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Surface chemistry of carbon: an atomistic approach

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Abstract - The surface chemistry of carbons can be examined from the points of view of the organic chemistry or of the structural properties of the materials. Referring to (i) reversible and irreversible adsorption of vapours on carbon surfaces and (ii) metallic derivates - carbon interactions, it was shown that both approaches are complementary.

INTRODUCTION

A large variety of carbon materials is industrially produced. For most applications, the surface chemistry of the carbons has a major influence on the performance of the material e.g. the carbon black dispersions in liquids, the dispersion of metallic compounds on carbon surfaces, the adsorption of vapours on activated carbons etc.

More than twenty years ago, the surface chemistry of carbons, carbon blacks in particular, was examined by several groups (ref. 1-3). In all cases the carbon surfaces were examined from the point of view of the organic chemistry : carbon and heteroelements, essentially oxygen and hydrogen, were considered to form chemical groups such as carboxyl -COOH, carbonyl and/or quinone C=O, hydroxyl and/or phenol -OH. Several methods, more or less specific of a given functional group or based on differences of acidity were developed and successfully used in many applications.

The utilization of surface chemical groups will be illustrated with two examples concerned with reversible (ref. 4-6) and irreversible (ref. 7) adsorption.

The characterization of porous structure of carbons by vapour adsorption may present serious difficulties due to the surface chemistry of the studied carbon. To illustrate that difficulty, we will take an example from the huge contribution of A.V. Kiselev (ref. 4-6) to the description of carbon surfaces.

The adsorption isotherms of benzene and methanol on an initial carbon black and on the same carbon after a slight oxidation were measured (fig.1). The methanol isotherm is significantly affected by surface oxidation while the benzene isotherm remains practically unchanged. Kiselev concluded that oxidation gives rise to a great number of functional groups on the surface, thus sharply increasing molecular adsorption and chemisorption of organic bases.

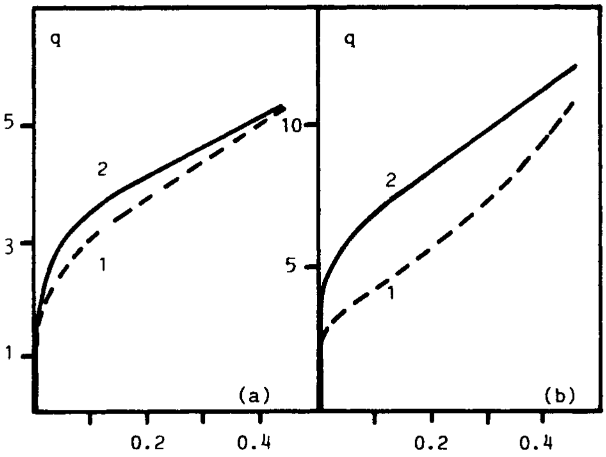


Fig. 1.
Adsorption isotherms (q in µmol /m^2) of (a) benzene and (b) methanol on

(1) original channel black and
(2) channel black oxidized with a mixture of nitric and sulfuric acids.

Irreversible adsorption is also affected by the chemistry of the carbon surface. As an example Papirer et al. (ref. 7) studied the irreversible adsorption of methanol at 473 K on two carbon blacks (Table I) ; the oxygenated groups content was determined by the method developed by H.P. Boehm (ref. 1).

As for the reversible adsorption of methanol, the irreversible adsorption depends upon chemical groups content : the higher the content per surface unit, the higher the ratio of grafted $-O-CH_3$ groups. The quantitative interpretation given by the authors is not, however, totally satisfactory. Indeed, for both carbon blacks, the surface amounts of grafted $-O-CH_3$ is more than twice the surface functional groups as determined from Boehm's method. This result shows that the organic approach on carbon surface, though very helpful, may not be enough for interpreting results.

The work of Boehm (ref. 1), Donnet (ref. 2) and Puri (ref. 3) on the chemistry of carbons were carried out in the late fifties and early sixties. At the same period, Ph. Walker Jr. and his group were trying to correlate surface and structural properties of graphitized carbon (ref. 8-9).

Graphitized carbons are anisotropic (fig. 2) ; the carbon atoms of the basal planes are less reactive than those of the prismatic faces. In a large domain of experimental conditions, the difference of reactivity is so high that carbon atoms can be classified into reactive and unreactive sites. The extent of "Active Surface Area" (A S A) corresponding to the area of active sites is thought to be a function of such properties of carbon as crystallite size and orientation, vacancy concentration in the basal plane and impurity concentration, type and location (ref.8).

