CHARACTERIZATION OF OXYGEN PLASMA-TREATED ACTIVATED CARBON

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Introduction

Plasmas offer an attractive alternative to more traditional methods for the surface modification of carbon fibers, mesocarbon microbeads, graphites, glassy carbons and carbon blacks. However, to the authors' knowledge, no previous work has been reported on the plasma surface modification of activated carbons, which could result in improvements in their performance as adsorbents and/or catalyst supports. An objective of this work was to explore the use of oxygen plasma to modify the porous texture and/or the surface chemistry of activated carbons. A second one was to establish the degree of access of the oxygen plasma to the porous network of activated carbons.

Experimental

The starting material was a commercial powdered activated carbon (Acticarbone 3S, from CECA-ATO), manufactured by steam activation of maritime pine wood, with the following producer's specifications: ash content, 3 wt.%; methylene blue index, 18; iodine index, 135; BET surface area, 1150 m^2g^{-1}. 1 g samples, ground to <63 μm, were exposed to an oxygen plasma in a Technics Plasma 200-G apparatus, working always under identical conditions (2.450 GHz, 150 W, 1 mbar, 19.9 mg cm^{-2}) while varying the time of exposure to attain a wide range of burn-off (b.o.) degrees (3.12 to 40.90 wt%).

Adsorption isotherms of N_2 (77 K) and CO_2 (273 K) were measured using a NOVA-1200 and various AUTOSORB volumetric gas sorption analyzers from Quantachrome (USA). Electrokinetic potentials (zeta potentials) were determined using a Laser Zee Meter 501. Point of zero charge values were measured following a method proposed by León y León et al.[1]. A Krüss Automatic Contact Angle Meter, model G1/G402, was used for measuring the advancing contact angles of water.

Results and Discussion

Figure 1 shows N_2 adsorption-desorption isotherms on fresh and plasma-treated samples. There is a small decrease in N_2 adsorption with increasing b.o. It was checked that the surface exposure of increasing amounts of low surface area (16 m^2g^{-2}) inorganic matter does not justify alone this decrease. As Table 1 shows, the BET surface area (S_{BET}) decreases from 1050 m^2g^{-1} (fresh

material) to 917 m^2g^{-1} (40.90% b.o.), as do the total pore volumes as established from adsorption at a relative pressure of 0.99 ($V_{P/P0\,=0.99}$). Micropore volumes calculated from the linear portion of the Dubinin-Radushkevich plots (V_{D-R}), also given in Table 1, decrease slightly as well upon plasma treatment. Adsorption isotherms of CO_2 at 273 K on the same samples were practically coincident at low relative pressures, but at higher relative pressures there was a small decrease in adsorbed amount with increasing b.o. As a consequence (Table 1), both D-R micropore volumes (V_{D-R}) and micropore surface areas ($S_{\mu p}$) decreased slightly with increasing b.o. The micropore width (L_0) changed little as a function of the b.o.
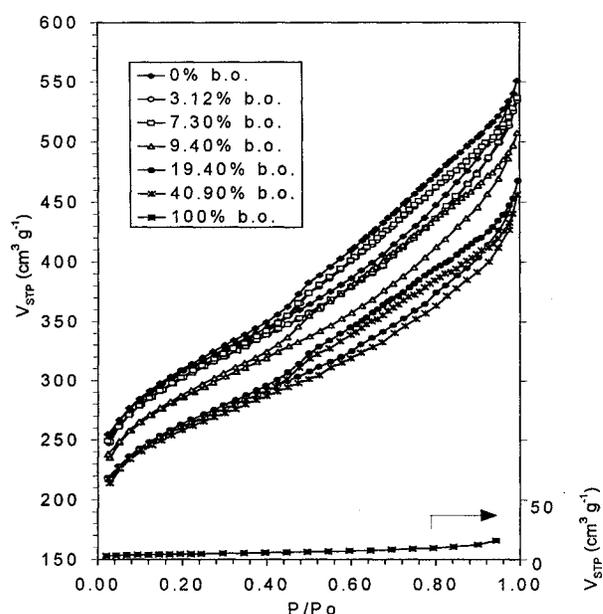

Figure 1. Adsorption isotherms of N_2 at 77 K on fresh and plasma-treated activated carbon samples.

The decrease in surface area with increasing b.o. can be attributed to gasification of carbonaceous matter constituting the pore walls, so that pores are widened and their contribution to the surface area becomes smaller. The small but gradual decrease in N_2/CO_2 surface area ratios from ca.

