Some insights into the evolution of support surface chemistry during the preparation of metal oxide-activated carbon catalysts by conventional wet impregnation

Nuevos avances sobre la evolución de la química superficial del soporte durante la preparación de catalizadores óxido metálico-carbón activado mediante impregnación húmeda convencional

A. Barroso Bogeat*[1], M. F. Alexandre Franco[2], C. Fernández González[2], V. Gómez Serrano[2]

[1] Departamento de Química Inorgánica, Facultad de Farmacia, Universidad de Salamanca, C/ Licenciado Méndez Nieto s/n, 37007 Salamanca, España

[2] Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias, Universidad de Extremadura, Avda. de Elvas s/n, 06006 Badajoz, España

**Corresponding author: adrianbogeat@usal.es*

Abstract

The present work is aimed at unveiling the evolution and changes undergone by the surface chemistry of a carbon support, with special attention to the oxygen-containing functionalities, during the different steps involved in the preparation of activated carbon (AC)-metal oxide (MO) catalysts by the conventional wet impregnation method. For such an aim, three series of catalyst samples have been prepared by impregnation of a commercial AC (Merck) with $Fe(NO_3)_3$ and $Zn(NO_3)_2$ aqueous solutions at 80 °C for 5 h, followed by oven-drying at 120 °C for 24 h, and then heat treatment at 200 or 850 °C for 2 h under inert atmosphere. Both the raw AC and the resulting samples were characterised in terms of their surface chemistry by FT-IR spectroscopy and measurement of pH of the point of zero charge. Chromene, pyrone, and ether type structures are by far dominant in the AC surface. The hydrolysis of Fe^{3+} and Zn^{2+} cations markedly influences the pH of the impregnation solution and thereby the oxidation of surface functional groups and structures of AC by the nitrate ion present in such solutions. Thus, the degree of oxidation is larger for the Fe^{3+} aqueous solution than for that of Zn^{2+}. During the impregnation step, phenolic hydroxyl or carboxylic acid groups as well as C-O-M bonds are usually formed on the AC surface by oxidation of chromene, 2-pyrone, and ether-type structures. Concerning the heat-treated samples, chemical changes are much stronger for the catalysts prepared at 850 °C as compared to those obtained at 200 °C. At the higher temperature, carboxylic acid groups, 4-pyrone, metal carboxylate structures, and C-O-M atomic groupings are formed.

Resumen

El presente trabajo tiene como objetivo desvelar la evolución y los cambios experimentados por la química superficial de un soporte carbonoso, con especial atención a las funcionalidades oxigenadas, durante las diferentes etapas implicadas en la preparación de catalizadores carbón activado (AC)-óxido metálico (MO) mediante el método de impregnación húmeda convencional. Para este propósito, tres series de catalizadores se han preparado mediante impregnación de un AC comercial (Merck) con disoluciones acuosas de $Fe(NO_3)_3$ y $Zn(NO_3)_2$ a 80 °C durante 5 h, seguida de secado en estufa a 120 °C durante 24 h y, por último, tratamiento térmico a 200 o 850 °C durante 2 h bajo atmósfera inerte. Tanto el AC de partida como las muestras resultantes fueron caracterizadas en términos de su química superficial mediante espectroscopía FT-IR y medida del pH del punto de carga cero. La superficie del AC está dominada por estructuras tipo cromeno, pirona y éter. La hidrólisis de los cationes Fe^{3+} y Zn^{2+} influye decisivamente sobre el pH de la disolución de impregnación y, en consecuencia, sobre la oxidación de los grupos funcionales y estructuras superficiales del AC por el ion nitrato presente en tales disoluciones. Así, el grado de oxidación es mayor para la disolución acuosa de Fe^{3+} que para la de Zn^{2+}. Grupos hidroxilo fenólico y ácido carboxílico, así como enlaces C-O-M, se forman sobre la superficie del AC durante la etapa de impregnación por oxidación de estructuras tipo cromeno, 2-pirona y éter. En cuanto a las muestras tratadas térmicamente, los cambios químicos son mucho más intensos para los catalizadores preparados a 850 °C en comparación con los obtenidos a 200 °C. A la máxima temperatura de tratamiento se forman grupos ácido carboxílico, 4-pirona, estructuras de carboxilatos metálicos y grupos atómicos C-O-M.

