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Activated Carbons for Applications in Catalysis: the point of view of a physical-chemist¹

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Abstract

This paper is a concise review on the principal physical-chemical techniques available to investigate the structural and surface properties of activated carbons (ACs) for catalytic applications. The same activated carbon has been characterized by an incredible amount of techniques: Solid State-Nuclear Magnetic Resonance, X-Ray Powder Diffraction and Raman spectroscopy for structural characterization, X-ray Photoelectron Spectroscopy, Inelastic Neutron Scattering and FT-IR spectroscopy for surface analysis, instead. The main goal is to discuss the advantages and disadvantages of all the techniques and to propose a multi-technique approach that should help in avoiding misinterpretations, as often found in the specialized literature.

1. Introduction

Activated Carbons (ACs) are materials composed almost entirely by carbon atoms. Their peculiarity is the extremely high value of surface area (well above $1000 \text{ m}^2\cdot\text{g}^{-1}$) that makes them interesting for industrial applications. They are produced starting from carbon-rich sources, having either organic (nutshells, coconut husk, wood or agricultural wastes) or fossil (peat, lignite, coal or petroleum pitch) origins. The heterogeneity of the sources allows tuning easily the intrinsic structural and surface properties of this class of materials, according to their final use. On the other hand, this variability makes difficult to generalize the properties of these materials both from the structural and from the surface point of view. Fig. 1 shows the typical aspect of an AC at different scale levels. Typically, ACs are fine powders (Fig. 1a) with an average particle size in the order of tens of micrometers. Each particle is constituted by small-sandwiched graphitic platelets, each of those is decorated by a different amount and type of functional groups (Henning and von Kienle 2010; Marsh and Rodríguez-Reinoso 2006; Schlögl 2008).

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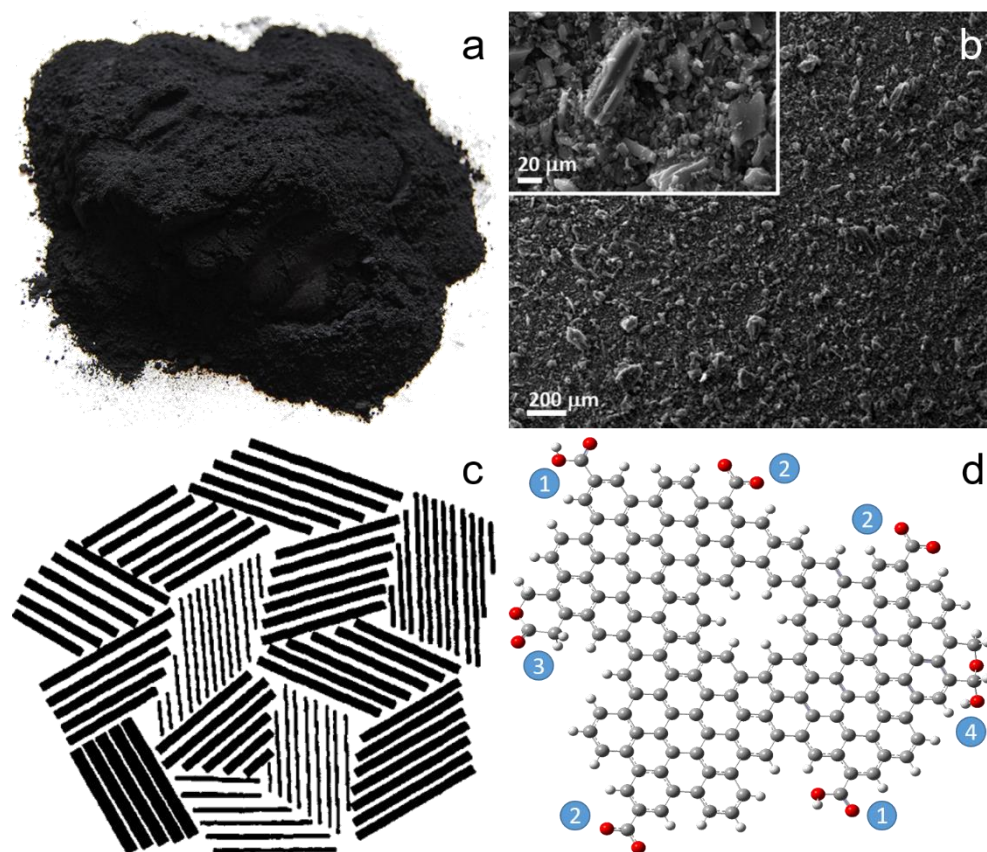


Fig. 1. Aspect of an AC of wood origin at different scale levels, from macro- (part a) to micro-scale (part b), from meso- (part c) to nano-scale (part d). Part d shows an example of possible surface groups, such as carboxylic acids (1), carboxylates (2), lactones (3), lactols (4) and CH groups, present at the edges of a sp^2 domain, as well as a possible defect (H-terminated hole).

ACs are largely employed for several technological applications, ranging from filtration, to gas trapping and catalysis (Antolini 2009; Chai et al. 2004; Deng et al. 2010; Dicks 2006; Kadirvelu et al. 2003; Maass et al. 2008; Muradov 2001; Park et al. 2003; Pernicone et al. 1998; Phan et al. 2006; Rotunno et al. 2006; Rouquerol et al. 2014; Sevilla and Mokaya 2014; Sircar et al. 1996; Steigerwalt et al. 2001; Voropaev et al. 2009; Wang et al. 2006; Watson et al. 2013; Wigmans 1989; Zhang et al. 2009; Zhao et al. 2008). The reasons at the basis of the large industrial interest upon ACs stand behind the relative low cost of production with respect to the characteristics shown by these materials, such as their low weight and very large values of specific surface area, their thermal and chemical stability, the easiness of tuning their structural and surface properties during production and post-production, and the possibility of changing their macroscopic aspect. Their low cost derives mainly by the raw materials, which are often wastes. This brings some drawbacks, namely the incredible heterogeneity depending on the raw materials that makes their properties source-dependent. For this reason, setting a robust method of analysis to properly characterize ACs in the correct way is extremely important.

