

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

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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 partículas 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 sistema 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.

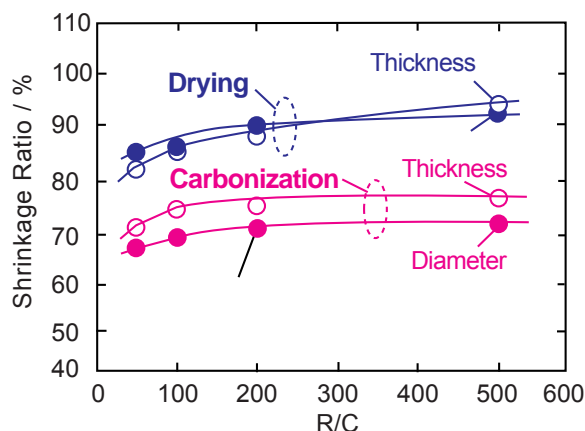


Figure 2. Shrinkage ratio of the obtained disks.
Figura 2. Relación de encogimiento de los discos obtenidos.

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.

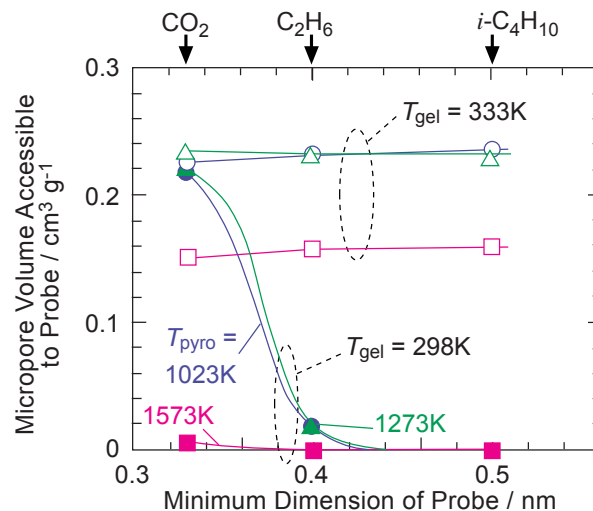


Figure 4. Estimation of inlet size of the surface pores of typical carbon gel microspheres.

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 accessibility 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

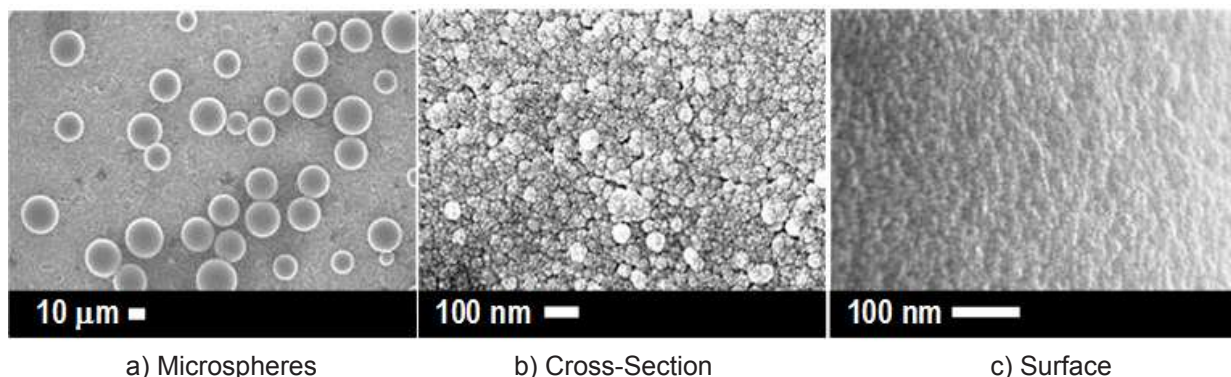


Figure 3. SEM micrograph of typical microsphere samples.
Figura 3. Microfotografía SEM de muestras de microesferas típicas.

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.

