

## The Versatility of Carbon Materials

Francisco Rodríguez-Reinoso

*Laboratorio de Materiales Avanzados. Departamento de Química Inorgánica.*

*Universidad de Alicante. E-03080 Alicante. Spain*

<http://www.ua.es/grupo/lma>; [reinoso@ua.es](mailto:reinoso@ua.es)

### 1. Introduction

The element carbon is the fourth most abundant in the planet. It is unique amongst the elements with its enormous variety of structural formats and chemical bonding. Major advances to the understandings of carbon materials began in the 1940s with the development of nuclear reactors where graphite was used as a neutron moderator. Carbon science grew rapidly from the knowledge gained in those days with the realization of how wide variations in structure and assembly of imperfect graphene layers created the wide range of carbon materials with such versatility in properties. The names of synthetic graphites, their composites, synthetic diamond, carbon fibers, fullerenes, nanotubes and activated carbon are well established. The almost explosive growth in carbon science since 1964 can be seen by scanning the pages of the journal Carbon, as well as the contents of the review series of Chemistry and Physics of Carbon started in 1965. The lecture will present a brief description of the carbon materials used in my studies over a 45 year period, with an emphasis on their versatility.

### 2. Carbon adsorbents

The production of porous carbons utilizes the non-fusing characteristics of natural organic materials on carbonization (heating in an inert atmosphere). The macromolecular cross-linked systems of the lignocellulosic constituents of, *e.g.* shells of coconuts and almonds, wood, and coals such as lignites remain after carbonization. Small molecules are released during this process with the spaces, so remaining, now called 'pores' being firmly established within the carbon. This porosity has been utilized for hundreds of years, but especially since World War I, with the introduction of respirators incorporating porous carbon derived from coconut shells, the so-called activated carbon

Over recent decades an industry has developed for the manufacture of activated carbons with a worldwide production in the order  $10^6$  tonnes. International Environmental Agencies require the strictest of control of emissions from industry involving air and water quality. Contaminants in air and water have to be removed and activated carbons are able to meet this challenge. As a result the market now offers literally hundreds of activated carbons specially tailored to work in specific problem areas.

How do activated carbons work? They are highly porous, with most porosity being in the range of the micropores ( $< 2$  nm) that originates intense dispersive forces which retain an adsorbed molecule such as a gaseous pollutant. Additionally, mesoporosity (2-50 nm in size) and macroporosity (larger than 50 nm) act as transport pores enabling adsorption to take place within the microporosity in acceptable periods of time. Because porosity is the space between the defective graphene layers of structure it tends to be slit-shaped so aiding the adsorption process [1,2]. The surfaces of activated carbons are predominantly hydrophobic (inert), a property of great value when adsorbing a pollutant from a high-humidity gas phase and from aqueous solutions. However, even this property can be modified by surface oxidation to replace hydrophobicity with hydrophilicity so enabling polar molecules to be adsorbed with greater efficiency. Additionally, versatility of activated carbons materials is seen when they can be

manufactured in such physical forms as powders, grains, pellets, fibers, clothes, felts and even monoliths. Considering these characteristics it is correct to state that activated carbon is a universal adsorbent with an unparalleled versatility.

This versatility is further demonstrated in the effects that the precursor, the activation procedure and the pre- and post-treatments have on the properties of the final activated carbon adsorbent and, consequently, in the many different applications that they have. Thus, it is possible to prepare a set of different activated carbons from the same precursor but using different activation procedures [3]. The adsorption isotherm of nitrogen at 77 K is a principal diagnostic tool in the characterization and differentiation of activated carbons. Different shapes of these adsorption isotherms reflect differences in extents and distributions of pore sizes within the carbons. As such these can have completely different applications. Our research group in the University of Alicante has extensively researched into different methods of activation in order to improve the development of porosity as required for the many applications [4-6]. As indicated above, the introduction of oxygen surface complexes by recommended procedures alters the chemical characteristics of the carbon surface and, hence produces a change in the adsorption characteristics of the carbon. Thus, it was shown [5] that the adsorption isotherm for water on a typical activated carbon, without oxygen surface complexes, is type III, showing very low interaction between the molecules of water and the carbon surface. However, when the sample was oxidized in air, or hydrogen peroxide or a nitric acid solution the interaction of water with the carbon surface increased and the uptake at low relative pressures was increased.

