



The effect of the gradual thermal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon

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Received 11 September 2001; accepted 8 May 2002

Abstract

The physicochemical properties, surface chemical structure and some catalytic properties of a series of carbons prepared by nitric acid oxidation of an activated carbon and subsequent heat treatment under vacuum and mild temperature conditions (423–573 K) were studied. The porous structure characteristics of the partially evacuated samples were estimated from low-temperature nitrogen adsorption data. The thermal analysis and the quantitative determination of surface functional groups by selective neutralization of bases and pH-metric titration were carried out. The dehydration of 2-methylpropan-2-ol was used as a test reaction. While gradual annealing in vacuum alters the surface only slightly, it does differentiate strongly the number and the acidic strength of the surface groups. Progressive heating under mild conditions removes mainly those surface groups that are located in macropores or on the outer surface of the carbon. According to TPD results, the decomposed surface groups are single carboxylic groups, as expected. The decomposition of single, strong carboxylic groups is accompanied by rearrangements of other carboxylic groups with the simultaneous formation of additional cyclic structures like anhydrides, lactones or lactols. Catalytic tests support our previous findings that oxidized carbons have a high dehydration activity. This activity is controlled not only by the number and the strength of acidic groups, but also by their accessibility. There exists an optimum concentration of surface acidic groups above which the activity decreases due to steric restrictions.

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Keywords: A. Activated carbon; B. Catalyst, surface treatment, oxidation; C. Temperature programmed desorption

1. Introduction

The porous structure and surface chemistry of activated carbon are important properties in connection with its adsorbent behavior. The surface functional groups further influence in a decisive way the ionic exchange and the catalytic and electronic properties of this carbon material [1–5]. These facts explain the long-standing interest in studying the surface chemistry of activated carbon, and

especially carbon–oxygen complexes. The surface groups most often suggested are carboxyl, phenolic hydroxyl, and quinone carbonyl groups. Slightly fewer in number are the reports of ether, peroxide, ester groups, lactones, carboxylic acid anhydrides and cyclic peroxides [1,3,6,7].

Because of the presence of such surface oxides, carbons can be used not only for oxidation reactions but also for acid–base reactions (e.g. etherification and decomposition of alcohols, vinyl and alkene polymerization) [8].

However, the application of activated carbon as a catalyst or catalyst support, as well as its regeneration, requires the use of higher temperatures, and this may result in the loss of oxygen groups. As a result, activated carbon needs, in some instances to be subjected to further

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oxidation treatment in order to re-establish its surface chemistry. This is why the formation and thermal stability of the oxygen groups have been of interest for many years and are still topics of current interest. Two general methods of forming oxygen functional groups involve the use of oxidizing gases or solutions [1]. Among the oxidative modification techniques, nitric acid oxidation is the best known. In addition, perchloric, sulfuric and phosphoric acids, hypochlorite, permanganate, bichromate and hydrogen peroxide can also be used to oxidize the carbon surface [1,5].

There are many reports on the studies of thermal stability of carbon surface oxides. However, most of them concern thermal stability at relatively high temperatures (at 573 K and above) (see Refs. in Table 2). The data on transformations of oxygen groups upon moderate heating of an activated carbon are rather scarce. Therefore, the aim of this study was to describe the effects of progressive heating with respect to the chemical and catalytic properties of oxidized activated carbon.

2. Experimental

2.1. Carbon oxidation

The commercial granulated activated carbon D43/1 from Carbo-Tech Aktivkohlen GmbH (Essen, Germany) was used. The carbon was de-ashed with conc. hydrofluoric and hydrochloric acids by Korver's method [9] and desorbed under vacuum (10^{-2} Pa) at 423 K for 2 h. Subsequently, the ashless carbon was oxidized with conc. nitric acid at 353 K for 3 h; then, after cooling, it was repeatedly washed with redistilled water until nitrates had been completely removed, and dried at 303 K. Finally, the oxidized carbon was desorbed under vacuum at 423 K for 2 h (DOx423) and divided into four portions. Three of these portions were then heated under vacuum (10^{-2} Pa) for 2 h at 473 K (DOx473), 523 K (DOx523) and 573 K (DOx573), in order to decompose some of the oxygen surface groups. All the samples thus prepared were subsequently handled in ambient air.

2.2. Carbon characterization

The porous texture of the carbons was determined from the nitrogen adsorption isotherm at 77 K using density functional theory (DFT) [10] and the Dubinin–Astakhov model [11]:

$$W_{DA} = W_0 \exp\{- (A/\beta E_0)^n\}$$

where W_0 is the total micropore volume, E_0 is the characteristic energy of adsorption, A is the adsorption potential, β and n are the affinity coefficient and parameter of the DA equation, respectively. In addition, the mean

micropore width (L_{mic}) and geometric surface area of micropores (S_g) were calculated by means of the model of slit shaped pores [11]:

$$L_{mic} = 10.8/(E_0 - 11.4)$$

$$S_g = \frac{2 \times 10^3 W_0}{L_{mic}}$$

The adsorption measurements were conducted volumetrically in an automatic ASAP 2010 Sorptomate (Micromeritics, Atlanta, USA). Before the experiment the samples were heated at 423 K under vacuum (10^{-5} Torr) to constant pressure. The DFT calculations were performed using the DFT software from Micromeritics Instrument Corporation.

Thermogravimetric analysis of the oxidized carbon was conducted in an inert atmosphere (He, 20 dm³/h) using an OD 102 derivatograph (Paulik–Paulik–Erdy, Budapest, Hungary) in the 293–1273 K range.

The surface oxygen groups were characterized by temperature-programmed desorption (TPD-QMS) of the decomposition products and acid–base titration. The TPD-QMS experiments were carried out in a flow reactor coupled to a quadrupole mass spectrometer (Dycor M200, Pittsburgh, USA) for the analysis of the gases evolved during thermolysis [12]. To avoid water physisorption all tubing and connections were heated at 373 K. The spectrometer was interfaced to a microcomputer for equipment control and data acquisition. In these experiments, dry, finely-ground carbon samples (0.25 g) were heated at 10 K/min to 973 K, while He was passed through at a flow rate of 25 ml/min. The temperature and selected mass signals—12, 14, 16, 17, 18, 28, 30, 32 and 44 amu—were monitored at 15 s intervals. The TPD spectra were deconvoluted using the non-linear least-squares procedure based on the Levenberg–Marquardt algorithm assuming a Gaussian peak shape.

The acidic group content was determined according to Boehm's [6] method by neutralization with bases of increasing strength (sodium bicarbonate— $pK_a = 6.37$, sodium carbonate— $pK_a = 10.25$, sodium hydroxide— $pK_a = 15.27$ and sodium ethoxide— $pK_a = 20.58$), while the number of basic groups was estimated by neutralization with 0.05 M hydrochloric acid. To make a second assessment of the acidic and basic properties, potentiometric titrations were carried out by means of the 'point-by-point' method [13]. Known portions of each carbon (0.5 g) were mixed with 50 ml of mixtures with a different pH (pH = 1–13) containing various quantities of 0.1 M NaCl, 0.1 M NaOH and 0.1 M HCl and then shaken mechanically for 48 h. The ionic strength was kept constant ($I = 0.1$). After this 48 h period, the pH values of the suspensions were determined using a glass electrode; an aliquot of the supernatant liquid was then back-titrated with hydrochloric acid or sodium hydroxide. Additionally, the acidities (pHs) of

carbon slurries in 0.1 M NaCl after 48 h were determined. The titration curves were differentiated using a quadratic interpolation procedure.

