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Thermochimica Acta 345 (2000) 165–172

thermochimica
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Thermogravimetric and adsorption studies of oxidized active carbons by using different probe molecules

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Received 15 June 1999; received in revised form 7 September 1999; accepted 6 October 1999

Abstract

Two coal-based active carbons were treated with hydrogen peroxide, perchloric acid and nitric acid at room temperature as well as with nitric acid at boiling temperature. This treatment, depending on the chemical nature of oxidizing agent, caused noticeable changes in their surface properties and porous structure. Structural changes caused by oxidative treatment of these carbons were estimated on the basis of nitrogen adsorption isotherms. However, the resulting surface changes were evaluated on the basis of water adsorption isotherms as well as thermogravimetric data for water, *n*-butanol and *n*-heptane thermodesorption. It was shown that nitric acid oxidation caused greatest changes in the surface and structural properties of the carbons studied. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Active carbons; Oxidation; Surface properties; Adsorption; Thermodesorption

1. Introduction

Active carbons are widely used as adsorbents, catalysts as well as catalyst supports [1–3]. In addition to the unique pore structure, their surface properties play also an important role. It is known that the carbon surface possesses both acidic and basic groups. For example, it was shown that acidic sites on the carbon surface control some organic reactions [4,5]. The surface activity of active carbons is mostly associated with the oxygen containing complexes such as carboxyl, carbonyl, phenolic and lactone groups.

There are numerous physical and chemical methods, which can be used for modification of active carbons, e.g., heat treatment in an oxidizing gas phase, treatment with oxidizing liquid agents, coating, deposition and chemical bonding [1]. Among these methods, the liquid-phase oxidation is often used because of its simplicity and efficiency. This treatment can change the surface and structural properties of active carbons, and consequently, can affect their sorption and catalytic behavior.

The aim of the present work is to study changes in the surface and structural properties of active carbons treated with aqueous solutions of different oxidizing strength such as hydrogen peroxide, perchloric acid and nitric acid. The structural changes were evaluated on the basis of nitrogen adsorption data, whereas their surface properties were determined from water vapor adsorption isotherms as well as from thermodesorp-

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PII: S0040-6031(99)00375-5

tion data for water, *n*-butanol and *n*-heptane. The latter data were measured by employing high-resolution thermogravimetry.

2. Experimental

2.1. Samples

Two coal-based active carbons AG5 and WD from the Gryfskand Company (Hajnowka, Poland) were studied in the current work. The treatment of these active carbons was carried out at room temperature with solutions of hydrogen peroxide (30%), perchloric acid (30%) or nitric acid (68%) for 3 h, respectively. The abbreviations for oxidized carbons consist of the carbon code (AG5 or WD) and the oxidizing agent code: O for hydrogen peroxide, N for nitric acid and Cl for perchloric acid. The AG5 and WD carbons were also oxidized with 68% nitric acid solution at its boiling temperature for 3 h and these intensively treated samples are denoted in the text as AG5-N* and WD-N*, respectively. All samples were washed with distilled water until oxidizing agent was removed and then dried at 110°C for 3 h.

2.2. Thermogravimetric measurements

These measurements were performed in nitrogen atmosphere using a model TGA 2950 high-resolution thermogravimetric analyzer from the TA Instruments, Inc. (New Castle, DE). The maximum heating rate was set to 5°C/min. The resolution and sensitivity parameters were 4 and 6, respectively. Prior thermogravimetric (TGA) measurements each sample was degassed at 110°C under vacuum for 3 h. The weight change of the blank samples as well as those exposed for 1.5 h to the saturated vapors of water, *n*-butanol and *n*-heptane were measured. The TGA results were analyzed in order to obtain information about changes in the surface properties of active carbons caused by oxidation. In addition, the ash content of the samples was measured on the same instrument in air at 800°C until the constant weight was observed.

2.3. Adsorption isotherms

Adsorption measurements were carried out at −196°C by using a model ASAP 2010 volumetric adsorption analyzer from Micromeritics, (Norcross, GA). This instrument allows accurate measurements of adsorption data starting from very low relative pressure (10^{-7}). Prior adsorption measurements all samples were degassed at 110°C under vacuum for 3 h. The obtained isotherms were used to analyze the pore structure of the samples under study. The total pore volume of the samples was calculated from the amount adsorbed at relative pressure of 0.995 and the BET surface area was evaluated at the relative pressure range from 0.04 to 0.14 [6,7]. The micropore volume and mesopore surface area was obtained by the α_s-plot method using the BP280 carbon black as the reference material [8]. The intercept and slope of the α_s-plot were used to calculate the micropore volume and mesopore surface area, respectively. Details can be found elsewhere [9].