TABLE 1. Reaction between methanol and carbon blacks surfaces

Carbon black	N_2 S_{BET} (m^2/g)	Oxygenated groups content (group/nm²)	Irreversible grafted $-O-CH_3$ (per nm²)
Monarch 1300*	560	1.45	4
Mogul L*	138	2.72	6

* from Cabot Corp.

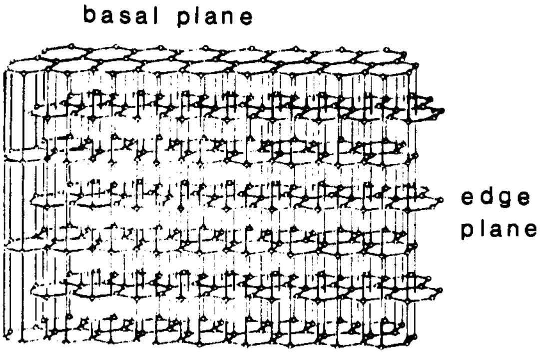


Fig. 2. Graphite structure

Walker defined a procedure to determine ASA of carbons. After the material was outgassed at 1220 K under vacuum, ASA was determined from the amount of surface oxygen complexes formed at 570 K under an initial oxygen pressure of 66.5 Pa. The number of oxygen complexes can be determined either from the weight uptake of the sample or by measuring carbon monoxide and dioxide evolved in a subsequent outgassing at 1220 K ; it was shown that CO and CO_2 are primary species of oxide complexes decomposition (ref. 9).

The ambitious undertaking of correlating the structural properties of different carbons to their ASA could not be achieved at that time. The concept of ASA was, however, extremely useful to understand the reactivity of carbon materials. The difference of reactivity can be ascribed to the fact that different carbons have, initially, different amounts of active surface area (ASA) and that their ASA changes to different extents with burn-off.

If the total surface area as determined by gas adsorption is quoted TSA, the surface density of active sites A* is equal to the ratio ASA/TSA ; the surface density of active sites corresponds to the proportion of surface carbon atoms active according to Walker's method with respect to the total number of surface carbon atoms.

The variation of A* with burn-off for different carbons is illustrated on table 2. It appears clearly that A* changes sharply in the early stages and then remains almost constant for a wide range of burn-off : after the gasification of the first carbon layers of the materials, the surface renewed during the entire oxidation exhibits the same active site density, which can be considered as a constant, a kind of fingerprint of the material.

The organic chemistry and structural approaches of the surface chemistry of carbons have been introduced with a few examples. Of course, a relation must exist between both approa-

TABLE 2. Variation of A* with burn-off

Material	Conditions of oxidation	Burn-off (%)	A* (%)
Graphitized carbon	dry air	0	0.1
black (V3G)		3	1.7
	773 K	10	2.7
(HTT 2770 K)		30	4.3
		50	4.3
Type I carbon felt	dry air	0	3.8
(HTT 2270 K)	923 K	17	8.5
		50	8.0
Coal char (10)	$H_2O/H_2/Ar$	0	60
		20	30
	1233 K	40	20
		60	20
		80	20
Coal char (11)	CO_2/N_2 (5 %)	0	11
		10	8
		30	4
(HTT 1670 K)	1223 K	50	4
		75	3

ches. It makes sense to consider that oxygenated functions are formed on active sites when the carbon material, after having been prepared at elevated temperature, is put in the presence of atmosphere at lower temperature or by oxidation in the liquid phase. In the absence of diffusion limitation or steric hindrance a simple correlation between both measurements would be expected. Practically, as pointed out by the two following examples, the correlation is not straightforward.

The oxygenated functions of V3G oxidized in air at 1473 K have been titrated by cyclic voltametry (ref. 12). The oxygen surface complexes are mainly quinone and phenol groups whose contents are 20 and 3 µeq/g, respectively. The total chemisorbed oxygen from which the ASA is computed is equal to 92 µeq/g ; it thermally desorbs mainly as CO and a small proportion as CO_2 : the chemical functions represent one fourth of the total active sites available.

J. Dentzer (ref. 13) measured by NaOH titration the acidic content of Carbolac 1 (oxidized carbon black produced by Cabot Corporation). He found 1.4 µeq/g while the value computed from ASA is 0.83 meq/g. As chemical functions are formed on active sites, their content might not be higher than the value from ASA : it is expected that carbon dioxide adsorbs on the polar surface of Carbolac 1 and is neutralized by NaOH.