1. Introduction

Activated carbon (AC, hereafter) is a porous carbon material widely employed not only as adsorbent but also as catalyst and catalyst support [1–3]. Such an extensive use chiefly arises from its unique and excellent properties, among which the high specific surface area, tunable porous structure, and very rich surface chemistry are worth mentioning. Concerning this latter, a number of works have revealed the pivotal role played by the surface chemical features of AC in catalytic processes due to its broadly varied reactivity, thus governing the dispersion of the catalytic active phase, its loading, and even the catalytic activity and/or selectivity [4–9]. In the field of carbon-based materials, the term “surface chemistry” commonly refers to the chemical nature and properties of their surface, which is essentially made up of unpaired electrons and several heteroatoms [10]. These latter are present in markedly different quantities and bonded to the carbon skeleton, thus forming a variety of surface functional groups and structures identical to those typically described for aromatic organic compounds [10,11]. Among the various heteroatoms found in ACs, oxygen is by far the most abundant and important, followed by nitrogen and to a much lesser extent hydrogen and phosphorus. In fact, carbon-oxygen functional groups not only influence the surface behaviour, wettability, or electrical, adsorptive, and catalytic properties of ACs, but also allow tailoring and tuning the surface chemistry for a given specific application by means of functionalisation [12].

On the other hand, metal oxides (MO, henceforth) are ubiquitous materials in heterogeneous catalysis due to their redox and acid-base properties, which allow them to take part in chemical processes involving the exchange of electrons, protons, and oxide ions. Therefore, a combination of AC and MO properties in a single hybrid catalyst may render it more versatile in catalysis processes and this redounds the number of applications.

The present work is aimed at preparing a series of AC-MO catalysts by conventional wet impregnation of a commercial AC support with $Fe(NO_3)_3$ and $Zn(NO_3)_2$ aqueous solutions under mild conditions and subsequent heat treatment of the resulting products at higher temperatures. Then, the as-prepared catalysts are characterised by means of FT-IR spectroscopy and measurement of the point of zero charge with a view to shedding light on the evolution and changes undergone by the surface chemistry of the carbon support, with special attention to the oxygen functional groups and structures, during the set of steps involved in the preparation of the samples (i.e., soaking, oven-drying, and calcination). The results obtained in previous characterisation studies of both AC and the freshly prepared AC-MO catalysts have been previously reported elsewhere [13–18].

2. Experimental

2.1. Materials and reagents

As received without any additional treatment, a commercial granular AC purchased from Merck (Darmstadt, Germany), 1.5 mm average grain size, was employed as support. This carbon material had been previously characterised by our research group in terms of its elemental chemical composition, surface chemistry, and textural features, the results being reported elsewhere [13,14,17]an attempt is made here to identify not only pyrone and chromene type structures but also their isomers in a commercial activated carbon (Merck; AC. Briefly, AC possesses a much lower ash content (i.e., around 4.7 wt.%) as compared to other activated carbons, and it is an essentially microporous material (micropore volume, 0.36 $cm^3 \cdot g^{-1}$; apparent surface area, 711 $m^2 \cdot g^{-1}$) with a noticeable contribution both of meso- and macroporosity (mesopore volume, 0.15 $cm^3 \cdot g^{-1}$; macropore volume, 0.21 $cm^3 \cdot g^{-1}$).

Metal nitrates (i.e., $Fe(NO_3)_3 \cdot 9H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$), which are as a rule readily soluble in water, were selected as metal oxide precursors and supplied by Panreac (Barcelona, Spain; reagent grade).

2.2. Preparation of the AC-MO catalysts

Metal oxide phases were supported on the pristine AC material by using a conventional wet impregnation method in two successive stages, according to the procedure previously described in detail elsewhere [14,16]activated carbon (AC. Briefly, AC was soaked at 80 °C for 5 h in an aqueous solution prepared by dissolving the appropriate amount of the metal nitrate precursor (i.e., precursor to AC mass ratio of 1:1). Then, the resulting impregnated solids were oven-dried at 120 °C for 24 h and finally heat-treated at either 200 or 850 °C for 2 h under dynamic inert atmosphere. Overall, three series of AC-MO catalysts were obtained depending on the heating temperature (i.e., 120, 200, and 850 °C) and therefore three samples for each employed metal precursor (i.e., $Fe(NO_3)_3 \cdot 9H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$). These samples have been denoted as MT, with M standing for the initial letter of the symbol for the metal and T for the heat treatment temperature.

