Development of carbon materials for catalysis, energy and environmental applications

Desarrollo de materiales de carbón para catálisis y aplicaciones energéticas y medioambientales

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Abstract

The development of carbon materials with tuned surface properties has been the core business of the Laboratory of Catalysis and Materials (LCM) for the past 25 years. LCM recent and relevant achievements in the field are highlighted in this overview, focusing on catalysis and additional energy and environmental applications.

Resumen

El desarrollo de materiales de carbón con propiedades superficiales controladas ha sido la actividad prioritaria del Laboratorio de Catálisis y Materiales (LCM) durante los últimos 25 años. En este breve resumen se destacan los logros más relevantes y recientes del LCM centrados en el campo de la catálisis y las aplicaciones energéticas y medioambientales.

1. Introduction

Among other relevant and unique properties offered by carbon materials, their texture and surface chemistry can be easily tuned to suit specific applications [1]. Beyond the traditional carbons (graphite, carbon blacks and activated carbons), a whole new range of materials is now available, including nanosized carbons (carbon nanotubes and nanofibers; graphene-based materials; nanodiamonds) and nanostructured carbons (carbon gels; ordered mesoporous carbons). These materials are *graphenic* in structure (in the case of nanodiamonds there will always be a few layers of disordered sp^2 carbon at the surface), and can be functionalized by reaction of different compounds with the unsaturated carbon atoms at the edges of the graphene layers and at basal plane defects, leading to a variety of surface functional groups. In addition, heteroatoms (O, S, N, B, etc.) can be incorporated into the graphene layers during synthesis, thereby modifying the surface properties of the carbon materials.

A range of experimental techniques has been used for the characterization of the surface functional groups on carbon materials, but their quantitative assessment is a major challenge. Temperature programmed desorption (TPD) is the technique of choice for the quantitative analysis of the surface oxygen functional groups. These decompose by releasing CO and CO_2 (and also H_2O) in different temperature ranges, as shown in Figure 1. Deconvolution procedures for the evolved CO and CO_2 profiles provide reliable estimates for the amounts of individual oxygen
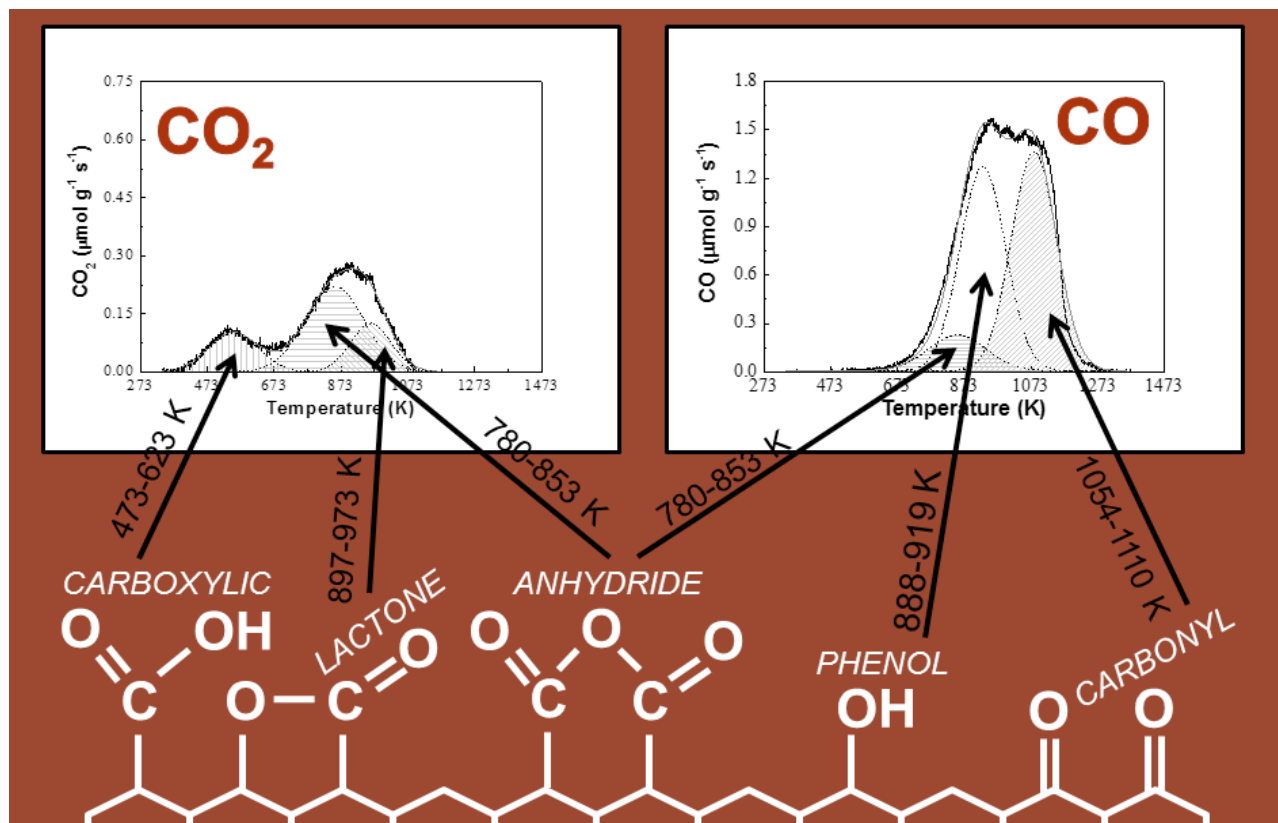