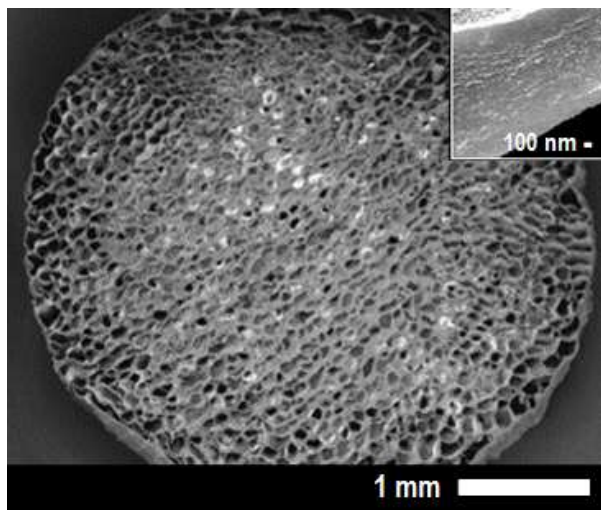


Figure 5. Cross sectional SEM image of a typical monolithic RF gel microhoneycomb.

Figura 5. Imagen SEM de la sección transversal de un típico 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.

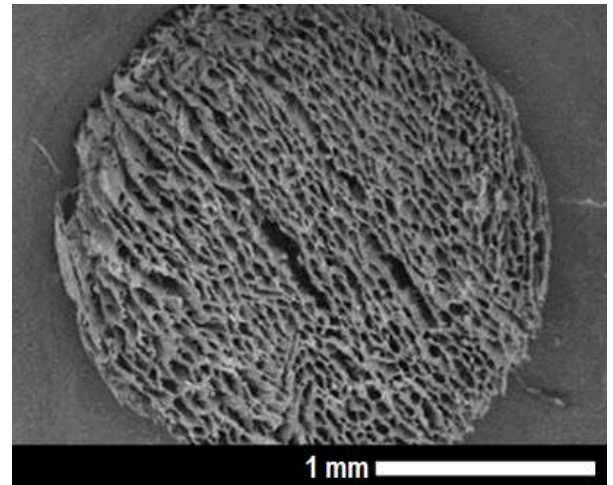


Figure 6. Cross sectional SEM image of a typical monolithic carbon gel microhoneycomb.

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 microhoneycomb. 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.

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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.

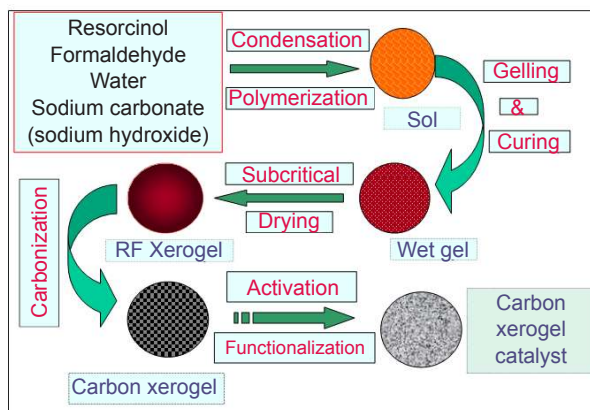


Figure 1. Steps in the synthesis of a carbon xerogel catalyst.
Figura 1. Etapas de síntesis de un catalizador de xerogel de carbón.

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 °C, one day each); water removed by sequential exchange with acetone (initially containing 5% acetic acid) and cyclohexane, followed by drying overnight at 80 °C; carbonisation at 800 °C (ramp @ 3 °C min⁻¹) under nitrogen flow (100 cm³ 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 m²/g for sample 37CXUA and 645 m²/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

