

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

## Activated carbons for applications in catalysis: the point of view of a physical-chemist

### This is the author's manuscript

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1633133> since 2017-05-11T16:34:58Z

*Published version:*

DOI:10.1007/s12210-017-0603-5

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



# UNIVERSITÀ DEGLI STUDI DI TORINO

***This is an author version of the contribution published on:***

*Questa è la versione dell'autore dell'opera:*

*[Rend. Fis. Acc. Lincei, 2017, p. 1-14, DOI: 10.1007/s12210-017-0603-5]*

***The definitive version is available at:***

*La versione definitiva è disponibile alla URL:*

*[<http://link.springer.com/article/10.1007%2Fs12210-017-0603-5>]*

# *Activated Carbons for Applications in Catalysis: the point of view of a physical-chemist<sup>1</sup>*

Andrea Lazzarini

Department of Chemistry, NIS Centre and INSTM, University of Turin, Via Giuria 7, Turin, I-10125, Italy.

E-mail: andrea.lazzarini@unito.it

## **Abstract**

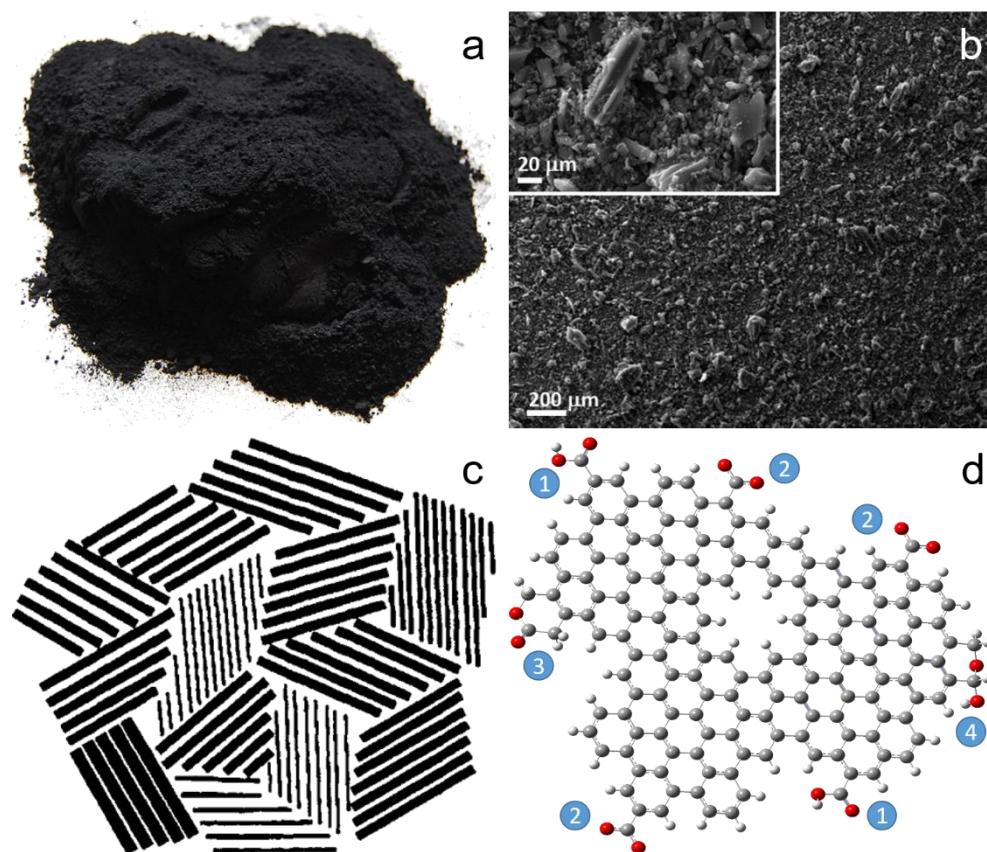
This paper is a concise review on the principal physical-chemical techniques available to investigate the structural and surface properties of activated carbons (ACs) for catalytic applications. The same activated carbon has been characterized by an incredible amount of techniques: Solid State-Nuclear 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).

---

<sup>1</sup> This contribution is the written, peer-reviewed version of a paper presented by a participant to the Conference "Concepts in catalysis: from heterogeneous to homogeneous and enzymatic catalysis", held at Accademia Nazionale dei Lincei in Rome on February 25-26, 2016.



**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 N<sub>2</sub>) 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 (HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, KMnO<sub>4</sub>) (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 sp<sup>2</sup> 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.

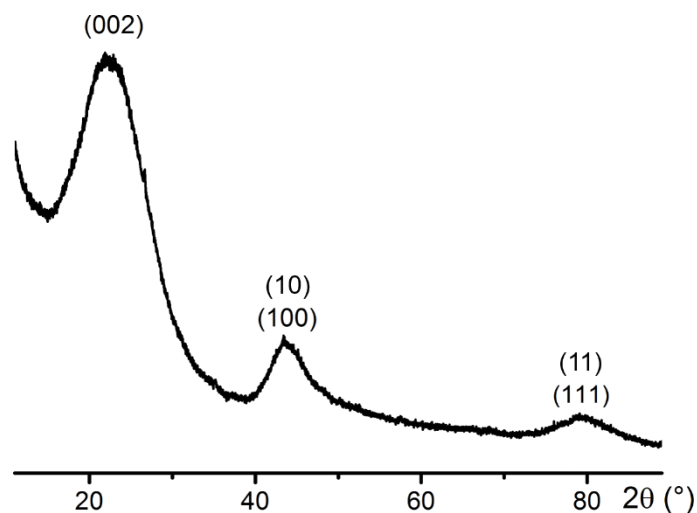
Adsorption based methods are the most powerful to measure the pore size-distribution and the surface area of porous materials (such as ACs). The values obtained for specific surface area depend on the method of measurement, the size of the probe molecule and the measurement temperature. N<sub>2</sub> 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 m<sup>2</sup>·g<sup>-1</sup>, 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  $80^\circ$ , 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.

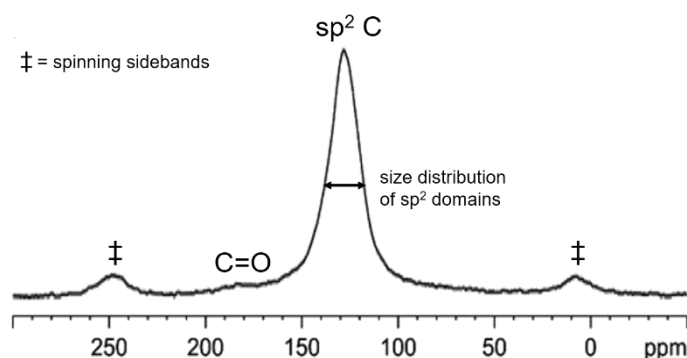
According to the specialized literature, the lateral size ( $L_a$ ) of the  $sp^2$  crystallites can be evaluated from the width of the (100) and (111) peaks by using the Scherrer equation (Eq. 1):

