

Textural and Chemical Surface Modifications Produced by Some Oxidation Treatments of a Glassy Carbon

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This paper deals with the modifications of the chemical surface functionalities and the textural changes of a glassy carbon produced by three oxidizing agents: ozone, hydrogen peroxide, and oxygen plasma. The chemical surface changes are evaluated by using Fourier transform infrared spectroscopy, temperature-programmed desorption–mass spectrometry, and chemical titrations of the surface functionalities by using the Boehm method. The textural modifications are studied by mercury porosimetry and by N₂ and CO₂ adsorption at 77 and 273 K, respectively. Ozone is a more effective oxidizing agent than H₂O₂ and oxygen plasma. It is able to introduce much larger amounts of oxygen functionalities on the surface than the other oxidizing agents. Moreover, the textural characteristics of the original sample remain almost unchanged after the treatments with oxygen peroxide and with oxygen plasma, while ozone produces modifications in surface area and mesoporosity. Nevertheless, ozone modifications of surface area seem to be partially produced by the fixation of the oxygen functionalities at the entrance of the micropores which partially hinder the access of the adsorbates.

1. Introduction

The use of carbon materials in adsorption and catalysis is related to their textural properties and chemical surface groups. The textural properties are determined by the surface area and porosity, while the chemical surface groups mainly consist of oxygen-containing functionalities. Most of the carbon materials have a polymodal distribution of pores, and therefore their selectivity in the adsorption and catalytic processes is not relevant. This can be improved by using carbon materials with controlled porosity, such as for example activated carbon fibers or glassy carbons. The latter are currently prepared by carbonization of organic copolymers in such a way that glassy carbon with tailored porosity can be obtained by controlling the experimental conditions and the raw material.^{1–3} Nevertheless, the carbon materials obtained under these conditions usually contain very limited amounts of chemical surface groups, which is a drawback if they are going to be used in adsorption and catalytic processes.⁴ There are several methods to increase the

concentration of chemical surface groups in carbon materials. Many of them involve chemical treatments in aqueous solution, and some are gas–solid reactions.^{5–8} The results of these treatments are highly dependent on the oxidant character of the reactive species and on the nature of the carbon material. Glassy carbons are rather inert to the oxidation, and therefore only strongly oxidant substances are able to introduce chemical surface groups on the surfaces of these materials in an appreciable amount.

The aim of this paper is to study the changes produced in a glassy carbon by a highly oxidant reactive species, namely, ozone (standard reduction potential, $E^\circ = +2.076$ V). The study is focused on the influence of several parameters (temperature of treatment, time, and ozone concentration) on the variation of the content of chemical surface groups. The results of the ozone treatments are compared to those obtained by oxidation with H₂O₂ aqueous solution and with oxygen plasma. For this purpose, the chemical and textural characteristics of the samples have been investigated. Chemical structure was measured using several complementary techniques: Fourier transform infrared (FTIR) spectroscopy, chemical titration of the surface groups, and temperature-programmed desorption (TPD). The textural properties were determined by mercury porosimetry and adsorption of nitrogen and carbon dioxide.

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2. Experimental Section

The starting material was a glassy carbon, P3M, which was obtained by carbonization of poly(furfuryl alcohol) in nitrogen flow at relatively low temperature (773 K). Details of the preparation of glassy carbons are given elsewhere.⁹ The ozonation treatments of P3M were carried out in an experimental setup consisting basically of an oxygen source, a Sander-labor ozone generator, a tubular cylindrical furnace, and a 2 cm i.d. hastelloy C reactor provided with a different gas inlet and outlet. A thermocouple connected to a temperature controller was installed at the middle of the reactor, and two other temperature meters were at the entrance and exit.

About 200 mg of carbon sample was placed inside a quartz capsule that was put in the center of the reactor. The system was first heated to the desired heat treatment temperature (HTT) under flowing nitrogen (flow rate = 20 L/h). The heating rate was 10 K/min, and the soak time was 5 min. Then, the nitrogen gas was switched to the oxygen–ozone mixture (flow rate = 20 L/h) which was held at the HTT for the selected residence time. When this time had elapsed, the system was cooled to room temperature in nitrogen.

