STABILITY TOWARDS HEATING AND OUTGASSING OF ACTIVATED CARBON OXIDIZED IN THE LIQUID PHASE

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ABSTRACT

The stability of the surface state of activated carbon oxidized in the liquid phase is checked under conditions of heating and outgassing. The oxidation was performed using aqueous solutions of H_2O_2, O_3, ClO_2, H_2SO_4, HNO_3, $HClO_4$, KIO_4 and $KMnO_4$. Also, the pH was varied in the case of H_2O_2, KIO_4 and $KMnO_4$, and the concentration was varied for HNO_3, KIO_4 and $KMnO_4$. The oxidizing agent strongly influences the thermal stability of the surface oxides that are removed by heat treatment between 35 and 800°C. It is generally higher for the substances with acidic properties; in particular HNO_3, but only when a concentrated solution is used in the oxidation of carbon. The release of surface oxides takes place to a larger extent for O_3 and HNO_3, although for the latter substance it depends on the concentration of the solution. In contrast to these oxidizing agents, thermally unstable oxygen complexes are not formed with ClO_2. In the treatment with a saturated solution of $KMnO_4$, the formation of insoluble substances which decompose on heating appears probable. The thermal stability and the removal of surface oxides or reaction products increases at acidic pH values; this is affected by the concentration of HNO_3 or $KMnO_4$ but not by the concentration of KIO_4. The results do not always agree with those obtained when the samples are outgassed under vacuum. Thus, discrepancies are observed in the influence of pH and concentration on the stability.

INTRODUCTION

Activated carbon (AC) possesses adsorbent and catalytic properties which are the basis of most of its laboratory uses and industrial applications. In the processes which take place when the material is used, a property with an outstanding role is the chemical nature of its surface. In particular, the surface oxides, named oxygen functional groups and complexes, may affect the adsorption of organics and inorganics from solution by modifying the capacity, mechanism and rate [1], and even the adsorbate composition [2]. They also influence the adsorption mechanism of a number of catalysed reactions such as the desulphurization of industrial gases in fuel-processing

technology [2]. These facts explain the growing interest in the study of the formation and properties of the oxygen surface complexes. They are frequently formed by oxidation of AC with oxidizing agents either in the gaseous phase (air, carbon dioxide and steam) or in solution ($KMnO_4$, HNO_3, Cl_2, etc.) [1].

Study of the stability of the surface state of oxidized AC allows us to obtain information on the extent to which the surface oxides are formed and on the specificity of the oxidizing agent–carbon interactions. This information is essential for the selective formation of oxygen surface complexes. Moreover, the thermal stability may be an important property for the regeneration of AC and in applications of the material which involve heat treatment. So far, in most studies carried out on the subject, the composition of the gases evolved during the heat treatment of carbons was determined [3]. It was frequently used to gain information on the type of surface oxides arising from particular treatments [1]. However, comparative studies on the stability of the surface state of AC upon its oxidation in liquid phase using a variety of oxidizing agents have not been carried out. To fill this gap, the present work is devoted to the determination of the influence of such variables as the solute (H_2O_2, O_3, ClO_2, H_2SO_4, HNO_3, $HClO_4$, KIO_4 and $KMnO_4$), the pH and concentration of the solution.

EXPERIMENTAL

About 4 g of AC, which had been previously heat-treated at 950°C for 5 h in an N_2 atmosphere, were mixed with 50 ml of an aqueous solution of varying solute, pH or concentration. In the case of O_3, an O_2–O_3 stream was made to pass in upward direction through the mixture of carbon and water

TABLE 1

Codes, pH and concentration of solutions used in the oxidation of AC

Codes [a]	pH	Concentration	Codes [a]	pH	Concentration
AC			$HClO_4$–S	S	2.25 M
H_2O_2–S	S	30 vol.%	D-KIO_4–S	S	10^{-2} M
H_2O_2–A	A	30 vol.%	C-KIO_4–S	S	Saturated
H_2O_2–B	B	30 vol.%	C-KIO_4–A	A	Saturated
O_3–S	S	2×10^{-4} M	C-KIO_4–B	B	Saturated
ClO_2–S	S	10^{-2} M	D-$KMnO_4$–S	S	10^{-2} M
H_2SO_4–A	A	1.6×10^{-2} M	C-$KMnO_4$–S	S	Saturated
D-HNO_3–S	S	10^{-2} M	C-$KMnO_4$–A	A	Saturated
C-HNO_3–S	S	14.37 M	C-$KMnO_4$–B	B	Saturated