This paper is intended to give an overview of some of the physical-chemical techniques suitable for investigating both structural and surface properties of ACs for applications in catalysis. A deep understanding of the ACs' properties is of primary importance for the complete knowledge of the catalyst's performances as a whole and often is determinant to avoid or postpone the catalysts deactivation (Albers et al. 1999; Albers et al. 1994; Albers et al. 2001; Aramendia et al. 1999a; Aramendia et al. 1999b; Argyle and Bartholomew 2015; Auer et al. 1998; Bartholomew 2001; Besson and Gallezot 2003; Burmeister et al. 1993; Card et al. 1983; Forzatti and Lietti 1999;

Gampine and Eyman 1998; Groppi et al. 1998; Konova et al. 2004; Kurtz et al. 2003; Lee and Trimm 1995; Mowery and McCormick 2001; Narui et al. 1999; Ordonez et al. 2001; Pellegrini et al. 2011; Pernicone et al. 1998; Prieto et al. 2013; Ryndin et al. 1989; Schanke et al. 1995; Swaan et al. 1994; Vizcaino et al. 2007; Zhang et al. 1996). The selected techniques are surely not exhaustive of all the possible experimental methods that can be applied to ACs, but they have been chosen on the basis of the personal experience of the author. The final message, however, is the same irrespective of the considered techniques: in order to obtaining a complete picture of these complex systems, the largest number of characterization techniques should be employed, otherwise the risk of a misleading interpretation of the experimental results grows rapidly.

This work would not be possible without the strict collaboration of our research group and Chimet S.p.A. (<http://www.chimet.com/en/catalyst>), who provided us along many years a large variety of ACs and related catalysts.

2. Classification of activated carbons

ACs are prepared starting from already carbonized materials, such as peat and coal, or via pyrolysis in inert atmosphere (Ar or N₂) of C-rich precursors, having either fossil or organic origin. The activation to which the “activated” term is referred is the process that leads to the development of surface area and porosity and the introduction of a variable amount of functional groups. The activation procedure can be divided into 2 main groups (Ahmadpour and Do 1996; Bansal et al. 1988; Figueiredo et al. 1999; Girgis et al. 2002; Illan-Gomez et al. 1996; Jagtoyen et al. 1992; Laine and Yunes 1992; Marsh and Walker Jr 1979; Marsh et al. 1984; Teng et al. 1998; Wigmans 1989):

- *Physical activation*, during which the porosities are produced by the effect of steam at high temperature, usually between 600 °C and 1200 °C;
- *Chemical activation*, in which the raw material is first impregnated with chemical agents, typically acids or strong bases (such as phosphoric acid or potassium hydroxide), and then treated at temperatures lower (450–900 °C) than those adopted for physical activation.

It is well established that ACs differ significantly according to the activation process. Physical activation leads to more regular structures (similar to turbostratic carbon) with a small amount of surface functionalities, with lower values of surface area and micropores volume. Chemical activation leads to more irregular structures with a consistent amount of surface functionalities, with higher values of surface area and micropores volume. An even finer tuning of the ACs properties can be achieved through a post-activation treatment, such as oxidation or graphitization. *Oxidation*, usually performed in liquid phase by using a wide range of reagents (HNO₃, H₂O₂, KMnO₄) (Acedoramos et al. 1993; Gomezserrano et al. 1991; Pradhan and Sandle 1999) causes the formation of a large number of oxygenated functional groups on the surface of ACs. *Graphitization* instead, drives to the condensation of sp² platelets, which lose the functional groups acquired during the activation process. This treatment is performed at temperatures above 2000 °C in inert atmosphere (Asaka et al. 2011; Fuertes and Alvarez 2004; Ōya and Marsh 1982) or between 800 °C and 1000 °C in the case of catalytic graphitization (Barbera et al. 2014; Sevilla and Fuertes 2006; Zhai et al. 2011).

ACs subjected to oxidation or graphitization treatments show different gas sorption property and a different behavior in the stabilization of metal nanoparticles (Serp and Figueiredo 2009).

3. A critical review on the main physical-chemical characterization techniques for ACs.

Despite the large amount of literature devoted to the structural and surface characterization of ACs for catalytic applications (Henning and von Kienle 2010; Marsh and Rodríguez-Reinoso 2006; Schlögl 2008), conflicting information and highly fragmented results are often found. Due to the intrinsic complexity of ACs, a single technique is not able to render a complete picture of the overall properties of these materials. Instead, a wide range of complementary techniques is needed to characterize ACs both from a structural and surface point of view. In the following, the main characterization techniques used to investigate ACs will be discussed, highlighting the information brought by each of them, as well as the advantages and the limitations.

3.1 Morphological analysis

The definition of the morphology of ACs is strictly dependent on the dimension scale we are interested in. Usually, to study these properties the most used techniques are microscopies in general. *Scanning Electron Microscopy* (SEM) is the most applied in the study of the morphology of ACs (Guo and Lua 2000; Phan et al. 2006; Saka 2012; Tay et al. 2009; Tseng and Tseng 2005; Yang and Qiu 2010) (Fig. 1b). With this technique is also possible to investigate the porosities of activated carbons. However, SEM gives the possibility to observe the external dimensions of the pores, without any possibility to measure the total amount of the specific surface area of ACs. For catalytic applications, the value of surface area is extremely important, since larger surface area means larger space for active phase of the catalyst to interact with the reactants. Moreover, pores can be directly involved in the reaction, influencing the selectivity towards the desired products.