Figure 1. Schematic representation of oxygen surface groups on carbon, and their analysis by deconvolution of TPD profiles.
Figura 1. Esquema de los grupos superficiales de oxígeno sobre carbón, y su análisis a partir de la deconvolución de los perfiles obtenidos por DTP.

groups. These methodologies were originally described in a seminal LCM paper [2], subsequently updated [3]. S-containing groups decompose by releasing SO and SO_2 species, and can also be determined by TPD.

Alternatively, the nature and concentration of O-, N- , B- and S-containing surface groups can be determined by deconvolution of the corresponding XPS spectra. This method is quite adequate for nano-sized carbons, but misleading results may be obtained in the case of porous carbons, since the concentration of the functional groups will in general be higher at the external surface layers, which are those probed by the photoelectrons; thus, the surface concentrations determined by XPS may not be representative of the material as a whole [4].

2. Functionalization methodologies

There are several reasons for the introduction of functional groups on the surface of carbon materials: to create anchoring sites for the adsorption of ions and molecules; to enhance dispersion in a desired reaction medium; to improve miscibility with polymer or oxide matrices, enhancing adhesion; on the other hand, these groups may act as active sites in catalysis.

Among the oxidizing agents that can be used to incorporate oxygen groups onto the carbon material surface, concentrated nitric acid and diluted oxygen are those most frequently used for wet and dry methods, respectively [5]. However, considerable changes in the textural properties of the carbon material may occur, especially in the case of high severity oxidizing treatments.

Textural changes can be minimized by hydrothermal oxidation with diluted nitric acid (< 0.30 mol/L). This method was developed in our group in order to finely adjust the amount of oxygenated surface groups on a carbon material to a desired degree. The extent of carbon surface functionalization was found to be strongly dependent on the concentration of nitric acid and temperature, and the amounts of each type of oxygenated group could be correlated with the acid concentrations used [6,7]. The method has also been applied with sulfuric acid, leading to the incorporation of sulfonic acid groups [8].

Conventional methods used for nitrogen functionalization include high temperature treatments with nitrogen containing gases and carbonization of nitrogen containing compounds or polymers. On the other hand, N-doped carbon xerogels with large mesopore surface areas can be obtained by adding a nitrogen precursor, such as urea or melamine, during synthesis [9]. More recently, we developed a simple and effective dry method for N-doping of carbon nanomaterials such as carbon nanotubes (CNTs) and graphene oxide (GO), which avoids the use of solvents and production of wastes [10]. The method involves ball-milling the carbon material together with a nitrogen precursor, followed by a thermal treatment under inert atmosphere. Large amounts of nitrogen can be incorporated in this way, in the form of quaternary nitrogen, pyridinic, and pyrrolic groups.

3. Carbon materials for catalysis

Carbon materials can be used as catalyst supports or as catalysts on their own. In both cases, the surface chemistry is of paramount importance. Nevertheless, the textural properties are also relevant, as they condition the access of reactants to the active sites and the course of eventual deactivation phenomena. Thus, mesoporous carbons are preferred, especially for reactions in the liquid phase, in comparison to activated carbons which have large micropore volumes [5]. In addition, carbon materials can be useful as catalyst promoters, for instance in photocatalysis.

