We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Designing Nanostructured Carbon Xerogels

Esther G. Calvo, J. Ángel Menéndez and Ana Arenillas
*Instituto Nacional del Carbón (CSIC), Oviedo,
 Spain*

1. Introduction

Until the discovery of carbon gels in 1890, inorganic gels had dominated sol-gel literature. Traditional inorganic gels based upon hydrolysis-condensation reactions of metal alkoxides are well known as a result of their high specific surface areas and their unique morphological and structural properties (De Sousa et al., 2001). Some of the precursors used for the preparation of such inorganic gels are aluminates, titanates and borates but the most frequently employed alkoxides are alkoxysilanes, leading to the extensively investigated silica gels (Mauritz, 1998; Zareba-Grodz et al., 2004). The reaction mechanism of silica gels is based on the hydrolysis of alkoxysilanes to yield silicic acid moities, $\text{Si}(\text{OH})_4$, which spontaneously condensate to generate, after a sequence of specific stages, the final silica gel consisting of siloxane groups (Si-O-Si) within its framework and silanol groups (Si-OH) on its surface (Salazar-Hernández et al., 2009). Some of the attractive features of silica gels are: the tailored textural and structural properties, abundance and low cost, high sorption capacity, very high thermal shock resistance, insolubility in most solvents and lower index of refraction compared to other inorganic gels. It is for these reasons that they are used in a wide range of industrial applications including catalysis, chromatography, drug delivery and ion exchange (Qu et al., 2008; Teng et al., 2010).

It was the great interest aroused by inorganic gels, especially in the case of silica gels, in different fields of application together with the advantages associated with sol-gel methods, i.e. low temperature processing, the high homogeneity of final products and the possibility of controlling their surface properties (Houmard et al., 2009), that persuaded Pekala and co-workers to go an step further and apply this sol-gel methodology to the synthesis of organic gels (Pekala, 1989). The first organic gel was obtained by sol-gel polymerization of resorcinol and formaldehyde under alkaline conditions and supercritical drying. This produced a material called organic aerogel, consisting of interconnected colloidal particles approximately 10 nm in diameter. Properties such as low density, highly porous material and high versatility of the sol-gel process turned the carbon gel into a prominent member of the “carbon family”.

Basically, an organic gel is a solid nanostructure comprised of nano-sized pores and interlinked primary particles obtained by means of polymerization reactions between hydroxylated benzenes and aldehydes, and then subjected to a drying process. The most commonly used monomers are resorcinol and formaldehyde (Al-Mutasheb & Ritter, 2003; Czzakel et al., 2005; Job et al., 2004; Tian et al., 2011a; Zhang et al., 2007; Zhu et al., 2007; Zubizarreta et al., 2008a) but, there are other potential combinations such as phenol/formaldehyde (Mukai et al., 2005a; Scherdel & Reichenauer, 2009; Teng & Wang,

2000), phenol/furfural (Dingcai & Ruowen, 2006; Long et al., 2008a; Pekala et al., 1995), phenol/melamine/formaldehyde (Long et al., 2008b), cresol/formaldehyde (Li et al., 2001; Zhu et al., 2006), etc. As shown in Figure 1, the formation of organic gels involves the following stages: (i) formation of a three-dimensional polymer in a solvent, known as gelation step, (ii) curing period where the crosslinking of previously formed polymer clusters (particles) takes place and, finally, (iii) drying step, that can be performed under subcritical, supercritical or freezing conditions, resulting in xerogels, aerogels and cryogels, respectively (Al-Mutasheb & Ritter, 2003; Czzakel et al., 2005; Job et al., 2004; Zubizarreta et al., 2008a). The last step needed to produce carbon gels is carbonization, with the purpose of removing any remaining oxygen and hydrogen groups, yielding a thermally stable nanostructure mainly composed of carbon. This carbonization is usually performed at high temperatures (approximately 600-1000 °C) under an inert atmosphere, such as N₂, He or Ar (Al-Mutasheb & Ritter, 2003; Calvo et al., 2011a; Lin & Ritter, 2000; Job et al., 2004). However, as will be discussed in Section 2.2 of this chapter, it is possible to use other reactive gases in order to modify the chemical composition of carbon gels (Kang et al., 2009).

Fig. 1. Schematic representation of the steps involved in the synthesis of organic gels.

All the synthesis steps, referred to in the preceding paragraph, interfere in the development of the porosity of carbon gels. This gives an idea not only of the versatility of this type of carbonaceous materials but also of their complexity, since most of variables involved in the synthesis procedure are not independent, i.e. each one influences not only in certain properties of the gel but may also modify the effect of other variables (Job et al., 2006; Quin & Guo, 2001). The most important parameters that affect the properties of carbon gels are the pH of the precursor solution and the nature and concentration of the reactants, since variations in these parameters cause significant changes in the final porous properties of the carbon gel, making it possible to go from a totally non-porous material to a very highly porous carbon gel by only modifying one of these parameters. However, there are also other variables to consider such as temperature and time of gelation and curing stages, the nature of the solvent and addition of surfactants during the drying step, as these also have an important influence on the development of different properties of carbon gels (Al-Mutasheb & Ritter, 2003; Job et al., 2007a; Kraiwattanawong et al., 2011; Matos et al., 2006; Tian et al., 2011b). In so far as the carbonization step is concerned, there are several parameters that

have a notable impact on the final characteristics of carbon gels, these include the carbonization temperature and time or the nature and flow rate of the carrier gas (Al-Mutasheb & Ritter, 2003; Lin & Ritter, 2000; Tamon et al., 1998).

The increasing popularity of carbon gels is largely due to their unique and controllable physicochemical properties such as their specific surface areas ranging from about 500 to 1200 m² g⁻¹, high pore volumes, low density, excellent electrical conductivity, high purity and the possibility of synthesizing them in the form of monoliths, powders, microspheres or thin films, with high packing densities (some of these shapes are shown in Figure 2) (Al-Mutasheb & Ritter, 2003; Juárez-Pérez et al., 2010; Mahata et al., 2008). The combination of these properties makes carbon gels the perfect candidates for diverse applications such as supercapacitors, fuel cells, desalination systems, catalyst supports, liquid and gas-phase adsorbents, etc. (Calvo et al., 2008; Frackowiak & Béguin, 2001; Moreno-Castilla et al., 2005; Zheivot et al., 2010; Zubizarreta et al., 2010). However, despite the large number of advantages associated with carbon gels, there are still some applications where it is preferable to use activated carbons as a result of their low production costs. The method of synthesis of carbon gels is the main hindrance to their implantation at industrial scale because with conventional methods, where gelation, curing and drying stages are performed in conventional furnaces, several days are required to produce the final materials. Of the three stages involved in the synthesis of organic gels, drying is the most expensive. This is due to, except in the case of subcritical drying, under supercritical and freezing conditions, it is necessary to perform solvent exchanges, which requires several days, and in the most extreme conditions of drying entails a substantial increase in production costs (Liu et al., 2006; Tamon et al., 2000; Zhang et al., 2007). Consequently, the research in this field is being addressed to the development of faster and cheaper methods of synthesizing carbon gels in order to make them more attractive and competitive than the activated carbons used until now (Calvo et al., 2008, 2011; Conceição et al., 2009; Tonamon et al., 2006; Zubizarreta et al., 2008b). Some of these works are based on the use of different types of electromagnetic radiation as a heating source for one or several stages of the synthesis process. As will be explained in more detail in Section 2.4, microwave and ultrasonic radiation are the most widely investigated of the new synthesis techniques, being the results very promising not only because they meet the target of lower production times and costs but also they produce carbon gels with properties similar to those obtained using more established methods (Calvo et al., 2008, 2011; Zubizarreta et al., 2008b).

Fig. 2. Carbon xerogels presented in different shapes.

To increase the porosity of carbon gels or to enrich their chemical structure, carbon gels can be subjected to various activation, oxidation and doping processes. Activation processes can be performed during or after the carbonization step and the properties of the final carbonaceous material will be greatly influenced by the sequence used. The purpose of activation is to increase the surface area and pore volume created during the synthesis of organic gels and to promote pore widening, especially in the case of narrow pores (Contreras et al., 2010; Silva et al., 2009; Zubizarreta et al., 2008c). In Section 2.2, the different types of activation processes and the corresponding properties of carbonaceous materials produced are reviewed in more detail but, by way of introduction it may be said that there are two types of activation processes, chemical and physical activation, both with their respective advantages and disadvantages, and each of them generating carbon gels with specific textural and structural characteristics (Contreras et al., 2010). The surface areas of most carbon gels vary between 600-700 m² g⁻¹, but after an activation process, this value may increase to 2000-3000 m² g⁻¹. In other words, the porosity may be tripled which is a great advantage in applications that require highly porous materials such as supercapacitors, hydrogen storage or catalysis.

There are several published works that deal with ways to modify the chemical nature of carbon gels by means of doping or oxidizing processes in order to widen their range of applications (Gryzb et al., 2010; Job et al., 2007b; Lee et al., 2011; Sepheri et al., 2009; Silva et al., 2009; Zubizarreta et al., 2010). The porous texture of carbon gels is a crucial property in most of the fields of application. However, it is not the only one that determines the performance as the surface chemistry is also a key factor. Thus, several studies focus on the incorporation of oxygen functional groups by means of different oxidation processes (Mahata et al., 2008; Silva et al., 2009), the incorporation of nitrogen groups by using nitrogen-containing monomers or post-synthesis treatments (Gorgulho et al., 2009; Kang et al., 2009; Long et al., 2008b; Pérez-Cadenas, 2009) and the modification of carbon gels with the incorporation of metal species into the carbon framework (Bekyarova & Kaneko, 2000; Chandra et al., 2011; Cotet et al., 2006; Job et al., 2007b; Liu et al., 2006; Tian et al., 2010). In the synthesis process of carbon gels based on sol-gel methodology, these above-mentioned treatments can be performed using different reagents and conditions, making it necessary to optimize the operating conditions to meet the requirements of each individual case. In Section 2.3, different types of oxidative treatments and doping processes will be discussed in the light of the characteristics of the carbon gels produced. There are a lot of variables suitable to be adjusted in order to tailor the properties of the final carbon gel. All these tailored characteristics of the designed material (i.e. porous, chemical, mechanical characteristics) are described in Section 3 and directly connected to both the operating conditions of the synthesis of the materials and the suitability of the further application. Due to the great versatility of these kind of materials there are a wide range of applications in very different fields like adsorption (in gas and liquid media), catalysis, energy storage, etc. A review of these possible application fields are presented in the Section 4 of this chapter.

2. Synthesis of nanostructured carbon xerogels

Carbon gels are polymeric nanostructured carbon materials that can be synthesized by different procedures, all of them based on a hydrolysis-condensation reaction between hydroxybenzenes and aldehydes. There are several precursors that can be used to develop carbon gels including phenol, resorcinol or cresol in the case of hydroxybenzenes whereas as aldehyde it is possible to use formaldehyde, furfural, etc. (Czzakel et al., 2005; Dingcai &

Rouwen, 2006; Long et al., 2008a, 2008b; Pekala et al., 1995; Scherdel & Reichenauer, 2009). Amongst all the possible variations, probably the most commonly synthesized carbon gels are those based on resorcinol and formaldehyde, although in order to reduce the cost of the materials involved in the synthesis process, some less expensive precursors, such as phenol (Mukai et al., 2005a; Scherdel & Reichenauer, 2009; Teng & Wang, 2000) or cellulose (Gryzb et al., 2010), have attracted interest in recent years. Another important parameter for the preparation of carbon gels is the reaction media because there are several available solvents such as deionised water (Job et al., 2004; Pekala, 1989; Zhu et al., 2007), acetone (Berthon et al., 2001) or methanol (Zubizarreta et al., 2008a). It goes without saying that the least expensive reaction media is water, although other solvents are preferred in certain conditions in order to obtain specific final properties. Once the reagents involved in the sol-gel process have been selected, the recipe for producing carbon gels is the following. First, hydroxybenzene, aldehyde, solvent and catalyst are mixed in suitable molar ratios and then the solution is heated in order to obtain a stable crosslinked gel, which is saturated with solvent and it must next be dried. As will be seen throughout this section, there are several drying methods resulting in materials with different properties (Czzakel et al., 2005; Job et al., 2005). The last essential step for obtaining carbon gels is thermal stabilization, i.e. treatment at high temperature under inert atmosphere, yielding a thermally and chemically stable carbon gel.

Fig. 3. Different stages involved in the synthesis process of carbon gels.

Figure 3 shows the main stages involved in the synthesis process of carbon gels by means of the polycondensation of a hydroxylated benzene and an aldehyde (resorcinol and formaldehyde in this particular case). These stages are as follows: (i) sol-gel reaction, i.e. the formation and crosslinking of polymeric particles, (ii) drying of the solvent-saturated gel and, finally, (iii) carbonization of the organic gel to yield the final carbon gel.

2.1 Synthesis steps for organic gels

As already mentioned at the beginning of Section 2, the synthesis process of organic xerogels is clearly divided into two main steps: (i) polymerization and crosslinking reactions between resorcinol-formaldehyde aggregates (gelation and curing stages) and, (ii) drying process. Each step plays an important role in determining the final properties of the xerogel, and therefore deserves a detailed description.

2.1.1 Polymerization and crosslinking

The polymerisation and crosslinking reactions, also referred as the gelation and curing processes, take place during the sol-gel reaction between resorcinol and formaldehyde. According to some published works (Lin & Ritter, 1997; Pekala & Alviso, 1992), the polymerisation mechanism includes two steps: (i) addition reaction to form hydroxymethyl derivatives of resorcinol and, (ii) condensation of hydroxymethyl derivatives to form methylene or methylene ether bridged compounds. After these reactions a polymer is formed and, as a consequence, the initial solution loses fluidity, producing a special material called gel, and the time which it takes for the gel formation is named *gelation time*. The curing step of the gel is an extension of the process whereby the crosslinking of polymeric aggregates previously formed in the gelation stage is favoured, so that a three-dimensional crosslinked polymer is obtained.

As can be seen in the reaction scheme represented in Figure 4, the formation of resorcinol anions via the abstraction of hydrogen is enhanced by the basic media. Resorcinol is a trifunctional fenolic compound that is able to add formaldehyde molecules in three different positions (2, 4 and 6), but these uncharged molecules are less reactive than the corresponding resorcinol anions. Therefore, when there are OH^- anions in the reaction media, the hydrogen of resorcinol molecules is abstracted promoting the formation of hydroxymethyl derivates. In the second stage, the condensation of these hydroxymethyl derivates proceeds via acidic media, generating colloidal particles that start to crosslink producing aggregates with a diameter of around 7-10 nm (Al-Mutasheb & Ritter, 2003).

Fig. 4. Mechanism of resorcinol-formaldehyde polymerization (based on reference Al-Mutasheb & Ritter, 2003).

According to this mechanism, the initial pH of the solution is a very important operating condition because it controls the polymerisation, the subsequent crosslinking and therefore, the final porous texture of carbon gels. It is for this reason that some compounds are usually added to the reactants in order to modify the pH of the media. Some authors claim that these compounds are simply pH regulators and therefore not the usually named catalysts (Job et al., 2005) while others postulate that the nature of the compound used (i.e., an ion) is going to have a direct bearing on the pH and therefore it is a real catalyst (Fairén-Jiménez et al., 2006; Tian et al., 2011b). In any case, independently on the nature of the compound used the R/C (resorcinol/catalyst molar ratio), is a parameter usually mentioned in the synthesis receipt and it is directly related with the pH of the reaction media. Therefore, at high catalyst concentrations, i.e. as the pH increases, the first addition reaction is favoured and therefore, very branched and unstable aggregates are formed, leading to smaller more interconnected polymer particles (see Figure 5b). The condensation reaction resulting from such small particles produces materials with smaller pores (Lin & Ritter, 1997; Job et al., 2004). In contrast, when the initial pH decreases, the formation of hydroxymethyl derivatives is slow; this results in a smaller number of resorcinol anions. Naturally, polymeric particles have enough time to grow, producing large but weakly branched aggregates. The condensation of such less interconnected polymeric particles leads to higher pore sizes, illustrated in Figure 5c. Therefore, it is possible to affirm that the pH of the precursor solution plays a very important role in the sol-gel reaction because it determines the size of the polymeric particles formed during the gelation and curing stages and, accordingly, the size of the pores in the final carbonaceous material (Calvo et al., 2011a; Lin & Ritter, 1997; Job et al., 2004; Zubizarreta et al., 2008a).

Fig. 5. Schematic representation of the influence of the pH of the precursor solution on the final nanostructure of the carbon gels obtained.

2.1.2 Drying

Once a stable three-dimensional polymer has been obtained, it is necessary to remove the solvent used as the reaction media. There are different types of drying methods, each of which produces materials with different properties. Therefore drying is another synthesis condition that needs to be taken into account when trying to control the final properties of the nanostructure organic gel (Czzakel et al., 2005; Job et al., 2005). The most widely drying methods used are: (i) subcritical drying, i.e. drying the gels by simple evaporation of the solvent (at ambient pressure and temperatures of around 100-150 °C); (ii) supercritical drying, which means eliminating the solvent in supercritical conditions (high pressures and temperatures), and (iii) freeze-drying, i.e. the solvent is frozen and then removed by sublimation. A scheme of the different ways of eliminating the solvent is presented in Figure 6, whilst a more detail description of each of them and their influence on the final properties of the carbon gels is described below.

Fig. 6. Scheme of the different ways of removing the solvent used in the synthesis of organic gels.

The drying of organic gels under subcritical conditions is based on the evaporation of the solvent. Unlike other types of drying, by means of subcritical conditions, the formation of a liquid-vapour interface takes place. Therefore, when the solvent inside the pores of the material evaporates, the pores are subjected to high tension which causes the partial collapse of the structure. In order to reduce the capillary forces responsible for the partial destruction of porous texture, according to some published works (Krai wattanawong et al., 2011; Lee et al., 2010) before performing the evaporation of the water used as solvent, it can be exchanged with another solvent with a lower surface tension. Possible candidates to substitute for water could be, for example, acetone or cyclohexane (the surface tension of water at 20 °C is $72.25 \times 10^3 \text{ Nm}^{-1}$ while in the case of acetone and cyclohexane it is 23.7×10^3 and $25.5 \times 10^3 \text{ Nm}^{-1}$, respectively). However, it must be said that in some cases the partial

shrinkage of the structure when water is used as a solvent may not be of any significant if the porous texture desired for a specific application is micro or micro-mesoporosity and an easy and cheap process is required. When the solvent is eliminated by evaporation, the resulting organic gel is called xerogel. This kind of drying is the cheapest and easiest to perform, and usually the process is quite rapid (i.e. hours). Furthermore, according to some recent studies (Calvo et al., 2011a; Job et al., 2006; Leonard et al., 2005; Zubizarreta et al., 2008b) if the different evaporation conditions (i.e. the type of the solvent used, the temperature of evaporation, the carrier gas used during evaporation, use of vacuum, microwave heating, etc.) are correctly selected, it is possible to control the porous texture in order to obtain either microporous, micro-mesoporous or micro-macroporous materials.

