

Thermogravimetric study of activated carbon oxidized with H_2O_2

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Abstract

Using activated carbon (AC) and H_2O_2 in aqueous solution, the influence of the method of preparation of samples on the stability of the surface state toward heating and outgassing was investigated. In the preparation of samples, AC was treated with H_2O_2 solutions of varying concentration or pH, and containing Fe^{2+} , Fe^{3+} , ethanol or ether. Also, the outgassing of AC and the contact between the intermediate products and the oxidizing solutions were effected under controlled temperature and time conditions. The mass of sample increased markedly when AC was oxidized at pH 2.5, especially when outgassing at $350^\circ C$ or for 6 h. The variations in mass at uncontrolled pH and at pH 11.5 were only slight. In the study on the thermal behavior, the samples were heated in a thermobalance between 30 and $800^\circ C$ in N_2 and outgassed in a gas adsorption apparatus ($150^\circ C$ at 133×10^{-6} Pa, for 12 h). The results of the thermogravimetric analysis showed that the mass decrease of AC increased above $600^\circ C$. The stability of the surface state was mainly influenced by pH changes in the H_2O_2 solution and by the outgassing time of AC. The addition of ethanol or ether to the oxidizing solution lowered the stability. The mass loss was strongly dependent on the oxidation method of AC. Outgassing of the samples significantly increased the mass loss with regard to the heat treatment carried out to the same temperature.

Keywords: Activated carbon; DTG; Hydrogen peroxide; Oxidation

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1. Introduction

Important applications of activated carbon are based on the surface chemistry of the material. For example, the removal of trace amounts of heavy metals from waste waters is due to specific ion-exchange properties of activated carbon. To enhance such properties, the carbon surface is usually chemically modified by introducing oxygen. This combines with the carbon atoms and oxygen functional groups are formed. In some applications and in the regeneration of activated carbon, the material is, however, heated at high temperatures and this results in loss of oxygen groups. Due to this, in some instances activated carbon needs to be subjected to a further oxidation treatment in order to reestablish its surface chemistry. These facts show that the formation and the thermal stability of the oxygen groups are topics of current interest. Two general methods to form oxygen functional groups involve the use of oxidizing gases or solutions [1]. Numerous studies have been made on the thermal decomposition of surface oxides as produced by various activation procedures [2]. In a previous study [3], a series of oxidants (H_2O_2 , O_3 , ClO_2 , etc.) were used in the treatment of activated carbon and the stability of the surface state of the samples toward heating and outgassing was investigated [3]. Using H_2O_2 only, the influence of the method of preparation of the samples is studied in this work.

2. Experimental

An activated carbon from Merck (1.5 mm, AC) was used. The oxidation method of AC was described in detail elsewhere [4]. The general procedure consisted of two successive stages of outgassing and oxidation carried out to avoid contact of the intermediate product with air. In each experiment, an H_2O_2 solution (50 cm^3) was brought into contact with the freshly outgassed sample of AC. All dilute solutions were prepared from a commercial H_2O_2 solution (Panreac; 110 vol, 33% w/v; CS). A few drops of an H_2SO_4 or NH_4OH concentrated solution were added to the H_2O_2 solutions for pH changes. Also, H_2O_2 solutions containing either 25 ppm Fe^{2+} or Fe^{3+} or 5 cm^3 ethanol or ether in 50 cm^3 of solution were used. The iron salts used were $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Fe}_2(\text{SO}_4)_3$ (Probus). After their preparation, the products of H_2O_2 oxidation were first oven-dried at 60°C for 24 h and then stored in a desiccator with CaCl_2 . Codes and specific conditions of preparation of the samples are shown in Table 1. D-0 and D-4 were prepared by using CS and a solution obtained by mixing 12.5 cm^3 CS with 37.5 cm^3 water. In the preparation of the rest of the samples, an H_2O_2 solution of intermediate concentration (25 cm^3 H_2O_2 plus 25 cm^3 water) was used [4].