3.1 Carbon as support

3.1.1 Carbon-supported metal catalysts

The functional groups on the surface of the support provide anchoring sites for the metal precursors and facilitate their access to the inner porosity by increasing the hydrophilicity of the carbon. The catalyst properties will be mainly determined by the precursor-support interactions. In particular, when the catalysts are prepared by impregnation in excess solution, it is essential to maximize the electrostatic interactions between the metal precursor ions in solution and the charged groups on the surface of the carbon, which depend on the pH of the solution and the point of zero charge (PZC) of the support [5]. These procedures were recently reviewed in the context of carbon-supported metal catalysts for fuel cells [11].

In the field of water purification, bimetallic catalysts supported on carbon materials were developed for the selective reduction of nitrate ions to nitrogen. The Pd-Cu catalyst supported on basic carbon materials was found to be the most active and selective [12]. The same catalyst system performed equally well in the reduction of bromate ions [13].

The conversion of biomass-derived raw materials into chemicals and fuels provides ample opportunities for the development of efficient carbon-supported catalysts. For instance, we have investigated the liquid phase selective catalytic oxidation of glycerol (a sub-product of biodiesel production), focusing on the synthesis of fine chemicals with high added value, such as glyceric acid. Different carbon materials were used as supports for gold nanoparticles, including CNTs, activated carbons and carbon xerogels. Surface oxygen was found to be detrimental to the catalyst activity, while the presence of narrow pores led to enhanced selectivity to glyceric acid. Thus, the highest selectivity (75%) was obtained with gold supported on activated carbon [14].

The conversion of cellulose to platform chemicals involves an initial hydrolysis step leading to glucose, followed by catalytic hydrogenation or oxidation steps. However, the one-pot direct conversion of cellulose can be achieved with efficient carbon-based catalysts, as we recently demonstrated for the oxidation of cellobiose to gluconic acid [15] and for the hydrogenation of cellulose to sorbitol [16]. In the first case, mesoporous carbons (xerogels and ordered mesoporous carbons) were functionalized with phenolic groups, providing active sites for cellobiose hydrolysis, while supported gold nanoparticles (1% loading) provided sites for oxidation of the glucose intermediate. A remarkable 80% selectivity to gluconic acid was obtained in a short reaction time [15]. For cellulose hydrogenation, we used Ru (0.4% loading) supported on activated carbon. When the
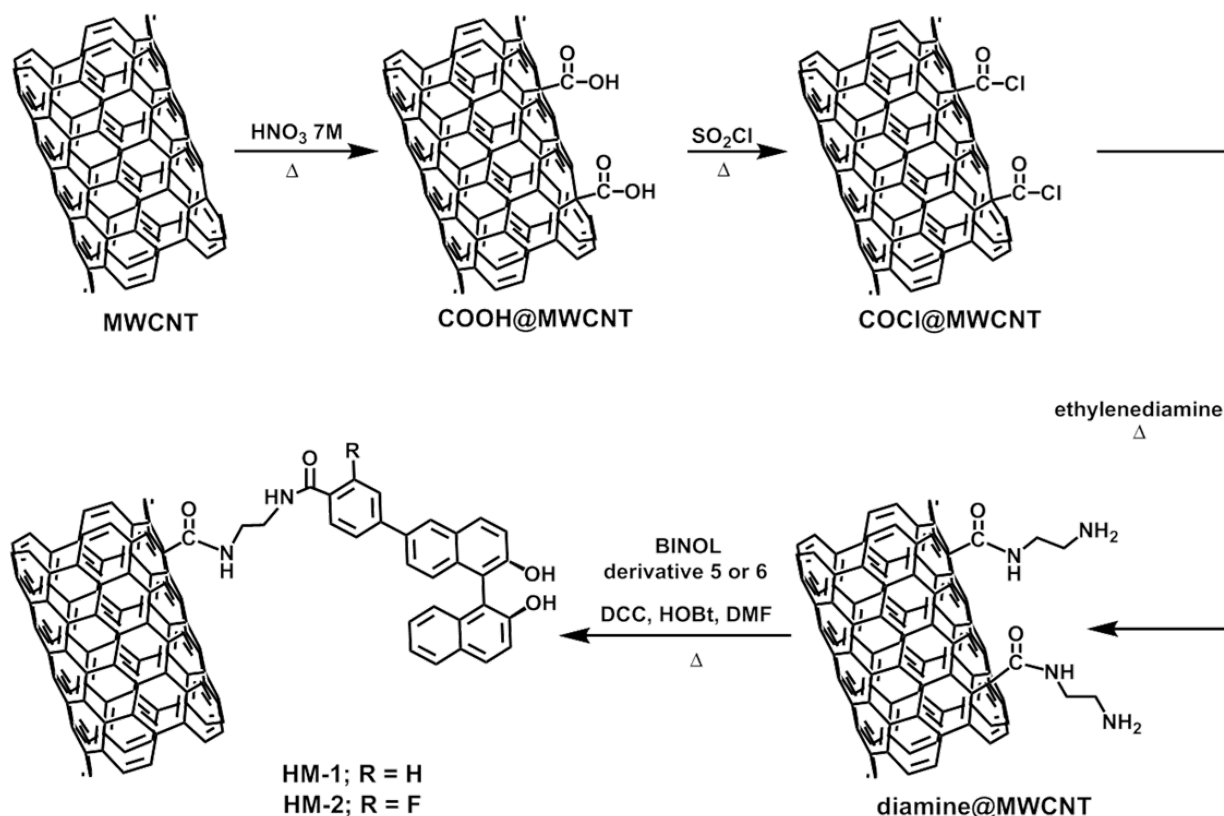
Figure 2. Strategy for the immobilization of (*S*)-BINOL derivatives onto carbon nanotubes. Reprinted from reference [17] with permission from Wiley-VCH.