Traditionally, although the most widely drying method used is supercritical drying, it is also the most expensive and complicated. Based on the removing of the solvent under high pressure and temperature, it is the best way to preserve the porous texture and structural properties created during the synthesis of the gels. The materials prepared by this method are called aerogels. In order to soften the conditions of supercritical drying, the solvent is usually replaced by CO₂ before its elimination under supercritical conditions. The temperature needed to remove CO₂ is lower than that of any organic solvent due to its lower surface tension, so most of the published studies on carbon aerogels make a preliminary exchange of solvent (Carrot et al., 2007; Liu et al., 2006; Tian et al., 2011a). The main problem is that the most commonly solvent used (i.e., water) needs to be exchange with an organic solvent, prior to be replacing by CO₂, complicating the procedure with several steps. Thus, the aqueous gels must to be placed in an organic solvent (i.e. acetone) for several days to completely remove the water and after that, the organic solvent is exchanged with liquid CO₂ which will finally be removed under supercritical conditions (Carrot et al., 2007). Another option is to remove the organic solvent directly under supercritical conditions, thereby by-passing the CO₂ exchange step (Liang et al., 2000; Wiener et al., 2004). However, although this second procedure avoids one of the steps in the drying process, the process usually requires more drastic operating conditions with respect to pressure and temperature apart from the fact that the aerogels obtained undergo a greater structure collapse and density than aerogels dried following the first recipe. Carbon aerogels are characterized by high pore volumes, which make these materials applicable in a huge number of application fields. However, the main disadvantage of supercritical drying, in addition to the difficulty and extremely high costs associated with the method, is the time needed to obtain dry gels as the solvent exchange steps require several days (Carrot et al., 2007; Job et al., 2005; Liu et al., 2006).

The third drying method, which results in materials called cryogels, is based on the freezing and subsequent removal of the solvent by sublimation. This method is an effective way of preparing gels with a controlled pore structure. The costs associated with freeze-drying are lower than those of supercritical drying, but it is still a more expensive method than drying by simple evaporation of the solvent (Yamamoto et al., 2001). In the case of aqueous gels, it is possible to freeze the water directly by placing the wet gel in a liquid nitrogen bath. Afterwards, the solvent is removed by sublimation under low pressures. This procedure can lead to dramatic changes in the density of the cryogels after freezing and also to the formation of megalopores or voids as a result of the creation of crystals inside the structure of the gels (Job et al., 2005; Kocklenberg et al., 1998). To prevent the formation of crystals which may deform the designed nanostructure of the polymer, the solvent is replaced before drying the gel. The most common solvent used for this purpose is t-butanol (Feaver

& Cao, 2006; Mukai et al., 2005b; Yoshimune et al., 2008), as it causes fewer changes in density than water and the vapour pressure is higher, which reduced the drying time. The advantage of this type of drying process is the possibility of obtaining high mesopore volumes (Yoshimune et al., 2008). As for the disadvantages, it should be highlighted that it is very difficult to prepare monoliths and in addition, in order to avoid the appearance of megalopores, it is necessary to perform a solvent exchange which entails an extra step and therefore an increase in time and costs.

To conclude this section of drying methods, it needs to be affirmed that the choice of drying conditions will determine the textural and structural properties of the final materials. Moreover, none of the drying methods are perfect, all three have their advantages and disadvantages (reported in Table 1), and the choice of method will depend on the requirements of the final applications.

DRYING METHOD	MATERIAL	ADVANTAGES	DISADVANTAGES
SUBCRITICAL	Xerogel	- Simple, rapid and cheap method	- Presence of capillary forces that destroy part of the initial porosity
		- High surface areas and pore volumes can be achieved	
SUPERCRITICAL	Aerogel	- No shrinkage of pore texture	- Requires high temperatures and pressures
			- Extremely high cost
FREEZE	Cryogel	- Low shrinkage	- Long times required
			- Necessary to perform, at least, one solvent exchange with CO ₂
		- Materials with higher pore diameter	- High cost, long time and complicated method
			- With aqueous gels, it is essential to exchange the solvent

Table 1. Summary of the main characteristics of the drying methods used in the field of carbon gels.

2.2 Thermal treatments of organic gels

The thermal treatment of the organic gels, i.e. carbonization, allows the removal of non-crosslinked organic chains, labile oxygen and hydrogen surface groups, resulting in thermally stable nanostructured materials formed mainly by carbon. This type of nanostructure endows the materials with a series of electrical, thermal and mechanical properties that are very useful in applications related to catalysts, energy storage, etc. (Al-Mutasheb & Ritter, 2003). The main targets of the carbonization step are to obtain thermally stable carbonaceous materials and promote the development of microporosity in the gels. The nanostructure developed during the synthesis of the organic gel usually remains intact

during the carbonization step, and therefore the meso and macroporosity obtained is preserved as it was previously designed. However, during the carbonization step the elimination of volatiles and labile matter leads to the formation of microporosity, mainly localized in the nodules of the polymer (see Figure 5a). Thus, the meso-macroporosity is controlled during the synthesis of organic gels while the microporosity is controlled independently during the carbonization step, which supposes a great advantage respect to design and control the porous texture of these materials. Usually, organic gels are carbonized by heating the samples in a furnace under inert atmosphere (i.e. N₂, Ar or He) for a specific period of time. Although most of the published works on carbon gels use N₂ or Ar as inert gas during the carbonization step, others use a reactive gas to modify the internal structure of the material. For example, K.Y. Kang et al. (Kang et al., 2008), showed that it was possible to perform the carbonization under an ammonia atmosphere (process known as ammonization). As a result, in addition to develop the microporosity of the samples, nitrogen functionalities are incorporated into the structure.

Like other steps involved in the synthesis process of organic gels, carbonization has also an important influence on the final properties of the material. The most important variables that have a significant influence on the characteristics of carbon gels are: temperature and time of carbonization, type of gas and flow rate used, heating device used, etc. Several authors have studied the influence of carbonization temperature on the porosity of carbon gels. Whereas some of these studies affirm that an increase in carbonization temperature leads to a loss of microporosity (Lin & Ritter, 2000). Others affirm the opposite, i.e. an improvement in microporosity when the temperature increases (Kang et al., 2008). C. Lin and J.A. Ritter (Lin & Ritter, 2008) evaluated the dependence of porous texture with carbonization temperature by performing the carbonization under N₂ flow at several temperatures (600, 750, 900, 1050 y 1200 °C). Their results reflected that the optimum temperature was 600 °C because as the temperature increased, smaller micropore volumes were reported. In addition, the present work shows that carbonization temperature does not influence the mesoporosity of the samples, which corroborates the affirmation that meso-macroporosity is developed during the synthesis of the organic gels while the appearance of micropores occurs during the subsequent carbonization stage (Al-Mutasheb & Ritter, 2003). Other work on the influence of carbonization temperature has also been carried out by K.Y. Kang et al. (Kang et al., 2008) but, in that case, the process was performed at 650, 850, and 950 °C under flows of nitrogen and ammonia. Results showed that higher temperatures promote the development of porosity. The bibliography, therefore, apparently contains contradictions regarding the real influence of the carbonization temperature on microporosity development of carbon gels. The reason for these divergences is probably that many other variables, such as the R/F molar ratio, the pH of the precursor solution, the type of catalyst used, etc., lead to different nanostructure materials that react in a different way with the increase of temperature. The nature of gas used during the carbonization may also have an effect on the porous and structural properties of carbon gels. Starting with the porous texture, most of the literature about carbon xerogels uses N₂ or Ar atmosphere as carrier during carbonization, resulting in materials with specific surface areas of approximately 600-700 m² g⁻¹ (Calvo et al., 2011a; Job et al., 2004; Matos et al., 2006; Zhu et al., 2007). However, it has been reported that the treatment of organic xerogels with ammonia produces carbon xerogels with specific surface areas above 1000 m² g⁻¹ (Kang et al., 2008). Moreover, differences in the chemical characteristics of the samples may also appear due to the nature of the atmosphere. For example, carbon xerogels prepared by

means of ammonia-assisted carbonization contain approximately 6-7 wt. % of nitrogen while in the case of organic xerogels carbonized under nitrogen atmosphere, the amount of nitrogen does not exceed 1 wt. %. These examples show the huge influence of the carbonization process on the final properties of carbon gels and, as in the case of the other synthesis variables, a correct choice of carbonization conditions allows to obtaining a material with the appropriate properties (both porous and chemical) for a specific application.

Carbon gels can be also subjected to activation processes after or during the carbonization step. The aim of activation processes is to increase the surface area and volumes of the pores created during the synthesis, and also to promote their widening, especially in the case of the narrower pores. Therefore, it is very common to activate carbon xerogels, where the porosity is narrower and lower, and they are usually used in applications where besides narrow mesopores a high volume of micropores are needed. It is generally accepted that there are two types of activation methods: physical activation, by means of CO₂, steam, or a combination of both (Lin & Ritter, 2000) and chemical activation, where the activation agent may be KOH (Fang & Binder, 2006; Macia-Agullo et al., 2007; Zubizarreta et al., 2008c), H₃PO₄ (Conceição et al., 2009; Jagtoyen et al., 1993), ZnCl₂ (Olivares-Martín et al., 2006), etc. In all cases, it is essential to optimize a number of variables due to their notable influence on the final porosity. Some of these variables are: temperature and time of activation, activating agent and precursor used (i.e., organic or carbon gels as precursor), amount of activating agent, gas flow and heating rate, etc. (Fang & Binder, 2006; Lozano-Castelló, 2002). Chemical activation processes take place in two stages: (i) the precursor is mixed with the activating chemical agent and this can be done in two different ways, by physical mixture, i.e. the two solid products are directly mixed in a mortar, or by wet impregnation, when the sample is mixed with a concentrated solution of the selected chemical agent for a specific time at low temperature (< 100 °C); in the latter case the slurry formed must be subsequently dried before the process is continued; (ii) the mixture is subjected to thermal treatment under an inert atmosphere up to a selected temperature that may range from 300 to 900 °C, depending on the activated agent used. When this thermal treatment is completed, the sample must be washed with water several times in order to remove traces of chemical agent. Finally, the sample is dried. One of the main disadvantages of this type of activation, apart from the higher cost of the activating agents (KOH, H₃PO₄ vs. CO₂ and steam water, for instance), is the washing stage since, in addition to lengthen the process, sometimes it is extremely difficult to completely remove all the traces of the residual activating agent. Despite these drawbacks, chemical activation has several advantages compared to physical activation including the lower temperature and activation time, higher yield and higher development of porosity achieved (Lozano-Castelló, 2002; Molina-Sabio et al., 2004; Teng & Wang, 2000). Physical activation consists of (i) thermal treatment of the precursor in an inert atmosphere and the successively controlled gasification of the carbonaceous material or (ii), the direct activation of the raw material in the presence of the activating gas. The main characteristics of physical activation are: higher temperatures than chemical activation (between 800-1100 °C), a more heterogeneous micropore size and very simple method (Okada et al., 2003). The effect of the type of precursor on the porosity of final materials is well known in the case of chemical activation, whereas in physical activation processes, further studies are needed to determine the relevance of this variable. Published works on chemical activation of organic and carbon gels have shown that in the case of carbon gels, chemical activation produces an increase in micropores volume without modifying the

mesoporous structure formed during the synthesis of the gels. However, when the chemical activation of organic gels is performed, mainly microporous materials are obtained since the mesoporosity created during the synthesis is severely damaged. This phenomenon again shows the versatility of these carbonaceous materials because, by means of chemical activation processes, only by varying the precursor used, it is possible to prepare mainly microporous materials with a small amount of mesopores or materials characterized by a high micropore volume but also by a significant amount of mesopores with a controlled size depending on the pH of the initial solution (Zubizarreta et al., 2008c). In chemical activation, several works in the literature evaluate the influence of the amount of chemical agent used on the final characteristics of the carbon gels. Usually, as the activating agent/precursor ratio increases, a further development of the microporosity takes place. However, it seems that there is a limit to this ratio, above which the specific surface area begins to decline. Thus, Zubizarreta et al. (Zubizarreta et al., 2008c) showed that in the chemical activation of different carbon xerogels with KOH, the activating agent/precursor mass ratio greatly influences (but not always in the same way) the porous texture of the activated carbon xerogels. The authors have used ratio values of 1, 2, 3 and 4 and observed that in some cases the maximum surface area was achieved with a ratio of 3, whilst with other samples the maximum was achieved using a ratio of 4. Different results were obtained depending on the pH of the initial solutions used to synthesize the materials. Highly microporous carbon xerogels can also be prepared by chemical activation with phosphoric acid (Conceição et al., 2009). In this work, several impregnation ratios were used and their influence on the final characteristics on the material was evaluated. It is noteworthy that for all the impregnation ratios employed, the mesoporosity of original samples was destroyed, which is consistent with the findings of other scientific studies (Zubizarreta et al., 2008c). In addition, the higher the impregnation ratio, the greater the development in porosity. However, it should be noted that differences between samples was not very significant, since with ratios of 1, a carbon xerogel with a specific surface area of $1525 \text{ m}^2 \text{ g}^{-1}$ was obtained while if the impregnation ratio was tripled, an increase in specific surface area of barely $200 \text{ m}^2 \text{ g}^{-1}$ was achieved.

From the examples showed in this section 2.2, both in carbonization and activation processes, is clear that the porous texture of carbon xerogels can be designed by modifying several synthesis conditions. This is of huge relevance as it reveals the carbon gels as a nanostructured material with a great potential as it is possible to tailor specific properties of this kind of materials to adequate them for an optimum behavior in a wide variety of scientific fields and applications.

2.3 Another post-synthesis treatments

As already mentioned, the most interesting characteristic of carbon gels is the possibility of tailoring the final properties in order to prepare them for a specific application (al-Mutasheb & Ritter, 2003; Czzakel et al., 2005; Job et al., 2004, 2005; Pekala, 1989; Zhang et al., 2007; Zhu et al., 2007; Zubizarreta et al., 2008a), control and design achieved by selecting the appropriate variables involved in the synthesis. There are many possible *bottoms to be pressed* to obtain the right results. Nevertheless, the porous texture is not the only factor that determines the optimum performance of the carbon gels in a specific application. Surface chemistry also plays a relevant role, due to the interactions between the fluids and the carbon surface (i.e. the possibility of redox reactions, charge transfer, different wettabilities depending on the surface chemistry, the blockage of reactive sites, etc. (Serdich et al., 2008)).

Therefore, there has been an increase in the number of published works focused on the tuning of the surface chemistry of carbon gels in recent years and these processes can be performed in several ways. For example, carbon gel functionalisation can be carried out with post-synthesis treatments, such as oxidation using different oxidizing agents, HNO_3 , H_2O_2 , air, etc. (Gryzb et al., 2010; Mahata et al., 2008), treatments with compounds such as ammonia, melamine or ammonia borane (Gorgulho et al., 2009; Pérez-Cadenas et al., 2009; Sepheri et al., 2009), with the aim of incorporating nitrogen and borane groups, respectively, into the structure of carbon gels. Alternatively, heteroatoms can be directly added during the synthesis using heteroatom-containing polymeric precursors, i.e. melamine, urea, cellulose acetate, etc. (Gryzb et al., 2010; Long et al., 2008b). Rather than in post-synthesis treatment, this is a modification of the synthesis receipt and therefore, the polymerization process would vary since the initial reactants are different.

Regarding to oxidative processes, oxygenated surface groups are incorporated using liquid-phase oxidants (e.g. nitric acid, hydrogen peroxide, ammonium persulphate) or gas-phase oxidants (i.e. air, steam, oxygen, etc.). The nature of the oxygenated functionalities incorporated depends not only on the type of oxidizing agent used, but also on the conditions in which the oxidative process is carried out. For example, N. Mahata and co-workers (Mahata et al., 2008), studied the type of oxygen surface groups created in carbon xerogel structures by means of three different oxidation treatments (oxygen plasma, nitric acid and diluted air). Of the three oxidative treatments, HNO_3 oxidation produces largest amount of carboxylic acid groups, but the amount of oxygen groups created is difficult to control and besides, high concentrations of HNO_3 are needed. Each of the three processes produces carbon xerogels with different surface chemistry. Consequently, the choice of oxidizing agent should be made according to the application requirements for which the carbon gels are intended. Another work focusing on the oxidation conditions of carbon xerogels with HNO_3 was published by Silva et al (Silva et al., 2009). In this work, HNO_3 -hydrothermal oxidation was carried out using several concentrations of nitric acid (from 0.01 to 0.30 mol l^{-1}) at different operating temperatures (between 120 and 200 °C) and the results show that both the concentration of HNO_3 and temperature notably influence on the level of oxygen functional groups created on the surface of carbon xerogels. There is a clear correlation between the degree of functionalization and the HNO_3 concentration used. The temperature of functionalisation may also affect the porosity of the final carbon xerogels. Unlike the partial blockage of the pores produced in oxidative processes with concentrated HNO_3 , the HNO_3 -hydrothermal method not only maintained the porous texture of carbon xerogels but also, when the operating temperature was fixed at 200 °C, there was even an increase in the specific surface area of carbon xerogels oxidized with a high concentration of HNO_3 solution. Another published study covering several types of carbon xerogels post-treatments, was performed recently by Grzyb and co-workers (Gryzb et al., 2010). A series of nitrogen and oxygen functionalised carbon xerogels were synthesized by means of different oxidative processes with HNO_3 and H_2O_2 , treatments with gaseous ammonia at high temperature and co-heating of carbon xerogels with melamine. All of these treatments give rise to a wide range of carbon xerogels, with different amounts and type of oxygen and nitrogen groups. This represents a breakthrough for applications that, besides a good porosity development, require materials with a rich surface chemistry. Out of all the post-synthesis treatments studied, it was found that ammonisation produces the most basic carbon xerogels not only because of the incorporation of basic N-groups, but also due to the reduction of acidic oxygen functionalities within the chemical structure of the carbon xerogels. Oxidation with nitric acid or hydrogen

peroxide introduces almost amount of oxygen (about 5 wt. %), while the character of these functionalities is quite different. XPS data reported in this work show that H_2O_2 oxidation mainly produces carbon xerogels with oxygen groups like alcohols and ethers, whereas nitric acid treatment incorporates esters, lactones and carboxylic groups into the structure of the carbon xerogels, results which are consistent with other scientific works.

