BOLETIN del
Grupo Español del Carbón

Indice

Preface

This issue of the Boletín del Grupo Español del Carbón (Spanish Carbon Group Bulletin) is dedicated to carbon gels. These are porous carbon materials prepared by the carbonization of organic gels obtained by the sol-gel polymerization of certain organic monomers, e.g., resorcinol and formaldehyde, in the presence of basic or acid catalysts. Sol-gel processing is a versatile method for synthesizing solid materials and is carried out in a liquid solution and at low temperatures, generally below 100 ºC.

An important step in the preparation of these materials is the technique used to dry the wet gel or hydrogel, because it affects the surface properties of the final carbon. Three main methods have been developed for this purpose, i.e., subcritical drying, supercritical drying and freeze-drying, which give rise to xerogels, aerogels and cryogels, respectively.

Research on carbon gels has grown rapidly since resorcinol-formaldehyde gels were first prepared by R.W. Pekala in 1989 [1]. This is largely due to their well-developed micro- and mesoporosity, whose size and volume can be controlled independently, and to their large surface area. In addition, they can be readily doped with other heteroatoms and obtained in varying forms such as powders, microspheres, monoliths and thin films. Thanks to these characteristics, they are used in adsorption, heterogeneous catalysis and electrochemical energy storage, among other applications [2-4].

Various authors have contributed to this special issue. Prof. A. Celzard and coworkers from the Université de Lorraine (France) show that carbon gels can be prepared from phenolic resources of natural origin such as tannin and lignin, significantly reducing the costs of the preparation process. Prof. S.R. Mukai from the Hokkaido University (Japan) describes the versatility of carbon gels to adopt different morphologies, attributable to their behavior as readily moldable fluids before their gelation. Prof. J.L. Figueiredo from the Universidade do Porto (Portugal) shows how the characteristics of carbon xerogels can be modified to ensure their adequate performance as metal-free catalysts for a wide variety of reactions in either liquid or gas phase. Finally, Prof. N. Job from the University of Liège (Belgium) addresses mass transport in carbon gels with tuned porosity, which is an important issue in many of the applications of these materials.

I wish to express my gratitude to all authors that have contributed with their time and effort to this special issue of the Bulletin.

Carlos Moreno-Castilla
Guest Editor

[1] Pekala RW. Organic aerogels from the polycondensation of resorcinol with formaldehyde. J Mat Sci 1989; V24(9):3221-3227.

[2] Fairén-Jiménez D, Carrasco-Marín F, Moreno-Castilla C. Adsorption of benzene, toluene and xylenes on monolithic carbon aerogels from dry air flows. Langmuir 2007; 23(20): 10095-101.

[3] Moreno-Castilla, C. Carbon gels in catalysis. In Serp P, Figueiredo JL, editors. Carbon materials for catalysis, New York: J. Wiley & Sons, 2009: Chapter 10.

[4] Zhang LL, Zhao XS. Carbon-based materials as supercapacitor electrodes. Chem Soc Rev 2009; 38(9):2520-2531.
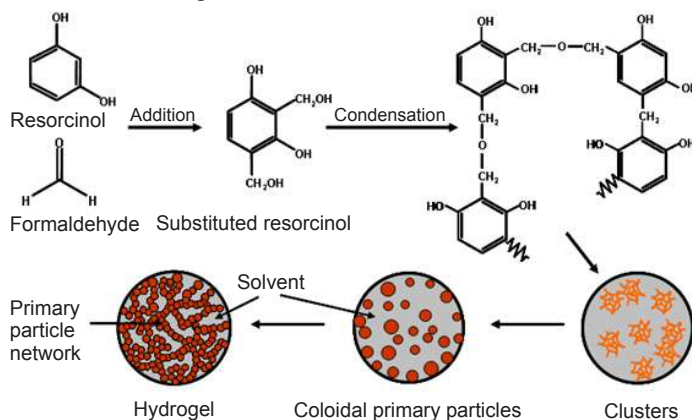
Sol-gel polymerization reaction of resorcinol and formaldehyde. Adapted from reference [1]

Carbon gels derived from natural resources
Geles de carbón de origen natural

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Abstract

Most carbon gels investigated so far and reported in the literature were prepared from resorcinol crosslinked with formaldehyde in water, and were generally dried with supercritical CO_2 before being pyrolysed. In the present paper, through some selected examples, we show how valuable carbon gels can be derived from other phenolic resources having a natural origin. Special emphasis is given to tannin and lignin, both derived from wood, as potential precursors of carbon aero- and cryogels. However, natural compounds not obeying the usual concepts of sol-gel chemistry may also be used for preparing carbon gels, such as cellulose, and even glucose. In the latter case, hydrothermal treatment forces the phase separation to occur, and leads to monoliths which can be advantageously converted into carbon aerogels by supercritical drying and subsequent pyrolysis.

Resumen

La mayoría de los geles de carbón investigados hasta ahora y citados en la literatura han sido preparados a partir de resorcinol reticulado con formaldehído en agua, y generalmente secados con CO_2 supercrítico antes de ser pirolizados. En este manuscrito, hemos seleccionado algunos ejemplos y mostramos como se pueden preparar excelentes geles de carbón a partir de compuestos fenólicos que tienen un origen natural. Especial mención merecen los taninos y ligninas, extraídos de la madera, como potenciales precursores de aero- y criogeles de carbón. Sin embargo, otros compuestos naturales que no obedecen al concepto habitual de la química de sol-gel también pueden ser usados para preparar geles de carbón, como la celulosa y la glucosa. En este último caso, el tratamiento hidrotermal fuerza la separación de fase, y conduce a monolitos que pueden ser convertidos en aerogeles de carbón por secado supercrítico y posterior pirólisis.

1. Introduction

Gels are, among other possible definitions that can be used for describing them, semisolid systems comprising two phases, solid and liquid, embedded in each other in such a way that the pores of the solid, filled with solvent, are of colloidal dimensions [1]. Removal of the liquid phase leads to a highly porous backbone, especially if supercritical of freeze drying has been carried out. The latter processes indeed prevent the shrinkage of the material (though never completely) and, therefore, the collapse of the pores induced by capillary forces can be minimized. Getting carbon gels is thus possible, as it is already the case for most carbonaceous solids, from the controlled pyrolysis of organic precursors, here organic gels, in non-oxidizing atmosphere.

From the simple aforementioned assertions, it can be concluded that using biopolymers or natural resources in general for preparing carbon gels involves several requirements. First, if the porous structure has to be maintained, the precursors should not melt when heated. Therefore, all chemical (i.e. crosslinked) gels might be used for that purpose, since chemical gels are insoluble, infusible, three-dimensional polymer networks. In contrast, jellies based on fruits and aspic based on gelatine, for example, are physical (i.e. coagulated) gels, and melt when heated. Then, the boiling and the pyrolysis of the resultant liquid lead to an ill-defined brittle residue, which is porous due to the evolution of gases, but which is certainly not a carbon gel. Nevertheless, infusible biopolymers which can be dissolved and next coagulated may also become precursors of carbon gels, provided that the porous structure made up by their entanglement can be maintained all along the drying and heat-treatment processes. This is the case of cellulose, whose carbon yield, however, is rather low.

Possible natural precursors for preparing carbon gels should thus be prone to gelation or at least to rigid entanglement, be infusible before or after being crosslinked, have a high carbon yield and be cheap. One advantage of using them is indeed, on top of their "greener" character, the correspondingly reduced cost of the resultant material. In the following, emphasis will be given to phenolic biopolymers such as tannin and lignin, especially well matching these requirements. They are described in section 2, and their use for preparing gels is developed in section 3 and partly in section 4. However, natural molecules not obeying the aforementioned requirements may, in some cases, also lead to carbon gels using special preparation processes such as hydrothermal treatment. Some examples are given in section 4.

2. Tannin and lignin as precursors of carbon gels

Tannin and lignin are both derived from plants, and especially from wood. There are fundamental differences between them, as explained below, but both share valuable characteristics such as very aromatic character, hence leading to a high carbon yield, around 45%, and ability of being easily crosslinked thanks to their number of reactive hydroxyl groups. Figure 1 shows the typical chemical structure of tannin and lignin, though that of lignin can just be a model, strongly depending on its vegetable origin and on the severity of its extraction process.

Tannins are extractible molecules, industrially exploited from wattle, pine and quebracho trees, for example. They are oligomers based on the repetition of the unit shown in Figure 1a, whose exact structure depends on the origin. For instance, wattle tannin has OH groups in positions 7, 3', 4' and 5', and the corresponding flavonoid units are mainly 4,6-linked, leading to water-soluble phenolic compounds with typical molecular weights ranging from 0.5 to 3.5 kDa [2]. Lignin is also a phenolic molecule, but is a three-dimensional, crosslinked, polymer. It is the

most common natural polymer after cellulose, and its role in plant tissues is cementing cellulose fibres. It is based on three phenylpropanoid monomers, as shown in Figure 1b-d, connected with each others through various inter-unit linkages, thus resulting in a complex macromolecular structure [3,4]. Lignin is generally considered as a waste material from the pulp and paper industry, and is most often used as fuel for the energy balance of pulping process.
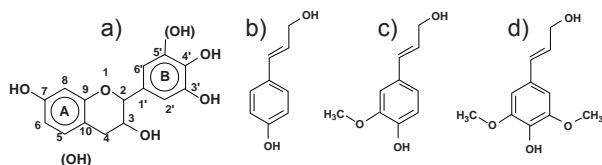
Figure 1. Chemical structure of: (a) the flavonoid unit of condensed tannins; (b)-(d) the structural units of lignin: (b) p-coumaryl alcohol; (c) coniferyl alcohol (guaiacyl); (d) sinapyl alcohol (syringyl).
Figura 1. Estructura química de: (a) la unidad flavonoide de taninos condensados; (b)-(d) las unidades estructurales de la lignina: (b) alcohol p-cumarílico; (c) alcohol coniferílico (guaiacilo); (d) alcohol sinapinílico (siringilo).

Tannin and lignin can be suitably crosslinked by aldehydes, such as formaldehyde, and are thus natural counterparts of resorcinol, from which most carbon gels have been prepared and investigated. However, tannin can be used either alone with formaldehyde for preparing organic gels and derived carbon gels [5], or in combination with other synthetic phenolic molecules such as phenol or resorcinol [6], whereas lignin can never be used alone. Whatever the way it is crosslinked, and as far as the authors know, lignin alone could never lead to homogeneous, stable, organic gels from which carbon gels might be prepared. Instead, hard precipitates are obtained. Nice, reproducible, gels could only be obtained by combining lignin with smaller phenolic molecules such as phenol [7], resorcinol [8] and tannin [9].

## 3. Carbon gels from tannin and lignin: selected examples

As explained above, tannin easily gels in the presence of formaldehyde. Unlike what is known for resorcinol, a broad range of pH can be successfully used with tannin, leading to materials having different porous structures, as demonstrated below. The typical pH of a tannin solution is close to 4.5, at which the reactivity with formaldehyde is the lowest, the highest

reactivity being found at pH lower than 3 and higher than 7. The pH can thus be advantageously increased or decreased through the use of any base or acid, respectively, abusively but very frequently referred to as "catalysts". As a consequence, the gelation time is strongly modified, and the highest BET surface areas of the resulting carbon aerogels, above 700 m^2/g, are found at pH 4 – 5, whereas the mesopore volumes increase with pH, up to 0.9 cm^3/g [5].

Carbon aerogels derived from tannin present a typical nodular structure, see Figure 2, and the average diameter of such nodules decreases when the pH increases. Such features are very usual for all other gels derived from phenolic precursors. The materials shown in Figure 2 were obtained by supercritical drying in acetone, which is as efficient as CO_2 for that purpose [10] but much cheaper. Combined with the fact that a very inexpensive precursor was used, tannin, these resultant carbon aerogels are 5 times cheaper than their resorcinol-based counterparts [5].

Instead of drying supercritically the monoliths before pyrolysis, freeze-drying can be carried out. The process is a bit longer, since it requires several steps of solvent exchange, but is cheaper. Carbon cryogels derived from mixtures of tannin and resorcinol were successfully prepared, in which both proportions of reactants and pH were changed. As a result, a much broader range of porous structures than those of typical resorcinol – formaldehyde gels could be obtained. Interestingly, pore size distributions (PSD) could be tuned through the pH for both tannin – formaldehyde (TF) carbon aerogels and tannin – resorcinol – formaldehyde (TRF) carbon cryogels, either shifting the PSD at rather constant mesopore volume (for TRF), or keeping the PSD centred on the same pore width but changing the mesopore volumes (for TF), see Figure 3 [5,6].

The porous structure of cryogels is different from that of aerogels of identical composition for two possible reasons. One is related to shrinkage during drying, which may be very different depending on the process. Thus, diluted gels can be freeze-dried with a much lower shrinkage than what can be observed when using supercritical solvents. As a consequence, extremely high porosities, but correspondingly low mechanical properties, are obtained. Such weak materials may then suffer a
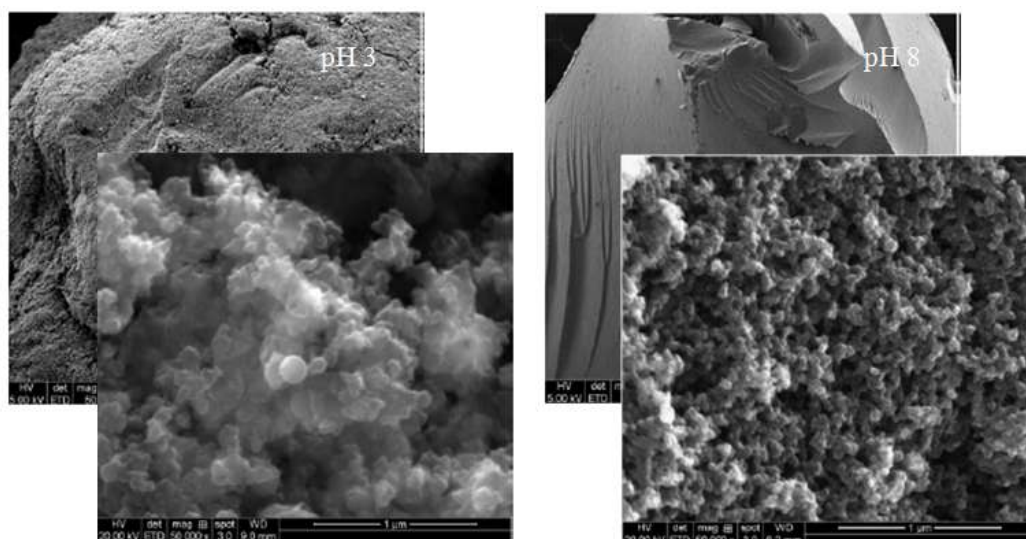
Figure 2. SEM pictures of tannin-based carbon aerogels prepared at two different pH. The effect of the pH on the porous structure is clearly seen even at low magnification (after [5]).
Figura 2. Fotografías MEB de aerogeles de carbón preparados a partir de tanino y a dos pH diferentes. El efecto del pH sobre la estructura porosa se ve claramente incluso al menor aumento (de [5]).
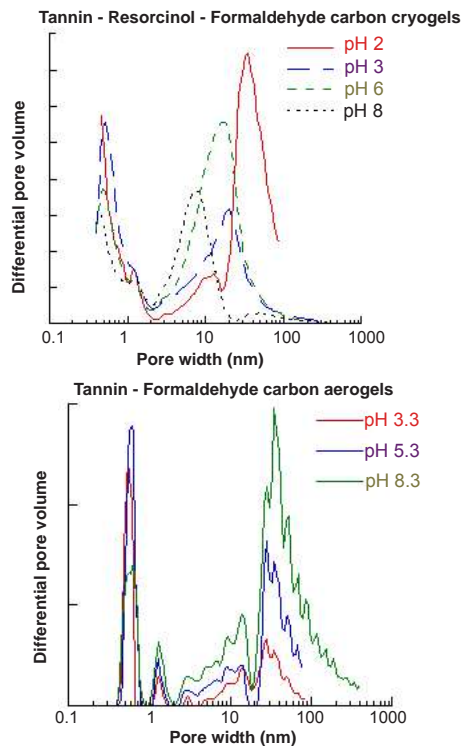
Figure 3. Pore size distributions of tannin – resorcinol – formaldehyde carbon cryogels (top) and tannin – formaldehyde carbon aerogels (bottom), showing the significant impact of the initial pH of the solution before gelation (after [5,6]).
Figura 3. Distribuciones de tamaño de poro en criogeles de carbón preparados a partir de tanino - resorcinol - formaldehído (arriba) y en aerogeles de carbón preparados a partir de tanino - formaldehído (abajo), mostrando el impacto significativo del pH inicial de la solución antes de la gelificación (de [5,6]).

