Role of surface phosphorus complexes on the oxidation of porous carbons

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Abstract

Chemical activation of olive stone with phosphoric acid produces activated carbons with relatively high content of P surface groups that remain very stable on the carbon surface at relatively high temperatures. Changes in the surface chemistry of a phosphoric acid activated carbon after subjecting it to thermal treatments in oxidizing and inert conditions are studied by temperature-programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and adsorption/desorption of NH_3. TPD and XPS results point out that P surface groups preferentially reacts with molecular oxygen, prior to carbon gasification, through the oxidation of C-P bond to form C-O-P ones, which are thermally stable at temperatures lower than 700 ºC. At higher temperatures, these C-O-P type surface groups decompose to less oxygenated P groups on the carbon surface (of C-P type) generating CO (and CO_2) in the gas phase. These C-P type surface groups seem to be very reactive and are (re)oxidized upon contact with air, even at room temperature, forming again C-O-P type groups. Thus, the presence of these oxygen-containing P surface groups with an interesting redox functionality of high chemical and thermal stability seems to be responsible of the high oxidation resistance and high oxygen content (once exposed to ambient air) of this type of porous carbons.

Keywords: phosphorus surface groups, carbon inhibition oxidation, surface redox functionality, activated carbon, temperature-programmed desorption, carbon reduction

1. Introduction

Activation of lignocellulosic materials with phosphoric acid is a well-established method for the preparation of activated carbons with a well-developed porous texture with potential uses in catalysis and adsorption applications. Besides, this method allows, depending on the activation conditions, the preparation of activated carbons with a relatively large amount of P surface complexes of very high thermal stability that confer to these carbonaceous solids high surface acidity and oxidation resistance, increasing the possibilities of these materials for applications in catalysis [1-10]. Another advantage is that these carbon materials can be prepared from different carbonaceous precursors, as agricultural wastes, that are abundant, environmentally friendly disposal and its cost decreases associated with activated carbon production. In the present study, olive stone, an important bio-waste of the agro-food industry in Spain, with a production of more than 450,000 tons/year [11], is used as carbon precursor.

The studies of phosphoric acid activated carbons by FTIR, XPS and solid-state NMR techniques pointed out that the remaining P over the surface of the carbon, directly generated during the preparation process under specific conditions, is most likely in form of C-O-P and C-P groups [1, 11-14] . However, some discrepancies are found in the literature associated to the chemical stability of the surface P in phosphorus-containing carbons. In a classic paper, Mckee *et al.* [15] suggested that the C-P-O bonds are not very stable at high temperatures. Oh and Rodriguez proposed an alternative configuration of these C-P-O bonds based on the formation of pπ–dπ bond by overlapping p orbitals between P and O. They suggested that this type of bonding in which P=O groups is replacing two edge carbon atoms would be thermally stable to high temperatures [16]. Lee and Radovic [17] showed that the structure with C-O-P bonding is more stable and able to survive longer than the structure with C-P-O

bonding, using quantum mechanical modelling. This was later supported by Puziy *et al.* [12, 13] based on IR, XPS and P-NMR methods, since high thermal treated carbons revealed a high contribution of condensed phosphates attached by C-O-P linkage to carbon matrix. Nevertheless, Wu and Radovic proposed later that the O-P bond in the C-O-P system is the weakest one based on ab initio molecular orbital calculations [14]. They concluded that when the treatment temperature is increased to high temperatures, the formation of C-PO_3 groups, probably, from decomposition of C-O-PO_3 ones seems to take place. Besides, the ab initio results showed that the C-P bond might be more stable than the C-O-P ones. On this question, Rosas *et al.* [7] observed the release of CO at high temperatures for phosphoric acid activated carbons during a TPD and this behavior was ascribed to the presence of C-O-PO_3 groups on the carbon surface at high temperatures that decompose to C-PO_3 ones.