Fig. 7. Main functionality groups that can be incorporated into carbon gels by post-synthesis treatments.

The doping of carbon gels with different metal species (i.e. metals, metal oxides, metal carbides) is another common post-synthesis process in carbon gels, since by means of this technique it is possible to modify their chemical nature, enlarge their surface area and improve their conductivity, thereby increasing the already known potential of this kind of carbonaceous materials. Despite the great interest in carbon gels due to the possibility of tailoring their porous texture, the presence of metal particles acting as active sites is required for specific applications. Consequently, several studies on the doping of carbon gels with transition and non-transition metals have emerged in recent years (Chandra et al., 2011; Job et al., 2007b; Lee et al., 2011; Liu et al., 2006). For example, in the particular case of energy storage in supercapacitors, carbon gels are very promising materials due to their attractive features. Supercapacitors assembled with these carbonaceous materials store energy mainly because of the formation of a double electric layer on electrodes surface. However, it is well known that specific capacitance can be increased as a result of redox reactions. Hence, in relation to this particular application, numerous studies have emerged on the synthesis of doped carbon gels. The species that are usually incorporated into carbon gel structures to improve their energy capacitance via pseudocapacitive processes are Ni, B, P, Cu, Ca, Co, Mn, etc. (Chandra et al., 2011; Cotet et al., 2006; Job et al., 2007b; Tian et al., 2010). Carbon gels have also received a great deal of attention as hydrogen storage media due to their good adsorption properties that are the result of their remarkable textural development. It has generally been accepted that the hydrogen storage capacity of carbon materials is directly related with their specific surface area and micropore volume (Tian et al., 2010; Zubizarreta et al., 2010). However, the storage

capacity values at room temperature are too low, which is a very serious problem for their application in mobile devices. In order to overcome this limitation, researchers have proposed a doping process of carbon materials to improve the interaction between the hydrogen and the carbon surface and, consequently, to enhance their hydrogen storage capacities. Zubizarreta and co-workers (Zubizarreta et al., 2010), reported the preparation of Ni-doped carbon xerogels by two methods (both post-synthesis treatments): dry impregnation and strong electrostatic adsorption, SEA. Their results showed that both treatments produce Ni-doped carbon xerogels with a small particle size (2-9 nm) and a good nickel dispersion, but dry impregnation method produces carbon xerogels with the higher amount of nickel incorporated. In contrast, the SEA method produces materials with a high interaction between C-Ni and besides, Ni particles with a very homogeneous size (around 2 nm) are obtained. Some of the samples prepared showed very good hydrogen storage capacities, with higher values than those of undoped carbon gels, making Ni-doped carbon xerogels good candidates for hydrogen storage systems. In another study on metal-doped carbon gels performed by Tian et al. (Tian et al., 2010), carbon gels were doped with metallic cobalt particles by means of two methods: (i) the addition of cobalt acetate solution to the carbon gels followed by thermal treatment and a reduction process, and, (ii) ion-exchange method. It was found that the size of the Co particles incorporated into the structure of the materials was between 2 and 8 nm when cobalt acetate solution was used and, besides that, these samples had higher surface area and micropore volume than the Co-doped carbon gels obtained by the ion-exchange method. The hydrogen storage capacity of both types of doped-materials was compared with that of the original undoped material and the results show higher values of hydrogen storage in both of the metal-doped carbon gels, although the process that presented the better results was doping with a solution of cobalt acetate.

All the studies listed in the bibliography point out the huge versatility of carbon gels and the great potential of these materials not only because their tuneable nanostructure but also because their chemical nature can be easily altered by post-synthesis treatments.

2.4 Novel and underdevelopment alternative synthesis conditions

Over the past few decade, a number of works on alternative methods of manufacturing carbon gels by means of different types of electromagnetic radiation (i.e. infrared, ultrasonic or microwave) have been published (Calvo et al., 2008; Kang et al., 2008; Tonamon et al., 2005, 2006; Wu et al., 2004). In some cases, irradiation is applied in order to improve the porous texture of the final products, whereas in other cases, the aim is to shorten the synthesis process, in order to make carbon gels more cost-competitive materials.

Wu et al. (Wu et al., 2004) prepared carbon gels from resorcinol, furfural and hexamethylenetetramine (HMTA), by means of a drying process that combines drying at room temperature, infrared lamp and high-temperature drying. This particular drying method gives rise to low-density carbon gels with a well-developed porosity development. However, although no solvent exchange or high operating pressures are involved, it is still a long drying procedure (about 34 hours). There are many works about polymerization reactions and other types of chemical processes that are accelerated by ultrasonic radiation (Neppolian et al., 2008; Riera et al., 2010; Suslick et al., 1999; Tonamon et al., 2005). Several authors have employed ultrasonic radiation in one or several steps to synthesize carbon gel. Ultrasonic has been found to be very a helpful strategy to increase reaction rates, yields of products and, thereby shortening the reaction time required. One of the studies that applies sonication to carbon gel is that published by Tonamon and co-workers in 2005 (Tonamon et al., 2007). These authors

synthesized resorcinol-formaldehyde carbon xerogels under different catalyst concentrations by means of ultrasonic irradiation using several intensities in order to evaluate the influence of sonication conditions on the porous texture of the materials. First, ultrasounds were applied to the resorcinol-formaldehyde mixture until a highly viscous sample was observed, and then the rest of the gelation and curing stages were completed by heating in a conventional furnace for 7 days. In all the samples prepared, the researchers found that ultrasonic irradiation improved the mesoporosity of the carbon gels, even in samples for which only a minor presence of mesopores could be expected (i.e. $S_{\text{BET}} = 650 \text{ m}^2 \text{ g}^{-1}$ and $V_{\text{meso}} = 0.53 \text{ cm}^3 \text{ g}^{-1}$ when the carbon xerogel was synthesized in the absence of sonication vs. $660 \text{ m}^2 \text{ g}^{-1}$ and $0.93 \text{ cm}^3 \text{ g}^{-1}$ if the intensity of the ultrasonic radiation was increased to 106 W cm^{-2}). In addition, it was observed that the higher the ultrasonic intensity, the shorter the gelation times and the higher the mesopore volume. In 2006, the same group of researches introduced a new variable in the synthesis process of carbon gels, i.e., drying by microwave technology (Tonamon et al., 2006). In some cases, the applied ultrasonic radiation to RF aqueous solutions and then they dried the samples by means of microwave radiation (after a water-exchange step using t-butanol in order to minimize the shrinkage of the structure). The results showed that the presence of mesopores was favored when ultrasonic and microwave radiations were combined (i.e. V_{meso} of $0.59 \text{ cm}^3 \text{ g}^{-1}$ and $0.46 \text{ cm}^3 \text{ g}^{-1}$ for resorcinol-formaldehyde carbon gels dried in a microwave oven with and without previous sonication process, respectively). Therefore, one of the conclusions of that work was that microwave drying was a new and efficient drying method for carbon gels because it resulted in time saving without destroying the meso-macroporosity of samples.

Microwave heating has been used to obtain different organic reactions for several years (Kappe, 2004; Menéndez et al., 2010). There are many processes involving carbon materials where microwave radiation is the main heating source used because of the good capacity of most carbon materials to absorb microwaves. The main advantage of microwave-assisted thermal processes is the saving of time, resulting in a reduction in the energy consumed, as a result of the different mechanism involved in the heating process (Menéndez et al., 2010). Thus, microwave radiation promises to be an effective technology in the field of carbon gels allowing their long synthesis time to be reduced and opening up a way to their application to industrial scale. As mentioned above, the first works that combine microwave heating and carbon gels are based on the application of this type of radiation in some stage of the synthesis process, i.e. during the drying stage (Zubizarreta et al., 2008b) or during the gelation and curing stages followed by drying in a vacuum oven (Kang et al., 2008). In all these cases, carbon gels with a good texture development were prepared in a considerably shorter time than by means of conventional heating but even so, the time required for their manufacture were too long. The next step would be the utilization of microwave heating for the entire synthesis process of carbon xerogels, i.e. during gelation, curing and drying stages. The first researchers that used microwave heating in the three stages involved in the synthesis process were Calvo et al. (Calvo et al., 2008), when in 2008 they have showed the possibility of obtaining RF carbon xerogels with similar characteristics to conventionally synthesized xerogels but with a considerable saving of time and energy (i.e. 3-4 hours under microwave radiation compared to several days by conventional heating). In addition, there are several other advantages of using microwave technology to fabricate carbon xerogels. According to a recent publication (Calvo et al., 2011a; Juárez-Pérez et al., 2010), by means of microwave heating is possible to determine the gelation point of the carbon xerogels during the sol-gel synthesis, which is essential for controlling the viscosity of the reaction media in order to obtain the carbon xerogel in an

specific form (i.e., sphere, monolith, film, etc.). Another advantage of microwave radiation is the possibility of preparing mesoporous carbon xerogels over a wider pH range than when using conventional methods (Calvo et al., 2011a). It was pointed out that, in addition to time saving and the ability to accurately determine the gelation time, mesoporous materials with a tailored mesopore size can be synthesized in a wider range of pH than in the case of conventional heating. For example, with microwave heating, a pH between 4.5 and 6.5 can be used to produce micro-mesoporous carbon xerogels and micro-macroporous materials when the initial pH is fixed at 3.1, while in the case of conventional methods, only a pH range of 5.8–6.5 serves micro-mesoporous carbon xerogels.

Fig. 8. The microwave device used in the synthesis of carbon xerogels (a) and a scheme showing the determination of the gelation point (b).

3. Properties of carbon gels

As already pointed out, the main advantage of carbon gels lies in the possibility of tailoring their porous texture to accomplish the requirements of the final application, and this can be achieved by selecting the appropriate synthesis conditions. While there is an abundant literature about the effect of the different stages of carbon gel synthesis (i.e. gelation, curing, drying, carbonization and activation) on the surface area, pore volume and pore size distribution (Czzakel et al., 2005; Job et al., 2004, 2005; Lin & Ritter, 2000; Matos et al., 2006; Zubizarreta et al., 2008a), the situation regarding the mechanical and chemical properties is quite different. Although, in some cases, these parameters may be slightly influenced by the synthesis procedure followed, it is usually necessary to carry out additional processes to produce any significant changes in the mechanical or chemical properties of carbon gels (Gryzb et al., 2010; Gorgulho et al., 2009; Job et al., 2007b; Lee et al., 2011; Pérez-Cadenas et al., 2009; Silva et al., 2009).

In this section, the main factors that have any impact on the final properties of carbon gels are reported. Each of the stages involved in the synthesis process is highlighted and explained. As can be seen in Table 2, there are several variables to be considered in the synthesis of carbon gels, which explains the versatility of these materials since they can be obtained with very diverse characteristics depending on the application which they are intended. However, this also has its downside because there are a large number of variables to consider and control. Moreover, these variables are on many cases interrelated, which

complicates their optimization. A different section will be assigned to each group of characteristics (textural, chemical and structural). Nevertheless, taking into account the information collected in the Table 2, it can be affirmed that: (i) all the variables involved in the different stages of synthesis have a remarkable effect on the porous texture of carbon gels but, in many cases, their influence on the chemistry and structure of these carbonaceous materials remains unknown; (ii) as regards the porosity of carbon gels, it might be said that each stage involved in the synthesis is very selective to a specific pore size. For example, it is possible to modify the macro/mesoporosity of samples by changing the pH of the precursor solution without affecting the development of microporosity, which is conditioned by the carbonization and activation steps (Calvo et al., 2008; Conceição et al., 2009; Job et al., 2004; Lin & Ritter, 2000; Zubizarreta et al., 2008c); (iii) in order to modify the chemistry of carbon gels, for example, by incorporating oxygenated functional groups, it is necessary to perform extra treatments (Gryzb et al., 2010; Silva et al., 2009).

3.1 Porous texture

In this section, the variables that influence the final porous texture of carbon gels are grouped according to the synthesis step and the corresponding operating conditions, in order to clarify the role that each stage plays.

3.1.1 Sol- gel process: pH, RF concentration or temperature and time of gelation and curing

Figure 9 shows a picture of four organic xerogels synthesized from resorcinol-formaldehyde solutions with a different initial pH (between 5.8 and 6.5). Intuitively it may be said that the pH of the precursor solution must be an important factor in the synthesis process of carbon gels because of the different colors of these four materials. Actually, numerous works (Al-Mutasheb & Ritter, 2003; Job et al., 2004; Zubizarreta et al., 2008a) have already established that the pH, or hydroxylated benzene/catalyst molar ratio, is the key factor that determines the meso/macroporous texture of carbon gels. As a general rule, as the initial pH increases, both the volume and the diameter of meso/macropores decrease, while there is no effect on the microporosity of the sample. That is to say, by means of a slight increase in the initial pH it is possible to go from micro-macroporous to micro-mesoporous materials and from these to exclusively microporous carbon gels (Calvo et al., 2011a; Zubizarreta et al., 2008a).

Fig. 9. Resorcinol-formaldehyde organic xerogels prepared from precursor solutions with different pHs: from left to right 5.8, 6.0, 6.2 and 6.5.

The effect of pH on the porosity of carbon gels can be explained by the polymerization mechanism between hydroxylated benzene and aldehyde molecules. Polymerization reaction between these two species occurs in two different stages: (i) the formation of hydroxymethyl derivatives and (ii) the condensation of these hydroxymethyl derivatives and their clustering. At a high initial pH the first stage is favored, giving rise to the formation of hydroxymethyl derivatives and then to the formation of highly branched clusters. These cross-linked and unstable clusters lead to small and interconnected particles that, after condensation, give rise to the formation of pores, mainly mesopores. On the other hand, a low initial pH leads to the formation of fewer but bigger clusters that finally result in materials with bigger pores in the macropore range (Job et al., 2004; Lee et al., 2010). This is shown in Figure 5.

From the abundant literature that shows the dependence of the porosity of carbon gels on the initial pH (Calvo et al., 2008, 2011a; Job et al., 2004; Zubizarreta et al., 2008a), it would appear that the maximum pH that can be used to synthesize porous carbon gels is about 7.0. What is more, when the carbon gels synthesized in this study were compared, it was observed that variations of only 0.2 units in the initial pH promote significant changes in the size of mesopores. For example, the maximum mesopore diameter for a RF carbon xerogel can change from 26 nm to 14 nm when an initial pH of 5.8 and 6.0 were used. The same trend was observed for two series of carbon xerogels synthesized under microwave and conventional heating (Calvo et al., 2008). In both cases, conventional and microwave-assisted synthesis, carbon xerogels with a higher pH have smaller mesopore size. Moreover, a more recent study (Calvo et al., 2011a) shows that for microwave-assisted synthesis, the pH window used for producing micro-mesoporous materials of different mesopore size is about two units of pH (between 4.5 and 6.5), whereas synthesis in a conventional stove has a smaller pH window (between 5.8 and 6.5). The pore size distributions of these xerogels are collected in Figure 10 in order to see the porous texture in relation to the initial pH and the type of heating device used. This example confirms that there are interactions between the variables involved in the synthesis process. It can be seen that the same variations in initial pH do not produce similar carbon xerogels due to a new variable, i.e. the type of heating device used.

Fig. 10. Pore size distribution of resorcinol-formaldehyde prepared with different pH and heating mechanisms: conventional (a) and microwave radiation (b) (adapted from reference Calvo et al., 2011a).

Conversely, the effect of the concentration of reagents on the porosity of carbon gels has not been studied in depth. Most published works on carbon gels synthesized from resorcinol-formaldehyde mixtures use a molar ratio $R/F = 0.5$ (Al-Mutasheb & Ritter, 2003; Job et al., 2004; Zhang et al., 2007; Zhu et al., 2007; Pekala, 1989). This is because formaldehyde only has one aldehyde group able to interact with other groups while resorcinol molecules display two hydroxyl groups. Nevertheless, some studies use a lower molar ratio R/F , that it is to say, a more diluted RF solution, leading to carbon gels with smaller particle sizes and, therefore, smaller pore sizes (Al-Mutasheb & Ritter, 2003).

The synthesis procedure of carbon gels found in most of the published literature involves the heating of the monomers solution at temperatures ranging between 70 and 90 °C for 3-5 days in order to perform the gelation and curing stages (Pekala, 1989). The synthesis temperature and time affect the porosity of resulting materials. However, according to the results reported by Job et al. (Job et al., 2006), the effect on the porous structure is not the same in every carbon gel because the most important variable in this sol-gel synthesis, i.e. the initial pH, again comes into play. These authors studied the effect of several combined parameters, gelation and ageing temperature (50, 70 and 90 °C) and ageing time (between 0 and 72 hours), in three series of organic xerogels obtained from precursor solutions with different pH. In all the examples shown, the increase in temperature leads to lower gelation times, which is consistent with other works (Al-Mutasheb & Ritter, 2003; Job et al., 2007a; Kim et al., 2001). Moreover, as the synthesis temperature increases, the ageing time may be shortened (i.e. samples synthesized at 50 °C do not reach stability after 72 hours while in the case of 70 or 90 °C, the polymerization reactions are completed after 24 or 48 hours, depending on the initial pH). In general, it can be said that increasing the synthesis temperature yields narrower pores but this statement does not apply in all cases due to the influence of the pH. If the ageing time is increased, higher surface areas and pores volume are achieved, but once the polymerization reaches stability, the increase in ageing time scarcely has any influence on the porosity of materials. However, it should be noted that it is not easy to establish trends for each of the variables involved in the sol-gel process because a slight change in one variable, like the pH, implies a variation in the effect of other parameters, for example the synthesis temperature.

3.1.2 Drying: Heating device and drying temperature

It is particularly difficult to establish a direct relationship between the drying method and the textural properties of carbon gels because the effects produced by other variables such as the initial pH, synthesis temperature and time can conceal it. However, according to some works in which aero, cryo and xerogels were compared, it was reported that carbon gels with a higher pore size, large mesopores and macropores, are mainly achieved under supercritical and freezing conditions. In contrast, carbon xerogels are susceptible to a high degree of shrinkage of their porous nanostructure due to the surface tensions caused by the solvent upon the vapor-liquid interface (Czzakel et al., 2005; Job et al., 2005; Qin et al., 2001). As a result of the partial collapse of their structure, carbon xerogels possess a smaller pore size than their aero and cryogel counterparts. However, it should be noted that several works suggest that it is possible to prepare meso-macroporous carbon xerogels by employing low values of initial pH, although with lower pores volume than aerogels and cryogels (Calvo et al., 2011a). Subcritical drying is the cheapest, simplest and fastest procedure, since the other two methods require extra processes of solvent exchange and extreme operating conditions. However, in general, the choice of the drying method is conditioned by the requirements of porosity in the final application.