The heat treatments of the samples were performed in a thermogravimetric apparatus, Mettler TA-3000, consisting of a TG-50 thermobalance (precision $\pm 2^\circ\text{C}$, temperature; $\pm 1 \mu\text{g}$, weight) and a TG-10 processor. About 100 mg of each individual sample were heated from 30 to 800°C (heating rate 5°C min^{-1}) in flowing N_2 (purity $>99.998 \text{ vol}\%$; flow rate $200 \text{ cm}^3 \text{ min}^{-1}$). The mass loss produced in the

Table 1
Codes and preparation of the samples

Sample	Dilution	pH	Outgassing		Contact	
			<i>T</i> /°C	<i>t</i> /h	<i>T</i> /°C	<i>t</i> /h
D-4	4	S	250	2	30	2
D-0	0	S	250	2	30	2
AM	2	A	250	2	30	2
BM	2	B	250	2	30	2
OT-30	2	A	30	2	30	2
OT-250	2	A	250	2	30	2
OT-350	2	A	350	2	30	2
Ot-0	2	A	250	0	30	2
Ot-2	2	A	250	2	30	2
Ot-6	2	A	250	6	30	2
Ot-12	2	A	250	12	30	2
CT-O ^a	2	A	250	2	0	2
CT-30	2	A	250	2	30	2
CT-50	2	A	250	2	50	2
CT-70	2	A	250	2	70	2
Ct-2	2	A	250	2	30	2
Ct-6	2	A	250	2	30	12
Ct-12	2	A	250	2	30	12
A-Fe ²⁺	2	A	250	2	30	2
B-Fe ³⁺	2	B	250	2	30	2
A-EtOH	2	A	250	2	30	2
A-Ether	2	A	250	2	30	2

Key: D, dilution; S, solution pH; A, pH 2.5; B, pH 11.5; M, medium; O, outgassing; *T*, temperature; *t*, time; C, contact. ^a The contact between the phases was established with the system at the indicated temperature.

outgassing of the samples (150°C at 133×10^{-6} Pa, for 12 h) was determined by using a conventional gas adsorption apparatus. Around 10 mg of sample were used in each experiment. Prior to outgassing, the samples were oven-dried at 110°C for 12 h.

3. Results and discussion

3.1. Mass variations in the H_2O_2 oxidation of AC

The percentage mass variation (PMV) values (Table 2) show a strong dependence of the mass of sample on the preparation method [4]. The great increase in mass for OT-350 and Ot-6, particularly, and the small variation in mass for all the

Table 2

Variations of mass in the preparation and heat treatments of the H₂O₂ samples

Sample	PMV ^a	HT-PML ^b				O-PML ^c
		30–800°C	30–150°C	150–400°C	400–800°C	
AC		10.5	7.8	0.6	2.1	3.5
D-4 ^d	0.2	4.1	1.0	1.4	1.7	3.3
D-0 ^d	0.1	4.2	1.0	2.1	1.1	3.9
AM	2.5	6.8	2.2	2.2	2.4	3.7
BM	0.1	2.6	0.6	0.7	1.3	2.3
OT-30	2.1	4.7	1.3	2.0	1.4	3.5
OT-250	2.5	6.8	2.2	2.2	2.4	3.7
OT-350	7.3	12.9	3.8	6.1	3.0	5.9
OT-0 ^e	2.1	5.5	1.0	2.8	1.7	4.6
Ot-2	2.5	6.8	2.2	2.2	2.4	3.7
Ot-6	5.7	6.6	1.6	2.7	2.3	2.9
Ot-12	3.1	7.2	1.9	2.9	2.4	1.9
CT-0	3.6	7.9	2.0	3.2	2.7	3.0
CT-30	2.5	6.8	2.2	2.2	2.4	3.7
CT-50	3.0	7.7	2.2	2.8	2.7	3.9
CT-70	1.6	5.9	2.2	1.5	2.2	3.2
CT-2	2.5	6.8	2.2	2.2	2.4	3.7
CT-6	1.8	6.3	2.6	1.8	1.9	4.5
CT-12	1.8	5.3	1.3	2.0	2.0	2.9
A-Fe ²⁺	2.0	8.5	1.6	3.5	3.4	4.7
B-Fe ³⁺ ^e	–0.2	3.9	0.7	1.1	2.1	2.0
A-ETOH	2.9	6.9	1.3	3.3	2.3	4.1
A-Ether	3.3	8.4	1.7	4.0	2.7	5.5