serious pore collapse during pyrolysis, leading to materials that are finally less porous than their aerogel counterparts, whose mechanical properties were higher due to lower amount of very wide pores. This phenomenon was observed for diluted tannin – formaldehyde cryogels, presenting a minimum of BET surface area (400 m^2/g) at pH 4 – 5 [11], i.e. at the pH at which a maximum was observed for tannin – formaldehyde aerogels (see above). Surface areas and micropore volumes as high as 1400 m^2/g and 0.55 cm^3/g, respectively, were measured at pH 7.5. The fact that NaOH used for adjusting the pH at this value, remaining inside the porosity and acting as an activating agent during the pyrolysis, thus leading to somewhat activated carbon gels, can not be discarded. The second reason for differences of porosity between aero- and cryogels is related to the nature of the solvent that has been used for freeze-drying. *Tert*-butanol is most frequently used, but is able to crystallise inside the porosity of the gels, leading to acicular crystallites and deeply modifying the resultant porosity. Figure 4 shows the example of carbon cryogels particles prepared from tannin and formaldehyde using the emulsion polymerization process formerly described by Yamamoto et al. [12], and in which needle-like pores are easily seen. Materials freeze-dried in water, whose ice volume is much bigger than that of the liquid phase, comprise even bigger pores. As a conclusion, foreseeing the kind of porosity that a carbon gel will have after drying and pyrolysis is totally impossible.

Preparing a chemical gel from any phenolic precursor assumes that the conditions of gelation are known and have been optimized. As explained above, high initial dilution of the precursor resin leads to high
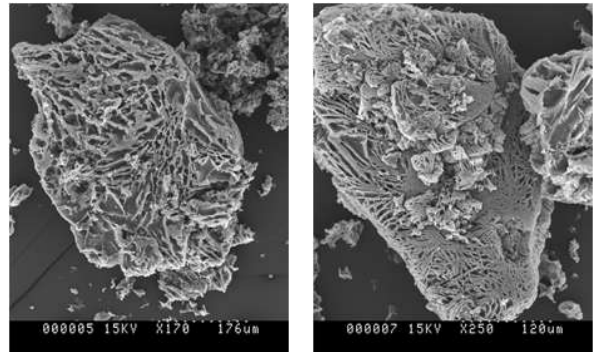
Figure 4. Needle-like macroporosity exhibited by carbon cryogel particles made by inverse emulsion polymerization of a tannin-formaldehyde solution, followed by freeze-drying in t-butanol and pyrolysis at 900°C.
Figura 4. Macroporosidad acicular que muestran las partículas de criogel de carbón sintetizadas por polimerización en emulsión inversa de una solución de tanino - formaldehído, seguida de liofilización en ter-butanol y pirólisis a 900°C.
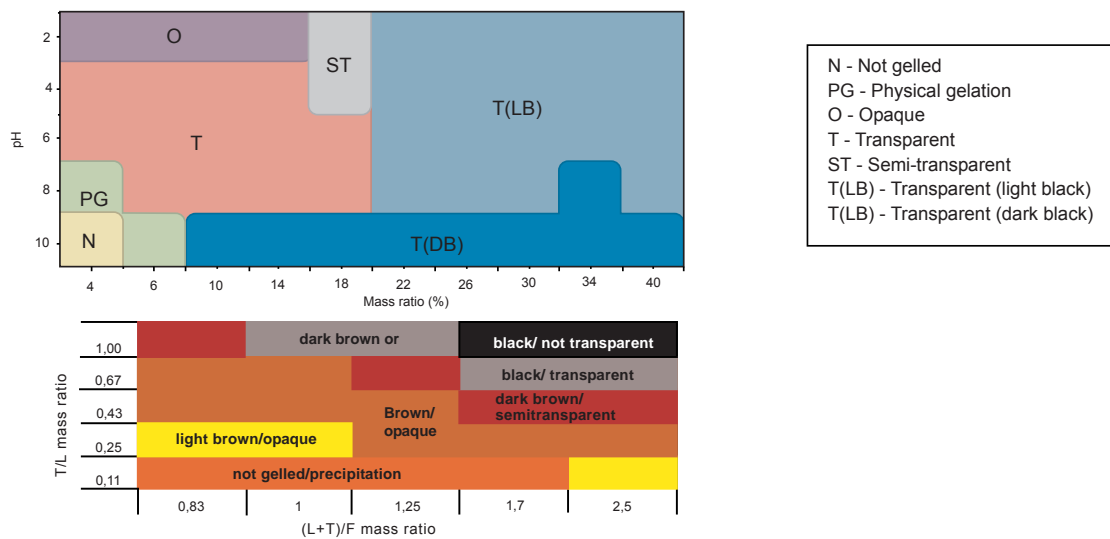
pore volumes, but the solid backbone is so weak that a significant part of the porosity is lost during drying and/or subsequent pyrolysis. Less diluted gels should thus be preferred, having a lower initial porosity, but whose major part will be maintained because they are stiffer, so they can finally present much more developed porous structure. Mechanical strength is indeed a very important parameter, directly related to porosity which can be controlled by initial dilution, pH and amount of crosslinker. There exists an optimum for each of these experimental parameters. Additionally, some values that these parameters may take can be in favour, or in contrast hinder and even prevent, gelation.

Therefore, for better understanding phenolic systems, building a phase diagram may be of great interest. This has been recently done by our group in the case of tannin – formaldehyde aqueous solutions, see below. The situation is more complicated when more than one phenolic molecule is present, such as in lignin – tannin or lignin – phenol systems. In the latter cases, some parameters must be fixed for avoiding multi-dimensional diagrams that would be impossible to represent. Figure 5 illustrates tannin – formaldehyde and tannin – lignin – formaldehyde diagrams as a function of a limited number of parameters. The existence of areas within which no gelation occurs, or within which reversible (physical) gels are obtained, is evidenced.

The organic gels presented in Figure 5, especially the aerogels, have been investigated recently [7,9] but still deserve additional studies. All stable chemical gels present the expected nodular structure, whatever the composition, and so do their carbonaceous derivatives. Both packing and average diameter of their nodules depend on the amount of crosslinker, pH and dilution of the resin. Pyrolysis leads to nice carbon aerogels, whose porous texture is still under investigation and will be published in the near future. The first results confirm the relevance of lignin as precursor of carbon gels, leading to surface areas higher than 500 m^2/g, just like for many other carbon gels derived from synthetic resources.

4. Carbon gels prepared from alternative methods or derived from other resources

The usual sol-gel chemistry used above is not necessarily involved for preparing organic monoliths from which carbon gels can be finally obtained. In other words, the classical scheme consisting in dissolving a precursor into a solvent, and whose

N - Not gelled
PG - Physical gelation
O - Opaque
T - Transparent
ST - Semi-transparent
T(LB) - Transparent (light black)
T(LB) - Transparent (dark black)

Figure 5. Phase diagrams of tannin – formaldehyde (TF, top) and tannin – lignin – formaldehyde (TLF, bottom, reprinted from [9] with permission) solutions, showing the kinds of materials obtained, depending on a limited number of experimental parameters (for TF: pH and dilution at constant T/F ratio = 1.35; for TLF: T/L proportions and amount of formaldehyde at fixed dilution = 26% and constant pH = 10). Supercritical, freeze-, or subcritical drying and pyrolysis of such gels leads to a very broad range of carbon gels, whose complete investigation is far from being accomplished.

Figura 5. Diagramas de fase de las disoluciones tanino - formaldehído (TF, arriba) y tanino - lignina - formaldehído (TLF, abajo, reproducido de [9] con permiso), mostrando las clases de materiales obtenidos, según un número limitado de parámetros experimentales (para TF: pH y proporción de la dilución a T/F constante = 1.35; para TLF: Proporción de T/L y cantidad de formaldehído a dilución fija = 26 % y pH constante = 10). El secado supercrítico, por liofilización, o subcrítico de esos geles y su posterior pirólisis conduce a una muy amplia gama de geles de carbón, cuya investigación completa está lejos de haberse finalizado.

crosslinking will lead first to a sol, i.e. to a very fine suspension of solid, and next to a gel through the gradual clustering of the suspended particles, can be more or less modified, depending on both the synthesis protocols and on the precursors.

For example, the phase separation leading to the occurrence of polymer particles and hence to a gel can be forced when hydrothermal conditions are used. In this case, separation between gelation and precipitation is not always easy, and some experimental conditions lead to an overlapping of these two regimes. In a general way, it can be assumed that a gel is formed when the size of the constitutive nodules is both "small" (say, a few nm to a few tens of nm) and homogeneous, unlike precipitates whose particles have all possible dimensions, and can be much bigger. Figure 6 thus shows the materials which could be derived from wattle tannin dissolved in aqueous solutions of different pH and submitted to 180°C under 1MPa.

Gels obtained this way are, just like their counterparts prepared by conventional sol-gel chemistry, based on rather spherical nodules. However, using hydrothermal conditions, neither crosslinker nor supercritical drying was required. The porosity was indeed fully maintained after normal (i.e. subcritical) drying in air and subsequent pyrolysis at 900°C. Thus, the sample shown at the left of Figure 6 had a BET surface area of 495 m^2/g [13]. Additionally, and interestingly, if not pure water but concentrated ammonia solution is used instead, direct functionalization of the precursor can be achieved, leading to hydrothermal carbons having nitrogen contents as high as around 15 wt.%. However, even if the term "hydrothermal carbon" has been widely used in the literature, the materials obtained directly from the autoclave should never be considered as authentic carbons, since their elemental carbon content is around 60 wt.% only. Therefore, an additional pyrolysis step is required for increasing the carbon content above 80%. Doing so, the materials functionalized with nitrogen loose part of the latter, which is decreased to a value (a few %)

which depends on the final temperature.

Hydrothermal treatment is also a very interesting process for getting carbons from precursors whose carbon yield is intrinsically low when directly pyrolysed in standard conditions, and/or whose gelation does not occur according to the classical sol-gel chemistry. Hydrothermal process indeed partly prevents the evolution of gases based on light elements such as C and N, and forces the phase separation to occur. When a highly dispersed monolith, based on very fine particles, is obtained, i.e. a true gel, its drying and subsequent pyrolysis may lead to a carbon gel derived from *a priori* unexpected precursors. The best examples have been reported by the group of Antonietti, using glucose as the main starting compound. A rather fibrous carbon aerogel could indeed be prepared from the hydrothermal treatment of a mixture of glucose and ovalbumin, see Figure 7. BET surface area and mesopore volume higher than 300 m^2/g and 0.5 cm^3/g, respectively, were measured after pyrolysis at 900°C. Due to the presence of protein among the precursors, this carbon aerogel was naturally doped with around 6 wt.% of nitrogen [14].

Such materials could also be easily doped by sulphur by simply incorporating a S source in the form of low amounts of either S-(2-thienyl)-L cysteine or 2-thiophene carboxaldehyde, leading to similar carbon aerogels as above, after supercritical drying and pyrolysis, but presenting special catalytic properties related to their surface composition [15]. Finally, borax has been recently suggested as both catalyst and structure-directing agent, allowing the preparation of monoliths from glucose treated in hydrothermal conditions. After supercritical drying and pyrolysis, carbon aerogels having different porous textures could be obtained, depending on the amount of borax. The highest BET surface area and mesopore volume were around 360 m^2/g and 0.4 cm^3/g, respectively [16]. As found in many other works before, the size of the constitutive nodules changed with the pH, hence with the amount of borax in this special case.
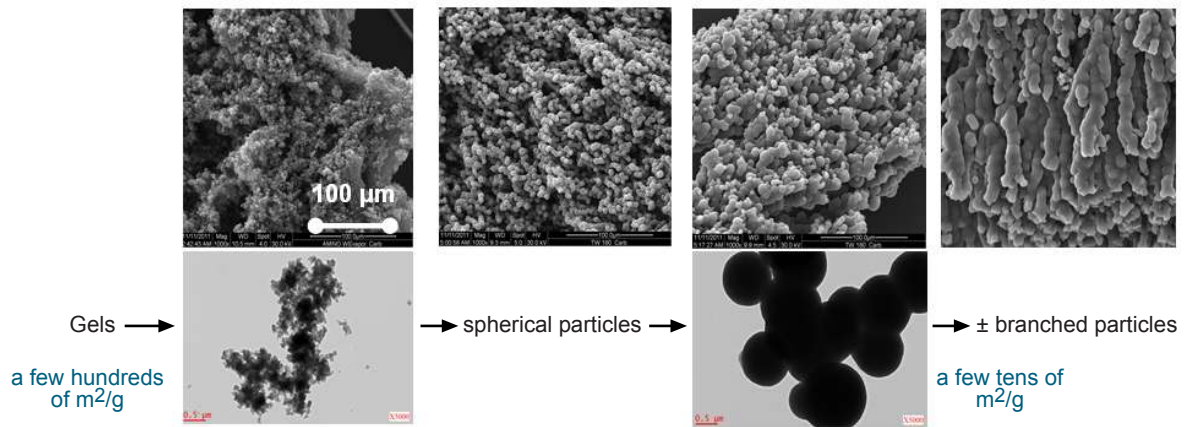
Figure 6. Various materials obtained by hydrothermal treatment of wattle tannin followed by pyrolysis at 900°C, using various pHs and conditions of dissolution. Those at the left are true carbon gels (after [13]). Even wider range of materials can be obtained by changing temperature, time and initial dilution.

Figura 6. Varios materiales obtenidos por tratamiento hidrotermal de tanino de acacia seguido de pirólisis a 900°C, usando varios pH y diluciones. A la izquierda, verdaderos geles de carbón (de [13]). Cambiando la temperatura, el tiempo y la dilución inicial se puede obtener una gama de materiales más amplia incluso.
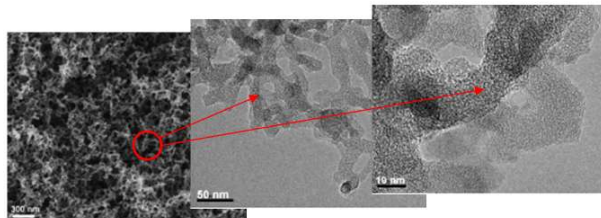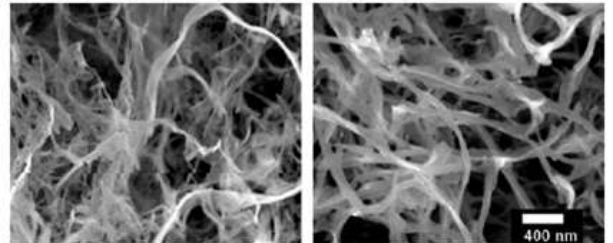

Figure 7. Fibrous carbon aerogels derived from the hydrothermal treatment of a mixture of glucose and ovalbumin (after [14], reproduced by permission of the Royal Society of Chemistry).
Figura 7. Aerogeles de carbón fibrosos preparados por tratamiento hidrotermal de una mezcla de glucosa y albúmina de clara de huevo (de [14], reproducido con el permiso de Royal Society of Chemistry).