The nature and concentration of these phosphorus functional groups on the surface of the carbon material has a significant influence on the catalyst performance, since this groups act as anchoring sites for the active phase in the preparation of supported catalysts or they can even be the active sites for specific catalytic reactions. In fact, activated carbons prepared by chemical activation using phosphoric acid have been successfully used as acid catalysts in alcohol dehydration reactions [3, 18] and for the decomposition of H_2O_2 [6]. The results reported for alcohols dehydration reactions show that the presence of oxygen in the reaction atmosphere not only leads to a significant enhancement of alcohol conversions, but also inhibits catalyst deactivation and allows steady state conditions to be reached. In addition to its use as solid acid catalyst, redox functionality has been also incorporated by impregnation of these phosphorus containing activated carbons with vanadium species, obtaining a bifunctional catalyst that is active for hydrocarbon partial oxidation reactions [4, 10].

The use of phosphoric acid activated carbons as catalysts supports for the selective oxidation of benzene, toluene, and xylene (BTX) [2] has also been reported. Oxygen plays a key role not only in all these catalytic processes, but also in the catalyst performance, since the carbon surface chemistry is modified during the reactions involving oxidizing conditions. Recent investigations have also showed that the presence of C-P type phosphorus groups enhances the functionalization of these materials with nitric acid [19]. Therefore, there is a growing interest on these materials in catalysis and the study of the chemical surface modification under oxidative conditions is investigated in the present work.

In addition to this, enrichment of surface oxygen groups on phosphoric acid activated carbons has been observed in most of the above mentioned works, despite the carbons were prepared at relatively high temperatures or were treated to high temperatures under inert conditions. In this sense, it would be of interest to study whether surface re-oxidation may take place on this type of activated carbon during different storage conditions. Therefore, the main purpose of the present work is to study the role of the P surface groups on carbon surface oxidation and reduction reactions. For that, an extensive study of the evolution of oxygen and P surface complexes of an activated carbon prepared by activation of olive stone with phosphoric acid before and after thermal treatments in air and inert atmosphere has been carried out using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). As a baseline, an activated carbon with similar textural characteristics, but without surface P groups, was also prepared by physical activation of olive stone (CO_2 partial gasification) at the same temperature.

2. Experimental Section

2.1. Activated carbons preparation

Two different activated carbons (with and without phosphorous) were prepared through different pathways: chemical activation with phosphoric acid and physical activation by partial gasification with CO_2. Olive stone waste was used as carbonaceous precursor, in both cases. The olive stone waste was cleaned with deionized water, dried at 100 ºC and ground with a roller mill to obtain samples of 400–800 μm particle size. For the chemical activation process, the raw material was impregnated with concentrated H_3PO_4 (85 wt. %, Sigma Aldrich) at room temperature, with a weight ratio of 2/1 (H_3PO_4 /olive stone) and dried for 24 h at 60 °C. The impregnated samples were activated at 800 ºC under continuous N_2 (purity 99.999%, Air Liquide) flow (150 cm^3 STP/min) in a conventional tubular furnace. The activation temperature was reached at a heating rate of 10 °C/min and maintained for 2 h. The activated sample was cooled inside the furnace under the same N_2 flow and then washed with distilled water until negative phosphate analysis in the eluate [20]. The resulting activated carbon, denoted by ACP2800, was dried at 60 °C and, then, grinded and sieved (100-300 μm).

For the physical activation process, a procedure described previously by our research group was followed [21], in which the gasification conditions, i.e. gasification temperature and reaction time, as well as the particle size, were set in order to warrant chemical reaction control to achieve a carbon burn-off value of around 55 %. An olive stone char was obtained by carbonizing the raw material under N_2 flow at 800 ºC. This char was heated under N_2 atmosphere to the gasification temperature (800 ºC). Then, the gas feed was switched to CO_2 (99.998 %, Air Liquide) with a flow rate of 150 cm^3 STP/min for 7 h. The resulting activated carbon, denoted by ACG800, was washed under stirring at room temperature for 1 h with 1% HCl in order to remove mineral components. ACG800 sample was chemical activated with H_3PO_4 following the same procedure than that performed to prepare ACP2800, resulting in ACG800-P2 carbon.

