carbons.

Figure 5 presents the absolute adsorption isotherms of water vapour onto some treated A2PS samples. The mechanism of water adsorption onto carbon adsorbents was proposed by Dubinin and Sierpinsky (Dubinin and Sierpinsky

1981). According to them, water molecules are first adsorbed on primary adsorption *centres (PAC)* with oxygen-containing surface functionalities and then adsorption occurs on secondary sites with adsorbed water molecules. An increase in the water vapour pressure leads to the formation of clusters of associated water molecules via the hydrogen bonding (Salame and Bandosz 1999; Salame et al. 1999; Gun'ko 2005; Choma et al. 1999). The isotherms *obtained* for the initial A2PS as well as for the water-treated samples can be assigned to type III of the IUPAC classification (Sing et al. 1985) that is characteristic for weak adsorbent-adsorbate interactions. Water molecules interact weakly with the carbon surface due to a small number of primary active centres corresponding to 0.60, 0.69 and 0.79 $\mu mol/m^2$ (Fig. 5, Table 4). These values were calculated using the DS equation (Dubinin and Sierpinsky 1981). The modification of A2PS with hydrogen peroxide causes a significant increase in the adsorption capacity compared with that for A2PS treated with water vapour (Fig. 5). Additionally, the isotherm shape for the former *modified with* 20 and 30% H_2O_2 changes significantly (isotherms transform into type I of the IUPAC classification) because of an increase in the amounts of primary adsorption sites: 0.79 (Fig. 5, curve 4), 2.02 (5) and 3.89 $\mu mol/m^2$ (6). Content of PAC for initial and treated SCN samples is also presented in Table 4. It can be seen that value of PAC, expressed in
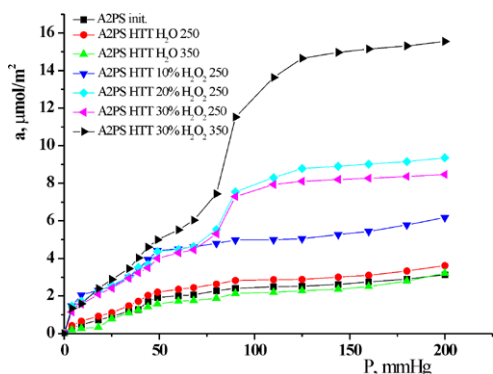
Fig. 6 The absolute adsorption isotherms of ammonia at 20°C on adsorbents prepared based on the carbon A2PS
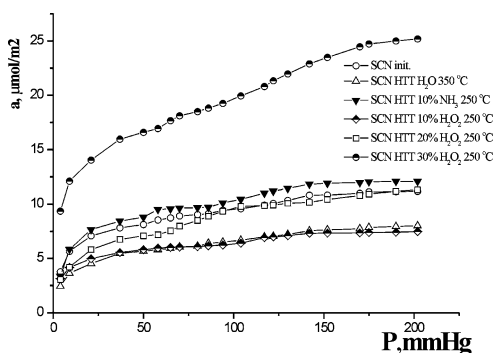
Fig. 7 The adsorption isotherms of ammonia recorded at 20°C on SCN samples

μmol/m^2, increases sharply with elevation of H$_2$O$_2$ concentration at 250°C while that considerably reduces at 350°C for both ACs.

As it could be expected, hydrothermal treatment of A2PS with hydrogen peroxide causes a significant increase in the adsorption of ammonia (Fig. 6) because of an increase in the number of acidic surface sites (Tomaszewski et al. 2005; Seredych and Bandosz 2007a; Seredych and Bandosz 2007b). The amounts of these groups increase much *more significantly* on the carbon treated with hydrogen peroxide than with water (Fig. 6). The course of isotherms *obtained for SCN* is similar (Fig. 7). (It should be noted that calculation of absolute isotherms for this AC is based on values of S_g rather than S_{BET}.) The stepped shape of the isotherm course (Figs. 6 and 7) can be due to structural and energetic heterogeneity of the samples.

The adsorbent heterogeneity can be analyzed on the basis of the distribution functions of Gibbs free energy of adsorption $f(\Delta G)$ (Fig. 8). The $f(\Delta G)$ distributions for benzene and water depend on both textural and chemical characteristics of initial and treated carbons. The structural changes in the treated A2PS and SCN carbons are rather opposite (Tables 1 and 3). Therefore a $f(\Delta G)$ peak at small $\Delta G = -1.5$ kJ/mol is observed on the adsorption of benzene onto initial SCN but it is absent for the treated SCN

samples, as well as for A2PS. As it is known (Salame and Bandosz 1999) the adsorption of benzene is sensitive to the presence of surface functionalities. The differences in the minimal and maximal $-\Delta G$ values are relatively small because the samples were modified under mild conditions. In the case of water, only the differences in maximal adsorption energies are found (Fig. 8). Generally, the modified samples are more heterogeneous in relation to benzene than water. This is evidenced by the differences between the minimal and maximal energies which are much larger for benzene than for water. Independent on the kind of initial carbon this difference is about 10–12 kJ/mol for benzene and 6–8 kJ/mol for water. Hydrothermal modification of A2PS and SCN reduces their energetic heterogeneity to some extent. This kind of treatment was earlier applied to change the AC surface chemistry but at minimal change in the porous structure (Tomaszewski et al. 2005) that allowed studying the effect of chemical heterogeneity of the AC surface on the mechanism of amphetamines adsorption. It was found that only a portion of the surface of oxidized carbons was accessible for the adsorbed probe compounds. The O-containing functionalities in the vicinity of entry into narrow pores made it difficult or even impossible for explosive substances—*nitroaromatic compounds* (Leboda et al. 2002) to locate in such pores due to strong specific interactions (Rodriguez-Reinoso et al. 1992). It is quite possible that such effects determine the shape and course of energy distribution functions (Fig. 8).