Figure 8. Fibrillar carbon cryogels derived from cellulose and pyrolysed at 600°C in nitrogen (left) and HCl (right). Reproduced from [20] with permission.
Figura 8. Criogeles de carbón fibrilares preparados a partir de celulosa y pirolizados a 600°C en nitrógeno (izquierda) y HCl (derecha). Reproducido de [20] con permiso.

Cellulose gels, aero- and cryogels, have been successfully prepared according to a number of techniques [17-21]. Cellulose could be used as such or as an ester: cellulose acetate. The former leads to physical (coagulated) gels, whereas the latter, through the use of isocyanate as crosslinker, leads to chemical gels. Both kinds of materials could be converted into carbon gels. Due to the fibrous nature of the precursor, the morphology of the resultant carbons was found to be fibrillar, thus was different from the traditional nodular structure most frequently reported so far. However, the characteristics of such gels are fully comparable with those based on phenolic precursors. For example, carbon aerogels derived from cellulose acetate (dried with supercritical CO_2) presented BET surface areas higher than 400 m^2/g [22] and mesopore volumes around 0.2 cm^3/g [23]. Because of such valuable characteristics, these materials could be successfully doped with noble metals and suggested as catalyst for PEM fuel cells [24]. From physical cellulose gels, fibrillar carbon cryogels have been obtained. These cryogels presented surface areas and mesopore volumes higher than 500 m^2/g and 0.6 cm^3/g, respectively [20]. Due to the low carbon yield of cellulose, these materials were advantageously pyrolysed in HCl, making the carbon yield increase from 15 to 30%, see Figure 8.

5. Conclusion

Producing carbon gels from natural resources, whether they are aerogels, cryogels or xerogels, was reported to be perfectly feasible, provided that the precursors are suitably chosen. Given that melting and extensive thermal decomposition should be absolutely avoided, most of the porous, organic, precursors are chemical gels of phenolic nature. However, other systems have been reported, whose main drawbacks, especially low carbon yield, could be got round through a preliminary hydrothermal treatment or through a pyrolysis in unusual atmospheres. Nevertheless, such methods are not enough when the precursor can not resist the pyrolysis step, such as materials mainly based on proteins. For example, soy-tannin aerogels recently reported could never be converted into their carbonaceous counterparts [25].

When compared to carbon gels made from synthetic molecules, biopolymer-derived carbon gels generally have very similar micropore volumes but possess higher macropore volumes and much broader mesopore size distributions. This finding is certainly related to the much higher molecular weight of structural units of bio-oligomers and biopolymers. Crosslinked phenolic biopolymers are indeed characterized by long polymer chains leading to steric hindrance, hence preventing the formation of very narrow pores related to high surface areas. This is well known for tannin oligomers, which are essentially branched and rigid, preventing the complete reactivity of all possible sites with formaldehyde. Additionally, the reaction with the crosslinker further provides a 3D-character to the polymer network, e.g. in the case of lignin, thus preventing the formation of very narrow pores. In contrast, organic and carbon gels based on smaller synthetic molecules, such as resorcinol, may present higher surface areas, higher mesopore volumes and narrower mesopore size distributions, but are significantly more expensive.

Anyway, and provided that their purity is high enough, carbon gels derived from natural resources are expected to have, and in some cases were already found to have, the same applications as those suggested for their synthetic counterparts, i.e., adsorbents, porous electrodes for electric double layer supercapacitors or secondary batteries, filling material for HPLC columns, catalyst supports, and heat insulators at high temperature.

6. Acknowledgements

7. References

[1] Brinker CJ, Scherer GW. Sol – gel science. The physics and chemistry of sol–gel processing. Academic Press, 1990.

[2] Pasch H, Pizzi A, Rode K. MALDI-TOF mass spectrometry of polyflavonoid tannins. Polymer 2001;42(18):7531–7539.

[3] Abreu HS, do Nascimento AM, Maria MA. Lignin structure and wood properties. Wood Fiber Sci 1999;31(4):426–433.

[4] Adler E. Lignin chemistry: past, present and futures. Wood SciTechnol 1977;11(3):169–218.

[5] Szczurek A, Amaral-Labat G, Fierro V, Pizzi A, Masson E, Celzard A. The use of tannin to prepare carbon gels. Part I. Carbon aerogels. Carbon 2011;49(8):2773–2784.

[6] Szczurek A, Amaral-Labat G, Fierro V, Pizzi A, Celzard A. The use of tannin to prepare carbon gels. Part II. Carbon cryogels. Carbon 2011;49(8): 2785–2794.

[7] Grishechko LI, Amaral-Labat G, Szczurek A, Fierro V, Kuznetsov BN, Celzard A. Lignin – phenol – formaldehyde aerogels and cryogels. Micropor Mesopor Mater 2012; 2013;168: 19-29.

[8] Chen F, Xu M, Wang L, Li J. Preparation and characterization of organic aerogels from a lignin – resorcinol – formaldehyde copolymer. Biores 2011;6(2):1261-1272.

[9] Grishechko LI, Amaral-Labat G, Szczurek A, Fierro V, Kuznetsov BN, Pizzi A, Celzard A. New tannin – lignin aerogels. Ind Crops Prod 2013;41(1):347-355.

[10] Amaral-Labat G, Szczurek A, Fierro V, Pizzi A, Masson E, Celzard A. Impact of depressurizing rate on the porosity of aerogels. Micropor Mesopor Mater 2012;152:240–245.

[11] Amaral-Labat G, Szczurek A, Fierro V, Stein N, Boulanger C, Pizzi A, Celzard A. Pore structure and electrochemical performances of tannin-based carbon cryogels. Biomass Bioenergy 2012;39:274-282.

[12] Yamamoto T, Sugimoto T, Suzuki T, Mukai SR, Tamon H. Preparation and characterization of carbon cryogel microspheres. Carbon 2002; 40(8):1345 –1351.

[13] Braghiroli F, Fierro V, Izquierdo MT, Parmentier J, Pizzi A, Celzard A. Nitrogen-doped carbon materials produced from hydrothermally treated tannin. Carbon 2012; 50(15): 5411-5420.

[14] White RJ, Yoshizawa N, Antonietti M, Titirici MM. A sustainable synthesis of nitrogen-doped carbon aerogels. Green Chem 2011;13(9):2428-2434. http://dx.doi.org/10.1039/C1GC15349H

[15] Wohlgemuth SA, White RJ, Willinger MG, Titirici MM, Antonietti M. A one-pot hydrothermal synthesis of sulfur and nitrogen doped carbon aerogels with enhanced electrocatalytic activity in the oxygen reduction reaction. Green Chem 2012;14(5):1515-1523.

[16] Fellinger TP, White RJ, Titirici MM, Antonietti M. Borax-mediated formation of carbon aerogels from glucose. Adv Funct Mater 2012;22(15):3254-3260.

[17] Tan, C, Fung, M, Newman, JK, Vu C. Organic aerogels with very high impact strength. Adv Mater 2001;13(9):644-646.

[18] Fischer F, Rigacci A, Pirard R, Berthon-Fabry S, Achard P. Cellulose-based aerogels. Polymer 2006;47(22):7636–7645.

[19] Jin H, Nishiyama H, Wada M, Kuga S. Nanofibrillar cellulose aerogels. Colloids Surfaces A Physicochem Eng Aspects 2004;240(1):63-67.

[20] Ishida O, Kim Dy, Kuga S, Nishiyama Y, Malcol Brown R. Microfibrillar carbon from native cellulose. Cellulose 2004;11(3,4):475-489.

[21] Innerlohinger J, Weber Hk, Kraft G. Aerocellulose: Aerogels and aerogel-like materials made from cellulose. Macromol Symp 2006;244:126-135.

[22] Guilminot E, Fischer F, Chatenet M, Rigacci A, Berthon-Fabry S, Achard P, Chainet E. Use of cellulose-based carbon aerogels as catalyst support for PEM fuel cell electrodes: Electrochemical characterization. J Power Sources 2007;166(1):104–111.

[23] Grzyb B, Hildenbrand C, Berthon-Fabry S, Bégin D, Job N, Rigacci A, Achard P. Functionalisation and chemical characterisation of cellulose-derived carbon aerogels. Carbon 2010;48(8):2297–2307.

[24] Rooke J, De Matos Passos C, Chatenet M, Sescousse R, Budtova T, Berthon-Fabry S, Mosdale R, Maillard F. Synthesis and properties of platinum nanocatalyst supported on cellulose-based carbon aerogel for applications in PEMFCs. J Electrochem Soc 2011;158(7):B779-B789.

[25] Amaral-Labat G, Grishechko LI, Szczurek A, Fierro V, Kuznetsov BN, Pizzi A, Celzard A. Highly mesoporous organic aerogels derived from soy and tannin. Green Chem 2012; 14(11): 3099-3106.

Controlling the Morphology of Carbon Gels
Control de la morfología de los geles de carbón

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Abstract

Carbon gels are unique porous carbons, which are typically obtained through the carbonization of resorcinol-formaldehyde gels. This material is practically an aggregate of nanometer-sized carbon particles. Nanopores, mostly in the size range of mesopores, exist between the particles. Smaller pores, micropores being the majority, also exist within the particles. Therefore, this material has a hierarchical pore system in which short micropores are directly connected to mesopores.

The precursor of carbon gels can be obtained through sol-gel transition. Therefore there is a high possibility that the morphology of the resulting carbon can be easily controlled using various molding methods. We have actually challenged the controlling of the morphology of carbon gels, and have succeeded in obtaining them in the form of disks, microspheres and microhoneycombs. Details of such carbon gels will be reported.

Resumen

Los geles de carbón son materiales porosos únicos que se obtienen normalmente mediante la carbonización de geles de resorcinol-formaldehído. Este material es prácticamente un agregado de parículas de carbono nanométricas. Los nanoporos, mayoritariamente en el intervalo de tamaño de los mesoporos, existen entre las partículas. Los poros más pequeños, mayoritariamente microporos existen también dentro de las partículas. Por tanto, este material tiene un sitema jerárquico de poros en el que los cortos microporos están directamente conectados a los mesoporos.

El precursor de los geles de carbon se puede obtener a través de una transición soil-gel. Por tanto hay alta posibilidad de que la morfología del carbón resultante se pueda controlar fácilmente usando diferentes métodos de moldeo. De hecho, hemos afrontado el reto de controlar la morfología de los geles de carbón y hemos tenido éxito al obtenerlos en forma de discos, microesferas y micro panales de abejas. Los detalles de estos geles de carbón se presentarán en este trabajo.

1. Introduction

Carbon gels are unique porous carbons which were introduced in the late 1980s by Dr. Pekala and his coworkers[1-3]. Carbon gels are practically an aggregate of carbon nanoparticles. The voids formed between the nanoparticles are in the mesopore size-range, so this material is widely renowned as a mesoporous carbon. Moreover, micropores exist within the nanoparticles. Therefore it can be said that this material has a hierarchical pore system of micropores and mesopores[4-6].

Carbon gels are usually synthesized through the following method [1-3]: First resorcinol is mixed with formaldehyde, and with the aid of a base catalyst such as sodium carbonate, substituted resorcinols are formed. Through polycondensation, colloidal particles are formed, and these particles coagulate and form a 3 dimensional network of particles which

is called a resorcinol-formaldehyde (RF) hydrogel. Carbon gels can be obtained by drying and carbonizing this material. In the drying process, special drying methods such as supercritical drying are typically used in order to suppress shrinkage and maintain the unique structure of RF hydrogels. We showed that a more economical drying method, freeze drying, can be used in place of supercritical drying [7, 8]. Microwave drying can also be used in limited cases [9, 10].

It is also well known that carbon gels have a high nanostructure controllability [5, 6]. For example, the size of the mesopores of carbon gels depends on the size of the nanoparticles which consist it, and the size of such nanoparticles can be controlled by the catalyst concentration of the starting solution, which means that the size of the mesopores can also be controlled indirectly by adjusting this concentration. Moreover, the volume of micropores can be easily increased using conventional activation methods without hardly affecting the size and volume of mesopores. Therefore if a method to give carbon gels a desired morphology without affecting its porous properties can be established, unique porous carbons, the micro-, meso- and macro-scale structures of which can be independently controlled to best match their usages will be obtained. In this report, the attempts our group has made to obtain such carbons will be introduced.

2. Disks

As the precursor of carbon gels, RF gels, are usually obtained through sol-gel transition, we expected that it would be quite easy to mold them into a simple disk form without using any binders. To verify this possibility, first starting solutions with typical compositions were prepared, and then they were poured into teflon molds of different thicknesses. After sol-gel transition occurred, the resulting RF hydrogels were released from the molds, and were subsequently freeze-dried and carbonized yielding carbon gel disks [11].


Figure 1. Typical disks obtained in this work.
Figura 1. Discos típicos obtenidos en este trabajo.

Fig. 1 shows a photograph of typical disks obtained through this method. The disk on the left side is an RF hydrogel, the one in the middle an RF cryogel, and the one on the right, a carbon cryogel. Significant shrinkage occurred during drying and carbonization, but distorted disks or disks with cracks were hardly obtained, which indicates that shrinkage occurred fairly isotropically. Fig. 2 shows how the shrinkage ratio depends on the catalyst concentration. Isotropic

shrinkage can also be confirmed from this graph. Therefore it can be concluded that monolithic carbon gel disks can easily be obtained through this method.
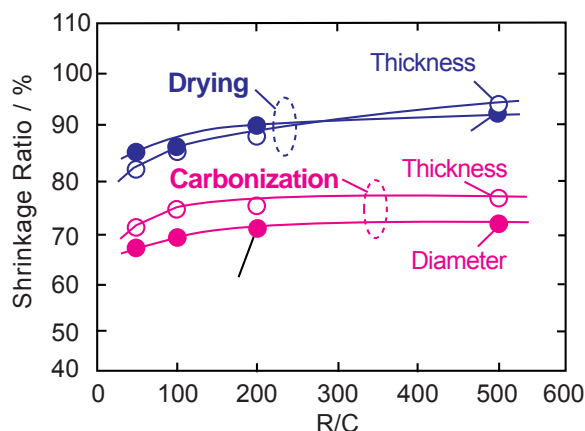
Figure 2. Shrinkage ratio of the obtained disks.
**Figura 2.** Relación de encogimiento de los discos obtenidos.

3. Microspheres

The next morphology to be explained about is microspheres. As the initial source of carbon gels is an aqueous solution, we assumed that they could be molded into microspheres through inverse emulsion polymerization. In order to verify this possibility, first a typical starting solution was prepared and was kept at a constant temperature T_{gel}, and just before the solution was about to transform to a gel, it was dispersed into a mixture of cyclohexane and SPAN80, a surfactant which was maintained at the same temperature T_{gel}. After agitating the resulting emulsion for 5 to 10 h, RF hydrogel microspheres were formed. Carbon gel microspheres were obtained by freeze drying and carbonizing these microspheres [12, 13].

Fig.3 shows SEM micrographs of typical microspheres obtained through this method. It can be seen that microspheres with diameters in the range of 5 to about 30 micrometers were obtained. The inner parts of the microspheres were found to be formed by nanoparticles, like typical carbon gels, but interestingly, macropores or large mesopores could not be found at the surface of the microspheres.

