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INDICE

Editorial

It gave me great pleasure to accept the invitation of Professor F. Maldonado to be the Invited Editor of this special issue of the Boletín del Grupo Español del Carbón dedicated to the carbon materials research developed by the Portuguese groups that for long time have been working in this thematic.

The preparation of the issue was not a difficult task. All the colleagues to whom I addressed an invitation to prepare a manuscript, showing the carbon materials related work developed in their research groups, were very receptive to the idea. This was not a surprise due to the close and fruitful collaboration that all of us have with Spanish colleagues. If there was any doubt, a brief look into the references of the various contributions is sufficient to come to that conclusion.

Preparing the "invitation list" was an easy issue. In fact, although the number of Portuguese research groups working on carbon materials is not very high, the quality of work developed is internationally recognized.

The first invitation was addressed to Professor José Luis Figueiredo who headed the group related with Catalysis and Materials in the Faculty of Engineering of University of Porto for more than 30 years. Among the numerous studies published by the group, one of the major achievements is the proposed methodology to characterize the surface functional groups based on the temperature programmed desorption results. The original paper was published in 1999 and so far it was cited by almost 1400 documents, some of them being studies published in 2016, proving the subject's relevance.

The other two groups, from University of Évora and New University of Lisbon, are also headed by well-known researchers who have been using carbon materials for different purposes. The group of Professor Peter Carrott and Professor Manuela Carrott have been interested in the preparation of carbons and in the assessment of the potentialities of the materials as adsorbents in gas and liquid phases processes. On the other hand, the research of the group headed by Professor Isabel Fonseca is mainly based on the use of carbon materials as catalysts.

Lastly, the interest of the University of Lisbon's group is currently focused on the preparation of biomass-derived carbons to be applied in the removal of pharmaceutical compounds in aqueous solution.

By choosing these four groups, the goal was to give an overview of the carbon materials' studies developed in Portugal, expecting that the texts would (and effectively did) include collaborations with other national groups whose main objective is not directly related with carbon materials.

The documents gathered in this issue show the large scope of the studies developed in Portugal in the field of carbon materials which, I hope, could lead to the establishment of even more Iberian collaborations.

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$_2$O) 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

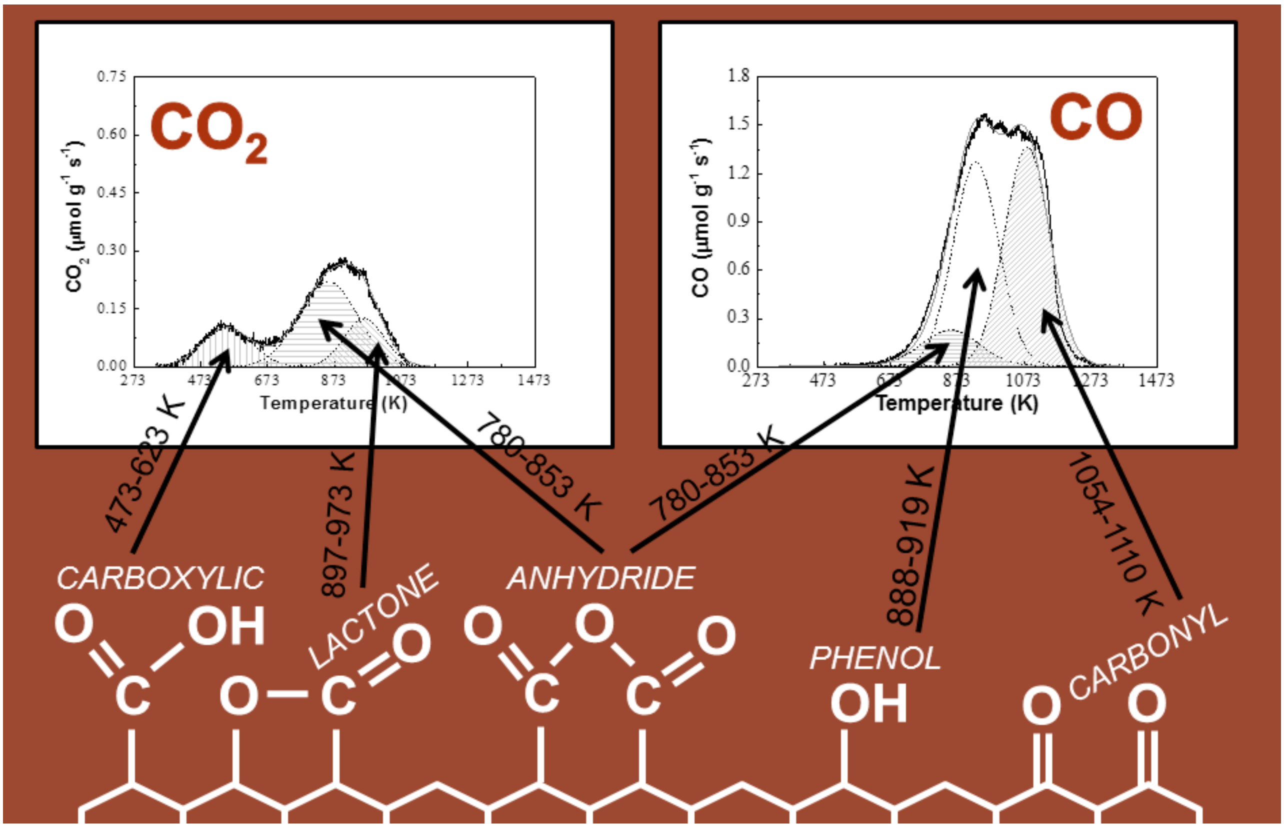

Figure 1. Schematic representation of oxygen surface groups on carbon, and their analysis by deconvolution of TPD profiles.

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

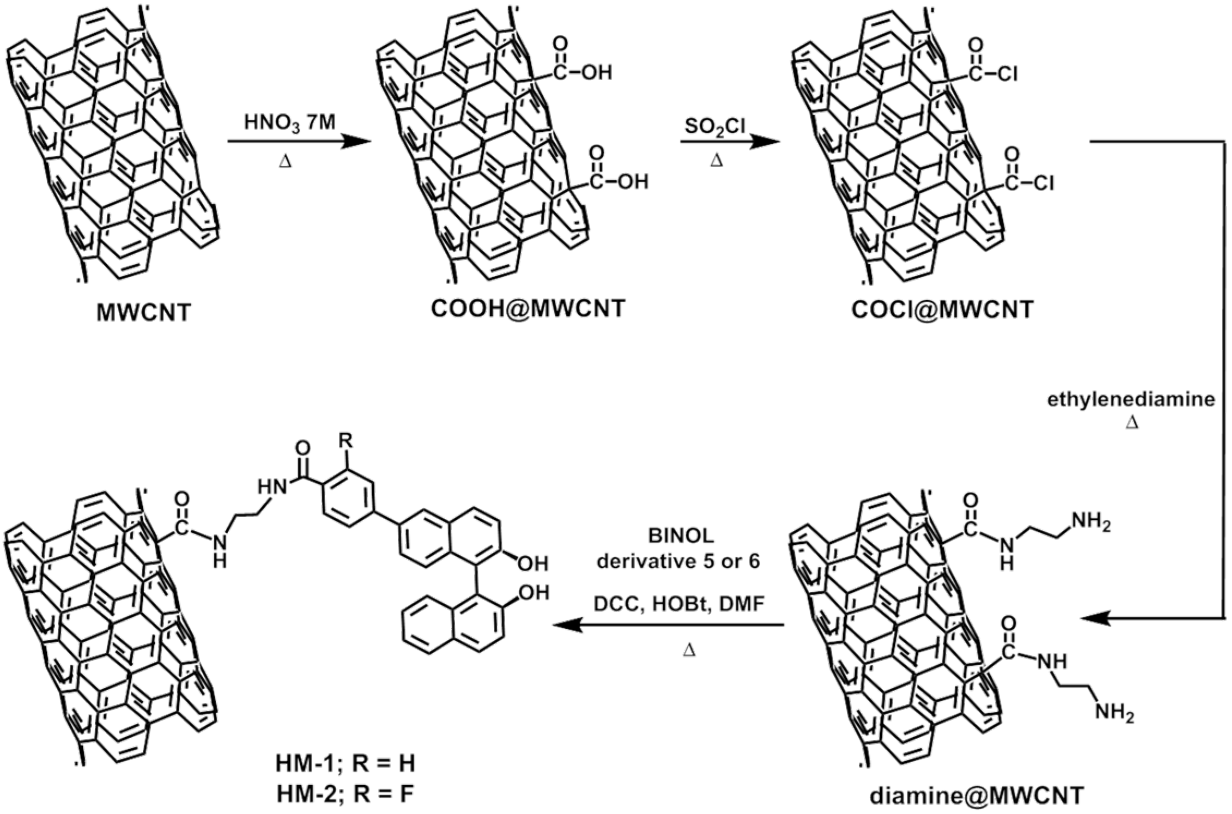

Figure 2. Strategy for the immobilization of (*S*)-BINOL derivatives onto carbon nanotubes. Reprinted from reference [17] with permission from Wiley-VCH.

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

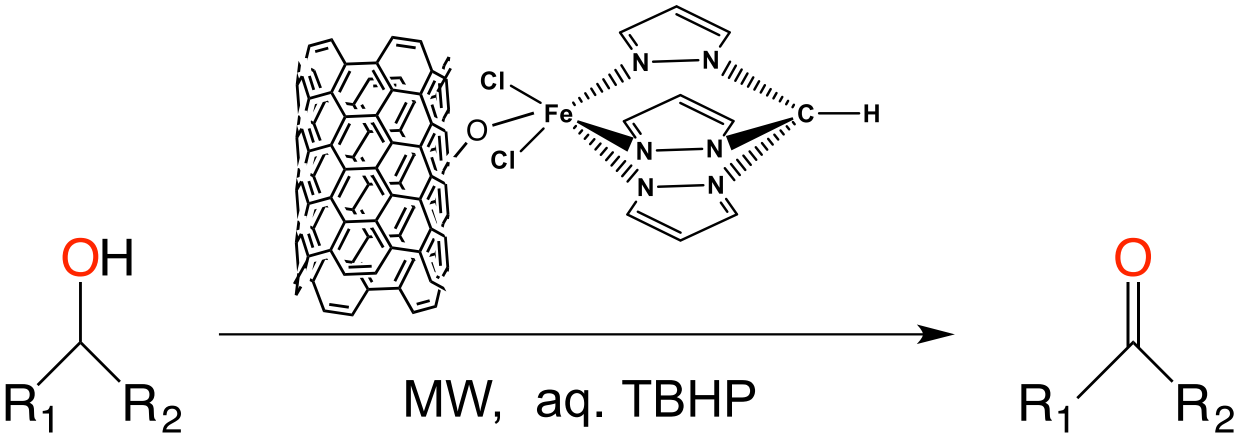

Figure 3. Oxidation of secondary alcohols to the corresponding ketones in the presence of the C-scorpionate complex $[FeCl_2\{\eta^3\text{-}HC(pyrazol\text{-}1\text{-}yl)_3\}]$ anchored on functionalized CNTs.

Figura 3. Oxidación de alcoholes secundarios a sus correspondientes cetonas en presencia del complejo C-escorpionato $[FeCl_2\{\eta^3\text{-}HC(pirazol\text{-}1\text{-}yl)_3\}]$ 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].

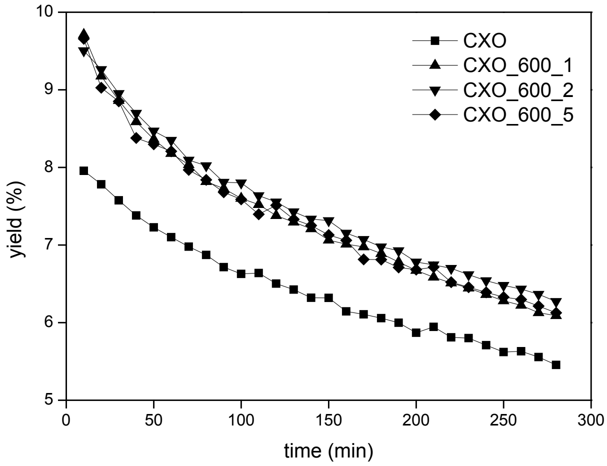

Figure 4. Isobutene yield at 375 ºC as a function of reaction time with oxidized carbon xerogels heat-treated at 600 °C for different times (1, 2 and 5 hours). Reprinted from [23] with permission from Elsevier.