^a PMV, percentage of mass variation in the preparation of the samples ($[(m_f - m_i)/m_i] \times 100$, where m_i is the initial mass of AC and m_f the final mass of sample). ^b HT-PML, percentage of mass loss in the heat treatment of the samples ($[(m_1 - m_2)/m_0] \times 100$, where m_1 and m_2 represent the mass at T_1 and T_2 ($T_1 < T_2$), respectively, and m_0 is the initial mass of sample). ^c O-PML, percentage of mass loss in the outgassing of the samples. ^d 30–100°C, 100–275°C and 275–800°C. ^e 30–100, 100–400°C and 400–800°C.

products oxidized with H₂O₂ solutions at uncontrolled pH and at pH 11.5 (for A-Fe³⁺ the PMV value is even negative), in contrast to the samples prepared at pH 2.5, should be noted. For the series OT, Ot, CT and Ct, the mass either generally increases progressively or varies rather irregularly. It also depends on the species (Fe²⁺, Fe³⁺, etc.) added to the H₂O₂ solution. In connection with these results it should be recalled that the PMV value represents the net mass balance associated with the treatment of AC with H₂O₂ solutions. Accordingly, the low PMV values obtained for a number of samples do not necessarily mean that surface oxygen complexes were not formed in the oxidation of AC because the incorporation of oxygen to the carbon might be followed by mass loss.

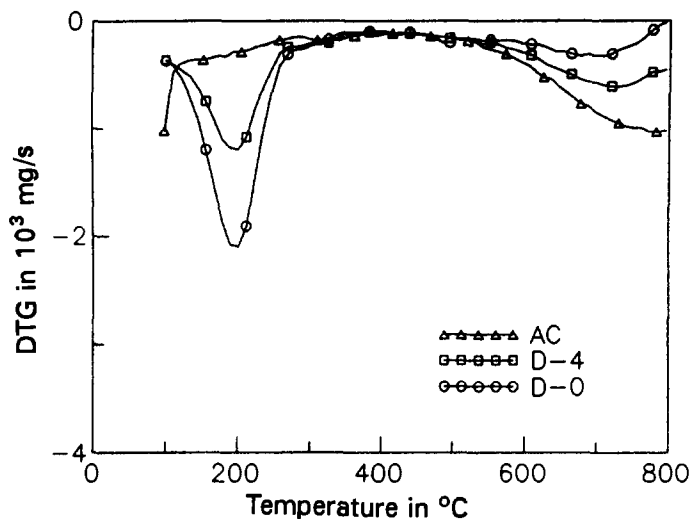


Fig. 1. DTG curves of AC, D-4 and D-0.

3.2. Thermal behavior of the samples

The weight loss effect shown by the DTG curve of AC (Fig. 1) below 150°C is attributable to the removal of mainly hygroscopic water (the 30–150°C region has been omitted from the curves for the sake of clarity). The significant decrease in the AC mass above 600°C was ascribed previously [5] to the ejection of volatile matter from the material on account of the heat treatment at temperatures higher than the manufacture temperature. Another possibility is the loss of oxygen surface groups, which must decompose at different temperatures [6–10]. Generally, the oxygen complexes formed on treatment of carbon with oxidizing gases are stable below the temperature of formation [2]. At higher temperatures their evolution occurs, the composition of the gases depending particularly on temperature and on the chemical nature of the oxygen complex. Otake and Jenkins [11] concluded that the oxygen groups present in HNO₃-oxidized and air-oxidized carbons are essentially completely decomposed by heat treatment to 1000°C in N₂, and also that the oxygen complexes can be divided into four groups according to the decomposition temperature and on whether they yield CO or CO₂. The presence of both high and low temperature complexes which generate CO₂ and CO was associated with the occurrence of chemically different complexes and/or the same complex existing on energetically different sites [11]. Using a wood-based, steam-activated carbon, Meldrum and Rochester [12] observed that a high proportion of C=O and C–O species were destroyed during heat treatment of the material in nitrogen at 800°C.