So next we analyzed the surface structure of the microspheres through the so-called molecular probe method. Fig. 4 shows the results where the micropore volume accessible to the probe molecule is plotted as a function of the minimum dimension of the probe molecule. It was confirmed that when T_{gel} was low and the carbonization temperature (T_{pyro}) was high, the surfaces of the microspheres tended to become

microporous, and in certain cases, microspheres in which even carbon dioxide cannot penetrate into could be obtained. This indicates that microspheres having mesoporous inner parts and surfaces with unique properties can be obtained through this method. Therefore, this method not only enables the synthesis of carbon gel microspheres, but also allows the controlling of the nanostructure of the surface of the resulting microspheres.
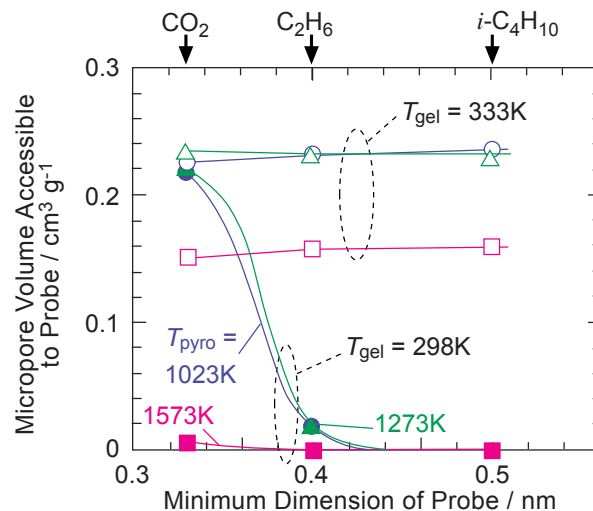

Figure 4. Estimation of inlet size of the surface pores of typical carbon gel microspheres.
Figura 4. Estimación del tamaño de entrada de los poros superficiales de microesferas típicas de geles de carbón.

4. Microhoneycombs

Porous carbons are usually synthesized in the form of particles, therefore the size of the particle determines the length of the diffusion paths within it. This means that the particle size must be small enough to ensure a high accessibilty to their inner parts. However as the voids formed between the particles provide paths or macropores to the material, the size of the particles also determines the resistance they cause when fluids are passed through them. So the particle size must be large to avoid significant resistance to flows. This means that a high accessibility to their inner part is a complete trade-off with a low resistance to flows. Indeed, there are many cases in which large particles are used just to avoid severe pressure drops. This dilemma can be avoided by changing the morphology of the material.

A microhoneycomb, which is a monolith having straight and aligned channels which sizes are in the micrometer range, and which channels are formed by nanoporous walls which thicknesses are also in the micrometer range is thought to be one example

a) Microspheres   b) Cross-Section   c) Surface
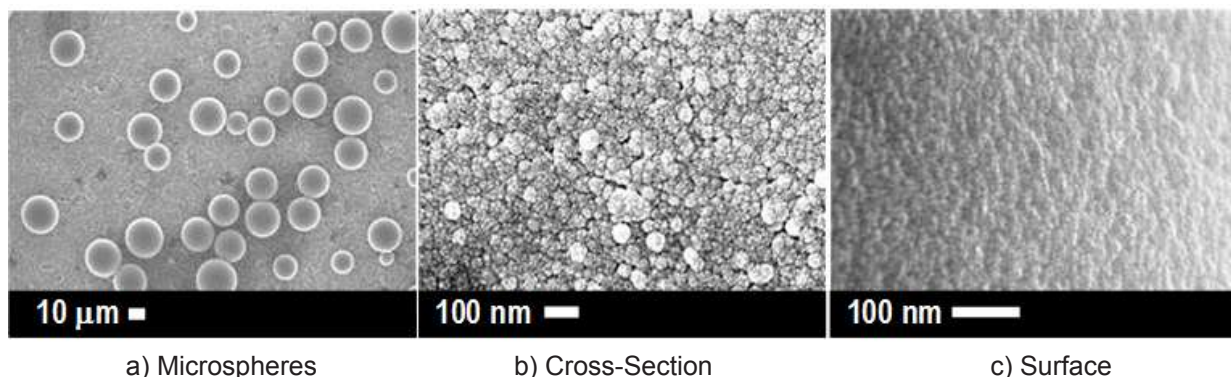
Figure 3. SEM micrograph of typical microsphere samples.
Figura 3. Microfotografía SEM de muestras de microesferas típicas.

of an ideal morphology. As the thickness of the walls is in the micrometer range, the diffusion paths within them are extremely short, and as the channels are straight and aligned, the resistance when fluids are passed through this monolith can be minimized. It was difficult, if not impossible to synthesize such microhoneycombs using conventional methods, but we found that such microhoneycombs can be synthesized through the sol-gel method using ice crystals as the template [14-16].

In the developed method, first a hydrogel precursor is prepared, and then this hydrogel is dipped at a constant rate into a cold bath which temperature was maintained below the freezing temperature of the gel. This freezing process is called unidirectional freezing. During this freezing process, an array of needle shaped ice crystals appears within the hydrogel and elongates in the freezing direction. This causes the hydrogel to be condensed between the growing ice crystals. So, a monolithic microhoneycomb as shown here could be obtained by thawing and drying the completely frozen material. As ice crystals act as the template in this method, we named it the ice templating method [14-16]. This method was originally developed using a silica hydrogel, but considering the similarity of hydrogels, we thought that this method will also be applicable to resorcinol-formaldehyde hydrogels.

We actually tested this possibility [17, 18]. First a typical starting solution was prepared, and through sol-gel polycondensation, rod type RF hydrogels were formed. As the catalyst was thought to disturb the growth of ice crystals, the hydrogels were thoroughly washed with distilled water. Then the samples were dipped at a constant rate into a cold bath. The obtained samples were aged, freeze-dried and carbonized yielding monolithic carbon gels.
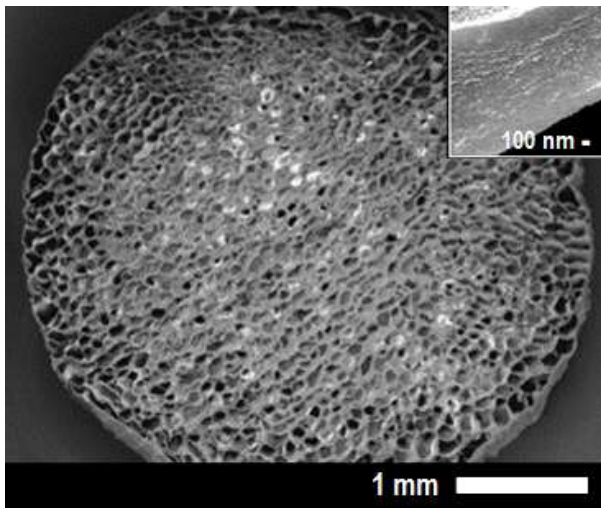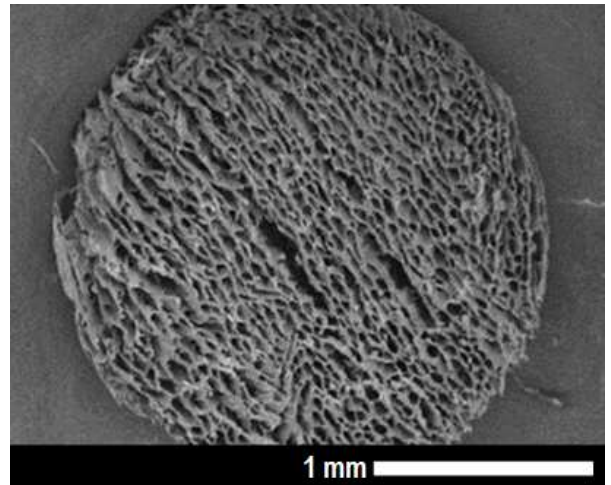

Figure 5. Cross sectional SEM image of a typical monolithic RF gel microhoneycomb.
Figura 5. Imagen SEM de la sección transversal de un típico gel RF monolítico en panal de abeja.

Figure 5 shows a SEM micrograph of the cross section of a typical sample obtained in this work. It can be noticed that the RF gel was successfully molded into the form of a microhoneycomb. Nanoparticles which are the origin of mesoporosity can be clearly distinguished in the enlarged micrograph of the honeycomb wall which indicates that the nanostructure of the gels is not altered by freezing. This was also confirmed through adsorption experiments. Therefore a mesoporous RF gel was

successfully obtained.

Figure 6. Cross sectional SEM image of a typical monolithic carbon gel microhoneycomb microhoneycomb.
Figura 6. Imagen SEM de la sección transversal de un típico gel monolítico de carbón en panal de abeja.

Next, we attempted to carbonize the RF gel microhoneycommb. Figure 6 shows a cross sectional SEM micrograph of a typical sample after carbonization. It can be noticed that although slight shrinkage occurs, the sample maintains its unique morphology. Therefore, it can be concluded that carbon gels having a unique microhoneycomb morphology can be obtained through ice templating.

5. Concluding Remarks

As was introduced in this article, we found that it is very easy to control the morphology of carbon gels. Therefore, not only the micro- and meso-structures, but also the macro-structure of this unique material can be tuned to best match its application. We are now investigating applications which can make full use of such carbon gels with controlled morphologies, and hope to report the results in the near future.

6. References

[1] Pekala RW. Organic aerogels from the polycondensation of resorcinol with formaldehyde, J. Mater. Sci. 1989; 24: 3221-3227.

[2] Pekala RW, Kong FM. A synthetic route to organic aerogels - mechanism, structure and properties. J. de Physique Coll. Suppl. 1989; 50: C4-33-40.

[3] Pekala RW. Synthetic control of molecular structure in organic aerogels. Mater. Res. Soc. Proc. 1990; 171: 285-292.

[4] Ruben GC, Pekala RW, Tillotson TM, Hrubesh LW. Imaging aerogels at the molecular-level. J. Mater. Sci. 1992; 27(16): 4341-4349.

[5] Yamamoto T, Yoshida T, Suzuki T, Mukai SR, Tamon H. Dynamic and static light scattering study on the sol-gel transition of resorcinol-formaldehyde aqueous solution. J. Colloid Interface Sci.2002; 245(2): 391-396.

[6] Yamamoto T, Mukai SR, Endo A, Nakaiwa M, Tamon H. Interpretation of structure formation during the sol-gel transition of a resorcinol-formaldehyde solution by population balance. J. Colloid Interface Sci. 2003; 264(2): 532-537.

[7] Tamon H, Ishizaka H, Yamamoto T, Suzuki T. Freeze drying for preparation of aerogel-like carbon. Dry. Technol. 2001; 19(2): 313-324.

[8] Yamamoto T, Nishimura T, Suzuki T, Tamon H. Control of mesoporosity of carbon gels prepared by sol-gel polycondensation and freeze drying. J. Non-Cryst. Solids 2001; 288(1-3): 46-55.

[9] Tamon H, Mukai SR, Nishihara H, Yoshida T, Yamamoto T, Tonanon N, Tanthapanichakoon W. Synthesis of Mesoporous Carbon Gels using Microwave Drying. Carbon 2003 (Oviedo).

[10] Tonanon N, Wareenin Y, Siyasukh A, Tanthapanichakoon W, Nishihara H, Mukai SR, Tamon H. Preparation of Resorcinol Formaldehyde (RF) Carbon Gels: Use of Ultrasonic Irradiation Followed by Microwave Drying. J.Non-Cryst. Solids 2006; 352(52-54): 5683-5686.

[11] Mukai SR, Kambara H, Hasegawa T, Tamon H. Binder-free Synthesis of Carbon Cryogel Tablets and their Performance as Electrodes for Electric Double Layer Capacitors. Carbon 2005 (Gyeongju).

[12] Yamamoto T, Sugimoto T, Suzuki T, Mukai SR, Tamon H. Preparation and characterization of carbon cryogel microspheres. Carbon 2002; 40(8): 1345-1351.

[13] Yamamoto T, Endo A, Ohmori T, Nakaiwa M, Mukai SR, Tamon H. Effect of drying method on gas adsorption characteristics of carbon gel microspheres. Dry. Technol. 2005; 23(9-11): 2119-2129.

[14] Mukai SR, Nishihara H, Tamon H. Porous properties of silica gels with controlled morphology synthesized by unidirectional freeze-gelation. Micropor. Mesopor. Mat. 2003; 63(1-3) 43-51.

[15] Mukai SR, Nishihara H, Tamon H. Formation of monolithic silica gel microhoneycombs (SMHs) using pseudosteady state growth of microstructural ice crystals. Chem. Commun. 2004; (7): 874-875.

[16] Nishihara H, Mukai SR, Yamashita D, Tamon H. Ordered macroporous silica by ice templating. Chem. Mater. 2005; 17(3): 683-689.

[17] Nishihara H, Mukai SR, Tamon H. Preparation of resorcinol-formaldehyde carbon cryogel microhoneycombs. Carbon 2004; 42(4): 899-901.

[18] Mukai SR, Nishihara H, Yoshida T, Taniguchi K-I, Tamon H. Morphology of resorcinol-formaldehyde gels obtained through ice-templating. Carbon 2005; 43(7): 1563-1565.

Carbon xerogels for catalytic applications
Xerogeles de carbón para aplicaciones catalíticas

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Abstract

The synthesis and properties of carbon xerogels are briefly described, emphasizing the methods used for tuning of their surface chemistry and textural properties, in order to design catalysts suitable for specific applications.

Resumen

La síntesis y las propiedades de los xerogeles de carbón han sido descritas brevemente, incidiendo en los métodos de preparación usados para la modificación de las propiedades texturales y la química superficial, con el objetivo de diseñar catalizadores adecuados para aplicaciones específicas.

1. Introduction

The versatility of carbon materials in catalysis is well documented in the literature, and has been the subject of a recent review [1]. Activated carbons and carbon blacks are the carbon materials which have traditionally been used in catalysis, either as catalyst carriers or as catalysts on their own. One of the drawbacks of activated carbons is that they are essentially microporous materials, while mesoporous materials would be advantageous for catalysis in order to minimize diffusion limitations and catalyst deactivation. However, various types of nanostructured carbon materials have been developed in recent years which offer quite interesting properties for catalytic applications. In particular, carbon gels can be produced by carbonization of organic gels obtained by the sol–gel polycondensation of organic monomers such as resorcinol and formaldehyde [2]; they are designated as aerogels, xerogels or cryogels according to the method used for drying the aqueous organic gels (supercritical drying, conventional drying and freeze drying, respectively). Carbon gels are materials of high porosity and surface area, controllable pore size, and can be shaped in various forms for practical applications (such as monoliths, thin films and pellets). By adequate tuning of their surface chemistry and textural properties, it is possible to design catalysts suitable for specific applications. Previous reviews focused mainly on metal-doped carbon gels [3,4], while here we will concentrate on the development of carbon xerogels as catalysts on their own, highlighting some of the most recent results reported.

2. Synthesis and properties

Similarly to any other solid catalyst, the catalytic performance of a carbon xerogel is determined by the nature, concentration and accessibility of its active sites, and these factors depend both on the physical and the chemical properties of the material.