Czakkel and co-workers (Czakkel et al., 2005) published in 2005 a study on carbon gels dried under different conditions, keeping the rest of variables involved in the synthesis process constant. They obtained a S_{BET} of 2650, 1010 and 891 $\text{m}^2 \text{g}^{-1}$ and a V_p of 2.05, 0.79 and 0.44 $\text{cm}^3 \text{g}^{-1}$, for cryogels, aerogels and xerogels, respectively, and concluded that freeze-drying promotes the formation of materials with a larger textural development. The same trend was also observed in another work in 2005 (Job et al., 2005), where three types of drying methods were studied but in this case, precursor solutions with different pH were used. Carbon cryogels presented a higher specific surface area and pore volume than the other types of carbon gel in three out of the five series studied, those with lower pH. No clear trend was observed in the sizes of the meso and macropores of aerogels and cryogels synthesized. Nevertheless, in the pH range evaluated, carbon xerogels were the materials with the smallest meso and macropores.

In the case of carbon xerogels, some studies report the porous texture differences resulting from evaporative drying under different conditions (Kraiwattanawong et al., 2011; Zubizarreta et al., 2008a). For example, carbon xerogels with a good textural development and significantly reduced synthesis time (up to 98%) were obtained using microwave heating (Zubizarreta et al., 2008b). Furthermore, as illustrated in Figure 11, the microwave process allows the tailoring of the porous texture of the carbon xerogels depending on the initial pH, or R/C.

Fig. 11. Influence of R/C molar ratio on the pore size distribution of different carbon xerogels dried by microwave heating (adapted from reference Zubizarreta et al., 2008b).

Another factor to be taken into account is the drying temperature. A number of studies show that the removal of the solvent should be performed with a smooth gradual increase in temperature in order to avoid the collapse of the porosity. In most of the works, the drying stage was carried out at approximately 85-150 °C for the necessary time to remove the solvent inside the structure of the material, but using very slow temperature programs (Job et al., 2005).

3.1.3 Carbonization: Temperature, heating rate and atmosphere used

The aim of the carbonization stage is, on the one hand, to obtain thermally stable materials, mostly composed of carbon atoms and, on the other hand, to develop the microporosity of carbon gels (Al-Mutasheb & Ritter, 2003; Quin & Guo, 2001). Variables such as final temperature or heating rate have a significant influence on the textural properties of carbon gels while the type of atmosphere (inert or reactive), in addition to its impact on porosity, has a notable repercussion on their surface chemistry.

Most published works on the influence of carbonization temperatures on the textural characteristics of carbon gels agree that increasing the temperature leads to materials with a lower surface area and pore volume (Lin & Ritter, 2000). Thus, the microporosity of carbon gels is reduced when the carbonization temperature is increased. However, it is necessary to discriminate between ultramicropores, pores with diameter less than 0.7 nm and supermicropores, in the 0.7-2.0 nm range. Lin and Ritter (Lin & Ritter, 2000), evaluated the effect of carbonization temperature (600, 750, 900, 1050 and 1200 °C) on these two groups of micropores and concluded that the decrease in the surface area at higher temperatures is mainly due to the smaller number of micropores in 0.4-0.7 nm range. The carbon gels reported in this work are also composed of micropores with a diameter between 1-2 nm, whose volume decreases at low temperatures (600-900 °C), while when the carbonization was performed at 1050 and 1200 °C, their volume increased indicating that high temperatures destroy ultramicropores but create a greater amount of larger micropores.

The carbonization temperature is the most important parameter in the pyrolysis processes. However, other factors such as heating rate and carbonization atmosphere have also some influence on the textural properties of carbon gels (Kang et al., 2009). Overall, the heating rates used during pyrolysis are around 5-15 °C (Wu et al., 2004; Yoshimune et al., 2008; Zubizarreta et al., 2008a) since higher heating rates would mean a lower microporosity development, as reflected by several works that evaluate the different conditions in the carbonization processes of several carbon materials (Kuo et al., 2005; Liou, 2004).

Regarding the influence of the carbonization atmosphere, it seems that inert gases produce the materials with the lowest textural development. For example, carbon gels prepared under a N₂ atmosphere usually have specific surface areas about 600-700 m² g⁻¹ (Calvo et al., 2008; Kraiwattanawong et al., 2011; Zubizarreta et al., 2008a), whereas this parameter can reach 1000 m² g⁻¹ when the pyrolysis step is carried out under ammonia or CO₂ atmosphere (Kang et al., 2009).

3.1.4 Activation: Physical or chemical activating agent, activating agent/precursor ratio, type of precursor and activation time and temperature

Usually the temperature used for physical activation range between 700-1100 °C for different lengths of time, ranging from few hours (Guo et al., 2009; Lin & Ritter, 2000; Nabais et al., 2008; Zhao et al., 2007) to 24 hours (Contreras et al., 2010). The activation time and temperature are very important variables since they can notably modify the microporosity of the resulting materials, and even the narrower mesoporosity. Usually, increasing the temperature promotes higher development of carbon gel microporosity. As an example, Lin and Ritter (Lin & Ritter, 2000), performed the physical activation of resorcinol-formaldehyde carbon xerogels with CO₂ at 1050 °C for several activation times: 0.5, 1, 2 and 3 hours. The carbon xerogels reported in this study were found to have

significant volume of micropores in the 0.6 nm range, micropores whose diameter is centered at approximately 1.3 nm and also mesopores ranging from 2-10 nm. The increase in the activation time produced a more developed pore structure since the total pore volume increased. The amount of ultramicropores increases until it reaches its maximum value after 2 hours of activation, while the volume of large micropores and smaller mesopores rises consistently with activation time. These results lead to the conclusion that in more prolonged activation processes, not only does the creation of micropores take place but also the destruction of the narrower micropores which are sometimes converted into large micropores and small mesopores. This phenomenon has also been found in another study performed by Contreras and co-workers (Contreras et al., 2010), where physical activation processes with CO₂ at 900 °C for 4, 8 and 16 hours resulted in carbon xerogels with specific surface areas of 1015, 1365 and 2180 m² g⁻¹, respectively, and micropores of size 1.0, 1.1 and 1.4 nm, corroborating the development of porosity and the widening of micropores with the increase in activation time. In the same publication, the influence of another variable involved in the activation processes, i.e. temperature, upon the porosity of materials was evaluated. Two activation temperatures were studied, 800 and 900 °C, and it was found that the highest temperature produced a greater development in microporosity, as reflected by the increase in S_{BET} , $V_{\text{DUB-N}_2}$ and $V_{\text{DUB-CO}_2}$. With these examples, it is possible to affirm that the development of microporosity increases with higher activation temperatures and times, i.e. as the burn-off increases, a phenomenon consistent with other works that deal with physical activation processes of different type of materials (Guo et al., 2009; Roman et al., 2008).

As expected, chemical activation processes are also conditioned by many variables such as the activation time and temperature, the amount of activating agent or type of precursor (Conceição et al., 2009; Contreras et al., 2010; Zubizarreta et al., 2007). With regard to the activating agent/precursor ratio, several studies have reported that the increase in the amount of chemical agent leads to materials with a higher textural development, although it should be pointed out that there is a maximum value above which surface area begins to decrease (Zubizarreta et al., 2008c). Conceição et al. (Conceição et al., 2009) published a work on the chemical activation with H₃PO₄ of resorcinol-formaldehyde aerogels using different impregnation ratio values (H₃PO₄/gel = 1, 2 and 3). The increase in the amount of H₃PO₄ leads to a higher total pore volume (i.e. 0.65, 0.94 and 1.41 cm³ g⁻¹ for samples obtained using impregnation ratios of 1, 2 and 3, respectively). The narrower micropores widen and, therefore, the volume of the ultramicropores decreases (i.e. 0.16, 0.15 and 0.13 cm³ g⁻¹), unlike the volume of supermicropores and narrower mesopores that increases with higher impregnation ratios, a phenomenon similar to that explained in the preceding paragraph regarding the effect of temperature on physical activation processes. This trend was also observed in chemical activation processes of RF xerogels by adding different amounts of KOH (Zubizarreta et al., 2008c). As the activating agent/precursor mass ratio increases, carbon xerogels evolve from exclusively microporous to micro-mesoporous materials when the A/P ratio is 4. As the KOH/precursor mass ratio increases, both the specific surface area and micropore volume increase but sometimes, when A/P > 3, both parameters decrease as a result of the widening of the micropores, which are then converted to narrow mesopores.

Another noteworthy variable in chemical activation processes is the type of precursor used. According to different works (Calvo et al., 2011b; Zubizarreta et al., 2008c), the chemical activation of carbon gels develops the microporosity notably without modifying

the pristine meso-macroporosity, as a result of the thermal stability of carbon gels. However, when carbonization and activation are simultaneous processes, the reactivity of the organic gels causes the destruction of most of the meso and macropores created during sol-gel synthesis, while the microporosity undergoes intense development. When chemical activation is performed after the carbonization step, it is possible to synthesize materials with a specific surface area of about $1500 \text{ m}^2 \text{ g}^{-1}$ and large mesopores volume ($S_{\text{BET}} = 1540 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{DUB-N}_2} = 0.69 \text{ cm}^3 \text{ g}^{-1}$ and $V_{\text{meso}} = 0.25 \text{ cm}^3 \text{ g}^{-1}$ for a carbon xerogel activated with KOH, (Zubizarreta et al., 2008c)) whereas when organic gels are used as activating precursors, there is an intense development of microporosity, which is reflected by S_{BET} values ranging from 2000 to $3000 \text{ m}^2 \text{ g}^{-1}$, although this is accompanied by a lower mesopores volume (i.e. $S_{\text{BET}} = 2037 \text{ m}^2 \text{ g}^{-1}$, $V_{\text{DUB-N}_2} = 0.82 \text{ cm}^3 \text{ g}^{-1}$ and $V_{\text{meso}} = 0 \text{ cm}^3 \text{ g}^{-1}$ (Zubizarreta et al., 2008c)).

As mentioned above, during the activation processes narrow mesopores may be created depending on the activation conditions. Therefore, it is important to discriminate between this type of mesopores and the meso- macroporosity that appears during the sol-gel synthesis of organic gels. The latter type of porosity is unable to remain intact when chemical activation of organic gels is carried out. However, in a recent work it has been shown that, under certain conditions, the chemical activation with KOH when microwave radiation is used as a heating source of organic xerogels, leads to materials with the meso-macroporosity of the original samples, in addition achieving remarkable amount of micropores (Calvo et al., 2011b).

Usually, chemical activation processes are performed at lower temperatures than physical activations, i.e. $700\text{--}850^\circ\text{C}$ when metal alkoxides, such as KOH or NaOH, are used as activating agent (Macia-Agullo et al., 2007; Raymundo-Piñero et al., 2005; Zubizarreta et al., 2008c), and temperatures ranging from $450\text{--}650^\circ\text{C}$ in the case of chemical activations with H_3PO_4 (Conceição et al., 2009, Qin et al., 2001). The influence of temperature on the pore structure of carbon gels has been more extensively studied in the case of physical activation processes, although there are also some studies about its effect on chemical activations. As the activation temperature increases, materials with a more developed porosity (i.e. higher surface area, micropore and also mesopore volumes) are formed. However, it is noteworthy that, as with the effect of the amount of activating agent, there is a maximum temperature above which porosity begins to decrease (Niu & Wang, 2008; Okada et al., 2003).

To sum up, by choosing suitable synthesis and post-processing conditions, it is possible to tailor the porosity of carbon gels, discriminating between micropores, mainly produced during carbonization and activation stages and meso-macropores, created during the sol-gel synthesis. It is therefore possible to obtain exclusively microporous carbon gels (suitable for H_2 storage and adsorption applications (Cabria et al., 2007; Mahata et al., 2008)), micro-mesoporous materials (for use as electrodes in supercapacitors (Calvo et al., 2008; Escribano et al., 1998; Frackowiak & Béguin, 2001)) or even meso-macroporous samples (for water treatments (Sanchez-Polo et al., 2007)).

3.2 Chemical properties

Unlike the porous textural properties, which can be easily controlled with the synthesis and processing conditions, the chemical nature of carbon gels is not usually influenced by the synthesis protocol followed during the sol-gel synthesis. Apart from the obvious influence of the chemical nature of the monomers used, it is only possible to create different chemical

characteristics when activation, oxidation or doping processes are employed (Contreras et al., 2010; Silva et al., 2009; Zubizarreta et al., 2008c).

Carbon gels are composed of approximately 92-98 wt. % carbon and the rest of the composition is divided between hydrogen and oxygen, regardless of the synthesis conditions such as initial pH, operating time and temperature, dilution, etc. (Calvo et al., 2011a). However, Zubizarreta et al. (Zubizarreta et al., 2008a) affirm that it is possible to synthesize carbon gels with a larger amount of oxygen by performing the drying step by means of microwave heating. The oxygen content of this type of carbon xerogels was about 6-8 wt. %, probably due to the fact that with microwave radiation, several secondary reactions take place, which would favour greater crosslinkage between organic gel and the more stable oxygenated groups (Caddick, 1995).

Activation processes, both physical and chemical, besides increasing considerably the microporosity, are able to increase the quantity of oxygen present in carbon gels of around 3-4 wt. % and, according to several published works, the higher the temperature and time of activation, the higher the amount of oxygenated groups created (Contreras et al., 2010). However, since the amount of oxygen inside the carbon gel structure is still low, the determination of the nature of these surface groups is no straightforward task (Contreras et al., 2010).

The pH_{PZC} , (i.e. the pH value at which the electrical charge density on the carbon surface is zero), of carbon gels synthesized from resorcinol-formaldehyde solutions generally ranges from 8-9.5, whatever the synthesis conditions used (Calvo et al., 2011a; Zubizarreta et al., 2008a; Lambert et al., 2009). This basic character is may be due to the presence of delocalized π electrons on the surface of the carbon gels, because of their aromatic character (Montes-Morán et al., 1998), and the presence of pyrone or chromene-like structures (Fuentes et al., 1998). When activation and/or oxidation processes are carried out, the point of zero charge is irreversibly modified, increasing or decreasing with respect to the value of the pristine material, depending on the nature of the oxygenated functionalities created (Mahata et al., 2008). Thus, Lambert et al. (Lambert et al., 2009) show that oxidation by nitric acid is able to modify the surface chemistry of resorcinol-formaldehyde carbon gels, by modifying their pH_{PZC} from ca 9.4 to 2.4.

The modification of surface chemistry of carbon gels by doping processes has been widely investigated because of the need for rich chemical nature and good conductivity of these materials in a wide range of areas (e.g. catalysis or energy applications) (Job et al., 2008; Lee et al., 2011; Moreno-Castilla et al., 1999, 2005; Zubizarreta et al., 2010). There are several methods for obtaining metal-doped carbon gels. Basically, they can be classified into three processes: (i) direct dissolution of the metal precursor in the resorcinol-formaldehyde mixture (Chandra et al., 2011; Maldonado-Hódar et al., 2003); (ii) use of a resorcinol derivative containing an ion exchange moiety that can be polymerized by sol-gel reactions (Baumann et al., 2002; Fu et al., 2005), and finally, (iii) deposition of the precursor metal either on organic or carbon gels (Mahata et al., 2008). In addition to the several types of doping processes, factors such as the nature and amount of metal precursor, operating temperature, etc. greatly determined the chemical properties of the resulting materials (Frackowiak & Béguin, 2001; Job et al., 2007b).

The effect of the amount of metal precursor on the final properties of carbon gels has been evaluated by Job et al (Job et al., 2007b), through the synthesis of RF carbon xerogels doped with Cu, Ni, Pd, and Pt, by the addition of complexing agents that react during the sol-gel process. The results of this work showed that the metal particle size varies with the

concentration of the complexing agent, and these metal particles remain inserted into the structure of the materials after the drying and pyrolysis stages. For example, Pd-doped carbon xerogels had metal particle sizes of about 20 nm at low concentrations of metal precursor while the size decreased to 3-5 nm, as the concentration of complexing agent increased. In the case of Cu and Ni-loaded carbon gels, the metal particle size was unchanged with the concentration of complexing agent because they were not incorporated inside the polymeric network of the material and, therefore, they sintered during the pyrolysis stage.

The influence of the processing temperature on the surface chemistry of carbon gels was studied by Maldonado-Hódar (Maldonado-Hódar et al., 2003). In this work, they reported the preparation of tungsten-doped carbon aerogels by means of sol-gel reactions between resorcinol, formaldehyde and ammonium tungsten mixtures. Two carbonization temperatures were selected (500 and 1000 °C), and their influence on the resulting materials was evaluated. By means of SEM images, it was possible to determine the distributions of the metal species created, showing a more homogeneous distribution when the sample was carbonized at 1000 °C. Moreover, the temperature determined the type of tungsten particles inside the carbon structure, since carbonization at 500 °C produced materials composed of needle-like WO₃ particles with a radius of few nanometres, while when the temperature was set at 1000 °C, as well as the same type of particles, a denser species with a certain dendritic character were obtained.

The surface chemistry of metal-doped carbon gels are also conditioned by the pH of the precursor solution (Bekyarova et al., 2000) like the textural properties. Bekyarova and Kaneko (Bekyarova et al., 2000) prepared Ce,Zr-doped carbon aerogels by adding metal salts to the resorcinol-formaldehyde solutions. Two pH values were selected, 3 and 7, results in materials with different features. The TEM images collected in this work showed that in the case of pH 7, the carbon aerogel was composed of bound particles of about 20 nm and, there was a homogeneous distribution of the metal species. However, the sample synthesized from a solution with pH 3 gave rise to spherical particles with diameters of about 3 µm and no doping particles were detected.

3.3 Mechanical properties

Carbon gels are composed of interconnected quasi-spherical nodules, forming a three-dimensional matrix, as reflected by the SEM photograph presented in Figure 12. As already mentioned, the diameter of these nanospheres and, therefore, the pore size is influenced by several synthesis conditions (Czzakel et al., 2005; Silva et al., 2009; Zubizarreta et al., 2008a). As regards to the initial pH, lower microspheres size are obtained as the initial pH increases, corresponding to highly compact structures. Zubizarreta et al. (Zubizarreta et al., 2008a) determined the influence of the pH on the structure of the carbon xerogels, noting that precursor solutions with pH 9 and 7 produced carbon xerogels with a compact and uniform structure while the sample obtained using pH 6 exhibited a low-compact structure and besides, the microspheres have hardly intuit.