Figura 2. Estrategia para inmovilizar derivados de (*S*)-BINOL sobre nanotubos de carbono. Reimpreso de [17] con permiso de Wiley-VCH.

catalyst was ball-milled together with the cellulose, an outstanding selectivity to sorbitol of almost 80% was reached [16].

3.1.2 Anchored metal complexes

Carbon materials are excellent supports for the covalent immobilization of metal complexes with catalytic activity, thus providing a route for the heterogenization of homogeneous catalysts in order to combine the advantages of both systems. A detailed account of our early work can be found in reference [1]. One of the most attractive immobilization procedures involves the introduction of functional groups on the carbon support, their subsequent derivatization, and reaction with molecules containing –OH or –NH$_2$ groups in order to form ester or amide linkages. As an example, the immobilization of chiral BINOL derivatives onto carbon nanotubes is shown in Figure 2 [17].

The heterogenization of transition metal complexes with C-scorpionate ligands is another promising topic of research, as these catalysts can be used for the oxidation of various substrates under mild conditions [18-20]. In this case, the C-scorpionate complexes were anchored via phenolate groups, as schematically shown in Figure 3.

3.2 Carbon as catalyst

Industrial applications of carbon as a catalyst on its own are limited to the synthesis of phosgene and related processes, but many other reactions can be catalyzed by metal-free carbons [1,4,5]. A selection of examples from our recent work is described in the next sections.

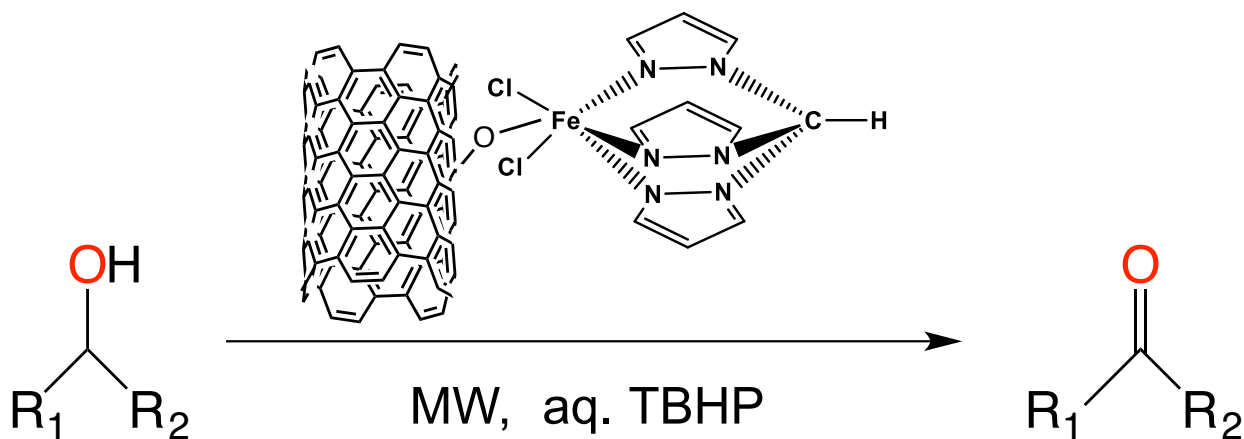### 3.2.1 Oxidative dehydrogenation of isobutane