[a] D and C represent dilute and concentrated solutions; S, A and B mean pH = solution pH, 2.5 and 11.5, respectively. (The pH was varied by adding a few drops of a concentrated solution of H_2SO_4 or NH_4OH to the solution of oxidizing agent.)

contained in a glass vessel. Carbon and a solution of the oxidizing agent remained in contact for 5 h at 25°C, and generally under a continuous agitation of 70 oscillations min^{-1}. The phases were then separated by filtration, and the solid was either thoroughly washed with distilled water for 1 month and then oven-dried at 110°C for 24 h or only dried. Sample codes and the pH values and concentrations of the solutions are shown in Table 1.

The stability of the surface state which resulted from the oxidation of carbon was checked under heating and outgassing conditions. Using a Mettler TA-3000 thermogravimetric unit, around 20 mg of sample were heated from 35 to 800°C in an N_2 dynamic atmosphere (200 cm^3 min^{-1}). The resulting DTG curves will allow us to compare the effects of weight loss associated with the heat treatment. After oven-drying at 110°C for 24 h, about 10 mg of sample were outgassed at 150°C for 12 h, at a pressure of 133×10^{-6} Pa, using a conventional gravimetric apparatus for gas adsorption. The mass loss will be used in this case to obtain information on the stability.

RESULTS AND DISCUSSION

Thermal stability

The oxidation of AC with solutes in aqueous solution gives rise to the formation of a surface state, the thermal stability of which depends on variables such as the oxidizing agent, pH and concentration of the solution. The substance used in the treatment of carbon influences not only the surface composition of the resulting material, which will be the determinant factor of the stability, but also the extent to which the oxidation process takes place. The product with a larger oxidizing power, i.e. with a higher positive value of the standard reduction potential, will promote the surface to a higher oxidation state and will diversify the interactions with carbon to a greater extent, as it is capable of acting on positions of the substrate which show less tendency to oxidize.

Figure 1 shows the DTG curves for AC and the samples prepared by oxidation of carbon with aqueous solutions of H_2SO_4, HNO_3 and $HClO_4$. All show a maximum weight loss centred between 40 and 50°C, which is associated with the release of water on heating. At temperatures above 100°C, the plot shows one peak for H_2SO_4–A and $HClO_4$–S, and two peaks for C–HNO_3–S. This indicates that in the treatment of carbon with the solution of HNO_3 a larger number of different surface groups which are thermally unstable between 35 and 800°C is formed. According to the location of peaks along the x-axis, the stability order for the surface state is $HNO_3 > H_2SO_4 > HClO_4$. In relation to the extent of formation of the surface groups, however, the variation sequence is $HNO_3 > HClO_4 > H_2SO_4$.
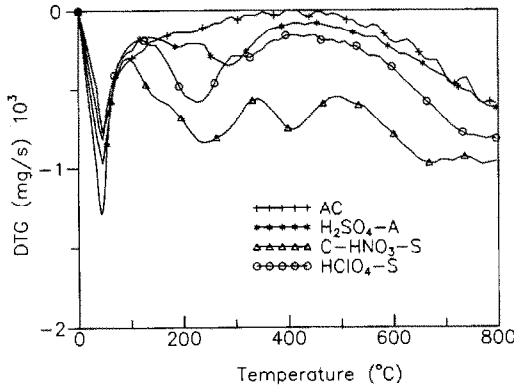
Fig. 1. DTG curves for AC and samples prepared by oxidation of AC with solutions of H_2SO_4, HNO_3 and $HClO_4$.

This behaviour is consistent with the moderate oxidizing power of H_2SO_4 [4] and $HClO_4$ [5] in the cold compared with HNO_3, together with the concentration of the solutions of H_2SO_4, HNO_3 and $HClO_4$.