The carbon samples were oxidized under a constant gas flow rate, using a different ozone concentration (C_{O_3}), HTT, or residence time (R_t). In this way, three series of experiments were carried out:

A-series: C_{O_3} = 50 mg/L, HTT = 25–150 °C, R_t = 1 h

B-series: C_{O_3} = 50 mg/L, HTT = 25–150 °C, R_t = 3 h

C-series: C_{O_3} = 30–65 mg/L, HTT = 25 °C, R_t = 3 h

Hereafter, the names of the samples of the A- and B-series contain the letter of the series and the temperature of treatment, while those of the C-series include the ozone concentration. The samples obtained by treatment of P3M with H_2O_2 and oxygen plasma are labeled P3M-ox2 and P3M-1% O_2 P, respectively. The preparation of the former involved the treatment with concentrated aqueous solution of H_2O_2 and further pyrolysis in N_2 flow at 773 K for 1 h. The latter was prepared by treatment with oxygen plasma produced in a microwave device. Details of the two oxidation methods are given elsewhere.^{7–9}

The infrared spectra were obtained in the 4000–450 cm^{-1} frequency range with 40 scans being taken at 2 cm^{-1} resolution using a Perkin-Elmer 1720 FT-IR spectrometer. Pellets were prepared by mixing powdered carbon and KBr (Merck, for spectroscopy) at a carbon/KBr ratio of 1:100. They were compacted at 10 tonnes/ cm^2 for 10 min. The spectrum of a pure KBr pellet was also recorded and used as the background.

The chemical analysis of the surface functionalities was carried out following the Boehm method,¹⁰ which uses aqueous solutions of bases of different strengths to determine the acidic groups: carboxyls, lactones, and phenols. For this purpose, different batches of 0.25 g of sample were in contact, at 298 K for 48 h, with 25 cm^3 of solutions of $NaHCO_3$ (0.1 M), Na_2CO_3 (0.05 M), and NaOH (0.1 M), respectively. Then the aqueous solutions were titrated with HCl. According to the method, $NaHCO_3$ neutralizes the carboxyl groups, lactones are determined by the difference between the groups neutralized by Na_2CO_3 and $NaHCO_3$, and the difference between the groups neutralized by NaOH and Na_2CO_3 is phenols. Moreover, the basic groups are analyzed in a similar way by neutralization with HCl solutions and further titration with NaOH. Temperature-programmed desorption connected to a mass spectrometer (TPD–MS) was also used to study the amounts and nature of the surface functionalities. For this purpose, 0.1 g of sample was conditioned at 398 K in He flow. Then, the temperature was increased up to 1273 K in a 60 cm^3/min He flow at a heating rate of 20 K/min. The evolved amounts of CO_2 , CO, H_2O , and H_2 were monitored by a mass spectrometer as a function of the temperature.

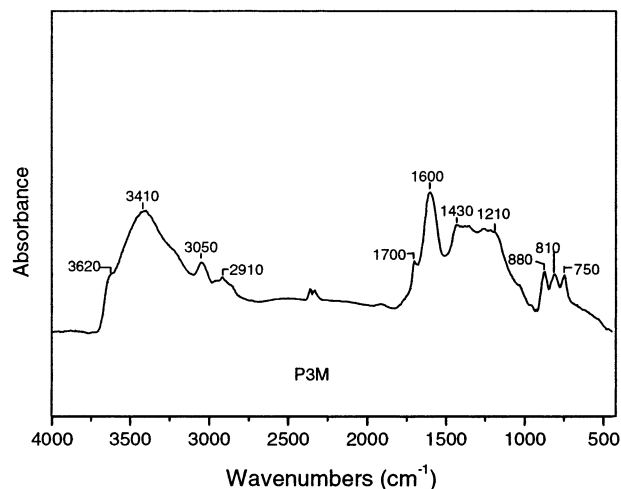


Figure 1. FTIR spectrum of P3M.

Table 1. Assignment of the Bands of the FTIR Spectrum of P3M^a

wavenumber (cm^{-1})	assignment	wavenumber (cm^{-1})	assignment
3410	$\nu(O-H)$	1600	$\nu(C=C)$ skeletal
3050, 2910	$\nu(C-H)$	1430–1210	$\delta(CH_2)$, $\delta(OH)$, $\nu(C-O)$
1700	$\nu(C=O)$	880, 810, 750	$\gamma(C-H)$

^a Symbols: ν , stretching; δ , bending (in-plane); γ , bending (out-of-plane).

Mercury porosimetry up to 4200 Kg/ cm^2 was used to determine the pore size distribution in pores larger than 3.6 nm in width. From this, the volumes of macropores ($\varnothing \geq 50$ nm in width) and mesopores ($3.6 \leq \varnothing \leq 50$ nm in width) were also obtained. The nitrogen and carbon dioxide isotherms were obtained at 77 and 273 K, respectively. They allow determination of the adsorbed amounts, by using the Brunauer–Emmett–Teller (BET) (for SN_2) and Dubinin–Radushkevich (for SCO_2) equations, and the surface areas accessible to these molecules.

3. Results and Discussion

3.1. FTIR Spectrum of P3M. The infrared spectrum of P3M (Figure 1) displays a number of absorption bands and shoulders, which are assigned as shown in Table 1.^{11–15} According to these band assignments, P3M contains oxygen surface groups in addition to the aromatic skeleton. The marked intensities of the bands at 3410 and 1700 cm^{-1} indicate that the concentrations of the oxygen groups are significant in the material. The intense, broad band centered at 3410 cm^{-1} is assigned to phenols, likely involved in hydrogen bonds. The absorption peak for nonbonded OH groups is barely perceptible as a shoulder at 3620 cm^{-1} . Although the phenol groups also absorb infrared radiation between 1500 and 1300 cm^{-1} and at 1200 cm^{-1} , the $\delta(OH)$ vibration is not of practical value for analysis¹¹ and the $\nu(C-O)$ vibration usually overlaps with other absorptions.¹² The broad band at wavenumbers below 1500 cm^{-1} suggests that $=C-O$ bonds containing ether type structures are also present in P3M.

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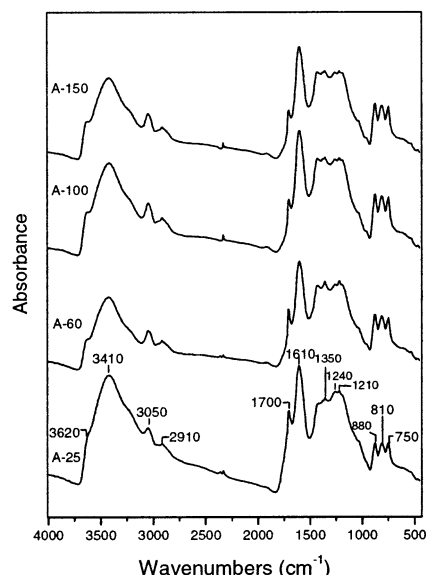


Figure 2. FTIR spectra of the A-series.

Such structures may include epoxides and aromatic ethers that absorb at 1250 cm^{-1} and between 1275 and 1200 cm^{-1} , respectively. Finally, the presence of carbonyl groups in P3M is revealed by the peak at 1700 cm^{-1} . This band position, which is quite sensitive to substituent effects,¹¹ is compatible at times with $\text{C}=\text{O}$ groups in aromatic aldehydes, ketones, and dimeric carboxylic acids. According to the literature, these oxygen surface groups absorb infrared radiation between 1710 and 1685 cm^{-1} ,¹³ at 1690 cm^{-1} ,¹² and between 1700 and 1680 cm^{-1} ,¹³ respectively. Lactone structures, which absorb at slightly higher wavenumbers,¹³ may also be responsible for this band, as it was earlier attributed¹⁴ to $\nu(\text{C}=\text{O})$ vibrations in α,β -unsaturated δ -lactones.

In relation to the carbon–hydrogen structures, the band at 3050 cm^{-1} is compatible with $\nu(\text{C}-\text{H})$ vibrations in aromatic rings, whose skeletal stretching vibrations may cause the spectral appearance of the strong band at 1600 cm^{-1} . The three bands at 880 , 810 , and 750 cm^{-1} are assigned to ring substitutions. These band positions are characteristic of one to three adjacent hydrogen systems.¹⁴ There are no bands for higher numbers of adjacent hydrogen atoms (e.g., a band in the 710 – 690 cm^{-1} range for five such atoms), which is consistent with ring condensations in the skeletal structure of P3M. On the other hand, the band at 2910 cm^{-1} is likely associated with vibration modes of methylene groups. It is in fact an overlapped band, resulting from two peaks at 2925 and 2850 cm^{-1} ,¹¹ corresponding to symmetric and asymmetric vibrations. The methylene groups should also contribute to the absorption of infrared radiation in the 1430 – 1210 cm^{-1} frequency range, owing to the wagging and twisting bending deformations.

3.2. Ozonation of P3M. 3.2.1. Influence of HTT.

Figure 2 shows the FTIR spectra obtained for the samples of the A-series. Compared to Figure 1, they are as a whole similarly shaped to that of P3M, which points out that most of the chemical structure of P3M is not modified by the treatment with ozone in the 25 – $150\text{ }^{\circ}\text{C}$ range for 1 h. This may be accounted for in terms of a hardly accessible porous structure of P3M to ozone since, as a result, the oxidation action of this chemical, despite its strong oxidizing power, would be mitigated. In this connection, it should be recalled here that the ozone molecule is bent and larger than the oxygen molecule, which is also present

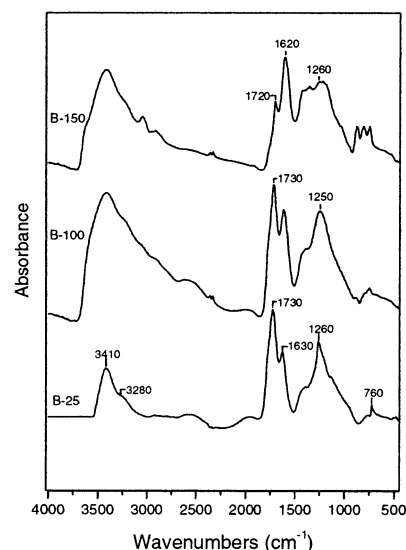


Figure 3. FTIR spectra of the B-series.

in the gas stream. Then, it is possible that oxygen partially hinders the oxidizing action of ozone.

The most interesting feature in the spectra of the ozonated samples, compared to that of P3M, is the increase in the intensity of the band at 1700 cm^{-1} . This means that the treatment produces $\text{C}=\text{O}$ bond containing structures. It is also noticeable that the intensity of the band at 1700 cm^{-1} is significantly higher for the sample ozonated at $25\text{ }^{\circ}\text{C}$ (A-25) and it decreases for the other samples prepared at higher HTTs. Therefore, the formation of $\text{C}=\text{O}$ -containing groups is favored at the lowest HTT ($25\text{ }^{\circ}\text{C}$). These results are consistent with the fact that ozone is thermally unstable,¹⁵ so that the concentration in the gas stream decreases as the HTT increases.

3.2.2. Influence of Ozonation Time. The FTIR spectra of the samples of the B-series, prepared by ozonation for 3 h, are collected in Figure 3. As compared to the spectrum of P3M, they show very important changes concerning both band positions and intensities, in particular for the products prepared at the lowest HTT (i.e., $25\text{ }^{\circ}\text{C}$). Thus, the band at 1700 cm^{-1} in the spectrum of P3M shifts to 1730 cm^{-1} and greatly increases in intensity in the spectrum of B-25. The band at 1600 cm^{-1} shifts to a higher wavelength (1630 cm^{-1}) and becomes weaker in the spectrum of B-25. This also occurs but even more drastically for bands in the 900 – 700 cm^{-1} frequency range, where just a peak is detectable. There is a significant decrease in the absorption of radiation in the region of 1500 – 1200 cm^{-1} . Finally, the bands at 3050 and 2910 cm^{-1} are absent from the spectrum of B-25 and the intensity of the band at 3410 cm^{-1} is lowered. The same spectral features of the B-25 spectrum can be observed for the spectrum of B-100. However, the changes that occurred in comparison to the P3M spectrum were less drastic when the HTT was $100\text{ }^{\circ}\text{C}$. Moreover, the whole spectrum of B-150 resembles that of P3M and only the intensity of the band at 1720 cm^{-1} is apparent.

The above-mentioned spectral modifications clearly show that the ozonation of P3M at 25 and $100\text{ }^{\circ}\text{C}$ for 3 h results in very important changes in the chemical structure of the material. A great part of the oxygen surface functionalities in the ozonated products are those that cause absorption of infrared radiation at 1730 cm^{-1} . This band is compatible with $\nu(\text{C}=\text{O})$ vibrations in monomeric carboxylic acids¹¹ and in lactone type structures.¹³ In a previous FTIR study on the oxidation of amorphous carbon by ozone at 300 K , the direct formation of COOH groups

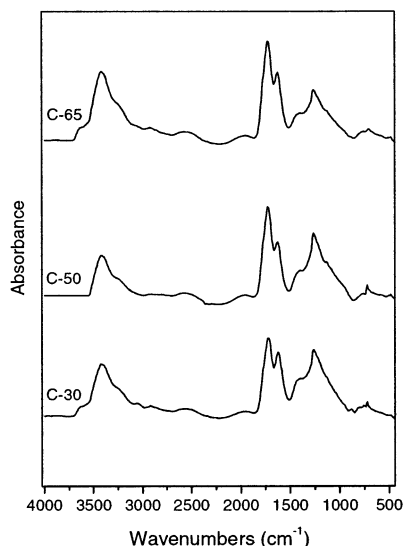


Figure 4. FTIR spectra of the C-series.

was also reported by Mawhinney and Yates¹⁶ on the basis of the spectral appearance of $\nu(\text{O}-\text{H})$, $\nu(\text{C}=\text{O})$, and $\nu(\text{C}-\text{O})$ bands. The carboxylic acid groups and the lactonic structures are probably formed by partial oxidation of aromatic rings, in agreement with the band displacement from 1600 to 1630 cm^{-1} and the important decrease of the intensity of this band. On the other hand, the ether groups (band at 1260 cm^{-1}) are the only oxygen structures of P3M that seem not to be affected by the ozonation treatment.

If one accounts for the practically unchanged spectra of Figure 2 and the above-mentioned new spectral features observed in Figure 3, it can be inferred that ozonation of P3M is strongly time dependent. The kinetic control of the ozonation of this material is likely related to the porous texture, being a mass-transfer-controlled process. In fact, if the diffusion of ozone in pores of the carbon substratum is somehow hindered, the effectiveness of the ozonation treatment increases with larger carbon/ozone contact. The 3 h ozonation treatment of P3M was effective not only at 25 °C but also at 100 °C. This indicates that at a higher temperature the unfavorable effect of ozone decomposition is offset to a certain extent by the greater accessibility of ozone to the porous texture of P3M.

3.2.3. Influence of Ozone Concentration. From the spectra of the samples of the C-series (Figure 4), it follows that the increase in concentration of ozone (C_{O_3}) in the gas stream raises the amount of $\text{C}=\text{O}$ structures. Furthermore, the effect is significantly larger in the C_{O_3} range between 30 and 50 mg/L than between 50 and 65 mg/L, which is in agreement with the weight loss (i.e., 2.50, 5.91, and 6.14% for $\text{C}_{\text{O}_3} = 30, 50$, and 65 mg/L, respectively) produced by the ozonation process of P3M. These results suggest that at high C_{O_3} values the dominant factor over the ozonation is the accessibility to the porosity of the carbon, which is probably hindered by the large concentration of $\text{C}=\text{O}$ structures produced at the earlier stages of the treatment.

3.3. Influence of the Oxidizing Agent. The above results suggest that P3M chemical groups are significantly modified by ozone treatments which are sensitive to variations in temperature, time, and ozone concentration. It is interesting to compare these results with those obtained by treatments of P3M with an aqueous solution of hydrogen peroxide and with oxygen plasma (see

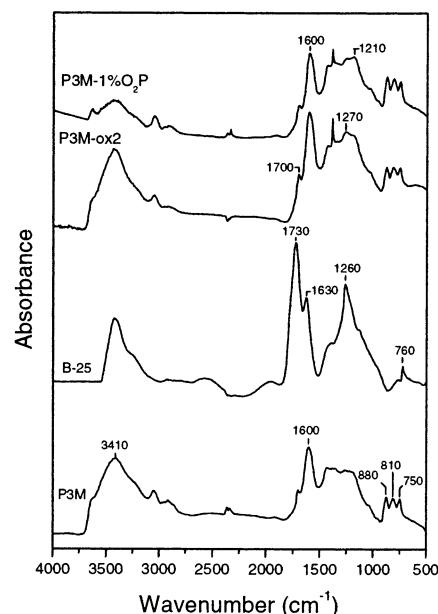


Figure 5. FTIR spectra of the different treatments.

Table 2. Chemical Surface Groups (mequiv g^{-1})

sample	carboxyls	lactones	phenols	basic
P3M	0.161	0.069	0.079	0.194
P3M-ox2	0.163	0.150	0.269	0.201
B-25	2.000	0.171	1.262	
P3M-1%O ₂ P	0.165	0.000	0.072	0.091

Experimental Section). The spectra of the original sample P3M and those obtained by the three treatments (B-25 for ozone) are shown in Figure 5. The spectra of P3M, P3M-1%O₂P, and P3M-ox2 display the same features, which means that the chemical structures of the three samples, regarded as a whole, are quite similar. Nevertheless, the differences in the intensity of the bands at 1210, 1700, and 3410 cm^{-1} suggest a higher concentration of $\text{C}=\text{O}$ groups and ether structures in P3M-ox2 and a lower concentration of OH groups in P3M-1%O₂P. Nevertheless, the most relevant fact in Figure 5 is that the spectrum of sample B-25 shows large differences with respect to those of the other samples. This suggests that the structural changes are very important when ozone is the oxidizing agent. In this case, not only methylene groups and ring substituent groups are transformed but also the aromatic structure of the carbon is affected. In particular, the formation of $\text{C}=\text{O}$ structures is very important as deduced by the very large intensity of the band at 1730 cm^{-1} . It is also noticeable in sample B-25 that the band at 3050 cm^{-1} assigned to $\text{C}-\text{H}$ vibrations in aromatic rings has disappeared and that there are clear modifications in other spectral regions, such as below 900 cm^{-1} .

The differences found by FTIR spectroscopy in the chemical surface nature of the samples have been further investigated by using other experimental techniques such as chemical titrations and TPD. The results of the chemical titrations, collected in Table 2, show that the treatments with hydrogen peroxide and oxygen plasma produce minor changes in the chemical surface group content.

This is probably because the oxidizing character of the former is not large enough ($E^\circ = 1.763 \text{ V}$) and because of the further pyrolysis of the sample at 773 K after the treatment in aqueous solution. On the contrary, in the case of the plasma treatment it accounts for the very strong oxidizing character so that the activation energy to react

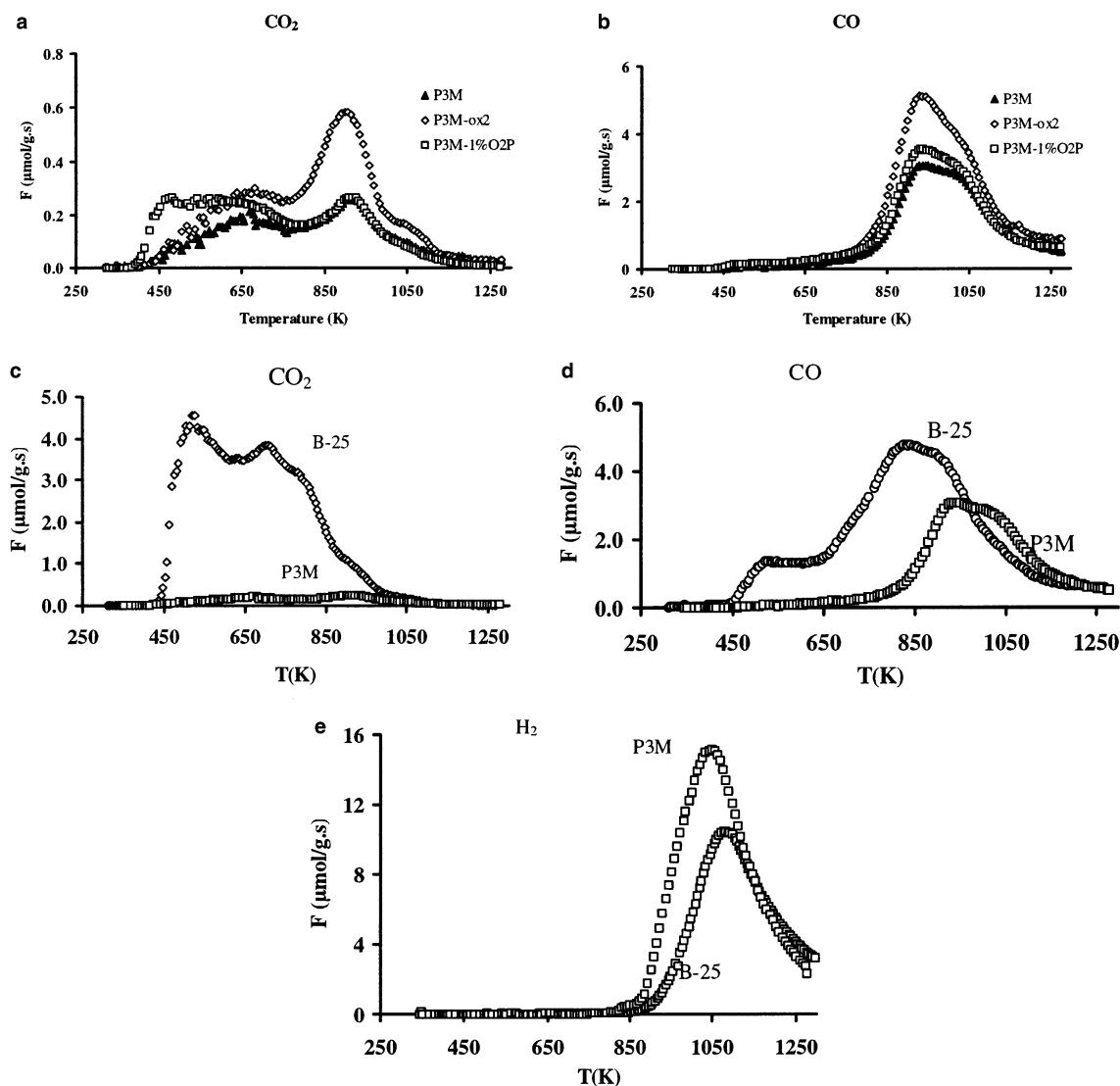


Figure 6. (a,b) TPD-MS profiles. Comparison of P3M, P3M-ox2, and P3M-1%O₂P. (c–e) Comparison of the TPD-MS profiles of P3M and B-25.

with carbon is almost negligible.^{17,18} For this reason, the main result of the reaction between P3M and oxygen plasma consists of the production of CO₂ and CO with a small increase in the fixation of oxygen groups on the surface. These data are in agreement with the results of the FTIR spectra of Figure 5, which show small changes in samples obtained by treatment with hydrogen peroxide and oxygen plasma (Table 2). In contrast with the other treatments, the reaction with ozone introduces a very large amount of acidic groups. This is particularly relevant for carboxyls and phenols, although the amount of lactones is 3-fold larger than in the original sample. This means that the large increase in intensity of the band at 1730 cm⁻¹ (Figure 5) in sample B-25 is probably due to these oxygen-containing groups.

The desorption profiles of CO₂ and CO obtained by TPD-MS are shown in Figure 6a,b for samples P3M, P3M-ox2, and P3M-1%O₂P. The plots show some modifications of the CO₂ and CO profiles of P3M-ox2 and P3M-1%O₂P compared to that of P3M. An increase is seen in the desorbed amount of carbon dioxide at 910 K and carbon

monoxide at 940 K, in particular for sample P3M-ox2. The maximum of the carbon dioxide evolution at 910 K may be attributed to lactones or anhydrides, whereas that of carbon monoxide at 940 K is probably due to phenols.¹⁹ The desorption profiles of sample P3M-1%O₂P are similar to that of P3M except for a small increase in CO₂ desorption at low temperature which was not detected by chemical titration because of the heating precondition for 24 h prior to the analysis. Therefore, the TPD-MS profiles are in agreement with FTIR and chemical analysis data, which support that the treatments with H₂O₂ and oxygen plasma produced small changes in the oxygen-containing groups on the surface of P3M.

Figure 6c–e shows CO₂, CO, and H₂ TPD-MS profiles, respectively, for samples P3M and B-25. It is seen that the increase in CO₂ desorbing groups in sample B-25 (Figure 6c) is very large in a very wide temperature range having two maxima at 550 and 750 K. The temperature of the first one coincides with a maximum in the CO desorption profile (Figure 6d) which suggests the existence of anhydride groups.^{19,20} Nevertheless, the amount of CO₂ desorbed around 550 K is much larger than the CO

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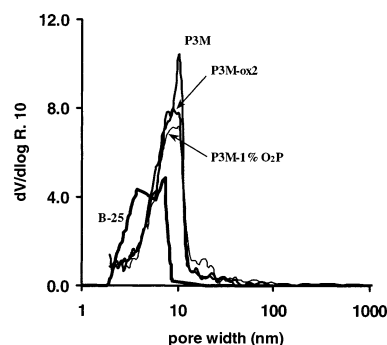
Table 3. Textural Characteristics

sample	V_3 (cm ³ /g)	V_2 (cm ³ /g)	W_0 (cm ³ /g)	S_{N_2} (m ² /g)	S_{CO_2} (m ² /g)
P3M	0.015	0.328	0.165	490	389
P3M-ox2	0.006	0.321	0.179	526	423
B-25	0.000	0.194	0.110	179	290
P3M-1%O ₂ P	0.019	0.368	0.142	449	334

desorbed, which suggests that there is also a large amount of carboxylic groups. In addition, the amount of CO₂ desorbing groups at relatively high temperatures, that is, between 650 and 900 K, is really large and it can be due to lactones and carboxylic groups.^{19,20} According to the data in Table 2, it is likely that most of these should be attributed to carboxylic groups. The CO desorption profile also shows a much larger amount desorbed by B-25 than by P3M. In addition, the profile of B-25 has two maxima at 550 and 850 K. The former has been already assigned to ether groups in agreement with the band at 1260 cm⁻¹ (Figure 5), while the latter is likely due to carbonyl and phenol groups in agreement with the data in Table 2. In contrast to the CO₂ and CO desorption profiles, the desorption of H₂ (Figure 6e) shows a smaller amount desorbed by B-25 than by P3M, which should be partially linked to the disappearance of the band at 3050 cm⁻¹ assigned to C–H vibrations and the large modifications in the 1430–1210 cm⁻¹ frequency range shown in Figure 5.

The surface areas and pore volumes of the samples are collected in Table 3. Regardless of the sample, the macropore volume V_3 ($\varnothing \geq 50$ nm in width) is negligible in any case. In the mesopore region, the volume V_2 ($3.6 \leq \varnothing \leq 50$ nm) in sample B-25 is clearly smaller than that of P3M and remains almost unchanged in samples P3M-ox2 and P3M-1%O₂P with respect to P3M. This can also be seen in the pore size distributions obtained by mercury porosimetry (Figure 7), which shows minor changes in samples obtained by H₂O₂ and oxygen plasma. However, a significant decrease and the shift of the maximum of the distribution in B-25 are apparent. The micropore volume, W_0 , obtained from the CO₂ adsorption isotherm also shows minor changes for samples P3M-ox2 and P3M-1%O₂P compared to P3M and a clear decrease for sample B-25. Then the data of the pore volumes point out that only the treatment with ozone produces significant changes in the pore network which should be related with the same reason argued above in relation to the chemical group modifications.

The surface areas measured by N₂ and CO₂ again show small modifications on samples obtained by treatments with H₂O₂ and plasma, but a significant decrease in S_{N_2} and S_{CO_2} in sample B-25 is seen. Moreover, in this sample $S_{N_2} < S_{CO_2}$, which suggests that there are constrictions which partially hinder the access of nitrogen at 77 K to the micropores.²¹ These could be produced by the large amounts of oxygen groups which have been fixed as a consequence of the treatment with ozone. It is known that the fixation of the chemical groups tends to be produced in the border of the entrance of the micropores as they are the most energetic sites.²² For these reasons, the surface areas of sample B-25 were also measured after the partial elimination of the chemical groups. For this purpose, the

**Figure 7.** Macro- and mesopore distributions.

sample was heated in He flow (in the same conditions of the TPD–MS experiments) at 550 and 750 K (Figure 6c,d) before the adsorption measurements. The N₂ and CO₂ surface areas after heating at 550 K are 180 and 298 m²/g for N₂ and CO₂, respectively. These values are almost coincident with those in Table 3, which means that the evolved oxygen chemical groups at 550 K did not hinder the access to the micropores. Nevertheless, the surface areas after heating at 750 K are 341 and 398 m²/g for S_{N_2} and S_{CO_2} , respectively. The new value of S_{CO_2} is coincident with that of P3M, suggesting that the chemical groups evolved at this temperature produce constrictions in the micropore network. This supports that the chemical groups partially hinder the nitrogen access to the microporosity and also the above suggestion (Figure 4) that the high O₃ concentration (65 mg/L) does not largely increase the fixation of the oxygen chemical groups because the previous fixed functionalities hinder the access of the reactive species. Moreover, this is in agreement with the previous suggestion in relation to the maximum at 750 K in Figure 6c which was assigned to highly stabilized oxygen groups (in the border of the pores). Also, even after the treatment at 750 K the N₂ surface area is smaller than that of CO₂, which means that there are still very stabilized oxygen chemical groups (Figure 6c) which partially hinder the access of this molecule. All these data seem to suggest that the ozone treatment at 25 °C for 3 h produces minor changes in the textural characteristics of the sample P3M although the chemical surface groups are largely increased. This is an interesting result as in many cases (i.e., molecular sieves) the aim is to preserve the network structure of the adsorbent and to increase the chemical functionalities which can act as active centers.

4. Conclusions

The ozonation of P3M is sensitive to the increase in temperature and time. The former has an unfavorable effect on the ozonation process for a shorter time, which has been associated with the thermal instability of ozone. The latter produces strong changes in the chemical structure of the material, provided that the temperature is 25 or 100 °C. A longer treatment results in a large extent of formation of C=O-containing structures from the aromatic structure of P3M. The products prepared at such temperatures also contain large amounts of C=C bonds in olefinic structures. However, ether type structures are not affected by the ozonation treatment. Ozone has proved to be a much more effective oxidizing agent than H₂O₂ and oxygen plasma. It is able to react even with the aromatic structure of the carbon. As a consequence, the amounts of oxygen groups introduced by ozone are much larger than those fixed by the other treatments. This higher effectiveness of the ozonation process in comparison to the other oxidizing treatments can have very important

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applications in those systems where chemical interactions at the surface level are involved. Particularly, the modification of the surface chemistry of carbon materials is critical to their use as catalysts and catalyst supports, and also this plays a very important role in binding carbon materials to organic resins in composite matrixes. The textural characteristics of the sample are not changed by H_2O_2 or plasma, while ozone produces modifications in mesoporosity and in surface area. However, the latter seem

to be caused by the fixation of the oxygen functionalities which partially hinder the access of the adsorbates.

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