The strong effect of weight loss between 150 and 400°C (for a large number of samples the maximum is centered at about 285°C in the DTG curves) indicates that for D-4 and D-0 (Fig. 1) the extent of removal of surface groups or species was influenced by the concentration of the H₂O₂ solution. Moreover, the thermal

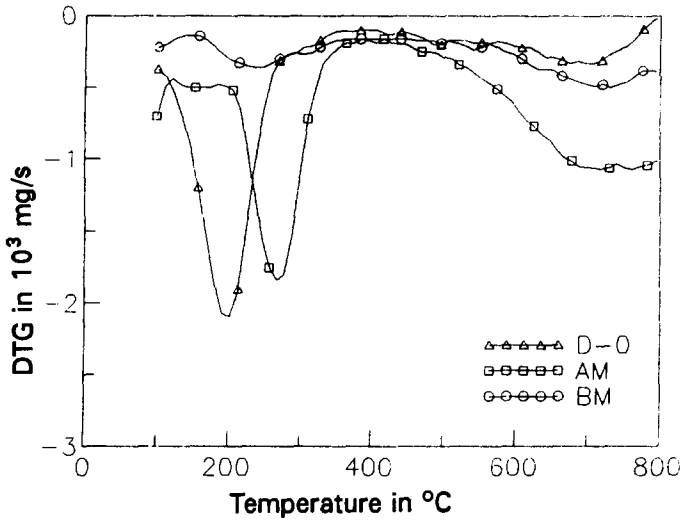


Fig. 2. DTG curves of D-0, AM and BM.

stability of the surface state of the samples depended on the pH of the oxidizing solution (Fig. 2). It varies in the sequence: AM > BM > D-0. Marked differences were also noted in the surface chemistry of these samples [4], as inferred from their FTIR spectra (Fig. 3). The concentration of oxygen surface groups (carbonyl,

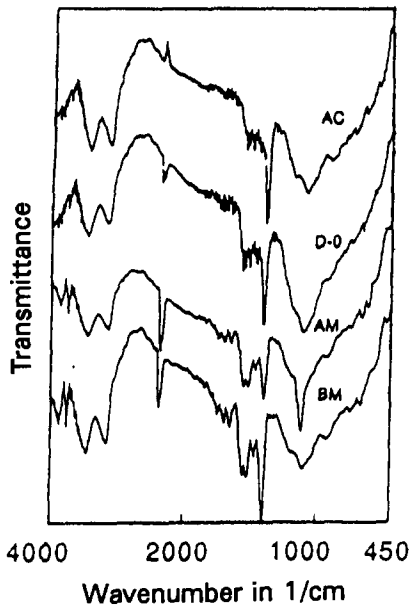


Fig. 3. FTIR spectra of AC, D-0, AM and BM.

hydroxyl, etc.) is different in the samples. The presence in the AM spectrum only of the sharp band at about 1120 cm^{-1} is probably a significant result, allowing for the fact that in this sample the weight loss takes place at higher temperatures. Such a band is presumably due to $\nu(\text{C-O})$ vibrations in cyclic ethers [4], and therefore it might be thought that this oxygen complex is involved in the mass decrease, although it is well known that the ether structures decompose at higher temperatures in the range $500\text{--}1000^\circ\text{C}$, yielding CO [13]. However, the greater mass loss at high temperatures for AM than for D-0 or BM is in accord with the magnitude of the mass increase produced in the preparation of the samples, as described above. Finally, it should be noted that the relative position of the maximum in the weight loss was similar to that for the products of AC oxidation, but without the previous outgassing of the material [3].