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

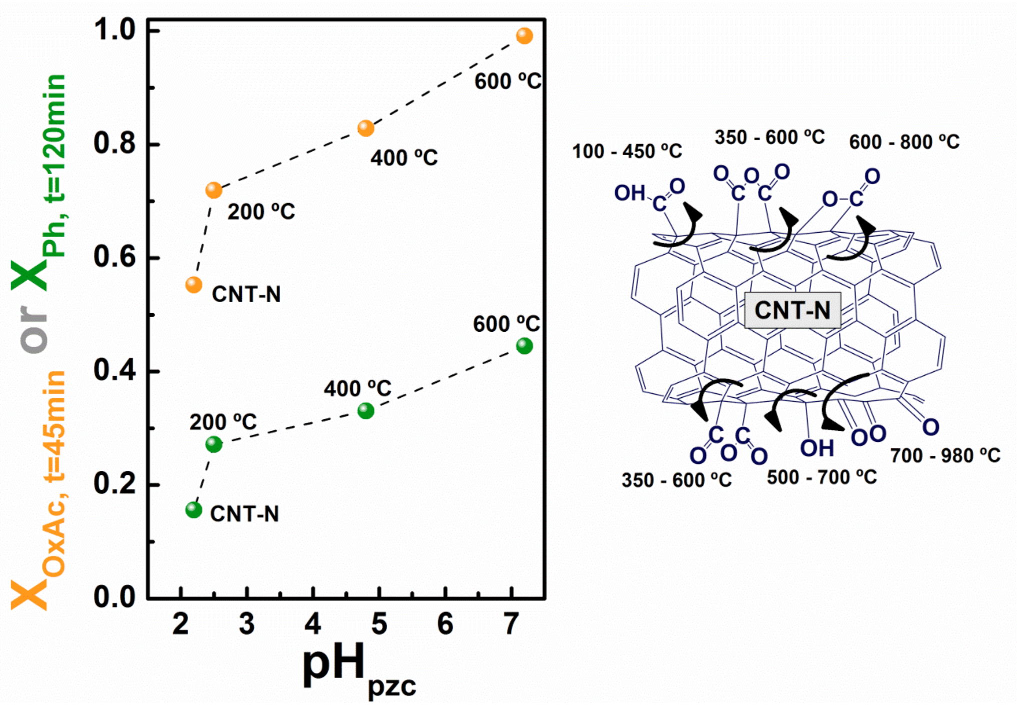

Figure 5. Oxalic acid (OxAc, orange points) and phenol (Ph, green points) degradation by CWAO using CNTs modified with nitric acid and subsequently treated at different temperatures. Adapted from [29] with permission from Elsevier.

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].

Acknowledgments

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References

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

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

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

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

[5] Figueiredo JL. Functionalization of porous carbons for catalytic applications. J. Mater. Chem. A 2013; 1: 9351-9364.

[6] Silva AMT, Machado BF, Figueiredo JL, Faria JL. Controlling the surface chemistry of carbon xerogels using HNO_3 hydrothermal activation. Carbon 2009; 47: 1670-1679.

[7] Romanos GE, Likodimos V, Marques RRN, Steriotis TA, Papageorgiou SK, Faria JL, Figueiredo JL, Silva AMT, Falaras P. Controlling and quantifying oxygen functionalities on hydrothermally and thermally treated single-wall carbon nanotubes. J. Phys. Chem. C 2011;115: 8534-8546.

[8] Morales-Torres S, Silva TLS, Pastrana-Martínez LM, Brandão ATSC, Figueiredo JL, Silva AMT. Modification of the surface chemistry of single and multi-walled carbon nanotubes by HNO_3 and H_2SO_4 hydrothermal oxidation for application in direct contact membrane distillation. Phys. Chem. Chem. Phys. 2014; 16: 12237-12250.

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

[10] Soares OSGP, Rocha RP, Gonçalves AG, Figueiredo JL, Órfão JJM, Pereira MFR. Easy method to prepare N-doped carbon nanotubes by ball milling. Carbon 2015; 91: 114-121.

[11] Figueiredo JL, Pereira MFR. Synthesis and functionalization of carbon xerogels to be used as supports for fuel cell catalysts. J. Energy Chemistry 2013; 22: 195–201.

[12] Soares OSGP, Órfão JJM, Pereira MFR. Nitrate reduction catalyzed by Pd–Cu and Pt–Cu supported on different carbon materials. Catal. Lett. 2010; 139: 97–104.

[13] Restivo J, Soares OSGP, Órfão JJM, Pereira MFR. Bimetallic activated carbon supported catalysts for the hydrogen reduction of bromate in water. Catal. Today 2015; 249: 213–219.

[14] Rodrigues EG, Pereira MFR, Chen X, Delgado JJ, Órfão JJM. Influence of activated carbon surface chemistry on the activity of Au/AC catalysts in glycerol oxidation. J. Catal. 2011; 281: 119-127.

[15] Eblagon KM, Pereira MFR, Figueiredo JL. One- pot oxidation of cellobiose to gluconic acid. Unprecedented high selectivity on bifunctional gold catalysts over mesoporous carbon by integrated texture and surface chemistry optimization. Appl. Catal. B: Environ. 2016; 184: 381-396.

[16] Ribeiro LS, Órfão JJM, Pereira MFR. Enhanced direct production of sorbitol by cellulose ball-milling. Green Chem. 2015; 17: 2973-2980.

[17] Monteiro CJP, Carabineiro SAC, Lauterbach T, Hubbert C, Hashmi ASK, Figueiredo JL, Pereira MM. *(S)*-BINOL immobilized onto multiwalled carbon nanotubes through covalent linkage: A new approach for hybrid nanomaterials characterization. ChemNanoMat 2015; 1: 178–187.

[18] Martins LMDRS, Peixoto de Almeida M, Carabineiro SAC, Figueiredo JL, Pombeiro AJL. Heterogenisation of a C-scorpionate FeII complex on carbon materials for cyclohexane oxidation with hydrogen peroxide. ChemCatChem 2013; 5: 3847–3856.

[19] Peixoto de Almeida M, Martins LMDRS, Carabineiro SAC, Lauterbach T, Rominger F, Hashmi ASK, Pombeiro AJL, Figueiredo JL. Homogeneous and heterogenised new gold C-scorpionate complexes as catalysts for cyclohexane oxidation. Catal. Sci. Technol. 2013; 3: 3056-3069.

[20] Ribeiro AP, Martins LM, Carabineiro SAC, Figueiredo JL, Pombeiro A. Portuguese Patent Application nº 109062, filed December 29th, 2015.

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

[22] Velásquez JJD, Suárez LMC, Figueiredo JL. Oxidative dehydrogenation of isobutane over activated carbon catalysts. Appl. Catal. A: Gen. 2006; 311: 51–57.

[23] Pelech I, Soares OSGP, Pereira MFR, Figueiredo JL. Oxidative dehydrogenation of isobutane on carbon xerogel catalysts. Catal. Today 2015; 249: 176–183.

[24] Martín-Sánchez N, Soares OSGP, Pereira MFR, Sanchez-Montero MJ, Figueiredo JL, Salvador F. Oxidative dehydrogenation of isobutane catalyzed by an activated carbon fibre cloth exposed to supercritical fluids. Appl. Catal. A: Gen. 2015; 502: 71-77.

[25] Rocha RP, Pereira MFR, Figueiredo JL, Carbon as a catalyst: Esterification of acetic acid with ethanol. Catal. Today 2013; 218-219: 51-56.

[26] Rocha RP, Sousa JPS, Silva AMT, Pereira MFR, Figueiredo JL. Catalytic activity and stability of multiwalled carbon nanotubes in catalytic wet air oxidation of oxalic acid: the role of the basic nature induced by the surface chemistry. Appl. Catal. B: Environ. 2011; 104: 330-336.

[27] Ribeiro RS, Silva AMT, Figueiredo JL, Faria JL, Gomes HT. The influence of structure and surface chemistry of carbon materials on the decomposition of hydrogen peroxide. Carbon 2013; 62: 97–108.

[28] Gonçalves AG, Figueiredo JL, Órfão JJM, Pereira MFR. Influence of the surface chemistry of multiwalled carbon nanotubes on their activity as ozonation catalysts. Carbon 2010; 48: 4369-4381.

[29] Rocha RP, Silva AMT; Romero SMM, Pereira MFR, Figueiredo JL. The role of O- and S-containing surface groups on carbon nanotubes for the elimination of organic pollutants by catalytic wet air oxidation. Appl. Catal. B: Environ. 2014; 147: 314–321.

[30] Restivo J, Rocha RP, Silva AMT, Órfão JJM, Pereira MFR, Figueiredo JL. Catalytic performance of heteroatom-modified carbon nanotubes in advanced oxidation processes. Chin. J. Catal. 2014; 35: 896–905.

[31] Rocha RP, Restivo J, Sousa JPS, Órfão JJM, Pereira MFR, Figueiredo JL. Nitrogen-doped carbon xerogels as catalysts for advanced oxidation processes, Catal. Today 2015; 241: 73-79.

[32] Rocha RP, Gonçalves AG, Pastrana-Martínez LM, Bordoni BC, Soares OSGP, Órfão JJM, Faria JL, Figueiredo JL, Pereira MFR, Silva AMT. Nitrogen-doped graphene-

based materials for advanced oxidation processes. Catal. Today 2015; 249: 192–198.

[33] Gomes HT, Miranda SM, Sampaio MJ, Figueiredo JL, Silva AMT, Faria JL. The role of activated carbons functionalized with thiol and sulfonic acid groups in catalytic wet peroxide oxidation. Appl. Catal. B: Environ. 2011; 106: 390-397.

[34] Wang W, Serp P, Kalck P, Faria JL. Visible light photodegradation of phenol on MWNT-TiO_2 composite catalysts prepared by a modified sol–gel method. J. Mol. Catal. A: Chem. 2005; 235: 194-199.

[35] Pastrana-Martínez LM, Morales-Torres S, Likodimos V, Figueiredo JL, Faria JL, Falaras P, Silva AMT. Advanced nanostructured photocatalysts based on reduced graphene oxide-TiO_2 composites for degradation of diphenhydramine pharmaceutical and methyl orange dye. Appl. Catal. B: Environ. 2012; 123-124: 241-256.

[36] Pastrana-Martínez LM, Morales-Torres S, Carabineiro SAC, Buijnsters JG, Faria JL, Figueiredo JL, Silva AMT. Nanodiamond-TiO_2 composites for heterogeneous photocatalysis. ChemPlusChem 2013; 78: 801–807.

[37] Pastrana-Martínez LM, Morales-Torres S, Papageorgiou SK, Katsaros FK, Romanos GE, Figueiredo JL, Faria JL, Falaras P, Silva AMT. Photocatalytic behaviour of nanocarbon-TiO_2 composites and immobilization into hollow fibres. Appl. Catal. B: Environ. 2013; 142–143: 101–111.

[38] Pastrana-Martínez LM, Morales-Torres S, Likodimos V, Falaras P, Figueiredo JL, Faria JL, Silva AMT. Role of oxygen functionalities on the synthesis of photocatalytically active graphene-TiO_2 composites. Appl. Catal. B: Environ. 2014; 158–159: 329–340.

[39] Sampaio MJ, Bacsa RR, Benyounes A, Axet R, Serp P, Silva CG, Silva AMT, Faria JL. Synergistic effect between carbon nanomaterials and ZnO for photocatalytic water decontamination. J. Catal. 2015; 331: 172–180.

[40] Silva CG, Sampaio MJ, Marques RRN, Ferreira LA, Tavares PB, Silva AMT, Faria JL. Photocatalytic production of hydrogen from methanol and saccharides using carbon nanotube-TiO_2 catalysts. Appl. Catal. B: Environ. 2015; 178: 82–90.

[41] Pastrana-Martínez LM, Silva AMT, Fonseca N, Vaz J, Figueiredo JL, Faria JL. Photocatalytic water reduction of CO_2 to methanol using graphene derivative-TiO_2 composites: Effect of pH and copper (I) oxide. Submitted for publication.

[42] Enterría M, Pereira MFR, Martins JI, Figueiredo JL. Hydrothermal functionalization of ordered mesoporous carbons: The effect of boron on supercapacitor performance. Carbon 2015; 95: 72-83.

[43] Silva TLS, Morales-Torres S, Figueiredo JL, Silva AMT. Multi-walled carbon nanotube/PVDF blended membranes with sponge and finger-like pores for direct contact membrane distillation. Desalination 2015; 357: 233–245.

Carbon Materials Research in Évora

La Investigación en Materiales de Carbono en Évora

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Abstract

An overview is presented of the work involving carbon materials which has been carried out in Évora by the Surface and Materials Chemistry Group. Current active interests related to the synthesis or preparation and surface modification of carbon materials, studies of gas phase and liquid phase applications and fundamental studies of adsorption, are highlighted.

Resumen

Este trabajo presenta una visión general del trabajo que se ha llevado a cabo en Évora por el Grupo de Química de Superficies y Materiales con materiales de carbono. Entre los intereses actuales del Grupo son de destacar la síntesis o preparación de nuevos materiales, la modificación de la química superficial de los materiales de carbono, el estudio de sus aplicaciones en las fases gaseosa y líquida, y los estudios fundamentales de adsorción.