The influence of other synthesis variables, such as the drying procedure, on the structure of carbon gels has been determined by several research groups. Regardless of the drying conditions, the structure of carbon gels is composed of interconnected spherical particles, although it is necessary to emphasize that the size of such spheres changes depending on the method used (Czzakel et al., 2005). Sometimes it is difficult to discriminate between the structures of carbon aerogels and cryogels. However, by means of SEM or TEM

photographs, it is possible to appreciate the smaller size of the microspheres of the carbon xerogels, as a result of the shrinkage of the structure (Czzakel et al., 2005).

One of the advantages associated with carbon gels is that they can be made with different morphologies, such as monoliths, although this monolithic shape is notably influenced by the synthesis conditions. There is a scientific work that has demonstrated the effect of the initial pH and the heating device used to evaporate the solvent, on the morphology of carbon xerogels (Zubizarreta et al., 2008a). With microwave heating, it was possible to preserve the monolithic shape of the carbon gel when a precursor solution with a high pH is used, whereas when the pH was low, the monolith broke into pieces as a result of its greater frailty. This confirms that the final carbon gel displays better mechanical properties as the initial pH increases.

Fig. 12. SEM image of resorcinol-formaldehyde carbon xerogel synthesised in a microwave oven using a precursor solution with a pH of 5.8.

Regarding the effect of the activation processes, both physical and chemical, on the mechanical properties of the resultant activated material, it has been observed that it is possible to obtain monoliths of physically activated carbon gels. However, when chemical activation is used, the process is more severe and it is not possible to retain the monolithic shape.

The porous, chemical and mechanical characteristics of carbon gels are related to the different synthesis steps and the operating variables involved in each stage. As a summary of this section this relationship is reported in Table 2. Although there are many works which deal with the designing of the carbon gel properties and the great potential of these materials, many variables require further study and adjustment with the aim of tailoring the properties of the final material for a specific application.

STEP	VARIABLES	POROUS TEXTURE	CHEMICAL PROPERTIES	STRUCTURAL PROPERTIES
SOLUTION, GELATION AND CURING	pH/catalyst	pH has no influence on microporosity and/or surface area (Calvo et al., 2011a; Job et al., 2004; Lin & Ritter,1997) Increasing pH yields a narrower mesoporosity (Calvo et al., 2011a; Job et al., 2004; Lin & Ritter,1997) Decreasing the pH increases the macroporosity (Zubizarreta et al., 2008a, Calvo et al., 2011a) As the pH increases, the gelation time (t_g) decreases (Calvo et al., 2011a; Juárez-Pérez et al., 2010)	Not influenced (Calvo et al., 2011a, Zubizarreta et al., 2008a)	Increasing the pH increases the mechanical resistance of the carbon xerogels (Zubizarreta et al., 2008a)
	RF concentration	A decrease in the RF concentration leads to a smaller pore size (Al-Mutasheb & Ritter, 2003; Petricevic et al., 2001)	Not influenced	Little studied
	Temperature	Very high synthesis temperatures cause a shrinkage of porosity	Not influenced	Little studied
SUBCRITICAL DRYING	Stove	Causes shrinkage of the pore structure (Al-Mutasheb & Ritter, 2003; Czzakel et al., 2005; Job et al., 2005)	Not influenced	Easy to obtain carbon xerogel monoliths
	Microwave	Slightly higher shrinkage of the pore structure (Zubizarreta et al., 2008b)	Higher oxygen content but few studies on this topic (Zubizarreta et al., 2008b)	It is difficult to obtain carbon xerogel monoliths directly, but the good control of gelation point leads to design the final shape (Calvo et al., 2011a; Mahata et al., 2008)
CARBONISATION	temperature	Increasing the temperature either increases (Husley et al., 1992; Lin & Ritter, 2000) or decreases the surface area and micropore volume (Kang et al., 2009) Little influence on meso or macroporosity	Increasing the temperature reduces the oxygen content (Al-Mutasheb & Ritter, 2003)	Little studied
	Heating rate	A high heating rate reduces the micropore volume (Kuo et al., 2005; Liou, 2004)	Little studied	Little studied
	Atmosphere	A carbonization atmosphere notably influences the porous texture of the carbon gels (Kang et al., 2009; Zubizarreta et al., 2008a)	Depending on the type of carbonisation atmosphere (Kang et al., 2009; Zubizarreta et al., 2008a)	Little studied

STEP	VARIABLES	POROUS TEXTURE	CHEMICAL PROPERTIES	STRUCTURAL PROPERTIES
ACTIVATION	Physical	Increasing activation the temperature and operating times leads to a more developed pore texture (Contreras et al., 2010; Lin & Ritter, 2000)	The oxygen content increases (Contreras et al., 2010)	Possible activation of the monoliths
		Activation of the organic xerogels destroys the meso-macroporosity created during the synthesis (except in a MW oven), but increases the microporosity and surface area considerably (Calvo et al., 2011b; Zubizarreta et al., 2008c)		
	Chemical	Activation of the carbon xerogels increases the microporosity without altering the meso-macroporosity (Al-Mutasheb & Ritter, 2003; Molina-Sabio et al., 2004; Zubizarreta et al., 2008c) The activating agent/carbon ratio influences the micropore volume considerably (Conceição et al., 2009; Zubizarreta et al., 2008c)	The oxygen content increases	The monoliths are usually destroyed (Zubizarreta et al., 2008c)

Table 2. Effect of the synthesis conditions on the properties of resorcinol-formaldehyde carbon gels.

4. Applications of carbon xerogels

All the characteristics already mentioned along this chapter make carbon xerogels very promising candidates for a wide range of applications such as adsorption (Long et al., 2009; Maldonado-Hódar et al., 2007; Ying et al., 2005), water treatment (Girgis et al., 2011; Shánchez-Polo et al., 2007), gas separation (Yamamoto et al., 2004) or enzymes support (Chaijitrakool et al., 2008). Besides the most common and referenced ones like catalysts support (Job et al., 2008; Lambert et al., 2010; Liu & Creager, 2010; Moreno-Castilla et al., 1999), electrode materials in electric double layer capacitors (Calvo et al., 2008; Frackowiak & Béguin, 2001; Sepheri et al., 2009; Zhang et al., 2007; Zhu et al., 2007) and hydrogen storage (Kang et al., 2009; Tian et al., 2010, 2011a, 2011b; Zubizarreta et al., 2010). In this section a brief review of all these applications of carbon xerogels are reviewed.

4.1 Catalysts support

Catalysis plays a decisive role in many reactions and technologies such as: energy supply by fuel cells, oxidation of organic compounds in liquid effluents, removal of SO_x and NO_x in order to reduce the pollution, synthesis of fine chemistry products, etc (Girgis et al., 2011; Machado et al., 2010; Moreno-Castilla et al., 2005; Pirard et al., 2011). Generally, two types of catalysis are distinguished: homogeneous catalysis, i.e. reactants and catalyst constitute just one phase and heterogeneous catalysis, it is to say, when catalyst is in a different phase respect to the reactants involved in the process. Both kind of catalysts display advantages

and drawbacks. For example, heterogeneous catalysts are much important at industrial scale as a result of their simple preparation procedure, high stability and the possibility of separating them from the reaction media in an easy way. Nevertheless, the disadvantages of heterogeneous catalysis are the presence of two different phases and the control of the active sites nature. On the other hand, regarding to homogeneous catalysis, although reactions take place in a single phase and catalysts can be tailored, their carriage in industrial processes is lower due to their sometimes limited stability and their difficult recovery (Choplin & Quignard, 1998; Djakovitch et al., 2004; Fontecha-Cámara et al., 2011).

Most of published works on carbon gels used in catalysis field are focused on heterogeneous processes and the great interest of carbon gels in this field research is due to their attractive features such as: tailored pore texture, possibility of enriching their surface chemistry by different processes, high packing density, high durability under harsh conditions, etc. (Cotet et al., 2006; Job et al., 2005; Moreno-Castilla et al., 1999; Teng & Wang, 2000). The major challenge in catalysis, together with the reduction of costs is to increase their activity and selectivity. The selectivity is a feature very difficult to manage but catalytic activity has been extensively studied in many publications in order to achieve a relationship between this parameter and the properties of the carbon material. Both surface chemistry and porous texture of carbon gels play an important role on catalytic processes. However, catalytic activity depends on the nature, amount and accessibility of their active sites for the reactants, and it is not always straightforward to correlate it with intrinsic characteristics of carbonaceous materials.

One of the first works found about catalytic performance of metal-doped carbon gels were published in 1999 by Moreno-Castilla and co-workers (Moreno-Castilla et al., 1999). This work was focused on the study of catalytic activity of chromium, molybdenum and tungsten oxide-doped carbon aerogels in the isomerisation reaction of 1-butene and the results showed that the best catalyst for this specific reaction was carbon aerogel based on tungsten oxide because of the higher surface acidity. The isomerization reaction of 1-butene in other structures was a widely investigated process since a hydrocarbon with higher octanoic value can be obtained and therefore, several research groups have performed studies on the effect of using metal catalysts supported on carbon materials for accelerating this reaction (Álvarez-Merino et al., 2000).

Carbon gels have also been explored as metal catalyst support for fuel cell applications. The fact of using carbon supported catalysts in fuel cells allows production costs to be reduced and performance and durability of the electrochemical system to be improved (Arbizzani et al., 2007; Job et al., 2008; Liu & Creager, 2010). One the most recent works in this research field was carried out by Liu and Creager (Liu & Creager, 2010). Resorcinol-formaldehyde carbon xerogels was used as supports for Pt particles, by means of impregnation-reduction method using H_2PtCl_6 as platinum precursor and formaldehyde as the reducing agent. Electrochemical results of the membrane-electrodes fabricated from Pt-deposited carbon xerogels with Nafion as electrolyte, were compared with those of Pt catalyst supported on a commercial carbon black. Pt-carbon xerogel catalysts displayed good intrinsic catalyst activity due to the higher size of Pt particles in these catalysts and besides, the cell performance normalized by Pt loading was slightly higher when Pt particles were supported on resorcinol-formaldehyde carbon xerogels. Job et al. (Job et al., 2008) also prepared Pt-carbon xerogel catalysts for fuel cell applications. The catalysts were synthesized following two different recipes: (i) impregnation of carbon xerogel with Pt precursor solution followed by reduction process and (ii) strong electrostatic adsorption

(SEA method). This latter method produced higher dispersion of Pt particles than the impregnation and consequent reduction, improving the performance of fuel cells in terms of Pt mass activity. Moreover, there are research groups that used bimetallic catalysts for energy production in fuel cells. For example, Figueiredo and co-workers (Figueiredo et al., 2006) evaluated the electrochemical performance of direct-methanol fuel cells (DMFCs) assembled with Pt-Ru catalyst supported on oxidized carbon xerogels and the results reported in that study demonstrated that resorcinol-formaldehyde carbon xerogels were effective as supports for Pt/Ru particles. Pt-Ru bimetallic catalysts were also prepared by Arbizzani and et al (Arbizzani et al., 2007) for their use as anodes in DMFCs. In that case, the carbon supports were mesoporous cryo and xerogel carbons and Pt-Ru catalysts were obtained by impregnation of carbon materials with H_2PtCl_6 and RuCl_3 in ethylene glycol and later chemical reduction. The activity of the catalysts were related with structural and morphological properties of carbonaceous supports and electrochemical results of fuel cells were also compared to those obtained with a Pt-Ru supported on a commercial carbon support, showing again the good behaviour of carbon gels as support catalysts.

Other chemical processes and/or reactions catalyzed by carbon gels are for example, oxidation of several organic compounds with the aim of reducing pollution in liquids effluents (Girgis et al., 2011; Maldonado-Hódar et al., 2004), toluene combustion reactions (Gomes et al., 2008; Maldonado-Hódar et al., 2007), growth of carbon nanofilaments and nanotubes (Fu et al., 2003), conversion of D-glucose into D-gluconic acid (Pirard et al., 2011), and a long list since this type of catalysts has infinite number of applications in many different research fields.

4.2 Electric energy storage

A large number of publications can be found in the literature about carbon gels as electrode materials in supercapacitors as a result of being highly porous materials with a good electric conductivity (Kim et al., 2001).

In electrochemical double layer capacitors, EDLC's, the main mechanism that governs charge storage processes is the formation of the electric double layer in the electrode/electrolyte interface (Frackowiak, 2007; Kötzt & Carlen, 2000). Theoretically, as specific surface area increases, higher energy storage capacitance is achieved, but actually the situation changes because the whole surface area of the electrode material is not electrochemically accessible, and therefore useful, when electrodes are immersed in the electrolyte. Many studies about carbon gels and supercapacitors have concluded that charge storage is performed in micropores whereas mesopores with a specific size are needed for a fast diffusion of electrolyte ions (Frackowiak & Béguin, 2001; Salitra et al., 2000; Vix-Guterl et al., 2005). Electrochemical studies on carbon gels with a mesopores size between 3-13 nm have resulted in very high specific capacitance values and also, in a stable capacitive performance of the supercapacitor (Escribano et al., 1998). Therefore, it has been generally accepted that a balanced porosity between micro and mesopores is preferable to reach the optimum performance of the supercapacitor. Carbon gels are very promising materials for this application since besides their high microporosity, mesopores with a specific and tailored size can be obtained varying the synthesis conditions, absent feature in the case of activated carbons. Moreover, carbon gels display other advantages when they are used as electrodes in supercapacitors such as their high conductivity, enabling the removal of the usual additive to promote this property employed with active carbons, possibility of obtaining them in several morphologies directly without the need

of binders, i.e. it would be feasible to prepare carbon gel films in order to directly use as electrodes, and high cycling-life (Pandolfo & Hollenkamp, 2006). It has been found specific capacitance values of carbon gels in aqueous electrolyte between about 100 F g⁻¹, in the case of an untreated carbon gel and 300 F g⁻¹, data corresponding to carbon gels textural and chemically modified by means of several post-synthesis treatments. Some specific capacitance values found in the literature for untreated carbon gels are for example from 153 to 194 F g⁻¹ in the case of several resorcinol-formaldehyde carbon xerogels with specific surface areas between 700-800 m² g⁻¹ (Zhang et al., 2007); 150 F g⁻¹ when the electrochemical performance were carried out using a basic aqueous media as electrolyte and RF carbon xerogel dried by microwave heating after a previous solvent exchange with acetone (Halama et al., 2010), or finally, 120 F g⁻¹ for a RF carbon xerogel with a S_{BET} of 594 m² g⁻¹ obtained by microwave-assisted synthesis (Calvo et al., 2011a). It should be noted that despite the lower energy storage capacitance shown in the case of this late carbon xerogel, it is a very promising material because it has been synthesized by microwave heating in few hours compared to several days needed in the other examples cited. Higher capacitance values are reported when activated carbon gels are used as electrode materials in supercapacitors. Zhu and co-workers (Zhu et al., 2007) and Wang et al. (Wang et al., 2008) performed the synthesis of activated carbon gels with KOH and studied their electrochemical performance as electrode materials in supercapacitors with basic aqueous electrolyte, and results reported by both research groups were 244 F g⁻¹ (Wang et al., 2008) and 284 F g⁻¹ (Zhu et al., 2007), comparable values to those shown by other carbonaceous materials commonly used as electrodes in supercapacitors (Kierzek et al., 2004; Lota et al., 2008; Shi, 1996).

The energy storage mechanism based on charges separation in the electrode/electrolyte interface is not the only mechanism that can carry out in supercapacitors. In fact, there is another type of energy storage, induced by faradaic reactions occurring in electrodes surface, which considerably enhances the capacitance of supercapacitors (Frackowiak & Béguin, 2001). These redox reactions promote so-called pseudocapacitance effects and they are caused due to the presence of heteroatoms in the surface of the carbon electrodes. Some of the heteroatoms which contribute to the energy storage by means of pseudocapacitive effects are, for example, O, N, P, B, some metals, etc. (Frackowiak, 2007; Kang et al., 2008; Tian et al., 2010). Moreover, together with the increase of energy capacitance, surface groups improve the wettability of electrodes in aqueous media, due to electrostatic interactions on the electrode surface with dipole moments of water molecules. There are many examples in the literature about the use of doped carbon gels as electrode materials for supercapacitors. In the case of nitrogen-doped carbon gels, the work presented by Kang and co-workers, mentioned in Section 2 (Kang et al., 2008), reported the preparation of nitrogen enriched carbon xerogels by means of ammonisation processes. In this study, three different carbon xerogels were compared both textural and electrochemically: RF carbon xerogel conventionally synthesized, RF carbon xerogel conventionally synthesized and carbonised under NH₃ atmosphere and, finally, a RF carbon xerogel prepared by microwave-assisted synthesis and carbonised with NH₃. The two samples subjected to NH₃-carbonization display similar nitrogen contents (between 2.6 and 3.2 wt. %), while the porous texture is noticeable different. Microwave assisted sample has around 1700 m² g⁻¹ of specific surface area opposite to 1080 m² g⁻¹ for its counterpart synthesized by conventional heating and also, the latter carbon xerogel has lower mesopore volume. This different porosity affects the electrochemical performance

of samples since conventional sample display a specific capacitance of 148 F g^{-1} vs. 185 F g^{-1} in the case of sample with larger porosity development. When these two carbon xerogels were compared to the sample pyrolysed under N_2 atmosphere, it was clearly demonstrated the profitable effects of nitrogen doping since although this last sample has a specific surface area close to $800 \text{ m}^2 \text{ g}^{-1}$, its energy storage capacitance is very poor as a result of the absence of nitrogen functionalities, i.e. the lack of reversible electrochemical reactions that increase the capacitance due to pseudo-faradaic processes. Other work that shows the improvement of energy storage due to the presence of heteroatoms was performed by Sepheri et al. (Sepheri et al., 2009). In that case, the functionalization was carried out during the synthesis process of organic gels since, once organic gels are synthesized but still wet, they were introduced in ammonia borane/trifluoroacetic acid solution in order to incorporate B and N atoms into the structure of resulting materials. This treatment promotes the presence of functional groups and besides, the increase of mesoporosity since the carbon gel mixed with AB solution possesses a mesopore volume of $1.57 \text{ cm}^3 \text{ g}^{-1}$ opposite to $1.17 \text{ cm}^3 \text{ g}^{-1}$ in the case of untreated carbon xerogel. Results about the chemical nature of these samples, show that the ammonia borane treatment allows the incorporation of borane and oxygen functionalities (2.2 and 11.4 wt. % of boron and oxygen for treated carbon xerogel vs. 0.0 and 3.8 wt. %, respectively, in the case of untreated sample) while nitrogen groups disappear during the carbonization step. The enrichment of surface chemistry together with the enhanced porous texture causes an increase of ca. 30 % in the specific capacitance values and also an improvement in the current density of supercapacitors.