126 **2.2. Thermogravimetric analysis**

127 Thermogravimetric analysis (TG) were performed in a CI Electronics MK2 balance
128 under air flow (150 cm^3 STP/min) from room temperature to 900 ºC at a heating rate of
129 10 ºC/min, with a sample weight of about 20 mg. Simultaneous thermal-gravimetric
130 analysis and differential thermal analysis (TGA/DTA Mettler-Toledo) was used for
131 investigating the re-oxidation process at room temperature after a thermal treatment at
132 900 ºC. In this way, sample weight variation and heat involved in the process were
133 simultaneously analyzed.

134 **2.3. Porous texture characterization**

135 The porous texture of the samples was characterized by N_2 adsorption–desorption
136 at -196 ºC and by CO_2 adsorption at 0 ºC, using an ASAP 2020 apparatus
137 (Micromeritics). Samples were previously out-gassed at 50 torr and 150 ºC for 8 h.
138 From the N_2 adsorption/desorption isotherm, the apparent surface area (A_{BET}) was
139 determined from the BET equation [22]. The micropore volume (V_{DR}) was obtained by
140 the Dubinin-Radushkevich (DR) method applied to the CO_2 and N_2 adsorption
141 isotherms [23]. The mesopore volume (V_{mes}) was determined as the difference between
142 the adsorbed volume of N_2 at a relative pressure of 0.95 and the micropore volume
143 (V_{DR}), covering only the pore sizes between 2 and 40 nm, according to the Kelvin
144 equation [24].

145 **2.4. Surface chemistry characterization and elemental composition**

146 Ultimate analysis of the carbons was carried out in a Leco CHNS-932 system,
147 being the oxygen content calculated by difference. The total amount of P was analyzed
148 by inductively coupled plasma optical emission spectrometry (ICP-OES).

149 The surface chemistry of the samples was analyzed by X-ray photoelectron
150 spectroscopy (XPS) using a *5700C model Physical Electronics* apparatus with *MgKα*

151 radiation (1253.6 eV). For the analysis of the XPS peaks, the C_{1s} peak position was set
152 at 284.5 eV and used as reference to locate the other peaks position. The deconvolution
153 of the peaks was done using Gaussian-Lorentzian curves and a Shirley type background
154 line.

155 Temperature-programmed desorption (TPD) profiles were obtained in a customized
156 quartz fixed-bed reactor placed inside an electrical furnace and coupled to a mass
157 spectrometer (Pfeiffer Omnistar GSD-301) and to non-dispersive infrared (NDIR) gas
158 analyzers (Siemens ULTRAMAT 22) in order to quantify CO, CO_2, H_2 and H_2O
159 (calibration error < 1%). In these experiments, c.a. 100 mg of the sample was heated
160 from room temperature to 1000 °C at a heating rate of 10 °C/min in nitrogen (purity
161 99.999%, Air Liquide) flow (200 cm^3 STP/min). The absence of any leak was carefully
162 checked before each experiment and the samples submitted to this thermal treatment
163 were denoted by -TT.

164 XPS and TPD analysis were also carried out in order to characterize the oxygen
165 surface groups (OSG) of the carbon catalyst generated after oxidations in air (purity
166 99.999%, Air Liquide) at different temperatures. The samples were heated from room
167 temperature up to 120, 180, 240, 325 and 350 ºC at a heating rate of 10 ºC/min in
168 nitrogen flow (200 cm^3 STP/min) that was changed to air at the same flow rate when the
169 chosen temperature was reached and maintained for 2 h. After these 2 hours of
170 experiment, the inlet gas was again changed to nitrogen until all the oxygen was
171 evacuated from the reactor and lines (followed by mass spectroscopy). Finally, a TPD
172 experiment was carried out up to 950 ºC in N_2 flow. The samples submitted to air
173 oxidation were denoted by -OT, where T is the air oxidation temperature.