1. Introduction

Research in adsorption and materials chemistry began in Évora in 1991 with a study financed by the Portuguese National Environmental Agency on the use of activated carbons for the removal of pollutants from water. Subsequently, what is now the Surface and Materials Chemistry Group of the Évora Chemistry Centre, concentrated most of its research activity in three major areas. On the one hand, the synthesis or preparation and surface modification of carbon and silica based porous materials. Although the latter will not be discussed here it is of interest to point out that the group have always maintained a strong and active interest in the synthesis and applications of pure and surface modified mesostructured mesoporous silicas. The second major area is gas phase and liquid phase applications of the materials developed, with emphasis on environmental control, gas separations and certain health related issues, as well as some catalytic studies. The third major area is related to fundamental studies of adsorption. Silica based materials, because of their more uniform and ordered mesoporous structure, have proven to be particularly useful for this type of study. However, some interesting results have also been obtained using carbon materials.

Besides the three major areas, the Surface and Materials Chemistry Group, usually in collaboration with other research groups, has also studied other materials, including zeolites, clays, polymer aerogels and molecularly imprinted polymers, as well as non-porous materials, including carbon blacks and non-porous polymers. With regard to the latter, it is of interest to mention that the group is currently participating in an EC Workgroup developing European Standards for the characterization of End-of-Life Tyres. Taking this together with the work on porous materials, this means that the group now has first-hand practical experience of measuring surface areas over 3 orders of magnitude from < 1 $m^2 g^{-1}$ to > 1000 $m^2 g^{-1}$, as well as porosity over 4 orders of magnitude from < 1 nm (by adsorption of N_2 at 77 K) up to 53 µm (by mercury porosimetry).

Over the years, the Surface and Materials Chemistry Group has collaborated with a large number of other research groups around the world. It is especially relevant to highlight here the long standing "carbon contacts" with two Spanish institutions, namely, the Universidad de Extremadura, which is actually the closest other university to the University of Évora, and the Instituto Nacional del Carbón (INCAR) in Oviedo. As well as various publications, joint patents between these institutions and the University of Évora have been obtained.

In the following sections, we will present an overview of some of the work involving carbon materials which the Surface and Materials Chemistry Group has carried out with current active interests highlighted. Only a few references, which can be considered a representative selection of the group's carbon work, are given [1-31].

2. Synthesis, preparation and surface modification of carbon materials

2.1. Bioresources

A recurring theme in the Surface and Materials Chemistry Group's work has been the valorization of residues arising from agricultural or industrial activities. Évora is situated in the Alentejo, which is the world's largest cork producing region, and it was natural therefore that we should be the first to study the transformation of cork into activated carbon [1, 2]. The Alentejo is also the home of Delta Cafés, which is one of the largest coffee roasting companies in Europe, and hence coffee manufacturing residues have also been used as activated carbon precursors [3, 4]. A significant research effort, with EC and national funding, was also put into the production of activated carbons from different types of lignin [5, 6]. Other bioresources which the group have investigated include almond shell [7], vine shoots [8], esparto grass [9], sunflower stems and olive stones. Work which is currently in progress is using chitosan, sacarose, fructose and different types of wood from the Benguela region of Angola and from the Dili region of Timor-Leste.

Both physical and chemical activation have been used. One of the novel features of the work, originally carried out with cork, was the use of "dry" chemical activation, which was found to have some advantages over the more usual "wet" chemical activation [2]. Similarly, hydrothermal carbonization is presently being developed as an interesting higher yield, and hence precursor and energy efficient, alternative to the traditional thermal carbonization [10, 11]. In conjunction with subsequent chemical activation, very high surface area (~ 2000 $m^2 g^{-1}$) materials with controllable porosity are being obtained.

2.2. Polymer precursors

Members of the Surface and Materials Chemistry Group were working with activated carbon fibres, more specifically viscose rayon based activated carbon cloths, before moving to Évora and this interest in microporous carbon fibres was continued using acrylic textile fibres and cloths as precursors [12-15]. Some work has also been carried out using cloths made from lyocell rayon. A particularly interesting feature of this work, carried out in collaboration with INCAR, was that it was found that microwave heating could be used as a rapid and clean method to modify the activated carbon fibres and to introduce molecular sieve properties [14, 15].

The principal centre for recycling of PET in Portugal is located in the Alentejo, which led us to study the use of recycled PET for producing activated carbons [16] and this line of work is still being actively developed. Following the same theme of valorization of residues, ongoing work, under a R&D Project supported by the FCT, is related to the conversion of MDF and PB composites, which are becoming available in increasingly large amounts, and lend themselves naturally to the formation of monolithic adsorbents. Low density carbon aerogels are another ongoing interest of the group and these have been prepared from both the usual resorcinol-formaldehyde (RF) polymer aerogels [17, 18] as well as from 2,4-dihydoxybenzoic acid-formaldehyde (DHBAF) polymer aerogels [19, 20]. One of the reasons for studying DHBAF aerogels is that the carboxyl hydrogens can be exchanged with metal ions which, after carbonization of the polymer, are converted into metallic nanoparticles, uniformly deposited on a mesoporous carbon support.

3. Gas phase and liquid phase applications of carbon materials

3.1. Gas phase applications

Gas phase applications, excluding fundamental adsorption and characterization studies, referred to below, have been directed towards the separation of gases, namely, N_2, O_2, CH_4 and CO_2 [14-16], CO_2 capture [20], VOC reduction and some catalytic processes. In the first case, various methods, including CVD, γ-irradiation and microwave treatment, have been used to induce molecular sieve properties in activated carbons prepared from different precursors and, under certain conditions, it has been possible to achieve selectivities for O_2/N_2 separation, for example, superior to those given by the widely used commercial Takeda carbon molecular sieves.

Studies of CO_2 capture have been based on surface modification of carbon aerogels by deposition of amines. Other alternative methods of modification, as well as non-carbon adsorbents, are currently being investigated. A novel aspect of this work, for the group, is the development of thermogravimetric analysis as a convenient and versatile technique for studying the equilibrium and kinetics of gas phase adsorption.

A long standing and ongoing characteristic of the Surface and Materials Chemistry Group is related to studies of the adsorption of hydrocarbons and alcohols and water vapour. It might be mentioned that many visiting PhD students have come to Évora specifically to carry out equilibrium and kinetic studies of adsorption with our equipment, as gravimetric adsorption equipment is not available in all laboratories. The adsorption of organic vapours is of some relevance in the context of VOC pollution, although the main focus of our own work is generally directed more towards characterization and fundamental studies of adsorption and is referred to below.

3.2. Liquid phase applications

The early studies carried out by the Surface and Materials Chemistry Group were related to the adsorption of metal ions [21, 22]. Subsequently, attention was switched to the adsorption of phenolic compounds [23-27] and then to pharmaceuticals and pesticides [28]. Environmental Persistent Pharmaceutical Pollutants (EPPPs) have been classified as "priority substances" by the EU, while both pharmaceuticals and pesticides are classified as Persistent Organic Pollutants (POPs). Hence, they are highly relevant to us as, on the one hand, agriculture and forestry based industries are amongst the principal economic motors of the Alentejo and, on the other, a number of Portugal's major water resources, including the Rivers Guadiana and Tagus (*Tejo*) and the Alqueva Reservoir, are, wholly or partially, in the Alentejo.

Studies of the adsorption of solutes from the liquid phase are generally carried out in batch mode. On the other hand, for our work currently in progress with MDF and PB based activated carbons, it was considered important to compliment these studies by developing procedures for carrying out adsorption studies in a flow system as well. Hence, kinetic and equilibrium adsorption studies of specific probe molecules, considered pollutants, such as phenolic compounds (including phenol) and dyes (including Neutral Red), by MDF and PB based activated carbons in both monolithic and powder form, has been studied in both batch and dynamic modes.

Studies related to health are one of the most recent areas of interest of the group, in particular the adsorption of metformin, a drug to treat diabetes, and fluoxetine, the active ingredient of many antidepressant drugs, in simulated gastric and intestinal fluids and very interesting results are being obtained. The group has produced carbon materials with the potential to treat intoxications, assuming the usual dose of activated carbon slurry to treat overdoses at hospital level and that the person had ingested a full box of pills. Recently, the adsorption of glucose using hybrid materials was also studied.

4. Fundamental studies of adsorption by carbon materials

4.1. Adsorption from the gas phase

One of the standard methods for analyzing vapour adsorption isotherms is the α_s method. In order to apply the method a standard or reference adsorption isotherm is needed and, with the exception of N_2 at 77K, these are rarely available. Part of our work is to evaluate the possibility of using adsorptives other than N_2 at 77 K and to publish standard data whenever possible. The adsorptives studied in most detail so far include benzene, methanol, ethanol and dichloromethane [29, 30].

Carbon aerogels are simultaneously micro and mesoporous and this leads to errors in the estimation of micropore volume when the α_s (underestimated) and DR (overestimated) methods are used. Initially, we resolved the problem by recurring to the nonane preadsorption method, which proved to be ideally suited for these materials [17, 18]. Subsequently, we were then able to validate the applicability of the QSDFT method, as opposed to the more common NLDFT method, for the characterization of the microporosity of carbon aerogels [19].

Ordered mesoporous materials are of great interest as model adsorbents. In this context, the Surface and Materials Chemistry Group have also carried out detailed studies of adsorption-desorption isotherms of aromatic and aliphatic hydrocarbons on various ordered mesoporous materials, including CMK-3 type mesoporous carbon [31]. This work is of particular interest, on the one hand, as it combines our experience with mesostructured silica and carbon adsorbents and, on the other, as it allowed us to evaluate the effect of adsorbent characteristics, such as surface chemistry, pore size and shape and pore opening size, on the adsorption behavior of different hydrocarbons of different size and polarity.

4.2. Adsorption from the liquid phase

Here, we will mention just two aspects of our work with carbon materials.

Adsorption from aqueous solutions is more complex than gas phase adsorption as i) there is competition between solute and solvent for adsorption space, ii) the solute will usually be present in different, frequently charged, forms, in proportions which vary according to the conditions and iii) the adsorbent surface may also have a charge which will also vary according to the conditions. In our work on the adsorption of metal species we developed a simple surface ionization / adsorption model and this was subsequently adapted for adsorption of organic solutes [21, 22, 26]. By a combination of solute adsorption at different concentrations and solution pH values, acid/base titrations, mass titrations and simulation of the model, it was possible to make estimates of surface ionization constants and, in the case of the metal species, adsorption equilibrium constants.

A more commonly used empirical equation for adsorption of organic solutes, which is also an integral feature of ASTM standard D3860 for the determination of the adsorptive capacity of activated carbon, is the Freundlich Equation. We presented an analysis of a solute solubility normalized form of the equation and its application to adsorption isotherms of various phenolic solutes indicated that two regimes of adsorption, characterized by an adsorption energy, E_{ads}, greater than or less than a critical value, E_{ca}, could be distinguished. When $E_{ads} > E_{ca}$, the shape of the adsorption isotherm is determined by solute-solid interactions. On the other hand, when $E_{ads} < E_{ca}$, solute-solution interactions become more important [25].

5. Acknowledgements

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6. References

[1] Carrott PJM, Ribeiro Carrott MML, Lima RP. Preparation of activated carbon `membranes' by physical and chemical activation of cork. Carbon. 1999;37:515-7.

[2] Carrott PJM, Ribeiro Carrott MML, Mourão PAM. Pore size control in activated carbons obtained by pyrolysis under different conditions of chemically impregnated cork. J Anal Appl Pyrolysis. 2006;75:120-7.

[3] Domínguez A, Menéndez JA, Fernández Y, Pis JJ, Valente Nabais JM, Carrott PJM, Ribeiro Carrott MML. Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. J Anal Appl Pyrolysis. 2007;79:128-35.

[4] Nabais JV, Carrott PJM, Ribeiro Carrott MML, Luz V, Ortiz AL. Influence of preparation conditions in the textural and chemical properties of activated carbons from a novel biomass precursor: The coffee endocarp. Bioresource Technol. 2008;99:7224-31.

[5] Carrott PJM, Suhas, Ribeiro Carrott MML, Guerrero CI, Delgado LA. Reactivity and Porosity Development during Pyrolysis and Physical Activation in CO_2 or Steam of Kraft and Hydrolytic Lignins. J Anal Appl Pyrolysis. 2008;82:264-71.

[6] Carrott PJM, Ribeiro Carrott MML, Suhas. Comparison of the Dubinin-Radushkevich and Quenched Solid Density Functional Theory approaches for the characterisation of narrow microporosity in activated carbons obtained by chemical activation with KOH or NaOH of Kraft and hydrolytic lignins. Carbon. 2010;48:4162-9.

[7] Nabais JMV, Laginhas CEC, Carrott PJM, Ribeiro Carrott MML. Production of activated carbons from almond shell. Fuel Proc Technol. 2011;92:234-40.