Figure 1 represents schematically the different steps in the synthesis of a carbon xerogel. The textural properties of the materials obtained are largely determined by the synthesis conditions, and various parameters can be modified in order to optimize the process, including the formaldehyde/resorcinol ratio, type and amount of catalyst, curing temperature, addition of other monomers (for instance, cresol), and drying procedure.
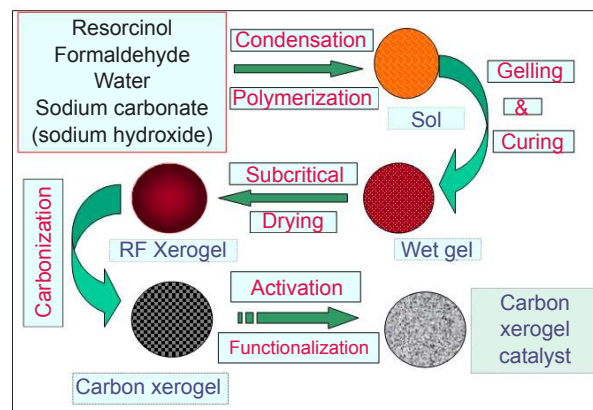

Figure 1. Steps in the synthesis of a carbon xerogel catalyst.
Figura 1. Etapas de síntesis de un catalizador de xerogel de carbón.

The method of drying the aqueous organic gel is one of the key factors for the synthesis of a mesoporous carbon. Indeed, it is necessary to prevent the collapse of the 3D network which may occur as result of the strong capillary forces of water, and this may be accomplished by solvent exchange. One recipe which is commonly used to produce carbon xerogels in our Laboratory is the following: formaldehyde/resorcinol ratio = 2.0; gelling and curing step performed over a period of three days (at 30, 50, and 75 ºC, one day each); water removed by sequential exchange with acetone (initially containing 5% acetic acid) and cyclohexane, followed by drying overnight at 80 ºC; carbonisation at 800 ºC (ramp @ 3 ºC min^{-1}) under nitrogen flow (100 cm^3 min^{-1}, 6 h). But in particular, the textural properties are most sensitive to the pH used in the sol-gel processing [5]. As an example, Figure 2 presents data for two carbon xerogels with quite different textural properties which were synthesized under similar conditions, except for the pH (adjusted with NaOH solution) which was 5.6 (sample 37CXUA) or 6.0 (sample 39CXUA). Figure 2a) shows the nitrogen adsorption isotherms, and Figure 2b) the corresponding mesopore size distributions. The BET surface areas of these samples are very similar (653 m^2/g for sample 37CXUA and 645 m^2/g for sample 39CXUA), but the average mesopore diameters are quite different: 16 nm for sample 37CXUA and 4 nm for sample 39CXUA.

Carbon xerogels (CX) have a graphitic structure, and so the active sites are expected to be found mainly at the edges of the graphene layers, where the unsaturated carbon atoms may chemisorb oxygen, water, or other compounds like ammonia, originating surface groups such as those represented schematically in Figure 3. Similar surface groups can be formed on basal plane defects. In addition, the π electron system of the basal planes contributes to the carbon basicity, affecting its adsorption and catalytic properties [6,7].

Both gas phase and liquid phase treatments can be used to generate oxygen groups on the surface of
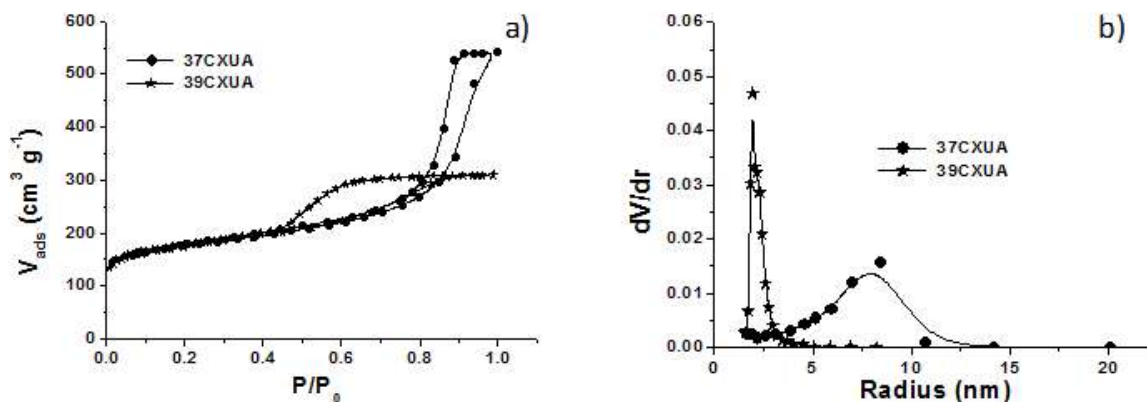
Figure 2. Textural properties of two carbon xerogels synthesized at different pH: a) nitrogen adsorption isotherms at 77 K; b) mesopore size distributions.
Figura 2. Propiedades texturales de dos xerogeles de carbón sintetizados a distintos valores de pH: a) isotermas de adsorción de N_2 a 77 K, b) distribución de tamaño de mesoporos.

carbon xerogels [8,9], while heating under inert atmosphere may be used to selectively remove some of these functions. Typical gas-phase activation consists of heating the CX sample up to a temperature in the range 350-450 ºC using 5% O_2 (diluted in N_2) with adequate duration of the isothermal heating period in order to achieve the desired burn-off (BO).
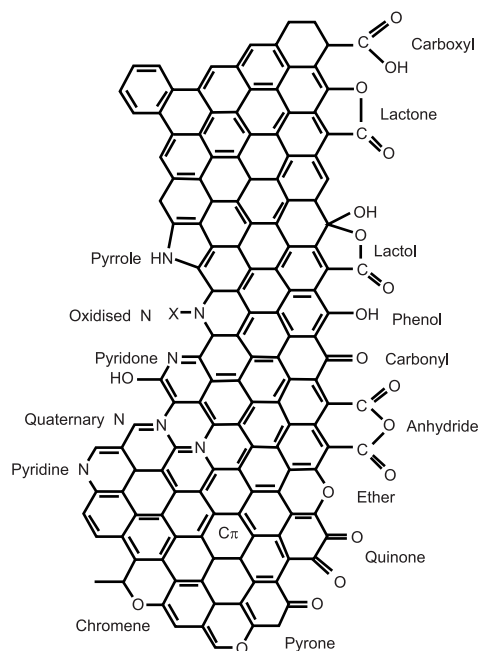
Figure 3. Nitrogen and oxygen surface groups on carbon. Reprinted from reference [7] with permission from Elsevier.
Figura 3. Grupos funcionales de nitrógeno y oxígeno en materiales de carbón. Reproducido de [7] con permiso de Elsevier.

Both the mesopore surface area and the micropore volume are expected to increase upon oxidation, as a result of the widening of existing pores and/or creation of new ones by selective gasification of structural components, or by the opening of some of the previously inaccessible pores [8]. On the other hand, liquid phase oxidation with nitric acid can be performed on a Soxhlet, with different acid concentrations and duration of the treatment, followed by washing with distilled water, and then drying at 110 °C [9]. Alternatively, a recently developed hydrothermal procedure can be used, allowing for a finer control of the extent of surface oxidation [10]. The textural changes are negligible when using low concentrations of nitric acid, but can be of the same

order of magnitude as those induced by gas phase oxidation when using higher concentrations.

The nature and concentration of the surface oxygen groups can be assessed by temperature-programmed desorption with mass spectrometry (TPD-MS), a method which has been improved in our group [11,12]. Upon heating, carboxylic acids and lactones release CO_2, while phenol and carbonyl groups release CO; carboxylic anhydrides decompose by releasing both CO and CO_2. As an example, Figure 4 shows the TPD spectra obtained with a carbon xerogel (sample 28CX-UA, average mesopore diameter = 28 nm) oxidised by two different methods, namely: treatment with HNO_3 7M in a Soxhlet, under reflux, for 3 hours (sample 28CX-NA), and oxidation in the gas phase with a mixture of 5% O_2 in N_2, at 415ºC for 30 hours, to a burn-off of 17% (sample 28CX-AR) [9]. The TPD profiles of nitric acid and air activated samples are quite different, but both show large increases in the amounts of evolved CO and CO_2 in comparison to the original sample. Deconvolution of the CO and CO_2 spectra can provide reliable estimates of the amounts of each type of oxygen group [11,12]. Activation by air creates mainly phenol and carbonyl groups. Nitric acid activation is most suitable to introduce carboxylic groups, but large amounts of phenol and carbonyl groups are also generated.

Nitrogen doping can be accomplished by the introduction of a nitrogen-containing precursor in the organic xerogel, such as urea and melamine [13,14], or by post-treatments with nitrogen compounds, such as ammonia, urea or amines. Different types of surface nitrogen groups can be obtained, as shown in Figure 3, which can be determined by deconvolution of XPS spectra [13-15]. The additional electrons provided by nitrogen increase the surface basicity. Moreover, the presence of nitrogen atoms in the carbon matrix, particularly in the case of pyridinic (N6) and pyrrolic (N5) groups, has been shown to enhance the catalytic activity of carbon materials in oxidation reactions [16,17].

3. Catalysis with carbon xerogels

Heterogeneous catalysts are generally classified into three groups, namely metals, non-stoichiometric metal oxides, and acids, each group showing catalytic activity for a defined set of reactions [18]. Interestingly, carbon materials can be active catalysts for reactions which are typical of all three classes, such as dehydrogenations, oxidations and reductions, and alkylation and dehydration, a fact that was recognized
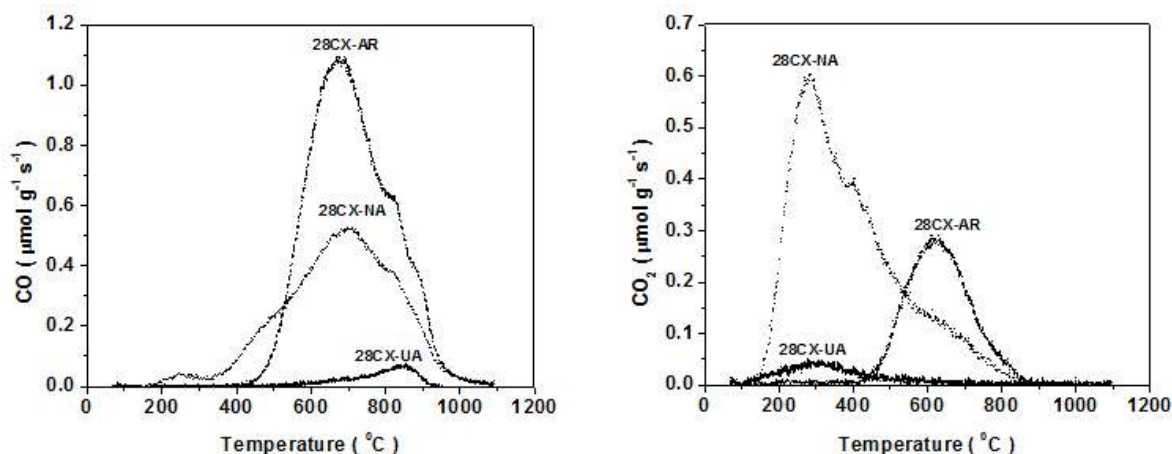
Figure 4. CO and CO$_2$ TPD spectra of activated and original carbon xerogel samples: original sample (28CX-UA); sample treated in nitric acid (28CX-NA); and sample treated in oxygen (28CX-AR). Adapted from reference [9]..

Figura 4. Perfiles de desorción térmica programada de CO y CO$_2$ para las muestras de xerogeles de carbón activados y originales: muestra original (28CX-UA); muestra tratada con ácido nítrico (28CX-NA); y muestra tratada con oxígeno (28CX-AR). Adaptada de [9].

long time ago [19]. The versatility of carbon as a catalyst [7, 20] stems from the rich variety of surface functional groups (Figure 3) which can act as active sites for different types of reactions. Selected examples are reviewed in the next sections, highlighting some of the recent results obtained in our group.

3.1 Carbon xerogels as acid catalysts

Acidic surface oxygen groups include carboxylic acids and anhydrides, lactones or lactols, and phenols (Figure 3). Previous reports with oxidized activated carbons showed that carboxylic acid groups are responsible for their catalytic activity in the dehydration of alcohols [21, 22]. But, in general, stronger active acid sites are required to catalyze other reactions, such as alkylations, esterifications, acetalizations and hydrolyses. Efficient acid catalysts for these reactions can be obtained by functionalization with sulfonic acid groups [23]. For instance, the activity of carbon xerogels treated with nitric acid and with sulfuric acid was recently assessed in the ring opening reaction of epoxides by alcohols and amines [24]. The introduction of sulfonic acid groups (CX treated with H$_2$SO$_4$) provided for the most active catalyst, the conversion of styrene oxide with ethanol reaching nearly 100 % at room temperature after 30 minutes, with a selectivity of 97 % towards 2-ethoxy-2-phenylethanol. However, similar performances were observed with both carbon xerogels in the reaction of styrene oxide with aniline [24].

Preliminary results for the esterification of acetic acid with ethanol were obtained in our group [25], using two different carbon xerogel catalysts: CX-HNO$_3$ (treated with HNO$_3$ 5M; acidity = 1.58 mmol g^{-1}) and CX-H2SO4 (treated with concentrated H$_2$SO$_4$; acidity = 1.91 mmol g^{-1}). As expected, the sample functionalized with sulphuric acid was the most active, with a yield of ethyl acetate of 52 % after 12 h, while only 13 % was obtained with sample CX-HNO$_3$ (T=70 °C; molar ratio ethanol/acetic acid=10; 0.2 g of catalyst). In order to establish a correlation with the concentration of the active sites, three samples were prepared with different amounts of sulfonic acid groups. Two samples were functionalized with concentrated H$_2$SO$_4$ at 150 ºC for 6 hours, but with different ratios of acid to solid (150 mL and 20 mL H$_2$SO$_4$ per gram of CX). The concentrations of sulfonic acid groups, determined by XPS, were 994 and 591 μmol g^{-1}, respectively. A third sample was obtained from the first one by heat treatment in helium at 250 ºC ([SO$_3$H] = 78 μmol g^{-1}). Figure 5 shows that the catalytic activity correlates nicely with the concentration of surface sulfonic acid groups.
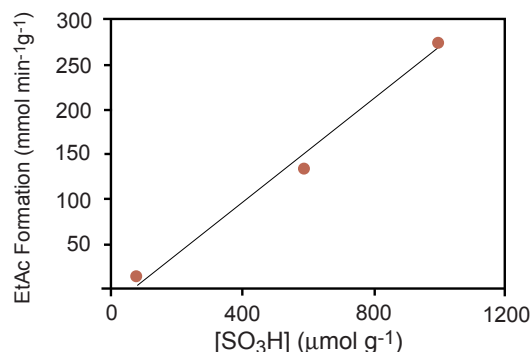
Figure 5. Correlation between the catalytic activity of carbon xerogels for the esterification of acetic acid with ethanol and the concentration of sulfonic acid groups.

Figura 5. Correlación entre la actividad catalítica de los xerogeles de carbón para la esterificación de ácido acético con etanol y la concentración de grupos sulfónicos.

3.2 Carbon xerogels as oxidation catalysts

The oxidative dehydrogenation of hydrocarbons (ODH) is one of the most interesting applications of carbon materials as catalysts. It has been established that the reaction involves the quinone-hydroquinone groups [26], as shown in Figure 6.

The active sites are the quinone groups (pairs of carbonyl groups at the edges of the carbon layers connected by a resonance structure), which are converted into hydroquinones, and regenerated back to the original sites by oxygen. This reaction has been intensively studied using activated carbons and carbon nanotubes as catalysts [7,20,26-28]. We have recently started to investigate the use of carbon xerogels as catalysts for the ODH, but no results have been reported so far.