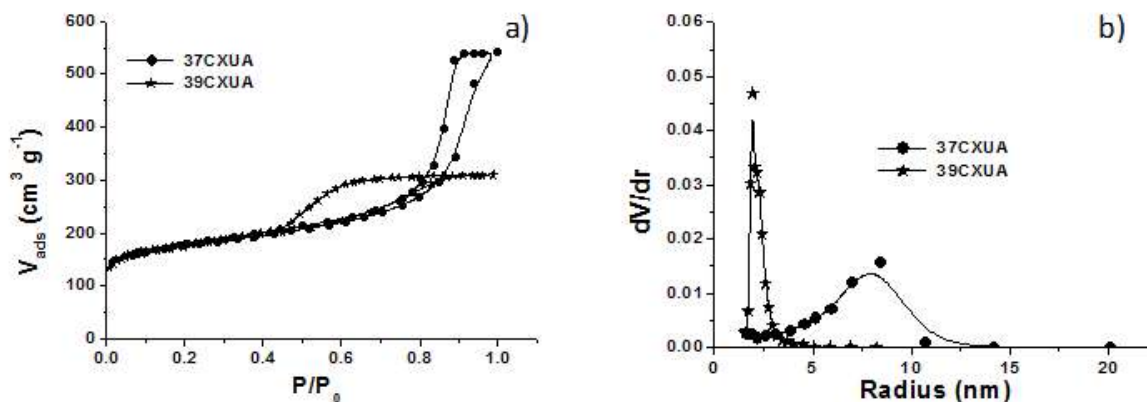


Figure 2. Textural properties of two carbon xerogels synthesized at different pH: a) nitrogen adsorption isotherms at 77 K; b) mesopore size distributions.

Figura 2. Propiedades texturales de dos xerogeles de carbón sintetizados a distintos valores de pH: a) isothermas 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 °C 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).

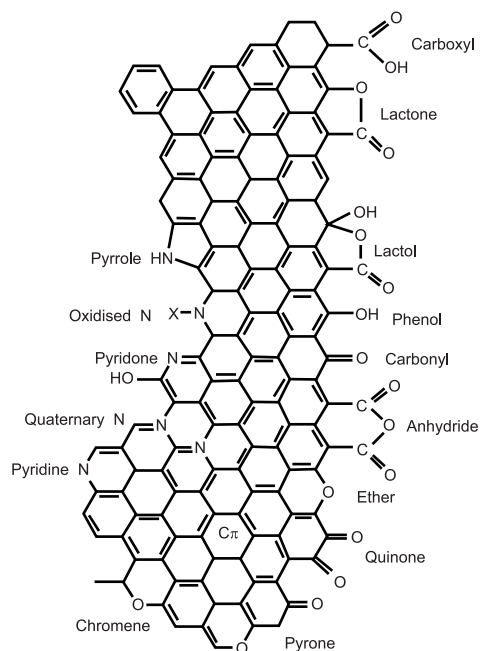


Figure 3. Nitrogen and oxygen surface groups on carbon. Reprinted from reference [7] with permission from Elsevier.

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 415°C 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