[8] Nabais JMV, Laginhas C, Carrott PJM, Ribeiro Carrott MML. Thermal conversion of a novel biomass agricultural residue (vine shoots) into activated carbon using activation with CO_2. J Anal Appl Pyrolysis. 2010;87:8-13.

[9] Nabais JMV, Laginhas C, Ribeiro Carrott MML, Carrott PJM, Amoros JEC, Gisbert AVN. Surface and porous characterisation of activated carbons made from a novel biomass precursor, the esparto grass. Appl Surf Sci. 2013;265:919-24.

[10] Román S, Valente Nabais JM, Ledesma B, González JF, Laginhas C, Titirici MM. Production of low-cost adsorbents with tunable surface chemistry by conjunction of hydrothermal carbonization and activation processes. Micropor Mesopor Mater. 2013;165:127–33.

[11] Nabais JMV, Laginhas C, Titirici MM. Activated carbons with high nitrogen content by a combination of hydrothermal carbonization with activation. Microporous and Mesoporous Materials. 2016;226:125-32.

[12] Carrott PJM, Nabais JMV, Ribeiro Carrott MML, Pajares JA. Preparation of activated carbon fibres from acrylic textile fibres. Carbon. 2001;39:1543-55.

[13] Nabais JMV, Carrott PJM, Ribeiro Carrott MML, Menéndez JA. Preparation and modification of activated carbon fibres by microwave heating. Carbon. 2004;42:1309-14.

[14] Carrott PJM, Nabais JMV, Ribeiro Carrott MML, Menéndez JA. Microwave heating as a novel method for introducing molecular sieve properties into activated carbon fibres. Carbon. 2004;42:227-9.

[15] Nabais JMV, Carrott PJM, Ribeiro Carrott MML, Padre-Eterno AM, Menéndez JA, Dominguez A, Ortiz AL. New

acrylic monolithic carbon molecular sieves for O_2/N_2 and CO_2/CH_4 separations. Carbon. 2006;44:1158-65.

[16] Carrott PJM, Cansado IPP, Ribeiro Carrott MML. Carbon molecular sieves from PET for separations involving CH_4, CO_2, O_2 and N_2. Appl Surf Sci. 2006;252:5948-52.

[17] Carrott PJM, Conceição FL, Ribeiro Carrott MML. Use of n-nonane pre-adsorption for the determination of micropore volume of activated carbon aerogels. Carbon. 2007;45:1310-3.

[18] Conceição FL, Carrott PJM, Ribeiro Carrott MML. New carbon materials with high porosity in the 1-7 nm range obtained by chemical activation with phosphoric acid of resorcinol-formaldehyde aerogels. Carbon. 2009;47:1874-7.

[19] Carrott PJM, Marques LM, Ribeiro Carrott MML. Characterisation of the porosity of polymer and carbon aerogels containing Fe, Ni or Cu prepared from 2,4-dihydroxybenzoic acid by n-nonane pre-adsorption and density functional theory. Micropor Mesopor Mater. 2010;131:75-81.

[20] Marques LM, Carrott PJM, Ribeiro Carrott MML. Amine-modified Carbon Aerogels for CO_2 Capture. Adsorpt Sci Technol. 2013;31:223-32.

[21] Carrott PJM, Ribeiro Carrott MML, Nabais JMV, Prates Ramalho JP. Influence of surface ionization on the adsorption of aqueous zinc species by activated carbons. Carbon. 1997;35:403-10.

[22] Carrott PJM, Ribeiro Carrott MML, Nabais JMV. Influence of surface ionization on the adsorption of aqueous mercury chlorocomplexes by activated carbons. Carbon. 1998;36:11-7.

[23] Mourão PAM, Carrott PJM, Ribeiro Carrott MML. Application of different equations to adsorption isotherms of phenolic compounds on activated carbons prepared from cork. Carbon. 2006;44:2422-9.

[24] Nabais JMV, Gomes JA, Suhas, Carrott PJM, Laginhas C, Roman S. Phenol removal onto novel activated carbons made from lignocellulosic precursors: Influence of surface properties. J Hazardous Mater. 2009;167:904-10.

[25] Carrott PJM, Mourão PAM, Ribeiro Carrott MML, Gonçalves EM. Separating surface and solvent effects and the notion of critical adsorption energy in the adsorption of phenolic compounds by activated carbons. Langmuir. 2005;21:11863-9.

[26] Carrott PJM, Ribeiro Carrott MML, Vale TSC, Marques L, Nabais JMV, Mourão PAM, Suhas. Characterisation of Surface Ionisation and Adsorption of Phenol and 4-Nitrophenol on Non-porous Carbon Blacks. Adsorpt Sci Technol. 2008;26:827-41.

[27] Cansado IPP, Mourao PAM, Falcao AI, Ribeiro Carrott MML, Carrott PJM. The influence of the activated carbon post-treatment on the phenolic compounds removal. Fuel Proc Technol. 2012;103:64-70.

[28] Cansado IPP, Nunes AS, Ribeiro Carrott MML, Carrott PJM. Adsorption Properties of Activated Carbons Prepared from Recycled PET in the Removal of Organic Pollutants from Aqueous Solutions. Adsorpt Sci Technol. 2010;28:807-21.

[29] Carrott PJM, Ribeiro Carrott MML, Cansado IPP, Nabais JMV. Reference data for the adsorption of benzene on carbon materials. Carbon. 2000;38:465-74.

[30] Carrott PJM, Ribeiro Carrott MML, Cansado IPP. Reference data for the adsorption of methanol on carbon materials. Carbon. 2001;39:193-200.

[31] Russo PA, Ribeiro Carrott MML, Carrott PJM. Hydrocarbons adsorption on templated mesoporous materials: effect of the pore size, geometry and surface chemistry. New Journal of Chemistry. 2011;35:407-16.

Synthesis of biomass-derived activated carbons for liquid phase application

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Abstract

In this communication an overview of the studies developed in the Adsorption and Adsorbent Materials Group related with the preparation of biomass-derived activated carbon materials is presented, highlighting the results of the most important research line of the group in the carbon materials thematic, i.e., the assessment of the potentialities of these materials as adsorbents of various pharmaceutical compounds from aqueous solution.

Resumen

En esta comunicación se presenta una visión general de los estudios que se realizan en el Grupo de Adsorción y Materiales Adsorbentes de la Universidad de Lisboa en la temática de los materiales de carbón. Estos trabajos se basan en la preparación de carbones activos derivados de biomasa y el estudio de sus aplicaciones como adsorbentes de diversos compuestos farmacéuticos en disolución acuosa. Aquí se han resaltado los resultados más importantes de esta línea de investigación.

1. Introduction

The present Adsorption and Adsorbent Materials Group (AAM) of the Centre of Chemistry and Biochemistry of the Faculty of Sciences of Lisbon University is the heir of the Adsorption Group that for more than 30 years developed studies mainly centered on the adsorption from gas phase on several porous materials, namely zeolites and clay-derived solids. As a natural enlargement of interests, in the late 90´s the group started to develop a new research line focused on carbon materials. The first studies were focused on the preparation of cork-derived materials followed by the evaluation of their performance in gas phase processes. However, being aware of the importance of the use of activated carbons in advanced water treatment technologies to allow an efficient removal of recalcitrant pharmaceutical compounds, the group turned the attention to this problematic. In this context, in the last 15 years the research line related with carbon materials has been centered on assessing the potentialities of different biomass-derived activated carbons as adsorbents of various pharmaceutical compounds detected all over the world. In the following, a description of the most relevant results will be presented, highlighting the studies where unexpected results allowed a deeper insight into the mechanism of these processes, what was only possible due to the establishment of collaborations with different research areas. The applied character of the studies drew the attention of the industry, which gave us the opportunity to integrate a QREN project team headed by the world leading company in cork processing.

The collaborations with Portuguese (Inorganic Chemistry Group of Faculty of Sciences from University of Porto (FCUP), Catalysis Group of Lisbon Superior Engineering Institute (ISEL) and Chemistry Department of Faculty of Science and Technology, New University of Lisbon (FCT-UNL)) and foreign, mainly Spanish (ADPOR Group, Dpt. Chemical Processes for Energy and Environment, Instituto Nacional del Carbón, (INCAR)) research groups was also fundamental to test the prepared materials in applications other than adsorption, being the developed works listed in the final of this communication.

Lastly, it must be mentioned that since our research interests have been centered on the field of carbon materials, the developed studies gave rise to several projects of undergraduate students, as well as MSc and PhD theses and, as a natural consequence, allowed numerous panel and oral presentations in international conferences, namely in Carbon or GEC congresses.

2. Investigation of different precursors for the synthesis of activated carbons

The industrial production of activated carbons is generally based on coal, wood and coconut shell, the first being a non-renewable feedstock with a progressively decrease of quality (high ash content), and the last largely available biomasses, but with variable price. In this context, the search of other sustainable alternatives for activated carbons precursors is a research subject that, although extensively reported in the literature, remains as a hot topic in the field of carbon materials. In fact, the use of carbon-rich agro-industrial residues as raw materials for the production of activated carbons is a possible strategy to add value to biomasses that otherwise would be landfilled or used as fuel. This approach decreases wastes and enables the production of goods, therefore contributing to a more circular economy and more sustainable industrial processes.

Due to the importance of cork for the Portuguese economy, cork powder waste was the first biomass residue explored by the group for the production of activated carbons. The first results revealed the potentialities of this biomass to prepare carbons with molecular sieve properties [1, 2] and, as previously mentioned, were the starting point of a new research line focused on the preparation of activated carbons. Cork powder has been extensively tested to prepare activated carbons by different activation methodologies [1, 3-9], being the obtained materials tested as adsorbents in both gas and liquid phase processes. The work developed received the attention of the industry and national funding entities, and the AAM group integrated the team of a consortium headed by Corticeira Amorins, the world leading company of cork processing industry (QREN5532–WaterCork). The close cooperation with the cork industry allowed AAM group to explore the potentialities of a large set of cork processing by-products as precursors of activated carbons (Figure 1(a)), namely granules of expanded corkboard.

The methodology developed during the project was protected by a National Patent [10], the work was published [11] and presented in the 2013 Carbon Conference. The scale-up of the methodology developed during the WaterCork project allowed the preparation of a large amount of cork-derived activated carbon, which was selected to be tested in the recently started LIFE Impetus project coordinated by researchers from LNEC (National Laboratory of Civil Engineering) Hydraulic and Environment Department. The project aims to evaluate several strategies to improve current barriers for controlling pharmaceutical compounds in urban wastewater treatment plants (LIFE14 ENV/PT/000739) where activated carbons may have a strategic importance.

Sisal fibres wastes, discarded by a rope industry (CORDEX), were also used as precursors of activated carbons (see Figure 1(b)) and further assayed as adsorbents of pharmaceutical compounds [12, 13], or as additives to TiO_2 in the photooxidation of phenol [14, 15].

The solid wastes generated during the processing of pine wood, and pine wood and coal blends in the pilot gasification facility of LNEG (National Laboratory of Energy and Geology) were chemically activated with K_2CO_3 [16, 17] obtaining porous carbons with apparent surface areas that reached 1500 $m^2\ g^{-1}$ when pine wood was the raw materials used to feed the gasification reactor (see Figure 1(c)).

More recently, a biodiesel production by-product – low particle size rapeseed recovered from warehouse air filtration system – was also assayed as precursor for the synthesis of reusable activated carbons (Figure 1(d)) for the adsorption of caffeine from aqueous solution [18].

Regarding less conventional methodologies, in the context of a FCT projects, the group has also developed mesoporous carbon materials through a template approach using porous clay heterostructures [19] and porous silica [20].

More recently, sugar-derived activated carbons (Figure 2) were obtained through a two-step procedure involving an initial hydrothermal carbonization for the synthesis of spherical hydrochars, which were further activated aiming the preparation of spherical activated carbons [21-23]. The results of this study illustrate the importance of the choice of the activating agent to tune the carbons properties, since the most commonly used agent, KOH, originated superactivated carbons, but at the expense of the spherical morphology and with very low preparation yields, while the K_2CO_3 mediated process maintained the spherical shape of the hydrochar along with a high developed microporous structure and preparation yields of ~ 50 % [21].

Chemical activation of different biomasses using essentially K_2CO_3 has been explored in the work developed in the AAM group, which allowed to gather a set of carbons with distinct textural, surface and morphological properties, which make them interesting materials for a wide range of possible applications, as it will be briefly described in the following sections.

3. Gas and Liquid phase applications

3.1.1 Gas phase

The first studies of the AAM group regarding the application of activated carbon materials were focused on their use in gas phase adsorption processes.

VOCs adsorption was studied with cork-derived activated carbons, in both powdered and granular forms [4, 8] and also with CMK-3, the carbon replica of ordered mesoporous silica SBA-15 [24].