Adsorption based methods are the most powerful to measure the pore size-distribution and the surface area of porous materials (such as ACs). The values obtained for specific surface area depend on the method of measurement, the size of the probe molecule and the measurement temperature. N₂ adsorption at 77 K is the most popular method for determining the surface area and characterizing the pore structure of activated carbons (Bradley and Rand 1995; Capelle and de Vooy 1983; Fernandez-Colinas et al. 1989a; Fernandez-Colinas et al. 1989b; Rodríguezreinoso et al. 1989; Sing 1994; Thommes et al. 2012). However, the determination of the micropores size distribution remains a difficult problem. Several mathematical models, such as the Langmuir theory (Langmuir 1918) or the BET theory (Brunauer et al. 1938), were developed for data interpretation. BET theory can be successfully applied to estimate the specific surface area of ACs, typically above 1000 m²·g⁻¹, making them one of the best supports for heterogeneous catalysis. However, the surface area values are often largely overestimated due to enhanced adsorption inside micropores of activated carbons (Rouquerol et al. 2007). For further information the reader is referred to the abundant literature on the topic (Marsh and Rodríguez-Reinoso 2006; Rouquerol et al. 2014).

3.2 Structural characterization

Despite the catalytic process takes place at the catalyst surface, the structure of the support may influence considerably its surface properties; recently we have demonstrated that structurally disordered ACs display a more functionalized surface (Lazzarini et al. 2016). The principal techniques giving information on the structure of ACs are *X-Ray Powder Diffraction*, *Raman spectroscopy* and *Solid-State Nuclear Magnetic Resonance*.

3.2.1 X-Ray Powder Diffraction (XRPD). This is the principal technique for studying the structure of crystalline materials. As mentioned previously, ACs may possess either a structure closer to nano-graphite or turbostratic carbons in the case of physical activation, or a quite disordered/amorphous structure in the case of chemical activation. Independently from their activation procedure, they possess quite small crystalline domains formed principally by low-

stacking-level sp^2 graphite-like platelets, decorated by a different amount of functional groups, as schematically illustrated in Fig. 1c-d. Unfortunately, the lateral dimension of the sp^2 domains usually do not exceed 2 nm in diameter, making XRPD of difficult interpretation. The typical XRPD pattern of an AC is shown in Fig. 2. It does not show distinct sharp diffraction peaks (like graphite), but only 3 very broad peaks. These peaks correspond to those typical of crystalline graphite, demonstrating that amorphous carbons are characterized by small graphitic islands (Fujimoto 2003; Houska and Warren 1954; Li et al. 2007; Shen et al. 1996; Zickler et al. 2006). The first peak at $2\theta = 23^\circ$ is similar to the (002) reflection of graphite, attributed to the stacking of the graphene layers (Houska and Warren 1954; Li et al. 2007; Zickler et al. 2006). The other two peaks, respectively at $2\theta = 44^\circ$ and 80° , correspond to the (100) and (111) reflections originating from the in-plane structure of graphitic crystallites (Houska and Warren 1954; Li et al. 2007; Zickler et al. 2006). Dealing with not-ordered systems, a more realistic description of the amorphous carbon phases, rather than as contribution of the single (100) and (111) reflections to the graphite XRD pattern, would be obtained by considering these XRD reflections being originated by the whole family of 10 and 11 plains (Inagaki et al. 2014; Vázquez-Santos et al. 2012; Zhai et al. 2011). Narrower peaks correspond to crystallites having a larger lateral dimension.

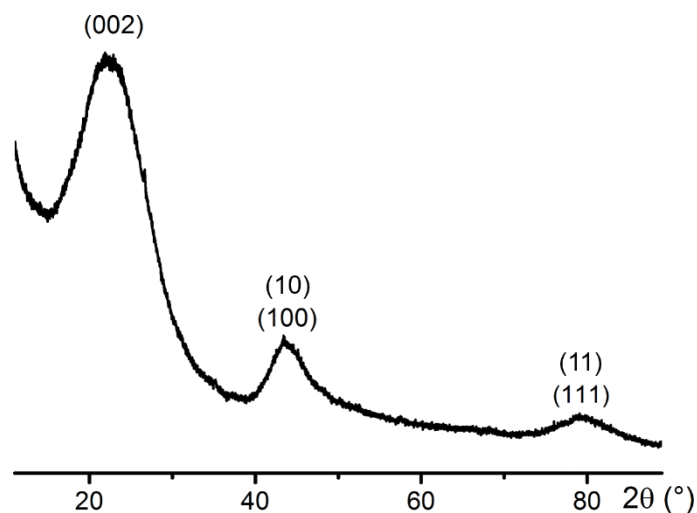


Fig. 2. XRPD pattern (counts VS angle) for a wood carbon chemically activated. Labels on diffraction peaks indicate their assignment.

According to the specialized literature, the lateral size (L_a) of the sp^2 crystallites can be evaluated from the width of the (100) and (111) peaks by using the Scherrer equation (Eq. 1):

$$L_a = (K \cdot \lambda) / (\beta \cdot \cos\theta) \quad (1)$$

where K is a dimensionless shape factor (usually 0.9), λ is the incident wavelength, β is the line broadening at half the maximum intensity (FWHM), θ is the Bragg diffraction angle. In the literature, discrepancies in the determination of the average crystallite size are present, depending on the different methodologies adopted for peak profile evaluation (Ungár et al. 2002); furthermore, also the defects (vacancies and heteroatoms) and strain of the carbon lattice may contribute to the diffraction broadening (Cuesta et al. 1998; Johnson et al. 1986; Zickler et al. 2006). For this reason, the evaluation of L_a obtained from the Scherrer equation for ACs should be considered only as semi-quantitative, and coupling the information obtained from XRPD with other structural techniques is highly recommended.