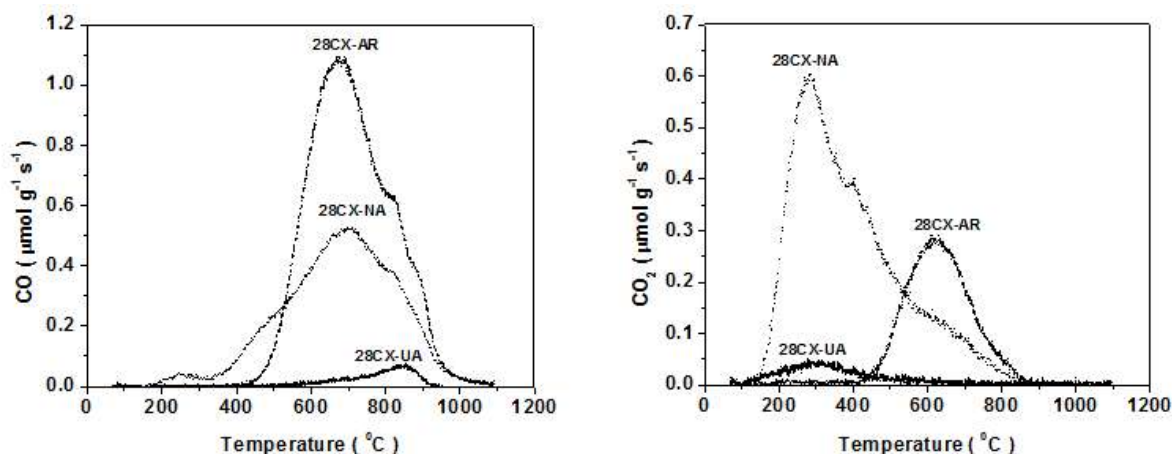


Figure 4. CO and CO₂ TPD spectra of activated and original carbon xerogel samples: original sample (28CX-UA); sample treated in nitric acid (28CX-NA); and sample treated in oxygen (28CX-AR). Adapted from reference [9].

Figura 4. Perfiles de desorción térmica programada de CO y CO₂ 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 H₂SO₄) 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-HNO₃ (treated with HNO₃ 5M; acidity = 1.58 mmol g⁻¹) and CX-H₂SO₄ (treated with concentrated H₂SO₄; 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-HNO₃ (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 H₂SO₄ at 150 °C for 6 hours, but with different ratios of acid to solid (150 mL and 20 mL H₂SO₄ 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 °C ([SO₃H] = 78 µmol g⁻¹). Figure 5 shows that the catalytic activity correlates nicely with the concentration of surface sulfonic acid groups.

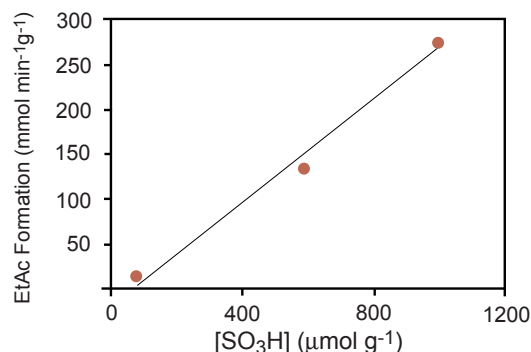


Figure 5. Correlation between the catalytic activity of carbon xerogels for the esterification of acetic acid with ethanol and the concentration of sulfonic acid groups.

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 NO₂ 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 O₂. It is assumed that oxygen is first chemisorbed on the active sites, reacting then with NO to form NO₂, as schematically shown in Figure 7.

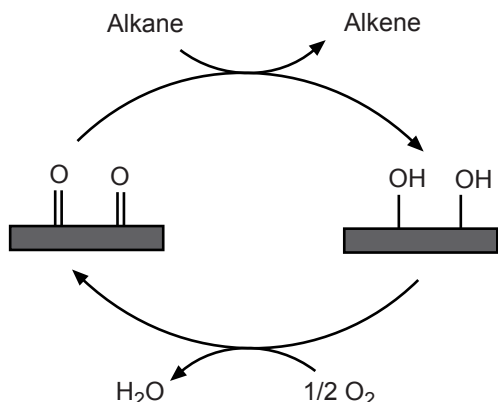


Figure 6. Catalytic cycle proposed for the oxidative dehydrogenation of hydrocarbons on carbon materials. Adapted from [7].

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].

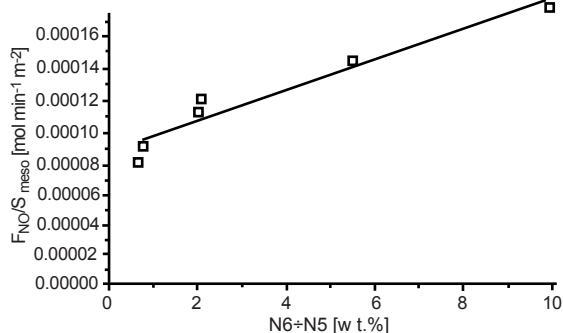


Figure 8. Rate of NO oxidation versus the concentration of pyridine and pyrrole groups.