The effect of weight loss centered at about 285°C is much stronger for OT-350 than for the other OT samples (Fig. 4). Above 400°C , the thermal behavior of OT-350 is similar to that of OT-250. For the Ot samples (Fig. 5), the decrease in mass occurs at temperatures markedly lower when AC was outgassed for shorter times. Thus, the degree of surface ‘cleaning’ of AC by the outgassing effect appears to influence the interaction of the H_2O_2 solution with the outgassed product, which is reflected in the stability of the surface state of the samples. The weaker effect for CT-70 than for the rest of the CT samples (Fig. 6) is consistent with the PMV values (Table 2), although similarities were observed in the surface chemistry of CT-70 and CT-0 [4]. The greater variation in mass at high temperatures for Ct-2 (Fig. 7) is also probably significant from the standpoint of the stability of the surface state. Moreover, it should be noted that the results of the thermogravimetric analysis obtained for these four series of samples tend to parallel

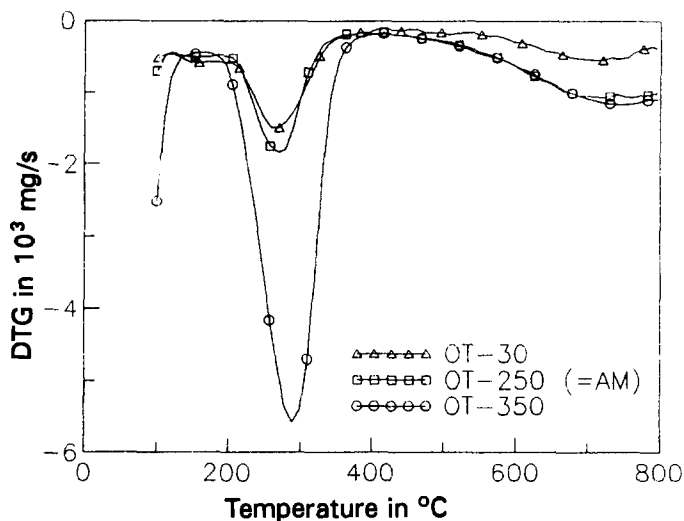


Fig. 4. DTG curves of the OT samples.

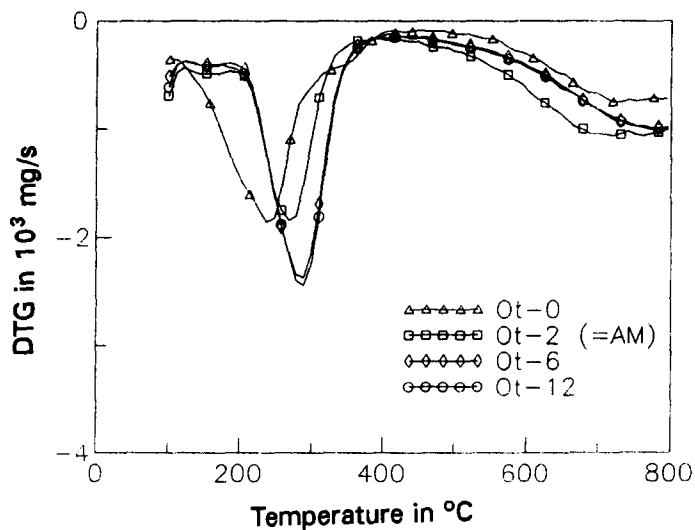


Fig. 5. DTG curves of the Ot samples.

