

FURTHER INSIGHTS INTO THE BASICITY OF CARBONS

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INTRODUCTION

The presence of oxygen on a carbon surface is known to have a profound influence on the behavior of this material as an acid or a base [1]. This in turn is crucial for the effectiveness of carbons as catalyst supports [2] and liquid-phase adsorbents [3]. However, carbon basicity is not only a consequence of the balance between acidic (e.g., carboxyl, phenol and lactone groups) and basic (e.g., pyrone and chromene-like structures) oxygen-containing groups and/or other surface groups with different heteroatoms. In fact, it has been shown [4,5] that the π -electrons within the graphene layer of a carbon material behave as a Lewis base. In the present work, we provide evidence that oxygen-free sites at the edges of the basal planes can also be important Lewis-base centers and we discuss the relative importance of these two kinds of sites in defining the basic character of carbon materials.

EXPERIMENTAL

A commercial activated carbon, Norit C-granular (Nc) was used as the starting material. Samples H950 and N950 were prepared by heating Nc to 950 °C at 25 °C/min for 3 h in a flow (150 mL/min) of ultra-high-purity H₂ or N₂, respectively. These samples were further heat-treated in a graphitization furnace in an inert atmosphere at 1800 and 2600 °C. (The corresponding sample designations are Nc/1800, H950/2600, etc.) Except for the microcalorimetric tests (see below), samples were exposed to ambient atmosphere and were stored for several days without taking any precautions prior to their characterization.

X-ray diffraction analyses were carried out using a Philips diffractometer. The parameters L_c and L_a , roughly corresponding to crystallite height and width, were estimated from (002) and (100) peaks, while the d-spacing between the graphene layers was determined from the (002) peak.

The point of zero charge (PZC) was determined by mass titration [6]. Elemental analysis was determined using a LECO CHN-600 instrument; oxygen content was estimated by difference.

Microcalorimetric tests were performed in a

Calvet-type apparatus [7]. Samples H950 and N950 were first prepared *in situ* and then gravity-transferred to the adsorption cell (avoiding any contact with atmospheric O₂); they were subsequently evacuated for 24 h at 10⁻³ Torr. The amount and type of the active sites left on the surface of the carbons after treatment was titrated by adding sequentially known doses of O₂ at 30 and 150 °C. Oxygen adsorption isotherms, as well as plots of heats of O₂ adsorption vs. surface coverage, were obtained from these experiments.

RESULTS AND DISCUSSION

The PZC data, the results of chemical analyses and structural parameters obtained from the XRD analyses are shown in Table I. As shown in previous work [8], treatment in H₂ is much more effective than that in N₂ for passivating the carbon surface against O₂ adsorption; it does so by eliminating the most reactive carbon sites. Thus, upon atmospheric exposure, carbon N950 has a higher oxygen content than H950. On the other hand, most of the O-containing surface groups are of acidic nature; hence carbon H950 possesses a higher PZC than N950.

The basic character of H950 could be due, at least in part, to the presence of some O-containing basic groups. However, as its oxygen content is very low (molar O/C is ~0.002), the basicity of this carbon comes from the Lewis-base character of the basal plane [4,5] and of O-free edge sites.

Microcalorimetric studies show the presence and importance of the O-free edge sites. Indeed, samples H950 and N950 contain some active sites that adsorb oxygen only at an elevated temperature (see Figure 1). These sites, which are stable at room temperature, have adsorption energies <70 kcal/mol and they are very similar in both energies and amount for N₂- and H₂-treated carbons. In contrast, sites of higher adsorption energies were eliminated during the treatment with hydrogen; indeed, the microcalorimetric fingerprint of H950 does not show the presence of such active sites [8].

The stable O-free edge sites have been postulated to be divalent, s²p²-hybridized in-plane σ pairs, with localized π electrons [8,9]. The

electron density of these sites makes them Lewis-base centers in the presence of Lewis acids.

Treatments at very high temperature (e.g., 1800 and 2600 °C) also destroy the sites of high adsorption energies, by surface annealing [10], yielding carbons with very low or virtually null (samples treated at 2600 °C) oxygen content, even upon air exposure. The acidic or basic character of such samples should, therefore, be governed by the structure of the carbon and not by its oxygen-containing groups. In this context, a very significant result is the lower PZC value for samples subjected to 2600 °C than for those subjected to 1800 °C. The existence of this PZC maximum can be explained by

postulating that at high temperatures (e.g., >1800 °C) the observed basicity is a result of 'competition' between Lewis-base-type edge sites and Lewis-base basal plane sites. The concentration of the former is known to decrease with increasing size of the graphene layers (see Table I). This appears to have a dominant effect on carbon basicity. The concomitant increase in the concentration of basal plane sites is not sufficient compensation [11]. Also, the accompanying increase in the degree of π - π overlap, as the d-spacing decreases, appears to contribute to a decrease in the basic character of the Lewis-base basal plane sites.

Table I. Points of zero charge, chemical analyses and structural parameters of the carbons.

Carbon	PZC (pH units)	Chemical Analyses ⁽¹⁾				Structural Parameters, Å		
		wt% C	wt% H	wt% N	wt% O ⁽²⁾	d ₀₀₂	L _c	L _a
Nc	2.5	82.3	2.3	0.3	15.1	3.78	9.0	nd
N950	5.2	94.2	0.6	0.6	4.6	3.78	10.8	30.4
H950	9.0	99.0	0.4	0.3	0.3	3.78	10.1	35.4
Nc/1800	8.9	99.6	< 0.01	0.2	0.2	3.68	11.1	41.7
N950/1800	8.8	nd	nd	nd	nd	3.68	10.3	40.5
H950/1800	8.5	99.7	< 0.01	0.2	0.1	3.68	11.3	48.6
Nc/2600	7.6	100	< 0.01	< 0.01	< 0.01	3.44	18.1	52.0
N950/2600	7.5	100	< 0.01	< 0.01	< 0.01	3.44	18.1	62.4
H950/2600	7.2	nd	nd	nd	nd	3.44	20.4	78.2

(1) dry and ash-free basis; (2) obtained by difference; nd = not determined.

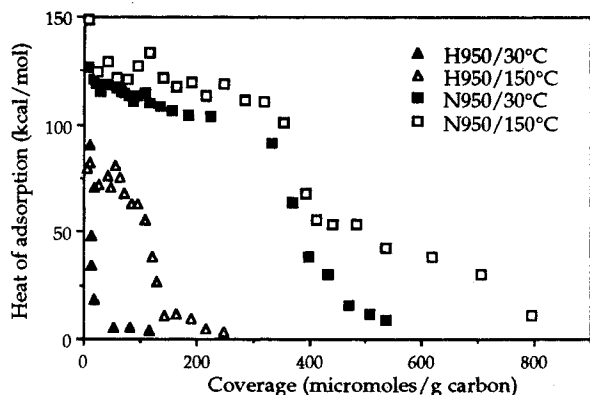


Figure 1. Surface coverage dependence of differential heats of O₂ adsorption at 30 and 150 °C.

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