Textural and chemical characterization of microporous carbons

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Abstract

Several methods for the characterization of the porous texture (adsorption of vapors and gases, immersion calorimetry) and chemical nature—mainly oxygen surface groups (selective titration and temperature programmed desorption) of activated carbons are analyzed. The results for several series of activated carbons show that a simple and convenient evaluation of volume of micropores and heterogeneity of the micropore size distribution can be obtained by combining the results from adsorption of N_2 at 77 K and CO_2 at 273 K. On the other hand, for microporous carbons the micropore size distribution obtained by adsorption and immersion calorimetry are very coincident. It has been found for carbons oxidized with different chemicals that there is a correlation between selective titration and TPD. Finally, the relative importance of the porous texture and oxygen surface groups of activated carbon on the adsorption capacity and enthalpy of immersion for molecules with different polarity has been evaluated, and it has been shown that the specific interactions between the polar molecules and the surface groups play an important, although not exclusive, role in both adsorption and immersion. In the case of non-polar molecules, only the porous texture of the carbon conditions the amount adsorbed and the enthalpy of immersion. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Activated carbon; Microporosity; Functional groups; Adsorption; Immersion calorimetry

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1. Introduction

Microporous carbons are a very important class of materials, the best known of which is activated carbon due to its wide range of applications and the large world annual production (around 400 000 tons). Activated carbons are used for gas- and liquid-phase adsorption processes because they have large internal surface areas which are the result of the activation process [1−4].

A characteristic feature of activated carbons is the large internal surface located within a network of narrow pores, where the bulk of the adsorption takes place. The adsorption energy is greatly enhanced in narrow pores; for ideally slit-shaped pores having a width of two molecular dimensions, the potential energy of adsorption is approximately twice as large as on a flat graphite surface [5]. The size and shape of the narrow pores also play a role in the selectivity of adsorption through molecular sieve effects.

Like many other carbons, microporous carbons also contain chemically active centers, responsible for specific interactions and whose distribution within the structure is of great importance from the point of view of their practical use in adsorption processes [6]. Most of the characterization of activated carbons was centered in the past around the physical structure, mainly the porosity, by adsorption techniques, but it is now widely accepted that a complete characterization of adsorbent carbons must include their chemical structure.

After a description of the physical and chemical structure of microporous carbons (mainly activated carbons), this report presents a set of results for different series of carbons deduced from physical adsorption of vapors and gases coupled with immersion calorimetry, which are complemented with data on their chemical structure. These results provide a complete characterization of the carbons and explain their adsorptive behavior in respect of different types of molecules.

2. The structure of microporous carbons

Porous carbons are a non-graphitic class of carbon, characterized by internal surface areas ranging from 500 to over 3000 m^2/g. Non-graphitic carbons are

divided into two categories, the graphitizable and non-graphitizable carbons [7]. The non-graphitizable carbons, also called chars, constitute carbonization products from wood, fruit shells, brown coals, lignites and highly volatile bituminous coals [8]; these materials do not pass through a fluid phase during pyrolysis and carbonization. Activated carbon, the best known example of porous carbon, is derived from chars which have been partially gasified with steam or carbon dioxide to increase their porosity; alternatively, chemical activation of the precursor with a chemical such as zinc chloride, phosphoric acid, etc. is another important industrial process for the manufacture of activated carbons.

Porous carbons are constituted by imperfect sections of graphitic lamellae of small size, which are crumpled and have many structural defects, bonded together to create a three-dimensional network, the spaces between them constituting the carbon porosity, as shown in Fig. 1 [9]. The variations in size, shape, deformation and cross-linking among the lamellae not only cause differences in porosity, but also in physical properties such as bulk density, hardness, etc. The porosity is classified into three groups [10]: micropores (width less than 2 nm); mesopores (width between 2 and 50 nm) and macropores (width greater than 50 nm). Micropores contribute most to the high surface areas of activated carbon and provide high adsorptive capacities for molecules of small dimensions such as gases and most solvents. Mesopores are important for the adsorption of larger molecules and, together with macropores, are transport pores to the interior of the particles and microporosity.

Microporous carbons can be produced from almost all naturally occurring organic materials, which are three-dimensional polymeric or macromolecular networks composed of cellulose and lignin associated with their botanical morpholo-
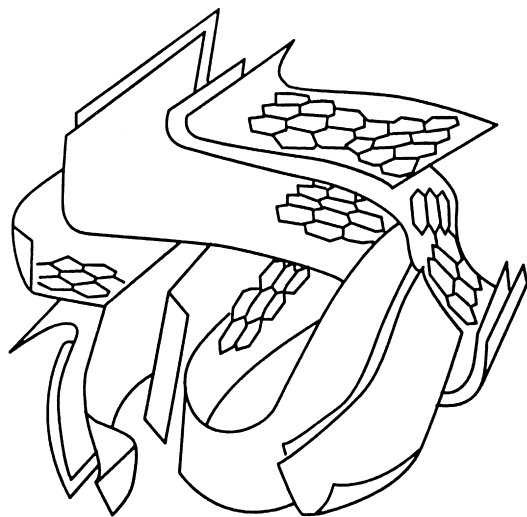

Fig. 1. Schematic representation of the structure of activated carbon.

gies. During pyrolysis (also called primary carbonization, heat treatment up to 600°C) and carbonization (also called secondary carbonization, heat treatment above 600°C) a large change in the polymeric network is produced. In the typical case of cellulosic precursors, the material loses small volatile molecules such as water and carbon dioxide together with a series of aliphatic acids, carbonyls, alcohols, etc. in the temperature range up to 600°C. There is an increase in C/H and C/O ratios and as the temperature increases within the carbonization range the network becomes more carbonaceous and more aromatic, with formation of clusters of six-membered ring systems randomly bonded. It is the spaces between these bonded clusters which constitute the microporosity of the char.

The char obtained by carbonization of cellulosic materials and coal is essentially microporous, but the microporosity may become filled or partially blocked with the tars and other decomposition products. In order to increase the volume of this microporosity further, gasification of carbon material is needed. This is usually accomplished by reaction with steam or carbon dioxide above 800°C, by which the gas molecules penetrate the interior of the char particle to remove carbon atoms. The activation conditions are critical since the removal of carbon atoms must be internal in order to increase the micropore volume; external gasification has to be avoided because this is a simple removal of external carbon atoms without any increase in porosity. This means that the gas molecule (carbon dioxide or water) needs to penetrate through the char porosity and to orientate itself so that the oxygen atom is transferred and bonded to the carbon atom of the char network and the resultant carbon monoxide molecule (after decomposition of the oxygen surface group) has subsequently to be desorbed from the network [11,12].