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

where  $K$  is a dimensionless shape factor (usually 0.9),  $\lambda$  is the incident wavelength,  $\beta$  is the line broadening at half the maximum intensity (FWHM),  $\theta$  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  $^{13}\text{C}$  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  $^1\text{H}$  spin polarization, followed by cross polarization transfer to  $^{13}\text{C}$  and its signal detection. This is used in order to enhance the signal of nuclei with a low gyromagnetic ratio (such as  $^{13}\text{C}$ ) by magnetization transfer from nuclei with a higher gyromagnetic ratio ( $^1\text{H}$ ). Therefore, ACs having a larger amount of H-terminations give  $^{13}\text{C}$  CPMAS NMR spectra with a better signal-to-noise ratio. The  $^{13}\text{C}$  NMR spectra of ACs is usually dominated by a broad peak centered around 125 ppm, which is characteristic of  $\text{sp}^2$ -hybridized carbon in condensed aromatic rings (Fig. 3). The line width of the signal is usually quite broad, due to a large distribution of  $\text{sp}^2$  islands having a different size. We have recently demonstrated that the distribution of the  $\text{sp}^2$  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.**  $^{13}\text{C}$  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,  $^{31}\text{P}$  nucleus can also be probed with CPMAS SSNMR. The  $^{31}\text{P}$  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 ( $\nu_0$ ). The energy difference ( $\nu_{\text{vibr}}$ ) 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 ( $\lambda_{\text{exc}}$ ) for carbon-based materials are 514 nm (green light) and 244 nm (deep UV light). The first one gives information mainly on the  $\text{sp}^2$  domains,



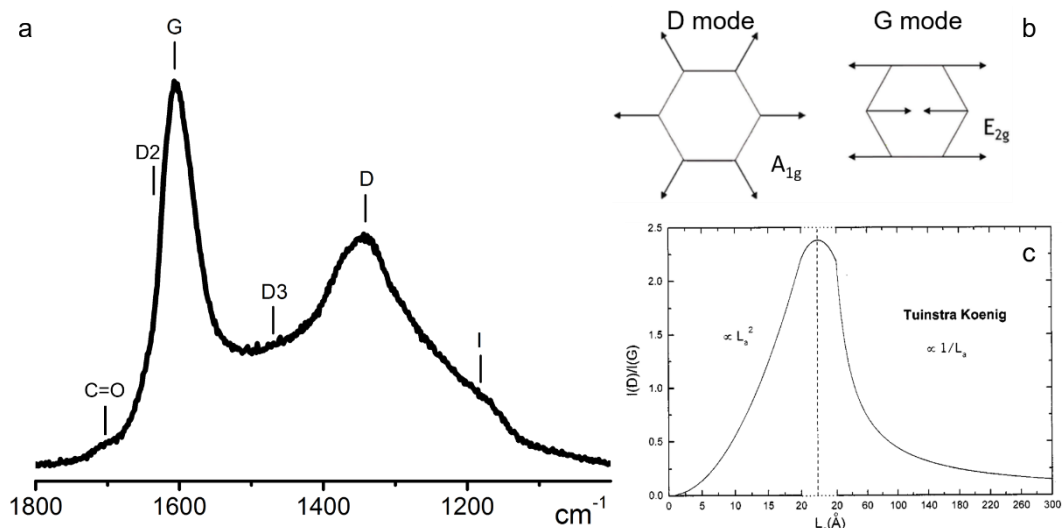
because that wavelength has a strong selectivity towards the  $\pi$  states of  $sp^2$ -hybridized carbon species (Wada and Solin 1981). UV Raman, instead, excites both the  $\pi$  and the  $\sigma$  states; therefore it is able to probe both  $sp^2$  and  $sp^3$  carbon species (Gilkes et al. 1997). 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  $1600\text{ cm}^{-1}$  (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  $1580\text{ cm}^{-1}$ . The  $20\text{ cm}^{-1}$  shift is typical of disordered graphitic systems and is explained by considering the overlap of a second band (D2, around  $1620\text{ cm}^{-1}$ ), 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  $1350\text{ cm}^{-1}$  (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  $1450\text{ cm}^{-1}$ , is attributed to randomly distributed amorphous carbon on the interstitial position of the graphitic islands (Jawhari et al. 1995). The I band around  $1150\text{ cm}^{-1}$ , 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  $1700\text{ cm}^{-1}$ , 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.

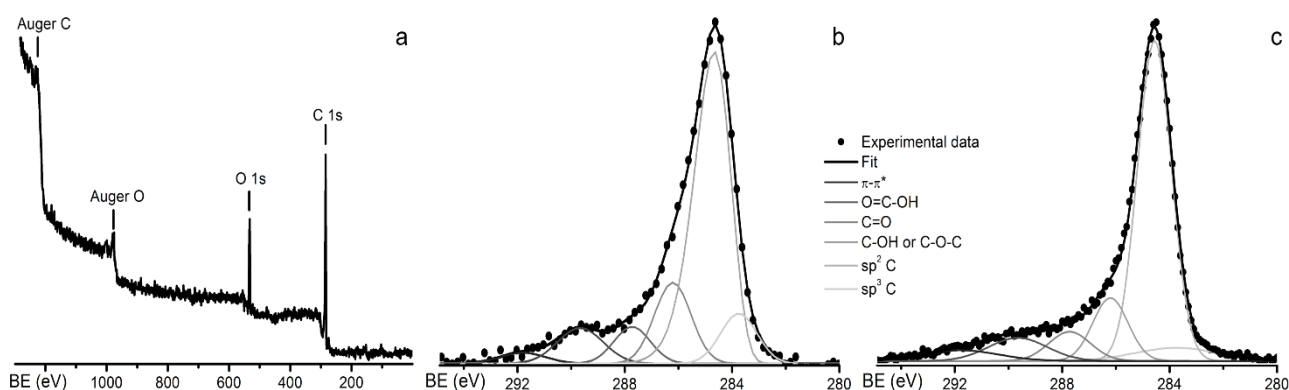
H and O are the most abundant heteroatoms in ACs, the former found in the C-H terminations of the graphitic platelets, and the latter present in a variety of different functional groups having an acid (carboxyls and anhydrides, lactones and phenols), basic (quinones, pyrones), or neutral (carbonyls and 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;  $\text{Na}_2\text{CO}_3$  carboxyl and lactone groups and  $\text{NaHCO}_3$  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  $\text{sp}^2$  carbon. Carbon species with  $\text{sp}^3$  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  $\pi$ - $\pi^*$  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  $1600\text{ cm}^{-1}$  is assigned to  $\nu(\text{C}=\text{C})$  vibrational modes of conjugated  $\text{sp}^2$  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  $\text{H}_3\text{PO}_4$ , 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).

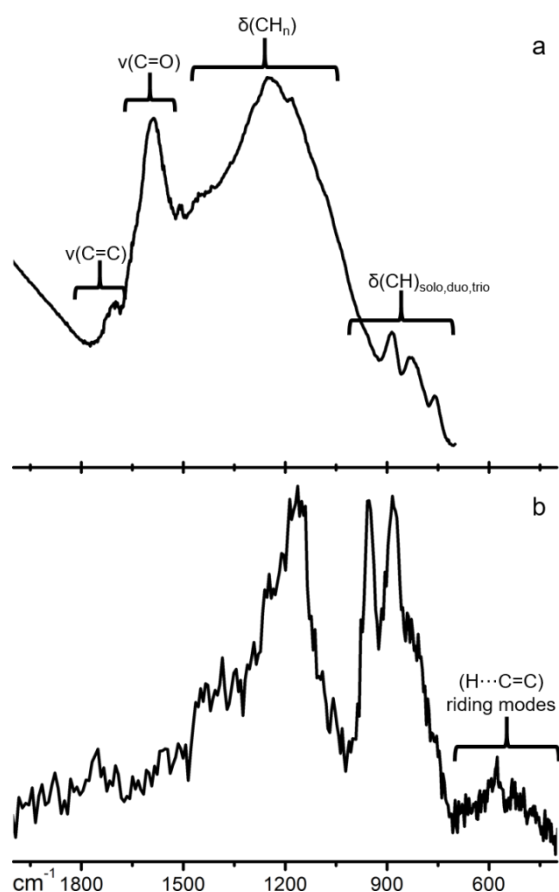
d) Absorption bands in the  $1800\text{--}1700\text{ cm}^{-1}$  region, are indicative of O-containing surface groups (e.g. a band around  $1700\text{ cm}^{-1}$  is typical of carbonyl or carboxyl species, while a band around  $1800\text{ cm}^{-1}$  is characteristic for anhydrides) (Lin-Vien et al. 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  $\text{sp}^2$  platelets constituting the AC, since smaller  $\text{sp}^2$  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  $\text{sp}^2$  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  $950\text{ cm}^{-1}$ , 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, <sup>13</sup>C and <sup>31</sup>P 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 sp<sup>2</sup> 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.