2.3. Catalytic activity

The decomposition of 2-methylpropan-2-ol was conducted in a fixed-bed flow-type reactor working at atmospheric pressure, using helium as carrier gas. The reagent analysis was performed by on-line gas-chromatography [14]. The catalytic tests were carried out in the range 343–413 K, using 120 mg of catalyst, at a 2-methylpropan-2-ol partial pressure of 64.7×10^2 Pa. The reagent was fed at a space time of 617.3 kg/s/mol.

3. Results and discussion

3.1. Porous structure

We have already demonstrated that both the commercial activated carbon D43/1 and its nitric acid oxidized form possess a well-developed porous structure with a high micro- and macroporosity [13]. However, as for other carbon materials, some decrease in pore volume after the nitric acid treatment was observed [13,15–19]. This is a consequence of the fixation of part of surface oxygen complexes at the entrance of the pores which increases their constriction (in other words, not all the micropores are accessible to N_2 molecules), or of widening of the microporosity [15]. The estimated values of the specific surface area (S_{N_2}), the micro- (V_{mic}) and mesopore volume (V_{meso}) calculated using DFT theory, and the D–A equation parameters (W_0 , B_0 , n , S_g and L_{mic}) for the oxidized carbons (Table 1), indicate that only small changes in porosity result from the gradual heating of the oxidized carbon. Annealing under vacuum only slightly enhances micro- (V_{mic} , W_0) and mesoporosity (V_{mes}), and the mean width of micropores (L_{mic}). The increase in the number of pores of greater width with increasing heating temperature was then confirmed by the pore size distributions calculated from density functional theory (Fig. 1). The decreasing value of parameter n (Table 1) indicates that the microporosity has become less uniform.

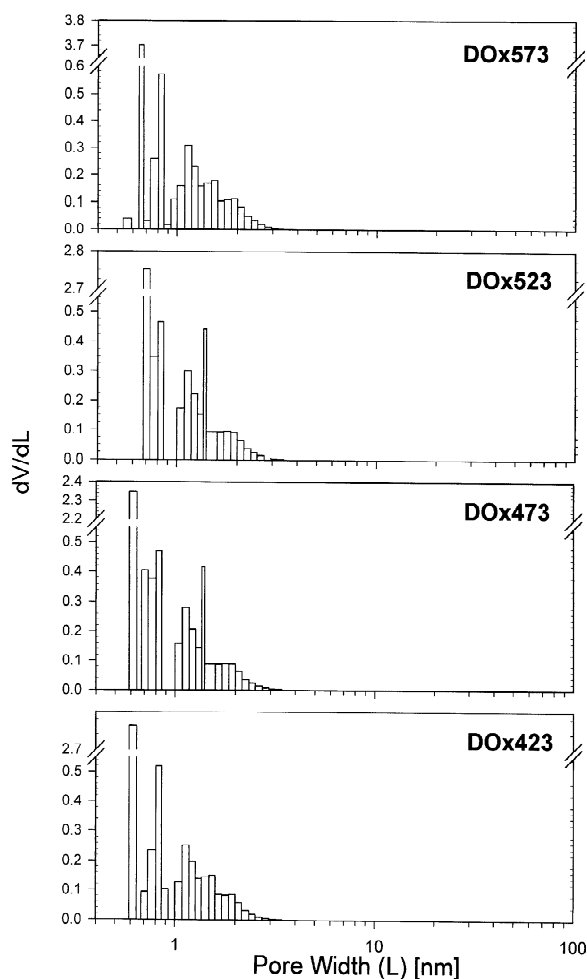


Fig. 1. Pore size distribution curves of the evacuated oxidized carbon samples.

A part of oxygen surface complexes is fixed at the entrance of the pores [15]. Therefore, the observed small changes in the micro- and mesoporosity suggest that progressive heating under mild conditions removes mainly surface groups located in macropores or on the exterior carbon surface under the removal conditions applied.

Table 1
Textural characteristics of the desorbed oxidized carbons

Oxidized carbon	Specific surface area S_{N_2} (DFT) (m^2/g)	Micropore volume, V_{mic} (DFT) (cm^3/g)	Mesopore volume V_{mes} (DFT) (cm^3/g)	Micropore surface area S_g (DA) (m^2/g)	Micropore volume W_0 (DA) (cm^3/g)	Characteristic energy, E_0 (kJ/mol)	n	Micropore width L_{mic} (nm)
DOx423	798	0.335	0.026	785	0.414	21.63	1.92	1.06
DOx473	799	0.340	0.032	787	0.430	20.78	1.79	1.09
DOx523	767	0.350	0.033	759	0.447	20.57	1.66	1.18
DOx573	804	0.358	0.043	752	0.457	20.28	1.77	1.22

3.2. TPD results

The DTG curve for the oxidized carbon DOx423 (Fig. 2) handled in ambient air after desorption at 423 K indicates a maximum weight loss centered around 363 K, which is associated with the release of physically sorbed water. In the range 450–800 K, the plot shows two peaks at about 553 and 703 K. Above 800 K there is an additional minimum centered at around 1000 K. After progressive heating under vacuum of the DOx423 carbon, the peak at 553 K decreases and shifts to higher temperatures, whereas the intensity of the peaks located at higher temperatures increases.

The observed minima on the DTG curves above 450 K follow the peaks on the product profiles recorded during TPD measurements of the carbon DOx423 (Fig. 3). The main products evolved are water ($m/e = 18$), carbon monoxide ($m/e = 28$) and carbon dioxide ($m/e = 44$). Small amounts of nitrogen oxide ($m/e = 30$) and molecular oxygen ($m/e = 32$) were also evolved.

There is some controversy in the literature [5–7,16–32] with respect to the assignment of TPD peaks to specific surface groups, because the peak temperatures are known

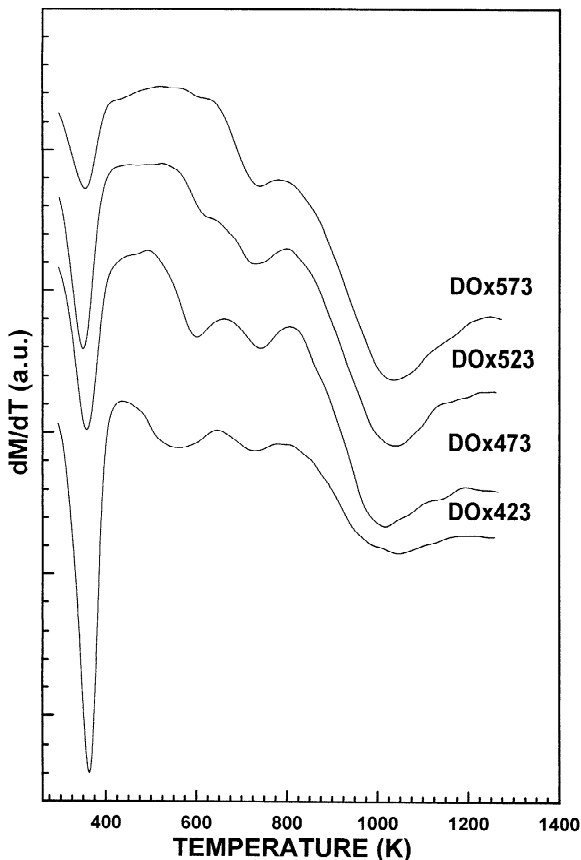


Fig. 2. DTG curves of the evacuated oxidized carbon samples.