Qin and other researchers (Qin et al., 2011), also reflect the improvement of capacitive performance of supercapacitors by means of nitrogen functionalization of electrodes. Unlike the other two mentioned examples, the electrochemical devices assembled were asymmetric supercapacitors, where $\text{Ni(OH)}_2/\text{Co(OH)}_2$ composite works as anode and an activated carbon gel/melamine resin composite as cathode material, strategy widely used in others research groups (Ganesh et al., 2006; Staiti & Lufrano, 2010). The followed recipe to perform the functionalization of materials was quite different respect to the other two published studies. On the one hand, resorcinol-formaldehyde carbon gel was synthesized and chemically activated with KOH and secondly, a melamine resin was prepared in order to use it as nitrogen source. Both samples were mixed in water with ultrasonic radiation and afterwards, the resulting material was pyrolysed and activated with KOH causing the activated nitrogen enriched carbon/carbon gel composite. Results show that activated organic gel has a specific surface area of $1670 \text{ m}^2 \text{ g}^{-1}$ opposite to $1848 \text{ m}^2 \text{ g}^{-1}$ for the nitrogen enriched composite, demonstrating that, as in previous cases (Kang et al., 2008; Sepheri et al., 2009), treated carbon gels display high porosity development. The composite also has an important amount of heteroatoms since XPS measurements show 2.1 and 13.3 % of nitrogen and oxygen content, for such sample. Electrochemical results reported in this work corroborate the higher energy storage as a result of redox reactions in the electrode surface since specific capacitance values were 103 F g^{-1} in the case of using the activated carbon gel as cathode material and 224 F g^{-1} when the supercapacitor was assembled with the nitrogen enriched composite. The difference in specific surface area between two samples was only 11 % while the electrochemical performance was enhanced about 50 %, indicating that the presence of pseudocapacitive interactions allow the global capacitance of supercapacitor to be increased.

As reflected in Section 2 of this chapter, there are lots of research groups working on doping processes of carbon gels with metal species in order to prepare higher porous and

conductive materials. Therefore, one of the final applications of these metal-doped carbon gels is as energy storage systems. One of the more recent works dealing with doping processes of carbon gels for their use in supercapacitors was published by Lee and co-workers (Lee et al., 2011). The doping method was performed either by impregnation of manganese oxide on carbon gel power or by impregnation onto monolith material and the resulting carbon gels was electrochemically characterized. The best specific capacitance values were found in the case of impregnation of power form (i.e. 135 F g^{-1} for Mn-doped carbon aerogel obtained by impregnation onto power form opposite to 108 F g^{-1} in the best case when the impregnation was carried out with the monolithic material).

4.3 Hydrogen storage

As a result of the scarcity of fossil hydrocarbon resources, hydrogen is becoming a promising substitute for these fossil fuels in mobile applications. In addition to achieve the independence of fossil fuels, the use of hydrogen represents an environmentally friendly technology since allows the production of zero emission vehicles. However, the main requisite to a successful implementation is to store and transport the hydrogen in a safe and easy way (Dillon & Heben, 2001; Schimmel et al., 2004; Zubizarreta et al., 2009). Many researches have showed great attention to solve this hydrogen storage problem by means of several methodologies: high pressure, low temperature, metal or complex hydrides and porous materials, being the latter one of the most attractive solutions. High specific surface areas with narrow micropore size distributions are required for high-efficiency physical adsorption of hydrogen. As already mentioned, the possibility to tailor the micro-mesoporosity of carbon gels besides their surface chemistry makes them suitable materials for hydrogen storage devices (Kabbour et al., 2006; Tian et al., 2010, 2011, Zubizarreta et al., 2010).

There are a large number of published works about carbon gels and hydrogen storage that try to determine the interaction mechanism between H_2 and carbonaceous support and the relationship between adsorption capacities and textural and morphological properties of sorbent material. Regarding to the texture of nanoporous carbon materials, most of the studies conclude that there is a linear relationship between hydrogen storage capacity and surface area and micropore volume, but these are not the only influencing factors, since micropore diameter plays a key role in the final storage capacity. In other words, for hydrogen storage application is so important a high micropore volume as well as a narrow micropore size distribution (De la Casa-Lillo et al., 2002; Gadiou et al., 2005; Jordá-Beneyto et al., 2008). According to several published works (Gadiou et al., 2005; Jordá-Beneyto et al., 2008), micropores with a pore size of approximately 0.7-0.9 nm promotes higher hydrogen sorption capacities. In contrast, regarding to smaller mesopores, there is not a clear relationship between mesopore diameter and process of hydrogen storage. Zubizarreta et al. (Zubizarreta et al., 2009) have published a study based on the hydrogen sorption capacity of several carbon materials, including three resorcinol-formaldehyde carbon xerogels with different porous texture and morphology. In most samples, it has been found that in H_2 adsorption experiments performed at 77 K, the gravimetric storage capacity increases with the narrow micropore volume, analogous results to those reported in the literature about hydrogen storage on other kind of materials such as activated carbon (Akasaka et al., 2011; Cabria et al., 2007; Gadiou et al., 2007; Jordá-Beneyto et al., 2008; Xua et al., 2007) or metal organic frameworks, MOFs (Hirscher & Panella, 2007; Thomas, 2007), for example.

Fig. 13. Gravimetric and volumetric storage capacity of several hydrogen storage systems

For an optimum hydrogen storage capacity in solid materials, besides a well developed porous texture, there is another important feature to take into account, which is their surface chemistry. Experimental results about hydrogen storage on porous materials show that at low temperature, the dominant mechanism in the hydrogen storage process is based on microporous adsorption. However, as the temperature increases or the pressure decreases, chemical structure begins to have noticeable relevance in the mechanism of H₂ adsorption. Therefore, with the aim of changing the hydrogen/carbon interaction and therefore, enhancing the hydrogen storage capacity at room temperature or low pressure, several researches have used doped carbon materials. Some of the heteroatoms used to modify the surface properties and to achieve an enhanced hydrogen adsorption are N, B, Ni, Co, etc. (Kabbour et al., 2006; Tian et al., 2010; Zubizarreta et al., 2010). As already reflected in Section 2, carbon gels can undergo different doping processes, which is a great interest to solve the limitation of poor hydrogen uptake at room temperature. It can be found a remarkable number of studies related to hydrogen storage on doped carbon gels. However, it should be noted that, as a result of the large number of variables involved in the storage process (i.e. temperature and pressure of hydrogen storage, porous texture of carbon gels, amount and particle size of the heteroatom incorporated into the structure of carbon materials, etc.) it is very difficult to find several publications agreeing with the values of hydrogen storage capacity. For example, Kabbour et al (Kabbour et al., 2006) have published in 2006 a study about Co and Ni-doped carbon gels for hydrogen storage. The gravimetric hydrogen storage values reported were 2.1 and 2.3 wt.% for Co and Ni-doped carbon gels, respectively, when the hydrogen sorption experiments were performed at 77 K and low pressure (pressure between 0 and 2.5 bar). Other work about Co-doped carbon gels for H₂ storage shows a value of hydrogen storage capacity of 4.38 wt.% under lower temperature and high pressure conditions (Tian et al., 2010), but it should be said that the carbon gels used as adsorbent material in both works displays very different textural properties (i.e. $S_{\text{BET}} = 1667 \text{ m}^2 \text{ g}^{-1}$ in 157 versus ca $1000 \text{ m}^2 \text{ g}^{-1}$ in 156), which could explain the notable difference in hydrogen storage capacities. Zubizarreta et al. (Zubizarreta et al., 2010) also investigated the performance of Ni-doped carbon gels in hydrogen storage systems and reported one of the higher values of gravimetric hydrogen storage capacity for this type of

carbonaceous materials. The best Ni-doped carbon xerogel synthesized in that work, whose specific surface area is $1727 \text{ m}^2 \text{ g}^{-1}$ with a Ni content of 2.7 wt.%, exhibits a value of hydrogen storage capacity of 6 wt.% at 77 K and 40 bar. It is very complicate to compare all these results with those found with other doped carbonaceous materials used in hydrogen storage applications (i.e. activated carbons (Akasaka et al., 2011; De la Casa-Lillo et al., 2002; Takagi et al., 2004), nanotubes (Gao et al., 2010; Lamari et al., 2002; Schimmel et al., 2004; Surya et al., 2009) or nanofibers (De la Casa-Lillo et al., 2002; Kim et al., 2008)). The hydrogen storage capacity of Ni-doped carbon gels compared with other hydrogen storage systems is collected in Figure 13. Regarding to the gravimetric storage capacity, the Ni-doped xerogel shows analogous and even higher values to other materials reported in the figure when the experiments were carried out at -196°C and 40 bar but, as reflected at the beginning of this paragraph, the increase of the temperature produces an important decrease of the hydrogen storage capacity, thus the Ni-doped carbon xerogel at 25°C is far from that the DOE had proposed for the year 2010.

4.4 Other applications

As already reflected in this chapter, the sol-gel reaction allows textural and chemical properties to be tailored but, in addition, it is possible to control other important characteristic of these carbonaceous materials, such as their morphology. As pointed out in Section 1, carbon gels can be synthesized with several shapes: monolith, films, powder, spheres, etc. and morphology may be one of the key factors that could determine the good or bad performance of carbon gels in some specific applications. An example of the relevance of the morphology is the use of carbon xerogel spheres as columns filler for gas separation. A research group from INCAR-CSIC has recently prepared resorcinol-formaldehyde carbon spheres with different sphere size depending on the synthesis procedure followed and has studied their performance as material sieves for separation of N_2/CO_2 gas mixtures (some of their results reported in Figure 14). On the one hand, it can be seen pictures with carbon spheres of different size and on the other hand, N_2 and CO_2 monitoring curves that show that CO_2 can be separated as a result of the porosity and basicity of the carbon xerogel spheres.

Fig. 14. Carbon xerogel spheres and their potential as fillers for gas separation systems.

In the literature, there is some example about carbon gels designed for gas separation applications. In fact, Zheivot et al. (Zheivot et al., 2010) published in 2010 a study about the production of several phenol-formaldehyde carbon xerogels and their use as adsorption materials in gas chromatography. Results reported showed that microporous carbon xerogels can be prepared varying the synthesis conditions and they can be successfully used as adsorbents to concentrate the impurities of light hydrocarbons and gaseous products of many catalytic reactions. Liquid phase adsorption can also be performed with carbon gels. In 2007, Sanchez-Polo and other researchers (Sánchez-Polo et al., 2007) analyzed the efficiency of Ag-doped carbon aerogels for the removal of several ions (Br^- and I^-) from drinking waters. The doping of resorcinol-formaldehyde aerogels was carried out by the addition of silver acetate as catalyst instead of the commonly used sodium carbonate. The study confirmed that the synthesis of mainly meso and macroporous carbon aerogels with an important amount of Ag particles could be carried out and the resulting materials displayed good adsorption capacities. The performance of carbon aerogels as adsorption materials was compared with the adsorption capacity of a commercial activated carbon that turned out to be lower. Other published work about carbon gels as liquid phase adsorbents was carried out by Girgis et al. (Girgis et al., 2011). In that study, the synthesis of carbon xerogels with difference porous texture was carried out and also the performance as adsorbent materials of two cationic dyes was evaluated. The main conclusion extracted from that publication is that carbon gels are good adsorbing materials in remediation processes since their adsorption capacities towards Methylene blue and Rhodamine B are comparable to conventional activated carbons. There is other recent work that includes the removal of several compounds from liquid effluents by using carbon gels as adsorbent materials (Figueiredo et al., 2011) but in this case, adsorption capacities collected are worse or similar than those shown by activated carbons, indicating that carbon xerogels do not seem to be an feasible option to remove colour from the effluents.

5. Conclusion

Carbon xerogels are nanostructured materials of a huge versatility since they can be synthesized with (i) different porous texture at micro-, meso- and macropore scale, (ii) different surface chemistry and (iii) different final shape. Moreover, all these properties can be tailored by adjusting the synthesis conditions, so it is possible, at least in theory, to obtain nanoporous carbon materials on-demand. However, the main problem to be solved in order to obtain a material with certain predetermined characteristics lies in the large number of variables that is necessary to control during their synthesis and to the fact that some of these variables are not independent. In consequence, one of the main drawbacks for the extensive use of these materials is to define the appropriate synthesis conditions and achieve them in a competitive way in terms of costs and operating time. Despite to the fact that great progress has been done in this sense -for example microwave induced synthesis has reduced the time of the carbon xerogels synthesis from days to hours with an important reduction in the costs of production- there is still need a step forward giving the opportunity to vast research field. Thus, it seems not risked to assure that as investigations on this matter reveals new information the great versatility of the carbon xerogels will make them important members of the family of the nanostructured materials with applications in numerous new, or existing, technologies ranging from electricity storage to drug delivery.

6. Acknowledgment

Authors would like to thanks the Spanish Ministerio de Ciencia e Innovación (Ref. MAT2008-00217/MAT) for the financial support. EGC also acknowledges FICYT for the research grand received.

7. References

- Akasaka, H.; Takahata, T.; Toda, I.; Ono, H.; Ohshio, S.; Himeno, S.; Kokubu, T.; Saitoh, H. (2011). Hydrogen storage ability of porous carbon materials fabricated from coffee bean wastes. *International Journal of Hydrogen Energy*, Vol. 36, (580-585).
- Al-Mutasheb, S.A.; Ritter, J.A. (2003). Preparation and Properties of Resorcinol-Formaldehyde Organic and Carbon gels. *Advanced Materials*, Vol. 15 (101-114).
- Álvarez-Merino, M.A.; Carrasco-Marín, F.; Moreno-Castilla, C. (2000). Tungsten catalysts supported on activated carbon: II. Skeletal isomerization of 1-butene. *Journal of Catalysis*, Vol. 192, (374-380).
- Arbizzani, C.F.; Beninati, S.; Manfredi, E.; Soavi, F.; Mastragostino M. (2007). Cryo and xerogel carbon supported PtFu for DMFC anodes. *Journal of Power Sources*, Vol. 172, (578-586).
- Baumann, T.F.; Fox, G.A.; Satcher, J.H.; Yoshizawa, R.; Fu, R.; Dresselhaus, M.S. (2002). Synthesis and characterization of copper-doped carbon aerogels. *Langmuir*, Vol. 18, (7073-7076).
- Bekyarova, E.; Kaneko, K. (2000). Structure and Physical Properties of Tailor-Made Ce,Zr-Doped Carbon Aerogels. *Advanced Materials*, Vol. 12, (1625-1628).
- Berthon, S.; Barbieri, O.; Ehrburger-Dolle, F.; Geissier, E.; Achard, P.; Bley, F.; Hecht, A.-M.; Livet, F.; Pajonk, G.M.; Pinto, N.; Rigacci, A.; Rochas, C. (2001). DLS and SAXS investigations of organic gels and aerogels. *Journal of Non-Crystalline Solids*, Vol. 285, (154-161).
- Burdinova, T.; Ekinici, E.; Yardim, F.; Grimm, A.; Björnbom, E.; Minkova, V.; Goranova, M. (2006). Characterization and application of activated carbon produced by H₃PO₄ and water vapour activation. *Fuel Processing Technology*, Vol. 87, (899-905).
- Cabria, I.; López, M.J.; Alonso, J.A. (2007). The optimum average nanopore size for hydrogen storage in carbon nanoporous materials. *Carbon*, Vol. 45, (2649-2658).
- Caddick, S. (1995). Microwave Assisted Organic Reactions. *Tetrahedron*, Vol. 51, (10403-10432).
- Calvo, E.G.; Ania, C.O.; Zubizarreta, L.; Menéndez, J.A.; Arenillas, A. (2008). Exploring new routes in the synthesis of carbon xerogels for their applications in electric double-layer capacitors. *Energy & Fuels*, Vol. 24 (3334-3339).
- Calvo, E.G.; Juárez-Pérez, E.J.; Menéndez, J.A.; Arenillas, A. (2011a). Fast microwave-assisted synthesis of tailored mesoporous carbon xerogels. *Journal of Colloid and Interface Science*, Vol. 357 (541-547).
- Calvo, E.G.; Ferrera-Lorenzo, N.; Arenillas, A.; Menéndez, J.A. (2011b). Mesopores role in electrochemical performance of activated organic xerogels obtained by microwave radiation. *III Symposium on Hydrogen, Fuel Cells and Advanced Batteries, Hyceltec*, Abstract Book, p. 465, PO-15 (Zaragoza) 2011, ISBN: 978-84-938668-8-4.
- Carrot, P.J.M.; Conceição, F.L.; Carrot, M.M.L.R. (2007). Use of n-nonane pre-adsorption for the determination of micropore volume of activated carbon aerogels. *Carbon*, Vol. 45, (1310-1313).