#### 5. Acknowledgements

The author would like to acknowledge C. Lamberti, E. Groppo, M. R. Chierotti and R. Gobetto from University of Turin, A. Piovano from ILL, G. Agostini from ESRF, S. Rudić from ISIS facility and R. Pellegrini from Chimet S.p.A. for the scientific and human contributions to the realization of this work.

## References

- Acedoramos M, Gomez serrano V, Valenzuelacalahorro C, Lopezpeinado AJ (1993), Oxidation of Activated Carbon in Liquid-Phase - Study by FT-IR. *Spectr Lett*, 26: 1117-1137 doi:10.1080/00387019308011598
- Adib F, Bagreev A, Bandosz TJ (1999), Effect of surface characteristics of wood-based activated carbons on adsorption of hydrogen sulfide. *Journal of Colloid and Interface Science*, 214: 407-415 doi:10.1006/jcis.1999.6200
- Ahmadpour A, Do DD (1996), The preparation of active carbons from coal by chemical and physical activation. *Carbon*, 34: 471-479 doi:[http://dx.doi.org/10.1016/0008-6223\(95\)00204-9](http://dx.doi.org/10.1016/0008-6223(95)00204-9)
- Albers P, Burmeister R, Seibold K, Prescher G, Parker SF, Ross DK (1999), Investigations of Palladium Catalysts on Different Carbon Supports. *Journal of Catalysis*, 181: 145-154 doi:<http://dx.doi.org/10.1006/jcat.1998.2279>
- Albers P, Deller K, Despeyroux BM, Prescher G, Schafer A, Seibold K (1994), SIMS XPS Investigations on activated carbon catalyst support. *Journal of Catalysis*, 150: 368-375 doi:10.1006/jcat.1994.1355
- Albers P, Deller K, Despeyroux BM, Schafer A, Seibold K (1992), XPS SIMS Study On The Surface-Chemistry Of Commercially Available Activated Carbons Used As Catalyst Supports. *Journal of Catalysis*, 133: 467-478 doi:10.1016/0021-9517(92)90254-f
- Albers P, Pietsch J, Parker SF (2001), Poisoning and deactivation of palladium catalysts. *Journal of Molecular Catalysis A: Chemical*, 173: 275-286 doi:[http://dx.doi.org/10.1016/S1381-1169\(01\)00154-6](http://dx.doi.org/10.1016/S1381-1169(01)00154-6)
- Albers PW, Bösing S, Lansink Rotgerink H, Ross DK, Parker SF (2002), Inelastic neutron scattering study on the influence of after-treatments on different technical coke of varying impurity level and their  $sp^2/sp^3$  character. *Carbon*, 40: 1549-1558 doi:[http://dx.doi.org/10.1016/S0008-6223\(02\)00018-0](http://dx.doi.org/10.1016/S0008-6223(02)00018-0)
- Albers PW, Pietsch J, Krauter J, Parker SF (2003), Investigations of activated carbon catalyst supports from different natural sources. *Physical Chemistry Chemical Physics*, 5: 1941-1949 doi:10.1039/b212210n
- Ania CO, Parra JB, Pis JJ (2004), Oxygen-induced decrease in the equilibrium adsorptive capacities of activated carbons. *Adsorpt Sci Technol*, 22: 337-351 doi:10.1260/0263617041514875
- Antolini E (2009), Carbon supports for low-temperature fuel cell catalysts. *Appl Catal B-Environ*, 88: 1-24 doi:10.1016/j.apcatb.2008.09.030
- Aramendia MA et al. (1999a), Influence of the reaction conditions and catalytic properties on the liquid-phase hydrodechlorination of chlorobenzene over palladium-supported catalysts: Activity and deactivation. *Journal of Catalysis*, 187: 392-399 doi:10.1006/jcat.1999.2632
- Aramendia MA, Borau V, Garcia IM, Jimenez C, Marinas JM, Urbano FJ (1999b), Influence of the reaction conditions and catalytic properties on the liquid-phase hydrodebromination of bromobenzene over palladium supported catalysts: activity and deactivation. *Appl Catal B-Environ*, 20: 101-110
- Argyle MD, Bartholomew CH (2015), Heterogeneous Catalyst Deactivation and Regeneration: A Review. *Catalysts*, 5: 145-269 doi:10.3390/catal5010145
- Asaka K, Karita M, Saito Y (2011), Graphitization of amorphous carbon on a multiwall carbon nanotube surface by catalyst-free heating. *Applied Physics Letters*, 99: 091907 doi:10.1063/1.3630132
- Atkins P, de Paula J (2009). In: *Elements of Physical Chemistry* (5th ed.). Oxford U. P., Oxford, p 459

- Auer E, Freund A, Pietsch J, Tacke T (1998), Carbons as supports for industrial precious metal catalysts. *Applied Catalysis A: General*, 173: 259-271 doi:[http://dx.doi.org/10.1016/S0926-860X\(98\)00184-7](http://dx.doi.org/10.1016/S0926-860X(98)00184-7)
- Bansal RC, Donnet J-B, Stoeckli F (1988) *Active Carbon*. Marcel Dekker, New York, USA
- Barbera K, Frusteri L, Italiano G, Spadaro L, Frusteri F, Perathoner S, Centi G (2014), Low-temperature graphitization of amorphous carbon nanospheres. *Chin J Catal*, 35: 869-876 doi:10.1016/s1872-2067(14)60098-x
- Bartholomew CH (2001), Mechanisms of catalyst deactivation. *Appl Catal A-Gen*, 212: 17-60 doi:10.1016/s0926-860x(00)00843-7
- Benaddi H, Legras D, Rouzaud JN, Beguin F (1998), Influence of the atmosphere in the chemical activation of wood by phosphoric acid. *Carbon*, 36: 306-309 doi:[http://dx.doi.org/10.1016/S0008-6223\(98\)80123-1](http://dx.doi.org/10.1016/S0008-6223(98)80123-1)
- Besson M, Gallezot P (2003), Deactivation of metal catalysts in liquid phase organic reactions. *Catalysis Today*, 81: 547-559 doi:10.1016/s0920-5861(03)00153-6
- Beyssac O, Goffé B, Petitet J-P, Froigneux E, Moreau M, Rouzaud J-N (2003), On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 59: 2267-2276 doi:[http://dx.doi.org/10.1016/S1386-1425\(03\)00070-2](http://dx.doi.org/10.1016/S1386-1425(03)00070-2)
- Biniak S, Szymański G, Siedlewski J, Świątkowski A (1997), The characterization of activated carbons with oxygen and nitrogen surface groups. *Carbon*, 35: 1799-1810 doi:[http://dx.doi.org/10.1016/S0008-6223\(97\)00096-1](http://dx.doi.org/10.1016/S0008-6223(97)00096-1)
- Blume R, Rosenthal D, Tessonnier J-P, Li H, Knop-Gericke A, Schlögl R (2015), Characterizing Graphitic Carbon with X-ray Photoelectron Spectroscopy: A Step-by-Step Approach. *ChemCatChem*, 7: 2871-2881 doi:10.1002/cctc.201500344
- Boehm HP (1994), Some Aspects of the Surface-Chemistry of Carbon-Blacks and Other Carbons. *Carbon*, 32: 759-769 doi:10.1016/0008-6223(94)90031-0
- Boehm HP (2002), Surface oxides on carbon and their analysis: a critical assessment. *Carbon*, 40: 145-149 doi:10.1016/s0008-6223(01)00165-8
- Boehm HP, Diehl E, Heck W, Sappok R (1964), *Surface Oxides of Carbon*. *Angewandte Chemie International Edition*, 3: 669-677 doi:10.1002/anie.196406691
- Bradley RH, Rand B (1995), On the Physical Adsorption of Vapors by Microporous Carbons. *Journal of Colloid and Interface Science*, 169: 168-176 doi:10.1006/jcis.1995.1018
- Brunauer S, Emmett PH, Teller E (1938), Adsorption of Gases in Multimolecular Layers. *Journal of the American Chemical Society*, 60: 309-319 doi:10.1021/ja01269a023
- Budinova T, Ekinci E, Yardim F, Grimm A, Björnbom E, Minkova V, Goranova M (2006), Characterization and application of activated carbon produced by H<sub>3</sub>PO<sub>4</sub> and water vapor activation. *Fuel Processing Technology*, 87: 899-905 doi:<http://dx.doi.org/10.1016/j.fuproc.2006.06.005>
- Burmeister R, Despeyroux B, Deller K, Seibold K, Albers P (1993) On the XPS-Surface Characterization of Activated Carbons Resp Pd/C Catalysts and a Correlation to the Catalytic Activity. In: Guisnet M, Barbier J, Barrault J, Bouchoule C, Duprez D, Perot G, Montassier C (eds) *Heterogeneous Catalysis and Fine Chemicals Iii*, vol 78. *Studies in Surface Science and Catalysis*. Elsevier Science Publ B V, Amsterdam, pp 361-368
- Capelle A, de Voys F (1983) *Activated Carbon... a Fascinating Material: Some Thoughts on Activated Carbon*. Norit N.V., Amersfoort
- Card RJ, Schmitt JL, Simpson JM (1983), Palladium-carbon hydrogenolysis catalysts: The effect of preparation variables on catalytic activity. *Journal of Catalysis*, 79: 13-20 doi:10.1016/0021-9517(83)90285-3
- Castiglioni C, Tommasini M, Zerbi G (2004), Raman spectroscopy of polyconjugated molecules and materials: confinement effect in one and two dimensions. *Philosophical Transactions of*