An important part of our research was devoted in the 1980's and 1990's to the detailed characterization of the porous carbons we prepared. Thus, it was demonstrated that the adsorption of nitrogen at 77K in carbons with the smallest of microporosity could be kinetically restricted when the pore size approximates to that of the nitrogen molecule (0.36 nm). In such cases the 'as-measured' adsorption isotherm would be far from the 'true' isotherm obtained under equilibrium conditions (up to several weeks were needed for some chars obtained from lignocellulosic materials). To overcome this limitation, the adsorption was studied of carbon dioxide (molecular dimension 0.33 nm) at the much higher temperature of 273 K but with the relative pressure covered being much smaller, 0.03 versus 1.0 for N<sub>2</sub> at 77 K, with the range of porosity covered being much smaller and only in the most narrow of the micropores. For this reason we recommend that a complete characterization of porosity should include the adsorption of CO<sub>2</sub> at 273 K [7,8]. Accordingly, the nitrogen adsorption provides the total volume of micropores whereas the carbon dioxide isotherm provides the volume of the most narrow micropores (up to about 0.7 nm); the difference giving the volume of micropores in the size range between 0.7 and 2.0 nm. This procedure is now followed by most researchers in the field of activated carbon. However, we have recently found that even carbon dioxide may have some kinetic restrictions in narrow microporosity and, consequently, care must also be taken when carrying out the adsorption of this gas at 273 K [9].

A variation of activated carbon structure is found in carbon molecular sieves (CMS), these being carbons with extremely uniform micropore distributions able to distinguish between molecular species as a function of their molecular dimension, molecular shape or kinetics of adsorption. CMSs play an important role in many technological applications such as gas separation, catalyst support, gas storage, energy storage, *etc.* Our group has been able to prepare CMSs for these applications [10,11]. As an example, recent results [12] include the adsorption kinetics for the separation of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub> on CMSs with a very large apparent surface areas (above 3000 m<sup>2</sup> g<sup>-1</sup>), thus

coupling two very important aspects in a gas separation process, large adsorption capacity and separation selectivity.

A further aspect of the versatility of carbon adsorbents is that it is possible to prepare monoliths of high density for gas storage in which conformation is carried out without the use of a binder. A combination of the right precursor (simple lignocellulosic materials) and a chemical activation with phosphoric acid or zinc chloride produces solid discs [13,14] that can store amounts of methane as high as 150 V/V at the traditionally accepted pressure of 3.5 MPa. When the precursor is a petroleum residue and the activating agent KOH it is also possible to produce binderless solid monoliths with very high surface areas and a relatively high storage of hydrogen at 77 K [15]. However, these values have to be further increased if there is to be a possibility for hydrogen storage. These monoliths also are very adequate for the use as electrodes in supercapacitors [16,17]. Furthermore, some of these later CMSs are able to separate the main components of flue gas and at the same time to be able to exhibit a very high storage capacity for carbon dioxide, a way which may help with further transportation and sequestration of carbon dioxide. Some additional developments have taken place in the preparation of carbons with high mesoporosity directly from lignocellulosic materials (instead of the costly synthesis from mesoporous silica using a template procedure). Some of these mesoporous carbons have as much as 80% of their pore volume in mesopores [18].

### **3. Carbon materials in catalysis**

Carbon materials are also important in the area of catalysis where they behave as a heterogeneous catalyst or as catalyst support, the possibilities being a direct result of their uniqueness in terms of both their porosity and surface functionality. This is another example of the versatility of carbon materials. Before these characteristics were accepted by researchers working in heterogeneous catalysis, the use of carbon materials in catalysis was more of an art than of a science. It is now, when knowledge of both parameters is recognized, that practicalities are beginning to be opened up and it is accepted that carbon offers an unparalleled versatility in the tailoring of catalysts to meet specific needs. However, further research is still needed to reach a better understanding of the roles of surface area, porosity, chemical inertness and surface functionality in order to exploit them in the design of truly unique catalysts [19,20]. A test of the importance of carbon in catalysis is shown by the many reviews published in the last few years [19,20], the organization of specific conferences (*e.g.*, Carbocat, held every two years) and the publication of specific books (the last one being *Carbon Materials for Catalysis*, published in 2009 by P. Serp and J.L. Figueiredo [21]).

### **4. Components of Carbon Structure**

An important part of research into graphite is now relatively old. But this subject area does not stand still. The last few years have seen an increasing interest in isotropic graphite and related materials, many of which are intended for application in automotive industries, aero-spatial transportation, high-speed trains, rockets, *etc.* The main precursors for these materials are coal-tar or petroleum pitches, as used in the industrial production of many carbon artifacts. Again, no other element shows such versatility in structural forms. Traditionally, cokes were produced that, when appropriately calcined or graphitized, could lead to the highly anisotropic anodes as used or the production of aluminium or steels. Subsequently, it was realized that control of the pyrolysis of petroleum residues could be used for the synthesis of the so-called isotropic graphites [22,23]. The term "isotropic graphite" could be enigmatic until it is pointed out that the

reason for this term is that the material is composed of very small graphitic crystals randomly present in the solid in such a way that no preferential orientation in any property is macroscopically observed (hence isotropic). They have a high bulk density ( $\sim 2.0 \text{ g cm}^{-3}$ ), high isotropy (0.9 to 1.1), high purity and, importantly, they can be sintered without the need of a binder. Applications include pistons and sealing rings for automobiles. Here, we have carbon materials entering into the subject of tribology with doping of the isotropic graphite with an extra metal or alloy [24,25]. The chemical inertness of graphites can be improved by doping with, *e.g.* boron, silicon, titanium, zirconium, *etc.* [26-28].

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