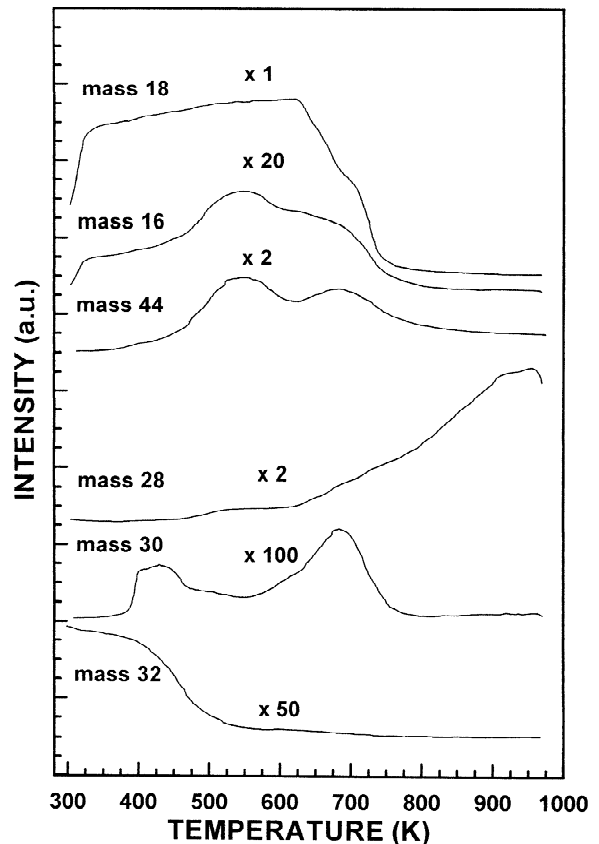


Fig. 3. TPD profiles of the oxidized carbon DOx423.

to be affected by the porous texture of the material, the heating rate and the geometry of the experimental system used [29]. However, some general trends have been established, as summarized in Table 2. Thus, a CO_2 peak results from carboxylic acid at low temperatures, and from anhydrides, lactones or lactols at higher temperatures; carboxylic anhydrides give rise to both a CO and a CO_2 peak; phenols, ethers and carbonyls (and quinones) produce a CO peak. In general, the TPD spectra obtained with carbon materials show composite CO and CO_2 peaks, so it is desirable to try to deconvolute them before the surface composition is estimated [29].

The CO_2 desorption profile of DOx423 given in Fig. 3 is to some extent similar to that obtained for other activated carbons oxidized by HNO_3 [16–19,21–23,28–31], and it is indicative of the occurrence of chemically different complexes and/or the same oxygen complex existing at energetically different sites [18,19,21,25–28,31]. The CO_2 profile shows two broad overlapping peaks located at about 553 and 680 K. As carboxyl groups are thermally less stable than anhydrides or lactones, the peak that appears at 545–590 K is tentatively assigned to carboxyl groups, the second peak to anhydrides, lactones or lactols. According to Otake and Jenkins [21] as well as de la Puente et al.

Table 2
Temperature regions of decomposition of individual carbon surface oxides

Surface group	Desorption gas	Temperature of desorption (K)	References
Carboxylic groups	CO ₂	453–473, 573	5
		575	18
		523	21
		473–523	22
		523–573	23
		550	28
		373–673	29
	520–560	30	
Carboxylic anhydrides	CO, CO ₂	700–775	18
		900	21
		1073–1173	22
		710–930	28
		820	29
		680–720	30
Lactones	CO ₂	623–673	22
		723	23
		463–923	25,26
		710–930	28
		940	29
Peroxides	CO ₂	823–873	22
		870	30
Phenolic and hydroquinonic groups	CO	873–973	22
		823	23
		975, 1110	28
		890–910	29
		900–930	30
Carbonylic and quinonic groups	CO	1073–1173	22
		973–1253	25
		975, 1110	28
		1060–1100	29
Ethers	CO	823	23
		1100	29
Pyrone structures	CO, CO ₂	1273	22
		1173, 1473	38

[23], only single carboxyl groups decompose at 545 K, while adjacent carboxylic and/or phenolic groups are dehydrated to anhydride or lactone groups, which then decompose at about 680 K. The tail after the second peak up to 973 K may suggest the presence of further chemically different lactones and/or the same oxygen complex existing in different environments.

The CO desorption profile of DOx423 is shown in Fig. 3: a very broad peak with the maximum at about 950 K and a small peak at 550 K. At this temperature nitrogen oxide also evolves owing to the decomposition of nitrogen surface groups. The smaller peak on the NO profile at

about 423 K results from traces of adsorbed nitrogen oxide formed during nitric acid treatment. In addition, adsorbed molecular oxygen evolves up to the same temperature.

In all TPD experiments the first product evolved was water, followed by CO₂ and CO. The water desorption profile of sample DOx423 presents an intense broad flattened peak at 620 K with a shoulder at 710 K. The poorly resolved data are due to pore diffusion/readsorption effects [24]. According to Harding et al. [33] these effects may be associated with the high interaction energy of water molecules in clusters around primary adsorption centers. However, in spite of the fact that all connections

and tubing were heated, the physisorption of water on some cold parts of the experimental setup cannot be ruled out. Acidic oxygen complexes forming hydrogen bonds with water act as primary adsorption centers on the carbon surface [33]. Usually, the release of loosely bound water molecules on heating is observed up to 400 K, while the evolution of water H-bonded to oxygen complexes takes place above 450 K [18,19,21,23,24,27–29], in a temperature region where water is also formed as a result of the condensation of adjacent carboxylic or phenolic groups [18,19,21,23,27,28]. Since the intensity of the H₂O profile is considerably higher than that of the CO₂ and CO profiles for DOx423 carbon, one may infer that at least part of the water desorbed above 450 K originates from H-bonded water associated with acidic oxygen complexes [18,21,23,24,27–29].

The simultaneous evolution of a considerable amount of H-bonded water as well as water formed by the condensation of surface groups may lead to strong overlapping of corresponding peaks, which may form a poorly resolved profile, as was observed in our case.

As can be expected, a gradual heating of the oxidized carbon DOx423 in vacuum diminishes the intensity of CO₂ desorption profiles (Fig. 4), especially of the peak centered at ca. 550 K assigned to single carboxyl groups. In addition, a more distinct peak appears at about 400 K, which is ascribed to chemisorbed CO₂ in micropores, formed during annealing. The considerable decrease in the amount of CO₂ evolved is followed by only minor changes in the quantity of CO evolved (Fig. 5).

The significant evolution only of CO₂ below 613 K indicates that mainly single, carboxylic structures are removed or transformed into other structures (e.g. anhydrides, lactones or lactols) during or after gradual heating.

As the annealing temperature gradually increases, so

does the final temperature at which water is evolved completely (Fig. 6). However, after heating at 573 K water disappears at lower temperatures. The disappearance of water at higher temperatures than carbon dioxide for the samples evacuated above 423 K (Figs. 4 and 6) indicates that some water is formed from structures other than carboxyls. It is known [34–37] that during the storage of outgassed samples in ambient air, phenolic and carbonyl groups are formed as a result of oxygen or water being chemisorbed on the outgassed carbon surface. As the samples were handled in air after heating, these additional molecules of desorbed water may be due to the presence of adjacent phenolic groups formed during storage, which are subsequently dehydrated to ether bridges between rings during evacuation or a TPD run [19,23]. These phenolic and carbonyl structures may also be responsible for the transformations of single carboxyl groups during heating. The formation of hydroxyl and carbonyl groups in the vicinity of a carboxyl group leads to the respective formation of lactones or lactols during heating [19,21,23].