Natural gas components adsorption was evaluated in one of the first works published by the group in carbon materials [3] and also more recently in a study with the superactivated sucrose-derived carbons [21]. This last work allowed to highlight the importance of the chemical activating agent to assure the enhancement of the carbons performance for a given task. In fact, the carbons obtained by K_2CO_3 activation of sucrose-derived hydrochars presented high performance for landfill gas or biogas upgrade (better than the best performing carbon in the literature) mainly due to their high packing densities and tailored micropore size distributions. On the opposite, the activated carbon obtained by KOH activation of the hydrochar presented a higher apparent surface area (» 2400 m^2g^{-1} vs 1500 m^2g^{-1}) at the expense of the spherical morphology, leading to a material with a very low packing density, and consequently lower adsorption capacity per volume than the K_2CO_3 derived sample. Additionally, the extensive textural characterization allowed to justify the high methane storage capacity in a volume basis of one of the K_2CO_3 derived samples, since the maximum of the micropore size distribution of this sample is centered in the predicted pore width for enhanced methane storage (0.8 nm).

3.1.2 Liquid phase

As it was mentioned the assessment of the carbons as adsorbents of pharmaceutical compounds is nowadays the most important research line of the group, concerning the carbon materials thematic. The relevance of this type of studies is recognized by the scientific community and government entities, since trace level contamination of water bodies with pharmaceutical compounds were detected in the last decades of the XX century [25-27]. Nowadays, monitoring studies all over the world confirm this reality, as the result of the high consumption of prescription and non-prescription medicines combined with the inefficiency of the implemented wastewater treatment technologies to assure an effective barrier to this particular class of compounds. Pharmaceutical compounds are considered emerging contaminants, and to this date the European Parliament has included diclofenac (anti-inflammatory & analgesic), 17a-ethynilestradiol and 17β-estradiol (both contraceptive hormones), in the first watch list of Directive 2013/39/EU, which will allow to gather more monitoring data, thus facilitating the determination of appropriate measures to address the risk posed by these substances.

Since activated carbons adsorption has been considered one of the best available technologies for the removal of pharmaceutical compounds, the research of the AAM group in this thematic has been focused on the adsorption of several pharmaceutical active compounds commonly detected in river water, sea water and some also in drinking water. So far

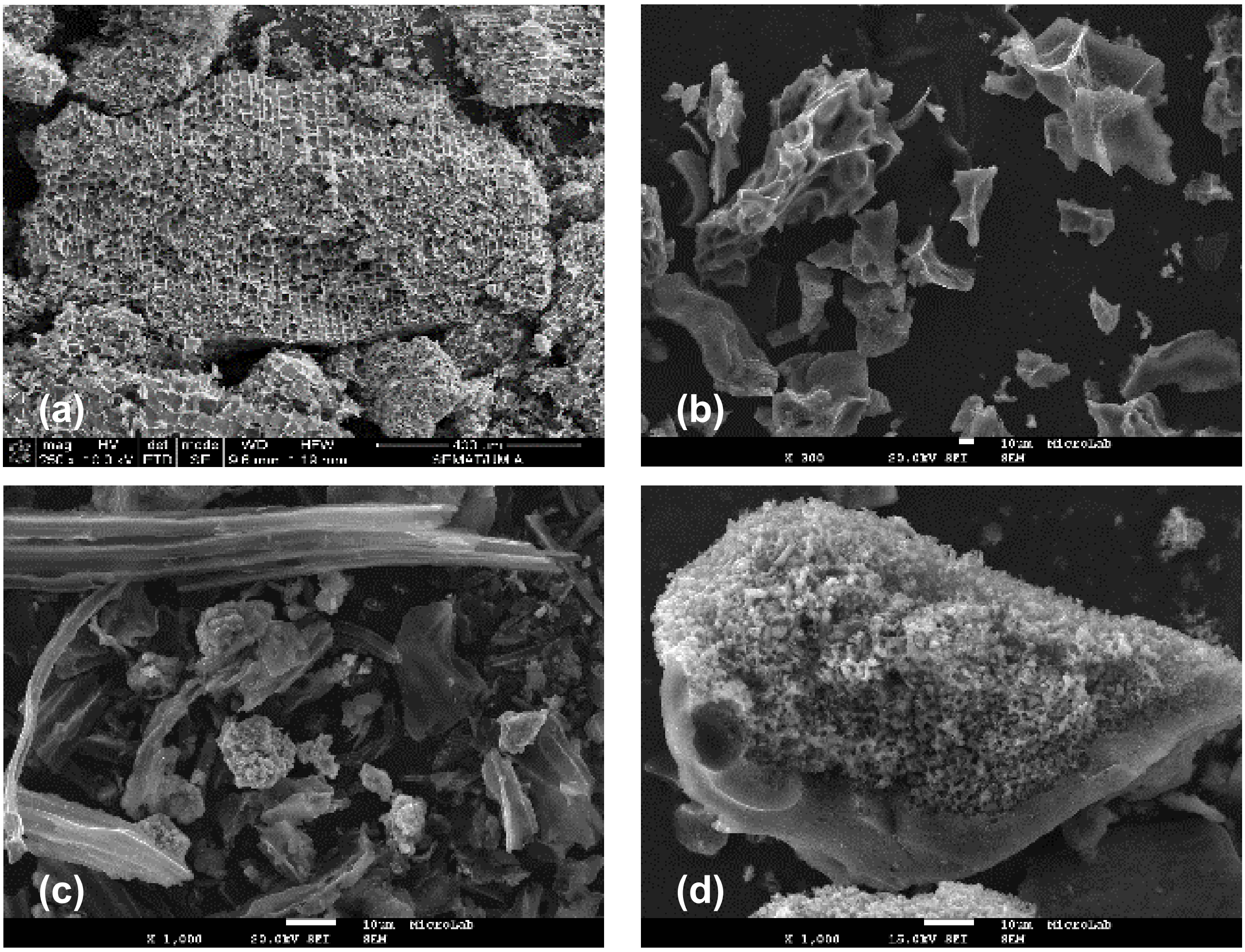


Figure 1. SEM imagens of activated carbons obtained from distinct raw materials: (a) cork - steam activation; (b) sisal - copper loaded and K_2CO_3 activated; (c) fly ash from pine gasification process - K_2CO_3 activated; and (d) rapeseed - K_2CO_3 activated.

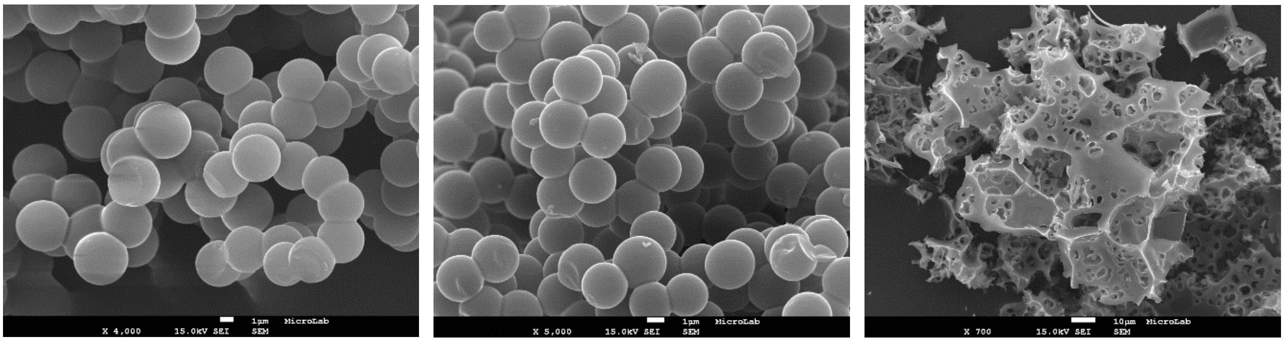


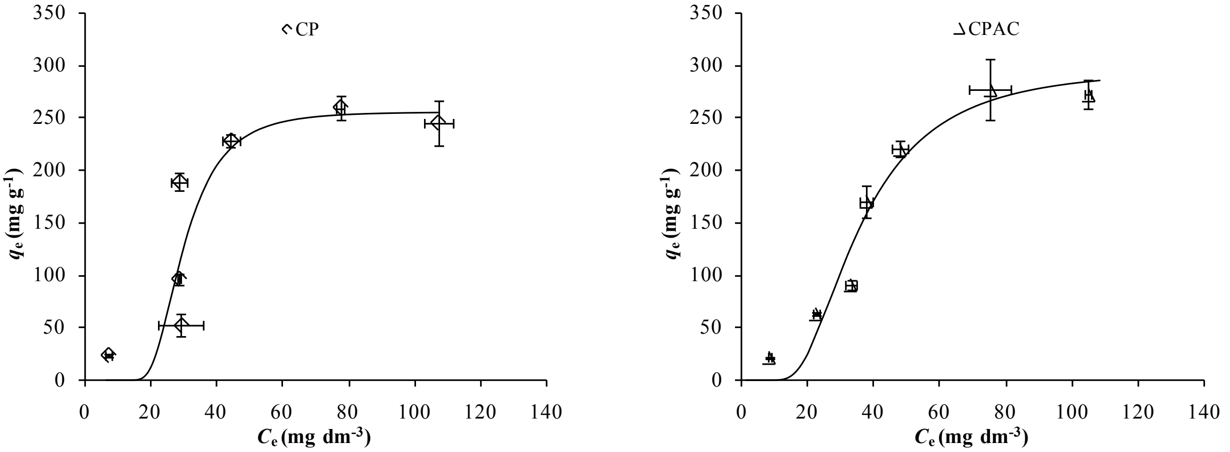
Figure 2. SEM images of (a) sucrose-derived hydrochar, (b) activated carbon obtained by physical impregnation of the hydrochar with K_2CO_3, and (c) activated carbon obtained by KOH activation of the hydrochar (solution impregnation).

studied target compounds were ibuprofen [6, 9, 11, 12, 22, 28], paracetamol [7, 11, 12, 16, 17, 22, 29] and acetylsalicylic acid [11], clofibric acid [5, 11, 22, 28, 30], caffeine [17, 22, 31] and iopamidol [11, 13, 22].

The performance of activated carbons is strongly dependent on the interactions adsorbent-adsorbate, but also on adsorbate-liquid media and adsorbent-liquid media, so the effect of several experimental parameters, such as solution pH, temperature, co-solvent addition and water hardness has also been explored. Some of the most relevant conclusions of the works developed by the AAM group in this thematic are described in the following.

Clofibric acid: is one of the most persistent drug residues detected in the aquatic environment worldwide, and besides being the metabolite and active principle of blood lipid regulators, it also represents the class of acidic pharmaceuticals. The studies evaluating clofibric acid adsorption onto activated carbons revealed that the increase of solution pH always lead to the decrease of the activated carbons performance as a consequence of the deprotonation. The resulting anionic specie has higher solubility/higher solvation energy [5, 30] preventing the interaction of the specie with the carbon surface. As reproduced in Figure 3, the adsorption isotherms of this compound at pH 3 (pH $< pK_a$) onto cork-based and commercial sample present an uncommon sigmoidal shape revealing the existence of a cooperative process.

Regarding water hardness, our recently published results show that the complexation of the deprotonated specie with calcium ($CaClof^+$ and $CaClof_2$) favors



igure 3. Clofibric acid adsorption isotherms on cork-based (CPAC) and commercial (CP) activated carbons at 30 ºC and solution pH 3.6 (distilled water solution with 10 % methanol (V/V)). Symbols correspond to the experimental data, whereas lines represent the fitting to the Dubinin-Astakhov equation. Error bars are included. Adapted from [5] with permission from Elsevier.

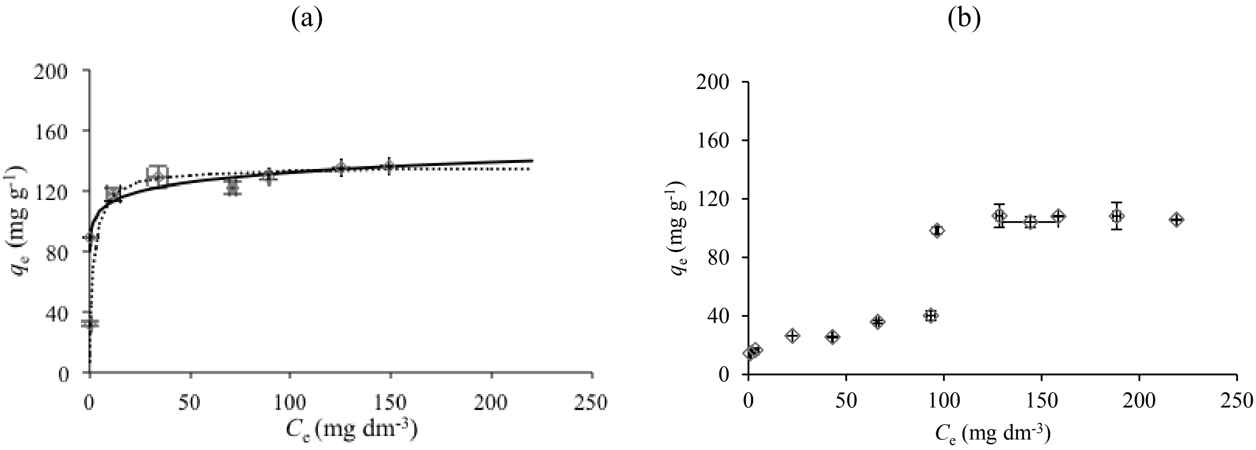
its adsorption onto activated carbons, partially overcoming the decreased adsorption observed at higher pH values [30]. Since this complexation can also occur for other acidic pharmaceuticals, the insights of this work afforded an explanation to results previously reported in the literature for other molecules, and is of crucial importance in the design of improved water treatment processes.