the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 362: 2425-2459

- Centrone A, Brambilla L, Renouard T, Gherghel L, Mathis C, Müllen K, Zerbi G (2005), Structure of new carbonaceous materials: The role of vibrational spectroscopy. *Carbon*, 43: 1593-1609 doi:<http://dx.doi.org/10.1016/j.carbon.2005.01.040>
- Chai GS, Yoon SB, Yu JS, Choi JH, Sung YE (2004), Ordered porous carbons with tunable pore sizes as catalyst supports in direct methanol fuel cell. *J Phys Chem B*, 108: 7074-7079 doi:10.1021/jp0370472
- Chen US, Su HY, Wang CH, Shih HC, Hsieh CT, Chen JM (2008), Oxygen/Carbon Ratio Effects on Surface-Modified Carbon Nanotubes. *J Nano Res*, 2: 77-84
- Chierotti MR, Gobetto R (2013), NMR crystallography: the use of dipolar interactions in polymorph and co-crystal investigation. *CrystEngComm*, 15: 8599-8612 doi:10.1039/c3ce41026a
- Cuesta A, Dhamelincourt P, Laureyns J, Martinez-Alonso A, M. D. Tascon J (1998), Comparative performance of X-ray diffraction and Raman microprobe techniques for the study of carbon materials. *Journal of Materials Chemistry*, 8: 2875-2879 doi:10.1039/a805841e
- Darmstadt H, Roy C, Kaliaguine S (1994), ESCA Characterization of Commercial Carbon-Blacks and of Carbon-Blacks from Vacuum Pyrolysis of Used Tires. *Carbon*, 32: 1399-1406 doi:10.1016/0008-6223(94)90132-5
- Deng Q, Li XY, Zuo JE, Ling A, Logan BE (2010), Power generation using an activated carbon fiber felt cathode in an upflow microbial fuel cell. *J Power Sources*, 195: 1130-1135 doi:10.1016/j.jpowsour.2009.08.092
- Desimoni E, Casella GI, Cataldi TRI, Salvi AM, Rotunno T, Dicroce E (1992), Remarks on the Surface Characterization of Carbon-Fibers. *Surf Interface Anal*, 18: 623-630 doi:10.1002/sia.740180809
- Dicks AL (2006), The role of carbon in fuel cells. *J Power Sources*, 156: 128-141 doi:10.1016/j.jpowsour.2006.02.054
- El-Sayed Y, Bandoz TJ (2003), Effect of increased basicity of activated carbon surface on valeric acid adsorption from aqueous solution activated carbon. *Physical Chemistry Chemical Physics*, 5: 4892-4898 doi:10.1039/b306983b
- Fernandez-Colinas J, Denoyel R, Grillet Y, Rouquerol F, Rouquerol J (1989a), Significance of N<sub>2</sub>-Adsorption and Ar-Adsorption data for following the Pore Structure Modifications of a Charcoal during Activation. *Langmuir*, 5: 1205-1210 doi:10.1021/la00089a014
- Fernandez-Colinas J, Denoyel R, Rouquerol J (1989b), Adsorption of Iodine from Aqueous Solutions on to Activated Carbons: Correlation with Nitrogen Adsorption at 77K. *Adsorpt Sci Technol*, 6: 18-26 doi:10.1177/026361748900600103
- Ferrari AC (2007), Raman spectroscopy of graphene and graphite: Disorder, electron-phonon coupling, doping and nonadiabatic effects. *Solid State Communications*, 143: 47-57 doi:<http://dx.doi.org/10.1016/j.ssc.2007.03.052>
- Ferrari AC, Robertson J (2000), Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B*, 61: 14095-14107
- Ferrari AC, Robertson J (2001), Origin of the 1150-cm<sup>-1</sup> Raman mode in nanocrystalline diamond. *Physical Review B*, 63: 121405
- Ferrari AC, Robertson J (2004), Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond. *Phil Trans R Soc Lond A*, 362: 2477-2512 doi:10.1098/rsta.2004.1452
- Ferrari AC, Rodil SE, Robertson J (2003), Interpretation of infrared and Raman spectra of amorphous carbon nitrides. *Physical Review B*, 67: 155306
- Figueiredo JL, Pereira MFR, Freitas MMA, Órfão JJM (1999), Modification of the surface chemistry of activated carbons. *Carbon*, 37: 1379-1389 doi:[http://dx.doi.org/10.1016/S0008-6223\(98\)00333-9](http://dx.doi.org/10.1016/S0008-6223(98)00333-9)

