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On the use of calorimetric techniques for the characterization of carbons: A brief review

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Abstract

In this paper, the use of calorimetric techniques to characterize different carbon materials is reviewed. The focus of the review is on the use of calorimetric techniques to assess chemical properties of carbons (e.g. nature of surface groups, hydrophobic/hydrophilic character, acidic/basic behavior, etc.), and a small section is dedicated to the application of calorimetry in determining the physical properties of carbons (e.g. surface areas, pore size distribution, etc.). The following techniques are described: immersion and flow-adsorption calorimetry and gas-adsorption microcalorimetry. Several representative examples of the use of calorimetry techniques to evaluate both physical and chemical properties are presented. It is demonstrated that calorimetry has provided unique insights into the structure and chemistry of active sites on the surface of various carbons. © 1998 Elsevier Science B.V.

Keywords: Calorimetry; Carbon characterization; Carbon materials

1. Introduction

As early as 1927 [1], the heats of adsorption of several gases and vapors on charcoal were measured using an ice calorimeter. In 1931, Bull et al. [2] used a vacuum calorimeter to assess the reaction between carbon and oxygen at low pressures and room temperature. Heats of adsorption at 273 K of different inorganic [3] and organic gases [4] were used by Beebe et al. to investigate correlations between the surface properties of carbon blacks and their rubber reinforcing ability. Despite the success of these early examples, and many others associated with the characterization of other materials [5], calorimetry has never been employed widely for carbon characterization. In fact, its use has been confined to a relatively small number of investigators who have used calorimetry for specific problems.

The aim of this paper is to review the limited number of examples of the use of calorimetry for the characterization of the physical and chemical surface properties of carbons. The results indicate great promise for calorimetric studies of the physical structure (i.e. textural properties) of carbons, especially when used in conjunction with more classic techniques based on the physical adsorption of gases and vapors. Three types of calorimetric methods have been employed for the study of surface chemistry of carbons: immersion; flow adsorption; and gas-adsorption calorimetry.

Immersion- and flow-adsorption calorimetry measure the heat of adsorption released by a sample which is immersed either in a liquid or in a stream of a carrier liquid and a probe compound as a function of the amount adsorbed. These two techniques have been found to be specially useful in the study of hydrophobic/hydrophilic nature of carbons and it also improved understanding of surface acidity/basicity.

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However, these techniques only provide average heat values, the chief value of which is to allow different carbons to be compared/contrasted. The method also provides a general understanding of the impact of different treatments on the number of surface groups present on a carbon. In contrast, gas-adsorption microcalorimetry determines the heats generated by the adsorption of measured doses of a gas or vapor which can be used to obtain information regarding the types and concentrations of active sites on carbon surface, the strength of interaction with various gases and vapors and an understanding of the precise chemistry/arrangement of active sites.

2. The physical structure of carbons

The most commonly used technique for the characterization of the texture of carbons (i.e. surface areas, molecular sieve properties, pore size distribution, etc.) is the physical adsorption of gases and vapors; however, sometimes immersion calorimetry, with probes of various molecular dimensions, is also used [6–11]. The basis of this technique is the measurement of the heat evolved when a solid, either degassified or partially covered by an adsorbed film, is brought into contact with a nonreacting liquid. Dubinin's theory provides the theoretical background for the volume filling of micropores [12] and its extension to immersion calorimetry developed by Stoeckli et al. [13–15]. Thus, the micropore volume $W_0(L_c)$ filled by a liquid of critical molecular dimension L_c, can be calculated by the following expression:

$$W_0(L_c) = (\Delta h_i(\exp) - h_i S_e) 2 V_m \beta E_0 \times (1 + \alpha T)(\pi)^{(1/2)} \quad (1)$$

where $\Delta h_i(\exp)$ is the experimental enthalpy of immersion of the carbon in the liquid, α the thermal expansion coefficient, V_m the molar volume of the liquid and h_i the specific enthalpy of wetting of the external surface of the carbon (S_e). For carbons with relatively small external surface areas, the term $h_i S_e$ can be neglected. In all other cases, h_i has to be estimated from experiments with nonporous carbons of a known surface area. Using this technique, the accessibility of the micropores can be assessed reasonably well. The external surface area (S_e) can also be calculated if calorimetry is used in combination with conventional isotherms of the corresponding vapor.