Figure 2 shows the DTG curves for the samples obtained by treating carbon with solutions of H_2O_2, O_3, ClO_2 and KIO_4 without modifying the pH, and Fig. 3 shows the corresponding curve for the sample prepared with $KMnO_4$. The peak located between 215 and 220 °C in the plots of H_2O_2–S, O_3–S and C-KIO_4–S denotes the formation of the same type of surface group when the oxidation is performed with H_2O_2, O_3 and KIO_4. This peak is somewhat more marked for O_3–S, despite the much lower concentration of the solution used in the case of O_3. In addition, the O_3–S curve shows a highly pronounced maximum at 120 °C, which is absent from the plots of H_2O_2–S and C-KIO_4–S. Therefore, the oxidation of carbon with O_3 is a more sensitive and less specific process than with H_2O_2 or KIO_4. This
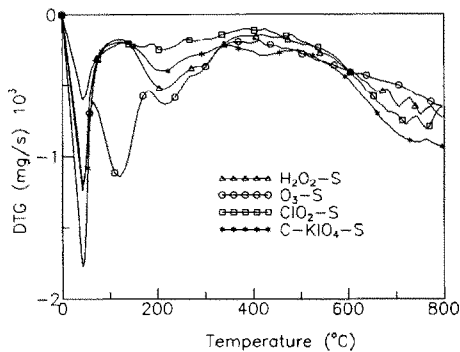

Fig. 2. DTG curves for samples prepared by oxidation of AC with solutions of H_2O_2, O_3, ClO_2 and KIO_4.
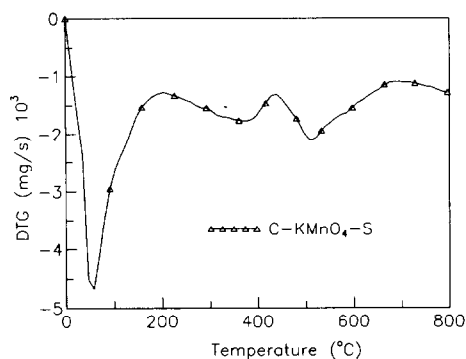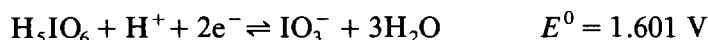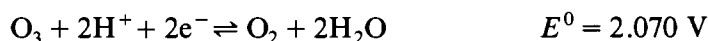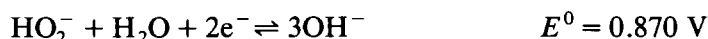
Fig. 3. DTG curve for the sample prepared by oxidation of AC with the saturated solution of $KMnO_4$ at the solution pH.

behaviour is compatible with the oxidizing power of these substances under conditions of identical pH and solution concentration, as indicated by their standard reduction potentials in acid and alkaline solutions: acid solution, $a_{H^+} = 1$
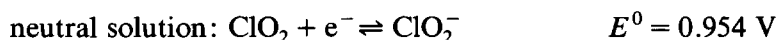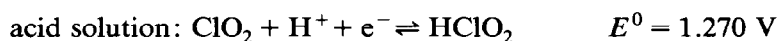
$$O_3 + 2H^+ + 2e^- \rightleftharpoons O_2 + 2H_2O \qquad E^0 = 2.070 \text{ V}$$

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^0 = 1.776 \text{ V}$$

$$H_5IO_6 + H^+ + 2e^- \rightleftharpoons IO_3^- + 3H_2O \qquad E^0 = 1.601 \text{ V}$$

basic solution, $a_{OH^-} = 1$

$$O_3 + 2H_2O + 2e^- \rightleftharpoons O_2 + 2OH^- \qquad E^0 = 1.240 \text{ V}$$

$$HO_2^- + H_2O + 2e^- \rightleftharpoons 3OH^- \qquad E^0 = 0.870 \text{ V}$$

$$H_3IO_6^{-2} + 2e^- \rightleftharpoons IO_3^- + 3OH^- \qquad E^0 = 0.700 \text{ V}$$

The smaller weight loss that results for $C-KIO_4-S$ in comparison with H_2O_2-S suggests that the formation of surface oxides is at least in part conditioned by the size of the oxidizing species in solution. It might take place through the control of accessibility to the carbon surface.

