Carbon xerogels for catalytic applications
Xerogeles de carbón para aplicaciones catalíticas

J. L. Figueiredo

Laboratório de Catálise e Materiais (LCM), Laboratório Associado LSRE/LCM, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.
* Corresponding author: jlfig@fe.up.pt

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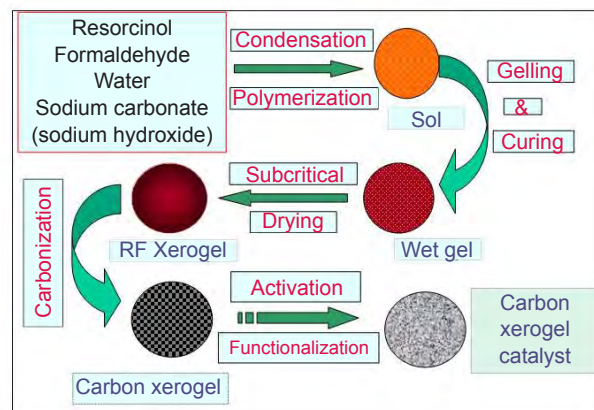
Figure 1. Steps in the synthesis of a carbon xerogel catalyst.
Figura 1. Etapas de síntesis de un catalizador de xerogel de carbón.

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
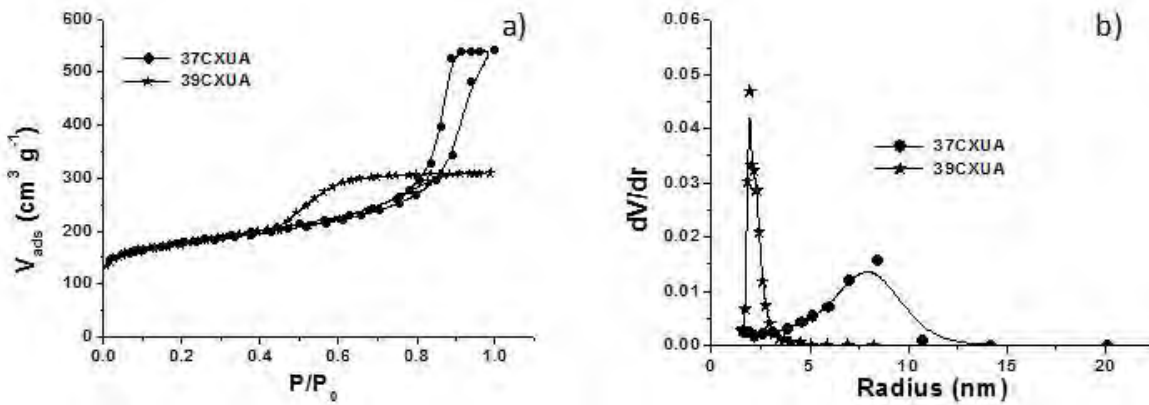
Figure 2. Textural properties of two carbon xerogels synthesized at different pH: a) nitrogen adsorption isotherms at 77 K; b) mesopore size distributions.
Figura 2. Propiedades texturales de dos xerogeles de carbón sintetizados a distintos valores de pH: a) isotermas de adsorción de N_2 a 77 K, b) distribución 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).
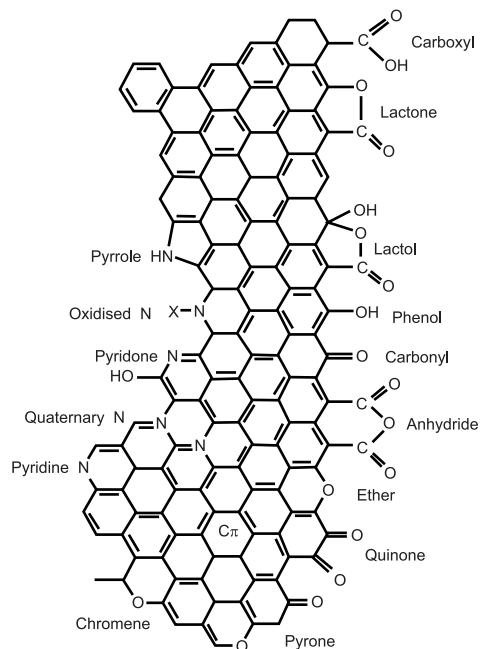
Figure 3. Nitrogen and oxygen surface groups on carbon. Reprinted from reference [7] with permission from Elsevier.
Figura 3. Grupos funcionales de nitrógeno y oxígeno en materiales de carbón. Reproducido de [7] con permiso de Elsevier.

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
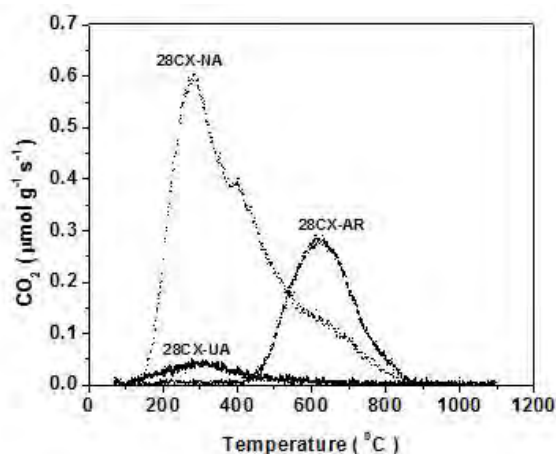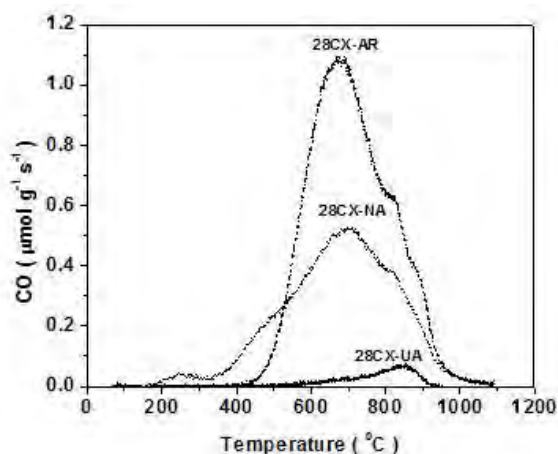
Figure 4. CO and CO$_2$ TPD spectra of activated and original carbon xerogel samples: original sample (28CX-UA); sample treated in nitric acid (28CX-NA); and sample treated in oxygen (28CX-AR). Adapted from reference [9]..