Stoeckli et al. utilized this technique for the characterization of the porous structure of a wide variety of carbon materials, such as activated carbons [6,13], activated carbon fibers [7] and sulfur-impregnated activated carbon [8]. Recently, Denoyel et al. [9] evaluated the surface area and micropore size distribution of activated carbons using nonporous carbon black as a reference and assuming that the enthalpy of immersion per surface area was proportional to the surface available to the immersion liquid. The same technique was also used by Rodríguez-Reinoso et al. [11] to assess the physical properties of a series of activated carbons. Their results are summarized in Table 1. As can be seen, except for carbons D-8 and D-19 for which the surface accessible to 2,2 dimethylbutane and isooctane is much lower than the BET surface areas, the values calculated using calorimetry are similar to those obtained from the physical adsorption of nitrogen. In the case of benzene, it was observed that the narrower the microporosity of the carbon the higher is the difference between the surface areas derived from nitrogen adsorption and from the enthalpies of immersion in benzene. This fact can be explained by taking into account that in very narrow

Table 1
Apparent surface areas of activated carbons (m^2/g) [11]

	BET	Immersion calorimetry		
Carbon	N_2 (77 K)	Benzene	2,2, Dimethylbutane	Isooctane
D-8	647	754	117	66
D-19	797	917	542	463
D-34	984	1114	958	928
D-52	1271	1402	1192	1243
D-70	1426	1552	1357	1460

micropores of the width of nitrogen molecules, the BET method only considers one of the walls of the micropore underestimating the actual surface area, whereas immersion calorimetry reflects the interaction of benzene with both walls [9].

Immersion calorimetry appears to be a simple and less-time consuming technique than conventional methods based on gas adsorption. However, this technique has also some limitations especially when used in the characterization of microporous carbons. For instance, the accessibility of molecules of large critical dimension to the micropore system can be restricted in carbons presenting constrictions at the entrance of the pores, and so surface areas measured with immersion calorimetry may differ from the actual area [6]. Information obtained from this technique should, therefore, be complemented with the use of, at least, one additional adsorption test.

A different approach employing differential scanning calorimetry (DSC) was utilized recently by Stasczuk [16] to determine the pore size distribution of activated carbons. This technique is based on the fact that the freezing point of water adsorbed on a carbon surface is proportional to the pore radius [17]. Thus, DSC peaks obtained at temperatures ranging 228–263 K are associated with the freezing of water in pores of different radii and their shapes reflect the structural heterogeneity of a given porous carbon.

3. The surface chemistry of carbons

3.1. Immersion- and flow-adsorption calorimetry

The surface of a carbon can be considered as a combination of basal planes of hydrophobic nature and polar sites at the edges of the carbon layers that form the graphite crystals. The edge-carbon atoms are frequently combined with oxygen, forming different functional groups, which act as primary sites in the adsorption of water molecules [18]. For this reason, even the most hydrophobic carbons can contain a certain amount of hydrophilic sites.