As mentioned above, the shapes of the CO₂ and CO profiles suggest the presence of additional peaks. In an attempt to find them, the CO₂ and CO profiles were deconvoluted using a Gaussian multi-peak function, on the assumption of a normal distribution of the desorption activation energies arising from corresponding heterogeneity sites distribution (see Fig. 7). It has recently been demonstrated by Figueiredo et al. [29] and Nevskaiia et al. [30] that such a function can be used quite successfully for deconvoluting the TPD spectra of oxidized microporous carbons.

The presence of several overlapping peaks in the CO₂ and CO spectra is also suggested by the results of intermittent TPD experiments for different carbons oxidized in various ways [31].

The individual peaks of the resolved spectra in Fig. 7 are

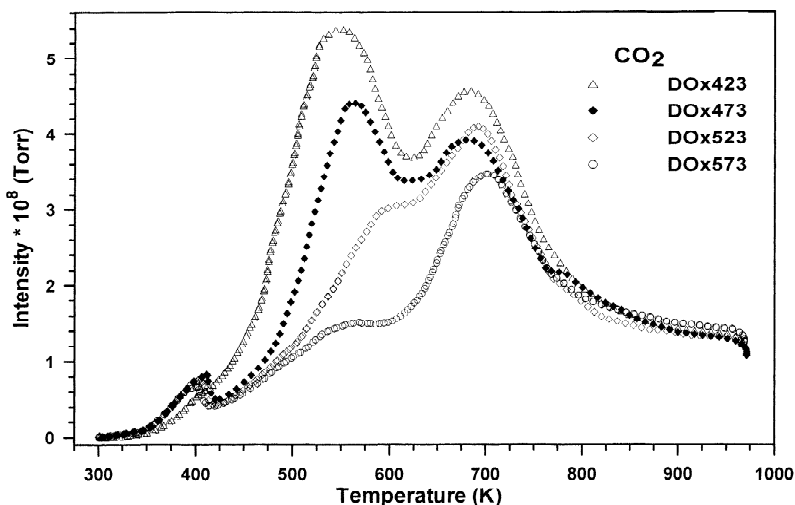


Fig. 4. CO₂ profiles for carbons DOx423, DOx473, DOx523 and DOx573.

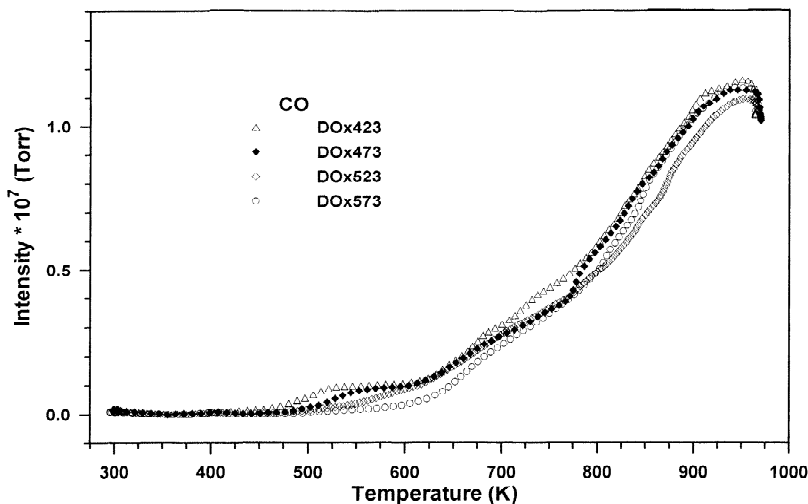


Fig. 5. CO profiles for carbons DOx423, DOx473, DOx523 and DOx573.

situated at temperatures similar to those recorded by other researchers for different oxidized carbons [18,19,21,23,25–32], especially to those obtained by Figueiredo et al. [29]. They found that CO₂ and CO were removed from oxidized carbon in several overlapping peaks at temperatures very close to those we obtained by TPD spectral fitting.

The CO₂ profile of carbon DOx423 can be fitted by five overlapping peaks at 416, 545, 683, 793 and 944 K. The peaks at 790 and 940 K can be assigned to various lactones/lactols or similar structures located in a different environment. It is assumed that the lactones present on the carbon surface exist in the form of *f*-lactones (γ -lactones) or unsaturated *n*-lactones (δ -lactones) [38,39]. For molecular species, the γ -lactones are quite stable, whereas the δ and higher lactones are much less so [38]. The surface

γ -form is also likely to be more stable than the δ and higher lactonic species. Thus, the peaks at 790 and 940 K can be ascribed to the δ - and γ -like lactones, respectively.

The resolved CO₂ spectra for the evacuated samples support suggestions that annealing alters not only the number but also the distribution of functional groups. There is an additional peak at 470–510 K. This peak reaches its maximum value for the DOx523 sample. The appearance of this peak may be due to rearrangements during heating or to exposure to the atmosphere [29,32,37]. For example, Koresh et al. [32] observed such a peak on the CO₂ TPD spectra for fresh carbon fibers after their exposure to humid air. It is postulated that this peak may have resulted from the decomposition of some acid structures such as resorcinol 2-carboxylic acid [28].

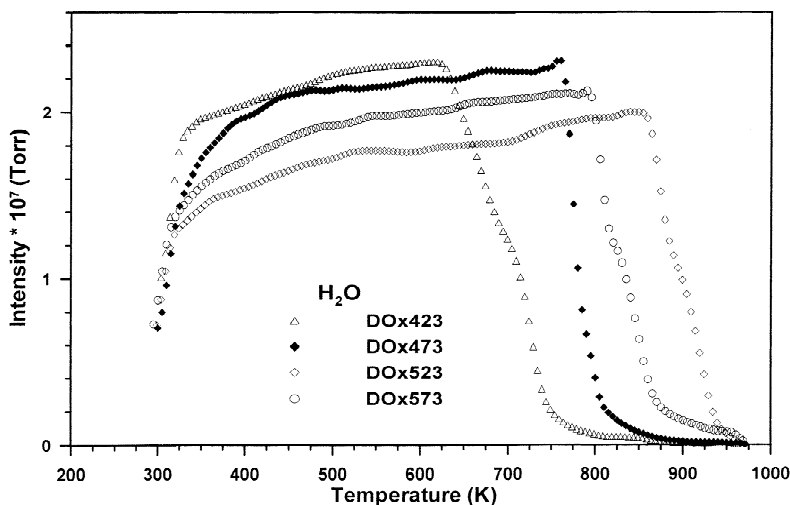


Fig. 6. H₂O profiles for carbons DOx423, DOx473, DOx523 and DOx573.