Different experimental techniques such as X-ray and HRTEM (high resolution transmission electron microscopy), coupled with adsorption experiments with molecules of various sizes and shapes, have confirmed that the structure of microporous carbons such as activated carbon consist of aromatic sheets and strips resembling a mixture of wood shavings and crumpled paper with spaces—micropores—between them. The micropores may be considered, locally at least, as slit-shaped [13]. Dark-field HRTM micrographs of activated carbons indicate local parallelism between the aromatic sheets and strips, but this does not necessarily apply to all pores [14].

Although the microporosity is the main reason for the large adsorptive capacity of porous carbons such as activated carbon, the chemical composition of the surface also plays an important role in the adsorption behavior. Activated carbon is invariably associated with appreciable amounts of heteroatoms such as oxygen and hydrogen chemically bonded to the structure, and with inorganic ash components.

Oxygen surface groups are by far the most important in influencing the surface characteristics and adsorption behavior of activated carbon, and as such they have attracted much attention in the last few years [2]. Their role in activated carbon adsorption properties will be shown in a later section. However, basic information on their formation and structure will be presented first.

At the edge of the basal planes of carbon atoms in the structure, where bonding in the plane is terminated, there are unsaturated carbon atoms. These sites are
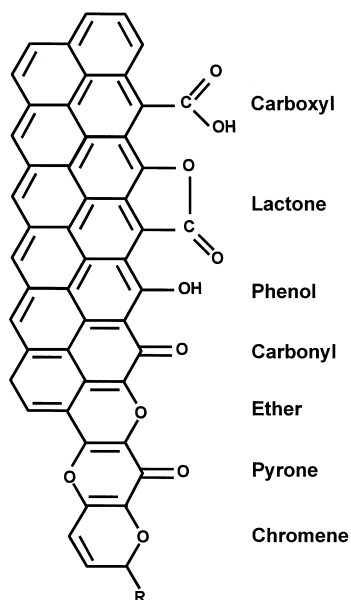
Fig. 2. Examples of oxygen functional groups on carbon surfaces.

associated with high concentrations of unpaired electrons and, therefore, play a significant role in the chemisorption of oxygen. When molecular oxygen is introduced to an outgassed carbon surface, it is either physically (reversibly) or chemically (irreversibly) adsorbed on the surface. Which predominates depends mainly on temperature; as the temperature is increased, the chemisorption of oxygen increases and the molecules dissociate into atoms that react chemically with the atoms of carbon to form oxygen surface compounds [15].

Carbon−oxygen surface complexes can also result from reaction with many other oxidizing gases (ozone, nitrous oxide, nitric oxide, carbon dioxide, etc.), and with oxidizing solutions (nitric acid, sodium hypochlorite, hydrogen peroxide, etc.), allowing the modification of the nature and amount of oxygen surface complexes of a given carbon.

The precise nature of carbon−oxygen structures is not entirely established but the results of many studies using different experimental techniques conclude that there may be several types of oxygen functional groups, as shown in Fig. 2 [16]; the presence of these surface groups gives activated carbons an acid-base character.

Although the study of the chemistry of these carbon surfaces has for the most part involved indirect methods of investigation, such as selective neutralization and temperature programmed desorption, it could be ascertained that carbons have on their surface oxygen surface groups with various acidities [16]. Thus, the selective neutralization studies carried out by Boehm [17] on several carbons suggested that $NaHCO_3$ neutralized carboxylic acid functionalities, Na_2CO_3 neutralized both

carboxylic acids and lactone and NaOH neutralized carboxylic acids, lactone and phenols.

On the other hand, temperature programmed desorption carried out on carbons show that the oxygen surface groups decompose upon heating, the evolved gases consisting mainly of CO_2 at lower temperatures and predominantly CO at higher temperatures. Tremblay et al. [18] suggested that CO_2 evolution is due to the decomposition of surface carboxyl and lactone, while decomposition of carbonyl, quinone and anhydride groups are responsible for CO evolution. More details about temperature programmed desorption of surface groups will be given in another section. The exact nature of these surface groups has been investigated further by studying specific chemical reactions and by spectroscopic techniques [6,15–17], and there is general agreement on the following two facts: (i) there is a variety of acidic functionalities with different acid strengths, especially quinone, phenols and carboxyl groups, and (ii) the acidity of a carbon generally increases with its oxygen content.

Basic functionalities have not received as much attention as acidic groups, but oxygen-containing and oxygen-free basic sites have been postulated to coexist on carbon surfaces [19]. However, one of the reasons why not enough information is available on the nature of basic groups is the lack of adequate evaluation methods for basic groups.

3. Textural characterization

Adsorption of gases and vapors is one of the most widely used techniques for the characterization of microporous carbons [20]. The first step is obtaining the adsorption isotherm and then to quantify the pore volume (or surface area) by application of different methods such as Dubinin-Radushkevich [21], BET [22], or α_s [5]. Alternatively a technique such as n-nonane preadsorption can also be used [5]. However, the determination of the micropore volume is not straightforward since the results are a function of both the method used to analyze the adsorption isotherm and the adsorptive selected, because the micropore filling mechanism is conditioned by the pore width/molecular dimension ratio (d_p/σ) and not by the absolute value of the pore width [5]. Consequently, a good approach would be to use the adsorption of various adsorptives and to apply different approximations to a series of microporous carbons with gradual evolution of pore dimension. This is the approach used here because it not only permits a check of the different methods applicable, but also of the strategy needed for the evaluation of the microporosity of porous carbons such as activated carbon.

There is one series of activated carbons which has been very thoroughly characterized, series D [23–29]. It was prepared by carbonization of olive stones and further activation at 825°C under a flow of carbon dioxide to cover a wide range of burn-off (8–70%, value included in the nomenclature). The porous nature of the char, constituted by narrow and uniform micropores, partly blocked by some tarry substances [30], and the activation process used (slow gasification rate), in

which the creation of microporosity predominates in the first stages of the process and widening of porosity at medium-to-high burn-off, provides a series of carbons ranging from almost exclusively microporous, with narrow and uniform pore width, to carbons with very high micropore volume and wide and heterogeneous micropore size distribution.

Table 1 includes the values for micropore volume of some carbons of series D, deduced by different experimental methods:

1. physical adsorption of N_2 at 77 K. The analysis of the adsorption isotherms was carried out by application of the Dubinin-Radushkevich (DR) equation, $V_0(N_2)$, and the α_s method (using a non-porous carbon of the same nature as standard reference [31]), V_α,
2. adsorption of CO_2 at 273 K and analysis of the adsorption isotherm by application of the DR equation, $V_0(CO_2)$,
3. preadsorption of n-nonane. n-Nonane is used to fill the micropores of the carbon before carrying out the adsorption of N_2 at 77 K. The difference between the total adsorption isotherm of N_2 at 77 K on the clean and preadsorbed carbon yields the micropore volume, $V(NP)$. An additional value has been deduced, V_n, corresponding to the volume of n-nonane retained by the carbon after outgassing at room temperature, before carrying out the adsorption of N_2 at 77 K.

The similarity of results for carbons such as D-8 and D-34 indicates that when the microporosity of these two carbons is narrow and uniform all theoretical and experimental approaches used are equally valid to determine the microporosity of activated carbon. There are only small differences in the values of V_n, which are slightly lower than $V(NP)$ because n-nonane is not filling all micropores but is blocking the entrance of some of them; this would not affect the value of $V(NP)$ but would yield low values of V_n. In fact, the difference is larger for the carbon with narrower microporosity, D-8, as expected.

For carbons with large burn-off (e.g. D-70), for which the pore size distribution is wider and more heterogeneous, it is possible to distinguish two sets of experimental values. The DR equation and the α_s method for the adsorption of N_2 at 77 K give similar values of micropore volume, which are larger than the values deduced from the adsorption of CO_2 at 273 K and n-nonane preadsorption. In this type of carbon there is an overlapping between the primary micropore filling taking place in narrow micropores (involving the interaction of individual molecules with the wall

Table 1
Micropore volume (cm^3/g) of activated carbons

Carbon	$V_0(N_2)$	V_α	$V_0(CO_2)$	$V(NP)$	V_n
D-8	0.26	0.25	0.26	0.26	0.16
D-34	0.39	0.39	0.36	0.38	0.31
D-70	0.67	0.64	0.48	0.52	0.47

of the pore of molecular dimensions—in the range $d_p = \sigma - 2\sigma$) and the secondary micropore filling occurring in wider micropores (pore width $d_p = 2\sigma - 5\sigma$), involving nitrogen−nitrogen interactions (but no capillary condensation). There is not a clear frontier between primary and secondary micropore filling, as denoted by the curvature of the DR and α_s plots for carbon D-70 [26].

The results of Table 1 for $V_0(N_2)$ and V_α, together with the values of micropore volume obtained by application of the DR equation to the adsorption isotherms of vapors such as benzene, cyclohexane, 2,2-dimethylbutane and iso-octane for the same series of carbons [25,26], show that the values of $V_0(N_2)$ and V_α can be associated to the total volume of micropores of the carbon, this including narrow and wide micropores.

The second set of values for carbon D-70 is constituted by $V_0(CO_2)$ and $V(NP)$ or V_n, and they are lower than $V_0(N_2)$ and V_α. If one takes into account that the range of relative pressure used in the adsorption of CO_2 at 273 K is very low (up to about 0.03 if the adsorption is carried out up to atmospheric pressure) the adsorption will be limited to the primary micropore filling in narrow micropores and consequently $V_0(CO_2)$ will be the volume of narrow micropores. On the other hand, the fact that the n-nonane preadsorption, when n-nonane is so strongly adsorbed in the microporosity that is not eliminated by outgassing at room temperature before the adsorption of N_2 at 77 K, gives the same value of micropore volume as the adsorption of CO_2 at 273 K is a further test of the validity of $V_0(CO_2)$ as a measure of the narrow microporosity. This means that a simple and convenient evaluation of the microporosity of activated carbons can be carried out by analysis of the adsorption isotherms of N_2 at 77 K and CO_2 at 273 K, since both provide complementary information of the micropore volume and the heterogeneity of its pore size. This approach, proposed by Rodríguez-Reinoso and coworkers some years ago [24], is widely used in the characterization of activated carbons.

Various attempts have been made to employ physical adsorption of vapors and gases for the evaluation of the micropore size distribution of porous carbons. The most direct approach would be to use a selection of molecular probes of different size and shape. Fig. 3 includes plots of micropore volume obtained by application of the DR equation to the adsorption of n-butane and iso-butane at 273 K and benzene, 2,2-dimethylbutane and iso-octane at 298 K, as a function of the minimum molecular dimension, for all carbons of series D. As a reference, the micropore volumes deduced from the adsorption of N_2 at 77 K, have been included for each carbon. The volume of micropores for carbon D-8 is small and decreases with increasing dimension of the adsorptive molecule, showing a clear molecular sieve effect for the larger molecules. The lack of accessibility of 2,2-dimethylbutane and iso-octane as compared with smaller molecules, the large equilibrium time needed to reach adsorption equilibrium for all adsorptives, and the smaller values deduced from the preadsorption of n-nonane (see Table 1) confirm the narrow pore size of this carbon. There is also a small molecular sieving effect for carbon D-19, which is not found in any of the other carbons with larger burn-off. For samples D-34, D-52 and D-70 all adsorptives give a similar value of micropore
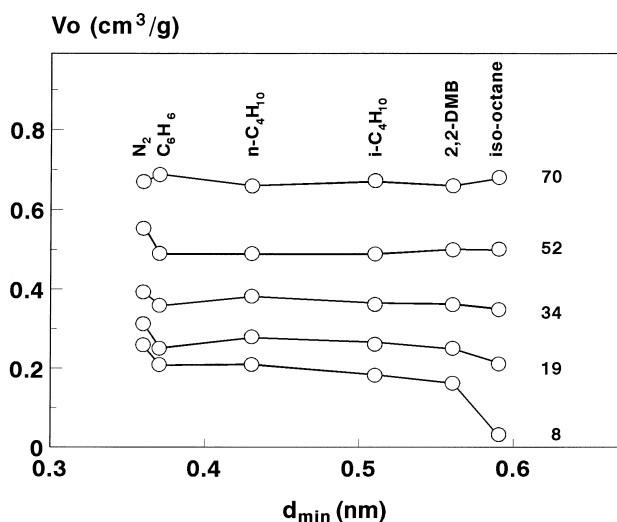
Fig. 3. Micropore size distributions deduced from physical adsorption of probe molecules (series D).

volume, thus indicating that all of the adsorptives are accessible to the porosity, which is at least of the minimum dimension of iso-octane, 0.59 nm.

Although the use of molecular probes is an unambiguous procedure to determine the volume of porosity accessible to each molecular dimension, it is however a very tedious experimental procedure and it is then convenient to see whether other experimental methods could be used for the same purpose. The measurement of the heat evolved when an outgassed solid becomes in contact with a liquid is the principle of immersion calorimetry [2,32]. The experimental enthalpy of immersion, $-\Delta H_i$ (J/g) can be converted into volume of micropores and surface area by using an appropriate non-porous reference carbon, and if the liquids used have different molecular dimensions it is possible to construct a pore size distribution similar to those shown in Fig. 3.

Stoeckli and coworkers [33,34] relate the enthalpy of immersion to the micropore volume (V_0) and characteristic energy (E_0) of the micropore filling theory of Dubinin. Consequently, the enthalpy of immersion of a liquid on a given carbon is a function of both the volume of micropores and the average micropore size, as well as the characteristics of the liquid. Table 2 compares the volume of micropores deduced from adsorption of benzene, 2,2-dimethylbutane and iso-octane (DR equation) and immersion calorimetry. In the case of benzene, the values are coincident except for carbon D-70, for which the three values deduced from immersion calorimetry are similar but lower than the values obtained from adsorption. This may be explained by considering that this carbon has a wide pore size distribution, with an important contribution of wide micropores (also called supermicropores by Dubinin) [21,35]. It is very probable that this range of porosity is detected by adsorption to a larger extent than immersion calorimetry because the

Table 2
Micropore volume (cm^3/g) of activated carbons obtained from physical adsorption and immersion calorimetry

Carbon	Benzene		2,2dmb		i-Octane	
	ads.	inm.	ads.	inm.	ads.	inm.
D-8	0.21	0.22	0.16	0.04	0.03	0.01
D-19	0.25	0.26	0.25	0.20	0.21	0.15
D-34	0.36	0.36	0.36	0.37	0.35	0.32
D-52	0.49	0.49	0.50	0.49	0.50	0.47
D-70	0.69	0.56	0.66	0.58	0.68	0.57

filling of these micropores takes place by the cooperative effect of secondary micropore filling, including adsorbate−adsorbate interactions, which are not detected by immersion calorimetry. There are also large discrepancies in the values for carbon D-8; the volumes deduced from benzene are similar but the immersion data for 2,2-dimethylbutane and iso-octane are lower than the adsorption data. This effect may be caused by both the selection of the characteristic energy E_0 giving the average micropore size (which has been taken as characteristic of the carbon, independently of the liquid used for immersion) and the fact that the two molecules are not accessible to the whole of the microporosity. As the accessibility of the liquid increases the values obtained from adsorption and immersion become more similar.

In order to calculate the surface area of a carbon from immersion data Denoyel and coworkers [36,37] calculate the specific enthalpy of immersion, ΔH_i (J/m^2) for a carbon in different liquids using a non-porous carbon black as reference, assuming that the enthalpy of immersion is proportional to the surface accessible to the liquid, independently of the shape and size of the pores. The surface area accessible to benzene, 2,2-dimethylbutane and iso-octane has been calculated for the carbons of series D using a graphitized carbon black (V3G) as reference surface [38]. The calculated values are given in Table 3, together with the BET surface area deduced from the adsorption of N$_2$ at 77 K. Except for carbon D-8 and D-19, with molecular sieving effects to large molecules, the surface areas accessible to 2,2-dimethylbutane and iso-octane are very similar to the BET surface areas. The minimum dimensions of nitrogen (0.36 nm) and benzene (0.37 nm) are very similar and consequently one could expect that both should have access to the same range of microporosity. However, the surface area calculated from benzene immersion is larger than the BET value and this can be interpreted assuming that the adsorption of nitrogen underestimates the surface area of activated carbons as compared with a free surface such as in carbon black. Thus the BET method, when applied to very narrow micropores (of the order of one nitrogen molecule), 'detects' only one wall of the pore, underestimating the surface area of the pore. However, immersion calorimetry 'detects' the interaction of the molecule with the

Table 3
Apparent surface areas of activated carbons

Carbon	BET	Immersion calorimetry		
	N_2 (77 K)	Benzene	2,2dmb	i-Octane
D-8	647	754	117	66
D-19	797	917	542	463
D-34	989	1114	958	928
D-52	1271	1402	1192	1243
D-70	1426	1552	1357	1460
V3G	62	—	—	—

two walls of the pore. The narrower the pore, the larger than unity will be the $S_{\text{benzene}}/S_{\text{BET}}$ ratio. This does not apply to 2,2-dimethylbutane and iso-octane for carbons D-34, D-52 and D-70 because the microporosity of these carbons may accommodate two molecules of nitrogen and at least one organic molecule. In fact, the presence of some residual narrow microporosity could be the reason for the high surface area measured by benzene even in carbon D-70.

The analysis of data from Tables 1 and 2 indicates that the adsorption of N_2 at 77 K, CO_2 at 273 K and immersion calorimetry of liquids with different molecular dimensions permit a complete characterization of the microporosity of activated carbons (information on larger size porosity may be easily obtained by means of mercury porosimetry). These techniques have been used to analyze the effect of activating agent (carbon dioxide or steam) on the development of microporosity upon activation of a char.

Three series of activated carbons have been prepared from a common precursor, olive stones, carbonized under a flow of nitrogen at 850°C for 2 h [39]: (i) series D, activated with carbon dioxide at 825°C (activation rate, 1%/h); (ii) series W, activated with steam at 800°C (activation rate, 2.1%/h); and (iii) series H, activated with steam at 750°C (activation rate, 1%/h). Table 4 includes the volume of micropores deduced from the adsorption of N_2 (77 K) and CO_2 (273 K) and application of the DR equation. The volume of pores measured by mercury porosimetry for some carbons of the three series have also been included in Table 4. Fig. 4 corresponds to the micropore size distribution, expressed as micropore volume as a function of the minimum dimension of the molecules used in immersion calorimetry [40]. There is, for a given series, an increase in the volume of micropores with increasing activation. However, such an increase is gradual for small molecules such as nitrogen or benzene, but for larger molecules (e.g. iso-octane and α-pinene) the increase is fast in the first stages of activation. Since at low degrees of activation (low burn-off) the order of accessible volume to the liquids is benzene > 2,2-dimethylbutane > iso-octane > α-pinene, which corresponds to the increase in minimum molecular dimension, it can be deduced that at low burn-off, the carbons exhibit some molecular sieving effect, which is not

Table 4
Pore volume (cm^3/g) for activated carbons series D, W and H

Carbon	$V_0(N_2)$	$V_0(CO_2)$	V_{Hg}
D-8	0.26	0.26	0.21
D-34	0.39	0.36	0.47
D-70	0.67	0.48	0.78
W-10	0.24	0.23	0.22
W-41	0.47	0.30	0.57
W-71	0.73	0.31	1.15
H-8	0.24	0.21	0.25
H-37	0.39	0.28	0.51
H-74	0.55	0.29	0.94

present at high burn-off. The more important differences among the three series can be summarized as follows:

1. The more important widening of the microporosity produced by steam in respect to carbon dioxide for carbons up to about 23% burn-off. Thus, while the differences between the volume of pores accessible to benzene and 2,2-dimethylbutane are still appreciable for D-19 (activated with carbon dioxide), such differences are not observed for carbons H-22 and W-23 (activated with steam);
2. The increase in the volume of micropores as from 40% burn-off for carbons activated with steam is smaller than for carbons activated with carbon dioxide. This different development of microporosity is characteristic of the activating agent, since carbons of series H and W have a similar behavior (although carbons of series W, prepared at higher temperature, develop microporosity to a larger extent than carbons of series H).

The results of Table 4 are in good agreement with the data of Fig. 4, although they provide additional information. Thus, $V_0(N_2)$ and $V_0(CO_2)$ are coincident for carbon D-8, indicating that the microporosity is narrow and uniform [24]. The values become differentiated with increasing activation, but $V_0(CO_2)$ also increases with activation. Consequently, the effect of activation with carbon dioxide is simultaneously creation and widening of small-size micropores, the later effect predominating at burn-off larger than 30−40% since the differences between $V_0(N_2)$ and $V_0(CO_2)$ are very noticeable in sample D-70. There is simultaneously an increase in the volume of meso- and macroporosity (V_{Hg}), although the proportion of macropores is high in all carbons [39].

Activation with steam (series W and H) differs from activation with carbon dioxide in the development of narrow microporosity, lower in the former, especially at high burn-off, since $V_0(CO_2)$ remains almost constant with increasing activation. Since $V_0(N_2)$ increases, this means that only widening of the existing micropores is taking place when activating with steam. The consequence of this effect is a smaller
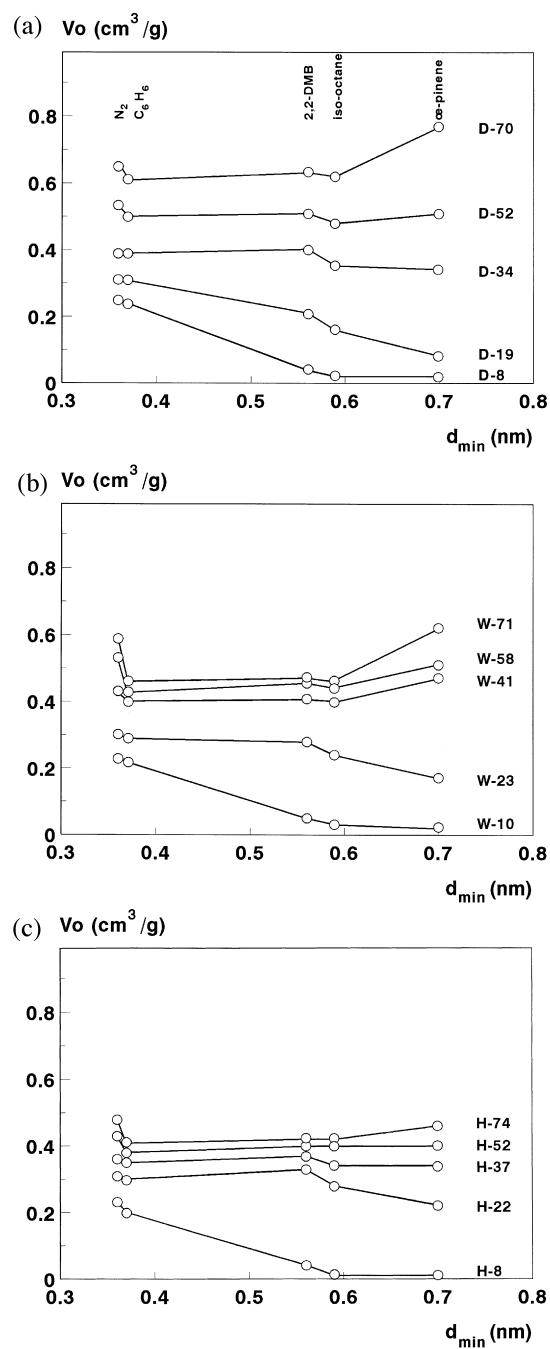
Fig. 4. Micropore size distribution deduced from physical adsorption (N$_2$) and immersion calorimetry for series D, W and H.

development of microporosity and larger development of meso- and macroporosity for series W and H. Not only are the values of V_{Hg} larger in series W and H, but also there is a different distribution of the volume of the three pore size ranges, the mesoporosity predominating in carbons of the two series activated with steam. The reason for this different behavior of the two activating agents, and the important role of the activation temperature in the activation process has already been described elsewhere [13,39,41].

4. Chemical characterization

The chemical characterization of a carbon surface is mainly concerned with the determination of the amount of heteroatoms and their type of bonding to the carbon skeleton, i.e. the nature of the surface groups [16,42]. Oxygen is the more common heteroatom in porous carbons and there is a series of oxygen surface groups of interest for their adsorption properties. Since most activated carbons are prepared by a thermal process (i.e. gasification of a char at high temperature in the presence of carbon dioxide, steam or a mixture of them) the resultant product usually possesses a low amount of oxygen surface groups [6], mostly originated by chemisorption of oxygen from air, and it is usual practice to increase their amount by oxidation of the carbon in air or with solutions of nitric acid, hydrogen peroxide, etc., without essentially modifying the porous texture. After oxidation, oxygen becomes bound to the carbon skeleton thus forming structures with different chemical and thermal stability. Thermal treatment of the oxidized carbon under an inert atmosphere (TPD) produces the selective decomposition of the oxygen groups, thus permitting the determination of the amount and nature of the oxygen surface groups [18].

Fig. 5 includes the TPD profiles for CO_2 and CO of a carbon prepared by activation in steam at 750°C (carbon H-0) and the carbon resulting from its oxidation with a solution of nitric acid [43], followed by washing in distilled water and drying at 110°C (carbon H-110). The amount of CO_2 evolved for carbon H-0 is very small since the decomposition of oxygen groups to CO_2 is produced at temperatures lower than that used during activation (750°C). Consequently, carbon H-0 only has surface groups decomposing to CO, with a maximum at 880°C, a temperature which is higher than the activation temperature. Oxidation with nitric acid (carbon H-110) leads to the creation of a variety of oxygen structures with a wide range of thermal stability. At low temperature (200−500°C), there is predominance of the so-called low temperature CO_2 groups, mainly due to carboxylic groups. There is in the 600−800°C range an appreciable amount $CO_2 + CO$ groups (anhydride groups, also called high temperature CO_2 groups), overlapping with CO groups evolving from other structures such as phenol, lactone, etc. up to 1000°C. Integration of the area under the corresponding peaks allows the determination of the amounts of CO_2 and CO evolved from the carbon.

As mentioned in Section 2, the oxygen surface groups can also be determined by selective titration, so that for instance NaOH titrates carboxyl, lactone and phenolic
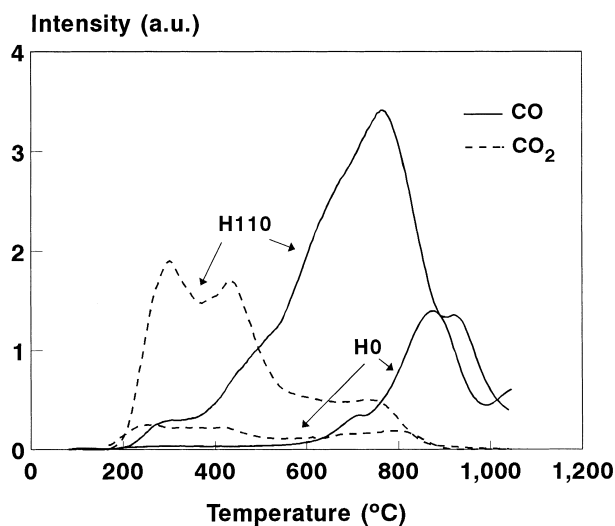
Fig. 5. CO and CO_2 profiles for carbons H-0 and H-110.

groups whereas $NaHCO_3$ titrates carboxyl groups only. Selective titration with NaOH and $NaHCO_3$ has been carried out on physically activated carbons with a range of pore size and oxidized with air (A), or solutions of hydrogen peroxide (P) or nitric acid (N) [44]. Fig. 6 includes the results of the titrations, and it is shown
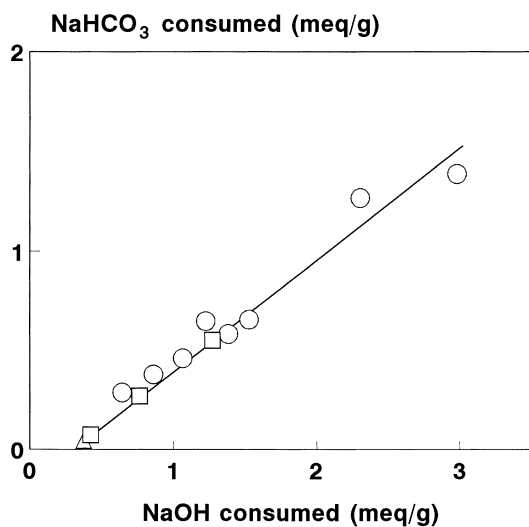

Fig. 6. Relation between $NaHCO_3$ (mequiv./g) and NaOH (mequiv./g) consumption by selective titration for carbons oxidized with air ($\triangle$), hydrogen peroxide ($\square$) and nitric acid ($\bigcirc$).

that the amount of $NaHCO_3$ consumed for all oxidized carbons is lower (about half) than the amount of NaOH consumed, the data fitting a straight line. This means that independently of the type of oxygen surface group present there is a relationship between the amounts consumed of NaOH and $NaHCO_3$. Other authors [17,42] have described linear relationships between the amounts consumed of NaOH, $NaHCO_3$, Na_2CO_3 and NH_4OH for different activated carbons. This behavior has been justified assuming that the acidity of the different surface groups is a function not only of the nature of the surface group (with its corresponding fixed value of pK_a) but also of its position in the carbon skeleton. In any case, these relations show the difficulty in differentiating the oxygen surface groups by selective titration.

There have been many attempts to relate the results obtained by selective titration and TPD for a large number of activated carbons and other porous and non-porous carbons and it was found that there is a relationship between the groups titrated by NaOH and those decomposing to CO_2 [44−47]. This is the case for the oxidized activated carbons described here, and Fig. 7 shows that there is a linear relationship with the slope of the line being near unity. This means that the groups evolving as CO_2 (corresponding to the decomposition of mainly carboxyl groups) lead, upon hydrolysis, to acids that can be stoichiometrically titrated by NaOH (according to the pK_a they could be carboxyl, lactone or phenolic groups). Consequently the correlation (Fig. 7 indicates that the acidic structures are monobasic) could only be explained if there is a phenolic group in conjunction with a carboxylic group. The phenolic group does not decompose to CO_2 but it would be titrated by NaOH.

5. Effect of texture and surface chemistry on adsorption and immersion calorimetry

The adsorbate−adsorbent interaction in physical adsorption is a function of the polarity of the solid surface and the adsorptive. The mainly non-polar character of the surface in activated carbon will favor the adsorption of non-polar molecules by a non-specific mechanism, but the adsorption of polar molecules can be increased by an adequate modification of the chemical nature of the carbon surface (e.g. by oxidation), since this will produce an increase in the adsorptive−surface interaction.

Several activated carbons were oxidized under mild conditions to avoid important modification of the original porosity, and they were used to analyze the effect of the oxygen surface groups in the adsorption of molecules with different polarity: nitrogen, sulfur dioxide, methanol and water [48]. The adsorption isotherms shown in Fig. 8 correspond to an activated carbon (M-0) with a very small amount of oxygen surface groups because it was prepared by physical activation and later heat-treated in hydrogen at 950°C. The amounts adsorbed for all adsorptives, expressed as volume of liquid, are very similar near saturation, thus obeying the Gurvitsch rule, but they are very different at low relative pressures, where the order of adsorption is $N_2 > SO_2 > CH_3OH > H_2O$. These differences are ex-
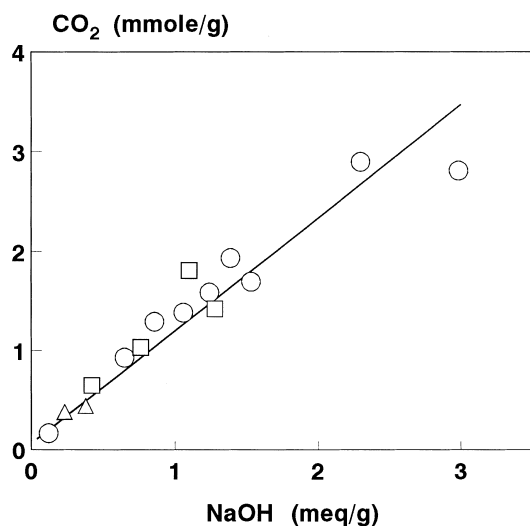
CO$_2$ (mmole/g)

Fig. 7. Relation between CO$_2$-evolving groups and acidity measured by NaOH titration (mequiv./g) for carbons oxidized with air (△), hydrogen peroxide (□) and nitric acid (○).

plained considering that the amount adsorbed by the carbon is the result of a competition between adsorbent−adsorbate interactions and the adsorptive−adsorptive interactions in the gas phase. The more intense the adsorptive−adsorptive interactions are, the smaller the interaction of the molecules with the carbon surface will be and, consequently, the smaller will be the amount adsorbed at low relative pressure. Very probably the adsorptive−adsorptive interaction will be a function of the permanent polar moment of the molecule (N$_2$ = 0; SO$_2$ = 1.6D; CH$_3$OH = 1.7D; H$_2$O = 1.8D) and, additionally, of the presence of intermolecular hydrogen bonding in methanol and water. In the particular case of water, besides the stronger hydrogen bonding one has to consider the weak non-specific interaction with the carbon surface due to the non-hydrophilic nature of the carbon. These factors are the main reason for the lack of micropore filling by water at low relative pressure, when this is possible for nitrogen. The shape of the adsorption isotherms, type V, indicates that the water−carbon interaction is very weak and consequently a relative pressure of around 0.5 is needed for the adsorption process to start, very probably through certain active centers. Once a few water molecules are adsorbed on the active centers, more molecules become bound by hydrogen bonding, this forming a series of water islands on the carbon porosity.

When the carbon is oxidized, for instance with a solution of nitric acid, there is an increase in the number of oxygen surface groups and this opens the possibility of specific interactions with the adsorptive, thus modifying the adsorption isotherm, especially at low relative pressures. In order to show the changes, the isotherms of Fig. 8 for carbon M-0 and those for the oxidized carbon (M-15N) have been
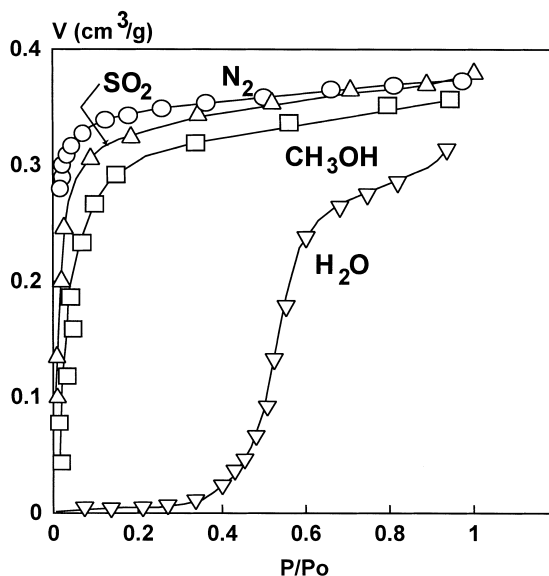
Fig. 8. Adsorption isotherms of N_2 (77 K), SO_2 (262 K), CH_3OH (298 K) and H_2O (298 K) for carbon M-0.

included in Fig. 9 as DR plots. The increase in oxygen content (2.90 and 4.02 mmol of CO_2 and CO, respectively as deduced from TPD for carbon M-15N, in respect to 0.14 and 0.25 mmol of CO_2 and CO for carbon M-0) [44] does not modify the adsorption process of a non-polar molecule such as nitrogen, but the effect is increasingly noticeable for the other molecules in the order $SO_2 < CH_3OH < H_2O$, thus showing that in addition to the non-specific carbon−adsorbate interaction there are other specific interactions with the oxygen surface groups. The extreme case corresponds to water for which there is a considerable increase in the amount adsorbed at low relative pressures, thus confirming that the adsorption of water starts by specific interactions of the water molecule with oxygen groups at the surface [48,49]. The adsorption of SO_2 and CH_3OH is intermediate between nitrogen and water, the non-specific interactions (dispersion forces) being more important for the former.

Direct evidence of the interaction governing the adsorption process could be obtained by immersion calorimetry. In order to establish the role of the oxygen surface groups of the carbon on the enthalpy of immersion in liquids of different polarity, a physically activated carbon (H-0) oxidized in nitric acid (H-110) has been heat-treated at different temperatures under an inert atmosphere to selectively eliminate the oxygen surface groups introduced by oxidation [43]. The liquids used for immersion were benzene, methanol and water.

The TPD profiles for the original and oxidized carbons were shown in Fig. 5 and the amount of CO_2 and CO evolving on TPD are given in Table 5, together with
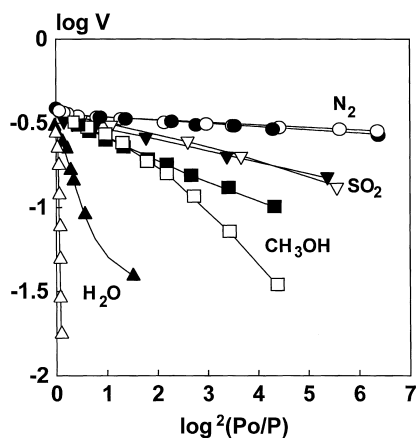
Fig. 9. DR plots for carbons M-0 (open symbols) and M-15N (closed symbols).

the data for the heat-treated carbons (the treatment temperature is included in the nomenclature of the carbons). The results indicate that there is a progressive elimination of groups decomposing to CO_2 and CO with increasing temperature of the heat treatment, with an important change at 500°C. For H-500 most of the groups decomposing to CO_2 have evolved whereas the amount of groups decomposing to CO has decreased only slightly, the decomposition taking place at higher temperature. On the other hand, the amount of oxygen surface groups of the original carbon H-0 (activated with steam at 750°C) is intermediate between H-700 and H-800.

The treatment of the carbon with nitric acid produces a slight decrease of the surface area of the carbon (see Table 5) since the oxygen bound to the carbon skeleton partially blocks the entrance of the microporosity. Progressive elimination of the surface groups by thermal treatment has two effects: (i) elimination of the micropore constrictions, and (ii) slight activation of the carbon (oxygen atoms leave the carbon surface bound to carbon atoms to form CO_2 and CO) and, conse-

Table 5
Oxygen surface groups evolved as CO and CO_2 (mmol/g) and BET surface area (m^2/g) of activated carbons

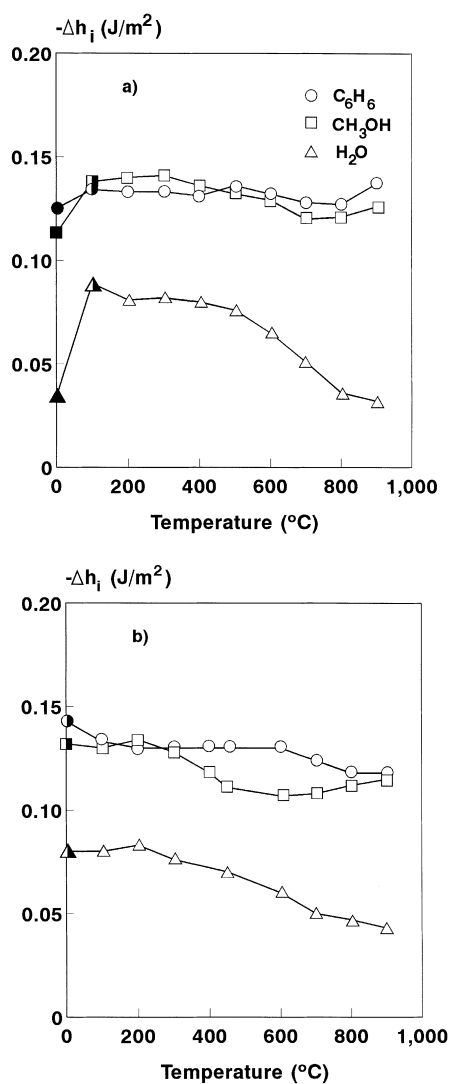| Carbon	S_{BET}	CO_2	CO
H-0	926	0.12	0.82
H-110	852	1.17	3.32
H-200	860	0.95	3.30
H-500	950	0.28	2.94
H-700	956	0.12	1.76
H-900	979	0.04	0.25

Fig. 10. Evolution of the areal enthalpies into benzene, methanol and water as a function of temperature for (a) activated carbons and (b) graphite.

quently, the surface area of carbon H-900 is somewhat larger than that of carbon H-0.

Since the changes in the carbon surface area affect the enthalpy of immersion of the carbons in liquids, to analyze the effect of the surface groups on the heat of immersion it is convenient to use the areal enthalpy of immersion (J/m^2). These values have been plotted as a function of the heat treatment temperature in Fig. 10a. For the sake of comparison Fig. 10b includes the data obtained by Barton and

Harrison [50] for a graphite outgassed at different temperatures. The similarity of the two figures is remarkable considering the large difference in the structure of the two carbon materials. Thus, the enthalpy per unit area for benzene is not only constant (and consequently, independent of the chemical nature of the carbon surface) but additionally the two sets of values of Fig. 10 are similar (≈ 0.13 J/m^2), this indicating that the energetic contribution due to the interaction of benzene with the surface of the micropores is the same as with the non-porous surface of the carbon. This confirms the convenience of determining the surface area of activated carbons using immersion calorimetry in benzene when a non-porous carbon is used as the reference, independently of the chemical nature of the carbon.

For methanol, the enthalpy per unit area of a carbon heat-treated at 900°C is similar to that of graphite (≈ 0.12 J/m^2) and slightly increases (up to ≈ 0.14 J/m^2) when the carbon has oxygen surface groups. The larger enthalpy of immersion registered when the carbon has groups evolving as CO_2 (at temperatures below 500°C, Table 5) indicates that the methanol molecule interacts with these groups, very probably throughout the formation of hydrogen bonds, in addition to the non-specific carbon−methanol interaction. These results are in good agreement with those described for the adsorption of methanol vapor (Fig. 9).

As in the case of adsorption, it is in the enthalpy of immersion in water where the role of oxygen surface groups is more clearly shown. Thus, there is a noticeable increase in ΔH_i for the oxidized carbon and there is a decrease when the heat treatment is above 500°C. The parallelism in the evolution of ΔH_i (H_2O)—Fig. 10a—and the evolution of oxygen surface groups (Table 5) shows that the groups decomposing to CO affect mainly the enthalpy of immersion, although the interaction of the oxygen-free carbon surface with the water molecule is also very important. In fact, the latter interaction must be responsible for the adsorption of water on the activated carbon oxidized and later reduced in hydrogen at 900°C (Fig. 8), for which adsorption starts at a relative pressure of 0.4. However, adsorption for the oxidized carbon begins at relative pressures below 0.1 (Fig. 9), as a consequence of the contribution of the interaction of the water molecule with the oxygen surface groups of the carbon.

The evolution of the enthalpy of immersion in water for activated carbon and graphite is very similar, again highlighting the role of the oxygen surface groups. Furthermore, the enthalpy of immersion in water for carbon H-900, with a small amount of surface groups, is rather near the value for graphite outgassed at 900°C. If one assumes that the structural units of an activated carbon are of the order of 100 times smaller than in graphite, the proportion of carbon atoms in the edges of the crystallites as compared with those on the basal plane is much larger in activated carbons. Since the enthalpy per unit area is the same in both materials one has to assume that once the surface groups are eliminated upon heat treatment there are no preferential sites (according to their position in the carbon structure) for the interaction of water molecules with the carbon atoms. In any case, this interaction is much lower than the interaction of the water molecule with the groups decomposing as CO.

6. Conclusions

Industrial applications of porous carbons are based on both their porosity and chemical nature and, consequently, their characterization is of great importance. The determination of the volume of micropores is not straightforward since it is a function of the adsorptive selected and the method used to analyze the corresponding adsorption isotherm. With the results obtained in the characterization of a series of activated carbons of gradually increasing porosity by adsorption of several gases and vapors and n-nonane preadsorption, it is found that a simple and convenient evaluation of the microporosity (volume of micropores and heterogeneity of pore size) can be attained by adsorption of N_2 at 77 K and CO_2 at 273 K. It has also been shown that immersion calorimetry in liquid hydrocarbons with different molecular dimensions is a convenient technique to determine the surface area and micropore size distribution of activated carbons, the results being similar to those obtained by adsorption of the same hydrocarbons (which is a more tedious experimental method).

The determination of the oxygen surface groups of the carbons has been carried out by selective titration and by TPD, and it has been shown that there is a correlation between the amounts of NaOH and $NaHCO_3$ consumed and also between the amount of NaOH consumed and the amount of CO_2 evolved in TPD. These correlations are independent of the oxidising agent used, thus indicating the difficulty in differentiating the various surface groups, very probably because of the effect not only of the surface group in itself but also its position in the carbon skeleton.

The effect of the texture and chemical nature of activated carbon in adsorption and immersion processes of molecules with different polarity has also been analyzed, and it has been shown that for non-polar molecules (e.g. nitrogen or benzene), the effect is almost nil for both the amount adsorbed and the enthalpy of immersion, but it is very important for polar molecules (especially when the dimensions are small, as for water). The specific interactions of the oxygen surface groups with the adsorbate play a predominant role, although not the only one, and the amount adsorbed or the enthalpy of immersion considerably increase with the amount of surface groups.

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