The two previous examples point out the difficulty to correlate chemical and structural characterization of carbon surfaces. Actually, both approaches must be considered to interprate interfacial behaviour of carbon materials as shown in the two studies of :

- adsorption of silver diammine complexes from the liquid phase
- deposition of phthalocyanine from the gas phase.

1) Adsorption of silver diammine complexes on carbon surfaces

Silver supported by carbon surfaces can be used as a catalyst. The adsorption of silver precursor, $Ag(NH_3)_2^+$ in the present case, is associated with the reduction of the adsorbed species into metallic silver by the carbon surface (ref. 14, 15). The morphology of the silver particles depends on the adsorption conditions of the silver complex. Therefore, it is of interest to understand more precisely the interaction between the diammine complex and the carbon surface. The adsorption of silver on V3G carbon black as a function of time has been measured for different levels of burn-off (ref. 16). In all experiments, the initial concentration of $Ag(NH_3)_2NO_3$ in 0.1 N NH_3 was equal to 6 mmol /liter.

Since the adsorption of cations requires interactions with the solid, a relationship between silver adsorption and the number of active sites of the carbon surface should be found. The amount of silver fixed after 1 and 24 h of adsorption is plotted in Fig. 3 as a function of ASA. An almost linear relationship is indeed observed between the amount of silver adsorbed after a given period of time and the ASA of carbon. This result indicates that silver diammine interacts with the active sites of the carbon surface, whatever the chemical group. It means that the interaction is specific with respect to active sites but non specific with respect to the functionality of chemical groups of the surface.

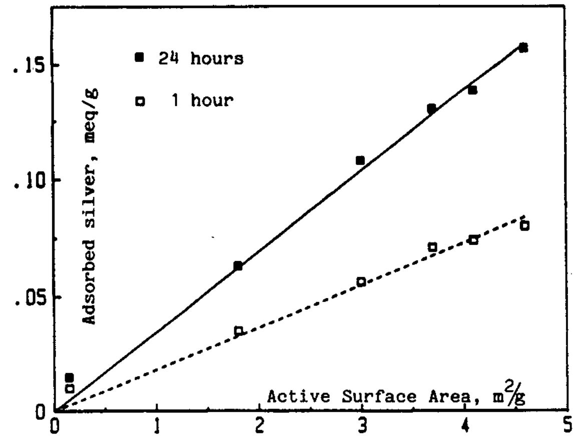


Fig. 3. Amount of silver diammine adsorbed after 1 and 24 h as a function of the active surface area of V3G.

TABLE 3. Adsorption of silver diammine cation on Carbolac 1*

Temperature of pyrolysis	Total acid groups (μeq/g)	Silver content (μeq/g)
Initial carbon	1400	1270
770 K	840	1090
1070 K	70	925

* from Cabot Corp.

Results obtained with V3G can be confirmed with another carbon substrate : Carbolac 1 before and after pyrolysis at high temperature (Table 3).

The acid functions content as titrated with sodium hydroxide decreases with the temperature of pyrolysis. After treatment at 1070 K, it is reduced 20-fold while the amount of exchanged silver is slightly modified. This result shows that the silver cations react with non acid functional groups. It is known, that after thermal decomposition of superficial acid groups, the carbon surface, when put into contact with the atmosphere, readsorbed oxygen with the formation of oxygenated complexes— essentially non-acidic (ref. 17, 18). A thermal treatment of Carbolac 1 modifies the nature of surface functional groups without significantly affecting the number of sites.

The adsorption and decomposition of silver cation on V3G and Carbolac leads to the conclusion that the adsorption is not the result of a specific exchange with a given type of functional group but rather with the extent of active sites whatever the type.

2) Phthalocyanine deposition from the gas phase

Iron phthalocyanine and polyphthalocyanines deposited on carbon electrodes are efficient catalysts for the electrochemical reduction of oxygen in metal-air batteries and alkaline fuel cells. We have studied (ref. 19) the coverage of V3G surface by iron phthalocyanine (PcFe). Experimental conditions for evaporation of PcFe at 750 K and condensation at 500 K on the carbon substrate as well as the characterization of deposits are described elsewhere (ref. 19, 20). Initial V3G and V3G gasified to 50 % burn-off in a flow of dry air have been used. Their ASA values are indicated in table 2.