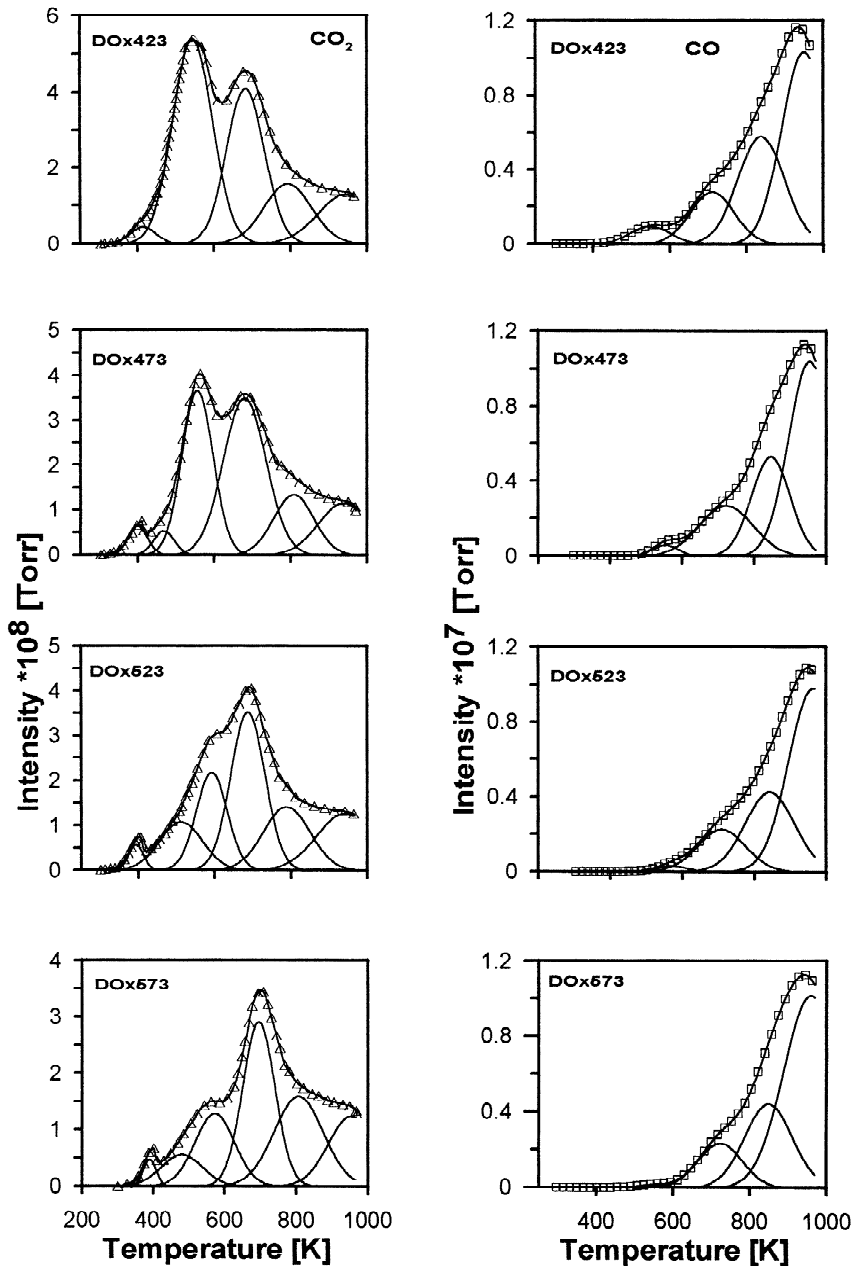


Fig. 7. Deconvoluted CO_2 and CO profiles for the desorbed oxidized carbons.

As mentioned above [34–37], phenolic and carbonyl groups are formed when outgassed samples are stored in ambient air. Thus, the formation of hydroxyl groups in the nearest neighborhood of carboxyl groups may lead to the formation of the above mentioned resorcinol 2-carboxylic acid-like structures [28].

The CO profile for all samples can be fitted by four peaks centered at about 550, 720, 840 and 950 K (Fig. 7). All of these CO desorption temperatures were found earlier

with other carbons oxidized by different methods [25–28]. The different CO peaks are indicative of the existence of chemically different surface complexes or the same complex existing in a different environment.

The amounts of desorbed CO_2 (peak near 690 K) and CO (peak near 710 K) are very similar, because the anhydrides decompose to yield one molecule of CO and one of CO_2 . This then confirms the suggestion that the peak at 690 K on the CO_2 profile and the peak at 710 K on

the CO profile should be assigned to anhydride structures. The appearance of a small CO desorption peak at a low temperature (550 K, may be due to the thermal decomposition of carbonyl groups in α -substituted ketones and aldehydes [27,28].

As mentioned above, the amount of CO evolved by annealed samples is nearly constant. However, the amount of desorbed CO corresponding to the peaks at 840 and 950 K is observed to increase at the expense of the peaks at lower temperatures. It seems that the formation of phenolic and carbonyl groups on the outgassed carbon surface after exposure to ambient air is responsible for this compensatory effect [34–37]. Thus, the peak at 840 K on the resolved CO profiles can be assigned to phenol or hydroquinone groups, but the peak at 950 K to thermally more stable oxides like semiquinones or quinones.

These phenolic and carbonyl structures may also be responsible for transformations of single carboxyl groups during annealing under vacuum. The dehydration of adjacent carboxyl and phenolic or carbonyl groups leads to the respective formation of additional lactones or lactols during heating [19,21,23].

3.3. Acid–base properties

The results of the Boehm titration and the acidities (pHs) of carbon slurries in 0.1 M NaCl (Table 3) show that the carbons demonstrate mainly acidic properties. The outgassing at gradually increasing temperatures enhances to some degree the basic properties of the carbons at the expense of their acidic properties. There is a considerable decrease in the number of groups of strong (carboxylic, $pK_a < 6.37$) and medium acid strength (carboxylic groups and lactones, $6.37 < pK_a < 10.25$) along with a simultaneous distinct increase in the content of neutral groups ($15.27 < pK_a < 20.58$) and, to some extent, of weak acid groups ($10.25 < pK_a < 15.27$) (quinone and phenolic structures, respectively) (Fig. 8). The most pronounced decrease in concentration of strong acid groups occurred in sample DOx423 heated at 573 K.

As we reported earlier [13], there are several inflection points ($pH_0 \sim 2.1$, $pH_1 \sim 4.0$, $pH_2 \sim 8.0$, $pH_3 \sim 11.1$, and $pH_4 \sim 12.6$) on the pH-metric titration curve of the oxidized carbon DOx423 (Fig. 9). The inflection point at $pH \sim 2.1$ corresponds to weak basic sites ($pK_b \sim 1.9$), the other to the

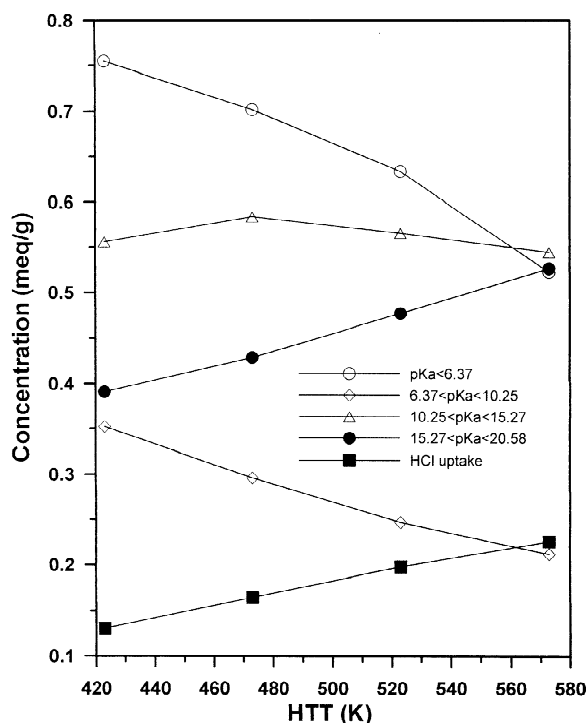


Fig. 8. Effect of gradual heat treatment on the concentration of surface oxides of different acidity.