2.3. Characterisation of the AC-MO catalysts

The as-prepared AC-MO catalyst samples were characterised in terms of their surface chemical features by means of FT-IR spectroscopy and measurements of the pH of the point of zero charge. These jointly provided a detailed picture of the evolution and changes undergone by the surface chemistry of the carbon support as a result of the soaking, oven-drying, and heating steps involved in the preparation of the supported catalysts.

2.3.1. Fourier-FT-IR spectroscopy

FT-IR spectra were registered for both the raw AC support and the freshly prepared catalyst samples by using a PerkinElmer Spectrum 100 spectrophotometer, in the wavenumber range from 4000 to 400 cm^{-1} and averaging the data from 8 successive scans taken at 2 cm^{-1} resolution. Prior to acquiring these spectra, sample/KBr pellets with a total mass of 238 mg and a sample to KBr mass ratio of 1:1900 were prepared following the procedure described in detail elsewhere [13]an attempt is made here to identify not only pyrone and chromene type structures but also their isomers in a commercial activated carbon (Merck; AC. The spectrum for a pure KBr pellet with approximately the same mass as the sample pellets was recorded and employed as background.

2.3.2. pH of the point of zero charge (pH_{pzc})

The pH_{pzc} for both the AC and the supported catalysts was measured by using the procedure proposed by Newcombe et al [19]. In brief, a set of 0.01 mol·L^{-1} NaCl aqueous solutions at pH of around 2, 4, 6, 8, and 10 were prepared by adjusting these values with either 0.1 mol·L^{-1} HCl or NaOH aqueous solutions. Then, the pH_{pzc} for each sample was determined from the plot of pH of the initial solution against pH of the corresponding supernatant after a soaking time of 48 h.

3. Results and discussion

3.1. Infrared analysis

The results obtained in the study of the pristine AC employed as support by means of FT-IR spectroscopy have been previously discussed elsewhere [13]an attempt is made here to identify not only pyrone and chromene type structures but also their isomers in a commercial activated carbon (Merck; AC, so they are herein summarised only for the sake of comparison. The infrared spectrum recorded for the AC is depicted in Figure 1, while the main band assignments and positions are summarised in Table 1. The most prominent feature of this spectrum is the very strong band centred at around 1720 cm^{-1}, which is ascribed to the *v*(C=O) vibration of both carboxylic acid groups and 2-pyrone structures, which are involved in hydrogen bonding. Moreover, the presence of carboxylic acid groups in the carbon support is further evidenced by the couple of bands registered at 1279 and 901 cm^{-1}. On the other hand, a large number of spectral features, such as the bands and shoulders at 1657, 1636, 1249, 1024, 740, and so on, cm^{-1}, are tentatively attributed to chromene and/or pyrone type structures (which are henceforth referred to as CPS in the text). Furthermore, the band appearing at about 1024 cm-1 is associated with ether type structures. Finally, the total content of phenolic hydroxyl groups (C-OH) in the AC surface is expected to be low, according to the small absorption of infrared radiation observed at around 1200 cm^{-1}.

The infrared spectra registered for the three catalyst samples of *FT* series are plotted together in Figure 2 for comparison purposes. As compared to that obtained for the raw AC (see Figure 1), the spectrum of F120 displays two stronger and well-defined bands located at 1726 and 1283 cm^{-1}, whereas the band at 1021 cm^{-1} is markedly weaker. Accordingly, it is likely that during the impregnation of the AC support with the Fe^{3+} aqueous solution (starting pH 1.54) CPS are oxidised as well and transformed into carboxylic acid groups. In addition, infrared absorption decreases in the range from 1236 to 1165 cm^{-1} while the band at 1112 cm^{-1} is significantly broader and stronger, all these spectral changes being consistent with the presence of C-O-Fe atomic groupings. These latter are formed by C-OH and Fe-OH condensation reactions accompanied by water release. Also, O_2 chemisorbed in the F120 sample may absorb infrared radiation nearby 1112 cm^{-1}. Furthermore, the scarcely visible shoulder at around 1386 cm^{-1} reveals that the content of residual nitrate groups (NO_3^-) is rather low in F120.