- Fillaux F, Papoular R, Bennington SM, Tomkinson J (1995a), Inelastic neutron scattering study of free proton dynamics in coal. *Journal of Non-Crystalline Solids*, 188: 161-168 doi:[http://dx.doi.org/10.1016/0022-3093\(95\)00101-8](http://dx.doi.org/10.1016/0022-3093(95)00101-8)
- Fillaux F, Papoular R, Lautié A, Tomkinson J (1994), Inelastic neutron-scattering study of the proton dynamics in carbons and coals. *Carbon*, 32: 1325-1331 doi:[http://dx.doi.org/10.1016/0008-6223\(94\)90119-8](http://dx.doi.org/10.1016/0008-6223(94)90119-8)
- Fillaux F, Papoular R, Lautié A, Tomkinson J (1995b), Inelastic neutron-scattering study of the proton dynamics in coals. *Fuel*, 74: 865-873 doi:[http://dx.doi.org/10.1016/0016-2361\(95\)00017-Y](http://dx.doi.org/10.1016/0016-2361(95)00017-Y)
- Forzatti P, Lietti L (1999), Catalyst deactivation. *Catalysis Today*, 52: 165-181 doi:10.1016/S0920-5861(99)00074-7
- Fuertes AB, Alvarez S (2004), Graphitic mesoporous carbons synthesised through mesostructured silica templates. *Carbon*, 42: 3049-3055 doi:10.1016/j.carbon.2004.06.020
- Fujimoto H (2003), Theoretical X-ray scattering intensity of carbons with turbostratic stacking and AB stacking structures. *Carbon*, 41: 1585-1592 doi:[http://dx.doi.org/10.1016/S0008-6223\(03\)00116-7](http://dx.doi.org/10.1016/S0008-6223(03)00116-7)
- Galué HA (2014), Decoding the infrared signatures of pyramidal carbons in graphenic molecular nanostructures of interstellar origin. *Chemical Science*, 5: 2667-2676 doi:10.1039/c4sc00890a
- Gampine A, Eyman DP (1998), Catalytic hydrodechlorination of chlorocarbons. 2. Ternary oxide supports for catalytic conversions of 1,2-dichlorobenzene. *Journal of Catalysis*, 179: 315-325 doi:10.1006/jcat.1998.2223
- Gilkes KWR, Sands HS, Batchelder DN, Robertson J, Milne WI (1997), Direct observation of  $sp^3$  bonding in tetrahedral amorphous carbon using ultraviolet Raman spectroscopy. *Applied Physics Letters*, 70: 1980-1982 doi:<http://dx.doi.org/10.1063/1.118798>
- Girgis BS, Yunis SS, Soliman AM (2002), Characteristics of activated carbon from peanut hulls in relation to conditions of preparation. *Materials Letters*, 57: 164-172 doi:[http://dx.doi.org/10.1016/S0167-577X\(02\)00724-3](http://dx.doi.org/10.1016/S0167-577X(02)00724-3)
- Gokagac G, Leger JM, Hahn F (2003), Behaviour of bimetallic Pt-Pd carbon-supported catalysts in methanol electrooxidation. *ZNaturforsch(B)*, 58: 423-432
- Gomez-serrano V, Acedoramos M, Lopezpeinado AJ, Valenzuelacalahorro C (1991), Stability Towards Heating and Outgassing of Activated Carbon Oxidized in the Liquid-Phase. *Thermochim Acta*, 176: 129-140 doi:10.1016/0040-6031(91)80268-n
- Groppi G, Cristiani C, Forzatti P, Berti F, Malloggi S (1998) High temperature combustion of methane over hexaaluminate-supported Pd catalysts. In: Parmaliana A, Sanfilippo D, Frusteri F, Vaccari A, Arena F (eds) *Natural Gas Conversion V*, vol 119. *Studies in Surface Science and Catalysis*. Elsevier Science Bv, Amsterdam, pp 71-76
- Guo J, Lua AC (2000), Preparation of activated carbons from oil-palm-stone chars by microwave-induced carbon dioxide activation. *Carbon*, 38: 1985-1993 doi:10.1016/S0008-6223(00)00046-4
- Harris RK (2012). In: Wasylishen RE, Ashbrook SE, Wimperis S (eds) *Encyclopedia of Magnetic Resonance*, vol Chichester, UK. John Wiley & Sons Ltd, pp 857-869
- Harris RK, Wasylishen RE, Duer MJ (2009) *NMR Crystallography*. John Wiley & Sons Ltd, Chichester, UK
- Henning K-D, von Kienle H (2010) Carbon, 5. Activated Carbon. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. doi:10.1002/14356007.n05\_n04
- Honeybone PJR, Newport RJ, Walters JK, Howells WS, Tomkinson J (1994), Structural properties of amorphous hydrogenated carbon. II. An inelastic neutron-scattering study. *Physical Review B*, 50: 839-845

- Houska CR, Warren BE (1954), X-Ray Study of the Graphitization of Carbon Black. *Journal of Applied Physics*, 25: 1503-1509 doi:<http://dx.doi.org/10.1063/1.1702373>  
<http://www.chimet.com/en/catalyst>.
- Illan-Gomez MJ, Garcia-Garcia A, Salinas-Martinez de Lecea C, Linares-Solano A (1996), Activated carbons from Spanish coals .2. Chemical activation. *Energy Fuels*, 10: 1108-1114 doi:10.1021/ef950195+
- Inagaki M, Toyoda M, Tsumura T (2014), Control of crystalline structure of porous carbons. *RSC Adv*, 4: 41411-41424 doi:10.1039/C4RA06730D
- Jagtoyen M, Thwaites M, Stencil J, McEnaney B, Derbyshire F (1992), Adsorbent Carbon Synthesis from Coals by Phosphoric-Acid Activation. *Carbon*, 30: 1089-1096 doi:10.1016/0008-6223(92)90140-r
- Jawhari T, Roid A, Casado J (1995), Raman spectroscopic characterization of some commercially available carbon black materials. *Carbon*, 33: 1561-1565 doi:[http://dx.doi.org/10.1016/0008-6223\(95\)00117-V](http://dx.doi.org/10.1016/0008-6223(95)00117-V)
- Jeong HK et al. (2008), Evidence of graphitic AB stacking order of graphite oxides. *Journal of the American Chemical Society*, 130: 1362-1366 doi:10.1021/ja076473o
- Jia YF, Xiao B, Thomas KM (2002), Adsorption of metal ions on nitrogen surface functional groups in activated carbons. *Langmuir*, 18: 470-478 doi:10.1021/la011161z
- Jimenez M, Lesaffre N, Bellayer S, Dupretz R, Vandebossche M, Duquesne S, Bourbigot S (2015), Novel flame retardant flexible polyurethane foam: plasma induced graft-polymerization of phosphonates. *RSC Adv*, 5: 63853-63865 doi:10.1039/c5ra08289g
- Johnson CA, Patrick JW, Mark Thomas K (1986), Characterization of coal chars by Raman spectroscopy, X-ray diffraction and reflectance measurements. *Fuel*, 65: 1284-1290 doi:[http://dx.doi.org/10.1016/0016-2361\(86\)90243-7](http://dx.doi.org/10.1016/0016-2361(86)90243-7)
- Kadirvelu K, Kavipriya M, Karthika C, Radhika M, Vennilamani N, Pattabhi S (2003), Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solutions. *Bioresour Technol*, 87: 129-132 doi:10.1016/s0960-8524(02)00201-8
- Konova P, Naydenov A, Venkov C, Mehandjiev D, Andreeva D, Tabakova T (2004), Activity and deactivation of Au/TiO<sub>2</sub> catalyst in CO oxidation. *J Mol Catal A-Chem*, 213: 235-240 doi:10.1016/j.molcata.2003.12.021
- Kozlowski C, Sherwood PMA (1986), X-Ray Photoelectron Spectroscopic Studies of Carbon-Fiber Surfaces VII-Electrochemical Treatment in Ammonium Salt Electrolytes. *Carbon*, 24: 357-363 doi:10.1016/0008-6223(86)90238-1
- Kurtz M, Wilmer H, Genger T, Hinrichsen O, Muhler M (2003), Deactivation of supported copper catalysts for methanol synthesis. *Catal Lett*, 86: 77-80 doi:10.1023/a:1022663125977
- Laine J, Yunes S (1992), Effect of the preparation method on the pore size distribution of activated carbon from coconut shell. *Carbon*, 30: 601-604 doi:[http://dx.doi.org/10.1016/0008-6223\(92\)90178-Y](http://dx.doi.org/10.1016/0008-6223(92)90178-Y)
- Langley LA, Villanueva DE, Fairbrother DH (2006), Quantification of surface oxides on carbonaceous materials. *Chemistry of Materials*, 18: 169-178 doi:10.1021/cm051462k
- Langmuir I (1918), The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *Journal of the American Chemical Society*, 40: 1361-1403 doi:10.1021/ja02242a004
- Lazzarini A et al. (2016), A comprehensive approach to investigate the structural and surface properties of activated carbons and related Pd-based catalysts. *Catal Sci Tech*, 6: 4910-4922
- Lee JH, Trimm DL (1995), Catalytic Combustion of Methane. *Fuel Processing Technology*, 42: 339-359 doi:10.1016/0378-3820(94)00091-7
- Li ZQ, Lu CJ, Xia ZP, Zhou Y, Luo Z (2007), X-ray diffraction patterns of graphite and turbostratic carbon. *Carbon*, 45: 1686-1695 doi:<http://dx.doi.org/10.1016/j.carbon.2007.03.038>
- Lin-Vien D, Colthup NB, Fateley WG, Grasselli JG (1991) *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*. Academic Press, London, UK