presence of various acidic surface groups of different acid strength. According to some authors [5–7,37] the basic sites are probably pyrone-like structures incorporated in a carbon matrix. The determined pK_a values of acidic groups are similar to those reported by other authors for various carbons treated with nitric acid [40–44]. It is commonly assumed [42,44] that pK_a values lower than 8 are characteristic of carboxylic groups, while the higher pK_a values are assigned to phenolic groups. However, the acidity of a surface functional group can be strongly influenced by the chemical environment of adjacent groups [41,45–50]. In addition, the carbon backbone may also affect the relevant pK_a values. Thus, the strongly acidic sites ($pK_{a1} \sim 4.0$) can be ascribed to carboxylic groups as well as to phenolic functionalities in the vicinity of quinone structures [51]. It is well known [47–49,51] that hydroxyquinones as well as hydroxynaphthoquinones are acids comparable in strength

Table 3

Acid–base properties of the desorbed oxidized carbons, according to Boehm's method [6]

Oxidized carbon	pH	Uptake (meq/g)				
		NaHCO ₃	Na ₂ CO ₃	NaOH	EtONa	HCl
DOx423	3.08	0.725	1.107	1.663	2.054	0.131
DOx473	3.39	0.702	0.998	1.582	2.011	0.165
DOx523	3.75	0.634	0.881	1.447	1.924	0.198
DOx573	4.02	0.523	0.735	1.280	1.807	0.226

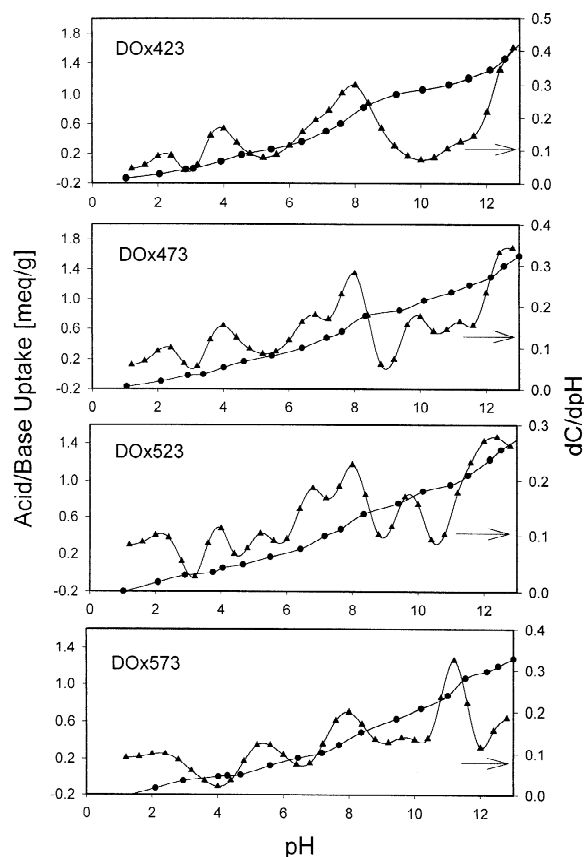


Fig. 9. pH-metric titration curves for the desorbed oxidized carbons.

to carboxylic acids. Their high acidity is usually attributed to the resonance effect in the formed anions (tautomeric effect) [44,46]. The weakly acidic sites ($pK_{a3} \sim 11.1$ and $pK_{a4} \sim 12.6$) are assigned to phenolic groups adjacent to other phenolic or carboxylic groups, respectively [41,42]. The inflection points at $pH \sim 8$ may result from the presence of phenolic groups or weak carboxyl groups formed during the hydrolysis of surface β -lactones or lactols [39].

Evacuation of the DOx423 carbon samples in the 473–573 K temperature range leads to the generation of additional inflection points on the pH-metric titration curves. After heating at 473 K two new ones appear at $pH \sim 6.7$ and $pH \sim 9.8$, while outgassing at 523 K generates another one at $pH \sim 5.3$.

The pH-metric measurements indicate that the oxidized carbon samples (DOx423) gradually evacuated and then exposed to air demonstrate the presence of other structures with a different acidity. These results are consistent with the TPD data. As mentioned above, these new structures may form during the partial desorption or rearrangement of some acidic groups of high or medium strength, as well as during the chemisorption of oxygen or water on an

outgassed carbon surface upon exposure to air at ambient temperature during storage. The inflection points at $pH \sim 5.3$ and $pH \sim 9.8$ may suggest the presence of *p*-hydroxybenzoic acid [45,46] or dihydroxyquinone-like structures [47,49], whereas the inflection point at $pH \sim 6.7$ may indicate the existence of β -lactones [39,46].

3.4. Catalytic properties

As can be expected from our earlier results [14,52], the catalytic tests in the flow mode indicate that the oxidized carbons investigated reveal considerable catalytic activity in the dehydration of 2-methylpropan-2-ol (Fig. 10). The only recorded product was isobutene. Previously, we showed that dehydration of secondary alcohols over oxidized carbons occurs on the outer surface of the carbon with the participation of strongly acidic surface groups—carboxylic structures [14,52]. The high degree of conversion of the bulky molecules of 2-methylpropan-2-ol ($\phi = 0.548$ nm [53]) over the oxidized carbons further supports this suggestion. However, there is a discrepancy between the dehydration activity and the surface acidity (Fig. 11). In spite of the lower acid group content, because of the evacuation of samples at gradually increasing temperatures, their activity increases. The sample desorbed at 523 K demonstrates the maximum activity, which diminishes at a higher outgassing temperature (573 K).

One factor that probably plays an important negative role in the dehydration of alcohol is steric hindrance. Previous results indicate that, at a higher degree of oxidation of a carbon surface, there is a decrease in catalytic activity during dehydration of secondary aliphatic alcohols [14,52]. It seems that the presence of too many

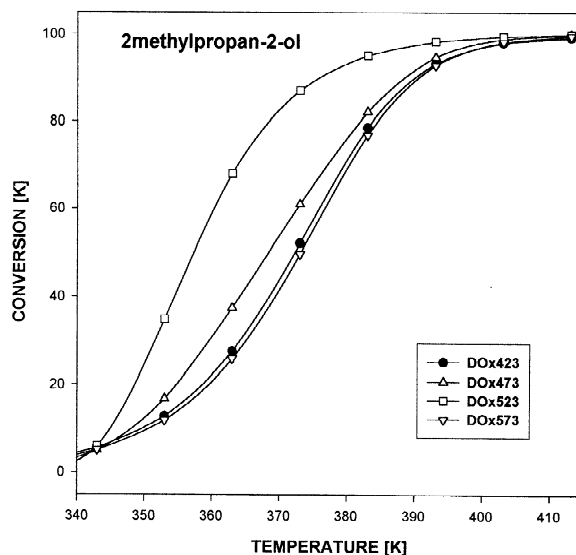


Fig. 10. Catalytic activity of the desorbed oxidized carbons during dehydration of 2-methylpropan-2-ol in continuous flow mode.