Another reaction which has been carried out with carbon xerogel catalysts is the oxidation of NO [29]. This is an interesting route for the control of NO emissions, since the NO$_2$ formed can be subsequently removed by absorption in water. The NO conversions are quite high, showing that carbon xerogels are efficient catalysts for NO oxidation. A

conversion of 98 % was obtained at room temperature with a concentration of NO of 1000 ppm and 10 % of O_2. It is assumed that oxygen is first chemisorbed on the active sites, reacting then with NO to form NO_2, as schematically shown in Figure 7.
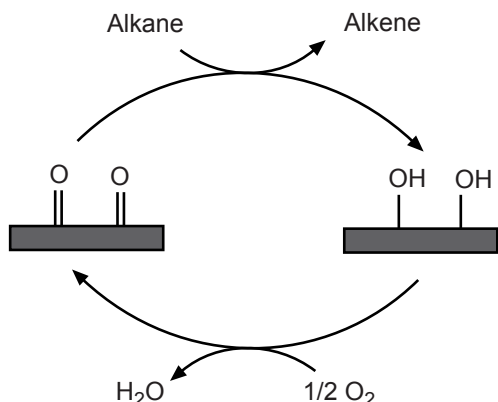
Figure 6. Catalytic cycle proposed for the oxidative dehydrogenation of hydrocarbons on carbon materials. Adapted from [7].
Figura 6. Mecanismo catalítico propuesto para la deshidrogenación oxidativa de hidrocarburos en materiales de carbón. Adaptada de [7].

The incorporation of nitrogen was found to improve significantly the catalytic activity of the carbon xerogels [29], the rate of NO oxidation increasing with the concentration of pyridine and pyrrole groups, as shown in Figure 8, in agreement with theoretical predictions [16].
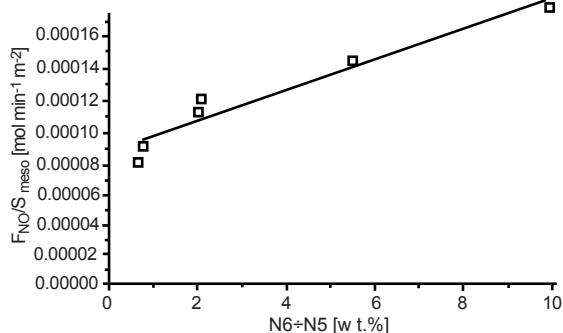
Figure 8. Rate of NO oxidation versus the concentration of pyridine and pyrrole groups.
Figura 8. Velocidad de oxidación de NO en función de la concentración de los grupos piridina y pirrol.

3.3 Carbon xerogels as catalysts for Advanced Oxidation Processes

Advanced oxidation processes (AOPs) is the collective designation of a set of chemical treatments designed to remove (mainly) organic pollutants from water and waste water by oxidation via highly reactive hydroxyl radicals. Among others, oxygen (or air), hydrogen peroxide or ozone can be used as oxidizing agents, the processes being called wet air oxidation (WAO), wet peroxide oxidation (WPO) and ozonation, respectively. Various types of catalysts have been used in these processes, but it has been shown recently that carbon materials without any supported metal or oxide phase can be highly active for the complete mineralization of the organic pollutants or their intermediate oxidation products into CO_2 and inorganic ions [7,20]. In this way, the costs associated with the use of expensive metal or oxide catalysts, and the danger of leaching of these catalytic phases into the effluents, are avoided.

We have already reported on the performance of carbon xerogel catalysts for the wet air oxidation of aniline [30] and nitro-aromatic compounds [31], for the wet peroxide oxidation of dyes [32], and for the ozonation of different types of dyes and also of oxalic acid, a common end-product of the oxidation of dyes which is refractory to non-catalytic ozonation [33].

Figure 9 presents data for the total organic carbon (TOC) removal during the ozonation of a dye (C.I. Acid Blue 113) catalyzed by carbon xerogels [33]. Three carbon xerogels with an average mesopore diameter of 37 nm were used as catalysts, namely the original material (XC0, S_{meso} = 329 m^2 g^{-1}, pH_{pzc} = 7.8), a HNO_3 oxidized sample (XC1, S_{meso} = 440 m^2 g^{-1}, pH_{pzc} = 3.1), and a thermally treated sample (XC2, S_{meso} = 252 m^2 g^{-1}, pH_{pzc} = 8.7). The results clearly show that the best performance is achieved with the basic carbons: XC2 > XC0 > XC1.
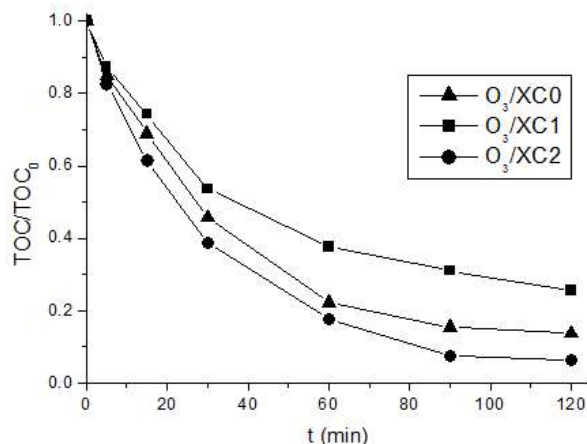

Figure 9. Normalized TOC removal in the ozonation of C.I. Acid Blue 113 at room temperature with carbon xerogel catalysts of different surface chemistry. Adapted from [33].
Figura 9. Eliminación de COT mediante la ozonización de C.I. Azul ácido 113 con xerogeles de carbón con distinta química superficial a temperatura ambiente. Adaptada de [33].

It should be stressed here that the removal of colour, that is, the degradation of the dye, is very fast even without a catalyst; thus, complete decolourisation was achieved by ozone at room temperature in less than 15 minutes [33]. However, single ozonation cannot remove most of the TOC in solution, showing that some of the dye degradation products still remain in solution. Mineralization degrees close to 100% require the presence of a catalyst, and carbon xerogels with a basic surface are capable of approaching this performance.

The AOPs reaction mechanisms are complex, and may involve a combination of homogeneous and
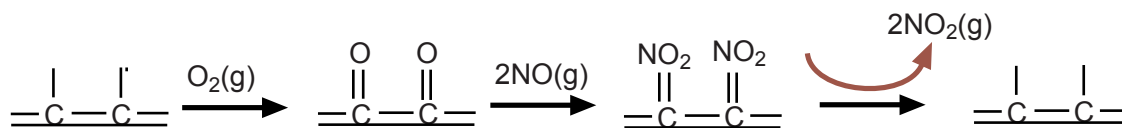
Figure 7. Proposed steps in the oxidation of NO on carbon xerogels.
Figura 7. Etapas propuestas en la oxidación de NO en xerogeles de carbón.

heterogeneous steps. In the case of ozonation, it is accepted that the carbon catalyst accelerates the decomposition of ozone. The delocalized π-electron system, or the surface basic groups (pyrone, chromene, pyrrole, cf. Figure 3) have been identified as the active sites for decomposition of ozone, leading to the formation of free radical species in solution, such as $HO^{\cdot}$, and also of surface free radicals ($O^{-\cdot}$, $O_2^{-\cdot}$, $O_3^{-\cdot}$). Thus, both pathways (homogeneous and heterogeneous) can be responsible for the oxidation of the organic compounds [34].

4. Conclusion

The physical and chemical properties of carbon xerogels can be easily modified by selecting the synthesis conditions and/or by suitable post-treatments, so that these materials can perform adequately as metal-free catalysts for a large variety of reactions, both in the liquid or in the gas phase. Selected examples from recent reports were reviewed in this paper, highlighting the performance of carbon xerogels as solid acid catalysts and also as oxidation catalysts. Further advances in the field require the proper identification and quantification of the active sites involved in each application.

Acknowledgments

References

[1] Serp P, Figueiredo JL (eds.). Carbon Materials for Catalysis. John Wiley & Sons, 2009.

[2] Pekala RW. Organic aerogels from the polycondensation of resorcinol with formaldehyde. J. Mater. Sci.1989; 24: 3221-3227.

[3] Moreno-Castilla C, Maldonado-Hódar FJ. Carbon aerogels for catalysis applications: An overview. Carbon 2005; 43: 455–465.

[4] Moreno-Castilla C. Carbon Gels in Catalysis. In: Philippe Serp and José Luís Figueiredo Eds. Carbon Materials for Catalysis. John Wiley & Sons, 2009 p. 373-399.

[5] Job N, Pirard R, Marien J, Pirard JP. Porous carbon xerogels with texture tailored by pH control during sol–gel process. Carbon 2004; 42: 619-628.

[6] Boehm HP. Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon 1994; 32: 759-769.

[7] Figueiredo JL, Pereira MFR. The role of surface chemistry in catalysis with carbons. Catal. Today 2010; 150: 2-7.

[8] Samant PV, Gonçalves F, Freitas MMA, Pereira MFR, Figueiredo JL. Surface activation of a polymer based carbon. Carbon 2004; 42: 1321-1325.

[9] Mahata N, Pereira MFR, Suárez-García F, Martínez-Alonso A, Tascón JMD, Figueiredo JL. Tuning of texture and surface chemistry of carbon xerogels. J. Colloid Interface Sci. 2008; 324: 150–155.

[10] Silva AMT, Machado BF, Figueiredo JL, Faria JL. Controlling the surface chemistry of carbon xerogels using HNO3 hydrothermal activation, Carbon 2009; 47: 1670-1679.

[11] Figueiredo JL, Pereira MFR, Freitas MMA, Órfão JJM. Modification of the surface chemistry of activated carbons. Carbon 1999; 37: 1379-1389.

[12] Figueiredo JL, Pereira MFR, Freitas MMA, Órfão JJM. Characterization of active sites on carbon catalysts. Ind. Eng. Chem. Res. 2007; 46: 4110-4115.

[13] Gorgulho HF, Gonçalves F, Pereira MFR, Figueiredo JL. Synthesis and characterization of nitrogen-doped carbon xerogels. Carbon 2009; 47: 2032-2039.

[14] Pérez-Cadenas M, Moreno-Castilla C, Carrasco-Marín F, Pérez-Cadenas AF. Surface Chemistry, Porous Texture, and Morphology of N-Doped Carbon Xerogels. Langmuir 2009; 25: 466-470.

[15] Lahaye J. The chemistry of carbon surfaces. Fuel 1998; 77: 543-548.

[16] Strelko VV, Kuts VS, Thrower PA. On the mechanism of possible influence of heteroatoms of nitrogen, boron and phosphorus in a carbon matrix on the catalytic activity of carbons in electron transfer reactions. Carbon 2000; 38: 1499-1503.

[17] Stöhr B, Boehm H, Schlögl R. Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate. Carbon 1991; 29: 707-720.

[18] Bond GC. Catalysis by Metals. Academic Press, NY. 1962.

[19] Coughlin RW. Carbon as adsorbent and catalyst. Ind. Eng. Chem. Prod. Res. Dev. 1969; 8: 12-23.

[20] Figueiredo JL, Pereira MFR. Carbon as Catalyst, In: Philippe Serp and José Luís Figueiredo Eds. Carbon Materials for Catalysis. John Wiley & Sons, 2009 p. 177-217.

[21] Moreno-Castilla C, Carrasco-Marin F, Parejo-Perez C, Ramon MVL. Dehydration of methanol to dimethyl ether catalyzed by oxidized activated carbons with varying surface acidic character. Carbon 2001; 39: 869-875.

[22] Szymanski GS, Karpinski Z, Biniak S, Swiatkowski A. The effect of the gradual termal decomposition of surface oxygen species on the chemical and catalytic properties of oxidized activated carbon. Carbon 2002; 40: 2627-2639.

[23] Budarin VL, Clark JH, Luque R, Macquarrie DJ. Versatile mesoporous carbonaceous materials for acid catalysis. Chem. Commun. 2007; 634-636.

[24] Matos I, Neves PD, Castanheiro JE, Perez-Mayoral E, Martin-Aranda R, Duran-Valle C, Vital J,

Rego AMB, Fonseca IM. Mesoporous carbon as an efficient catalyst for alcoholysis and aminolysis of epoxides. Appl. Catal. A: General 2012; 439-440: 24-30.

25 Figueiredo JL, Rocha RP, Pereira MFR. Carbon, a versatile catalyst. Carbon2012, The Annual World Conference on Carbon, June 17-22, 2012. Krakow, Poland.

26 Pereira MFR, Órfão JJM, Figueiredo JL. Oxidative dehydrogenation of ethylbenzene on activated carbon catalysts: 1- Influence of surface chemical groups. Appl.Catal.A: General 1999; 184: 153-160.

27 Zhang J, Liu X, Blume R, Zhang A, Schlögl R, Su DS. Surface-modified carbon nanotubes catalyze oxidative dehydrogenation of n-butane. Science 2008; 322: 73-77.

28 Zhang J, Su DS, Zhang A, Wang D, Schlögl R, Hébert C. Nanocarbon as robust catalyst: Mechanistic insight into carbon-mediated catalysis. Angew. Chem. Int. Ed. 2007; 46: 7319-7323.

29 Sousa JPS, Pereira MFR, Figueiredo JL. NO oxidation over nitrogen doped carbon xerogels. Applied Catalysis B: Environmental 2012; 125: 398–408.

30 Gomes HT, Machado BF, Ribeiro A, Moreira I, Rosário M, Silva AMT, Figueiredo JL, Faria JL. Catalytic properties of carbon materials for wet oxidation of aniline. Journal of Hazardous Materials 2008; 159: 420-426.

31 Apolinário AC, Silva AMT, Machado BF, Gomes HT, Araújo PP, Figueiredo JL, Faria JL. Wet Air Oxidation of Nitro-Aromatic Compounds: Reactivity on Single- and Multi-Component Systems and Surface Chemistry Studies with a Carbon Xerogel. Appl. Catal. B: Environmental 2008; 84: 75-86.

32 Ribeiro RS, Fathy NA, Attia AA, Silva AMT, Faria JL, Gomes HT. Materiais de Carbono como Catalisadores no Processo de Oxidação Catalítica com Peróxido de Hidrogénio. XXIII Congreso Iberoamericano de Catálisis, Santa Fé, Argentina, 2-7 septiembre, 2012.

33 Orge CA, Sousa JPS, Gonçalves F, Freire C, Órfão JJM, Pereira MFR. Development of Novel Mesoporous Carbon Materials for the Catalytic Ozonation of Organic Pollutants. Catal. Lett. 2009; 132: 1-9.

34 Faria PCC, Órfão JJM, Pereira MFR. Activated carbon and ceria catalysts applied to the catalytic ozonation of dyes and textile effluents. Appl. Catal. B: Environ. 2009; 88: 341-350.

Mass transport in carbon gels with tuned porosity
Transferencia de masa en geles de carbón con porosidad a medida

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Abstract

Diffusional limitations in carbon gel-supported catalysts are often encountered despite their open structure. However, the analysis of mass transport is rarely taken into account in studies dealing with catalyst preparation and test using these nanostructured carbons as supports. Any catalytic system should be first subject to mass transport analysis before any conclusion can be drawn about relationships between the physico-chemical properties and the measured activity of the catalyst.

Resumen

Pese a su estructura abierta, a menudo se observan limitaciones difusionales en catalizadores soportados en geles de carbono. Sin embargo, en los diversos estudios de preparación y testeo de catalizadores soportados en estos materiales nanoestructurados, pocas veces se lleva a cabo un análisis de transferencia de masa. Así, antes de obtener cualquier conclusión sobre la relación entre las propiedades fisicoquímicas y la actividad de un catalizador, el sistema debería someterse a un análisis de trasporte de masa.

1. Introduction

Porous carbon materials are widely used in many applications: adsorption in liquid or gas phase, gas separation, supports for catalysts, electrocatalysis, materials for batteries, etc. In all these processes, the pore texture of the chosen carbon material plays a major role. Indeed, whatever the above-mentioned application, species which can be adsorbates, reactants or ions must circulate within the pore texture. The control of the carbon pore texture is thus key to an efficient process.