The use of calorimetry can be very helpful in the quantification and determination of the nature of the hydrophobic and hydrophilic sites. Thus, flow-adsorption calorimetry was used by Groszek [19] to determine the proportion of basal plane and polar sites in graphite powders. He used the preferential heats of adsorption of *n*-dotriacontane (for the basal plane) and *n*-butanol (for the polar sites) on the carbon samples immersed in *n*-heptane to quantify the two kind of sites. The same technique was used for other carbon materials, such as carbon blacks, chars and activated chars [20], to obtain surface graphiticity and surface polarity indices. These indices provide a quantitative measure of the affinity of carbon surface for polar and nonpolar substances and are, therefore, related to the hydrophilic/hydrophobic nature of the carbons. For a graphitized carbon subjected to oxidation treatment, very good agreement was found between the active surface area (ASA) [21–23] (determined by chemisorption of O_2) and the calorimetric method employing the physical adsorption of *n*-butanol (see Table 2). More specifically, the surface areas of hydrophobic and hydrophilic surface sites were measured for a large number of different carbons, using a slight variation of the method mentioned above [24]. Hydrophilic and hydrophobic sites were related to the integral heats of displacement of 1-butanol from *n*-heptane and water solutions, respectively. For nonporous carbons, the heats of adsorption determined by flow-adsorption microcalorimetry were found to provide estimates of the relative proportions of hydrophilic and hydrophobic surface sites. In the case of microporous carbons the heats of adsorption are enhanced, resulting in the estimates of surface areas of hydrophobic and hydrophilic sites that may be significantly higher than the corresponding BET surface areas. However, the comparison of the two heats also permits the evaluation of the relative hydrophobicity or hydrophilicity of such carbons.

Information regarding the surface chemistry of coals can also be obtained by using this method. Thus, changes in coal surface polarity due to heat/oxidation

Table 2
Increase in surface areas caused by activation treatment of graphitized carbon black [20]

	Surface areas (m^2/g)		
Burn off (wt%)	BET, N_2 (77 K)	ASA [a]	Polar area [b]
0	73	0.15	0.14
30	97	4.1	4.5

[a] Determined by O_2 chemisorption.

[b] Determined by adsorption of *n*-butanol from *n*-pentane.

treatments, as well as the relative amount of strong and weak acid surface sites, on coals of different ranks were evaluated following the similar procedure [25]. In this case, acid sites were estimated from the heats of preferential adsorption of ammonium hydroxide from a dilute solution of water. Another example of the use of preferential heats of adsorption, of tert-butyl derivatives of phenol and pyridine from isooctane solutions, for the study of the surface chemistry of coals can be found in the paper of Fowkes et al. [26]. In that work, the number and strength of acidic and basic sites present on the surface of five coals of different rank was quantified. Tert-butyl derivatives of phenol and pyridine were chosen because of their 'limited penetration' into the bulk region of the coal, so that they do not dissolve into the coal. The heats of interaction between seven coals and their derived liquids with 13 acids of different strength were measured by Arnett and Ahsan [27] using flow titration and immersion calorimetry. They found that, in all cases, reactions with the coal-derived liquids were more exothermic than with the parent coals. It also appears that the enthalpy of immersion in strong acids involves quite a complex set of interactions in addition to the simple acid/base interaction.

The surface chemistry of carbon fibers used in advanced composites has also been investigated by means of calorimetry [28,29]. For instance, the acid–base character of several commercial carbon fibers was determined employing pulsed and continuous flow microcalorimetry techniques [29]. Using the pulsed flow method, the preferential heats of adsorption of 22 probes of different organic acids and bases from *n*-heptane were measured. These preferential heats-of-adsorption 'fingerprints' were found to be valuable in characterizing the surface chemistry of the carbon fibers and were used to rank carbon fibers with respect to the potential work of adhesion in a fiber–matrix interaction. A good correlation was found between the adsorption heats of acids and bases and the level of surface oxidation was determined by means of ESCA.

As mentioned above, oxygen functionalities on the surface of a carbon are postulated to act as primary water adsorption centers. Working independently, different authors found that these primary adsorption sites play a significant role in the enthalpy of immersion of carbons in water [30–41]. Thus, Dacey et al. [30] measured the heats of adsorption of water on carbon. They observed that the heat of adsorption of water was very close to the heat of vaporization except at very low coverage, in case where the heat of adsorption was considerably higher. The authors concluded that water is first adsorbed on the outer surface of the carbon and then migrates into the pores. In another early study, Wade [32] found a considerable drop in the heat of immersion when the carbon studied was degassed between 900 and 1000°C.