Adsorption isotherms of water vapor were measured on the degassed carbon samples at 25°C by a volumetric method of liquid microburettes [2]. According to this method the amount adsorbed is determined from the lowering of the liquid adsorbate meniscus in a calibrated microburette with a correction for the dead volume of the apparatus. The liquid microburette method is suitable to measure adsorption for adsorbates, the saturation vapor pressure of which is not to small at the temperature of measurement, e.g., water, ethanol, benzene. A detailed description of this method is given elsewhere [2].

3. Results and discussion

3.1. Nitrogen adsorption studies

The oxidation treatment alters not only the surface properties of the carbons studied but also their pore structures [10,11]. These changes were first characterized on the basis of nitrogen adsorption isotherms. The pore structure parameters were calculated from these isotherms and are shown in Table 1. Nitrogen adsorption isotherms for unmodified and modified samples of the AG5 carbons are presented in Fig. 1. As can be seen, the amount adsorbed on the AG5-Cl and AG5-N carbons is greater than that measured on the corresponding unmodified sample. It means that the treatment with perchloric acid and nitric acid altered significantly the overall porosity of AG5. However,

Table 1
Pore structure parameters and the percentage[a] of thermodesorbed adsorbates from the unmodified and oxidized carbons studied

Samples	S_{BET} (m^2/g)	S_{meso} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	Ash (%)	Water (%)	*n*-butanol (%)	*n*-heptane (%)
WD	1194	124	0.65	0.48	20.9	31	24	24
WD-O	1018	92	0.56	0.44	10.7	27	26	21
WD-CL	991	89	0.54	0.43	2.0	25	23	18
WD-N	958	70	0.51	0.42	2.6	32	17	20
WD-N*	459	38	0.25	0.20	3.4	22	13	10
AG5	880	66	0.48	0.39	16.9	24	23	19
AG5-O	922	80	0.51	0.40	14.4	27	17	21
AG5-CL	1006	86	0.55	0.44	4.8	28	26	21
AG5-N*	993	71	0.54	0.44	7.3	30	11	21
AG5-N[a]	497	49	0.28	0.21	5.8	22	13	13

[a] A correction for the mass change of the blank samples was used.

this effect was negligible for the samples oxidized with hydrogen peroxide. All treated samples except AG5-N* showed higher BET surface areas and total pore volumes. A comparison of nitrogen adsorption isotherms indicates that chemical modification with concentrated nitric acid changed significantly the pore structure of the AG5 active carbon. The influence of mineral matter should be also noted. The treatment of active carbons by oxidizing solutions may cause the dissolution of some inorganic species that may block the entrance of micropores. The original AG5 carbon contains about 16.9% ash while after modification this value decreased to ca. 14.4% for AG5-O, 4.8% for AG5-Cl, 7.3% for AG5-N, and 5.8% for AG5-N* (see Table 1).

Nitrogen adsorption isotherms for unmodified and modified samples of the WD series are shown in Fig. 2. The influence of oxidizing treatment is different for this carbon than for AG5. The oxidation at room temperature caused a decrease in the amount adsorbed at high relative pressures, whereas a significant increase in the amount adsorbed at low pressures was observed for the samples oxidized with nitric acid. Both the BET surface area and total pore volume decreased showing that the porous structure of

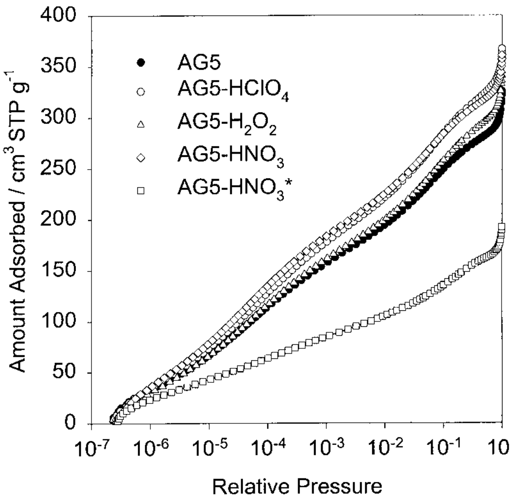

Fig. 1. Nitrogen adsorption isotherms for unmodified and oxidized AG5 carbons.