1.22 (fresh material) to 1.16 (40.90% b.o.) suggests that, as the b.o. increases, either mesopores/large micropores are lost, or small micropores are created. Given that, according to Table 1, the volume of small micropores remains fairly constant while the total pore volume decreases significantly with increasing b.o., the parallel decrease in surface area must be due to loss of mesopores or large micropores with little effect on the small micropores.

Table 1.Textural parameters of activated carbon samples.

b.o. (%)	N₂, 77 K			CO₂, 273 K		
	S_{BET} $(m^2\,g^{-1})$	$V_{P/P^o=0.99}$ $(cm^3\,g^{-1})$	V_{D-R} $(cm^3\,g^{-1})$	V_{D-R} $(cm^3\,g^{-1})$	$S_{\mu p}$ $(m^2\,g^{-1})$	L_0 (nm)
0	1050	0.852	0.427	0.3695	858	1.634
3.12	1022	0.826	0.415	0.3664	851	1.645
7.30	1021	0.830	0.415	0.3673	853	1.638
9.40	1010	0.785	0.408	0.3598	835	1.633
19.40	955	0.724	0.392	0.3517	817	1.628
40.90	917	0.706	0.374	0.3412	792	1.626

Zeta potential-pH curves of the fresh and plasma-oxidized samples are shown in Figure 2. The untreated carbon exhibits an isoelectric point (IEP) at a pH≈3.5, and the negative value of the zeta potential increases monotonically with the suspension pH evidencing that adsorption of ions from the suspension occurs. The IEP is known to provide an estimate of the acidity of the solid surface, which increases as the IEP is shifted to lower pHs; based on this, the plasma oxidation treatment of the activated carbon clearly increases its acidity, especially at low burnoffs. However, at b.o.'s ≥10 wt% it remains practically constant (Fig. 2). It would seem that, after a certain time of plasma treatment, the formation by oxidation of acidic groups on the surface of the activated carbon occurs at the expense of their uptake by burning. Interestingly, an increase in the negative value of the zeta potential at acidic pHs, attributed to the formation of acidic groups at the surface, was also reported by Esumi et al.[2] after oxygen plasma treatment of mesocarbon microbeads.

Point of zero charge (PZC) measurements showed an identical value of 10.2 for the fresh and 3.12% b.o. samples. Unlike the IEP, the PZC accounts for the total surface charge (external and internal) of the particles. Therefore, the PZC-IEP difference has been suggested[3] to provide a measure of the surface charge distribution of the porous carbon. Then, these two samples, with PZC-IEP differences of 6.7 and 8.9, respectively, have more negatively charged external than internal surfaces. The oxygen plasma treatment progressively increased the PZC-IEP difference, this result evidencing a preferential oxidation of the external surface. The internal surface of the untreated activated carbon preserves, however, a net basic character after oxygen plasma treatment.
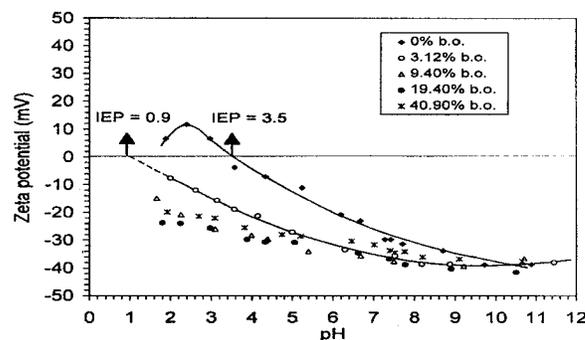

Figure 2. Zeta potential of fresh and plasma-treated samples as a function of the suspension pH.

The activated carbon studied did not agglomerate to form pellets with a flat surface. To overcome this limitation, contact angles were measured on the surface of compressed discs prepared from a mixture of sample and AgI (binder). The contact angles on the surfaces of these discs exhibit similar values for the fresh material (43.6±2.0 deg) and samples plasma-treated to b.o.s of 3.12 (42.6±1.2 deg) and 40.90 wt% (40.3±2.8 deg). Possible explanations for this lack of variation are either that the measurement of the contact angle with water is not sensitive enough to detect the changes associated with the oxygen plasma treatment, or that there was some artifact during the preparation of the samples.

Conclusions

Textural characterization (N₂/77 K and CO /273 K) evidences moderate decreases in surface area and pore volume following the oxygen plasma treatment. Oxygen plasma-treated samples have more negatively charged external than internal surfaces, *i.e.*, preferential oxidation of the external surface takes place with formation of acidic functional groups. The limit to the penetration of the oxygen plasma into the porous network of activated carbons seems to lie at the meso-supermicropore level, the reaction progressing according to the "contracting sphere" model of gas-solid reactions[4].

References

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