4 Conclusions

The hydrothermal modification of porous structure and surface properties for activated carbons was studied at relatively low temperatures (250–400°C). The modification effects related to changes in structural *parameters* and surface chemistry depend on the kind of a modifier (H$_2$O vapour, H$_2$O$_2$ or NH$_3$ solutions), nature of carbon adsorbent and treatment temperature. Modification with water, hydrogen peroxide and ammonia *under studied HTT conditions* causes negative changes, as a rule, i.e. reduction in the specific surface area and the *pore volume* from a few to 25 percent in the case of carbons prepared from fruit stones (A2PS, KAU) and characterized by $S_{BET} \approx 1000$ m^2/g and $V_p = 0.5$–1.0 cm^3/g. Meanwhile, destruction of porous network due to burning of carbon of pore walls, especially as result of H$_2$O$_2$ concentration increase, is observed. The latter leads to diminution of specific surface area and pore volume for micro- and mesopores and *increase* of nonideality of the pore shape. Maximal changes are characteristic for KAU samples subjected to double HTT and HTT with 50% hydrogen peroxide. HTT under these conditions also promotes transformation of part of micropores into mesopores. Thus,

Fig. 8 The distribution functions $f(\Delta G)$ of Gibbs free energy (ΔG) of adsorption of (**a**), (**b**) benzene and (**c**), (**d**) water onto activated carbons (**a**), (**c**) A2PS and (**b**), (**d**) SCN differently treated
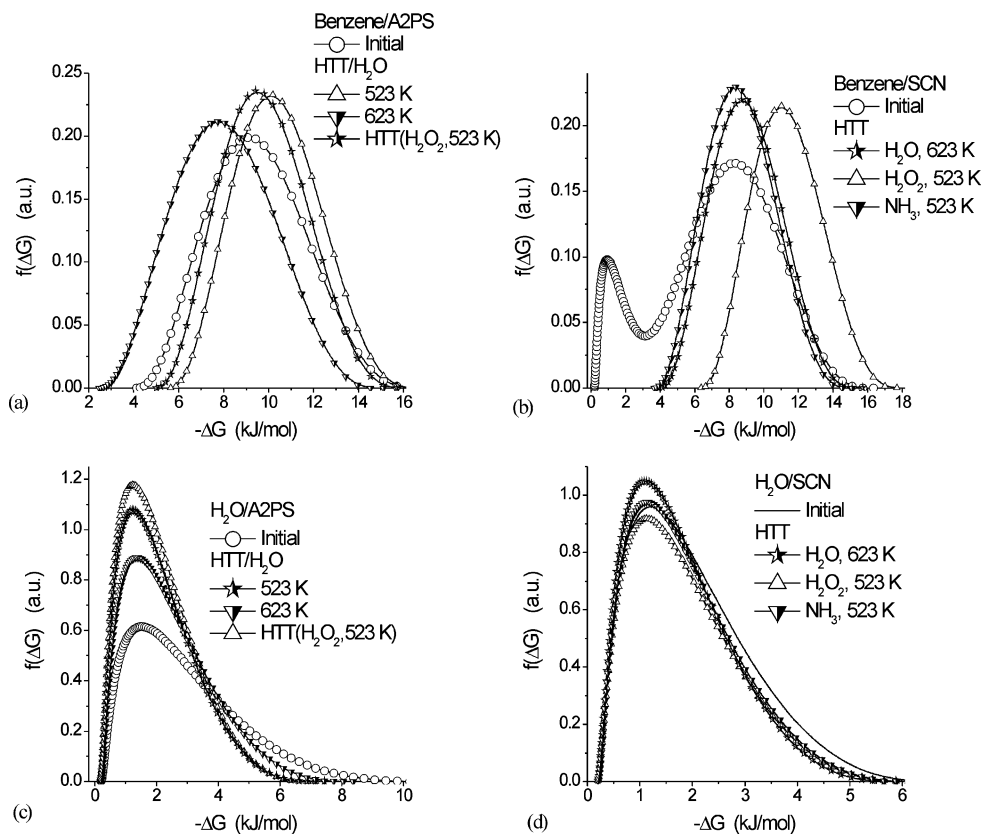
fraction of mesopores in the initial sample is about 30% whereas that for sample, modified with 50% H_2O_2, equals more than 60%, i.e. increases in 2 times.

The changes are much larger and mainly positive for carbon SCN characterized by much smaller $S_{BET} \approx 200$ m^2/g and $V_p \approx 0.3$ cm^3/g i.e. HTT of this AC causes its activation since specific surface area S_{BET} and pore volume increase more than in 2 times. At the same time, the magnitude of this effect is not so great if the data of adsorption of water are used *for calculation of specific surface area (geometrical surface determined from water vapour adsorption increases in 1.35 times)*. In other words, the value of effect is determined by the accessibility of pores for the molecules of adsorbate.

HTT of ACs in the autoclave causes significant increase of oxygen functionalities at surface, including groups possessing acid properties, and consequently, *increasing* of adsorption capacities with respect to polar substances: water, ammonia and benzene.

Therefore, this method allows *to change porous structure of carbons to a lesser extent and to modify their surface structure to a greater extent. Besides, hydrothermal modification of A2PS and SCN slightly reduces energetic heterogeneity of their surface.*

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