- Lopez GP, Castner DG, Ratner BD (1991), XPS O 1s Binding-Energies for Polymers Containing Hydroxyl, Ether, Ketone and Ester Groups. *Surf Interface Anal*, 17: 267-272 doi:10.1002/sia.740170508
- Maass S, Finsterwalder F, Frank G, Hartmann R, Merten C (2008), Carbon support oxidation in PEM fuel cell cathodes. *J Power Sources*, 176: 444-451 doi:10.1016/j.jpowsour.2007.08.053
- Marsh H, Rodríguez-Reinoso F (2006). In: *Activated Carbon*. Elsevier, Oxford, UK,
- Marsh H, Walker Jr PL (1979), The effects of impregnation of coal by alkali salts upon carbonization properties. *Fuel Processing Technology*, 2: 61-75 doi:[http://dx.doi.org/10.1016/0378-3820\(79\)90032-8](http://dx.doi.org/10.1016/0378-3820(79)90032-8)
- Marsh H, Yan DS, O'Grady TM, Wennerberg A (1984), Formation of active carbons from cokes using potassium hydroxide. *Carbon*, 22: 603-611 doi:[http://dx.doi.org/10.1016/0008-6223\(84\)90096-4](http://dx.doi.org/10.1016/0008-6223(84)90096-4)
- Mawhinney DB, Yates Jr JT (2001), FTIR study of the oxidation of amorphous carbon by ozone at 300 K - Direct COOH formation. *Carbon*, 39: 1167-1173 doi:[http://dx.doi.org/10.1016/S0008-6223\(00\)00238-4](http://dx.doi.org/10.1016/S0008-6223(00)00238-4)
- Meldrum BJ, Rochester CH (1990a), Fourier-transform infrared study of surface species on carbon mixed with KBr and reacted with CO<sub>2</sub>, O<sub>2</sub> and CO. *Journal of the Chemical Society, Faraday Transactions*, 86: 3647-3652 doi:10.1039/ft9908603647
- Meldrum BJ, Rochester CH (1990b), In situ infrared study of the modification of the surface of activated carbon by ammonia, water and hydrogen. *Journal of the Chemical Society, Faraday Transactions*, 86: 1881-1884 doi:10.1039/ft9908601881
- Meldrum BJ, Rochester CH (1990c), In situ infrared study of the surface oxidation of activated carbon dispersed in potassium bromide. *Journal of the Chemical Society, Faraday Transactions*, 86: 2997-3002 doi:10.1039/ft9908602997
- Meldrum BJ, Rochester CH (1990d), In situ infrared study of the surface oxidation of activated carbon in oxygen and carbon dioxide. *Journal of the Chemical Society, Faraday Transactions*, 86: 861-865 doi:10.1039/ft9908600861
- Moreno-Castilla C, Carrasco-Marín F, Mueden A (1997), The creation of acid carbon surfaces by treatment with (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. *Carbon*, 35: 1619-1626 doi:[http://dx.doi.org/10.1016/S0008-6223\(97\)00121-8](http://dx.doi.org/10.1016/S0008-6223(97)00121-8)
- Moreno-Castilla C, Ferro-García MA, Joly JP, Bautista-Toledo I, Carrasco-Marín F, Rivera-Utrilla J (1995), Activated Carbon Surface Modifications by Nitric Acid, Hydrogen Peroxide, and Ammonium Peroxydisulfate Treatments. *Langmuir*, 11: 4386-4392 doi:10.1021/la00011a035
- Moreno-Castilla C, López-Ramón NV, Carrasco-Marín F (2000), Changes in surface chemistry of activated carbons by wet oxidation. *Carbon*, 38: 1995-2001 doi:[http://dx.doi.org/10.1016/S0008-6223\(00\)00048-8](http://dx.doi.org/10.1016/S0008-6223(00)00048-8)
- Mowery DL, McCormick RL (2001), Deactivation of alumina supported and unsupported PdO methane oxidation catalyst: the effect of water on sulfate poisoning. *Appl Catal B-Environ*, 34: 287-297 doi:10.1016/S0926-3373(01)00222-3
- Muradov N (2001), Catalysis of methane decomposition over elemental carbon. *Catalysis Communications*, 2: 89-94 doi:[http://dx.doi.org/10.1016/S1566-7367\(01\)00013-9](http://dx.doi.org/10.1016/S1566-7367(01)00013-9)
- Nakamoto K (1978) *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. John Wiley & Sons, New York
- Narui K, Yata H, Furuta K, Nishida A, Kohtoku Y, Matsuzaki T (1999), Effects of addition of Pt to PdO/Al<sub>2</sub>O<sub>3</sub> catalyst on catalytic activity for methane combustion and TEM observations of supported particles. *Appl Catal A-Gen*, 179: 165-173 doi:10.1016/S0926-860X(98)00306-8
- Noh JS, Schwarz JA (1989), Estimation of the Point of Zero Charge of Simple Oxides by Mass Titration. *Journal of Colloid and Interface Science*, 130: 157-164 doi:10.1016/0021-9797(89)90086-6

- Noh JS, Schwarz JA (1990), Effect of HNO<sub>3</sub> Treatment on the Surface-Acidity of Activated Carbons. *Carbon*, 28: 675-682 doi:10.1016/0008-6223(90)90069-b
- Ordóñez S, Díez FV, Sastre H (2001), Characterisation of the deactivation of platinum and palladium supported on activated carbon used as hydrodechlorination catalysts. *Appl Catal B-Environ*, 31: 113-122 doi:10.1016/s0926-3373(00)00270-8
- Óya A, Marsh H (1982), Phenomena of catalytic graphitization. *Journal of Materials Science*, 17: 309-322
- Papirer E, Li S, Donnet JB (1987), Contribution to the Study of Basic Surface Groups on Carbons. *Carbon*, 25: 243-247 doi:10.1016/0008-6223(87)90122-9
- Park GG, Yang TH, Yoon YG, Lee WY, Kim CS (2003), Pore size effect of the DMFC catalyst supported on porous materials. *Int J Hydrog Energy*, 28: 645-650 doi:10.1016/s0360-3199(02)00140-4
- Pellegrini R, Agostini G, Groppo E, Piovano A, Leofanti G, Lamberti C (2011), 0.5 wt.% Pd/C catalyst for purification of terephthalic acid: Irreversible deactivation in industrial plants. *Journal of Catalysis*, 280: 150-160 doi:<http://dx.doi.org/10.1016/j.jcat.2011.03.012>
- Pernicone N, Cerboni M, Prelazzi G, Pinna F, Fagherazzi G (1998), An investigation on Pd/C industrial catalysts for the purification of terephthalic acid. *Catalysis Today*, 44: 129-135 doi:10.1016/s0920-5861(98)00183-7
- Phan NH, Rio S, Faur C, Le Coq L, Le Cloirec P, Nguyen TH (2006), Production of fibrous activated carbons from natural cellulose (jute, coconut) fibers for water treatment applications. *Carbon*, 44: 2569-2577 doi:10.1016/j.carbon.2006.05.048
- Piovano A et al. (2015), Progress in the Characterization of the Surface Species in Activated Carbons by means of INS Spectroscopy Coupled with Detailed DFT Calculations. *Advances in Condensed Matter Physics*, 2015: 803267 doi:10.1155/2015/803267
- Pradhan BK, Sandle NK (1999), Effect of different oxidizing agent treatments on the surface properties of activated carbons. *Carbon*, 37: 1323-1332 doi:10.1016/s0008-6223(98)00328-5
- Prieto G, Zecevic J, Friedrich H, de Jong KP, de Jongh PE (2013), Towards stable catalysts by controlling collective properties of supported metal nanoparticles. *Nat Mater*, 12: 34-39 doi:10.1038/nmat3471
- Proctor A, Sherwood PMA (1983), X-ray photoelectron spectroscopic studies of carbon fibre surfaces—II. *Carbon*, 21: 53-59 doi:[http://dx.doi.org/10.1016/0008-6223\(83\)90156-2](http://dx.doi.org/10.1016/0008-6223(83)90156-2)
- Puziy AM, Poddubnaya OI, Martínez-Alonso A, Suárez-García F, Tascón JMD (2002), Synthetic carbons activated with phosphoric acid: I. Surface chemistry and ion binding properties. *Carbon*, 40: 1493-1505 doi:[http://dx.doi.org/10.1016/S0008-6223\(01\)00317-7](http://dx.doi.org/10.1016/S0008-6223(01)00317-7)
- Puziy AM, Poddubnaya OI, Socha RP, Gurgul J, Wisniewski M (2008), XPS and NMR studies of phosphoric acid activated carbons. *Carbon*, 46: 2113-2123 doi:<http://dx.doi.org/10.1016/j.carbon.2008.09.010>
- Reis MJ, Dorego AMB, Dasilva JDL, Soares MN (1995), An XPS Study of the Fiber-Matrix Interface Using Sized Carbon-Fibers as a Model. *Journal of Materials Science*, 30: 118-126 doi:10.1007/bf00352140
- Rodríguezreinoso F, Garrido J, Martínmartínez JM, Molinasabio M, Torregrosa R (1989), The combined use of different approaches in the characterization of Microporous Carbons. *Carbon*, 27: 23-32 doi:10.1016/0008-6223(89)90153-x
- Rotunno F et al. (2006) Preparation of Pd/C catalysts: from the Pd-precursor solution to the final systems. In: *Studies in Surface Science and Catalysis*, vol Volume 162. Elsevier, pp 721-728. doi:[http://dx.doi.org/10.1016/S0167-2991\(06\)80973-0](http://dx.doi.org/10.1016/S0167-2991(06)80973-0)
- Rouquerol J, Llewellyn P, Rouquerol F (2007) Is the BET equation applicable to microporous adsorbents? In: P.L. Llewellyn FR-RJR, Seaton N (eds) *Studies in Surface Science and Catalysis*, vol Volume 160. Elsevier, Amsterdam, pp 49-56. doi:[http://dx.doi.org/10.1016/S0167-2991\(07\)80008-5](http://dx.doi.org/10.1016/S0167-2991(07)80008-5)

- Rouquerol J, Rouquerol F, Llewellyn P, Maurin G, Sing KSW (2014) Adsorption by Powders and Porous Solids: Principles, Methodology and Applications. Academic Press, Oxford, UK
- Ryndin YA, Stenin MV, Boronin AI, Bukhtiyarov VI, Zaikovskii VI (1989), Effect of Pd/C Dispersion on its Catalytic Properties in Acetylene and Vinylacetylene Hydrogenation. *Applied Catalysis*, 54: 277-288 doi:10.1016/s0166-9834(00)82370-2
- Sadezky A, Muckenhuber H, Grothe H, Niessner R, Pöschl U (2005), Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon*, 43: 1731-1742 doi:<http://dx.doi.org/10.1016/j.carbon.2005.02.018>
- Sadykova YM, Dalmatova NV, Voronina YK, Burirov AR, Pudovik MA, Mitrasov YN, Sinyashin OG (2015), Modification of Bicyclic Phosphonates Based on Resorcinols and Its Derivatives via the Mannich Reaction. *Heteroatom Chem*, 26: 224-230 doi:10.1002/hc.21252
- Saka C (2012), BET, TG-DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl<sub>2</sub>. *J Anal Appl Pyrolysis*, 95: 21-24 doi:10.1016/j.jaap.2011.12.020
- Salame, II, Bandosz TJ (1999), Study of water adsorption on activated carbons with different degrees of surface oxidation. *Journal of Colloid and Interface Science*, 210: 367-374 doi:10.1006/jcis.1998.5918
- Salame, II, Bandosz TJ (2003), Role of surface chemistry in adsorption of phenol on activated carbons. *Journal of Colloid and Interface Science*, 264: 307-312 doi:10.1016/s0021-9797(03)00420-x
- Schanke D, Hilmen AM, Bergene E, Kinnari K, Rytter E, Adnanes E, Holmen A (1995), Study of the Deactivation Mechanism of Al<sub>2</sub>O<sub>3</sub>-Supported Cobalt Fischer-Tropsch Catalysts. *Catal Lett*, 34: 269-284 doi:10.1007/bf00806876
- Schlögl R (2008) 2.3.15 Carbons. In: *Handbook of Heterogeneous Catalysis*. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany. doi:10.1002/9783527610044.hetc0020
- Sears VF (1992), Neutron scattering lengths and cross sections. *Neutron News*, 3: 26-37 doi:10.1080/10448639208218770
- Serp P, Figueiredo JL (2009) *Carbon Materials for Catalysis*. John Wiley & Sons, Hoboken, USA
- Sevilla M, Fuertes AB (2006), Catalytic graphitization of templated mesoporous carbons. *Carbon*, 44: 468-474 doi:10.1016/j.carbon.2005.08.019
- Sevilla M, Mokaya R (2014), Energy storage applications of activated carbons: supercapacitors and hydrogen storage. *Energy Environ Sci*, 7: 1250-1280 doi:10.1039/c3ee43525c
- Shafeeyan MS, Daud W, Houshmand A, Shamiri A (2010), A review on surface modification of activated carbon for carbon dioxide adsorption. *J Anal Appl Pyrolysis*, 89: 143-151 doi:10.1016/j.jaap.2010.07.006
- Shen TD, Ge WQ, Wang KY, Quan MX, Wang JT, Wei WD, Koch CC (1996), Structural disorder and phase transformation in graphite produced by ball milling. *Nanostructured Materials*, 7: 393-399 doi:[http://dx.doi.org/10.1016/0965-9773\(96\)00010-4](http://dx.doi.org/10.1016/0965-9773(96)00010-4)
- Sing KSW (1994), Physisorption of Gases by Carbon-Blacks. *Carbon*, 32: 1311-1317 doi:10.1016/0008-6223(94)90117-1
- Sircar S, Golden TC, Rao MB (1996), Activated carbon for gas separation and storage. *Carbon*, 34: 1-12 doi:10.1016/0008-6223(95)00128-x
- Smith M, Scudiero L, Espinal J, McEwen J-S, Garcia-Perez M (2016), Improving the deconvolution and interpretation of XPS spectra from chars by ab initio calculations. *Carbon*, 110: 155-171 doi:<http://dx.doi.org/10.1016/j.carbon.2016.09.012>
- Steigerwalt ES, Deluga GA, Cliffler DE, Lukehart CM (2001), A Pt-Ru/graphitic carbon nanofiber nanocomposite exhibiting high relative performance as a direct-methanol fuel cell anode catalyst. *J Phys Chem B*, 105: 8097-8101 doi:10.1021/jp011633i