3.2.2 Solid-State Nuclear Magnetic Resonance (SS-NMR). The local structure of ACs can be probed by ^{13}C CP/MAS SSNMR measurements, which gives complementary information respect to

X-ray diffraction. Indeed, SSNMR can provide structural information on materials having a strong lack of long-range order, as in the case of activated carbons (Harris 2012; Harris et al. 2009). While diffraction experiments reveal topological data, SSNMR experiences connections and distances at local and intermediate length scales (Chierotti and Gobetto 2013). CPMAS (Stejskal et al. 1977) exploits a pulse sequence for direct excitation of ^1H spin polarization, followed by cross polarization transfer to ^{13}C and its signal detection. This is used in order to enhance the signal of nuclei with a low gyromagnetic ratio (such as ^{13}C) by magnetization transfer from nuclei with a higher gyromagnetic ratio (^1H). Therefore, ACs having a larger amount of H-terminations give ^{13}C CPMAS NMR spectra with a better signal-to-noise ratio. The ^{13}C NMR spectra of ACs is usually dominated by a broad peak centered around 125 ppm, which is characteristic of sp^2 -hybridized carbon in condensed aromatic rings (Fig. 3). The line width of the signal is usually quite broad, due to a large distribution of sp^2 islands having a different size. We have recently demonstrated that the distribution of the sp^2 domains is narrower for a wood carbon chemically activated than for a physically activated carbon (Lazzarini et al. 2016). In addition to the signal at 125 ppm, in some cases a weak peak around 180 ppm can be observed, which is indicative of the presence of oxygen-containing surface functional groups.

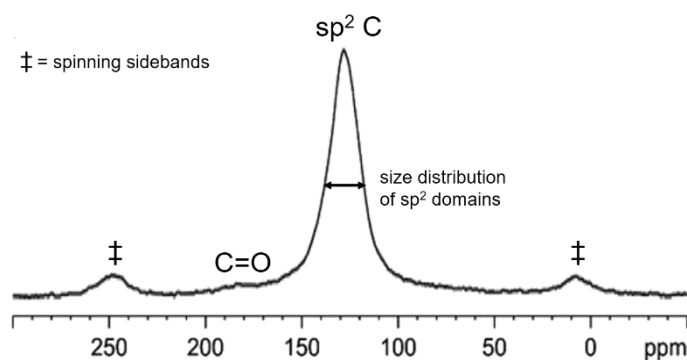


Fig. 3. ^{13}C CPMAS SSNMR spectrum (intensity VS shift) of a wood carbon chemically activated. The main assignments are also reported.

In the case of phosphoric acid activated carbons, ^{31}P nucleus can also be probed with CPMAS SSNMR. The ^{31}P CPMAS NMR spectrum is usually characterized by two main signals, centered around 1.3 and 14.1 ppm. The first one is characteristic of phosphates, i.e. phosphorus bound to four oxygen atoms, likely contained in the residual inorganic ashes of the activation process. On the contrary, the resonance at 14.1 ppm is attributed to phosphonates, i.e. organo-phosphorous compounds containing one P-C bond, revealing that at least a fraction of phosphorous has functionalized the carbon (Benaddi et al. 1998; Budinova et al. 2006; Jimenez et al. 2015; Puziy et al. 2002; Puziy et al. 2008; Sadykova et al. 2015).

3.2.3 Raman spectroscopy. Raman spectroscopy is among the most powerful technique to study the structure of activated carbons. It is based on the inelastic light scattering of a monochromatic light (the so-called Raman Effect), obtained with a laser source in the range between near IR and UV. The laser light excites framework vibrations (phonon modes) and the backscattered photons come out with a lower ($\nu_0 - \nu_{\text{vibr}}$) or higher ($\nu_0 + \nu_{\text{vibr}}$) energy with respect to the incoming photons (ν_0). The energy difference (ν_{vibr}) correspond to the excited vibrational mode. For a vibration to be Raman active it should involve a change in the electric polarizability, while there are no restrictions on the dipole moment (as for FT-IR spectroscopy). This is very useful for ACs, which are entirely composed by C-C bonds without any dipole moment, but with a good polarizability (Lin-Vien et al. 1991). The typical wavelengths of excitation (λ_{exc}) for carbon-based materials are 514 nm (green light) and 244 nm (deep UV light). The first one gives information mainly on the sp^2 domains,

because that wavelength has a strong selectivity towards the π states of sp^2 -hybridized carbon species (Wada and Solin 1981). UV Raman, instead, excites both the π and the σ states; therefore it is able to probe both sp^2 and sp^3 carbon species (Gilkes et al. 1997). Since the shape, position and intensity of the Raman fingerprints are laser-line dependent, a multi-line method should provide a complementary investigation and a more advanced Raman approach (Ferrari and Robertson 2004). It is also true that, despite UV radiation seems more promising for the analysis of this class of materials, most of the Raman spectra on ACs reported in the literature are obtained by using $\lambda_{\text{exc}} = 514$ nm. For this reason, we will limit the discussion to this excitation wavelength.