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 °C 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 °C ([SO$_3$H] = 78 μmol g^{-1}). Figure 5 shows that the catalytic activity correlates nicely with the concentration of surface sulfonic acid groups.
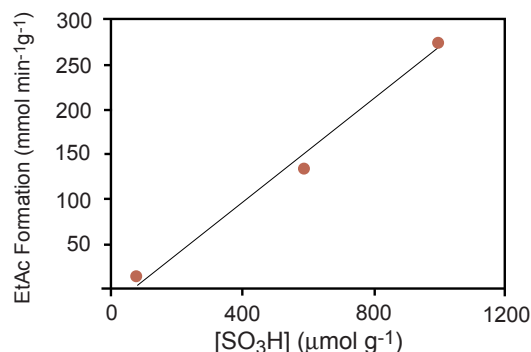
Figure 5. Correlation between the catalytic activity of carbon xerogels for the esterification of acetic acid with ethanol and the concentration of sulfonic acid groups.

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.
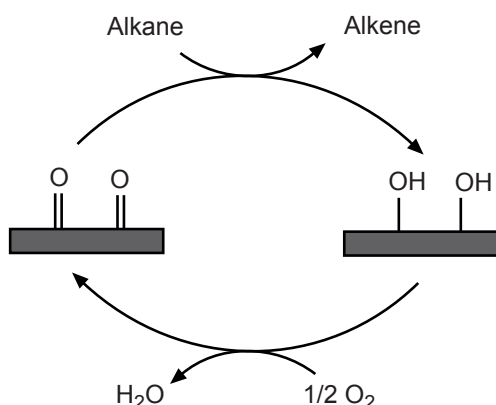
Figure 6. Catalytic cycle proposed for the oxidative dehydrogenation of hydrocarbons on carbon materials. Adapted from [7].
Figura 6. Mecanismo catalítico propuesto para la deshidrogenación oxidativa de hidrocarburos en materiales de carbón. Adaptada de [7].

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].
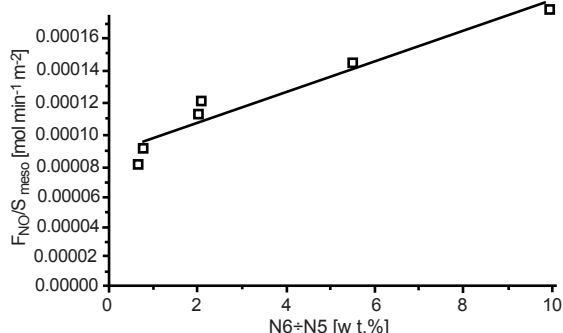
Figure 8. Rate of NO oxidation versus the concentration of pyridine and pyrrole groups.
Figura 8. Velocidad de oxidación de NO en función de la concentración de los grupos piridina y pirrol.

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.
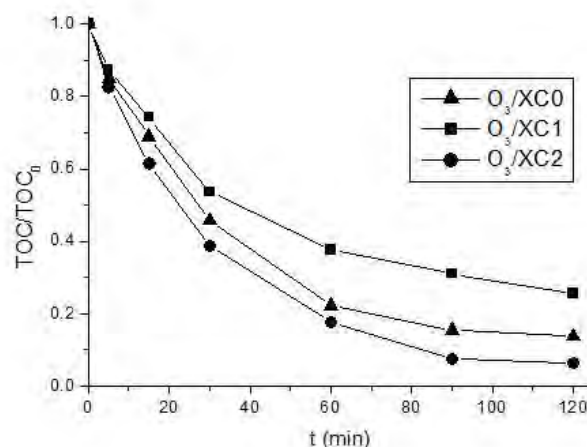

Figure 9. Normalized TOC removal in the ozonation of C.I. Acid Blue 113 at room temperature with carbon xerogel catalysts of different surface chemistry. Adapted from [33].
Figura 9. Eliminación de COT mediante la ozonización de C.I. Azul ácido 113 con xerogeles de carbón con distinta química superficial 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
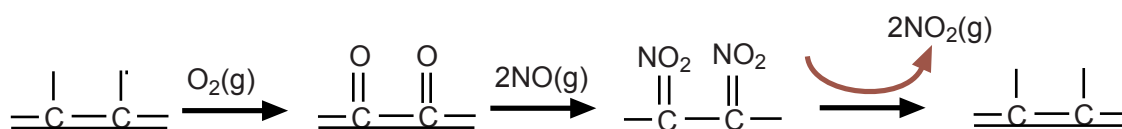
Figure 7. Proposed steps in the oxidation of NO on carbon xerogels.
Figura 7. Etapas propuestas en la oxidación de NO en xerogeles de carbón.

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

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