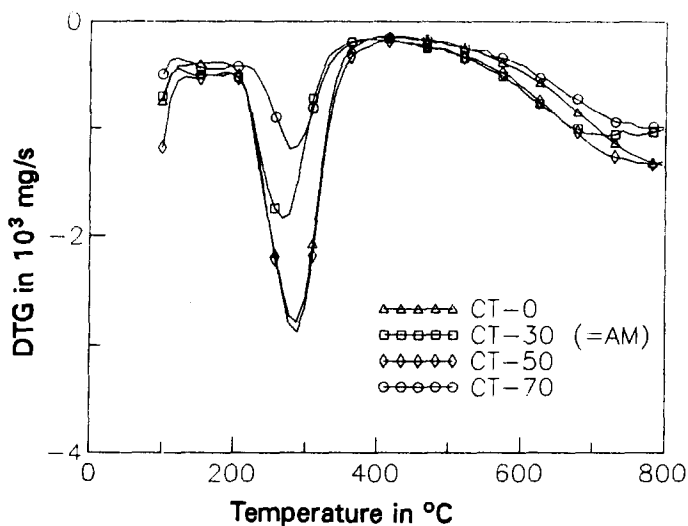


Fig. 6. DTG curves of the CT samples.

those provided by FTIR spectroscopy [4]. This is illustrated by the broad band located between 1300 and 900 cm^{-1} , which was shown in the spectra of AC and Ot-0.

The DTG curves of BM and B-Fe^{3+} show no weight loss effect at temperatures lower than 400°C (Fig. 8), nor was the absorption band at 1120 cm^{-1} found in the FTIR spectra of these samples [4]. In contrast, the presence of bands in the 1760

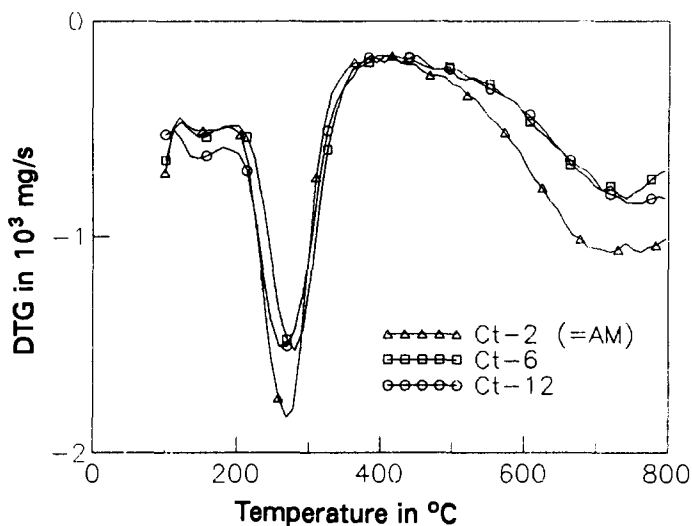
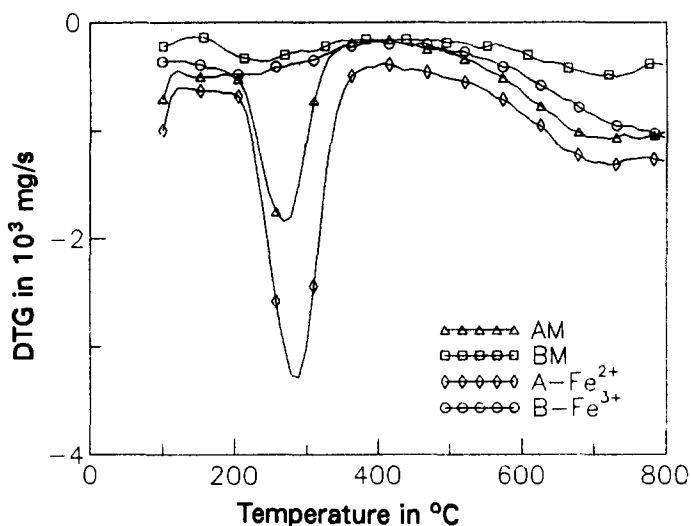


Fig. 7. DTG curves of the Ct samples.