The typical Raman spectrum of an activated carbon collected with $\lambda_{\text{exc}} = 514$ nm is shown in Fig. 4. This AC has been chosen because the corresponding Raman spectrum contains all the possible signals observable in the spectrum of an AC. It is dominated by 2 intense bands, attributed to vibrational modes involving sp^2 carbon species of disordered microcrystalline domains. The signal around 1600 cm^{-1} (G band) is due to the stretching of sp^2 C-C bonds (either in aromatic rings or chains) (Henning and von Kienle 2010; Marsh and Rodríguez-Reinoso 2006; Schlögl 2008). For crystalline graphite, this mode has E_{2g} symmetry (Fig. 4b) and gives a band around 1580 cm^{-1} . The 20 cm^{-1} shift is typical of disordered graphitic systems and is explained by considering the overlap of a second band (D2, around 1620 cm^{-1}), which is ascribed to the same kind of vibrational mode, but involving surface “graphene-like” layers (i.e. not sandwiched between two other layers) (Beysac et al. 2003; Castiglioni et al. 2004; Sadezky et al. 2005; Tommasini et al. 2011; Wang et al. 1990) or sp^2 nanostructures with a strained geometry (Galué 2014). The position of the G band indicates that the graphene stacking order is very low in ACs and that graphite-like platelets are also partially defective. The second intense signal in the Raman spectrum around 1350 cm^{-1} (D band) is usually assigned to a lattice breathing mode with A_{1g} symmetry (Fig. 4b) that is forbidden in ideal graphitic crystals but becomes Raman active in the presence of structural disorder (Castiglioni et al. 2004; Ferrari 2007; Henning and von Kienle 2010; Marsh and Rodríguez-Reinoso 2006; Schlögl 2008; Tommasini et al. 2011).

The analysis of the G and D bands can be useful to define the order degree in ACs. In principle, the relative ratio between the intensity of the D and G bands – $I(D)/I(G)$ – should correlate with the degree of structural disorder. Since long time, the intensity ratio between the two bands has been inversely correlated with carbon cluster dimension (according to the Tuinstra-Koenig correlation, TK) (Tuinstra and Koenig 1970) and considered as an indicator of the size of the graphitic domains in ACs (Fig. 4c). More recently, it has been proposed that the TK correlation is applicable only to graphitic domains having a lateral dimension larger than about 2 nm. Indeed, the intensity of the D band is proportional to the probability of finding a six-fold ring in the cluster, which is again proportional to the cluster size. Therefore, for sp^2 platelets having dimensions below 2 nm the development of a D band in the Raman spectrum indicates ordering, which is exactly the contrary for graphitic clusters larger than 2 nm (Ferrari and Robertson 2000). Fig. 4c summarizes the behavior of $I(D)/I(G)$ with the sp^2 cluster size and the limits of TK correlation. It is clear that the analysis of the Raman spectrum for ACs (which are highly defective materials) is not straightforward and, once more, coupling with the results obtained from complementary techniques is mandatory to avoid misinterpretation.

The Raman spectrum shown in Fig. 4a displays 2 additional bands. Both these signals have been ascribed to stretching vibrations involving an amorphous carbon phase, which can be present in variable amounts in ACs. The D3 band, observed between the G and the D bands around 1450 cm^{-1} , is attributed to randomly distributed amorphous carbon on the interstitial position of the graphitic islands (Jawhari et al. 1995). The I band around 1150 cm^{-1} , originated from the

coexistence of sp^3 phase and conjugated non-aromatic polyenes, present as pending groups of graphitic platelets (Ferrari and Robertson 2001). Finally, a very weak band is observed around 1700 cm^{-1} , which is due to the $\nu(\text{C}=\text{O})$ vibrations of oxygenated groups at the surface of the AC. The contributions in this spectral region are usually very weak, since Raman spectroscopy gives mainly information on the bulk of the investigated material.

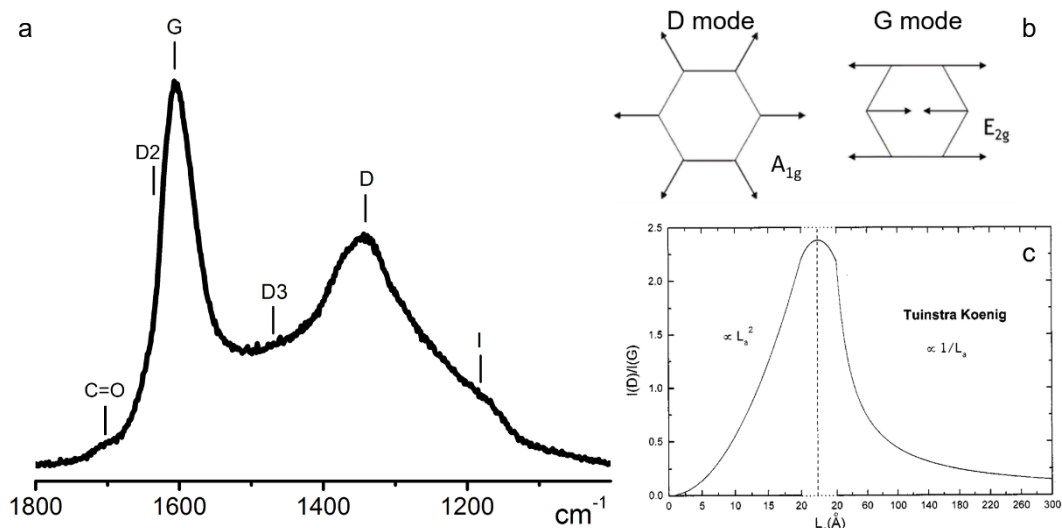


Fig. 4. Part a) Typical Raman spectrum ($\lambda_{\text{exc}} = 514\text{ nm}$; counts VS Raman shift) of a chemically activated carbon and assignment of the main features. Part b) Schematic representation of the G and D vibrational modes. Part c) Dependence of the $I(\text{D})/I(\text{G})$ ratio as a function of the lateral size (L_a) of the sp^2 domains.

3.3 Surface characterization

The surface of ACs is the most relevant part of the catalyst. Several functional groups can be present at the surface of ACs, depending on their origin and on the activation procedure, as well as on the post-activation treatments. The catalytic performances of a catalyst based on ACs are strongly influenced by the nature, the concentration and the accessibility of the surface groups. In fact, the surface functional groups influence the formation of surface intermediates, the wettability of the carbon in different solvents, the interaction with the active phase, the thermal stability and many other relevant properties. For these reasons, a deep characterization of the surface chemistry of ACs is mandatory to understand the catalytic performances.

H and O are the most abundant heteroatoms in ACs, the former found in the C-H terminations of the graphitic platelets, and the latter present in a variety of different functional groups having an acid (carboxyls and anhydrides, lactones and phenols), basic (quinones, pyrones), or neutral (carbonyls and ethers) nature. Oxygen containing groups can be detected with several techniques, such as *Chemical Titration*, *X-ray Photoelectron Spectroscopy (XPS)* and *FT-IR spectroscopy*. H-terminations can be efficiently probed with neutrons and in particular by *Inelastic Neutron Scattering (INS)*.

3.3.1 Chemical Titration. Classical acid/base titration, proposed by Boehm (Boehm 1994; Boehm 2002; Noh and Schwarz 1990; Salame and Bandosz 2003), can be used to quantify the basic and acid groups present at the carbon surface. To this aim, the AC is contacted with a standard basic or acid solution for long time, followed by a back-titration of the solution (Ania et al. 2004; El-Sayed and Bandosz 2003). The principle of this technique is that different surface functionalities can be probed as a function of their neutralization behavior (Boehm et al. 1964; Noh and Schwarz 1989). The amount of acid functionalities is measured assuming that NaOH neutralizes carboxyl, phenol

and lactone groups; Na_2CO_3 carboxyl and lactone groups and NaHCO_3 only carboxyl groups (Boehm 1994; Jia et al. 2002; Tamon and Okazaki 1996). Surface basic sites can be quantified by using HCl as titrant agent (Jia et al. 2002; Papirer et al. 1987). Back-titration using NaOH and HCl respectively (Adib et al. 1999; Jia et al. 2002; Salame and Bandosz 1999), determines the amount of acid or basic functional groups. The main drawback of this technique is that it usually determines about half of the total oxygen content available in the activated carbon (Noh and Schwarz 1989; Shafeeyan et al. 2010), being the neutral groups not detectable.

3.3.2 X-ray Photoelectron Spectroscopy (XPS). XPS is maybe the most surface sensitive and selective technique for the investigation of ACs functional groups. It measures the kinetic energy and the number of photoelectrons excited by a monochromatic X-ray beam and escaping from the first 10 nm of the surface of the material. Dealing with the detection of electrons, XPS requires ultra-high vacuum ($P < 10^{-9}$ mbar) regime. For ACs a few hundreds eV of incident radiation energy is sufficient to obtain a good signal coming from core levels of light elements (C 1s at 284.2 eV, O 1s at 543.1 eV and N 1s at 409.9 eV). In most of the cases, the C 1s XPS signal is the most informative signal, since it provides also information on the oxygen containing functional groups.

A typical C 1s XPS spectrum of a chemically activated carbon is shown in Fig. 5. It is characterized by a dominant peak with a pronounced tail at higher BE, indicating the presence of various functional groups at the carbon surface. For this reason, the C 1s XPS spectra are usually analyzed by deconvolution into different components. The seminal deconvolution method (Biniak et al. 1997; Puziy et al. 2008) involves the use of 6 gaussian peaks, as shown in Fig. 5. The most intense band is a tailed peak located around 284.5 eV and assigned to graphitic sp^2 carbon. Carbon species with sp^3 hybridization contribute at slightly lower BEs with respect to the aromatic C-C peak. The long tail at higher binding energies indicates the presence of C-O bonds with different nature. In particular, the contributions of alcohol (C-OH) or ether (C-O-C) groups, carbonyl groups (C=O), and carboxyl (O=C-OH) and/or ester (O=C-O-C) groups can be well separated. The last tiny signal around 292 eV is a satellite peak due to π - π^* shake-up transitions in aromatic rings (Albers et al. 1992; Biniak et al. 1997; Darmstadt et al. 1994; Desimoni et al. 1992; Kozlowski and Sherwood 1986; Proctor and Sherwood 1983; Reis et al. 1995; Xie and Sherwood 1989).

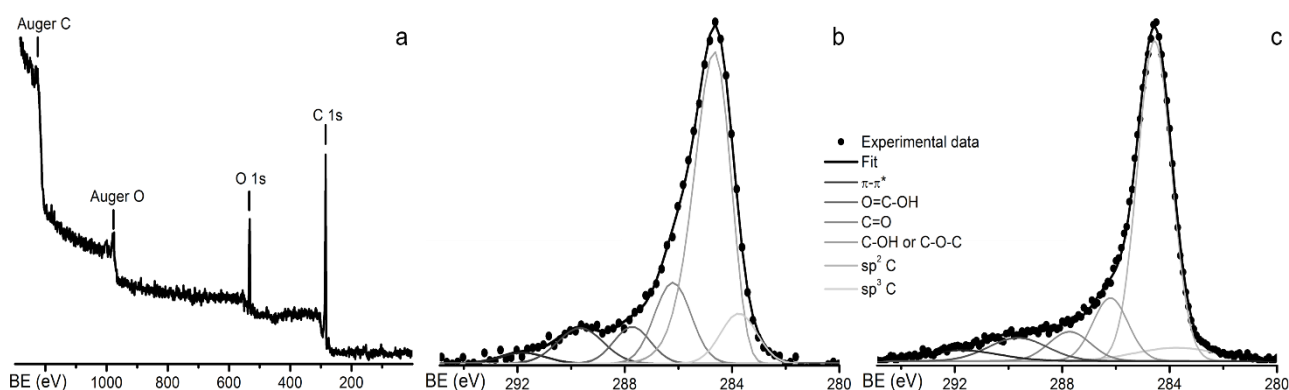


Fig. 5. Part a) Survey spectrum of a chemical AC. From this spectrum, it is possible to recognize also the presence of other elements (i.e. O) present at the surface of the carbon. Part b) and c) C 1s XPS spectrum of the same activated carbon, after background subtraction and deconvolution of the different contributions of C species to the total spectrum. Spectrum in part b) was collected with a laboratory instrument, the one in part c) was collected by using synchrotron radiation. All the spectrum are reported in counts VS binding energy.

Very recently, this deconvolution method has been improved by Smith *et al.* (Smith et al. 2016), by adding a peak near 285 eV to account for defective species.

In the literature are present several different procedures for C 1s XPS peak fit. The objective difficulties are due to an overall sum of the possible different interpretations given to those spectra. The first problem to be faced is the peak shape of C 1s spectra, which is affected by contributions from defects and functional groups that are often not sufficiently deeply analyzed. ACs spectrum shape may be influenced not only by the overlap between all the carbon species present in the sample, but also affected by the electronic structure of the sample (e.g. intrinsic conducting or semi-conducting behavior of the samples). For these reasons, the number of peaks used to fit C 1s XPS spectra of carbon based materials can vary considerably (Biniak et al. 1997; Blume et al. 2015; Chen et al. 2008; Jeong et al. 2008; Langley et al. 2006; Lopez et al. 1991; Smith et al. 2016). An additional source of incomprehension is the choice of the photon source that affects the observed line shapes. This is clearly visible comparing the broader spectrum collected with a non-monochromatic laboratory ESCA instrument (Fig. 5b) with respect to the one collected on APE beamline at ELETTRA Sincrotrone Trieste (Fig. 5c). The shape of the spectrum in Fig. 5b is less defined, and this could affect the quantitative evaluation of different chemical species present in the sample. Moreover, it could affect the shape and number of fitted peaks, leading to additional misinterpretations (Blume et al. 2015).

3.3.3 FT-IR Spectroscopy and Inelastic Neutron Scattering (INS). Both techniques can be defined as vibrational spectroscopies, although they are based on different probes (photons for FT-IR and neutrons for INS) and therefore they give complementary information. IR spectroscopy is sensitive to those chemical species having at least a vibrational mode associated with changes in the dipole moment (Atkins and de Paula 2009). INS instead, is extremely powerful in detecting vibrations involving the hydrogenous species. Applied to ACs (Albers et al. 2002; Albers et al. 2003; Fillaux et al. 1995a; Fillaux et al. 1994; Fillaux et al. 1995b; Honeybone et al. 1994; Piovano et al. 2015), neutron scattering is almost element selective with respect to H atoms, since the incoherent scattering cross section of H is 80.26 barn, against 0.001 barn of C and 0.0008 barn of O (Sears 1992). Having no selection rules, the signals intensity is proportional only to the amount of each chemical species present under the neutron beam, making INS a quantitative technique. The main drawbacks of this technique are the need of a large amount of sample (on the gram scale) and the need of large scale facilities for the production of neutrons, making this technique extremely costly. On the contrary, IR spectroscopy is one of the most affordable and versatile technique for surface science investigation.

FT-IR spectroscopy has been long exploited to characterize activated carbons (Mawhinney and Yates Jr 2001; Meldrum and Rochester 1990a; Meldrum and Rochester 1990b; Meldrum and Rochester 1990c; Meldrum and Rochester 1990d; Moreno-Castilla et al. 1997; Moreno-Castilla et al. 1995; Moreno-Castilla et al. 2000) and carbon-supported catalysts (Gokagac et al. 2003; Venter and Vannice 1989), despite the fact that IR spectra of ACs are difficult to be obtained, because of problematic sample preparation, scarce light transmission and uneven light scattering. Moreover, the electronic structure of carbon materials makes them absorbing all the radiation through the visible region and the infrared one, limiting the spectra collection in the conventional transmission mode. For these reasons, quite often the IR spectra of carbon-based materials contain spectral artefacts or distortions, which are unavoidable and complicate data interpretation. These problems can be partially avoided by performing the measurements in diffuse reflectance (DRIFT) mode.

Fig. 6a shows a typical DRIFT spectrum of a chemically activated carbon. Due to the difficulties in obtaining decent IR spectra, the assignment of the main absorption bands has not been trivial for a long time and numerous different interpretations are present in the literature. However, the following assignments seem to be now univocally defined:

a) The narrow and intense band centered around 1600 cm^{-1} is assigned to $\nu(\text{C}=\text{C})$ vibrational modes of conjugated sp^2 bonds belonging to graphitic islands (Ferrari et al. 2003). Its intensity may be influenced by the presence of oxygen atoms, causing an increase in the local dipole moment associated with these ring vibrations.

b) The intense and very broad absorption between $1300\text{--}1000\text{ cm}^{-1}$ is due to the overlap of many vibrational modes and it is extremely difficult to be deconvoluted. In-plane C–H bending modes (coupled with C–C collective modes) and modes related to geometrical distortion of the C–C skeleton should contribute in this region (Centrone et al. 2005; Ferrari et al. 2003). Dealing with carbons chemically activated H_3PO_4 , also P=O stretching vibration of phosphonate groups may contribute in the same spectral region ($1380\text{--}1140\text{ cm}^{-1}$) (Lin-Vien et al. 1991; Nakamoto 1978).