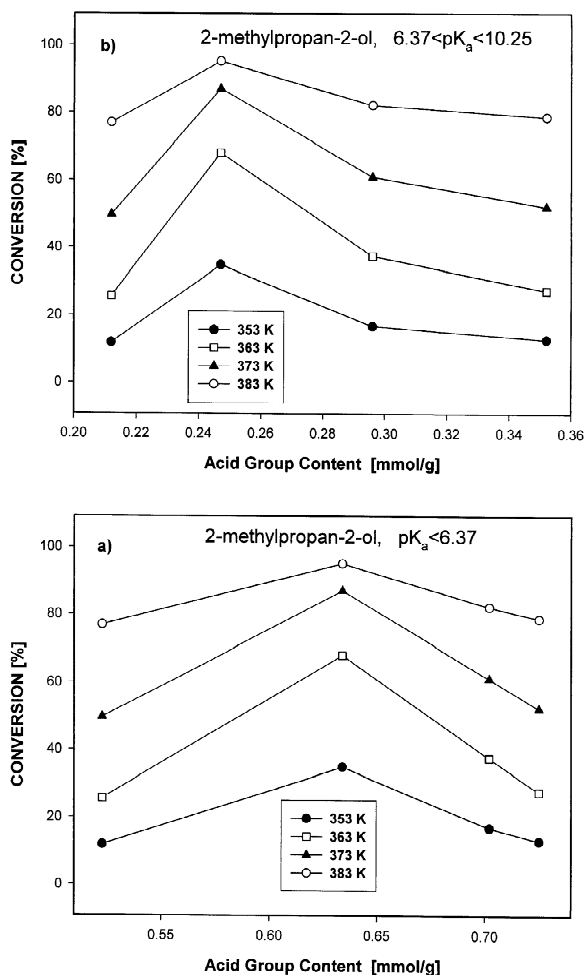


Fig. 11. The effect of surface groups of strong (a) and medium (b) acid strength on catalytic activity of the desorbed oxidized carbons during dehydration of 2-methylpropan-2-ol.

surface groups in the vicinity of catalytically active acid groups—carboxyls—may hinder the interactions between them and the bulky alcohol molecules or even prevent such interactions. It is known that the presence of adjacent polar functional groups leads to the formation of strong intermolecular hydrogen bonds between such groups. The decomposition of some carboxyls, as well as the rearrange-

ment of others, may remove existing steric restrictions to the reaction or facilitate access of the alcohol molecules to the catalytically active acidic groups.

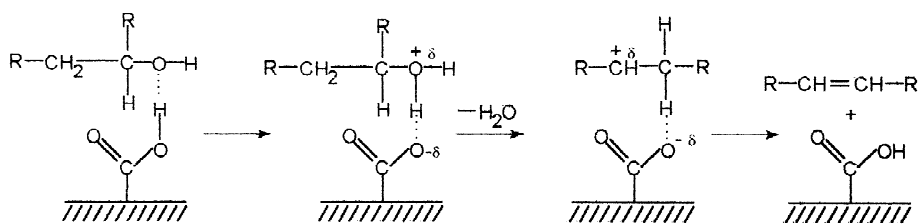
The formation of cyclic structures as a result of some carboxylic and/or hydroxylic groups (e.g. anhydrides and lactones) rearranging during annealing may be another important factor facilitating the dehydration of alcohols. These structures exhibit a high affinity for water [54]. As we reported earlier, the dehydration of secondary alcohols on the carbon catalysts proceeds according to the oxonium mechanism [14,52].

First, the alcohol molecule is protonated, then a water molecule is lost from the oxonium intermediate and an alkene is formed. Thus, the presence of additional cyclic structures facilitates the loss of water and, as a consequence, the dehydration activity may also increase.

4. Conclusions

The results of TPD experiments and the acid–base titrations indicate that outgassing at gradually rising temperatures with subsequent storage in air not only reduces the total number of acidic groups but also changes their distribution. The decomposed surface groups are single carboxylic groups. Some of the carboxylic groups are converted into cyclic structures (anhydrides, lactones or lactols). Other structures are also formed. The oxygen and water chemisorbed at unoccupied reactive sites at the carbon edges after exposure to the air participate in the formation of surface $-C=O$ and/or $-OH$ species [35–37]. The presence of such species in the vicinity of carboxyl or hydroxyl groups not only facilitates the formation of the above mentioned cyclic structures during subsequent heating, but also differentiates the acid strength of the surface groups.

In spite of the decreasing surface acidity, there is an increase in the dehydration activity of the partially evacuated carbon samples. The decomposition of some carboxyls and the rearrangement of the other acidic groups probably removes existing steric restrictions to the dehydration reaction or makes it easier for the alcohol molecules to reach the catalytically active acidic groups. Thus, the lower concentration of strongly acidic groups is compensated by the greater accessibility of the remaining



acidic groups. In addition, the formation during gradual heat treatment of considerable numbers of cyclic structures with a high affinity for water may also facilitate the dehydration.

Dehydration activity is thus controlled not only by the number and strength of acidic groups but also by their accessibility. There is an optimum concentration of acidic groups above which catalytic activity decreases.