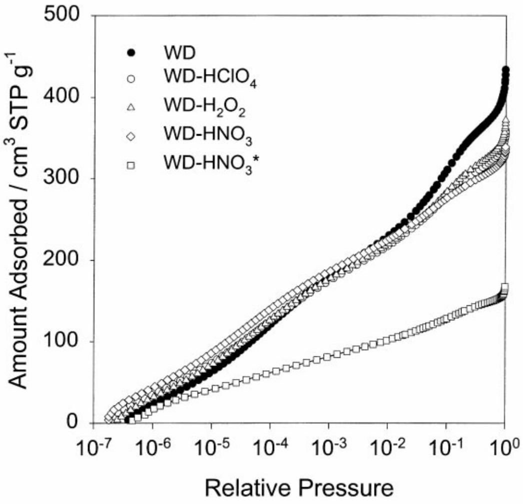

Fig. 2. Nitrogen adsorption isotherms for unmodified and oxidized WD carbons.

WD is more easily destroyed during oxidation treatment than in the case of AG5. If the mineral matter content is considered, this decrease should be more pronounced.

For intensively treated samples of AG5-N* and WD-N*, the BET surface area and total pore volume decreased significantly. This can arise from drastic treatment conditions, which caused not only dissolution of the mineral matter but also degradation of the pore structure, which resulted in widening micropores and consequently led to reduction of the surface area and total pore volume.

3.2. TGA measurements for the carbons studied

The oxidation of active carbons with concentrated acids caused dissolution of some inorganic impurities, destruction and/or formation of some pores as well as creation of oxygen complexes on the carbon surface. Thus, the TGA curves recorded in nitrogen for unmodified and oxidized carbons differ significantly (see Figs. 3 and 4). Especially, for intensively oxidized samples, AG5-N* and WD-N*, the TGA curves differ significantly from those for the remaining samples. They exhibit a gradual and pronounced mass loss until 1000°C, which indicates that strong oxidation changed not only the surface properties but also destroyed the carbon structure making its decomposition much easier. An intensive oxidation creates much more surface oxygen groups, which during heating evolve CO_2 and CO, thus increase the mass loss of the sample [12,13]. The weakly oxidized samples are much more stable in comparison to WD-N* and AG-5*.

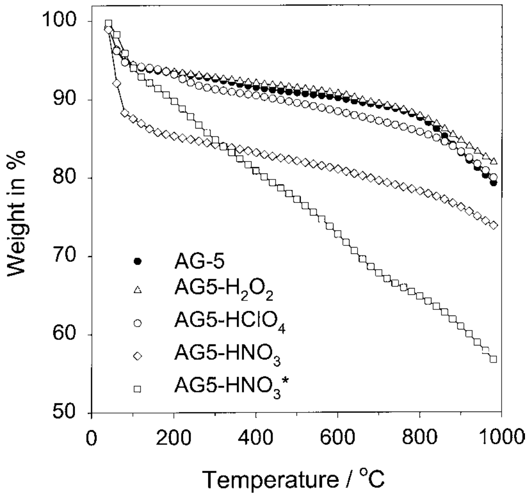

Fig. 3. TGA curves measured in nitrogen atmosphere for unmodified and oxidized AG5 carbons without initial degassing.

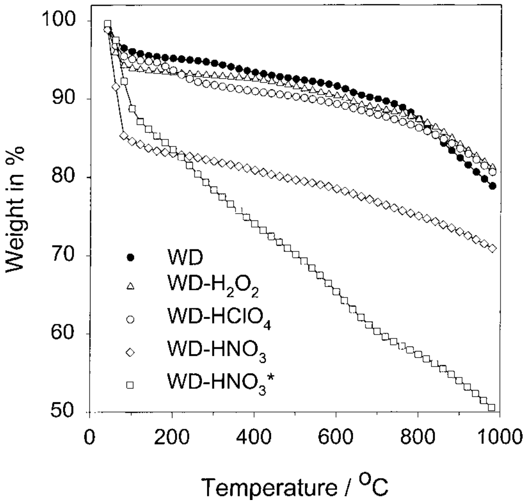

Fig. 4. TGA curves measured measured in nitrogen atmosphere for unmodified and oxidized WD carbons without initial degassing.