Iopamidol: is an iodinated contrast media more resistant to the biological degradation than other compounds of its class, possibly as a consequence of its branched side chains. This recalcitrant behavior, allied with the high dosages used in clinical exams, leads to its detection in wastewater treatment plants effluent and also in potable water. To study the adsorption of this voluminous pharmaceutical, both lab-made and commercial activated carbons were selected in order to assay materials with distinct pore structures. The results revealed a complex adsorption process characterized by two-step isotherms (Figure 4) that were rationalized considering the textural characterization data along with conductivity measurements and computational calculations. After demonstrating that iopamidol can be adsorbed as a monomer or in the form of aggregates, the uncommon isotherms configuration were interpreted as a consequence of a particular micropore distribution [32], i.e., when the sample does not have micropores with widths between 1.2 and 2.0 nm [13].

Paracetamol: is an over-the-counter medicine whose adsorption onto activated carbons has been extensively explored in the literature [33] and also by the AAM group [7, 11, 12, 16, 17, 22, 29, 34]. The study focused on the temperature dependence of the adsorption of paracetamol onto several activated carbons with distinct pore size networks, revealed all the possible dependences: positive, negative or no influence of the temperature. To understand the data obtained the adsorbed species were back-extracted and identified by ^{1}H NMR spectroscopy, proving that during the adsorption process, paracetamol oligomers are formed. The unexpected increase of adsorption capacity with the temperature was interpreted considering that when carbons do not present a continuous micropore size distribution, the energy associated with the adsorption process is enough to change the paracetamol dimer configuration, from the low energy geometry to a planar form. This evolution results in an accentuated decrease of the critical dimension which enables the access of paracetamol species to the narrow micropores of the activated carbons.

3.2 3. Other applications

Carbon materials developed in the AAM group have



(a) (b)

Figure 4. Iopamidol adsorption isotherms on (a) commercial carbon CP, and (b) on sisal-derived carbon S3. Symbols correspond to the experimental data, and in the case of sample CP dotted lines represent Langmuir equation fit and the solid lines the Freundlich equation fit. Adapted from [13] with permission from Elsevier.

been tested as catalysts and catalyst supports in collaboration with several research groups:

- Carbons prepared by template methodology were used as matrixes to anchor copper(II) bis(oxazoline) oxidovanadium (IV) acetylacetonate complexes, being the catalysts tested in asymmetric benzoylation of hydrobenzoin [35], and in the epoxidation of geraniol [36] reactions, respectively. In other studies, copper(II) aza-bis(oxazoline) and Mn(III) *salen* complexes were also immobilized on carbons replicas to prepare catalysts for the reaction of cyclopropanation of styrene [37] and epoxidation of *cis*-cyclooctene [38].
- Commercial and CMK-3 samples were used to prepared bifunctional carbon-supported platinum catalysts for hydroisomerization of *n*-alkanes, namely, *n*- decane [39].
- As-synthesised and copper doped sisal-derived carbons were tested in the photooxidation of phenol, either used alone or mixed with TiO_2 [14, 15].
- Sucrose-derived activated carbons prepared by KOH and K_2CO_3 activation of an hydrochar were recently tested for oxygen reduction reaction [23].

The potentialities of the commercial and lab-made carbons prepared by the AAM group as enrichment phases for sample preparation in analytical chemistry have been also explored, in order to quantify:

- drugs of abuse (morphine and codeine) [40]
- triazinic pesticides (atrazine, simazine and terbutylazine) [41]
- pharmaceutical compounds (ibuprofen and clofibric acid) [42]

The study focused on pharmaceuticals was made using cork-derived carbons using synthetic water, real water samples obtained from a wastewater treatment facility in the region of Lisbon and a biological sample (i.e. urine).

Acknowledgements

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References

[1] Carvalho AP, Cardoso B, Pires J, Brotas de Carvalho M. Preparation of activated carbons from cork waste by chemical activation with KOH. Carbon. 2003;41(14):2873-6.

[2] Carvalho AP, Cardoso B, Pires J, Carvalho MBd. Carvões obtidos por activação química de desperdícios de cortiça. Influência de diversos parâmetros experimentais. Actas do XVII Simpósio Ibero-Americano de Catálise, J. M. Órfão, J.L. Faria, J.L. Figueiredo (Eds), Porto, 16-21 Julho; 2000.

[3] Carvalho AP, Gomes M, Mestre AS, Pires J, Brotas de Carvalho M. Activated carbons from cork waste by chemical activation with K_2CO_3: Application to adsorption of natural gas components. Carbon. 2004;42(3):672-4.

[4] Carvalho AP, Mestre AS, Pires J, Pinto ML, Rosa ME. Granular activated carbons from powdered samples using clays as binders for the adsorption of organic vapours. Microporous and Mesoporous Materials. 2006;93(1-3):226-31.

[5] Mestre AS, Pinto ML, Pires J, Nogueira JMF, Carvalho AP. Effect of solution pH on the removal of clofibric acid by cork-based activated carbons. Carbon. 2010;48(4):972-80.

[6] Mestre AS, Pires J, Nogueira JMF, Parra JB, Carvalho AP, Ania CO. Waste-derived activated carbons for removal of ibuprofen from solution: role of surface chemistry and pore structure. Bioresource Technology. 2009;100(5):1720-6.

[7] Cabrita I, Ruiz B, Mestre AS, Fonseca IM, Carvalho AP, Ania CO. Removal of an analgesic using activated carbons prepared from urban and industrial residues. Chemical Engineering Journal. 2010;163(3):249-55.

[8] Cardoso B, Mestre AS, Carvalho AP, Pires J. Activated carbon derived from cork powder waste by KOH activation: preparation, characterization, and VOCs adsorption. Industrial & Engineering Chemistry Research. 2008;47(16):5841-6.

[9] Mestre AS, Pires J, Nogueira JMF, Carvalho AP. Activated carbons for the adsorption of ibuprofen. Carbon. 2007;45(10):1979-88.

[10] Martins SP, Mestre AS, Carvalho AP, Correia PB, inventors; Amorim Isolamentos, S.A., assignee. Processo de produção de carvão activado a partir de material de cortiça. PT 106637 B. Portugal patent PT 106637 B. 2012.

[11] Mestre AS, Pires RA, Aroso I, Fernandes EM, Pinto ML, Reis RL, et al. Activated carbons prepared from industrial pre-treated cork: Sustainable adsorbents for pharmaceutical compounds removal. Chemical Engineering Journal. 2014;253(0):408-17.

[12] Mestre AS, Bexiga AS, Proença M, Andrade M, Pinto ML, Matos I, et al. Activated carbons from sisal waste by chemical activation with K2CO3: Kinetics of paracetamol and ibuprofen removal from aqueous solution. Bioresource Technology. 2011;102(17):8253-60.

[13] Mestre AS, Machuqueiro M, Silva M, Freire R, Fonseca IM, Santos MSCS, et al. Influence of activated carbons porous structure on iopamidol adsorption. Carbon. 2014;77(0):607-15.

[14] Andrade MA, Carmona RJ, Mestre AS, Matos J, Carvalho AP, Ania CO. Visible light driven photooxidation of phenol on TiO2/Cu-loaded carbon catalysts. Carbon. 2014;76(0):183-92.

[15] Andrade MA, Mestre AS, Carmona RJ, Carvalho AP, Ania CO. Effect of the irradiation wavelength on the performance of nanoporous carbon as an additive to TiO2. Applied Catalysis A: General. 2015;507:91-8.

[16] Galhetas M, Mestre AS, Pinto ML, Gulyurtlu I, Lopes H, Carvalho AP. Carbon-based materials prepared from pine gasification residues for acetaminophen adsorption. Chemical Engineering Journal. 2014;240(0):344-51.

[17] Galhetas M, Mestre AS, Pinto ML, Gulyurtlu I, Lopes H, Carvalho AP. Chars from gasification of coal and pine activated with K2CO3: Acetaminophen and caffeine adsorption from aqueous solutions. Journal of Colloid and Interface Science. 2014;433(0):94-103.

[18] Batista MKS, Fonseca IM, Mestre AS, P.Carvalho A. Preparation and characterization of carbons obtained by chemical activation of rapeseed. XII Reunión del Grupo Español del Carbón, Madrid (Spain), 20-23 October 2013;

2000.

[19] Santos C, Andrade M, Vieira AL, Martins A, Pires J, Freire C, et al. Templated synthesis of carbon materials mediated by porous clay heterostructures. Carbon. 2010;48(14):4049-56.

[20] Pires J, Borges S, Carvalho AP, Silva AR. Porous Silicas and Respective Carbon Replicates for Adsorption and Catalysis. Adsorpt Sci Technol. 2010;28(8-9):717-26.

[21] Mestre AS, Freire C, Pires J, Carvalho AP, Pinto ML. High performance microspherical activated carbons for methane storage and landfill gas or biogas upgrade. Journal of Materials Chemistry A. 2014;2(37):15337-44.

[22] Mestre AS, Tyszko E, Andrade MA, Galhetas M, Freire C, Carvalho AP. Sustainable activated carbons prepared from a sucrose-derived hydrochar: remarkable adsorbents for pharmaceutical compounds. Rsc Adv. 2015;5(25):19696-707.

[23] Nunes M, Rocha IM, Fernandes DM, Mestre AS, Moura CN, Carvalho AP, et al. Sucrose-derived activated carbons: electron transfer properties and application as oxygen reduction electrocatalysts. Rsc Adv. 2015;5(124):102919-31.

[24] Saini VK, Andrade M, Pinto ML, Carvalho AP, Pires J. How the adsorption properties get changed when going from SBA-15 to its CMK-3 carbon replica. Separation and Purification Technology. 2010;75(3):366-76.

[25] Hignite C, Azarnoff DL. Drugs and drug metabolites as environmental contaminants: Chlorophenoxyisobutyrate and salicylic acid in sewage water effluents. Life Sci. 1977;20:337-41.

[26] Richardson ML, Bowron JM. The fate of pharmaceutical chemicals in the aquatic environment. J Pharm Pharmacol. 1985;37(1):1-12.

[27] Carvalho AP, Mestre AS, Andrade M, Ania CO. Ibuprofen in the Aquatic Environment: Occurrence, ecotoxicity and water remediation technologies. In: Carter WC, Brown BR, eds. Ibuprofen: Clinical pharmacology, medical uses and adverse effects: Nova Science Publishers 2013, p. 1-84.

[28] Andrade M, Parra JB, Haro M, Mestre AS, Carvalho AP, Ania CO. Characterization of the different fractions obtained from the pyrolysis of rope industry waste. Journal of Analytical and Applied Pyrolysis. 2012;95(0):31-7.

[29] Galhetas AM, Andrade MV, Mestre AS, Kangni-foli E, Brito MV, Pinto ML, et al. Influence of activated carbons textural properties on acetaminophen adsorption at different temperatures. Phys Chem Chem Phys. 2015;17:12340-9.

[30] Mestre AS, Nabiço A, Figueiredo PL, Pinto ML, Santos MSCS, Fonseca IM. Enhanced clofibric acid removal by activated carbons: Water hardness as a key parameter. Chemical Engineering Journal. 2016;286:538-48.

[31] Mestre AS, Marques SCR, Carvalho AP. Effect of the Alcohol Cosolvent in the Removal of Caffeine by Activated Carbons. Industrial & Engineering Chemistry Research. 2012;51(29):9850-7.

[32] Pinto ML, Mestre AS, Carvalho AP, Pires J. Comparison of Methods to Obtain Micropore Size Distributions of Carbonaceous Materials from CO2 Adsorption Based on the Dubinin-Radushkevich Isotherm. Industrial & Engineering Chemistry Research. 2010;49(10):4726-30.

[33] Carvalho AP, Mestre AS, Haro M, Ania CO. Advanced methods for the removal of acetaminophen from water. In: Javaherian A, Latifpour P, eds. Acetaminophen: Properties, clinical uses and adverse effects: Nova Science Publishers 2012, p. 57-105.