- Stejskal EO, Schaefer J, Waugh JS (1977), Magic-angle spinning and polarization transfer in proton-enhanced NMR. *J Magn Reson*, 28: 105-112 doi:[http://dx.doi.org/10.1016/0022-2364\(77\)90260-8](http://dx.doi.org/10.1016/0022-2364(77)90260-8)
- Swaan HM, Kroll VCH, Martin GA, Mirodatos C (1994), Deactivation of Supported Nickel-Catalysts during the Reforming of Methane by Carbon-Dioxide. *Catalysis Today*, 21: 571-578 doi:10.1016/0920-5861(94)80181-9
- Tamon H, Okazaki M (1996), Influence of acidic surface oxides of activated carbon on gas adsorption characteristics. *Carbon*, 34: 741-746 doi:10.1016/0008-6223(96)00029-2
- Tay T, Ucar S, Karagoz S (2009), Preparation and characterization of activated carbon from waste biomass. *J Hazard Mater*, 165: 481-485 doi:10.1016/j.jhazmat.2008.10.011
- Teng H, Yeh T-S, Hsu L-Y (1998), Preparation of activated carbon from bituminous coal with phosphoric acid activation. *Carbon*, 36: 1387-1395 doi:[http://dx.doi.org/10.1016/S0008-6223\(98\)00127-4](http://dx.doi.org/10.1016/S0008-6223(98)00127-4)
- Thommes M, Cychosz KA, Neimark AV (2012) Advanced Physical Adsorption Characterization of Nanoporous Carbons. In: Tascón JMD (ed) *Novel Carbon Adsorbents*. Elsevier, Oxford, pp 107-145. doi:10.1016/b978-0-08-097744-7.00004-1
- Tommasini M, Castiglioni C, Zerbi G, Barbon A, Brustolon M (2011), A joint Raman and EPR spectroscopic study on ball-milled nanographites. *Chemical Physics Letters*, 516: 220-224 doi:<http://dx.doi.org/10.1016/j.cplett.2011.09.094>
- Tseng RL, Tseng SK (2005), Pore structure and adsorption performance of the KOH-activated carbons prepared from corncob. *Journal of Colloid and Interface Science*, 287: 428-437 doi:10.1016/j.jcis.2005.02.033
- Tuinstra F, Koenig JL (1970), Raman Spectrum of Graphite. *The Journal of Chemical Physics*, 53: 1126-1130 doi:<http://dx.doi.org/10.1063/1.1674108>
- Ungár T, Gubicza J, Ribárik G, Pantea C, Zerda TW (2002), Microstructure of carbon blacks determined by X-ray diffraction profile analysis. *Carbon*, 40: 929-937 doi:[http://dx.doi.org/10.1016/S0008-6223\(01\)00224-X](http://dx.doi.org/10.1016/S0008-6223(01)00224-X)
- Vázquez-Santos MB, Geissler E, László K, Rouzaud J-N, Martínez-Alonso A, Tascón JMD (2012), Graphitization of highly porous carbons derived from poly(p-phenylene benzobisoxazole). *Carbon*, 50: 2929-2940 doi:<http://dx.doi.org/10.1016/j.carbon.2012.02.062>
- Venter JJ, Vannice MA (1989), DRIFTS investigation of the decomposition of ruthenium clusters on carbon and the subsequent ruthenium carbon catalysts. *Inorg Chem*, 28: 1634-1644 doi:10.1021/ic00308a008
- Vizcaino AJ, Carriero A, Calles JA (2007), Hydrogen production by ethanol steam reforming over Cu-Ni supported catalysts. *Int J Hydrog Energy*, 32: 1450-1461 doi:10.1016/j.ijhydene.2006.10.024
- Voropaev IN, Simonov PA, Romanenko AV (2009), Formation of Pt/C Catalysts on Various Carbon Supports. *Russian Journal of Inorganic Chemistry*, 54: 1531-1536
- Wada N, Solin SA (1981), Raman efficiency measurements of graphite. *Physica B+C*, 105: 353-356 doi:[http://dx.doi.org/10.1016/0378-4363\(81\)90274-6](http://dx.doi.org/10.1016/0378-4363(81)90274-6)
- Wang Y, Alsmeyer DC, McCreery RL (1990), Raman spectroscopy of carbon materials: structural basis of observed spectra. *Chemistry of Materials*, 2: 557-563 doi:10.1021/cm00011a018
- Wang ZB, Yin GP, Shi PF (2006), Effects of ozone treatment of carbon support on Pt-Ru/C catalysts performance for direct methanol fuel cell. *Carbon*, 44: 133-140 doi:10.1016/j.carbon.2005.06.043
- Watson VJ, Delgado CN, Logan BE (2013), Influence of Chemical and Physical Properties of Activated Carbon Powders on Oxygen Reduction and Microbial Fuel Cell Performance. *Environ Sci Technol*, 47: 6704-6710 doi:10.1021/es401722j
- Wigmans T (1989), Industrial aspects of production and use of activated carbons. *Carbon*, 27: 13-22 doi:[http://dx.doi.org/10.1016/0008-6223\(89\)90152-8](http://dx.doi.org/10.1016/0008-6223(89)90152-8)

- Xie Y, Sherwood PMA (1989), X-Ray Photoelectron-Spectroscopic Studies of Carbon Fiber Surfaces. Part IX: The Effect of Microwave Plasma Treatment on Carbon Fiber Surfaces. *Applied Spectroscopy*, 43: 1153-1158
- Yang JA, Qiu KQ (2010), Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. *Chemical Engineering Journal*, 165: 209-217 doi:10.1016/j.cej.2010.09.019
- Zhai DY, Du HD, Li BH, Zhu YA, Kang FY (2011), Porous graphitic carbons prepared by combining chemical activation with catalytic graphitization. *Carbon*, 49: 725-729 doi:10.1016/j.carbon.2010.09.057
- Zhang F, Cheng SA, Pant D, Van Bogaert G, Logan BE (2009), Power generation using an activated carbon and metal mesh cathode in a microbial fuel cell. *Electrochem Commun*, 11: 2177-2179 doi:10.1016/j.elecom.2009.09.024
- Zhang ZL, Tsipourari VA, Efstathiou AM, Verykios XE (1996), Reforming of methane with carbon dioxide to synthesis gas over supported rhodium catalysts .1. Effects of support and metal crystallite size on reaction activity and deactivation characteristics. *Journal of Catalysis*, 158: 51-63 doi:10.1006/jcat.1996.0005
- Zhao F, Rahunen N, Varcoe JR, Chandra A, Avignone-Rossa C, Thumser AE, Slade RCT (2008), Activated carbon cloth as anode for sulfate removal in a microbial fuel cell. *Environ Sci Technol*, 42: 4971-4976 doi:10.1021/es8003766
- Zickler GA, Smarsly B, Gierlinger N, Peterlik H, Paris O (2006), A reconsideration of the relationship between the crystallite size  $L_a$  of carbons determined by X-ray diffraction and Raman spectroscopy. *Carbon*, 44: 3239-3246 doi:<http://dx.doi.org/10.1016/j.carbon.2006.06.029>