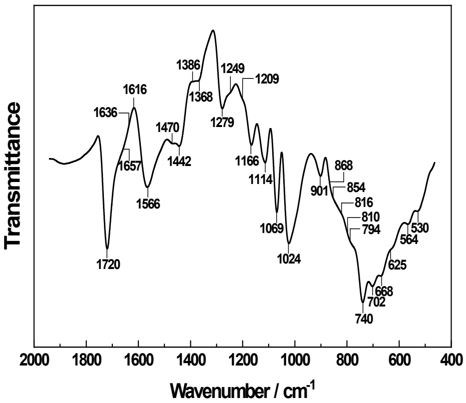

Figure 1. FT-IR spectrum registered for the raw AC support.

Figura 1. Espectro FT-IR registrado para el soporte AC.

Table 1. FT-IR spectrum of the AC support. Main band assignments.

Tabla 1. Espectro FT-IR del soporte AC. Asignaciones de bandas principales.

Spectral feature	Position / cm^{-1}	Assignment^a	Functional group / structure
Peaks	2972-2823	ν(C-H)	Chromene structures
		ν(O-H)	Quinone oximes
Band	1720	ν(C=O)	Carboxylic acid group, 2-pyrone structures
Shoulder	1657	ν(C=O)	Pyrone and chromene structures, carbonyl structures
Shoulder	1636	ν(C=C)	Pyrone and chromene structures
Band	1566	ν_s(C=C) skeletal	Aromatic ring
		ν(C=C)	2-pyrone structures
Band	1279	δ(O-H)-ν(C-O)	Carboxylic acid
		ν_{as}(=C-O-C)	4H-chromene
Shoulders	ca. 1249	ν_{as}(=C-O-C)	2H-chromene, 2-pyrone
Band	1024	ν_s(=C-O-C)	Chromene, pyrone, ether structures

^{a}Abbreviations: ν, stretching; δ, bending (in-plane); as, asymmetric; s, symmetric.

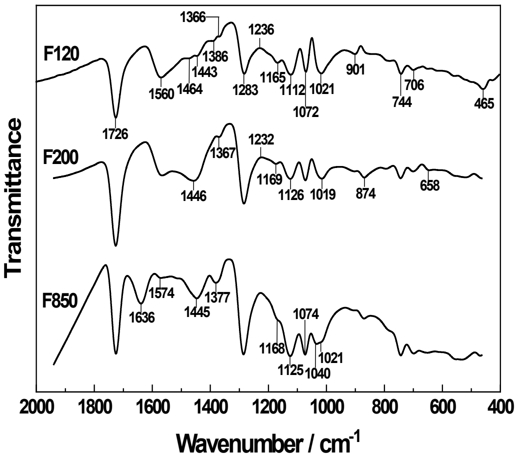

Figure 2. FT-IR spectra registered for the catalyst samples of *FT* series.

Figura 2. Espectros FT-IR registrados para las muestras de catalizador de la serie *FT*.

The greater intensity of the bands at 1726 and 1283 cm^{-1} for F200 than for F120 suggests that the heat treatment of this latter sample at 200 °C for 2 h under inert atmosphere promotes the formation of carboxylic acid groups to some extent. Similarly to the preparation of F120, these groups are likely generated from CPS since their total content is lower for the F200 catalyst sample than for F120, as revealed by the noticeably decreased intensity of the band at 1019 cm^{-1} observed in the F200 infrared spectrum. In this latter, infrared radiation absorption clearly decreases between 1232 and 1169 cm^{-1}, so phenolic -OH groups may also be involved in the oxidation processes. In this case, the oxidising agent should be any chemical species remaining up-taken after the preparation of F120, as the heat treatment of this sample at 200 °C in the preparation of the F200 catalyst is accomplished in nitrogen atmosphere.