For the samples oxidized at room temperature, oxidation changed slightly their TGA curves as shown in Figs. 3 and 4. The nitric acid oxidation is an efficient way to modify the carbon surface and to increase its hydrophilicity so that the TGA curves show greater mass loss below 150°C, which is related to thermodesorption of physically adsorbed water. Shown in Fig. 5 are the DTG curves for the AG5 carbons. Analogous TGA curves were obtained for the WD samples. As can be seen the oxidation generated an extra peak at about 120°C for the samples treated with nitric acid and an extra peak at 220°C for those treated with perchloric acid. This can be attributed to the decomposition of some functional groups. The TGA curves for the AG5-O and WD-O samples treated with hydrogen peroxide are quite similar to those for unmodified carbons because of the weak function of this oxidizing agent.

3.3. Water vapor adsorption studies

Adsorption isotherms of water vapor on unmodified and oxidized carbons were measured in order to show

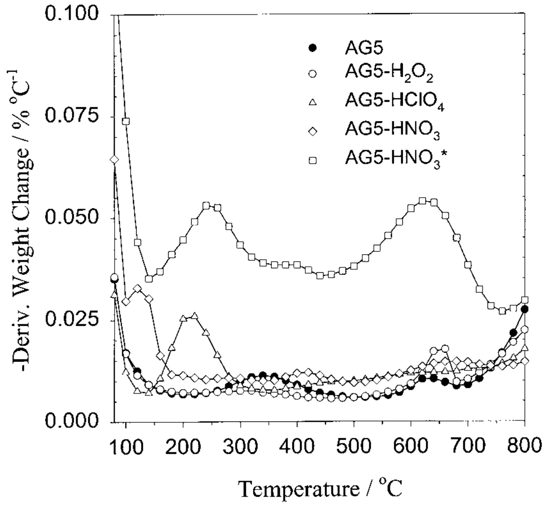

Fig. 5. DTG curves corresponding to those showed in Fig. 3.

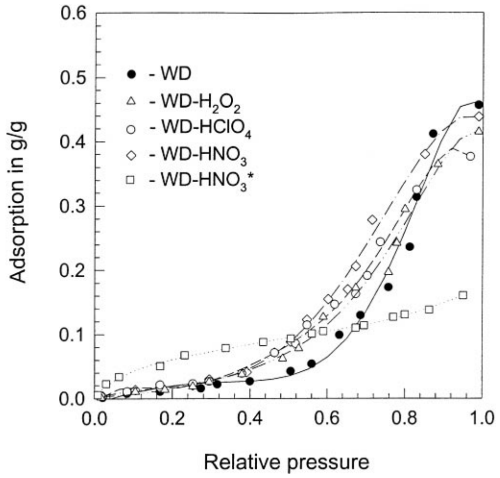

Fig. 7. Water adsorption isotherms for unmodified and modified WD carbons.

the change in their surface properties due to oxidation. These isotherms are shown in Fig. 6 for the AG-5 carbons and Fig. 7 for the WD carbons. As can be seen in these figures, acidic treatment at ambient temperature increased slightly adsorption at low relative pressures. This indicates that the oxidation truly altered the surface properties of the carbons studied, although their hydrophilicity did not change much because of mild oxidation conditions.

However, water adsorption isotherms changed significantly for the samples oxidized with nitric acid at boiling temperature. A significant increase in the water uptake is observed at low relative pressures ($p/p_0 < 0.5$) even though their porosity was partially destroyed as manifested by a substantial decrease in the total pore volume. Nevertheless, water adsorption at low relative pressures is very small for unmodified samples due to small amount of oxygen groups, which act as primary active sites in this process. This means that during strong oxidation a great amount of oxygen groups was created. In the range of high relative pressures the volume filling occurs and in this case the pore volume is a dominating factor. Thus, the adsorption uptake for unmodified samples was greater than that for strongly oxidized ones because the porosity of latter was partially destroyed due to acidic treatment at high temperatures.