- Chaijitrakool, T.; Tonamon, N.; Tanthapanichakoon, W.; Tamon, H.; Prichanont, S. (2008). Effects of pore characters of mesoporous resorcinol-formaldehyde carbon gels on enzyme immobilization. *Journal of Molecular Catalysis B: Enzymatic*, Vol. 55, (137-141).
- Chandra, S.; Bag, S.; Bhar, R.; Pramanik, P. (2011). Effect of transition and non-transition metals during the synthesis of carbon xerogels. *Microporous and Mesoporous Materials*, Vol. 138, (149-156).
- Choplin, A.; Quignard, F. (1998). From supported homogeneous catalysts to heterogeneous molecular catalysts. *Coordination Chemistry Reviews*, Vol. 17, (1679-1702).
- Conceição, F.L.; Carrot, P.J.M.; Ribeiro-Carrot, M.M.L. (2009). New carbon materials with high porosity in the 1-7 nm range obtained by chemical activation with phosphoric acid of resorcinol-formaldehyde aerogels. *Carbon*, Vol. 47, (1874-1877).
- Contreras, M.S.; Paez, C.A.; Zubizarreta, L.; Leonard, A.; Blacher, S.; Olivera-Fuentes, C.G.; Arenillas, A.; Pirard, J.-P.; Job, N. (2010). A comparison of physical activation of carbon xerogels with carbon dioxide with chemical activation using hydroxides. *Carbon*, Vol. 48, (3157-3168).
- Cotet, L.C.; Gich, M.; Roig, A.; Popescu, I.C.; Cosoveanu, V.; Molins, E.; Danciu, V. (2006). Synthesis and structural characteristics of carbon aerogels with a high content of Fe, Co, Ni, Cu and Pd. *Journal of Non-Crystalline Solids*, Vol. 352, (2772-2777).
- Czzakel, O.; Marthi, K.; Gueissler, K.; Laszlo, K. (2005). Influence of drying on the morphology of resorcinol-formaldehyde based carbon gels. *Microporous and Mesoporous Materials*, Vol. 86, (124-133).
- De la Casa-Lillo, M.A.; Lamari-Darkrim, F.; Cazorla-Amorós D.; Linares-Solano, A. (2002). Hydrogen storage in activated carbons and activated carbon fibers. *Journal of Physical Chemistry*, Vol. 106, (10930-10934).
- De Sousa, E.M.B.; Guimares, A.P.; Mohallem, N.D.S.; Lago, R.M. (2001). The effect of thermal treatment on the properties of sol-gel copper silica catalysts. *Applied Surface Science*, Vol. 183, (216-222).
- Dillon, A.C.; Heben, M.J. (2001). Hydrogen storage using carbon adsorbents: past, present and future. *Applied Physics A: Material Science Progress*, Vol. 72, (133-142).
- Dingcai, W.; Ruowen, F. (2006). Synthesis of organic and carbon aerogels from phenol-furfural by two-step polymerization. *Microporous and Mesoporous Materials*, Vol. 96, (115-120).
- Djakovitch, L.; Wagner, M.; Hartung, C.G.; Beller, M.; Koehler K. (2004). Pd-catalyzed Heck arylation of cycloalkenes: Studies on selectivity comparing homogeneous and heterogeneous catalysts. *Journal of Molecular Catalysis A: Chemical*, Vol. 219, (121-130).
- Escribano, S.; Berthon, S.; Ginoux, J.L.; Achard, P. (1998). Characterization of carbon aerogels. In: *Extended Abstract, Eurocarbon*, Strasbourg, France (841-842).
- Fairén-Jiménez, D.; Carrasco-Marín, F.; Moreno-Castilla, C. (2006). Porosity and surface area of monolithic carbon aerogels prepared using alkaline carbonates and organic acids as polymerization catalysts. *Carbon*, Vol. 44, (2301-2307).
- Fang, B.; Binder, L. (2006). A modified activated carbon aerogel for high-energy storage in electric double layer capacitors. *Journal of Power Sources*, Vol. 163 (616-622).
- Feaver, A.; Cao, G. (2006). Activated carbon cryogels for low pressure methane storage. *Carbon*, Vol. 44, (590-593).

- Figueiredo, J.L.; Pereira, M.F.R.; Serp, P.; Kalck, P.; Samant, P.V.; Fernandes, J.B. (2006). Development of carbon nanotube and carbon xerogels supported catalysts for the electro-oxidation of methanol in fuel cells. *Carbon*, Vol. 44, (2516-2522).
- Figueiredo, J.L.; Sousa, J.P.S.; Orge, C.A.; Pereira, M.F.R.; Orfão, J.J.M. (2011). Adsorption of dyes on carbon xerogels and templated carbons: influence of surface chemistry. *Adsorption*, Vol. 17, (431-441).
- Fontecha-Cámara, M.A.; Álvarez-Reinoso, M.A.; Carrasco-Marín, F.; López-Ramón, M.V.; Moreno-Castilla, C. (2011). Heterogeneous and homogeneous Fenton processes using activated carbon for the removal of the herbicide amitrole from water. *Applied Catalysis B: Environmental*, Vol. 101, (425-430).
- Frackowiak, E. (2007). Carbon materials for supercapacitor applications. *Physical Chemistry Chemical Physics*, Vol. 9 (1774-1785).
- Frackowiak, E.; Béguin, F. (2001). Carbon materials for the electrochemical storage of energy capacitors. *Carbon*, Vol. 39, (937-950).
- Fu, R.; Baumann, T.F.; Cronin, S.; Dresselhaus, G. (2005). Formation of Graphitic Structures in Cobalt- and Nickel-Doped Carbon Aerogels. *Langmuir*, Vol. 21, (2647-2651).
- Fu, R.; Dresselhaus, M.S.; Dresselhaus, G.; Zheng, B.; Liu, J.; Satcher, J.H.; Theodore, F.B. (2003). The growth of carbon nanostructures on cobalt-doped carbon aerogels. *Journal of Non-Crystalline Solids*, Vol. 318, (223-232).
- Fuentes, E.; Menéndez, J.A.; Suárez, D.; Montes-Morán, M.A. (1995). Basic surface oxides on carbon materials: A global view. *Langmuir*, Vol. 19, (3505-3511).
- Gadiour, R.; Texier-Mandoki, N.; Piquero, T.; Saadallah, S.; Parmentier, J.; Patarin, J. (2005). The influence of microporosity on the hydrogen storage capacity of ordered mesoporous carbons. *Adsorption*, Vol. 11, (823-827).
- Ganesh, V.; Pitchumani, S.; Lakshminarayanan, V. (2006). New symmetric and asymmetric supercapacitors based on high surface area porous nickel activated carbons. *Journal of Power Sources*, Vol. 158, (1523-1532).
- Gao, L.; Yoo, E.; Nakamura, J.; Zhang, W.; Chua, H.T. (2010). Hydrogen storage in Pd-Ni doped defective carbon nanotubes through the formation of CH_x ($x = 1, 2$). *Carbon*, Vol. 48, (3250-3255).
- Girgis, B.S.; Attia, A.A.; Fatthy, N.A. (2011). Potential of nano-carbon xerogels in the remediation of dye-contaminated water discharges. *Desalination*, Vol. 265, (169-176).
- Gomes, H.T.; Machado, B.F.; Ribeiro, A.; Moreira, I.; Rosario, M.; Silva, A.M.T.; Figueiredo, J.L.; Faris, J.L. (2008). Catalytic properties of carbon materials for wet oxidations of aniline. *Journal of Hazardous Materials*, Vol. 159, (420-426).
- Gorgulho, H.F.; Gonçalves, F.; Pereira, M.F.R.; Figueiredo, J.L. (2009). Synthesis and characterization of nitrogen-doped carbon xerogels. *Carbon*, Vol. 47, (2032-2039).
- Gryzb, B.; Hildenbrand, C.; Berthon-Frabry, S.; Béguin, D.; Job, N.; Rigacci, A.; Achard, P. (2010). Functionalisation and chemical characterization of cellulose-derived carbon aerogels. *Carbon*, Vol. 48, (2297-2307).
- Guo, S.; Peng, J.; Li, W.; Yang, K.; Zhang, L.; Zhang, S.; Xia, H. (2009). Effects of CO_2 activation on porous texture structures of coconut shell-based activated carbons. *Applied Surface Science*, Vol. 255, (8443-8449).
- Halama, A.; Szubzda, B.; Pasciak, G. (2010). Carbon aerogels as electrode material for electric double layer supercapacitors: Synthesis and properties. *Electrochimica Acta*, Vol. 55, (7501-7505).
- Hirscher, M.; Panella, B. (2007). Hydrogen storage in metal-organic frameworks. *Scripta Materialia*, Vol. 56, (809-812).

- Houmar, M.; Vasconcelos, D.C.L.; Vasconcelos, W.L.; Berthomé, G.; Joud, J.C.; Langlet, M. (2009). Water and oil wettability of hybrid organic-inorganic titanate-silicate thin films deposited via sol-gel route. *Surface Science*, Vol. 603, (2698-2707).
- Husley, S.S.; Alviso, C.T.; Kong, F.M.; Pekala, R.W. (1992). The effect of Pyrolysis Temperature and Formulation on Pore Size Distribution and Surface Area of Carbon Aerogels. In: *Peprint of Lawrence Livermore National Laboratory*, 1992.
- Jagtoyen, M.; Groppo, J.; Derbyshire, F. (1993). Activated carbon from bituminous coals by reaction with H_3PO_4 : The influence of coal cleaning. *Fuel Processing Technology*, Vol. 34, (85-93).
- Job, N.; Pirard, R.; Marien, J.; Pirard, J.-P. (2004). Porous carbon xerogels with texture tailored by pH control during sol-gel process. *Carbon*, Vol. 42, (619-628).
- Job, N.; Marie, J.; Lambert, S.; Berthon-Fabry, S.; Achard, P. (2008). Carbon xerogels as catalyst supports for PEM fuel cell cathode. *Energy Conversion and Management*, Vol. 49, (2461-2470).
- Job, N.; Panariello, F.; Marien, J.; Crine, M.; Pirard, J.P.; Leonard, A. (2006). Synthesis optimization of organic xerogels produced from convective air-drying of resorcinol-formaldehyde gels. *Journal of Non-Crystalline Solids*, Vol. 352, (24-34).
- Job, N.; Panariello, R.; Crine, M.; Pirard, J.-P.; Leonard, A. (2007a). Rheological determination of the sol-gel transition during the aqueous synthesis of resorcinol-formaldehyde resins. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 293, (224-228).
- Job, N.; Pirard, R.; Vertruyen, B.; Colomer, J.-F.; Marien, J.; Pirard, J.-P. (2007b). Synthesis of transition metal-doped carbon xerogels by cogelation. *Journal of Non-Crystalline Solids*, Vol. 353, (2333-2345).
- Job, N.; Thery, A.; Pirard, R.; Marien, J.; Kocon, L.; Rouzaud, J.-N.; Beguin, F.; Pirard, J.-P. (2005). Carbon aerogels, cryogels and xerogels: Influence of the drying method on the textural properties of porous carbon materials. *Carbon*, Vol. 43, (2481-2494).
- Jordá-Beneyto, M.; Lozano-Castelló, D.; Suárez-García, F.; Cazorla-Amorós, D.; Linares-Solano, A. (2008). Advanced activated carbon monoliths and activated carbons for hydrogen storage. *Microporous and Mesoporous Materials*, Vol. 112, (235-242).
- Juárez-Pérez, E.J.; Calvo, E.G.; Arenillas, A.; Menéndez, J.A. (2010). Precise determination of the point of sol-gel transition in carbon gels synthesis using a microwave heating method. *Carbon*, Vol. 48, (3305-3308).
- Kabbour, H.; Baumann, T.F.; Satcher, J.H.; Saulnier, J.A.; Ahn, C.C. (2006). Toward new candidates for hydrogen storage: High-Surface-Area Carbon Aerogels. *Chemistry of Materials*, Vol. 18, (6085-6087).
- Kang, K.-Y.; Lee, B.I.; Lee, J.S. (2009). Hydrogen adsorption on nitrogen-doped carbon xerogels. *Carbon*, Vol. 47, (1171-1180).
- Kappe, C.O. (2004). Microwave Heating in Modern Organic Synthesis. *Angewandte Chemie International Edition*, Vol. 43, (6250-6284).
- Kierzek, K.; Frackowiak, E.; Lota, G.; Gryglewick, G.; Machnikowski, J. (2004). Electrochemical capacitors based on highly porous carbons prepared by KOH activation. *Electrochimica Acta*, Vol. 49, (515-523).
- Kim, B.-J.; Lee, Y.-S.; Park, S.-J. (2008). A study on the hydrogen storage capacity of Ni-plated porous carbon nanofibers. *International Journal of Hydrogen Energy*, Vol. 33, (4112-4115).

- Kim, S.Y.; Yeo, D.H.; Lim, J.W.; Yoo, K.; Lee, K.; Kim, H. (2001). Synthesis and Characterization of Resorcinol-Formaldehyde Organic Aergoel. *Journal of Chemical Engineering of Japan*, Vol. 34, (216-220).
- Kocklenberg, R.; Mathieu, B.; Blacher, S.; Pirard, R.; Pirard, J.-P.; Sobry, R.; Van den Bossche, G. (1998). Texture control of freeze-dried resorcinol-formaldehyde gels. *Journal of Non-Crystalline Solids*, Vol. 225, (8-13).
- Kötz, R.; Carlen, M. (2000). Principles and applications of electrochemical capacitors. *Electrochimica Acta*, Vol. 45, (2483-2498).
- Krai wattanawong, K.; Tamon, H.; Praserttham, P. (2011). Influence of solvent species used in solvent exchange for preparation of mesoporous carbon xerogels from resorcinol-formaldehyde via subcritical drying. *Microporous and Mesoporous Materials*, Vol. 138, (8-16).
- Kuo, H.H.; Lin, J.H.C.; Pu, C.P. (2005). Effect of carbonization rate on the properties of a PAN/phenolic-based carbon/carbon composite. *Carbon*, Vol. 43, (229-239).
- Lamari, F.L.; Malbrunot, P.; Tartaglia, G.P. (2002). Review of hydrogen storage by adsorption in carbon nanotubes. *International Journal of Hydrogen Energy*, Vol. 27, (193-202).
- Lambert, S.; Job, N.; D'Souza, L.; Pereira, M.F.R.; Pirard, R.; Heinrichs, B.; Figueiredo, J.L.; Pirard, J.-P.; Regalbuto, J.R. (2009). Synthesis of very highly dispersed platinum catalysis supported on carbon xerogels by the strong electrostatic adsorption method. *Journal of Catalysis*, Vol. 261, (23-33).
- Lee, Y.J.; Chung, J.C.; Yi, J.; Baeck, S.-H.; Yoon, J.R.; Song, I.K. (2010). Preparation of carbon aerogels in ambient conditions for electric double-layer capacitor. *Current Applied Physics*, Vol. 10, (682-686).
- Lee, Y.J.; Jung, J.C.; Park, S.; Seo, J.G.; Baeck, S.-H.; Yoon, J.R.; Yi, J.; Song, I.K. (2011). Effect of preparation method on electrochemical property of Mn-doped carbon aerogel for supercapacitor. *Current Applied Physics*, Vol. 11, (1-5).
- Leonard, A.; Job, N.; Blacher, S.; Pirard, J.-P.; Crine, M.; Jomaa, W. (2005). Suitability of convective air drying for the production of porous resorcinol-formaldehyde organic and carbon xerogels. *Carbon*, Vol. 43, (1808-1811).
- Li, W.-C.; Lu, A.-H.; Guo, S.-C. (2001). Characterization of the microstructures of organic and carbon aerogels based upon mixed cresol-formaldehyde. *Carbon*, Vol. 39, (1989-1994).
- Liang, C.; Sha, G.; Guo, S. (2000). Resorcinol-formaldehyde aerogels prepared by supercritical acetone drying. *Journal of Non-Crystalline Solids*, Vol. 271, (161-170).
- Lin, C.; Ritter, J.A. (1997). Effect of synthesis pH on the structure of carbon xerogels. *Carbon*, Vol. 35, (1271-1278).
- Lin, C.; Ritter, J.A. (2000). Carbonization and activation of sol-gel derived carbon xerogels. *Carbon*, Vol. 38, (849-861).
- Liou, T.-H. (2004). Evolution of chemistry and morphology during the carbonization and combustion of rice husk. *Carbon*, Vol. 42, (785-794).
- Liu, B.; Creager, S. (2010). Carbon xerogels as Pt catalyst supports for polymer electrolyte membrane fuel-cell applications. *Journal of Power Sources*, Vol. 195, (1812-1820).
- Liu, N.; Zhang, S.; Fu, R.; Dresselhaus, M.S.; Dresselhaus G. (2006). Carbon aerogel spheres prepared via alcohol supercritical drying. *Carbon*, Vol. 44, (2430-2436).
- Liu, Z.; Wang, A.; Wang, X.; Zhang, T. (2006). Reduction of NO by Cu-carbon and Co-carbon xerogels. *Carbon*, Vol. 44, (2330-2356).

- Long, D.; Qiao, W.; Zhang, L.; Liang, X. (2009). Bimolecular adsorption behaviour on spherical carbon aerogels with various mesopore size. *Journal of Colloid and Interface Science*, Vol. 331, (40-46).
- Long, D.; Zhang, J.; Yang, J.; Hu, Z.; Li, T.; Chen, G.; Zhang, R.; Ling, L. (2008a). Preparation and microstructure control of carbon aerogels produced using m-cresol mediated sol-gel polymerization of phenol and furfural. *New Carbon Materials*, Vol. 23, (165-170).
- Long, D.; Zhang, J.; Yang, J.; Hu, Z.; Cheng, G.; Liu, X.; Zhang, R.; Zhang, L.; Qiao, W.; Ling, L. (2008b). Chemical state of nitrogen carbon aerogels issued from phenol-melamine-formaldehyde gels. *Carbon*, Vol. 46, (1259-1262).
- Lota, G.; Centeno, T.A.; Frackowiak, E.; Stoeckli, F. (2008). Improvement of the structural and chemical properties of a commercial activated carbon for its application in electrochemical capacitors. *Electrochimica Acta*, Vol. 53, (2210-2216).
- Lozano-Castelló, D.; Cazorla-Amorós, D.; Linares-Solano, A. (2002). Can highly activated carbons be prepared with a homogeneous micropore size distribution?. *Fuel Processing Technology*, Vol. 77, (325-330).
- Machado, B.F.; Gomes, H.T.; Serp, P.; Kalck, P.; Figueiredo, J.L.; Faria, J.L. (2010). Carbon xerogel supported noble metal catalysts for fine chemical applications. *Catalysis Today*, Vol. 149, (358-364).
- Maciá-Agulló, J.A.; Moore, B.C.; Cazorla-Amorós, D.; Linares-Solano, A. (2007). Influence of carbon fibers crystallinities on their chemical activation by KOH and NaOH. *Microporous and Mesoporous Materials*, Vol. 101, (397-405).
- Mahata, N.; Pereira, M.F.R.; Suárez-García, F.; Martínez-Alonso, A.; Tascón, J.M.D.; Figueiredo, J.L. (2008). Tuning of texture and surface chemistry of carbon xerogels. *Journal of Colloid and Interface Science*, Vol. 324, (150-155).
- Maldonado-Hódar, F.J.; Moreno-Castilla, C.; Carrasco-Marín, F.; Pérez-Cadenas, A.F. (2007). Reversible toluene adsorption on monolithic carbon aerogels. *Journal of Hazardous Materials*, Vol. 148, (548-552).
- Maldonado-Hódar, F.J.; Moreno-Castilla, C.; Pérez-Cadenas, A.F. (2004). Catalytic combustion of toluene on platinum-containing monolithic carbon aerogels. *Applied Catalysis B: Environmental*, Vol. 54, (217-224).
- Maldonado-Hódar, F.J.; Pérez-Cadenas, A.F.; Moreno-Castilla, C. (2003). Morphology of heat-treated tungsten doped monolithic carbon aerogels. *Carbon*, Vol. 41, (1291-1299).
- Matos, I.; Fernandes, S.; Guerreiro, L.; Barata, S.; Ramos, A.M.; Vital, J.; Fonseca, I.M. (2006). The effect of surfactants on the porosity of carbon xerogels. *Microporous and Mesoporous Materials*, Vol. 92, (38-46).
- Mauritz, K.A. (1998). Organic-inorganic hybrid materials: perfluorinated ionomers as sol-gel polymerization templates for inorganic alkoxides. *Materials Science and Engineering: C*, Vol. 6, (121-133).
- Menéndez, J.A.; Arenillas, A.; Fidalgo, B.; Fernández, Y.; Zubizarreta, L.; Calvo, E.G.; Bermúdez, J.M. (2010). Microwave Heating processes involving carbon materials. *Fuel Processing Technology*, Vol. 91, (1-8).
- Molina-Sabio, M.; Rodríguez-Reinoso, F. (2004). Role of chemical activation in the development of carbon porosity. *Colloids and Surface A: Physicochemical Engineering Aspects*, Vol. 241, (15-25).