As most prominent modifications, the spectrum recorded for the F850 catalyst sample displays a couple of medium intensity bands at 1636 and 1445 cm^{-1}, together with the weaker band centred at 1377 cm^{-1}. Moreover, this spectrum exhibits the band at 1125 cm^{-1} with increased intensity in comparison to that peaked at 1040 and 1021 cm^{-1}. In the case of the F850 catalyst, carboxylic acid groups, 4-pyrone structures as well as metal carboxylates could be formed due to the heating of F120 sample at 850 °C in inert atmosphere. Nevertheless, this heat treatment seems to favour the formation of C-O-M atomic groupings rather than of M-O-M atomic groupings. In this regard, the former groups may be generated with involvement of carboxylic acid groups, as for metal carboxylates with unidentate coordination [20], rather than of phenolic -C-OH groups, in view that the absorption increases nearby 1200 cm^{-1} for F850. In accordance with these results, it is likely that the main factor controlling the changes produced in the surface chemical composition of the catalyst samples is the reactivity of the metal oxide at high temperature.

The FT-IR spectra recorded for the catalyst samples of the *ZT* series are gathered in Figure 3. As far as the spectrum for Z120 is concerned, it displays three shoulders at around 1657, 1636, and 743 cm^{-1}. Moreover, the strong band located at 1024 cm-1 for the raw AC support is absence in the spectrum for Z120, likely because of overlapping bands. However, the increase in the absorption of infrared radiation observed between 1226 and 1161 cm^{-1} is indicative of the formation of phenolic C-OH groups from CPS as a result of the oxidation process. Such assumption is supported by the noticeable shift to lower frequencies and intensity decrease for the band appearing at 1714 cm^{-1} in the Z120 spectrum (i.e., for the carbon support it is centred at around 1720 cm^{-1}). Phenolic C-OH groups may also transform into C-O-Zn atomic groupings, as suggested by the development of the strong band at 1048 cm^{-1}. In this connection, it is also worth highlighting that the degree of hydrolysis is smaller for the Zn^{2+} cation as compared to Fe^{3+} cation, which should render the condensation reaction of C-OH and M-OH less likely. On the other hand, the band centred at 1048 cm^{-1} is also ascribable to O_2 chemisorbed on the Z120 surface. In any event, from the FT-IR spectrum registered for the Z120 sample it becomes evident that the effect of the impregnation of the AC with the Zn^{2+} precursor solution on the surface chemistry of the carbon support is less relevant than when a Fe^{3+} aqueous solution is employed. The much stronger band located at 1384 cm-1 for the Z120 spectrum than for its F120 counterpart reveals that the content of residual nitrate groups is much higher in the former catalyst sample.

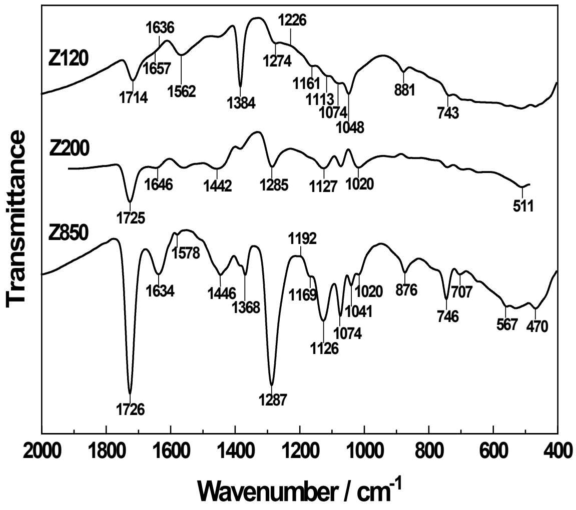

Figure 3. FT-IR spectra registered for the catalyst samples of *ZT* series.

Figura 3. Espectros FT-IR registrados para las muestras de catalizador de la serie *ZT*.

From the comparison of the FT-IR spectra registered for the Z120 and Z200 catalysts, it follows that the heat treatment of the former at 200 °C for 2 h in inert atmosphere leads to an increased concentration of carboxylic acid groups in the surface of the resulting Z200 catalyst sample. Regarding the spectrum for Z850, the presence of a large number of well-defined bands centred at 1726, 1634, 1446, 1368, 1126, 1074, 1041, 876, and 746 cm^{-1} is worth mentioning.