Figure 3. Oxidation of secondary alcohols to the corresponding ketones in the presence of the C-scorpionate complex [FeCl$_2$\{η^3-HC(pyrazol-1-yl)$_3$\}] anchored on functionalized CNTs.

Figura 3. Oxidación de alcoholes secundarios a sus correspondientes cetonas en presencia del complejo C-escorpionato [FeCl$_2$\{η^3-HC(pirazol-1-yl)$_3$\}] anclado sobre CNTs funcionalizados.

Previous research at LCM using activated carbon as catalyst highlighted the role of quinone surface groups as the active sites for the oxidative dehydrogenation (ODH) of hydrocarbons [21,22]. We have recently resumed research on this topic using oxidized carbon xerogels as catalysts for the ODH of isobutane [23]. Starting from a strongly oxidized carbon xerogel, catalyst samples with the same textural properties but with different amounts of active sites were prepared by heating under inert atmosphere at different temperatures. These samples were then tested in the ODH of isobutane in order to correlate their activity with the concentration of active sites, thus allowing the calculation of the turnover frequency (TOF). Although this is a mandatory requirement for benchmarking novel catalysts with those in current use for a given reaction, such quantitative data are scarce in the published literature, and TOFs for the ODH of lower alkanes had not been previously reported for carbon catalysts. Moreover, we were able to identify the negative role played by carboxylic groups, as shown in Figure 4, where the performance of the original oxidized catalyst (CXO) is compared with samples treated at 600 ºC. This temperature is too low to affect the concentration of the active sites (carbonyl/quinone groups), but is sufficient to remove all carboxylic groups. These groups are electrophilic, and their presence decreases the electron density at the active sites, thus lowering the catalyst activity. Therefore, in spite of having the same amount of active sites, CXO is less active than the thermally treated samples.

We have also investigated the effect of supercritical fluids on the performance of an activated carbon fiber cloth used as catalyst in the ODH of isobutane. Samples exposed to supercritical water exhibited the best performances, leading to high isobutene yields, selectivities close to 95%, and stable operation [24].
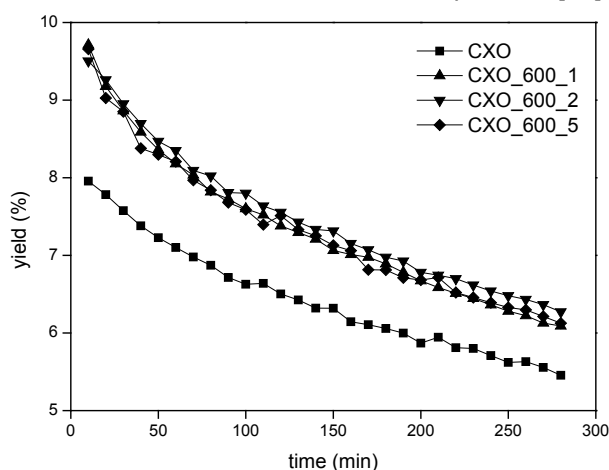

Figure 4. Isobutene yield at 375 ºC as a function of reaction time with oxidized carbon xerogels heat-treated at 600 °C for different times (1, 2 and 5 hours). Reprinted from [23] with permission from Elsevier.

Figura 4. Producción de isobuteno a 375 ºC en función del tiempo de reacción usando xerogeles de carbón oxidados y térmicamente tratados a 600 ºC a diferentes tiempos (1, 2 y 5 horas). Reimpreso de [23] con permiso de Elsevier.