References

- [1] Cookson Jr. JT. Adsorption mechanisms: the chemistry of organic adsorption on activated carbon. In: Cheremisinoff PN, Ellerbusch F, editors, Carbon adsorption handbook, Ann Arbor: Ann Arbor Science Publishers Inc, 1978, pp. 241–79.
- [2] Fabish nd TJ, Schleifer DE. Surface chemistry and the carbon black work function. Carbon 1984;22(1):19–38.
- [3] Mattson JS, Mark Jr. HB. Activated Carbon: Surface chemistry and adsorption from solution. New York: Marcel Dekker, 1971.
- [4] Neffe S. Evaluation of the pH-metric method for the determination of acidic groups on the surface of oxidized carbons. Carbon 1987;25:441–3.
- [5] Pun BR. In: Walker Jr. PL, editor, Chemistry and physics of carbon, Surface complexes on carbon, vol. 6, New York: Marcell Dekker, 1970, pp. 249–82.
- [6] Boehm HP. In: Pines H, editor, Advances in catalysis, Chemical identification of surface groups, vol. 16, New York: Academic Press, 1966, pp. 179–274.
- [7] Donnet JB. The chemical reactivity of carbons. Carbon 1968;6:161–76.
- [8] Radovic LR, Rodriguez-Reinoso F. In: Thrower PA, editor, Chemistry and physics of carbon, Carbon materials in catalysis, vol. 25, New York: Marcel Dekker, 1997, pp. 243–358.
- [9] Korver JA. Production of ash-free, active carbon. Chem Weekblad 1950;46:301–2.
- [10] Olivier JP, Conklin WB, Szombathely MV. In: Sing KSV, Unger KK, editors, Characterization of porous solids III, Determination of pore size distribution from density functional theory; A comparison of nitrogen and argon results, vol. 87, Amsterdam: Elsevier, 1994, pp. 81–9.
- [11] Stoeckli F, Huguenin D, Laederach A. On the characterization of carbon blacks by various techniques. Carbon 1994;32(7):1359–62.
- [12] Lomot D, Juszczak W, Pielaszek T, Kaszkur Z, Bakuleva TN, Karpiński Z, Wąsowicz T, Michalik J. Structure and reactivity of supported palladium catalysts. I. Pd/SiO₂ prepared from PdCl₂. New J Chem 1995;19(3):263–73.
- [13] Biniak S, Szymański G, Siedlewski J, Świątkowski A. The characterization of activated carbons with oxygen and nitrogen surface groups. Carbon 1997;35(12):1799–810.
- [14] Szymański GS, Rychlicki G. Importance of oxygen surface groups in catalytic dehydration and dehydrogenation of butan-2-ol promoted by carbon catalysts. Carbon 1991;29(4/5):489–98.
- [15] Pradhan BK, Sandle NK. Effect of different oxidizing agent treatments on the surface properties of activated carbons. Carbon 1999;37:1323–32.
- [16] Suh DJ, Park T-J, Ihm S-K. Effect of surface oxygen groups of carbon supports on the characteristics of Pd/C catalysts. Carbon 1993;31(3):427–35.
- [17] Krishnankutty N, Vannice MA. Effect of pretreatment on surface area, porosity, and adsorption properties of a carbon black. Chem Mater 1995;7:754–63.
- [18] Moreno-Castilla C, Ferro-Garcia MA, Joly JP, Bautista-Toledo I, Carrasco-Martin F, Rivera-Utrilla J. Activated carbon surface modifications by nitric acid, hydrogen peroxide, and ammonium peroxydisulfate treatments. Langmuir 1995;11:4386–93.
- [19] Vinke P, Van der Eijk M, Verbree M, Voskamp AF, Van Bekkum H. Modification of the surfaces of a gas-activated carbon and a chemically activated carbon with nitric acid, hypochlorite, and ammonia. Carbon 1994;32(4):675–86.
- [20] Rivin D. Surface properties of carbon. Rubber Chem Technol 1971;44(2):307–43.
- [21] Otake Y, Jenkins RB. Characterization of oxygen-containing surface complexes created on a microporous carbon by air and nitric acid treatment. Carbon 1993;31(1):109–21.
- [22] Zielke U, Huttinger KJ, Hoffman WP. Surface-oxidized carbon fibres: I. surface structure and chemistry. Carbon 1996;34(8):983–98.
- [23] De la Puente G, Pis JJ, Menendez JA, Grange P. Thermal stability of oxygenated functions in activated carbons. J Anal Appl Pyrolysis 1997;43:125–38.
- [24] Henschke B, Schubert H, Blöcker J, Atamny F, Schlögl R. Mechanistic aspects of the reaction between carbon and oxygen. Thermochim Acta 1994;234:53–83.
- [25] Marchon B, Carrazza J, Heinemann H, Samorjai GA. TPD and XPS studies of O₂, CO₂ and H₂O adsorption on clean polycrystalline graphite. Carbon 1988;26(4):507–14.
- [26] Marchon B, Tysoe WT, Carrazza J, Heinemann H, Samorjai GA. Reactive and kinetic properties of carbon monoxide and carbon dioxide on a graphite surface. J Phys Chem 1988;92:5744–9.
- [27] Moreno-Castilla C, Carrasco-Marin F, Mueden A. The creation of acid carbon surfaces by treatment with (NH₄)₂S₂O₈. Carbon 1997;35(10–11):1619–29.
- [28] Moreno-Castilla C, Carrasco-Marin F, Maldonado-Hodar FJ, Rivera-Utrilla J. Effects of non-oxidant and oxidant acid treatments on the surface properties of an activated carbon with very low ash content. Carbon 1998;36(1–2):145–51.
- [29] Figueiredo JL, Pereira M FR, Freitas MMA, Órfão JJM. Modification of the surface chemistry of activated carbons. Carbon 1999;37:1379–89.
- [30] Nevskaja DM, Santianes A, Muñoz V, Guerrero-Ruiz A. Interaction of aqueous solutions of phenol with commercial activated carbons: an adsorption and kinetic study. Carbon 1999;37(7):1065–74.
- [31] Haydar S, Moreno-Castilla C, Ferro-Garcia MA, Carrasco-Marin F, Rivera-Utrilla J, Perrard A, Joly J-P. Regularities in the temperature-programmed desorption spectra of CO₂ and CO from activated carbons. Carbon 2000;38:1297–308.
- [32] Avraham I, Danon A, Koresh JE. Study of carbon molecular sieve fibres by atmospheric TPD-MS of H₂O, CO and CO₂. J Chem Soc Faraday Trans 1998;94(13):1869–74.
- [33] Harding AW, Foley NJ, Norman PR, Francis DC, Thomas KM. Diffusion barriers in the kinetics of water vapor

- adsorption/desorption on activated carbons. *Langmuir* 1998;14:3858–64.
- [34] Kelemen SR, Freund H, Mims CA. The dependence of water adsorption and reaction on the structure of the carbon substrate. *J Vac Sci Technol A* 1984;2(2):987–90.
- [35] Miura K, Marimoto T. Adsorption sites for water on graphite. 4. Chemisorption of water on graphite at room temperature. *Langmuir* 1988;4:1283–8.
- [36] Menendez JA, Phillips J, Xia B, Radovic LR. On the modification and characterization of chemical surface properties of activated carbon: In the search of carbons with stable basic properties. *Langmuir* 1996;12:4404–10.
- [37] Carrasco-Martin F, Rivera-Utrilla J, Joly J-P, Moreno-Castilla C. Effects of ageing on the oxygen surface complexes of an oxidized activated carbon. *J Chem Faraday Trans* 1996;92:2779–82.
- [38] Barton SS, Evans MIB, Halliop E, MacDonald JAF. Anodic oxidation of porous carbon. *Langmuir* 1997;13:1332–6.
- [39] Garten VA, Weiss DE, Willis JB. A new interpretation of the acidic and basic structures in carbons. *Aust J Chem* 1957;10:295–308.
- [40] Leon y Leon CA, Solar JM, Calemma V, Radovic LR. Evidence for the protonation of basal plane sites on carbon. *Carbon* 1992;30(5):797–811.
- [41] Jagiello J, Bandosz TJ, Schwarz JA. Carbon surface characterization in terms of its acidity constant distribution. *Carbon* 1994;32:1026–8.
- [42] Bandosz TJ, Jagiello J, Contescu C, Schwarz JA. Characterization of the surfaces of activated carbons in terms of their acidity constant distributions. *Carbon* 1993;31(7):1193–202.
- [43] Jagiello J, Bandosz TJ, Putyera K, Schwarz JA. Determination of proton affinity distributions for chemical systems in aqueous environments using a stable numerical solution of the adsorption integral equation. *J Coll Interf Sci* 1995;172:341–6.
- [44] Bandosz TJ, Buczek B, Grzybek T, Jagiello J. The determination of surface changes in active carbons by potentiometric titration and water vapour adsorption. *Fuel* 1997;76(14/15):1409–16.
- [45] Albert A, Serjeant EP. Ionization constants of acids and bases. London: Methuen & Co. Ltd, 1962.
- [46] Weast RC, editor, CRC handbook of chemistry and physics, 57th edition, Cleveland: CRC Press, 1976, pp. D99–D103.
- [47] Schwartzbach G, Suter H. Reduction equilibria, acidity equilibria and absorption spectra of hydroxyquinones. *Helv Chim Acta* 1941;24:617–38.
- [48] Etlinger MG. Hydroxynaphthoquinones. I. Color and acidity. *J Am Chem Soc* 1950;72:3085–90.
- [49] Flaig W, Beutelspacher H, Riemer H, Kaelke E. Effect of substituents on the redox potential of substituted 1,4-benzoquinones. *Justus Liebigs Annalen Chem* 1969;719:96–111.
- [50] Caswell M, Schmir GL. Formation and hydrolysis of lactones and phenolic acids. *J Am Chem Soc* 1980;102:4815–21.
- [51] Dutta PK, Holland RJ. Acidic groups in coal and coal-derived materials. *Fuel* 1983;62:732–7.
- [52] Szymański GS, Rychlicki G. Catalytic conversion of propan-2-ol on carbon catalysts. *Carbon* 1993;31(2):247–57.
- [53] Marcus Y. The properties of solvents. Chichester: Wiley & Sons Ltd, 1998.
- [54] Rodriguez-Reinoso F, Molina-Sabio M, Gonzalez MT. Effect of oxygen surface groups on the immersion enthalpy of activated carbons in liquids of different polarity. *Langmuir* 1997;13:2354–8.