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 CO₂ 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 m² g⁻¹, pH_{pzc} = 7.8), a HNO₃ oxidized sample (XC1, S_{meso} = 440 m² g⁻¹, pH_{pzc} = 3.1), and a thermally treated sample (XC2, S_{meso} = 252 m² g⁻¹, pH_{pzc} = 8.7). The results clearly show that the best performance is achieved with the basic carbons: XC2 > XC0 > XC1.

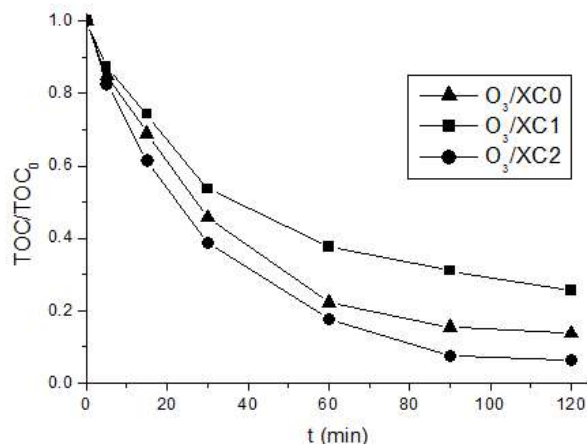


Figure 9. Normalized TOC removal in the ozonation of C.I. Acid Blue 113 at room temperature with carbon xerogel catalysts of different surface chemistry. Adapted from [33].

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

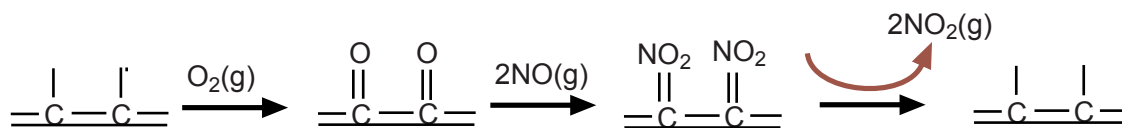


Figure 7. Proposed steps in the oxidation of NO on carbon xerogels.

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

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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 transporte 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 ($\sim 20 - 60$ 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

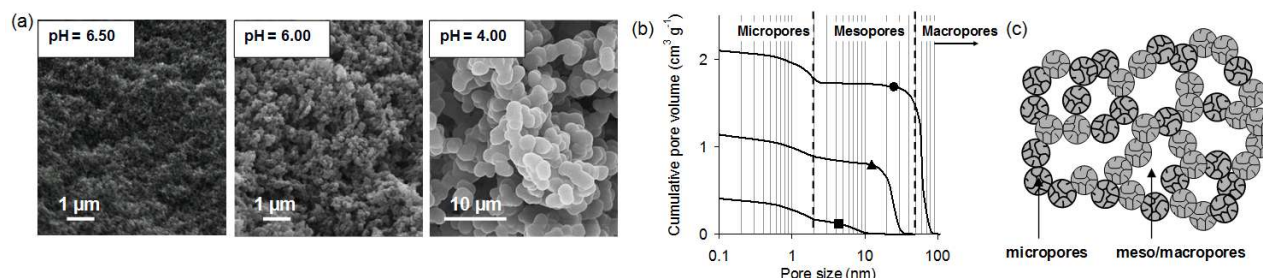


Figure 1. (a) Scanning electron micrographs of three carbon xerogels prepared at the same dilution ratio ($D = 5.7$) and various pH conditions. (b) Pore size distribution of carbon xerogels ($D = 5.7$) prepared at pH = 5.25 (\bullet), pH = 5.75 (\square) and pH = 6.25 (\triangle). (c) Carbon gel modeling: 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 (\bullet), pH = 5.75 (\square) and pH = 6.25 (\triangle). (c) Modelo de gel de carbón: nódulos esféricos 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 cm^3/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, C_e : 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.