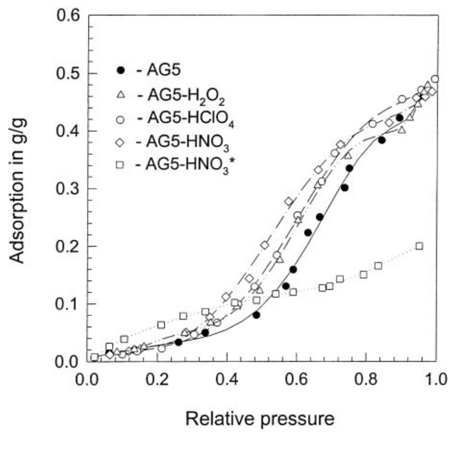

Fig. 6. Water adsorption isotherms for unmodified and modified AG5 carbons.

3.4. Thermodesorption of water, n-butanol and n-heptane

Acidic oxidation of active carbons changed not only their surface properties but also their pore structure (see Figs. 1 and 2; Table 1). Nitrogen adsorption study of unmodified and modified active carbons provided information about changes in the structural properties of oxidized carbons. However, nitrogen is not very good probe molecule for monitoring surface changes. It was shown previously [14–19] that thermodesorption of water, *n*-butanol and *n*-heptane can be used to

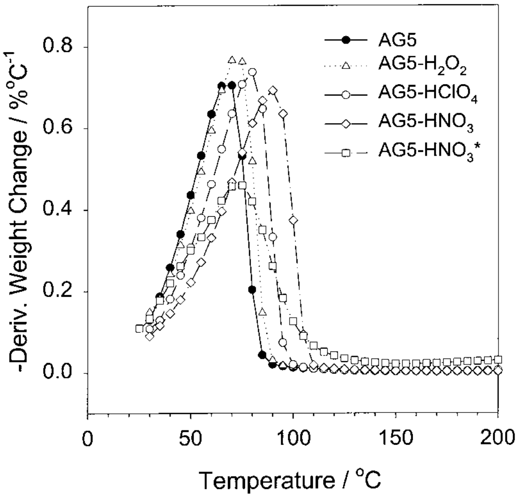

Fig. 8. The DTG curves for thermodesorption of water from unmodified and modified AG5 carbons.

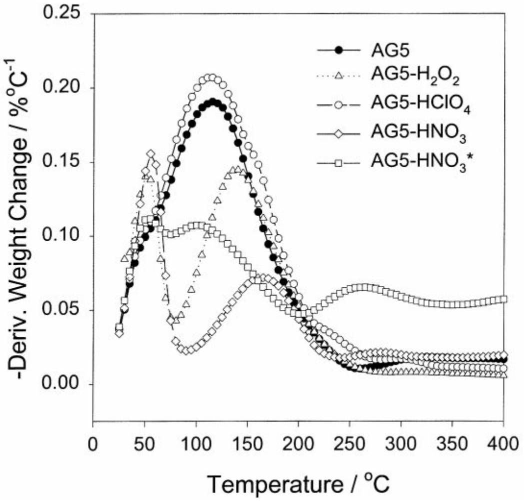

Fig. 9. The DTG curves for thermodesorption of *n*-butanol from unmodified and modified AG5 carbons.

monitor changes in the surface properties of active carbons. Therefore, these probe molecules were used in the current work to study the oxidized carbons. Shown in Fig. 8 is the DTG curve for water thermodesorption from the AG5 samples. Since water molecules are first adsorbed on surface oxygen groups via hydrogen bonding, and next these surface complexes are seeds for formation of water clusters, the TGA curves for the samples studied reflect this mechanism. The amount of water molecules interacting with the carbon surface is greater for strongly oxidized samples. As can be seen in Fig. 8, the temperature at which the maximums desorption rate appears to change gradually from AG5, AG5-O and AG5-Cl to AG5-N, excluding AG5-N*, the structure of which was partially destroyed due to aggressive oxidation with concentrated nitric acid. Also, the temperature required for complete thermodesorption increases in the same sequence. This means that the binding energy between active sites and adsorbed molecules increases in the same order, which is related to the strength of the oxidizing agent used.

Unlike water molecules, *n*-butanol can interact with both polar and unpolar regions of the carbon surface. The TGA curves for thermodesorption of *n*-butanol from the AG5 samples oxidized with nitric acid and hydrogen peroxide differ substantially for the remaining samples (see Fig. 9). These curves exhibit two distinct desorption peaks: one of them located about 50°C can be attributed to evaporation of the excess of *n*-butanol, and the second peak at higher temperature (ca. 150°C for AG5-O and 170°C for AG5-N) can be related to thermodesorption of this adsorbate. The observed shift of the second peak can be related to the greater amount of oxygen groups on the AG5-N surface, which was proved by water adsorption and thermodesorption. However, the concentration of surface oxygen groups is not only the factor that controls adsorption of *n*-butanol, which depends also on the hydrophobicity of the carbon surface. Due to hydrophobic interactions the main DTG peaks for *n*-butanol are shifted in direction of higher temperatures, i.e., 120–170°C, in comparison to the corresponding peaks for water thermodesorption, which are located below 100°C. Thus, a detailed interpretation of the DTG profiles for *n*-butanol is more difficult than for water. For instance, the DTG profiles for thermodesorption of *n*-butanol from the AG5 and AG5-Cl carbons exhibit one peak only around 120°C, which has similar shape for both samples except a small shoulder in the case of AG5-Cl. However, the DTG peaks for the strongly oxidized carbon, AG5-N*, are small and reflect its low adsorption capacity with respect to *n*-butanol because of a significant degradation of the

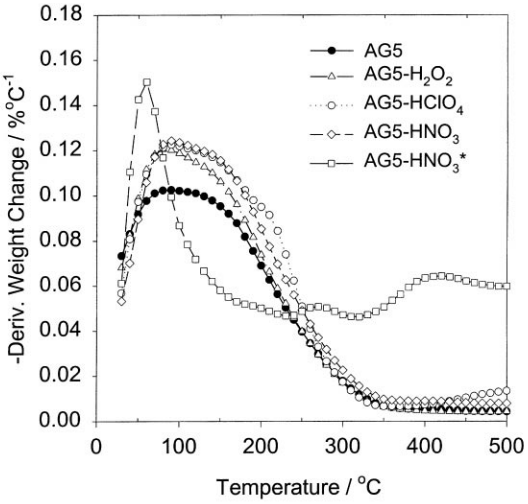

Fig. 10. The DTG curves for thermodesorption of *n*-heptane from unmodified and modified AG5 carbons.

pore structure of this sample during intensive oxidation process.

Shown in Fig. 10 are thermodesorption data for *n*-hetpane from the AG5 carbons. The DTG curves for the samples modified with different oxidants are quite similar and they end at the same temperature indicating that molecules of *n*-heptane interact with the carbon surface mainly via dispersive forces and, thus, do not probe effectively the surface changes. Microporosity seems to be a main factor that affects adsorption of *n*-heptane. The oxidizing treatment at room temperature increased the micropore volume of the AG-5 carbons studied and, consequently, caused an increase in the amount adsorbed of *n*-heptane. Similar results were obtained for the WD series but in this case the adsorption capacity decreased because of opposite changes in microporosity of these samples.

In comparison to the AG5 samples, the observed changes in the TGA curves for water, *n*-butanol and *n*-heptane thermodesorption from the WD carbons are smaller. The WD, WD-Cl, WD-N and WD-O samples exhibit very similar thermodesorption behavior for water. The maximum desorption rate occurred at similar temperature and thermodesorption was completed at about 105°C. Only the DTG profile for intensively treated sample, WD-N*, was significantly different indicating a greater amount of surface oxygen groups, which are able to interact with water molecules via hydrogen bonding.

The thermodesorption of *n*-butanol from the WD-N sample is analogous as in the case of AG5-N. However, the treatment of the WD carbon with perchloric acid did not change much its thermodesorption profile. It seems that perchloric acid was not efficient oxidizing agent for this carbon.

4. Conclusions

Two coal-based active carbons were oxidized with different oxidizing agents and nitrogen adsorption and thermogravimetry were used to investigate the changes in their pore structure and surface properties. It was shown that the surface properties of oxidized carbons can be studied by using high resolution thermogravimetry to measure thermodesorption of molecules of different polarity such as water, *n*-butanol and *n*-heptane. Also, it was found that the liquid-phase oxidation can change the pore parameters, especially for the carbons oxidized with nitric acid at higher temperatures.

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