3.2.2 Carbon materials for acid catalysis

Carbon materials can be easily functionalized with sulfonic acid groups and used as solid acid catalysts for such reactions as alkylations, esterifications, acetalizations and hydrolyses. We have recently reported on the esterification of acetic acid with ethanol, as a model acid-catalyzed reaction. Samples with different concentrations of sulfonic acid groups were tested, and a linear correlation between the rate of formation of ethyl acetate and the concentration of these groups was obtained; the calculated TOF was similar to those reported for other types of acid catalysts, but the activity was significantly reduced when the catalyst was reused in consecutive runs [25].

3.2.3 Carbon catalysts for Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are chemical treatments designed to remove pollutants from water and wastewater by oxidation mainly 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 that metal-free carbon materials can be highly active for the complete mineralization of the organic pollutants or their intermediate oxidation products into CO_2 and inorganic species. The corresponding reaction mechanisms are complex, and may involve a combination of homogeneous and heterogeneous steps [4].

Our earlier reports on the performance of carbon materials with different surface chemistry as catalysts for AOPs [26-28] showed that catalyst activity increases with the concentration of basic sites. Additional studies have revealed that acidic O-groups (carboxylic acids, anhydrides and phenol groups) have a strong negative impact on the catalyst activity, the conversion increasing as these groups are successively removed by thermal treatments, as shown in Figure 5 [29]. On the other hand, the presence of N-groups increases the activity of carbon materials as catalysts for AOPs [30-32]. S-groups also seem to play a positive role in the CWAO of phenol [29,30], possibly as a result of the production of highly active sulphate radicals, and in CWPO [33], but further studies are required to explain the reaction mechanisms involved.

3.2.4 Carbon catalysts for the oxygen reduction reaction

One of the major obstacles to the commercialization of fuel cell technologies is the huge amount of platinum required for the electrocatalysts. In particular, the state of the art cathode catalysts, where the oxygen reduction reaction (ORR) occurs, consist of carbon supported Pt, with metal loadings higher than 20%. However, it has been reported that N- and S-doped carbon materials, without any noble metal, can reach equivalent performances, and this has triggered a huge research effort in the field. We have recently started to investigate this topic, focusing on N-doped CNTs for ORR in alkaline medium. Our preliminary results highlight the role of pyridinic and quaternary nitrogen in determining the electrocatalytic ORR activity.

3.3 Carbon as promoter in photocatalysis

3.3.1 Photocatalytic degradation of organic pollutants

The heterogeneous photocatalytic degradation of organic pollutants proceeds mainly via
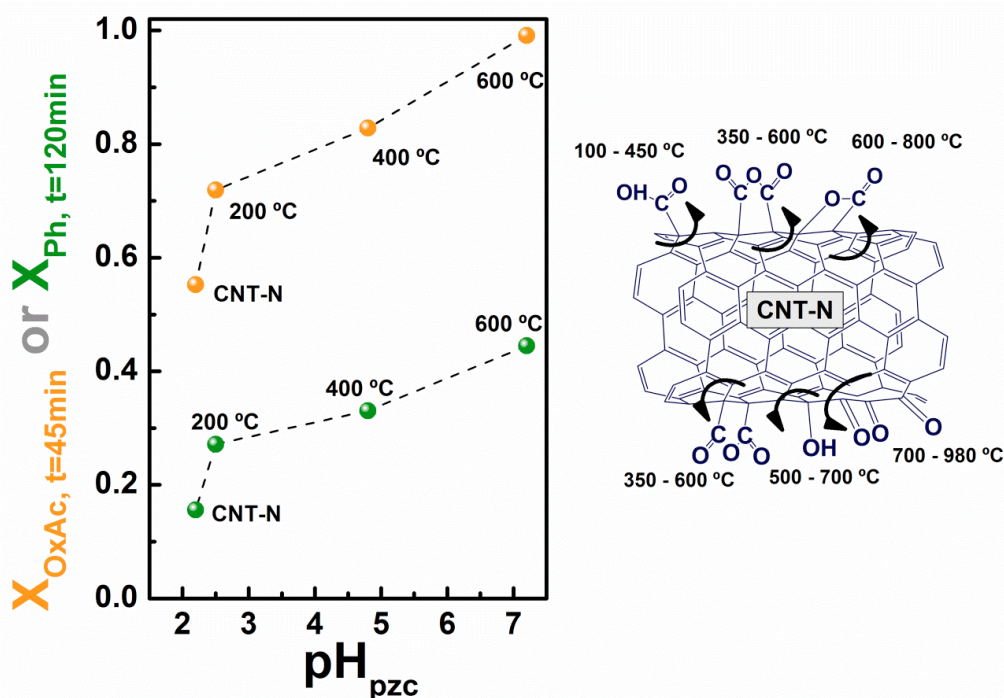
Figure 5. Oxalic acid (OxAc, orange points) and phenol (Ph, green points) degradation by CWAO using CNTs modified with nitric acid and subsequently treated at different temperatures. Adapted from [29] with permission from Elsevier.