However, carbons used in industrial applications or in electrochemical devices, such as activated carbons or carbon blacks, most often display quite inappropriate pore textures with regard to mass transport. The texture of activated carbons, for instance, is generally microporous, with low macropore or mesopore volumes, which often induces diffusional limitations during catalytic and adsorption processes. Carbon blacks, which are composed of microporous near-spherical particles of colloidal sizes (~ 20 – 60 nm), coalesced together as aggregates (1 – 100 µm), remain the elected material for Proton Exchange Membrane fuel cell electrodes [1]; however, the pore texture of the electrodes is quite dependant on the electrode processing because it is to a large extent defined by the packing of the carbon aggregates, which depends on the electrode manufacture technique.

These drawbacks call for the development of carbon materials with controllable and tunable pore texture. This is why so many recent works were dedicated to the preparation of synthetic porous carbon materials, with special attention to the control of the textural properties. Several routes were investigated in the last 20 years and, among the numerous new carbon materials developed, carbon gels, *i.e.* carbon xerogels, aerogels and cryogels, have been successfully used at laboratory scale as alternative to commercial carbons in several processes. The advantage of carbon gels is that their pore texture, *i.e.* pore size and pore volume, can be very accurately tuned within a wide range. As a result, one can adapt the pore texture of the used carbon with regard to the application in order to get rid of diffusional limitations encountered with mainly microporous materials. However, the elimination of mass transport limitations is not straightforward since it does not only depend on the pore size, but also on the void fraction, on the tortuosity of the pores and on the characteristic dimension of the catalyst pellet or particle. The aim of the present paper is to highlight the advantages of these materials in terms of mass-transport control, and to underline the precautions to be taken when using these *a priori* "diffusional limitation-free" materials.

2. Preparation of carbon gels with tuned pore texture

The preparation of carbon gels and the final pore texture obtained in function of the preparation recipe used is very well referenced in the literature [2]. Although alternatives can be found, most studies report the mixing of resorcinol and formaldehyde
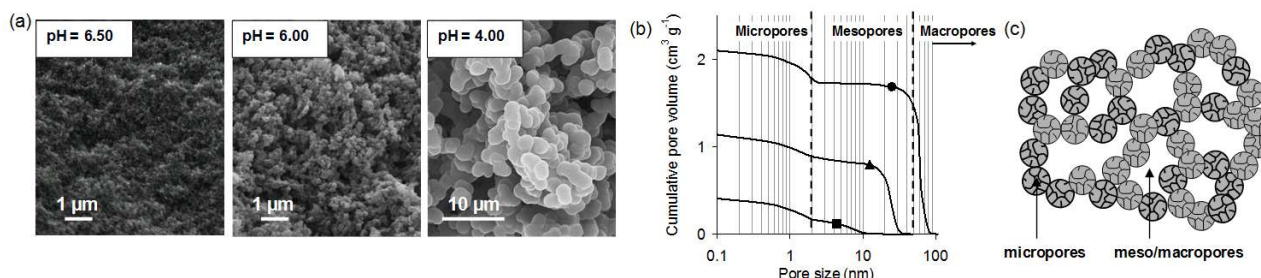
Figure 1. (a) Scanning electron micrographs of three carbon xerogels prepared at the same dilution ratio (*D* = 5.7) and various pH conditions. (b) Pore size distribution of carbon xerogels (*D* = 5.7) prepared at pH = 5.25 (●), pH = 5.75 (p) and pH = 6.25 (n). (c) Carbon gel modeling: covalently bonded microporous spherical-like nodules separated by meso/macropores.
Figura 1. Micrografías electrónicas de barrido de tres xerogeles de carbón preparados con la misma relación de dilución (*D* = 5.7) y diferentes pHs. (b) Distribución del tamaño de poros de xerogeles de carbón (*D* = 5.7) preparados a pH = 5.25 (●), pH = 5.75 (p) and pH = 6.25 (n). (c) Modelo de gel de carbón: nódulos esferoidales microporosos enlazados covalentemente separados por meso/macroporos.

(reagents) in water (solvent) and use of sodium carbonate as basification agent (also called 'base catalyst'). After gelation and ageing, the gel is composed of interconnected spherical nodules delimiting voids filled with the solvent. After drying and pyrolysis, the so-called 'string-of-pearl'-like structure remains (Fig. 1a) whatever the drying technique, although large variations in the final pore volume can be observed depending on the method used (evaporation, supercritical drying or freeze-drying). Pyrolysis induces the development of microporosity within the nodules. As a result, carbon gels display a bimodal pore texture (Fig. 1b): meso/macropores are delimited by the spacing between microporous nodules (Fig. 1c).

In order to change (tune) the pore texture of the final material, one can play on three main variables [3]: (i) the pH of the precursor solution, (ii) the dilution ratio, *i.e.* the water/reactants molar ratio and (iii) the drying technique. In a global way, the nodule size is mainly fixed by the pH of the precursor solution while the pore volume and pore size are mostly related to the dilution ratio and drying technique. However, the relationship between the synthesis/drying variables and the pore texture parameters is not straightforward. The dilution ratio, for instance, also impacts the nodule size, although to a less extent than the pH of the solution. The nature and concentration of ions also modifies the texture: for instance, adjusting two gels at the same pH with NaOH or $Mg(OH)_2$ leads to two different materials [4]. The drying technique impacts strongly the pore texture when the pores are small and when the dilution ratio is high. Indeed, in this case, evaporation leads to a shrunk material with low pore volume compared to materials obtained by supercritical drying or freeze-drying. However, as the solid fraction and pore size increases, capillary tensions induced by the curved liquid-vapor interface during evaporation decreases, and no shrinkage is observed whatever the drying technique [3]. Finally, the pore size and pore volume of carbon gels can be tuned independently within a wide range: from a few nm to a few µm, and from 0 to 5-6 cm³/g, respectively. This leaves plenty of room for adjustment with regard to the final application.

3. Use in mass-transport dependant processes
3.1. Heterogeneous catalysis

The deposition of active species on carbon gels is not more difficult than in the case of other carbon supports, but one of the advantages is that the surface chemistry can also be tuned by post-treatments [5], which further eases the impregnation with metal precursors for instance, or even the grafting of metal complexes. Many studies have reported the preparation of metal, alloy or oxide catalytic nanoparticles on such supports and their use in various catalytic processes [6]. However, few of them include the analysis of mass transport limitations in their discussion of results and, due to the lack of appropriate data, it is often difficult to determine whether the measured activity of the catalyst is diffusion-free or not. The danger here is to attribute reaction rate constancy or modifications to the physico-chemical characteristics of the catalyst (e.g. composition, surface chemistry, dispersion, etc.) while the system is in fact dominated by mass transport effects: in this case, the measured reaction rate is not the *specific* reaction rate, *i.e.* related to the physico-chemical properties of the catalytic sites, but an *apparent* reaction rate, somewhat falsified by mass-transport limitations.

This problem is quite classical in heterogeneous catalysis (Fig. 2) [7]: to reach the catalytic sites, reactants have first to diffuse through an external stagnant film of fluid outside the catalyst pellet and must then circulate within the pores of the support; products must then go the reverse way. In the case the reaction is intrinsically slow and the mass transport is fast enough, the concentration of reactants and products is quite homogeneous everywhere (Fig. 2a: *chemical regime*). However, when the kinetics of the reaction is fast and the diffusion rate is slow, a concentration gradient appears in the catalyst pellet and/or in the external stagnant film outside the pellet (Fig. 2b: *diffusional regime*). As a result, the reactant concentration at the catalytic site, C, which generally affects the kinetics of the reaction, is not that measured outside the catalyst pellet, Ce: the reaction rate measured by the experimenter is a mix between various reaction rates because each catalytic site actually 'sees' a different concentration of reactants (and products). Another consequence is that catalytic sites located at the pellet centre are almost useless because they are not reached by the reactants. The ratio between this *apparent* reaction rate, r_a, and the *specific* reaction rate, r_s, is called the *effectiveness factor* of the catalyst, η. This factor quantifies the gap between the true reaction kinetics over the catalytic sites and the reaction kinetics observed, which depends on the diffusion rate of the reactants and products in the external layer and within the pore texture of the support.
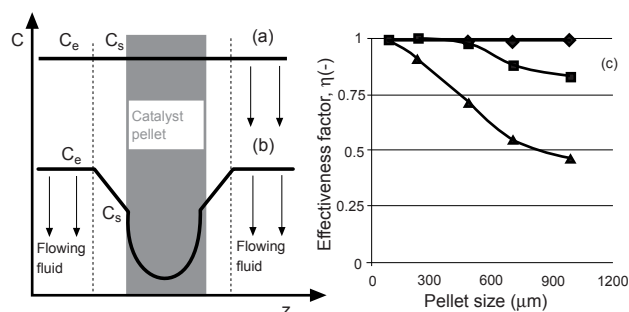
Figure 2. Mass transport in a catalyst pellet. (a) Reactant concentration profile in the case of *chemical regime*. (b) Reactant concentration profile in *diffusional regime*. Ce and Cs represent the concentration of a reactant in the flowing fluid and at the surface of the pellet, respectively. (c) Hydrodechlorination of 1,2-dichloroethane into ethylene on Pd-Ag/carbon xerogel catalysts, T = 573K. Effectiveness factor, η, as a function of the pellet size. Average pore size of the support: (p) ~10 nm, (n) ~30 nm, (u) ~70 nm. Data adapted from [8].
Figura 2. Transferencia de masa en una partícula de catalizador. (a) Perfil de concentración del reactivo en el caso de *régimen químico*. (b) Perfil de concentración del reactivo en *régimen difusional*. Ce and Cs representan la concentración del reactivo en el flujo y en la superficie de la partícula, respectivamente. (c) Hidrodecloración de 1,2-dicloroetano en etileno sobre catalizadores de Pd-Ag/xerogel de carbón, T = 573K. Factor de efectividad, η, en funcion del tamaño de partícula. Tamaño medio de poro del soporte: (p) ~10 nm, (n) ~30 nm, (u) ~70 nm. Datos adaptados de [8].

3.2. Determination of the external and internal limitations

In the case of carbon gels, like for any other porous material, selecting supports with 'large pores' does not necessarily mean that no diffusional problems will occur. As an example, Fig.2b shows the effectiveness factor of Pd-Ag catalysts supported on carbon xerogels with various meso/macropore

size in the case of hydrodechlorination of 1,2-dichloroethane into ethylene performed in gas phase at 573K [8]. One can observe that supports with small pore size lead to a rapid decrease of η, even with quite small pellets (500 μm). Larger pore sizes allow keeping the effectiveness factor equal to 1 for pellets of larger size (up to 7 mm by calculation in the case of 70 nm pores). Since too small pellets piled up in a reactor would lead to prohibitive pressure drop in the device, the possibility to use large pellets without loss of catalyst performance is obviously an advantage brought by an adequate pore texture of the support. However, increasing the temperature at 623K leads to internal diffusion limitations for pellets around 4 mm [8].

As a matter of fact, it is impossible to tell without any calculations or additional measurements whether kinetics is observed in chemical regime or not. So, before any discussion of the catalytic properties of carbon gel-supported catalysts, one must check that the obtained kinetics data are mass transport-free. In a practical way, *external limitations* can be detected by modifying the fluid flow rate (in the case of a continuous tubular reactor) or by changing the stirring speed (in the case of a continuous or discontinuous mixed reactor): these variables affect the thickness of the limit layer outside the catalyst pellet. *Internal limitations* can be detected by changing the pellet size: indeed, using smaller pellets obtained by grinding of larger ones would lead to a shorter average distance between the pellet surface and the catalytic sites and thus to a less severe internal concentration gradient. Note however that modifying the pellet size also decreases the thickness of the external film: so, the detection of internal limitations must be performed in the absence of external limitations.

If the catalytic properties of a sample are not independent of the flow rate or mixing and pellet size, the obtained data are not specific to the physico-chemical properties of the catalyst itself but are relevant to fluid dynamics. It is thus completely illusory to link any of the catalyst properties to the observed reaction rate. Additional measurements are not always easy to perform, but the presence of external or internal limitations can be deduced from calculation. The external diffusional limitations can be quantified by the fraction of external resistance f_e [7]:

$$(1) \quad f_e = 1 - \frac{C_s}{C_e} = \frac{r_a\, L_p}{k_d\, C_e}$$

where r_a is the apparent specific reaction rate per volume unit of catalyst, L_p is the characteristic dimension of the catalyst pellet (*i.e.*, the volume to surface ratio, equal to $d_p/6$ in the case of a sphere, d_p being the pellet diameter), C_e and C_s are the concentration of the limiting reactant in the bulk of the fluid phase and at the external surface of the catalytic pellet, respectively, and k_d is the external transfer coefficient. k_d can be estimated from correlations between the Sherwood (Sh), Reynolds (Re) and Schmidt (Sc) dimensionless numbers [7]. Indeed:

$$(2) \quad Sh = \frac{k_d\, d_p}{D_m} = Sh_0 + B Re^m Sc^{\frac{1}{3}} = Sh_0 + B\left(\frac{pud_p}{\mu}\right)^m \left(\frac{\mu}{pD_m}\right)^{\frac{1}{3}}$$

where Sh_0 is the Sherwood number in the absence of forced convection, D_m is the molecular diffusivity, d_p is the particle diameter, $\rho,\ \mu$ and w are respectively the density, the viscosity and the linear velocity of the fluid phase and B is a constant. In the case of a stirred reactor, the velocity of the fluid phase is calculated from the stirring speed of the reactor [7]. Specific correlations of the Eq. (2) form are available for many systems and under various conditions. All the parameters of these equations are characteristics of the fluid phase, reactor and catalyst pellet, which are normally accessible to the experimenter. The calculation of Sh and thus of f_e should not be a problem for usual reactors. Finally, if f_e is close to 1, one can conclude that no external limitations occur.

A quantitative approach to evaluate the influence of internal diffusion on the overall catalytic process consists in the calculation of the dimensionless Weisz modulus, ϕ, which is defined as the ratio between the apparent specific reaction rate and the diffusion rate of the reactant in the pore texture of the catalyst particle. For ϕ larger than 1, the internal diffusion limitations become rate-determining, and the observed reaction rate is falsified by mass transport within the pore texture. The Weisz modulus can be written as [7]:

$$(3) \quad \phi = \frac{r_a\, L_p^2}{D_e\, C_s}$$

where r_a is the apparent reaction rate per volume unit of catalyst, L_p is the characteristic dimension of the catalyst pellet, C_s is the concentration of the limiting reactant at the external particle surface, and D_e is the effective diffusivity through the catalyst pores. C_s is not easily determined unless the catalytic measurements are performed in the absence of external limitations, which is the usual way to proceed: in this case $C_s = C_e$. The effective diffusivity, D_e, is the diffusivity in the pores, D, corrected by the accessible void fraction, ε, and the pore tortuosity, ε [7]:

$$(4) \quad D_e = \frac{\varepsilon D}{\tau}$$

In liquid phase, D is the molecular diffusivity, D_m, available in tables. In gas phase and when the pores are small (typically < 100 nm), D is a combination of the both the molecular and the Knudsen diffusivities [9], the latter mechanism being related to diffusion in which collisions with the pore walls are predominant with regard to collisions between molecules. As a consequence, in Knudsen-type regime, the diffusivity changes with the pore size, which is not the case in molecular-type diffusion. Note also that the tortuosity of the catalyst support, τ, is often taken equal to $1/\varepsilon$.