c) The narrow bands in the $900\text{--}750\text{ cm}^{-1}$ region are due to the out-of-plane vibrations of C–H bonds at the edges (Centrone et al. 2005). It has been demonstrated that these vibrations are dependent on the number of adjacent hydrogen atoms. A band in the $860\text{--}910\text{ cm}^{-1}$ region accounts for an isolated hydrogen atom (solo), 2 bands at $800\text{--}810\text{ cm}^{-1}$ and $810\text{--}860\text{ cm}^{-1}$ account for two adjacent hydrogen atoms (duo), while 3 bands at $750\text{--}770\text{ cm}^{-1}$, $770\text{--}800\text{ cm}^{-1}$ and $800\text{--}810\text{ cm}^{-1}$ account for three adjacent hydrogen atoms (trio).

d) Absorption bands in the $1800\text{--}1700\text{ cm}^{-1}$ region, are indicative of O-containing surface groups (e.g. a band around 1700 cm^{-1} is typical of carbonyl or carboxyl species, while a band around 1800 cm^{-1} is characteristic for anhydrides) (Lin-Vien et al. 1991).

Fig. 6b shows a typical INS spectrum of an activated carbon. When normalized with respect to sample mass and acquisition time, the intensity of each signal is directly proportional to the amount of the corresponding species. Hence, the total spectrum intensity gives a rough indication of the surface area of the AC, since a larger surface area implies a larger amount of hydrogen terminations. Another effect influencing the total spectrum intensity is the dimension of the sp^2 platelets constituting the AC, since smaller sp^2 platelets correspond to a larger amount of edges (with H-terminations). The INS spectrum in Fig. 6b can be directly compared to the IR spectrum in Fig. 6a; but for INS the intensity of the bands is not subject to any selection rule. Other signals not present in the DRIFT spectrum can be identified as follows:

a) The weak and broad band in the $700\text{--}400\text{ cm}^{-1}$ region is mainly due to C–C torsion modes of C atoms at sp^2 edges, indirectly causing a substantial movement of the hydrogen atoms (riding vibrations) (Piovano et al. 2015), although in the same region also the acidic hydrogen of carboxyl groups present at graphitic platelets edges may weakly contribute (Piovano et al. 2015).

b) The intense band at 950 cm^{-1} , which is scarcely discussed in the literature, is assigned to the out-of-plane vibrations of C-H species belonging to irregular borders and vibrating not in phase (Piovano et al. 2015). This vibrational mode is not IR active and for this reason this band is not observed in the DRIFT spectrum.

It emerges that, INS and FT-IR spectroscopy when synergistically coupled to the investigation of the same AC, are tremendously efficient to characterize the surface species.

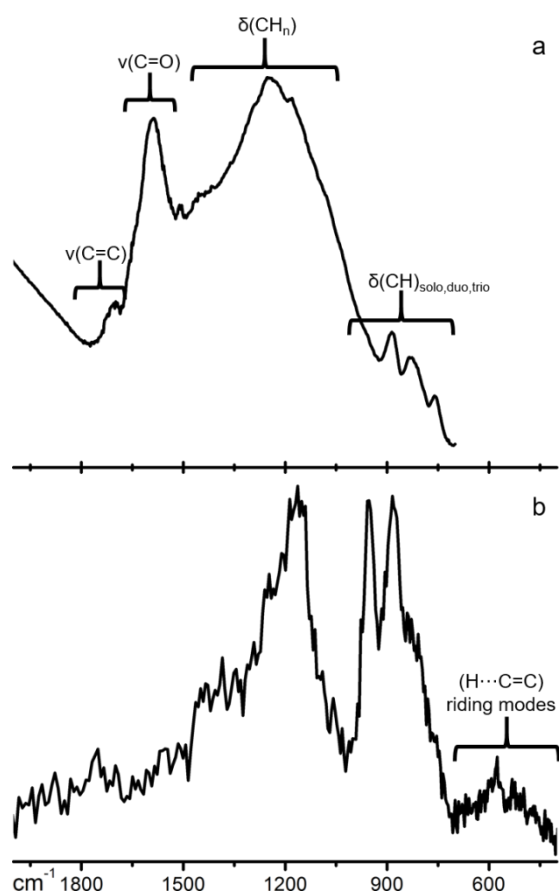


Fig. 6. DRIFT (part a) and INS (part b) spectra of a chemically activated carbon with assignments of the main absorption bands. Only the most significant spectral region is shown. Spectra are reported in Kubelka-Munk units (part a) and $S(Q,\omega)$ (part b) VS wavenumber.

4. Conclusions

The intention of this work is to define a robust guideline for the characterization of activated carbons for catalytic applications from a physical-chemical point of view. The whole set of techniques here described, when used in a complementary way, may shed light on the structural and surface properties of ACs in relation to their production methodology or the post-activation treatments. XRPD, ¹³C and ³¹P SS-NMR and Raman spectroscopy are able to describe ACs from a structural point of view, giving information on the stacking order and on the average dimension of graphite-like platelets, which are the building blocks of their structure. Chemical titration is able to probe acidity and basicity of carbons surface. XPS and FT-IR spectroscopies are fundamental in describing the oxygen-containing species present at the borders of the sp² domains. INS, thanks to its selectivity towards hydrogen atoms, is fundamental in probing C-H terminations typical of activated carbons. It is worth underlying that the same characterization methods can be extended to the investigation of all carbon-based materials (e.g. amorphous carbons, carbon fibers and nanotubes, graphene based materials, etc.), since they all present the same experimental drawbacks, related to their intrinsic heterogeneity and strong interaction with electromagnetic radiation.

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