174 Temperature-programmed desorption of ammonia (NH_3-TPD) was performed using
175 100 mg of catalysts saturated with NH_3 (20% vol in Helium) at 100ºC. After saturation,

176 the NH_3 weakly adsorbed was desorbed in a He flow at the adsorption temperature, until
177 no NH_3 was detected in the outlet gas. The TPD was performed by raising the
178 temperature up to 500 ºC at a heating rate of 10 ºC/min. Outlet NH_3 concentrations were
179 measured by mass spectroscopy (Pfeiffer Vacuum, OmniStar model).
180 Uncertainties were calculated using Student's t-values for 95 % confidence
181 intervals and random standard uncertainties per ASTM method, as detailed elsewhere
182 [25]. The uncertainties are presented in the tables.

183 **3. Results and discussion**

184 **3.1. Characterization of the activated carbons**

185 Table 1 summarizes the yields and the porous texture parameters of the original
186 activated carbons. The activated carbon obtained by gasification with CO_2, ACG800,
187 shows very low yield (13.5 ± 0.4 %, after carbonization and partial gasification).
188 However, the activated carbon prepared by chemical activation with H_3PO_4 at the same
189 temperature, ACP2800, presents a yield value of 38.7 ± 0.8 %, which is similar to those
190 obtained under similar conditions with other biomass residues [7, 11, 26]. The
191 activation agent, H_3PO_4, restricts the formation of tars and volatiles during the
192 carbonization process, thus increasing the yield of the remaining solid product [27].

193 **Table 1.** Yield and porous textural parameters values of the activated carbons[a].

	Yield	N_2 isotherm			CO_2 isotherm	
Sample	(%)	A_{BET} (m^2/g)	V_{DR} (cm^3/g)	V_{mes} (cm^3/g)	A_{DR} (m^2/g)	V_{DR} (cm^3/g)
ACG800	13.5 (0.4)	1355 (7)	0.570 (0.007)	0.064 (0.004)	870 (3)	0.349 (0.005)
ACG800-P2	10.3 (0.2)	1506 (9)	0.591 (0.009)	0.063 (0.004)	940 (4)	0.377 (0.004)
ACP2800	38.7 (0.8)	1380 (7)	0.514 (0.006)	0.654 (0.010)	662 (2)	0.265 (0.003)

194 [a]The uncertainties are provided in parentheses.
195
196 Both activated carbons show higher DR micropore volume values when N_2 is used
197 instead of CO_2 as the adsorbate gas, which indicates the presence of a wide microporous

198 texture [28]. The phosphoric acid activated carbon, ACP2800, presents higher values of
199 BET surface area and mesopore volume, which confirm that activation of olive stone
200 with phosphoric acid produces a significant contribution of mesoporosity. The activated
201 carbon ACG800, obtained by physical activation, presents a similar surface area, but
202 lower volume of mesopores.
203 The elemental composition and characterization of the surface chemistry of the
204 activated carbons are shown in Table 2. The main elements found on the surface of the
205 phosphoric acid activated carbons are carbon and oxygen, with lower, but still
206 significant amount of P. Nitrogen was also detected, but at very low concentrations,
207 probably being a remnant of nitrogen originally present in the carbon precursor.
208 Phosphoric acid appears to activate olive stone through the formation of phosphate and
209 polyphosphate bridges that crosslink biopolymer fragments, avoiding the contraction of
210 the structure by pyrolysis [18]. Most of the activating agent is removed during the
211 washing step, however part of the P is retained in the structure during the activation
212 process and seems to be stably bonded to carbon because they do not elute after the
213 washing step. The maximum amount of P surface groups that are introduced into carbon
214 structure during the activation process is attained at 700-800 ºC, according to previous
215 works [11, 18, 29]. The mass surface concentration of P determined by XPS (3.5 wt. %)
216 is very similar to that obtained by ICP-OES (3.7 wt.%) with uncertainties of 0.2 in each
217 case, indicating that P complexes are well distributed overall the carbon particles
218 surface, internal and external. No other inorganic elements were detected on the surface
219 of ACP2800, as they are removed by the phosphoric acid activation treatment. On the
220 other hand, the ACG800 surface is composed mostly by carbon and oxygen and no P
221 was found on it. Other mineral components like sodium, calcium and potassium, which
222 were originally present in the carbon precursor in very low amount, were removed to a