In addition, an absorption decrease is also noted for the band peaked at 1020 cm^{-1}. Accordingly, it becomes apparent that the heat treatment of the oven-dried Z120 sample at 850 °C brings about a significant development of oxygen-containing surface groups. To sum up, from the FT-IR spectra recorded for the couple of catalyst samples prepared by heat treatment at 850 °C (i.e., F850 and Z850) it is concluded that their surface chemistries are rather similar. Furthermore, according to the relative band intensities, the concentration of surface functional groups and structures or atomic groupings for these latter catalysts varies in the following order: Z850 > F850, carboxylic acid; F850 ≈ Z850, 4-pyrone; F850 ≈ Z850, C-O-M.

3.2. *pH_{pzc}*

The pH_{pzc} is 10.50 for the raw AC support [14]activated carbon (AC. As can be seen from Table 2, for the as-prepared AC-MO catalysts it is markedly lower than for the carbon substrate, irrespective of the metal oxide precursor and the heat treatment temperature. This observation is fully consistent with the increase in the content of acidic surface groups and decrease in the content of basic surface structures, as previously inferred from the corresponding FT-IR spectra. Furthermore, it is also found that the pH_{pzc} depends on the metal oxide precursor and the heat treatment temperature. Thus, samples prepared by impregnation with the Fe^{3+} aqueous solution exhibit pH_{pzc} values slightly lower than those observed for their counterparts obtained by impregnation with the Zn^{2+} aqueous solution. Such variation appears to be compatible with a greater presence of carboxylic acid groups in samples of *FT* series and of phenolic hydroxyl groups in those catalysts of *ZT* series. Concerning the influence of the heat treatment temperature, as compared to the samples oven-dried at 120 °C pH_{pzc} first slightly increases for catalysts prepared by heat treatment at 200 °C and then much more sharply for those obtained by heating at 850 °C, thus becoming close to the value measured for the AC support. Finally, it should be noted that although basic structures present in these latter samples must contribute to their basic character, band intensities associated with CPS do not directly correlate with pH_{pzc} values. Therefore, it is expected that other factors, such as the concentration of carboxylic acid groups and whether these functionalities are found as carboxylates or not, must also influence the surface basicity of the catalysts.

Table 2. pH_{pzc} values measured for the raw AC support and the as-prepared AC-MO catalyst samples.

Tabla 2. Valores de pH_{pzc} medidos para el soporte AC y las muestras de catalizador AC-MO preparadas

Sample	pH_{pzc}	Sample	pH_{pzc}	Sample	pH_{pzc}
AC	10.50				
F120	4.00	F200	4.10	F850	8.80
Z120	6.30	Z200	6.50	Z850	9.80

4. Conclusions

The preparation of three series of AC-MO catalyst samples has been carried out by means of the conventional wet impregnation method, consisting in three stages: (i) soaking of a commercial AC support with $Fe(NO_3)_3$ and $Zn(NO_3)_2$ aqueous solutions at 80 °C for 5 h, (ii) oven-drying at 120 °C for 24 h, and (iii) heat treatment at 200 or 850 °C for 2 h under inert atmosphere. The characterisation of the surface chemistry of the as-prepared materials by the FT-IR spectroscopy technique allows to draw the following main conclusions:

1. The impregnation of AC leads to the formation of phenolic hydroxyl and/or carboxylic acid groups as well as of C-O-M bonds to the detriment of CPS and ether type structures found in the raw carbon support. Accordingly, AC impregnation results in a marked increase of the acidic character of the carbon surface, as confirmed from pH_{pzc} measurements. C-O-M atomic groupings are formed by condensation of AC-OH groups and M-OH groups with water release.
2. The heat treatment of the oven-dried samples at 200 or 850 °C brings about stronger chemical modifications when heating at the highest temperature. For these catalysts, in general, carboxylic acid groups, 4-pyrone groups, metal carboxylates, and C-O-M atomic groupings are formed.
3. The chemical changes undergone by the AC surface as a result of its impregnation with the MO precursor solutions and subsequent oven-drying are essentially attributed to the oxidising action of chemical species present in these solutions, such as the nitrate ion, or generated during the soaking treatment. When heating at 200 or 850 °C, the chemical changes are mainly connected with the presence in the samples surface of chemisorbed O_2 and thermal effects at high temperature.