Fig. 8. DTG curves of AM, BM, A- Fe^{2+} and B- Fe^{3+} .

and 1500 cm^{-1} regions of the spectra, which were absent from the AC spectrum, proved that in the treatment of AC with the H_2O_2 solutions at alkaline pH, surface groups, i.e. carbonyl and carboxylate groups, ionic-radical structures, etc., were formed [4]. Accordingly, the results of the thermogravimetric analysis of the samples suggest that such groups were either thermally stable between 30 and 800°C or decomposed at different temperatures. The samples BM and B- Fe^{3+} are almost identical in thermal behavior. Some slight differences concern the mass losses at

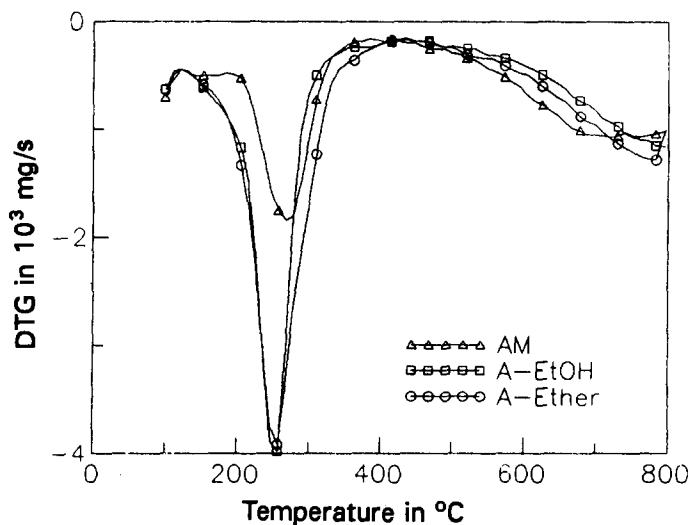
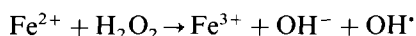


Fig. 9. DTG curves of AM, A-EtOH and A-Ether.

both low and high temperatures. For AM and A-Fe²⁺, their DTG curves (Fig. 8) indicate a greater mass loss for A-Fe²⁺. The increased oxidation of AC with Fe²⁺-H₂O₂ solutions was attributed to OH[•] radicals [14] generated as a result of the decomposition of H₂O₂ by the action of the ferrous salt [15–18]



Regarding the A-EtOH and A-Ether curves (Fig. 9), the maximum moves around 30°C toward lower temperatures. The decreased stability of the surface state may be connected with the removal of ethanol or ether from the samples. If so, these species remained in the oxidized products upon contact of H₂O₂ solutions with AC.

In order to obtain further information on the thermal behavior of the samples, the overall percentage of weight loss between 30 and 800°C was broken down into various fractions according to the temperature ranges of the maxima in the DTG curves. The values of HT-PML are given in Table 2. The weight loss for activated carbons at temperatures up to 900°C is usually low, ≈3–5% [12,19]. For AC, it is 10.5% to 800°C. The high mass loss between 30 and 150°C is attributable to the removal of adsorbed water as the material was not oven-dried prior to the heat treatment in the thermobalance. For the products of H₂O₂ oxidation, the HT-PML values corresponding to the range 30–800°C are larger than those of PMV. The release of surface species or functional groups of AC, which remained in the samples on treatment of the material, and also of those present in the samples on account of the interaction either of the H₂O₂ solutions with AC or of atmospheric components with the H₂O₂-treated products, contribute to the mass loss of the samples. In this connection it must be noted that the evolution of water up to 600°C was observed previously [20,21]. It was also suggested that adjacent carbonyl groups split off water to form cyclic acid anhydrides [22]. The variation of

HT-PML between 400 and 800°C for most series of samples is the same as that of PMV. In some instances, e.g the Ct series, the values of HT-PML and PMV are close for each sample. The greater mass loss for A-Fe²⁺ and OT-350 denotes the high stability of the surface species or functional groups present in these samples. In the other temperature ranges, the agreement between the values of HT-ML and PMV is, however, generally worse. The higher HT-PML between 150 and 400°C for D-4, D-0, BM and B-Fe³⁺ than for AC is also worth mentioning as it is in accord with the formation of surface groups when AC was oxidized with the H₂O₂ solutions at uncontrolled pH and at alkaline pH in the treatments of AC.

3.3. Mass loss in the outgassing of the samples

As reported previously by Puri [2], the oxygen complexes of carbon are stable, even under high vacuum. Regardless of the formation method, they do not generally decompose below 250°C [2]. The O-PML values (Table 2) show that outgassing of the samples produced an important mass loss. Comparison with the HT-PML values corresponding to the range 30–150°C indicates that the mass loss, except for AC, is greater than when the samples were simply heated to the same temperature, i.e. without the isothermal treatment at 150°C. Then, it seems likely that when the samples were outgassed at 150°C, surface species or groups were removed which were lost from the samples when they were heated at higher temperatures. It occurred only partially, as shown by the values obtained (these are omitted for the sake of brevity) by adding up the HT-PML values for the two lower temperature ranges, which are larger than those of O-PML. As expected, the O-PML value is high for OT-350, A-Ether and A-Fe²⁺ and low for BM and B-Fe³⁺. The small O-PML values for Ot-6 or Ot-12 are surprising because the PMV values are large for these samples.

References

- [1] P.N. Cheremisinoff and F. Ellerbusch (Eds.), Carbon Adsorption Handbook, Ann Arbor Science, Ann Arbor, Michigan, 1980.
- [2] B.R. Puri, in P.L. Walker, Jr. (Ed.), Chemistry and Physics of Carbon, Vol. 6, Marcel Dekker, New York, 1970.
- [3] V. Gómez-Serrano, M. Acedo-Ramos, A.J. López-Peinado and C. Valenzuela-Calahorro, Thermochim. Acta, 176 (1991) 129.
- [4] V. Gómez-Serrano, M. Acedo-Ramos, A.J. López-Peinado and C. Valenzuela-Calahorro, Fuel, 73 (1994) 387.
- [5] C. Valenzuela-Calahorro, A. Macías-García, Bernalte-García and V. Gómez-Serrano, Carbon, 28 (1990) 321.
- [6] R.C. Bansal, J.-B. Donnet and F. Stoeckli, Active Carbon, Marcel Dekker, New York, 1988, p. 31.
- [7] R.B. Puri and R.C. Bansal, Carbon, 1 (1964) 451.
- [8] M.T. Coltharp and N. Hackerman, J. Phys. Chem., 72 (1968) 1171.
- [9] S.S. Barton, D. Gillespie and B.H. Harrison, Carbon, 11 (1973) 649.
- [10] M. Voll and H.P. Boehm, Carbon, 8 (1970) 741.

- [11] T. Otake and R.G. Jenkins, *Carbon*, 31 (1993) 109.
- [12] B.J. Meldrum and C.H. Rochester, *Fuel*, 70 (1991) 57.
- [13] H. Jankowska, A. Swiatkowski and J. Choma, *Active Carbon*, Ellis Horwood, New York, 1991, p. 89.
- [14] I. Heard and F.E. Senftle, *Fuel*, 63 (1984) 221.
- [15] H.J.H. Fenton and H. Jackson, *J. Chem. Soc. (London)*, 75 (1989) 1.
- [16] J.O'M. Bockris and L.F. Oldfield, *Faraday Soc. Trans.*, 51 (1955) 249.
- [17] C. Walling, *Acc. Chem. Res.*, 8 (1975) 125.
- [18] W.G. Barb, J.H. Baxendale, P. George and K.R. Hargrove, *Faraday Soc. Trans.*, 47 (1959) 591.
- [19] J. Visser, in A. Capelle and F. Vooyos (Eds.), *Activated Carbon – A Fascinating Material*, N.V. Norit, Amersfoort, 1983, p. 57.
- [20] B.R. Puri, D.D. Singh and L.R. Sharma, *J. Phys. Chem.*, 62 (1958) 756.
- [21] B.R. Puri, and R.C. Bansal, *Carbon*, 1 (1964) 457.
- [22] J.S. Mattson and H.B. Mark, Jr., *Active Carbon*, Marcel Dekker, New York, 1971.