[34] Ruiz B, Cabrita I, Mestre AS, Parra JB, Pires J, Carvalho AP, et al. Surface heterogeneity effects of activated carbons on the kinetics of paracetamol removal from aqueous solution. Applied Surface Science. 2010;256(17):5171-5.

[35] Silva AR, Carneiro L, Carvalho AP, Pires J. Asymmetric benzoylation of hydrobenzoin by copper(II) bis(oxazoline) anchored onto ordered mesoporous silicas and their carbon replicas. Catal Sci Technol. 2013;3(9):2415-24.

[36] Dorbes S, Pereira C, Andrade M, Barros D, Pereira AM, Rebelo SLH, Araujo JP, Pires J, Carvalho AP, Freire C. Oxidovanadium(IV) acetylacetonate immobilized onto CMK-3 for heterogeneous epoxidation of geraniol. Microporous and Mesoporous Materials. 2012;160:67-74.

[37] Silva AR, Guimaraes V, Carvalho AP, Pires J. The role of the support properties in the catalytic performance of an anchored copper(II) aza-bis(oxazoline) in mesoporous silicas and their carbon replicas. Catal Sci Technol. 2013;3(3):659-72.

[38] Gaspar H, Andrade M, Pereira C, Pereira AM, Rebelo SLH, Araujo JP, Pires J, Carvalho AP, Freire, C. Alkene epoxidation by manganese(III) complexes immobilized onto nanostructured carbon CMK-3. Catalysis Today. 2013;203:103-10.

[39] Fernandes S, Andrade M, Ania CO, Martins A, Pires J, Carvalho AP. Pt/carbon materials as bi-functional catalysts for n-decane hydroisomerization. Microporous and Mesoporous Materials. 2012;163:21-8.

[40] Gonçalves AFP, Neng NR, Mestre AS, Carvalho AP, Nogueira JMF. Development of a Powdered Activated Carbon in Bar Adsorptive Micro-Extraction for the Analysis of Morphine and Codeine in Human Urine. Journal of Chromatographic Science. 2012.

[41] Neng NR, Mestre AS, Carvalho AP, Nogueira JMF. Powdered activated carbons as effective phases for bar adsorptive micro-extraction (BAµE) to monitor levels of triazinic herbicides in environmental water matrices. Talanta. 2011;83(5):1643-9.

[42] Neng NR, Mestre AS, Carvalho AP, Nogueira JMF. Cork-based activated carbons as supported adsorbent materials for trace level analysis of ibuprofen and clofibric acid in environmental and biological matrices. Journal of Chromatography A. 2011;1218(37):6263-70.

Mesoporous Carbon as effective and sustainable catalyst for fine chemistry

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Abstract

It is well known that activated carbon with well-developed porosity is a promising material that have been used for several applications, from adsorption to catalysis. Research in this field has intensified in recent years, looking for new and improved characteristics and applications. Our research group, recently renamed Materials for Adsorption and Catalysis group (MAC) in LAQV-REQUIMTE, has also devoted many research work in this subject, and has developed several collaboration works with other national and international research groups in the field.

Among our research group interests there is the study of catalytic properties of carbon materials and specifically mesoporous carbon. Some of the promising results were selected and summarized here, demonstrating that mesoporous carbon is an efficient and environmentally friendly heterogeneous catalyst.

Resumen

Es conocido que el carbón activado por su desarrollada porosidad es un material prometedor para varias aplicaciones, desde la adsorción a la catálisis. La investigación en este campo se ha intensificado en los últimos años, en busca de nuevas y mejoradas características y aplicaciones. Nuestro grupo de investigación, recientemente rebautizado grupo de materiales para la adsorción y catálisis (MAC) en LAQV-REQUIMTE, también ha dedicado muchos trabajos de investigación en este tema, y ha desarrollado varios trabajos en colaboración con otros grupos de investigación nacional e internacional.

Entre los distintos intereses de investigación de nuestro grupo se encuentra el estudio de las propiedades catalíticas de materiales de carbono y específicamente, de carbones mesoporosos. Algunos de los resultados más prometedores han sido seleccionados y se resumen aquí. Estos demuestran que el carbón mesoporoso es un catalizador heterogéneo eficiente y respetuoso con el medio ambiente.

1. Introduction

Countless of our daily consumed products are obtained resorting to catalytic procedures. Many of the catalysts traditionally employed in those processes show disadvantages such as high reaction temperature, prolonged reaction time, non-catalytic nature of the reagent, low conversion and low regioselectivity. Furthermore, in homogenous phase, other problems may occur dealing with the separation, isolation and purification of the product. Thus, the development of new and less expensive heterogeneous catalysts and their application in reactions with synthetic interest remains an important challenge. In fact, in recent years, heterogeneous catalysts [1- 3] and among them activated carbon [4-8], have attracted much attention as catalysts in the scope of green chemistry for fine-chemical synthesis.

Activated carbon is an extremely environmental friendly material with a very interesting porous structure that, depending on the precursor and preparation method, is very tuneable. Also this material present enormous versatility and high chemical and physical stability. As such, activated carbons with microporous structure have been employed successfully in several catalytic reactions [9-11]. However, mesoporous carbon with a different porous structure presenting meso and macro porous [12] may result in more efficient catalysts in terms of selectivity towards products among other advantages.

These mesoporous carbons are carbon gels that can be obtained through different procedures and display very interesting features about their structural characteristics, because they are very sensitive to the conditions used during gel synthesis and processing [13].

Resorcinol–formaldehyde (RF) aqueous gels are among the most studied systems [14]. Several thermal and chemical processes can be used to tailor the porous structure and the type and concentration of specific oxygen surface groups.

Carbon xerogels discussed here were synthesized by polymerization of resorcinol and formaldehyde. The surface of the activated carbon was oxidized in liquid phase with HNO_3 and then functionalized with H_2SO_4. The materials were tested in several acid catalyzed reactions with great success, such as the alcoholysis and aminolysis of epoxides, and the methoxylation of a-pinene.

2. Experimental

The mesoporous carbon samples were prepared according Lin and Ritter [14] by sol-gel technique. All reagents and solvents used in the preparation of resorcinol/formaldehyde aqueous gels and surface functionalization of the carbon xerogels were purchase from Aldrich and used as received.

An aqueous solution of resorcinol (R), formaldehyde (F) and sodium carbonate (C), was prepared in such a way that the solid material is 5% (wt./v) of the total volume, and in which the R/F mole ratio was fixed at 1:2 and the R/C mole ratio was fixed at 50:1.

The initial pH of the solution was adjusted to 6.10-6.20

with diluted HNO_3. The solution was sealed in a flask and magnetically stirred during 1 h. This procedure was followed by a thermal treatment at 85 ± 3 ºC during a week, without stirring. The gel obtained was washed with acetone for 3 days. Afterward it was dried under N_2 atmosphere in a tube furnace using a heating rate of 0.5 ºC/min. The temperature was heated up to 65 ºC and then held there for 5h, followed by a raise until 110 ºC and kept there for another 5h. Finally, the carbon xerogel was form by pyrolysis of the dried gel at 800 ºC for 3h in a N_2 atmosphere with both heating and cooling rates set at 0.5 ºC/min (CM).

For the oxidation of the carbon surface, the carbon xerogel (CM), was refluxed with a nitric acid solution (13M) for 6h (1 g/20 mL). After cooling the materials were washed with deionized water in soxhlet until neutral pH and then dried in oven at 110 ºC, thus obtaining the catalyst **CMN**.

The introduction of sulfonic groups in the carbon xerogel surface was achieved by placing the oxidized mesoporous carbon (**CMN**) in a concentrated sulfuric acid solution (1g of CMN/20 mL sulfuric acid solution) and heat it at 150 ºC for 13h under N_2 atmosphere. The obtained catalyst was washed with deionized water in soxhlet until pH 7 and then dried in oven at 110ºC (carbon **CMNS**).

The different mesoporous carbons were characterized after the oxidation of the surface to determine the features of the catalysts. Some characterization of the parent carbons before oxidation was also performed as a means of comparison. Chemical and textural characterization was obtained by elemental analysis, pH_{pzc}, TPD, BET and XPS.

3. Results

3.1 Carbons characterization

Although different batch of synthesized carbon gels may present slightly different overall values, the preparation of this material and subsequent surface modification treatments are very reproducible. [5-7]

Table 1 shows the textural characterization of the carbon samples for one of such batchs. According to IUPAC nomenclature, the synthesised carbons present a nitrogen adsorption-desorption isotherm type IV with a type H3 hysteresis loop, typical of materials with mesoporosity [15].

The textural properties of the mesoporous carbon reveal that the oxidation of the carbon with nitric acid (CMN) had no meaningful effect on the BET surface area, but some decrease of the mesoporous volume is observed. This may be due to the presence of functional groups in the entrance of the pores blocking the accessibility.

On the other hand, the posterior treatment with concentrated sulphuric acid resulted in a material with differences in the pore size distribution, probably due to the formation of new pores and the widening of existing pores by the acid.

The surface chemistry was characterized by TPD-MS, elemental analysis, XPS and pH_{PZC} and the main results are summarised in Table 2.

It is possible to conclude that the surface oxidation with HNO_3 was successful as the samples present a higher amount of oxygen and a lower value of pH_{PZC}. By XPS it was possible to detect sulfonic groups in the surface of sample CMNS, indicating that the introduction of these functional groups was also successful and these are probably the groups responsible for the increase in acidity reflected in the pH_{PZC} value.

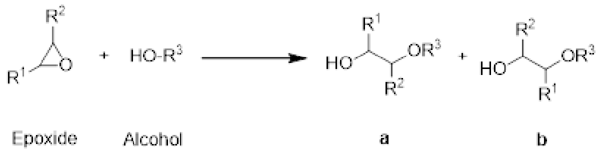
The results obtained with TPD are in quite accordance with the XPS and AE analysis. After oxidation with HNO_3 the samples present a pronounced increase in the functional group content and the most abundant functionalities are phenols and carboxylic groups,

An interesting observation from TPD results is that the carbon functionalised with sulfonic groups (CMNS) exhibits smaller amount of carboxylic acids, this fact supports the conclusion that the increase in acidity is due to the presence of sulfonic anchored groups.

3.2 Catalytic studies

3.2.1 Alcoholysis of epoxides

Mesoporous carbons CMN and CMNS were tested as catalysts in the ring opening reaction of epoxides. [7]



Scheme 1 - Reaction of epoxides with alcohols. Adapted from [7]

Table 1. Textural properties. Adapted from [7].

Catalyst	S_{BET} (m^2g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	V_T (cm^3g^{-1})	D_p (Å)
	B.E.T.	*t Method*	*DFT Method*	*Gurvitsh*	*BJH method*
CM	771	0.18	0.50	0.76	65.4
CMN	760	0.19	0.32	0.59	51.6
CMNS	797	0.20	0.51	0.79	74.5

Table 2. Surface chemistry characterization. Adapted from [7].

Sample	O/C	O/C	Total Oxygen	pH_{PZC}
	XPS *(atomic ratio)*	*E. A.* *(atomic ratio)*	*E. A.* *(atomic %)*	
CM	0.06	0.075	6.3	9.7
CMN	0.20	0.25	16.0	3.2
CMNS	0.19	0.29	20.2	2.4

Considering the reaction of styrene oxide and butanol at 80 ºC, both catalysts are active in the ring opening reaction but the functionalized carbon with sulfonic groups, CMNS, presents higher reactivity.

The reaction in the presence of catalysts CMN presented a 99 % conversion and 83 % selectivity for the product of interest **(b)** at 180 min of reaction time, while in the presence of CMNS it was possible to obtain the same values of conversion and selectivity in only 15 min.

These results suggest that strong acid sites in CMNS, sulfonic acid groups, are more active in this type of reactions. Table 3 presents the catalytic performance of catalyst CMNS with different epoxides, showing that the structure of the reactive has great influence.

3.2.2 Methoxylation of α-pinene

CMN and CMNS were employed in the reaction of methoxylation of α-pinene with success. [5]

Again both catalysts were active in the reaction studied. In this work CMN even outperformed the commercial carbon Norit also oxidized with HNO_3, revealing the textural relevance in the catalytic behavior of the samples. On the other hand CMNS presented higher initial reaction rate and higher conversion than CMN reinforcing the extreme importance of functional surface groups.