The surface area of PcFe as function of loading is plotted on Fig. 4. On the initial V3G, the surface area of PcFe increases only slightly, reaches a maximum of ca. 0.1 m^2/m^2 for a loading of 1 mg/m^2 and then slightly decreases. The results for the oxidized V3G are strikingly different. The surface area of PcFe reaches a maximum value of 0.25 m^2/m^2 for a load of 2 mg/m^2 and then remains constant. The surface chemistry of the carbon definitly influences the coverage of the substrate. A few questions arises : are both nucleation and growth steps depending on the surface chemistry of the substrate ; is the influence of surface chemistry specific of a given functional group ?

In Fig. 5, the number of PcFe particles per unit area of carbon support is plotted versus PcFe loading for initial and gasified V3G. The extrapolation of both curves at low loading gives the same number of nuclei for both substrates. Therefore, the surface chemistry does not influence the nucleation step.

In Fig. 6, we have compared the mean particle size $\bar{d}_S$ and the mean crystallite size $\bar{d}_B$ (determined by X ray) of the supported PcFe. Without entering in the details of the growth mechanism we have described elsewhere (ref. 19), it can be easily noticed that the surface activity of the substrate strongly influences the coalescence of PcFe particles. In particular, the coalescence of PcFe particles is prevented on the oxidized V3G.

An important point is now to establish what prevents this coalescence . The active surface area of such a carbon is usually covered with oxygen complexes mainly carbonyl and hydroxyl groups (ref. 8). Iron phthalocyanine exchanges coordinative bonds with a variety of molecules like pyridine and quinoline (ref. 21). A complex PcFe-H$_2$O with a bond between the

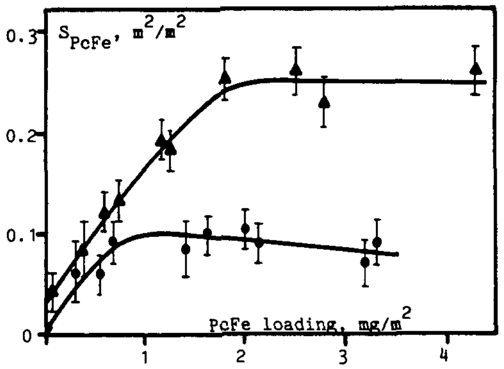


Fig. 4. Surface area of PcFe as function of loading on V3G (●) and activated V3G (▲).

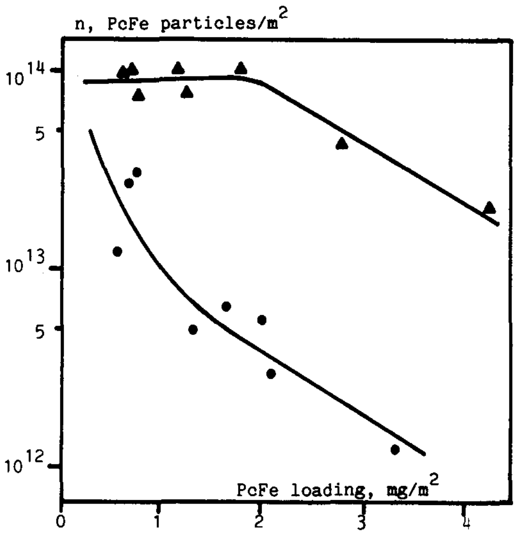
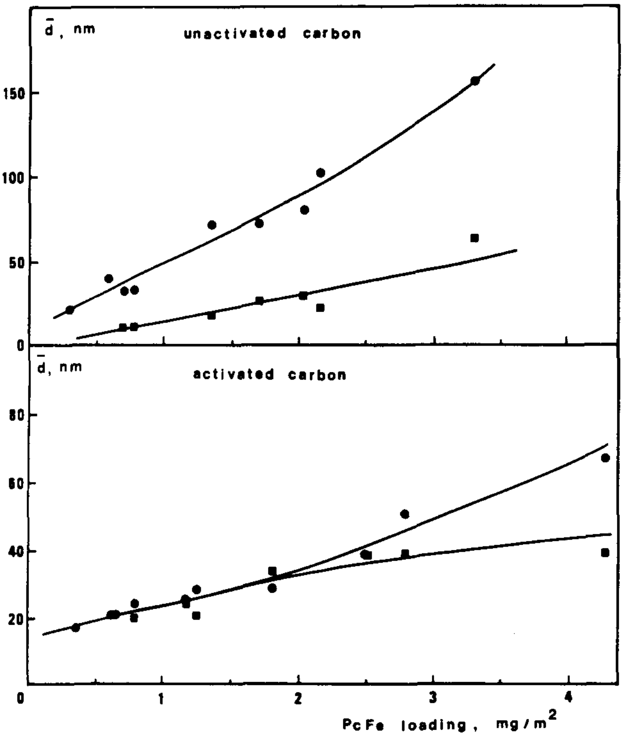