References

[1] Rodríguez-Reinoso F. The role of carbon materials in heterogeneous catalysis. Carbon 1998; 36:159–175.

[2] Rodríguez-Reinoso F, Sepúlveda-Escribano A. Carbon as catalyst support. In: Philippe Serp and José Luis Figueiredo Eds. Carbon materials for catalysis. John Wiley & Sons. 2009 p. 131–155.

[3] Barroso-Bogeat A, Fernández-González C, Alexandre-Franco M, Gómez-Serrano V. Activated carbon as a metal oxide support: A review. In: James F. Kwiatkowski Ed. Activated carbon: classifications, properties and applications. Nova Science Publishers. 2012 p. 297–318.

[4] Calafat A, Laine J, López-Agudo A, Palacios JM. Effect of surface oxidation of the support on the thiophene hydrodesulfurization activity of Mo, Ni, and NiMo catalysts supported on activated carbon. J. Catal. 1996; 162:20–30.

[5] Fraga MA, Mendes MJ, Jordão E. Examination of the surface chemistry of activated carbon on enantioselective hydrogenation of methyl pyruvate over Pt/C catalysts. J. Mol. Catal. A Chem. 2002; 179:243–251.

[6] Huang H-H, Lu M-C, Chen J-N, Lee C-T. Catalytic decomposition of hydrogen peroxide and 4-chlorophenol in the presence of modified activated carbons. Chemosphere 2003; 51:935–943.

[7] Moreno-Castilla C, Pérez-Cadenas AF, Maldonado-Hódar FJ, Carrasco-Marín F, Fierro JLG. Influence of carbon-oxygen surface complexes on the surface acidity of tungsten oxide catalysts supported on activated carbons. Carbon 2003; 41:1157–1167.

[8] Aguilar C, García R, Soto-Garrido G, Arriagada R. Catalytic wet air oxidation of aqueous ammonia with activated carbon. Appl. Catal. B Environ. 2003; 46:229–237.

[9] Bandosz TJ. Surface chemistry of carbon materials. In: Philippe Serp and José Luis Figueiredo Eds. Carbon materials for catalysis. John Wiley & Sons. 2009 p. 45–92.

[10] Barroso-Bogeat A, Alexandre-Franco M, Fernández-González C, Gómez-Serrano V. Activated carbon surface chemistry: Changes upon impregnation with Al(III), Fe(III) and Zn(II)-metal oxide catalyst precursors from NO3− aqueous solutions. Arab. J. Chem. 2019; 12:3963–3976.

[11] Jankowska H, Świątkowski A, Choma J. Active carbon. Ellis Horwood. 1991.

[12] Bandosz TJ, Ania CO. Surface chemistry of activated carbons and its characterization. In: Bandosz TJ Ed. Activated carbon surfaces in environmental remediation. Academic Press. 2006: p. 159–229.

[13] Barroso-Bogeat A, Alexandre-Franco M, Fernández-González C, Gómez-Serrano V. FT-IR analysis of pyrone and chromene structures in activated carbon. Energy and Fuels 2014; 28:4096–4103.

[14] Barroso-Bogeat A, Alexandre-Franco M, Fernández-González C, Gómez-Serrano V. Preparation of activated carbon-metal oxide hybrid catalysts: textural characterization. Fuel Process. Technol. 2014; 126:95–103.

[15] Barroso-Bogeat A, Alexandre-Franco M, Fernández-González C, Sánchez-González J, Gómez-Serrano V. Electrical conductivity of metal (hydr)oxide–activated carbon composites under compression. A comparison study. Mater. Chem. Phys. 2015; 152:113–122.

[16] Barroso-Bogeat A, Alexandre-Franco M, Fernández-González C, Gómez-Serrano V. Preparation and microstructural characterization of activated carbon-metal oxide hybrid catalysts: New insights into reaction paths. J. Mater. Sci. Technol. 2015; 31: 806–814.