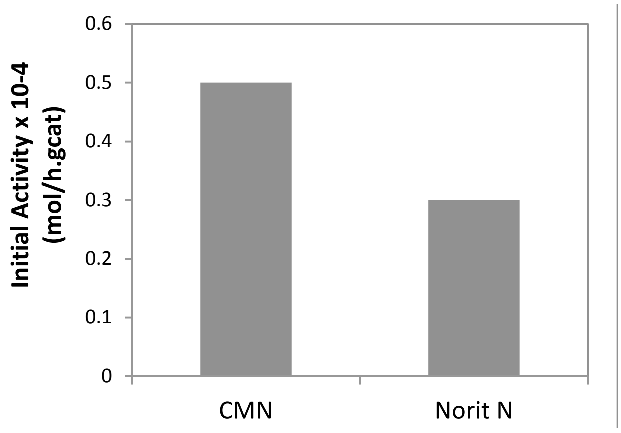


Fig 1. Methoxylation of α-pinene over activated carbon catalysts. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the α-pinene kinetic curve. Reaction conditions: T=60ºC; m_{cat}=0,2g; $n_{\alpha\text{-pinene}}$=9mmol; 50ml of methanol. Adapted from [5]

3.2.3 Synthesis of substituted quinolines

Another very interesting reaction to be studied under catalytic conditions applying carbons is the Friedlander reaction.

This is a very appealing area of research that may have great impact in the synthesis of important building blocks useful for the preparation of synthetic compounds with application in medicine, food, catalysis, dye, materials, refineries, and electronics. [16-17]

An example is the synthesis of substitute quinolones, an important class of nitrogen heterocycles. [6]

This work has been done by the research group in UNED with Doctor Elena Perez- Mayoral, presenting very promising results [6].

Among other activated carbons, the mesoporous carbon, also revealed to be able to catalyze the reactions. It performance was less effective than the other commercial ones studied, but this may be due to a lower amount of sulfonic groups incorporated in the surface.

Conclusion

These three woks were chosen to illustrate one of our group research lines, the study of catalytic behaviour of carbons.

The results summarised here exemplify that mesoporous carbon can be an effective catalyst in reactions of interest for the production of fine chemicals in the scope of green chemistry.

Mesoporous activated carbon proved to be effective catalysts for the ring opening reaction of epoxides affording the corresponding β-substituted alcohols with high conversion values and very good selectivity.

Also the HNO_3 oxidized carbon material and carbon material with sulfonic group were successfully used as acid catalysts in the methoxilation of α-pinene yielding α-terpinyl methyl ether as main product of the reaction.

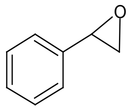
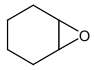
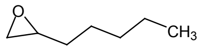
In a more complex reaction, as is the Friedlander, it presents lower performance but it is still capable of catalytic activity.

The textural properties of these materials, as well as the surface chemistry seems to be with great relevance for its performance. It is important to reinforce that the application of the catalysts reported here simplifies the experimental procedure, and allows the use of milder conditions.

Acknowledgement:

The results presented here were obtained in collaboration work with: Elena Perez-Mayoral e

Table 3 - Ring opening of substituted epoxide with ethanol. Adapted from [7].

Epoxide	Alcohol	T [ºC]	Time [min]	Conversion [%]	Selectivity to **b** [%]
	EtOH	r.t.	30	99	97
		50	15	99	96
		80	5	99	94
	EtOH	r.t.	120	89	100
		80	30	99	100
	EtOH	r.t.	24h	38	57
		80	4h	97	52

Conditions: Catalyst CMNS 0.1g, 3ml of alcohol, 1.5 mmol of epoxide.

Rosa Martin-Aranda from Departamento de Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED; Carlos Duran-Valle from Departamento de Química Orgânica e Inorgánica, Universidad de Extremadura; José Rodríguez-Mirasol and T. Cordero and Ramiro Ruiz-Rosas from Chemical Engineering Department, School of Industrial Engineering, University of Málaga

References

[1] Pita DS, Matos I, Fonseca IM, Ramos AM, Vital J, Castanheiro JE Methoxylation of α-pinene over heteropolyacids imomobilized in silica. Appl. Catal. A: Gen. 2010; 373: 140–146.

[2] Matos I, Pérez-Mayoral E, Soriano E, Zukal A, Martín-Aranda RM, López-Peinado AJ, Fonseca I, Čejka J Experimental and theoretical study of pyrazole N-alkylation catalyzed by basic modified molecular sieves. Chem. Eng. J. 2010; 161:377-383.

[3] Pérez-Mayoral E, Matos I, Nachtigall P, Položij M, Fonseca I, Vitvarová-Procházková D, Cejka J Intramolecular Hydroalkoxylation of Non-activated C-C Double Bonds Catalyzed by Zeolites: Experimental and Theoretical Study. ChemSusChem 2013; 6: 1021 – 1030.

[4] Ferreira P, Fonseca IM, Ramos AM, Vital J, Castanheiro JE Acetylation of glycerol over heteropolyacids supported on activated carbon. Catal. Comm. 2011; 12:573–576.

[5] Matos I, Silva MF, Ruiz-Rosas R, Vital J, Rodríguez-Mirasol J, Cordero T, Castanheiro JE, Fonseca IM Methoxylation of α-pinene over mesoporous carbons and microporous carbons: a comparative study. Micropor. Mesopor. Mat. 2014; 199:66–73.

[6] Lopez-Sanz J, Perez-Mayoral E, Soriano E, Omenat-Moran D, Duran CJ, Martin-Aranda RM, Matos I, Fonseca I Acid-Activated Carbon Materials: Cheaper Alternative Catalysts for the Synthesis of Substituted Quinolines. ChemcatChem 2013; 5:3736–3742.

[7] Matos I, Neves PD, Castanheiro JE, Perez-Mayoral E, Martin-Aranda R, Duran-Valle C, Vital J, Botelho do Rego AM, Fonseca IM Mesoporous carbon as an efficient catalyst for alcoholysis and aminolysis of epoxides. Applied Catalysis A: General 2012; 439– 440:24– 30.

[8] Durán-Valle CJ, Madrigal-Martínez M, Martínez-Gallego M, Fonseca IM, Matos I, Botelho do Rego AM, Activated carbon as a catalyst for the synthesis of N-alkylimidazoles and imidazolium ionic liquids. Catalysis Today 2012; 187(1):108–114.

[9] López-Pestaña JM, Ávila-Rey MJ, Martín-Aranda RM Ultrasound-promoted N-alkylation of imidazole. Catalysis by solid-base, alkali-metal doped carbons. Green Chem. 4 (2002) 628-630.

[10] López-Pestaña JM, Díaz-Terán J, Ávila-Rey MJ, Rojas-Cervantes ML, Martín-Aranda RM N-alkylation of imidazole by alkaline carbons Micropor. Mesopor. Mat. 2004; 67(1):87-94.

[11] Durán-Valle CJ, Fonseca I, Calvino-Casilda V, Picallo M, López-Peinado AJ, Martín-Aranda RM Sonocatalysis and alkaline-doped carbons: An efficient method for the synthesis of chalcones in heterogeneous media. Catal. Today 2005;107-108:500-506.

[12] Matos I, Fernandes S, Guerreiro L, Barata S, Ramos AM, Vital J, Fonseca IM The efect of surfactants on the porosity of carbon xerogels. Micropor. Mesopor. Mat. 2006; 92:38–46.

[13] Al-Muhtaseb SA, Ritter JA Preparation and Properties of Resorcinol–Formaldehyde Organic and Carbon Gels. Adv. Mater. 2003; 15:101-114.

[14] Lin C, Ritter JA Effect of synthesis pH on the structure of carbon xerogels. Carbon 1997; 35:1271-1278.

[15] Thommes M, Kaneko K, Neimark AV, Olivier JP, Rodriguez-Reinoso F, Rouquerol J, Sing KSW Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). Pure Appl. Chem. 2015; 87(9-10): 1051–1069.

[16] Egea J, de Los Rios C 1,8-Naphthyridine derivatives as Cholinesterases Inhibitors and Cell Ca2+ Regulators, a Multitarget Strategy for Alzheimer’s Disease. Curr. Top. Med. Chem. 2011; 11:2807–2823.

[17] Yan Z, Guang S, Su X, Xu H Near-Infrared Absorbing Squaraine Dyes for Solar Cells: Relationship between Architecture and Performance. J. Phys. Chem. C 2012; 116:8894–8900.

RESEÑA. XIII Reunión del Grupo Español del Carbón Alicante, 18 a 21 de Octubre de 2015

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La XIII Reunión del Grupo Español del Carbón tuvo lugar del 18 al 21 de octubre del pasado mes de octubre de 2015. En esta ocasión, la sede del evento fue Alicante, 22 años después de albergar la segunda reunión del grupo en el año 1993. La organización estuvo a cargo de la Universidad de Alicante, que celebró la reunión en el Hotel HUSA Alicante Golf, que ofreció a todos los participantes una gran acogida para este valorado evento.

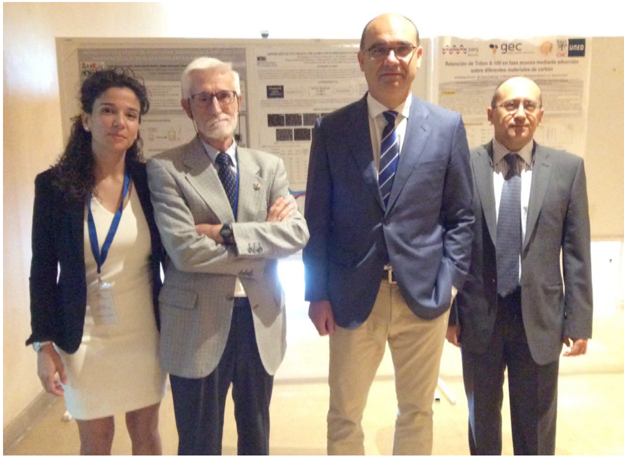
En la jornada inaugural se contó con la presencia del rector de la Universidad de Alicante, quien dio una grata bienvenida a todos los participantes. Así mismo, se hizo mención especial al Profesor Ángel Linares Solano por su gran trayectoria y dedicación a la investigación en materiales carbonosos, así como su aporte e inspiración al Grupo Español del Carbón desde su creación, ya que ha sido parte fundamental en el crecimiento del grupo.

La reunión tuvo una gran participación, con alrededor de 140 asistentes de todas partes del país, provenientes de diferentes universidades e institutos de investigación. Adicionalmente se contó con la participación de asistentes de grupos de investigación internacionales: Japón (1), Portugal (3), Brasil (1), Estados Unidos (1), Holanda (1) y México (2). Se presentaron dos conferencias plenarias, 55 comunicaciones orales y 104 en formato póster.

Los trabajos presentados se clasificaron en distintos temas de gran interés científico, relacionados con la “Generación sostenible de energía” (13), “Procesos de conversión del carbón” (4), “Preparación y caracterización de materiales de carbón” (31), “Nanomateriales, grafeno y materiales carbonosos avanzados” (25), “Aplicaciones en adsorción y catálisis” (31), “Aplicaciones en generación y almacenamiento de energía” (30), “Aplicaciones medioambientales” (25). Las conferencias plenarias estuvieron a cargo de: Dr. Carlos Moreno Castilla (Universidad de Granada), quien nos introdujo al estudio de las síntesis de esferas de carbono derivadas de reacciones de polimerización a bajas temperaturas y sus diversas aplicaciones, centrándose en sistemas de almacenamiento y conversión de energía; y el Dr. Fernando Rubiera (Instituto Nacional del Carbón – INCAR.CSIC), quien describió el estado actual de las tecnologías limpias de utilización del carbón.

De manera importante, hay que destacar los trabajos presentados en el 7º Premio GEC a Jóvenes Investigadores, todos de una calidad tal para ser merecedores del premio. Los tres finalistas del 7º Premio han sido los doctores José Miguel Bermúdez Menéndez, Esther Gómez Calvo e Isabel Martínez Berges, quienes presentaron su trabajo en la reunión y entre los cuales se seleccionó finalmente el ganador. El trabajo reconocido con este premio fue el presentado por la Dra. Isabel Martínez Berges, relacionado con los ciclos de carbonatación-calcinación de CaO como sistema de captura de CO_2, en el que ilustró nuevas tecnologías con alta eficiencia para la producción de energía.

Finalmente, se dio por concluida la reunión después de tres días de grandes debates en torno a los trabajos presentados, no sin tener la oportunidad de disfrutar de Alicante, su gastronomía, clima y el emblemático Castillo de Santa Bárbara. En la ceremonia de clausura se agradeció la participación de todos los asistentes y se invitó a la participación de la próxima Reunión del Grupo Español del Carbón, que se celebrará en Málaga (2017).



Dolores Lozano Castelló, presidenta del comité organizador de la XIII Reunión del GEC; Ángel Linares Solano, profesor del Departamento de Química Inorgánica de la UA; Manuel Palomar, Sanz rector de la UA y Diego Cazorla Amorós, presidente del GEC.

Fotografía de los finalistas del 7º Premio de Jóvenes Investigadores (J.M. Bermúdez Menéndez, E. Gómez Calvo e I. Martínez Berges), el presidente y el secretario del Grupo Español del Carbón.

Fotografía de los asistentes a la XIII Reunión del Grupo Español del Carbón en el salón de actos del Hotel Golf de Alicante.

Socios protectores del Grupo Español del carbón

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