- Montes-Morán, M.A.; Menéndez, J.A.; Fuentes, E.; Suárez, D. (1998). Contribution of the Basal Planes to Carbon Basicity: An Ab Initio Study of the $H_3O^+-\pi$ Interaction in Cluster Models. *The Journal of Physical Chemistry B*, Vol. 102, (5595-5601).
- Moreno-Castilla, C.; Maldonado-Hódar, F.J. (2005). Carbon aerogels for catálisis applications: An overview. *Carbon*, Vol. 43, (455-465).
- Moreno-Castilla, C.; Rivera-Utrilla, F.J.; Rodríguez-Castellón, J. (1999). Group of 6 metal oxide-carbon aerogels. Their synthesis, characterization and catalytic activity in the skeletal isomerization of 1-butene. *Applied Catalysis*, Vol. 183, (345-356).
- Mukai, S.R.; Tamitsuji, C.; Nishihara, H.; Tamon, H. (2005a). Preparation of mesoporous carbon gels from an inexpensive combination of phenol and formaldehyde. *Carbon*, Vol. 43, (2628-2630).
- Mukai, S.R.; Nishimura, H.; Yoshida, T.; Taniguchi, K.; Tamon, H. (2005b). Morphology of resorcinol-formaldehyde gels obtained through ice-templating. *Carbon*, Vol. 43, (1563-1565).
- Nabais, J.N.V.; Nunes, P.; Carrot, P.J.M.; Carrot, M.M.L.R.; García, A.M.; Díaz-Díez, M.A. (2008). Production of activated carbons from coffee endocarp by CO_2 and steam activation. *Fuel Processing Technology*, Vol. 89, (262-268).
- Neppolian, B.; Wang, Q.; Jung, H.; Choi, H. (2008). Ultrasonic-assisted sol-gel method of preparation of TiO_2 nano-particles. Characterization, properties and 4-chlorophenol removal application. *Ultrasonics Sonochemistry*, Vol. 15, (649-658).
- Niu, J.J.; Wang, J.N. (2008). Effect of temperature on chemical activation of carbon nanotubes. *Solid Stated Sciences*, Vol. 10, (1189-1193).
- Okada, K.; Yamamoto, N.; Kameshima, Y.; Yasumori, A. (2003). Porous properties of activated carbons from waste newspaper prepared by chemical and physical activation. *Journal of Colloid and Interface Science*, Vol. 262, (179-193).
- Olivares-Martín, M.; Fernández-González, C.; Macías-García, A.; Gómez-Serrano, V. (2006). Preparation of activated carbon from cherry stones by chemical activation with $ZnCl_2$. *Applied Surface Science*, Vol. 252, (5967-5971).
- Pandolfo, A.G.; Hollenkamp, A.F. (2006). Carbon properties and their role in supercapacitors. *Journal of Power Sources*, Vol. 157, (11-27).
- Pekala, R.W. (1989). Organic aerogels from the polycondensation of resorcinol with formaldehyde. *Journal of Materials Science*, Vol. 24, (3221-3227).
- Pekala, R.W.; Alviso, C.T. (1992). Carbon aerogels and xerogels. *Materials Research Society Symposium Proceedings*, Vol. 270, (3-14).
- Pekala, R.W.; Alviso, C.T.; Lu, X.; Gross, J.; Fricke, J. (1995). New organic aerogels based upon a phenolic-furfural reaction. *Journal of Non-Crystalline Solids*, Vol. 188, (34-40).
- Pérez-Cadenas, M.; Moreno-Castilla, C.; Carrasco-Marin, F.; Pérez-Cadenas, A.F. (2009). Surface chemistry, porous texture and morphology of N-doped carbon xerogels. *Langmuir*, Vol. 25, (466-470).
- Petricovic, R.; Glora, M.; Fricke, J. (2001). Planar fiber reinforced carbon aerogels for application in PEM fuel cells. *Carbon*, Vol. 39, (857-867).
- Pirard, S.L.; Diverchy, C.; Hermans, S.; Devillers, M.; Pirard, J.-P.; Job, N. (2011). Kinetics and diffusional limitations in nanostructured heterogeneous catalyst with controlled pore texture. *Catalysis Communications*, Vol. 12, (441-445).
- Qin, C.; Lu, X.; Yin, G.; Jin, Z.; Tan, Q.; Bai, X. (2011). Study of activated nitrogen-enriched carbon and nitrogen-enriched carbon/carbon aerogel composites as cathode materials for supercapacitors. *Materials Chemistry and Physics*, Vol. 126, (453-458).

- Qin, G.; Wei, W.; Guo, S. (2001). Semi-continuous drying of RF with supercritical acetone. *Carbon*, Vol. 41, (851-853).
- Qu, R; Wang, M.; Sun, C.; Zhang, Y.; Ji, C.; Chen, H.; Meng, Y.; Yin, P. (2008). Chemical modification of silica-gel with hydroxyl- or amino-terminated polyamine for adsorption of Au (III). *Applied Surface Science*, Vol. 255, (3361-3370).
- Quin, G.; Guo, S. (2001). Preparation of RF organic aerogels and carbon aerogels by alcoholic sol-gel process. *Carbon*, Vol. 39, (1935-1937).
- Raymundo-Piñero, E.; Azäis, P.; Cacciaguerra, D.; Cazorla-Amorós, D.; Linares-Solano, A.; Béguin, F. (2005). KOH and NaOH activation mechanisms of multiwalled carbon nanotubes with different structural organisation. *Carbon*, Vol. 43, (786-795).
- Riera, E.; Blanco, A.; García, J.; Benedito, J.; Mulet, A.; Gallego-Juárez, J.A.; Blasco, M. (2010). High-power ultrasonic system for the enhancement of mass transfer in supercritical CO₂ extraction processes. *Ultrasonics*, Vol. 50, (306-309).
- Roman, S.; González, J.F.; González-García, C.M.; Zamora, F. (2008). Control of pore development during CO₂ and steam activation of olive stones. *Fuel Processing Technology*, Vol. 89, (715-720).
- Salazar-Hernandez, M.M.; Leyve-Ramirez, M.A.; Gutierrez, J. A. (2009). Neutral alkoxysilanes from silica gel and N-phenyldiethanolamine. *Polyhedron*, Vol. 28, (4044-4050).
- Salitra, G.; Soffer, A.; Eliad, L.; Cohen, Y.; Aurbach, D. (2000). Carbon electrodes for double-layer capacitors. Relation between ion and pore dimensions. *Journal of Electrochemistry Society*, Vol. 147, (2486-2493).
- Sanchez-Polo, M.; Rivera-Utrilla, J.; Salhi, E.; von Gunten, U. (2007). Ag-doped carbon aerogels for removing halide ions in water treatment. *Water research*, Vol. 41, (1031-1037).
- Scherdel, C.; Reichenauer, G. (2009). Carbon xerogels synthesized via phenol-formaldehyde gels. *Microporous and Mesoporous Materials*, Vol. 126, (133-144).
- Schimmel, H.G.; Nijkamp, G.; Kearley, G.J.; Rivera, A.; de Jong, K.P.; Mulder, F.M. (2004). Hydrogen adsorption in carbon nanostructures compared. *Materials Science and Engineering B*, Vol. 108, (124-129).
- Sepheri, S.; Garcia, B.B; Zhang, Q.; Gao, G. (2009). Enhanced electrochemical and structural properties of carbon cryogels by surface chemistry alteration with boron and nitrogen. *Carbon*, Vol. 47, (1436-1443).
- Serdich, M.; Jurcakova, D.H.; Lu, G.Q.; Bandosz, T.J. (2008). Surface functional groups of carbons and the effects on their chemical character, density and accesibility to ions and electrochemical performance. *Carbon*, Vol. 46, (1475-1488).
- Shi, H. (1996). Activated carbons and double layer capacitance. *Electrochimica Acta*, Vol. 41, (1633-1639).
- Silva, A.M.T.; Machado, B.F; Figueiredo, J.L.; Faira, J.L. (2009). Controlling the surface chemistry of carbon xerogels using HNO₃-hydrothermal oxidation. *Carbon*, Vol. 47, (1670-1679).
- Staiti, P.; Lufrano, F. (2010). Investigation of polymer electrolyte hybrid supercapacitor based on manganese oxide-carbon electrodes. *Electrochimica Acta*, Vol. 55, (7436-7442).
- Surya, V.J.; Iyakutti, K.; Rajarajeswari, M.; Kawazoe, Y. (2009). Functionalisation of single-walled carbon nanotube with borane for hydrogen storage. *Physica E: Low-dimensional Systems and Nanostructures*, Vol. 41, (1340-1346).

- Suslick, K.S.; Price, G.J. (1999). Applications of ultrasound to materials chemistry. *Annual Review of Materials Science*, Vol. 29, (295-326).
- Takagi, H.; Hatori, H.; Yamada, Y.; Matsuo, S.; Shiraishi, M. (2004). Hydrogen adsorption properties of activated carbons from modified surfaces. *Journal of Alloys and Compounds*, Vol. 385, (257-263).
- Tamon, H.; Ishizaka, H.; Araki, T.; Okazaki, M. (1998). Control of mesoporous structure of organic and carbon aerogels. *Carbon*, Vol. 36, (1257-1262).
- Tamon, H.; Ishizaka, H.; Yamamoto, T.; Suzuki, T. (2000). Influence of freeze-drying conditions on the mesoporosity of organic gels as carbon precursors. *Carbon*, Vol. 38, (1099-1105).
- Teng, H.; Wang, S.-C. (2000). Preparation of porous carbons from phenol-formaldehyde resins with chemical and physical activation. *Carbon*, Vol. 38, (817-824).
- Teng, Z.; Han, Y.; Li, J.; Yan, F.; Yang, W. (2010). Preparation of hollow mesoporous silica spheres by a sol/gel emulsion approach. *Microporous and Mesoporous Materials*, Vol. 127, (67-72).
- Thomas, K.M. (2007). Hydrogen adsorption and storage on porous materials. *Catalysis Today*, Vol. 120, (389-398).
- Tian, H.Y.; Buckley, C.E.; Paskevicius, M.; Wang, S.B. (2011b). Carbon aerogels from acetic acid catalysed resorcinol-furfural using supercritical drying for hydrogen storage. *The Journal of Supercritical Fluids*, Vol. 55 (1115-1117).
- Tian, H.Y.; Buckley, C.E.; Paskevicius, M.; Sheppard, D.A. (2011a). Acetic acid catalysed carbon xerogels derived from resorcinol-furfural for hydrogen storage. *International Journal of Hydrogen Energy*, Vol. 36, (671-679).
- Tian, H.Y.; Buckley, C.E.; Sheppard, D.A.; Paskevicius, M.; Hanna, N. (2010). A synthesis method for cobalt doped carbon aerogels with high surface area and their hydrogen storage properties. *International Journal of Hydrogen Energy*, Vol. 35, (13242-13246).
- Tonamon, N.; Siyasukh, A.; Tanthapanichakoon, W.; Nishihara, H.; Mukai, S.R.; Tamon, H. (2005). Improvement of mesoporosity of carbon cryogels by ultrasonic irradiation. *Carbon*, Vol. 43, (525-531).
- Tonamon, N.; Wareenin, Y.; Siyasukh, A.; Tanthapanichakoon, W.; Nishihara, H.; Mukai, S.R.; Tamon, H. (2006). Preparation of resorcinol-formaldehyde (RF) carbon gels: Use of ultrasonic irradiation followed by microwave drying. *Journal of Non-Crystalline Solids*, Vol. 352, (5683-5686).
- Vix-Guterl, C.; Frackowiak, R.; Jurewick, K.; Friebe, M.; Parmentier, J.; Béguin, F. (2005). Electrochemical energy storage in ordered porous carbon materials. *Carbon*, Vol. 43, (1293-1302).
- Whang, J.; Yang, X.; Wu, D.; Fu, R.; Dresselhaus, M.S.; Dresselhaus, G. (2008). The porous structures of activated carbon aerogels and their effects on electrochemical performance. *Journal of Power Sources*, Vol. 185, (589-594).
- Wiener, M.; Reichenauer, G.; Scherb, T.; Frichke, J. (2004). Accelerating the synthesis of carbon aerogel precursors. *Journal of Non-Crystalline Solids*, Vol. 350, (126-130).
- Wu, D.; Fu, R.; Zhang, S.; Dresselhaus, M.; Dresselhaus, G. (2004). Preparation of low-density carbon aerogels by ambient pressure drying. *Carbon*, Vol. 42, (2033-2039).
- Xua, W.-C.; Takahashi, K.Y.; Matsuo, Y.; Hattoria, M. (2007). Investigation of hydrogen storage capacity of various carbon materials. *International Journal of Hydrogen Energy*, Vol. 32, (2504-2512).

- Yamamoto, T.; Endo, A.; Ohmori, T.; Nakaiwa, N. (2004). Porous properties of carbon gel microspheres for gas separation. *Carbon*, Vol. 42, (1671-1676).
- Yamamoto, T.; Nishimura, T.; Suzuki, T.; Tamon, H. (2001). Effect of drying conditions on mesoporosity of carbon precursors prepared by sol-gel polycondensation and freeze-drying. *Carbon*, Vol. 39, (2374-2376).
- Yang, K.Y.; Hong, S.J.; Lee, B.I.; Lee, J.S. (2008). Enhanced electrochemical capacitance of nitrogen-doped carbon gels synthesized by microwave-assisted polymerization of resorcinol and formaldehyde. *Electrochemistry Communications*, Vol. 10, (1105-1108).
- Ying, D.J.; Haji, Z.S.; Erkey, C. (2005). Dynamics of removal of organosulfur compounds from diesel by adsorption on carbon aerogels for fuel cell applications. *International Journal of Hydrogen Energy*, Vol. 30, (1287-1293).
- Yoshimune, M.; Yamamoto, T.; Nakaiwa, M.; Haraya, K. (2008). Preparation of highly mesoporous carbon membranas via sol-gel process using resorcinol and formaldehyde. *Carbon*, Vol. 46, (1031-1036).
- Zareba-Grodz, I.; Mista, W.O.; Strek, W.; Bukowska, E.; Hermanowick, K.; Maruszewski, K. (2004). Synthesis and properties of an inorganic-organic hybrid prepared by the sol-gel method. *Optical Materials*, Vol. 26, (207-211).
- Zhang, L.; Liu, H.; Wang, M.; Chen, L. (2007). Structure and electrochemical properties of resorcinol-formaldehyde polymer-based carbon for electric double-layer capacitors. *Carbon*, Vol. 45, (1439-1445).
- Zhao, N.; He, C.; Jiang, Z.; Lin, J.; Li, Y. (2007). Physical activation and characterization of multi-walled carbon nanotubes catalytically synthesized from methane. *Materials Letters*, Vol. 61, (681-685).
- Zheivot, V.I.; Molchanov, V.V.; Zaikovskii, V.I.; Krivoruchko, V.N.; Zaitseva, N.A.; Shchuchkin, M.S. (2010). Carbon xerogels: Nano and adsorption textures, chemical nature of the surface and gas chromatography properties. *Microporous and Mesoporous Materials*, Vol. 130, (7-13).
- Zhu, Y.; Hu, H.; Li, W.; Zhang, X. (2007). Resorcinol-formaldehyde based porous carbon as electrode material for supercapacitors. *Carbon*, Vol. 45, (160-165).
- Zhu, Y.; Hu, H.; Li, W.; Zhao, H. (2006). Preparation of cresol-formaldehyde carbon aerogels via drying aquagel at ambient pressure. *Journal of Non-Crystalline Solids*, Vol. 352, (3358-3362).
- Zubizarreta, L.; Arenillas, A.; Dominguez, A.; Menéndez, J.A.; Pis, J.J. (2008a). Development of microporous carbon xerogels by controlling synthesis conditions. *Journal of Non-Crystalline Solids*, Vol. 354, (817-825).
- Zubizarreta, L.; Arenillas, A.; Menéndez, J.A.; Pis, J.J.; Pirard, J.-P.; Job, N. (2008b). Microwave drying as an effective method to obtain carbon xerogels. *Journal of Non-Crystalline Solids*, Vol. 354, (4024-4026).
- Zubizarreta, L.; Arenillas, A.; Pirard, J.-P.; Pis, J.J.; Job, N. (2008c). Tailoring the textural properties of activated carbon xerogels by chemical activation with KOH. *Microporous and Mesoporous Materials*, Vol. 115, (480-490).
- Zubizarreta, L.; Arenillas, A.; Pis, J.J. (2009). Carbon materials for H₂ storage. *International Journal of Hydrogen Energy*, Vol. 34, (4575-4581).
- Zubizarreta, L.; Menéndez, J.A.; Marco-Lozar, J.P.; Pirard, J.P.; Pis, J.J.; Linares-Solano, A.; Cazorla-Amorós, A.; Arenillas, A. (2010). Ni-doped carbon xerogels for H₂ storage. *Carbon*, Vol. 48, (2722-2733).

Nanomaterials

Edited by Prof. Mohammed Rahman

ISBN 978-953-307-913-4

Hard cover, 346 pages

Publisher InTech

Published online 22, December, 2011

Published in print edition December, 2011

The book "Nanomaterials" includes all aspects of metal-oxide nano-structures, nano-composites, and polymer materials instigating with materials survey and preparations, growth and characterizations, processing and fabrications, developments and potential applications. These topics have utilized innovative methods of preparation, improvement, and continuous changes in multidimensional ways. The innovative frontiers are branching out from time to time to advanced nanotechnology. It is an important booklet for scientific organizations, governmental research-centers, academic libraries, and the overall research and development of nano-materials in general. It has been created for widespread audience with diverse backgrounds and education.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Esther G. Calvo, J. Ángel Menéndez and Ana Arenillas (2011). Designing Nanostructured Carbon Xerogels, Nanomaterials, Prof. Mohammed Rahman (Ed.), ISBN: 978-953-307-913-4, InTech, Available from: <http://www.intechopen.com/books/nanomaterials/designing-nanostructured-carbon-xerogels>

INTech
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen