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The role of surface chemistry in catalysis with carbons

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ABSTRACT

In addition to its use as a catalyst support, carbon can find application as a catalyst on its own, and a large number of applications of carbon as a catalyst, both in the liquid and in the gas phase, have been reported. Oxygen and nitrogen functional groups can perform as active sites, chemisorbing the reactants and forming surface intermediates of adequate strength. The role of surface chemistry in carbon catalysis is reviewed, with particular emphasis on those cases where the active sites have been properly identified, and useful activity correlations established.

1. Introduction

Carbon materials can be used as catalyst supports or as catalysts on their own. The first of these applications is well established, many carbon-supported catalysts being commercially available, especially in the field of Fine Chemicals production [1,2]. The subject has been comprehensively covered in several reviews [3–6].

Activated carbon has been used for a long time as a catalyst in the production of phosgene [7,8] and sulfur halides [9]. It is also used industrially for the simultaneous removal of SO_2/NO_x from flue gases, acting both as an adsorbent and as a catalyst [10–15].

In addition to these well established processes, a large number of applications of carbon as a catalyst, both in the liquid and in the gas phase, have been reported [16].

In many of the earlier publications there was an attempt to correlate the catalytic activity for a specific reaction with the physical properties (surface area and porosity) of the carbon material. Such correlations, when they exist, can provide only a partial view about the activity of the catalyst; indeed, the activity of a catalyst is determined by the nature, concentration and accessibility of its active sites, and only under particular conditions this is proportional to the surface area. In particular, catalyst deactivation and/or diffusion phenomena must be absent. Nevertheless, interesting correlations have been obtained in several cases, especially when a series of catalysts of different surface areas have been prepared from the same precursor material (thus ensuring that the intrinsic site activity is the same for each catalyst). In other cases, a critical pore size has been determined above which the carbon material can present stable activity for the specific reaction under investigation.

The decisive role of surface chemistry on the catalytic properties of carbon materials has long been recognized [17–19], but only recently it became possible to derive useful quantitative relationships.

The performance of a catalyst depends on the availability of suitable active sites, capable of chemisorbing the reactants and forming surface intermediates of adequate strength. Oxygen and nitrogen functional groups, which can be incorporated into the carbon materials by a variety of methods, play an important role in this context.

Relevant conclusions regarding the role of surface chemistry in carbon catalysis have been obtained by studying a series of catalysts prepared from the same carbon precursor with similar textural properties and different amounts of surface groups. It is then possible to correlate catalytic properties with the surface chemistry of the carbons. This approach has become possible because several methods are now available for the identification and quantification of the various types of functional groups on the surface of carbon materials [20].

This methodology has been used with success in a number of cases, such as the oxidative dehydrogenation of hydrocarbons, dehydration of alcohols, SO_2 oxidation, NO_x reduction, and various liquid phase processes for the oxidation of organic contaminants. These processes will be discussed, with particular emphasis on those cases where the active sites have been properly identified, and useful activity correlations established.

2. Characterization of the surface chemistry

In general, the carbon materials used in catalysis have the graphitic structure (activated carbons, carbon blacks, activated carbon fibers, carbon aerogels and xerogels).

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The presence of heteroatoms (O, N, H, Cl, S, . . .) bound to the edges of the graphene layers in the carbon material originates a variety of surface functional groups. Nitrogen functions are found when a nitrogen-containing precursor is used, or as a result of reaction with a nitrogen-containing reagent [21]. Oxygenated functions have been most extensively studied, since they are formed spontaneously by exposure of the carbon material to the atmosphere. The concentration of these groups can be further increased by oxidative treatments, either in the gas or liquid phase. Thermal treatments at increasing temperatures can then be used to remove selectively some of the groups formed. Acidic groups include carboxylic acids and anhydrides, lactones or lactols, and phenols, while carbonyl and ether oxygen are neutral or may form basic structures the nature of which is still open to debate, such as quinone, chromene and pyrone groups. In addition, the π electron system of the basal planes contributes to the carbon basicity [21–25]. Nitrogen functionalities were reviewed by Pels et al., Jansen and van Bekkum and Stanczyk et al. [26–29]. Fig. 1 summarizes the different oxygen and nitrogen functional groups which can be found on carbon surfaces.

In their pioneering studies, Boehm et al. [30–33] characterized the acidic oxygen groups by titration with bases of different strengths, while the basic sites were estimated by titration with HCl. Potentiometric titrations are another wet method of analysis [34–37] which can be used as an alternative to Boehm titrations. However, both methods fail to account for the total amount of oxygen present in the carbon material, which is usually ascribed to ether and carbonyl groups [23,24,38]. The application of infrared spectroscopy to characterize the surface chemistry of carbons has been the subject of a comprehensive review [39]. Special techniques, such as diffuse reflectance spectroscopy (DRIFTS), are quite useful in the identification of surface functional groups [40,41], especially when combined with other analytical tools [42].

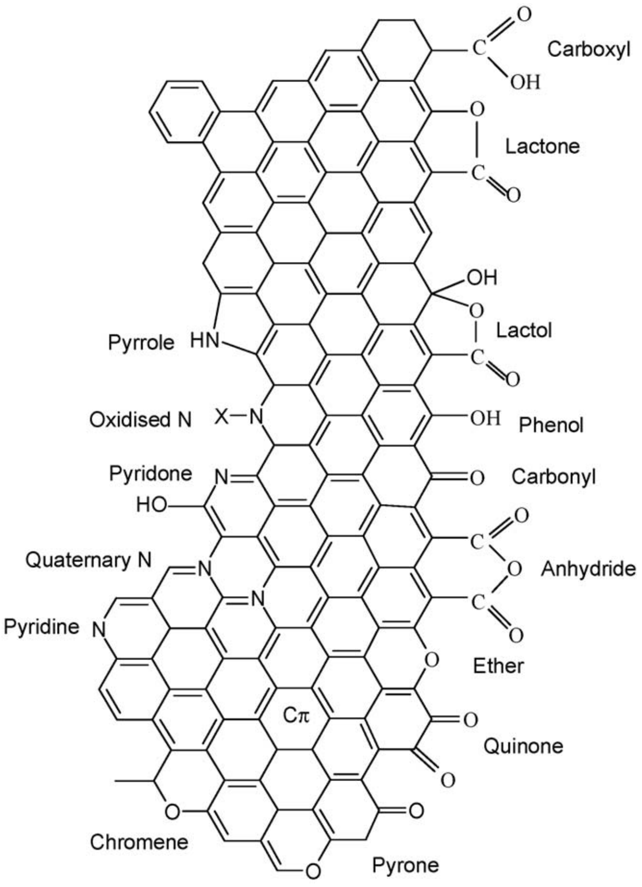

Fig. 1. Nitrogen and oxygen surface groups on carbon.

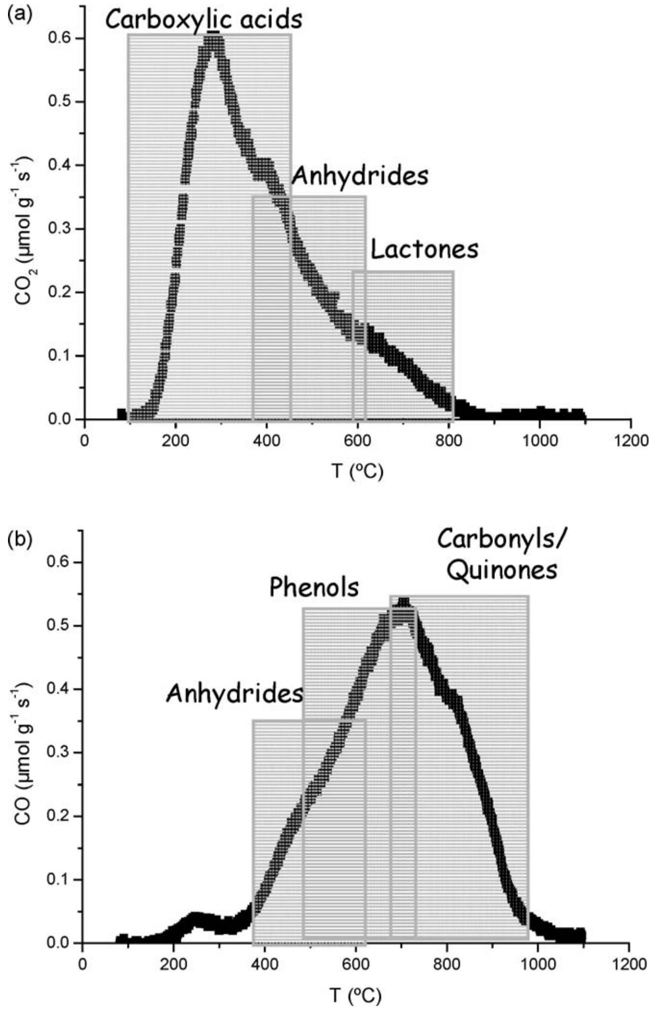

Fig. 2. Temperature ranges corresponding to the evolution of (a) CO_2 and (b) CO upon decomposition of the various types of oxygen functional groups.

Both X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD) can provide quantitative information on individual functional groups on the surface of carbon materials after deconvolution of the spectra. Suitable deconvolution procedures have been reported: deconvolution of O 1s and C 1s peaks in XPS [43–46]; deconvolution of evolved CO and CO_2 peaks in TPD [20,47–49]. XPS has also been used for the characterization of nitrogen-containing surface groups by deconvolution of the N 1s peak [26–29,50–52]. Table 1 summarizes the binding energies of the C 1s, O 1s and N 1s XPS peaks, while Fig. 2 summarizes the temperature ranges corresponding to the evolution of CO and CO_2 upon decomposition of the various types of oxygen functional groups.

Additional techniques which can be used to characterize functional groups on solid surfaces have been reviewed [53,54].

A vast amount of work has been devoted to the modification of the surface chemistry of carbon materials by chemical or thermal treatments, and to the comparison of different surface characterization techniques [27,38,54–63].

The results in Table 2 [20,64] show that the TPD method is able to account for the total oxygen content of activated carbons oxidized to different extents, while XPS leads to an overestimation which is due to the microporous nature of the materials (samples AC in Table 2). Much better agreement between the different methods is observed in the case of mesoporous carbons (samples CX in Table 2). Therefore, the TPD method is especially adequate for the characterization of oxygen functional groups on carbon

Table 1
Binding energies of the C 1s [43–45], N 1s [52] and O 1s [46] regions for the surface functional groups determined by XPS.

Region	Group	Binding energy (eV)
C 1s	Graphite, aromatics	284.6 ± 0.3
	Aliphatics, alpha carbons, $C–NH_2$	285.1–285.3
	Alcohols, phenols, CN	286.1 ± 0.3
	Carbon in keto-enolic equilibria, $C–NO_2$	286.4 ± 0.3
	Keto-groups	287.6 ± 0.3
	Carboxylic groups	289.1 ± 0.3
	Carbonate, CO_2	290.6 ± 0.3
	Plasmon loss	291.3 ± 0.3
O 1s	C=O	531.1 ± 0.3
	Hydroxyls, ethers and C=O in esters, amides, anhydrides	532.3 ± 0.3
	C–O in esters and anhydrides	533.3 ± 0.3
	Carboxylic groups	534.2 ± 0.3
	water	536.1 ± 0.3
N 1s	Pyridinic (N6)	398.7 ± 0.3
	Pyridonic or pyrrolic (N5)	400.3 ± 0.3
	Quaternary (N-Q)	401.4 ± 0.5
	Nitrogen oxides or nitrates (N-X)	402–405

Table 2
Oxygen contents (wt%) of porous carbon materials oxidized to different extents, determined by elemental analysis, TPD and XPS.

Sample	Elemental analysis	TPD	XPS
AC9	6.6	6.6	9.5
AC12	8.3	8.0	12
AC21	9.3	9.9	16
AC41	13	13	20
CX14	13	14	15
CX18	15	16	17

AC*n* = activated carbon and CX*n* = mesoporous carbon xerogel, where *n* = % burn-off (compiled from Refs. [20,64]).

materials with small porosity. Moreover, the assumptions which are made for the assignment of the TPD peaks [20,49] have been validated by a theoretical study of desorption mechanisms for oxygenated functionalities [65].

3. Carbon as a catalyst

Table 3 provides an overview of the various reactions that can be catalysed by carbon, together with the type of surface chemistry required or the nature of the active sites, when they have been identified [66]. In some cases, the reaction mechanisms have been clearly identified, and quantitative correlations were obtained between the catalyst activity and the concentration of the required active sites. Some of these results will be summarised in the following sections. Other reactions can be catalysed by functionalized carbons, but they are out of the scope of this short review. For instance, carbons functionalized with sulfonic acid groups can be efficient acid catalysts [67].

Table 3
Overview of the various reactions that can be catalysed by carbon, together with the type of surface chemistry required or the nature of the active sites.

Reactions	Surface chemistry/active sites
Gas phase	
Oxidative dehydrogenation	Quinones
Dehydration of alcohols	Carboxylic acids
Dehydrogenation of alcohols	Lewis acids and basic sites
NO_x reduction (SCR with NH_3)	Acidic surface oxides (carboxylic and lactone) + basic sites (carbonyls or N5, N6)
NO oxidation	Basic sites
SO_2 oxidation	Basic sites, pyridinic—N6
H_2S oxidation	Basic sites
Dehydrohalogenation	Pyridinic nitrogen sites
Liquid phase	
Hydrogen peroxide reactions	Basic sites
Catalytic ozonation	Basic sites
Catalytic wet air oxidation	Basic sites

3.1. Oxidative dehydrogenation

Alkhazov et al. [68] were the first to report on the use of activated carbons as catalysts for the oxidative dehydrogenation of ethylbenzene (ODE). Subsequent studies reported in the literature attempted to correlate the textural properties of the carbon materials and their activity in the ODE [69–73]. In general, it was found that coke deposition quickly blocked the small pores. A systematic study on the textural effects was published recently, using activated carbon fibers [74] and activated carbons [75]. The textural effects were found to be important up to an average pore width of 1.2 nm; for larger pores sizes, the surface chemistry was found to control catalyst performance.

Systematic studies on the role of surface chemistry in the ODE were reported by Pereira et al. [74,76–78] using activated carbons oxidized to different extents. The results obtained support the view that carbonyl/quinone groups on the surface are the active sites for this reaction, in agreement with earlier proposals [79,80]. In particular, a linear correlation was found between the activity in the ODE at 350 °C, and the concentration of the carbonyl/quinone surface groups [76]:

$$a = 3.87 \times 10^{-4}[\mathrm{Q}] + 0.71$$

where the activity a is in $\mu\mathrm{mol\,g^{-1}\,s^{-1}}$ and [Q] is the concentration of carbonyl/quinone groups ($\mu\mathrm{mol\,g^{-1}}$). The fact that there is a positive intercept shows that the reaction mixture (which contains oxygen) is able to introduce active sites onto the carbon surface.

The ODE has also been studied with nanocarbons (carbon nanotubes, onion carbon, carbon nanofibers) as catalysts, these materials offering the advantages of higher stability towards oxidation and less carbon formation [81–84]. These reports confirmed the essential role played by the carbonyl/quinone groups. The oxidative dehydrogenation of other hydrocarbons, such as propane on CNFs [85], isobutane over ACs [86] and butane on carbon nanotubes [87], has been explained in similar terms.

The ODE has been described by a redox cycle involving the quinone and hydroquinone surface groups, as schematically shown in Fig. 3. Selective oxidation reactions are frequently interpreted in terms of the so-called Mars-van Krevelen mechanism. However, the validity of some assumptions involved in this mechanism has been questioned recently [88], justifying the search for alternative kinetic models.

An outstanding performance of various nanocarbon catalysts (nanodiamond and carbon nanotubes with different wall thicknesses) was reported for the ODE, with stable activities over a period of 1500 min, and styrene selectivities as high as 95% [89]. The kinetic data obtained were well described by a Langmuir–Hinshelwood model, involving the dissociative adsorption of oxygen and noncompetitive adsorption of ethylbenzene on different sites. Moreover, isotopic tracer experiments suggested that C–H bond breaking is involved in the rate-determining step. Infrared spectroscopy supported the view that carbonyl/quinone surface groups are the active sites, in agreement with previous investigations by quasi-in situ XPS [90].

3.2. Dehydration of alcohols

The conversion of alcohols on carbon catalysts has been extensively studied [70,91–97]. Both dehydration and

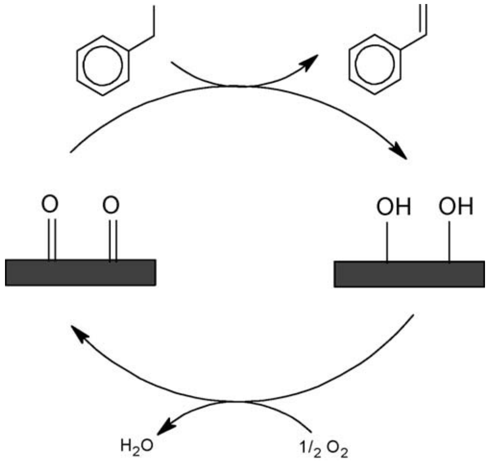

Fig. 3. Catalytic cycle proposed for the ODE.

dehydrogenation products can be formed. Using carbon catalysts oxidized to different extents and subsequently heat treated at different temperatures, it has been shown that alcohol dehydration is controlled not only by the number and strength of the carboxylic acid groups, but also by their accessibility [94,97]. The dehydration of methanol to dimethyl ether using oxidized activated carbons as catalysts was reported [95]. By treating the catalyst at increasing temperatures, in order to decompose the most unstable surface groups, the authors confirmed that the dehydration activity was due to the most strong carboxylic acid groups. Moreover, they reported a correlation between the activity and the H^+ concentration at the point of zero charge:

$$r_{\mathrm{DME}} = (2759 \pm 97)[\mathrm{H}^+]_{\mathrm{PZC}} + (0.53 \pm 0.25)$$

where r_{DME} ($\mu\mathrm{mol\,g^{-1}\,min^{-1}}$) is the rate of dimethyl ether formation at 453 K.

3.3. SO_x and NO_x abatement

The removal of SO_x and NO_x from gaseous effluents is an important field of application of porous carbons, where the adsorption capacity is combined with the catalytic activity of the carbon materials for oxidation and reduction [14,98].

Activated carbons are active catalysts for the oxidation of SO_2 into SO_3 and H_2SO_4 in the presence of O_2 and H_2O, but the role of surface chemistry in this process has been the subject of contradictory interpretations in the past.

In their work on the desulfurization activity of activated carbons, Raymundo-Piñero et al. [99,100] found that the SO_2 uptake in the presence of O_2 was determined by its oxidation into SO_3 inside the micropores, and an optimum pore size of about 0.7 nm was identified. It was also proposed that SO_3 was physically adsorbed in the micropores, rather than being chemisorbed. In addition, the activity was found to increase with the surface basicity. The introduction of nitrogen atoms into the carbon material increases the basicity and the desulfurization activity. In particular, it was found that the pyridinic groups are the most active for the catalytic oxidation of SO_2 both into SO_3 and H_2SO_4 [50], and a linear correlation between the activity (normalised by the BET surface area) and the concentration of pyridinic groups was obtained by these authors. However, the reaction mechanism is not yet fully understood. The catalytic activity of N-doped carbons in oxidation reactions has been explained in terms of the formation of superoxides, O_2^- [101] and also interpreted in terms of semiconductor properties [102]. This topic is the subject of a recent review [103].

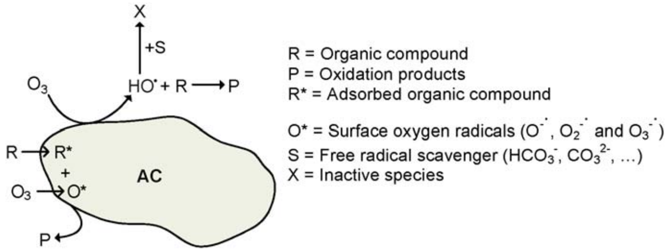

Fig. 4. Schematic representation of the main reaction pathways occurring during ozonation catalysed by activated carbon (AC). Adapted from Ref. [117].

The selective catalytic reduction of NO_x with ammonia (SCR), producing nitrogen and water, can also be efficiently catalysed by carbon materials at temperatures as low as 100–200 °C [104]. In this case, the reaction mechanism requires the formation of $CO^-(NH_4)^+$ and C(ONO) surface complexes; the active sites involved in the adsorption of NH_3 have been identified as carboxylic acids, lactones and phenols, while NO can be chemisorbed on carbonyl or pyridine surface groups [105,106].

3.4. Liquid phase processes for the oxidation of organic contaminants

Carbon as a catalyst has been used in several processes for the oxidation of organic compounds in liquid effluents, using air or oxygen (in catalytic wet air oxidation) [107–109], ozone [110–117] or hydrogen peroxide [118–121] as oxidants. The reaction mechanisms in the liquid phase are generally more complex, and may involve a combination of homogeneous and heterogeneous reaction steps; nevertheless, it is generally accepted that: the reaction mechanisms involve free radical species; basic carbons are the best catalysts; oxidation of the organic compounds may occur both in the liquid phase (homogeneous reaction) and on the catalyst surface.

The ozonation process is by far the most studied system, in particular in what concerns the investigation of reaction mechanisms. The scheme presented in Fig. 4 illustrates the main possible reaction pathways occurring in the ozonation of organic compounds. Several authors have reported that activated carbon accelerates the decomposition of ozone [122–126]. It is consensual that both textural and surface chemical properties influence that decomposition, the delocalised π electron system, or the oxygenated basic surface groups, such as chromene and pyrone [111], or the pyrrolic groups [112,126], being identified as the active centres for O_3 decomposition. Nevertheless, doubts on the mechanism still remain. According to the literature, two possible pathways can explain the decomposition of O_3 in the presence of activated carbon [115]. The first one assumes that activated carbon acts as an initiator for the decomposition of ozone, eventually through the formation of H_2O_2, yielding free radical species, such as $HO^\bullet$, in solution [127]. Another possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface free radicals (AC–O) [122], which may be any oxygen-containing active species on the surface of the activated carbon. These radicals can react with adsorbed organic species [128]. The mineralization of the organic compounds or their oxidation intermediates into CO_2 and inorganic ions (e.g. NO_3^-, NH_4^+, SO_4^{2-}) occurs both in the liquid phase through $HO^\bullet$ radical attack, and on the surface of the activated carbon.

4. Conclusions

The use of carbon as a catalyst was briefly reviewed, showing that interesting activity correlations can be established by adequate characterization of the carbon surface chemistry, in order to identify the nature and concentration of the active sites.

The redox couple quinone–hydroquinone was found to be involved in the oxidative dehydrogenation of hydrocarbons, while carboxylic acid groups were identified as the active sites for the dehydration of alcohols. Basic carbons are the most active for environmental catalysis applications, both in the gas and liquid phases.

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