Figura 5. Degradación de ácido oxálico (OxAc, puntos naranjas) y fenol (Ph, puntos verdes) por CWAO usando nanotubos de carbono modificados con ácido nítrico y tratados a diferentes temperaturas. Adaptado de [29] con permiso de Elsevier.

photogenerated hydroxyl radicals, and so falls under the definition of AOPs. The usual photocatalysts are semiconducting oxides, TiO_2 being the most popular. The photoactivity of TiO_2 can be improved by adding carbon materials, and the use of CNTs for this purpose was pioneered by LCM [34]. In addition to extended light absorption in the visible range, carbon materials have a promoting effect by inhibiting the electron-hole recombination processes. More recently, other types of nano-sized carbons were used in composites with TiO_2, such as GO [35] and nanodiamonds [36], with excellent results. In particular, a TiO_2-based composite with 4 wt.% of GO demonstrated the highest photocatalytic activity both under near-UV/Vis and visible light irradiation, outperforming the benchmark photocatalyst (Evonik P25 TiO_2). This composite was also incorporated into hollow fibres, showing good photoactivity and stability in continuous operation [37]. Adequate control of the carbon surface chemistry was found to be essential in the preparation of carbon composites with TiO_2 for photocatalysis [38].

We have also assessed the photocatalytic activity of ZnO (synthesized by CVD) combined with different types of nanocarbons [39]. In particular, the composite containing nitrogen-doped carbon nanotubes exhibited the highest photocatalytic activity for phenol degradation under simulated solar light irradiation.

3.3.2 Photocatalytic production of fuels

We have recently engaged in the development of new catalysts for efficient energy production, including solar fuels such as hydrogen from the photocatalytic reforming of biomass, and alcohols from the photoreduction of carbon dioxide. For hydrogen production from methanol and biomass-derived compounds, we used composites of CNTs and TiO_2 loaded with noble metals (Au, Pt, Ir and Pd). The highest conversion was reported with the Pt-loaded composite, highlighting the role of CNTs in promoting the dispersion of TiO_2 particles as well as their action as photosensitizers [40]. For the photocatalytic water reduction of CO_2 into renewable fuels (ethanol, methanol) under UV/vis light irradiation, we used Cu-loaded GO-TiO_2 composites [41].

4. Nanostructured carbon-based materials for energy and environmental applications

4.1 Hierarchical porous carbons for energy storage

Electrochemical double layer capacitors (EDLCs, or supercapacitors) are promising energy storage devices due to their high power density and small size. In principle, the capacitance increases with the specific surface area, but pore accessibility is also a key factor. Thus, the presence of well-developed ordered mesoporosity may increase the electrochemically active surface area by facilitating the diffusion of electrolyte ions. Further improvements in energy density can be achieved by promoting reversible faradaic reactions between the electrode surface and the electrolyte (pseudocapacitance). Thus, hybrid supercapacitors, combining both electrostatic and electrochemical storage mechanisms, can be obtained by enriching porous carbon materials with heteroatoms (N, O, S, P or B) or by decorating their surface with transition metal oxides. We have recently developed a hydrothermal route to produce boron doped ordered mesoporous carbons with tuned porosity and surface chemistry [42], and subsequent work will address the optimization of their properties in order to achieve high-performance supercapacitor electrodes.

4.2 Membranes for water desalination and treatment

The development of membranes for water desalination and treatment is a recent topic of research at LCM. The objective is to obtain novel composite membranes based on functionalized

nanocarbons (CNTs, GO) with enhanced physical and chemical properties, by tuning the surface chemistry of the nanocarbons and their respective loading in the membranes. The introduction of the optimal amount and type of functional surface groups is a crucial step in the development of membranes for new desalination technologies, because it will allow to tune the porosity and surface free energy of the membrane and the rejection properties of the active layer [8,43].

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