3.3. Heterogeneous catalysis on carbon gels

The case of carbon gels is more complicated since one clearly identifies two pore levels (Fig. 1b-c). Indeed, internal limitations could occur either at the meso/macropore level or at the micropore level if the catalytic species are located in the microporosity. With this particular double structure of granular pellet itself composed of porous spheres, one can imagine to perform the internal mass transport analysis at both levels, *i.e.* by calculating the Weisz modulus at the pellet (ϕ_p) and at the nodule (ϕ_n) level [8]. All parameters related to the solid must then be those related either to the pellet or to the nodule. For

instance, the characteristic dimension L_p and the void fraction ε are different when considering each level. In particular, the void fraction of the nodules is almost constant (~0.35) because the structure of the nodules and thus their microporosity is quite independent on the synthesis conditions of the pristine gel, unless the carbon gel is further activated to develop its specific surface area [10]; on the contrary, the void fraction of carbon gel monoliths strongly depends on the synthesis and drying pathway (see §2). As an example, the Weisz modulus was calculated at the pellet and nodule levels for Pd-Ag catalysts supported on carbon xerogels of various pore textures [8], and it was clearly demonstrated that, when present, the diffusional limitations occur at the meso/macropore level and not in the micropores. This can be explained by the difference of distance to be covered by the molecules in the meso/macropores (~ 500 µm for 1 mm pellets) compared to micropores (~ 10 – 100 nm) to reach the centre of either the pellet or the nodule; this clearly demonstrates that the pore size is not the only factor to be taken into account.

Another source of complication is the fact that the catalytic species may be not homogeneously dispersed in the porosity of the support. For instance, the active particles can be located in an outer layer of the pellet (core-shell configuration). In this case, the characteristic dimension, L_p, to be used in Eq. (1) and (3) is the thickness of this layer. Pirard *et al.* [11] studied the oxidation of D-glucose into D-gluconic acid on Pd-Bi/carbon xerogel catalysts in aqueous media; the catalytic species (Bi and Pd) were concentrated in an external layer of the catalyst pellets, as shown by physico-chemical characterization. Mass transport analysis was performed using the appropriate characteristic dimension; it showed that the kinetic measurements had been performed under diffusional regime and the authors concluded that measuring the true kinetic reaction rate implied to choose the experimental conditions within a very small range of values. This finally confirms that the measurement of the specific catalytic activity of catalysts supported on nanostructured carbons such as carbon gels is not an easy task; the choice of the experimental conditions should be subject to high caution.

Note that one could apply the same principles to adsorption; in this case, the reaction rate is replaced by the adsorption rate. Indeed, recent results have shown that the pore texture of carbon gels has the same impact on adsorption processes: the adsorption rate can be increased by selecting a support with appropriate pore texture [12], adsorption sites being more easily reached by the adsorbate molecules. This is quite interesting for purification systems or gas masks, for instance, where the transient adsorption of molecules occurs.

3.2. Electrocatalytic processes

The advantages of carbon gels in heterogeneous catalysis can be transferred to electrochemical devices such as Proton Exchange Membrane fuel cells. The catalytic layer of a PEM fuel cell is composed of Pt/carbon catalyst particles, interparticle voids and ionomer (Nafion®, usually), hot-pressed between a proton-exchange membrane and a gas diffusion layer (GDL) usually made of hydrophobic carbon felt [1]. A catalytic layer of a PEM fuel cell can be seen as a microreactor of heterogeneous catalysis where mass transports are complicated by (i) the presence of two fluid phases (gas and condensed water) and (ii) the proton transport via the ionomer network. Indeed, to be active, the metal (Pt) catalyst particles must be in contact with the carbon support and connected to the membrane *via* the ionomer. In addition, reactants (H_2 or O_2, protons and electrons) and water must circulate easily through the catalytic layers; in particular, the catalyst must be reached by the gas through the porous structure of the electrode. Usually, carbon blacks are used as support; however, the packing of the carbon black aggregates, and therefore the pore structure of the catalytic layers, depends on the carbon black nature and on the electrode processing [1]. Typically, at the air-fed cathode, where oxygen, proton and water transports hamper the oxygen reduction reaction, high potential losses due to diffusional limitations offset the cell performance [13]. This is compensated by the use of catalytic layers with high Pt loading, which increases the electrode cost.

The study of mass transport in such systems is not easy because some parameters of the above-written equations are not readily available. For instance, due to the presence of ionomer within the pore texture, the pore size and pore volume is different to that of the pristine carbon gel; this effect is reinforced by the fact that Nafion® swells when humidified, and that some water can condense within the pore texture, reducing further the available pore volume. As a first consequence, the true void fraction accessible to reactants, ε, is difficult to estimate. Concentrations C_e and C_s evolve with the position of the catalyst particles in the MEA, and correlations for the external transport, though available [14], strongly depend on the system geometry. At the moment, diffusional limitations are most often analyzed through the voltage loss analysis of the cell. The total voltage loss of the cell with regard to the reversible H_2/O_2 cell voltage can be decomposed into several components [15]: (i) the kinetic overpotential, η_{ORR}, due to the slowness of the O_2 reduction; (ii) the ohmic losses, η_{Ohm}, due to the resistance of the proton migration through the membrane and the electronic contact resistances; (iii) the mass-transport losses, or 'diffusion overpotential', η_{diff}. In such systems, kinetic and mass transport losses of the anode (H_2 side) can be neglected [15]. One can write:

$$(5) \quad E_{cell} = E_{rev} - \eta_{ORR} - \eta_{Ohm} - \eta_{diff}$$

where E_{rev} is the reversible H_2/O_2 cell voltage under the gas pressure and temperature of the cell. The first two contributions to the voltage loss can be measured. Briefly, η_{ORR} is obtained from measurements at low current densities, *i.e.* from data obtained in the near-absence of mass transport limitations and ohmic resistance (Tafel equation) [15]; η_{Ohm} is obtained by measurement of the ohmic resistance of the cell by impedance spectroscopy, performed *in situ*. Finally, all the other terms of Eq. (5) being known, η_{diff} can be deduced by difference. However, the overpotential attributed to mass transport, η_{diff}, remains a black box that actually encloses all the limitation sources that are not attributed to kinetic and ohmic phenomena through direct measurement. In particular it is difficult to determine where mass transport limitations occur in the catalytic layer. This question is still under investigation and remains of high importance in view of electrode optimization.
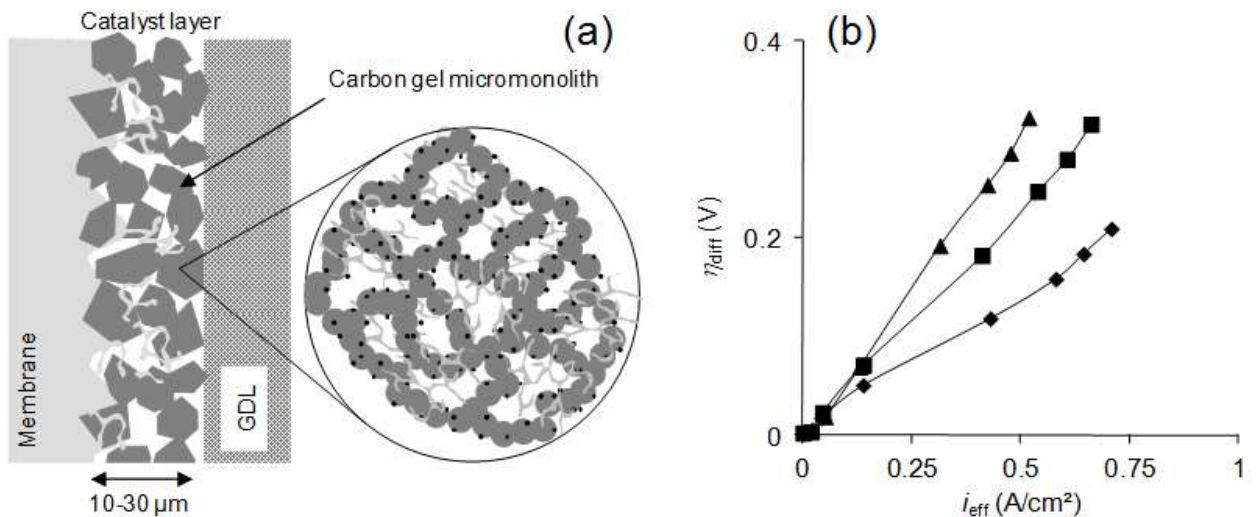
Figure 3. (a) Catalytic layer of a PEM fuel cell with Pt/carbon gel as catalyst; the micromonoliths are made of carbon gel that retains the pore texture of the pristine material, despite grinding. (b) Diffusion overpotential as a function of the current density calculated from measurements in PEM monocell with cathodes prepared from Pt/carbon xerogels of various average meso/macropore size and volume: (p) ~40 nm and 1.0 cm³/g, (n) ~85 nm and 1.8 cm³/g, (u) ~300 nm and 1.9 cm³/g. Adapted from [16].
Figura 3. (a) Capa catalítica de una pila de combustible PEM con Pt/gel de carbón como catalizador; los micromonolitos están hechos de gel de carbón que retiene la textura porosa del material original a pesar de la molienda. (b) Sobrepotencial de difusión en función de la densidad de corriente calculado de las medidas en una monopila PEM con cátodos preparados a partir de Pt/xerogeles de carbón de diferentes tamaño medio y volumen de meso/macroporos: (p) ~40 nm and 1.0 cm³/g, (n) ~85 nm and 1.8 cm³/g, (u) ~300 nm and 1.9 cm³/g. Adaptado de [16].

In search for new catalytic layer structures with low diffusion-induced potential losses, carbon gels constitute an interesting alternative to carbon blacks because their meso/macropore texture is totally independent on the electrode processing [16]; besides, the high purity of carbon gels ensures the absence of pollutants inherent to the support origin and detrimental to the electrocatalytic activity. In the electrode structure, the carbon black particle agglomerates are replaced by micromonoliths of carbon gel, which preserves the pores located in-between (Fig. 3a). These materials were used recently to prepare Membrane-Electrode Assemblies (MEAs) for air/H_2 [16-18] or air/methanol PEM fuel cells [19], and were mainly tested at the cathode of a monocell device. In both cases, the pore texture of the carbon gel was found to influence the cell performances: it was possible to decrease the diffusion-induced voltage losses by selecting carbon gels of appropriate pore texture (Fig. 3b). However, many variables influence the final electrode architecture and performance, and the optimization of the pore texture of the carbon support is still an open question.

4. Conclusions

Due to their pore texture versatility, carbon gels are attractive materials as (electro)catalyst supports because an accurate choice of the pore texture can decrease mass transport limitations encountered in operating catalytic processes. However, while few studies pay attention to this problem, the elimination of diffusional limitations is never obvious. As a result, any catalytic system should be first subject to mass transport analysis before any conclusion can be drawn about relationships between the physico-chemical properties and the measured activity of the catalyst. Despite their complex structure, carbon gel-supported catalysts can be studied following classical methods provided that their double-porosity structure is taken into account.

6. References

[1] Maillard F, Simonov P, Savinova ER. Carbon materials as supports for fuel cell electrocatalysts. In: Carbon Materials for Catalysis, Philippe Serp and José Luis Figueiredo Eds. Wiley, New York, 2009, p. 429-481.

[2] Elkhatat AM, Al-Muhtaseb S. Adv Mater 2011;23:2887-2903.

[3] Job N, Théry A, Pirard R, Marien J, Kocon L, Rouzaud JN, Béguin F, Pirard JP. Carbon 2005;43:2481-2494.

[4] Job N, Gommes CJ, Pirard R, Pirard JP. J Non-Cryst Solids 2008;354:4698-4701.

[5] Mahata N, Pereira MFR, Suárez-García F, Martínez-Alonso A, Tascón JMD, Figueiredo JL. J Coll Interf Sci 2008;324:150-155.

[6] Moreno-Castilla C. Carbon gels in catalysis. In: Carbon Materials for Catalysis, Philippe Serp and José Luis Figueiredo Eds. Wiley, New York, 2009, p. 373-400.

[7] Froment GF, Bischoff KB. Chemical Reactor Analysis and Design, 2nd ed., Wiley, New York, 1990.

[8] Job N, Heinrichs B, Lambert S, Pirard JP, Colomer JF, Vertruyen B, Marien J. AIChE J 2006;52:2663-2676.

[9] Satterfield CN. Mass Transfer in Heterogeneous Catalysis. Cambridge, MA: MIT Press; 1970.

[10] Contreras M, Páez C, Zubizarreta L, Léonard A, Olivera C, Blacher S, Pirard JP, Job N. Carbon 2010;48:3157-3168.

[11] Pirard SL, Diverchy C, Hermans S, Devillers M, Pirard JP, Job N. Catal Comm 2011;12:441-445.

[12] Almazán-Almazán MC, López-Domingo FJ, Domingo-García M, Léonard A, Pérez-Mendoza M, Pirard JP, López-Garzón FJ, Blacher S. Chem Eng J 2011;173:19-28.

[13] Gasteiger HA, Gu W, Makharia R, Mathias MF, Sompalli B. In: Wolf Vielstich, Arnold. Lamm and Hubert A. Gasteiger (Eds), Handbook of Fuel Cells – Fundamentals, Technology and Applications, Wiley, Chichester (UK), 2003, Vol. 3, p. 593.

[14] Li PW, Zhang T, Wang QM, Schaefer L, Chyu MK. J Power Sources 2003;114:63-69.

[15] Gasteiger HA, Kocha SS, Sompalli B, Wagner FT. Appl Catal B 2005;56:9-35.

[16] Marie J, Berthon-Fabry S, Chatenet M, Chainet E, Pirard R, Cornet N, Achard P. J Appl Electrochem 2007;37:147-153.

[17] Marie J, Chenitz R, Chatenet M, Berthon-Fabry S, Cornet N, Achard P. J Power Sources 2009;190:423-434.

[18] Job N, Marie J, Lambert S, Berthon-Fabry S, Achard P. Energ Convers Manage 2008;49:2461-2470.

[19] Arbizzani C, Beninati S, Manferrari E, Soavi F, Mastragostino M. J Power Sources 2007;172:578-586.

Reseña. Xerolutions, a company producing carbon gels, gets the Sodeco award

Last month of November, Xerolutions S.L. (http://www.xerolutions.com), a company that produces carbon xerogels, was awarded with the Sodeco 2012 award for business projects. The production of these materials is based on an innovative technology developed and patented by the promoter group, Ana Arenillas and J. Angel Menéndez, both from the INCAR-CSIC and members of the GEC. The material can be obtained with custom-designed properties for a particular application. The award panel took into account "the innovative nature of the project, which brings to market a new product, developed and patented by the promoter group, with multiple applications and in particular the production of electrodes for supercapacitors." The prize is worth 25,000 € for investment in the project.

David López, Almudena Trigo, Ana Arenillas and J. Angel Menéndez (1st, 2nd, 5th and 8th from the left, respectively) promoters of Xerolutions, receiving the Sodeco award from organizers and authorities.

Anuncio. XII Reunión del GEC

GRUPO ESPAÑOL CARBÓN

La ETSI Minas de la Universidad Politécnica de Madrid y la SD de Ingeniería Química de la Universidad Autónoma de Madrid tienen el placer de invitarles a la próxima Reunión del Grupo Español del Carbón que tendrá lugar en el Edificio Histórico de la ETSI de Minas de Madrid, los días 20 a 23 de Octubre de 2013.

Más información en http://www.minas.upm.es/gec2013.html

Esperamos contar con su asistencia.
Cordialmente, el Comité Organizador.

Socios protectores del Grupo Español del Carbón

Industrial Química del Nalón, S.A.
NalónChem

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