In contrast especially to O_3, the treatment of carbon with the solution of ClO_2 does not seem to affect the surface of the material appreciably, as the corresponding plot for ClO_2-S does not show the presence of well-defined peaks in the temperature interval between 35 and $800\,°C$. This was an unexpected result because chlorine dioxide is a strong oxidizing agent [5], which takes part in redox processes according to the following reaction schemes:

acid solution: $ClO_2 + H^+ + e^- \rightleftharpoons HClO_2 \qquad E^0 = 1.270 \text{ V}$

neutral solution: $ClO_2 + e^- \rightleftharpoons ClO_2^- \qquad E^0 = 0.954 \text{ V}$

Probably, illumination of the neutral solution of ClO_2 induces its rapid photodecomposition to a mixture of $HClO_3$ and HCl [5,6] which has a much

weaker oxidizing power than ClO_2, mostly in neutral and basic solutions, as shown, for instance, by the low value of the standard potential for the reduction reaction of $HClO_3$ at a basic pH:

$$ClO_3^- + H_2O + 2e^- \rightleftharpoons ClO_2^- + 2OH^- \qquad E^0 = 0.350 \text{ V}$$
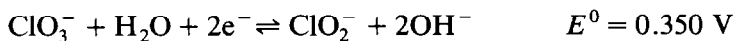
C-$KMnO_4$-S behaves thermally in a particular manner. Its DTG curve exhibits two peaks, situated at higher temperatures than for the other samples. It follows then that on treatment of carbon with the $KMnO_4$ solution either two different types of surface groups are formed, which are thermally more stable, or the corresponding weight losses are the result of decomposition of products formed in the $KMnO_4$-carbon reaction, which remain in the carbon pores, even after lengthy washing of the sample, because of their insolubility in water. This second supposition is supported by the fact that MnO_2 decomposes above about $530°C$ with the release of oxygen according to the reaction [6]

$$4MnO_2 \rightarrow 2Mn_2O_3 + O_2$$
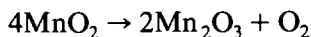
and that this manganese compound is probably formed in the reaction of $KMnO_4$ with carbon [3,7,8].

Comparison of the curves for H_2SO_4-A, C-HNO_3-S and $HClO_4$-S with those for H_2O_2-S, O_3-S and C-KIO_4-S shows that the effects of weight loss are always displaced to higher temperatures when the oxidation of carbon is carried out with solutions of substances which have acidic properties. This denotes a greater thermal stability of the surface state. Furthermore, the extent of formation of the corresponding surface oxides is greater for O_3 and HNO_3 and smaller for H_2SO_4, whereas it is rather similar for H_2O_2 and $HClO_4$. A reliable explanation of the results is not easy in this case because of the concurrence of differences in the oxidizing agent and the pH and concentration of the solution.

For a given substance, a pH change in the solution alters its oxidizing power and this will affect the stability and the degree of formation of the oxygen surface groups. The effect will depend only on the variation that the substance undergoes in its oxidizing capacity, a measure of which is the reduction potential value. This effect probably differs from that connected with the isolated presence of distinct solutes in solution, as in this case other factors may exert an influence; for example, the accessibility to possible positions for oxidation, which will be controlled by the size of the species in solution.

Figure 4 shows the DTG curves for the samples prepared using the concentrated solution of H_2O_2 at three different pH values. Apart from the peak associated with the removal of water, the plots all present a second peak between 215 and $225°C$, which appears as a shoulder in the case of H_2O_2-A. The weight loss is similar for H_2O_2-S and H_2O_2-A, and substantially smaller for H_2O_2-B. Therefore, the treatment of carbon with a
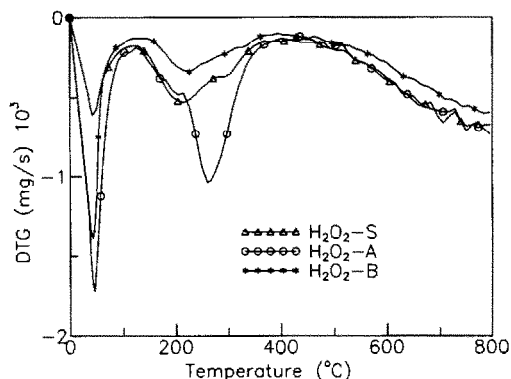
Fig. 4. DTG curves for the samples prepared by oxidation of AC with solutions of H_2O_2 at different pH values.

solution at pH 11.5 reduces formation of the surface oxides, which cause the mass loss when the samples are heated in the temperature interval studied. Moreover, only the curve for H_2O_2–A exhibits a peak centred at 264°C (it is found at a lower temperature than in the case of H_2SO_4–A, which is important as H_2SO_4 was the substance used to fix the pH at 2.5 in the H_2O_2 solution), which is more pronounced than that situated at about 220°C. Accordingly, the surface groups which arise from the oxidation of carbon possess a higher thermal stability and are formed to a larger extent when the treatment is performed at pH 2.5. This result is consistent with the variation produced in the oxidizing power of H_2O_2 by pH change, as shown by the reduction potential values given above for this substance.

KIO$_4$ behaves in some ways in a similar manner to H_2O_2. The DTG curves (see Fig. 5) present a maximum at around 220°C for C-KIO$_4$–S and C-KIO$_4$–B and at 260°C for C-KIO$_4$–A. Also, the peak becomes more
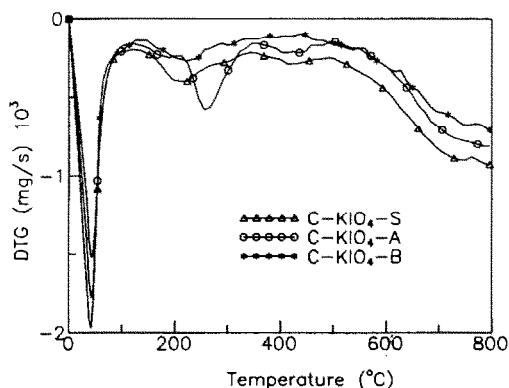

Fig. 5. DTG curves for the samples prepared by oxidation of AC with the saturated solution of KIO$_4$ at different pH values.
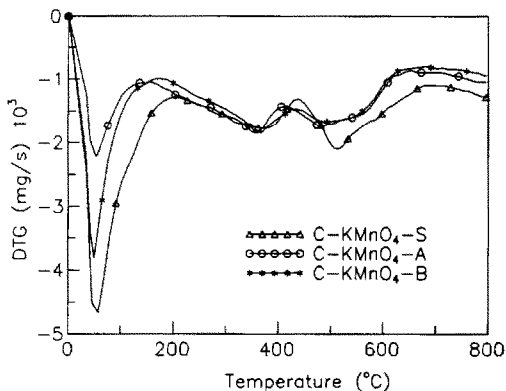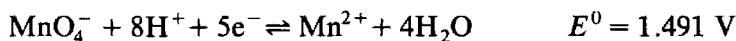
Fig. 6. DTG curves for the samples prepared by oxidation of AC with the saturated solution of KMnO$_4$ at different pH values.
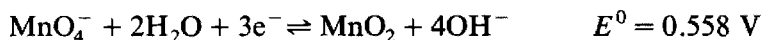
marked with the variation order C-KIO$_4$–B < C-KIO$_4$–S < C-KIO$_4$–A. As for H$_2$O$_2$, it follows that both the stability and the presence of the oxygen surface groups which are removed by heating are higher when the oxidation of carbon is carried out at pH 2.5. In contrast to H$_2$O$_2$, however, the treatment conducted at pH 2.5 does not give rise to formation of the surface oxides which are responsible for the weight loss centred at about 220°C, as indicated by the absence of a peak corresponding to that for C-KIO$_4$–A on the DTG curves.

The DTG curves for the samples prepared using a KMnO$_4$ saturated solution at several pH values are shown in Fig. 6. Besides the peak between 40 and 50°C, the plots show two weight loss maxima at temperatures above 350°C. The intensity of the second peak increases only when the oxidation is carried out at pH 2.5, which indicates the formation of a greater amount of surface complexes or, probably, reaction products, at such a pH value. This result agrees with the variation produced in the oxidizing power of KMnO$_4$ by pH change in the solution. The reduction potentials in acid and alkaline solutions are as follows:

Acid solution, $a_{H^+} = 1$

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O \qquad E^0 = 1.491 \text{ V}$$

Basic solution, $a_{OH^-} = 1$

$$MnO_4^- + 2H_2O + 3e^- \rightleftharpoons MnO_2 + 4OH^- \qquad E^0 = 0.558 \text{ V}$$

However, in view of the great difference that exists between these E^0 values, which is even larger than for H$_2$O$_2$, and the difference in concentration of the solution used, a higher influence of pH on the formation and removal of the surface groups or products was expected. Therefore, it seems that the oxidizing action of KMnO$_4$ is in some way prevented, possibly as a
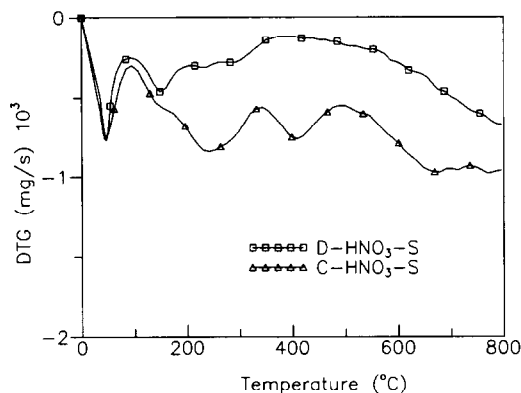
Fig. 7. DTG curves for samples prepared by oxidation of AC with solutions of HNO_3 varying in concentration.

result of the presence of insoluble substances in the carbon pores, which would prevent mass transport and suppress the redox process.

The concentration of the solution also influences the reduction potential value (the activity appears in the Nernst relationship) and hence the oxidizing capacity of each substance. For the oxidation of a porous material, the distinct presence of solute in the solution may affect both the diffusion of the substance (a proof of this is simply the increase in the adsorption of solutes from solution with increasing concentration) and the extent of oxidation. To check the possible effect of the concentration, a 10^{-2} M solution of HNO_3, KIO_4 or $KMnO_4$ was used in the treatment of carbon, together with a saturated or concentrated solution.

The DTG curves of D-HNO_3-S and C-HNO_3-S are shown in Fig. 7. Although the D-HNO_3-S plot presents only a single peak, centred at 151°C, the corresponding C-HNO_3-S plot shows two peaks, at 241 and 410°C, which are more pronounced and broader than the peak for D-HNO_3-S. These results prove the existence of notable influence of the HNO_3 solution concentration on the surface state in terms of the thermal stability and the extent and diversity of formation of surface oxides.

In contrast to HNO_3, the plots of D-KIO_4-S and C-KIO_4-S are almost coincident between 35 and 800°C, as is shown in Fig. 8. Therefore, the concentration of the KIO_4 solution does not affect the surface state that arises from the oxidation of carbon and undergoes alterations by heating over that temperature interval. Probably, the dilute solution is sufficiently concentrated to produce the complete oxidation of the positions which are active against this oxidizing agent.

The sample prepared by oxidation of carbon with the dilute solution of $KMnO_4$ behaves thermally in a different manner from those obtained by treatment with the saturated solution, as shown by the fact that the DTG curve of D-$KMnO_4$-S (see Fig. 9) has only a broad peak at 222°C. These
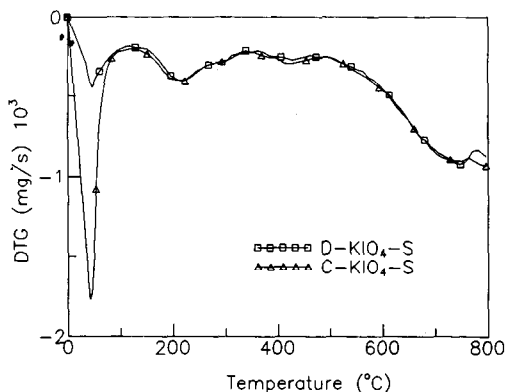
Fig. 8. DTG curves for samples prepared by oxidation of AC with solutions of KIO$_4$ varying in concentration.

results suggest that in a first stage of the reaction, KMnO$_4$ interacts with carbon to produce surface oxides which have a certain thermal stability, and there is no formation of those insoluble products that are presumably responsible for the prevention of mass transport.

Stability under outgassing conditions

The mass loss which occurs when the samples are outgassed under high vacuum must be associated with the removal not only of surface oxides but also of adsorbed water. This latter effect occurs despite the samples having been oven-dried at 110 °C for 24 h as, during the short time it takes to weigh the sample and then measure the length of the quartz spring in the adsorption apparatus, the samples adsorb water. The adsorption of moisture
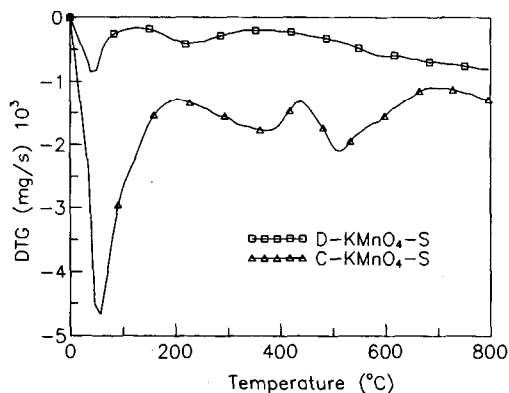

Fig. 9. DTG curves for samples prepared by oxidation of AC with solutions of KMnO$_4$ varying in concentration.

TABLE 2

Percentage of weight loss on outgassing of the samples under high vacuum

Sample	Wt.%	Sample	Wt.%
AC	0.96	$HClO_4$–S	1.53
H_2O_2–S	2.17	D-KIO_4–S	0.96
H_2O_2–A	1.87	C-KIO_4–S	1.74
H_2O_2–B	1.23	C-KIO_4–A	2.92
O_3–S	2.04	C-KIO_4–B	1.19
ClO_2–S	1.32	D-$KMnO_4$–S	1.19
H_2SO_4–A	2.36	C-$KMnO_4$–S	4.21
D-HNO_3–S	3.62	C-$KMnO_4$–A	3.20
C-HNO_3–S	3.07	C-$KMnO_4$–B	3.07

will have the upper limit of 0.96 wt.%, which is the percentage of weight loss for AC, if it is not affected by the oxidation of carbon. In fact, the data in Table 2 show that, except for D-KIO_4–S, the weight loss is higher for the oxidized products.

The large values of the percentage of weight loss correspond to the samples prepared by oxidation of carbon using concentrated solutions of $KMnO_4$ and HNO_3. According to previous results, the behaviour shown by the $KMnO_4$-treated samples is probably mostly the result of the loss of water which remained even after the drying treatment, as suggested by the significant presence of water in these samples, together with the prevention of mass transport that appears to take place in the case of these materials. For the HNO_3-treated samples, the mass loss must be connected with the removal of mainly surface oxides. As expected, the percentage of weight loss is relatively high for O_3–S, whereas it is small for ClO_2–S. However, the values for H_2O_2–S and C-KIO_4–A, which exceed that for O_3–S, are surprising.

The pH and the concentration of the solution exert a variable influence on the mass loss. This is more important for H_2O_2–S, C-$KMnO_4$–S and C-KIO_4–A; i.e. for the samples obtained by oxidation of carbon with solutions of H_2O_2 and $KMnO_4$ at the solution pH and of KIO_4 at acid pH. Finally, the percentage of weight loss is much smaller for D-$KMnO_4$–S and D-KIO_4–S than for C-$KMnO_4$–S and C-KIO_4–S, respectively. However, it is somewhat larger for D-HNO_3–S in comparison with C-HNO_3–S.

CONCLUSIONS

In this study on the stability under heating and outgassing conditions of the surface state of activated carbon oxidized in liquid phase, the results show that the oxidizing agent and the pH and concentration of the solution

exert a notable influence on the thermal stability and the extent and specificity of formation of the surface oxides, which are removed by heat treatment between 35 and 800 °C. Differences are observed in relation to the results obtained when the samples are outgassed under high vacuum.

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