Heats of immersion in water measured in an isothermal calorimeter [42,43] were also used by Barton et al. to elucidate the role of the different oxygen-containing surface groups as hydrophilic centers on different carbons [33–35], and carbon-treated surfaces [36]. For graphite [33] and carbon black [35] samples, they found that the heats of immersion in methanol and water, respectively, vary as a linear function of the total oxygen content of the surface, regardless of the actual structure (i.e. phenolic, carboxylic, carbonylic, lactonic, etc.) to which the oxygen atom is incorporated. The results corresponding to carbon black are summarized in Table 3. Combining immersion calorimetry with the BET surface area, and assuming 0.105 nm^2 as the area of an adsorbed water molecule, the number of layers of adsorbed water corresponding to the total number of sites $[a_0+s]$ and primary sites $[a_0]$ were also calculated. These results contrast with those reported by the same author [34] for a polyvinylidene chloride carbon, in which surface oxides desorbing as CO upon thermal treatment seem to have a linear dependency on the heat of immersion in water independently of the presence or absence of CO_2 desorbing oxide. It was concluded that the former sites are responsible for the initial adsorption of water at low relative pressures. A similar relation between the centers desorbed as CO from the surface of an active carbon and the heats of immersion in water was found by Stoeckli et al. [37]. More contradictory are the results reported by Puri et al. [38,39], who found that the heats of immersion of charcoal in water vary linearly with respect to oxygen functionalities evolved as CO_2.

Information regarding the surface chemistry of carbons can also be obtained from the evaluation of the immersion heats in alcohols [44–47]. Thus, the active hydrogen sites of the functional groups, such as hydroxyls or carboxyls, present on carbon blacks were

Table 3
Variation in the BET surface area, enthalpy of immersion, oxygen content and equivalent monolayers with the degree of oxidation of carbon black [35]

Sample	BET (m^2/g)	Δh_i (J/g)	[O] (mmol/g)	Equivalent monolayers	
				$[a_0+s]$	$[a_0]$
AR	100	7.9	0.545	0.40	0.40
1 h ox	123	16.2	1.74	0.900	0.80
2 h ox	123	17.9	1.95	0.966	0.826
4 h ox	126	22.6	2.24	1.18	1.08
8 h ox	149	30.5	3.41	1.26	1.07

evaluated from the interaction heats between those sites and various alcohols [46]. It was concluded that the interactions of the active hydrogen sites with the alcohol molecules is of electrostatic and hydrogen bonding type, whereas in the case of water, dissociation-hydration reactions are also involved. The heats of adsorption of the homologs of normal alcohol and fatty acid from the aqueous solution on active carbons were measured by Hukao and Takeda [47]. They found that the adsorption process has two stages, one of high energy at lower concentration and another of low energy at higher concentration. A similar phenomenon was reported by Corkill et al. [45] without discussion. Based on these results, Hukao and Takeda propose the existence of two kind of sites with different adsorption energies on the active carbons.

Also using immersion calorimetry, Bagreev and Tarasenko [48] showed the reversible character of halide sorption on activated carbon and the increase in the anion affinity of the activated carbon surface in the series $F^-<Cl^-<Br^-<I^-$.

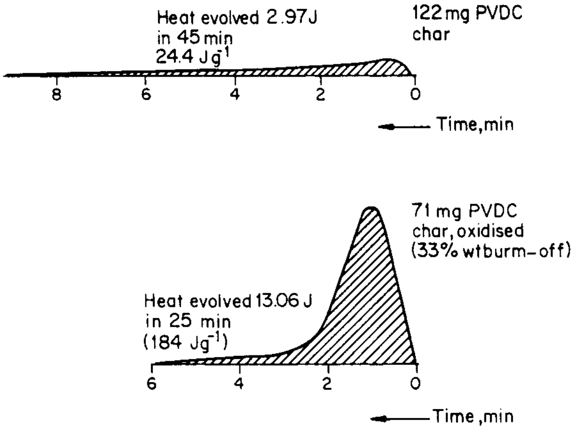

Fig. 1. Example of a typical plot obtained from immersion calorimetry. Heats of immersion of two PVDC chars in *n*-heptane [20].

As mentioned above, one common problem with the techniques based on immersion calorimetry is that only average heats of adsorption are obtained. This is illustrated in Fig. 1 which shows a typical plot obtained from immersion calorimetry. Thus, heats of immersion in water are related with the oxygen functionalities present on the carbon surface, but it is not possible to infer any information about the type of functionality by using this technique alone and the hydrophobic/hydrophilic character of the carbon can only be roughly estimated. The same problem exists for methods based on the evaluation of preferential heats of adsorption of different organic compounds. In this case, it is possible to obtain the estimates of relative proportions of hydrophilic and hydrophobic surface sites, but no information about the nature of these sites. In sum, there is not a single technique, calorimetric or any other, capable of providing a complete and accurate picture of the surface chemistry of carbons; however, immersion calorimetry provides information which complements the information obtained by other techniques.

3.2. Gas-adsorption calorimetry

The evaluation of the adsorption heats of gases and vapors on carbon surfaces can also be very useful in the study of carbon chemistry, both in the elucidation of the amount and nature of the different sites present or formed on the carbon surface, and as a means to clarify how changes in the surface chemistry of the carbon affect its adsorption properties. Although not large in number, some early studies of the differential heats of adsorption of gases on high surface area materials can be found [1–4,49–53]. The information that may, or may not be derived from differential calorimetric data has been clarified by Gow and Phillips in a relevant review [54] in which they have analyzed the mechanism of chemisorption and surface interaction in batch calorimetric systems. Calorimetric studies of oxygen adsorption onto carbon surfaces [2,55–60] have helped to determine the number, identity and chemistry of the various oxygen-containing surface groups that are invariably present on the surface of the majority of carbons and the nature of the active sites on which these groups are anchored.

Characterization of carbon supported metals [61,62] has also been carried out using a heat-flow differential microcalorimeter of original design. This calorimeter allows differential heats of adsorption and standard gas isotherms to be collected concomitantly so differential heats of adsorption can be plotted as a function of surface coverage [55,58]. Fig. 2 shows an example of the type of curves that can be obtained using this microcalorimeter. Compared to the integral heats obtained from immersion calorimetry (see Fig. 1), gas-adsorption microcalorimetry provides information regarding the change of the heat of adsorption with the surface coverage along with the total heat of adsorption and the total amount of gas adsorbed.

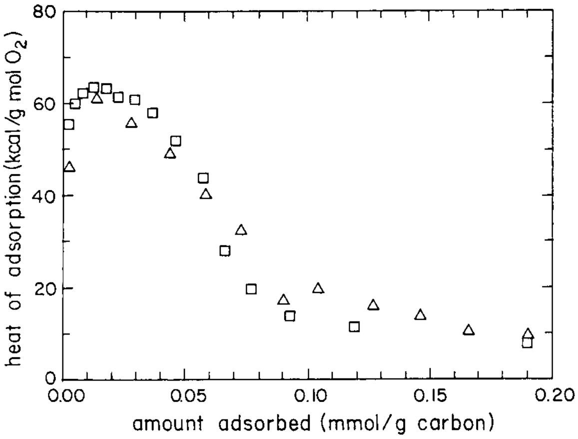

Fig. 2. Example of a typical plot obtained from adsorption microcalorimetry. Differential heats of adsorption of O_2 at 298 K on a HNO_3-treated Ambersorb [55].

The interaction between oxygen and the surface of a raw and catalytically promoted with potassium, calcium [63], sodium or magnesium [64] coal chars has also been studied by Gow and Phillips. Calorimetric studies supported the postulate that potassium catalyzes char gasification through a process in which a thin partially oxidized potassium film is alternately oxidized by the gas and reduced by the char. In contrast, calorimetric studies indicate that calcium and magnesium are relatively difficult to reduce and never form thin films. This is consistent with the finding that they are inactive gasification catalysts.

Microcalorimetric experiments were the key to explain the dramatic differences observed between H_2- and N_2-treated carbons [59,60]. It was found that carbon surfaces prepared by high-temperature N_2 treatments re-adsorbed oxygen even at room temperature and rapidly became re-acidified, while surfaces treated in high-temperature H_2 were not only basic, but they retained their basic character for long periods of time. These stable basic carbons, which do not adsorb oxygen at ambient laboratory conditions, were created by elimination of the most re/active unsaturated carbon atoms, either by high-temperature treatments in the presence of H_2 [59], or by a relatively low-temperature process in the presence of atoms of hydrogen [60]. In the second case, the presence of pellets of a Pt catalyst (which were physically mixed with the carbon) was required. Microcalorimetric tests indicated that the role of the platinum is to produce atomic hydrogen, which spills over onto the carbon surface.

All previous examples are based on the adsorption of oxygen on carbon surfaces. However, interesting information regarding the surface chemistry of carbons as well as the mechanisms of interaction between carbon surfaces and other gases or vapors can be obtained from the evaluation of the heats of adsorption of those gases. For example, isotherms and plots of the heats of adsorption vs. surface coverage of different gases and vapors adsorbed on graphite were obtained by Zarifyanz et al. [51]. They showed that irreversible adsorption of NO on "clean" graphite takes place to a much larger extent than O_2 adsorption on the same material and under the same conditions. This significant finding suggests that, for a given temperature, some of the active sites present on the surface of a carbon are accessible to molecules like NO but not to O_2 which requires a higher energy of activation.

The study of SO_2 adsorption on active carbons is of increasing interest because air pollution by sulfur dioxide has become a serious problem in industry. Calorimetry techniques have also been applied in this area [8,65]. Thus, determination of the molar SO_2 heat of adsorption on carbon samples subject to different oxidizing treatments was carried out by Davini [65] using an original gas chromatography method [66]. He found that SO_2 can be adsorbed on the surface of carbons by a mechanism which implies the formation of strong bonds between SO_2 and surface oxygenated functional groups with a basic nature.

The energetics of methane adsorption on activated carbons was recently studied using a Calvet microcalorimeter [67,68]. Heats of methane adsorption revealed that the surface functionalities of some oxidized carbons can block the narrowest pore entrances, which results in a decrease of the methane adsorption capacity of the carbon. Adsorption calorimetry was also used to study the thermodynamics of the adsorption process of the systems water/activated carbon [69] and ethanol/activated carbon [70].

The temperature regions of spontaneous oxidation of activated carbons loaded with volatile organic compounds (VOCs) were recently investigated by Wu and Leggett [71], using the so-called stopped-flow technique in combination with accelerating rate calorimetry.

Finally, as an example of how calorimetry is being used in the study and characterization of the most recently developed carbon materials, it is worth mentioning that oxygen-bomb combustion calorimetry was used to determine the standard energy of combustion of fullerene soot in arc discharge [72]; and that DSC measurements helped to determine the crystal structure of a new recently synthesized type of CCl_4-solvated-C-60, stable at room temperature and below [73].

In contrast with immersion calorimetry, gas-adsorption microcalorimetry provides precise information concerning the amount and type of the active sites existing or produced (e.g. by thermal desorption of the surface groups) on carbon surfaces. In addition, the energy of interaction of such sites with probe molecules of different gases and vapors can be evaluated with this technique. However, the nature of the complexes formed after the adsorption process has to be assessed by using a complementary technique.

4. Conclusions

It has been shown that calorimetry techniques have an excellent potential for the characterization of carbons. Important information concerning physical and chemical properties of carbon surfaces can be obtained when using the appropriate calorimetric technique. Immersion calorimetry when used in combination with a minimum of adsorption data can be very useful in textural characterization of microporous carbons yielding important information about the micropore system. Moreover, enthalpies of immersion of carbons in different liquids or heats of adsorption of gases on carbon surfaces can provide relevant information about the chemistry of the carbon surfaces and its influence on the sorption properties of the carbon. Although calorimetry alone is not able to completely characterize the complex surface chemistry of carbons, it is a very useful complement to other techniques. At present, calorimetry is relatively rarely employed for the characterization of carbons but work to date demonstrates the great potential value.

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