[17] Barroso-Bogeat A, Alexandre-Franco M, Fernández-González C, Gómez-Serrano V. Preparation of activated carbon-metal (hydr)oxide materials by thermal methods. Thermogravimetric-mass spectrometric (TG-MS) analysis. J. Anal. Appl. Pyrolysis. 2015; 116: 243–252.

[18] Barroso-Bogeat A, Alexandre-Franco M, Fernández-González C, Gómez-Serrano V. Physico-chemical characterization of activated carbon–metal oxide photocatalysts by immersion calorimetry in benzene and water. J. Therm. Anal. Calorim. 2016; 125:65-74.

[19] Newcombe G, Hayes R, Drikas M. Granular activated carbon: importance of surface properties in the adsorption of naturally occurring organics. Colloids Surfaces A Physicochem. Eng. Asp. 1993; 78:65–71.

[20] Palacios EG, Juárez-López G, Monhemius AJ. Infrared spectroscopy of metal carboxylates: II. Analysis of Fe(III), Ni and Zn carboxylate solutions. Hydrometallurgy. 2004; 72:139–148.

Adrián Barroso Bogeat (Villafranca de los Barros, Badajoz, October 19th 1987) obtained his Bachelor’s degree in Chemistry from the University of Extremadura (UEx, Spain) in 2010. He started his research career as a predoctoral fellow in the “Carbon Adsorbents-Adsorption” (ACA) group, leaded by Professor Vicente Gómez Serrano, at the Department of Organic and Inorganic Chemistry of UEx, supported first by a FPI fellowship from Junta de Extremadura (January 2011 to July 2012) and subsequently by a FPU fellowship from the Spanish Ministry of Education (July 2012 to January 2015). Adrián achieved his PhD in Chemical Science and Technology from UEx in December 2015, being awarded with the Extraordinary Doctorate Award and the 2016 Research Prize by the Spanish Royal Academy of Doctors. In February 2015, he joined the “Solid State Chemistry and Catalysis” group at the Department of Materials Science and Metallurgical Engineering and Inorganic Chemistry of the University of Cádiz (UCA). In this group, he occupied different positions: Research Assistant (February 2015 to August 2017), “Juan de la Cierva-Formación” Postdoctoral Fellow (September 2017 to August 2019), and Postdoctoral Research Associate (September 2019 to April 2021). Very recently, he obtained an Assistant Professor position at the Department of Inorganic Chemistry of the University of Salamanca (USAL).

His current research interests mainly focus on the field of heterogeneous catalysis, particularly the synthesis and physico-chemical characterisation of novel nanostructured catalysts based on rare earth oxides and first-row transition metals, as well as their testing in environmental protection related processes. Dr. Barroso Bogeat has also developed an intense research activity in the field of carbon materials and metal oxide-carbon hybrid materials, with a view to their applications in environmental protection, heterogeneous catalysis, and energy storage. In this regard, it is also worth highlighting his extensive experience in the study of the electrical properties of carbon materials, metal oxides, and carbon-based hybrid materials.

He has complemented his scientific formation with a three-month predoctoral stay at the Institute of Carbon Science and Technology (INCAR-CSIC, Oviedo, Spain) and a five-month postdoctoral stay at the Department of Chemistry of the University of Copenhagen (Denmark), this latter funded by the “José Castillejo Programme” of the Spanish Ministry of Education. During these stays, he was trained on the electrochemical characterisation of different carbon materials, as well as on electrocatalytic tests in solution by using electrodes based on rare earth oxides.

Finally, Dr. Barroso Bogeat has been a reviewer for several high impact journals in the fields of Materials Science and Chemistry and served as guest editor of a special issue of the *Catalysts* journal devoted to compiling some of the new research trends in rare earth oxide-based catalysts. He has also been member of the Organising Committee of the “XI Meeting of the Spanish Carbon Group” (Badajoz, Spain, October 2011) and Chairman of the Organising Committee of the “XIV Young Researchers Symposium of the Spanish Royal Society of Chemistry (RSEQ)” (Badajoz, Spain, November 2017). Since November 2018, he is president-elect of the Territorial Section of Extremadura (STExt) of the RSEQ.