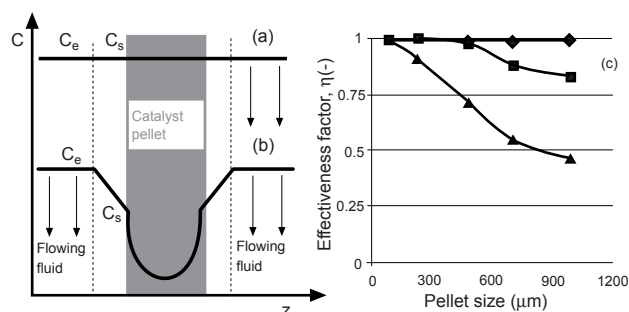


Figure 2. Mass transport in a catalyst pellet. (a) Reactant concentration profile in the case of *chemical regime*. (b) Reactant concentration profile in *diffusional regime*. C_e and C_s represent the concentration of a reactant in the flowing fluid and at the surface of the pellet, respectively. (c) Hydrodechlorination of 1,2-dichloroethane into ethylene on Pd-Ag/carbon xerogel catalysts, $T = 573\text{K}$. 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*. C_e and C_s 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, $T = 573\text{K}$. Factor de efectividad, η , en función 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:

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

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, ρ , μ 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, τ [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 ($\sim 500 \mu\text{m}$ for 1 mm pellets) compared to micropores ($\sim 10 - 100 \text{ nm}$) 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:

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

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.

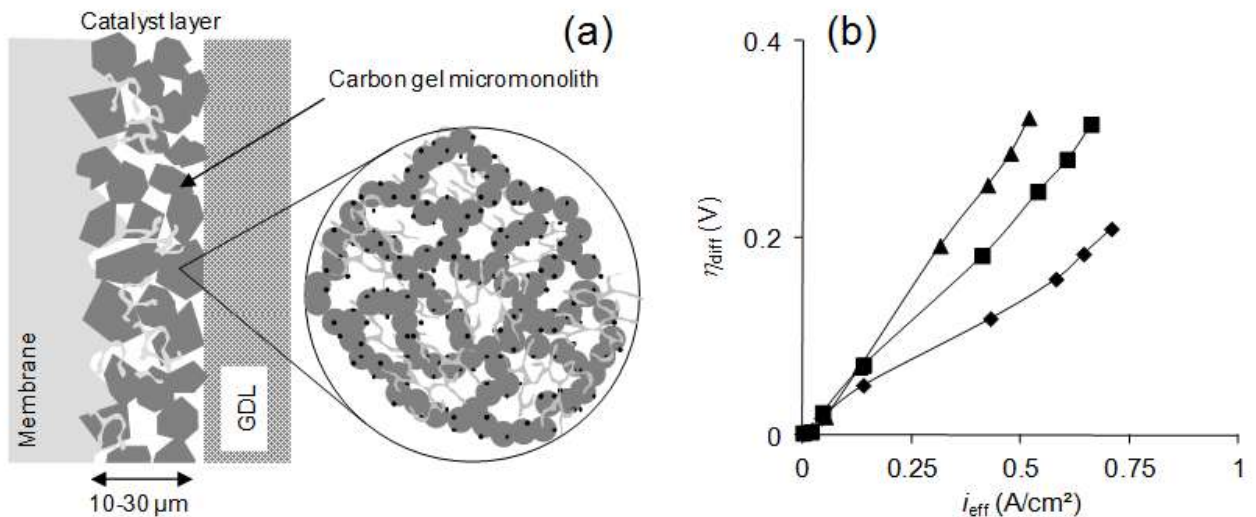


Figure 3. (a) Catalytic layer of a PEM fuel cell with Pt/carbon gel as catalyst; the micromonoliths are made of carbon gel that retains the pore texture of the pristine material, despite grinding. (b) Diffusion overpotential as a function of the current density calculated from measurements in PEM monocell 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/H₂ [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.

5. Acknowledgements

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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.
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