Fig. 5. Number of PcFe particles per unit of carbon support as function of PcFe loading : V3G (●), activated V3G (▲). →

metal atom and the water molecule has been noted in CCl_4 (ref. 22) and confirms our own results (ref. 20). Therefore, the higher stability of the PcFe particles on the activated carbon may originate from interfacial bonds with the oxygen complexes of the carbon surfaces as schematically drawn in Fig. 7. Upon removal of the oxygenated complexes, a decrease in the surface area of PcFe may be expected.

In order to verify this point, the oxygen groups of the carbon have been removed by H_2 treatment at 1220 K (ref. 23). Following this treatment, the carbon was cooled in H_2 and, under these conditions, the active surface area will be covered with chemisorbed hydrogen. Two samples having respectively 14.5 and 26 % PcFe in weight, have been prepared with the hydrogen-treated heterogeneous carbon. The corresponding surface areas of PcFe are compared to the previous one in Fig. 8. It is seen that after removal of the oxygen complexes the dispersion of PcFe decreases significantly and that the carbon behaves like the initial V3G support. Therefore the migration and the coalescence of the PcFe particles are considerably lowered by the presence of oxygenated groups which act as "anchors" for the supported particles.

In the case of the coverage of carbon surface by phthalocyanine from the gas phase, the organic chemistry approach of the surface reactivity combined with the concept of active sites leads to a good understanding of the growth of PcFe clusters.



← Fig. 6.
Comparison between the mean particle size $\bar{d}_S$ (●) and the mean crystallite size $\bar{d}_B$ (■) of supported PcFe.

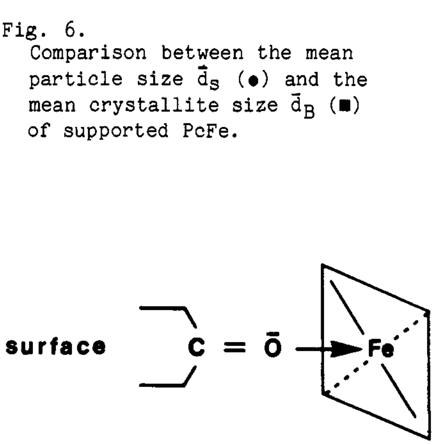


Fig. 7. Interaction between an oxygen complex and a PcFe molecule.

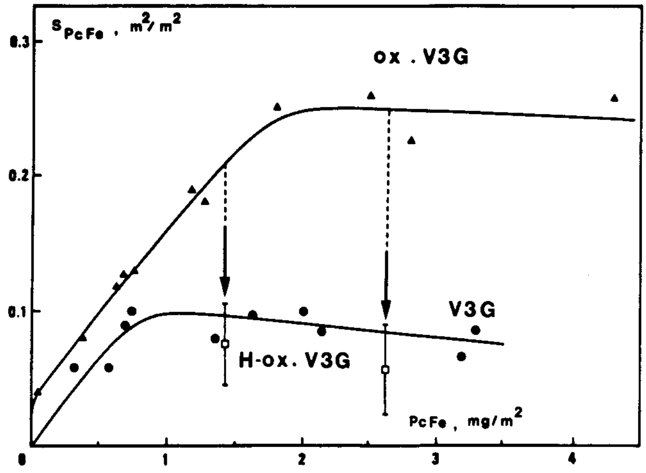


Fig. 8.
Surface area of PcFe supported on the activated and hydrogen-treated V3G (□) compared to the corresponding data on V3G (•) and activated V3G (▲).

CONCLUSION

The surface chemistry of carbons can be described in terms of functional groups with reference to the organic chemistry or in terms of Active Sites which are relevant to the structural organization of the material. The second approach which is referring to the difference between carbon atoms in the basal planes and in the prismatic planes can be considered as an atomistic approach of carbon reactivity.

Both approaches are necessarily linked since functional groups are formed on the active sites. The relation, however, is not straighforward and more has to be done for a better understanding of the relation between functional groups and the concept of actives sites. From the examples given in the present paper, it is important to emphasize the need to apply both approaches to each problem as in some cases a functional specificity is required but not in other cases. This is particularly true for adsorption studies. The ASA concept appears particularly well adapted to explain experimental results on carbon gasification.

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