large extent after a washing step, being present in quantity lower than 0.5 wt. %. In fact, the ash content for ACG800 sample is very low, 0.3% (Table 2). In the case of phosphoric acid activated carbons, the main inorganic constituent of the activated carbon ashes is phosphorus, in form of P_2O_5, as revealed by XPS analysis (not shown).

Table 2. Ash values, elemental composition and surface chemistry characterization (XPS) of the activated carbons [a].

	Ash	Elemental Analysis (wt. %)					XPS (wt. %)		
Sample	(wt. %)	C	O (by diff.)	H	N	S	C_{1s}	O_{1s}	P_{2p}
ACG800	0.3 (0.1)	93.2 (0.7)	4.7 (0.2)	1.2 (0.1)	0.5 (0.1)	0.1 (0.1)	97.8 (0.8)	3.2 (0.2)	-
ACG800-P2	3.7 (0.2)	87.9 (0.7)	6.7 (0.2)	1.3 (0.1)	0.4 (0.1)	0.0 (0.1)	90.2 (0.7)	7.3 (0.3)	2.5 (0.1)
ACP2800	6.0 (0.2)	82.4 (0.6)	9.3 (0.3)	1.9 (0.1)	0.4 (0.1)	0.0 (0.1)	87.3 (0.6)	9.2 (0.3)	3.5 (0.2)

[a]The uncertainties are provided in parentheses.

A very interesting feature observed here is that ACP2800 carbon contains a considerable amount of oxygen (9.3 ± 0.3 wt. %), despite having been activated in an inert atmosphere (N_2). In fact, the oxygen content in phosphoric acid activated carbons has also shown to reach a maximum for samples activated at 700-800 ºC and decreases at higher temperatures, in parallelism with the P content [11, 18, 29], which might suggest that incorporation of oxygen to the carbon surface is related to the P surface content.

Information about the chemical nature of OSG present in the activated carbons is obtained by analysing the XPS and TPD profiles. Figure S1 shows the C_{1s} spectrum for ACG800 and ACP2800 showing its deconvolution into six components according to the analysis of the C_{1s} region of carbon materials reported elsewhere [12, 13, 30]. The BE of carbon bound to phosphorus (C–P bonding) is between graphitic and aliphatic carbon bonds and thus cannot be clearly determined [31]. 62 and 15 % of surface carbon atoms for ACP2800 are graphitic and aliphatic, respectively, whereas those for ACG800 are 66 and 10%. About 20 % belongs to oxidized carbon.

245 The O_{1s} spectrum of ACP2800 sample (Figure 1a) shows a high contribution for
246 oxygen at a binding energy of 532.6 eV, which is characteristic of single bonded
247 oxygen in C-OH, C-O-C and/or C-O-P linkages. Compared to that of ACG800, the O_{1s}
248 spectrum for ACP2800 shows a more pronounce shoulder at lower binding energies,
249 characteristic of C=O and/or P=O groups (BE = 530.9 eV). A binding energy of 535.5
250 eV is related to chemisorbed oxygen and/or water [32].
251 The P_{2p} spectrum for ACP2800 (Figure 1b) shows a band with a main peak at a
252 binding energy of about 133.7 eV, which is characteristic of pentavalent
253 tetracoordinated phosphorus (PO_4) as in phosphates and/or polyphosphates [11, 13].
254 This broad band can be deconvoluted in different doublets with an area ratio of 0.5 and
255 a distance between peaks of 0.84 eV. Wu and Radovic assigned the peak at a binding
256 energy about 134.0 eV to C-O-P type bonds [14], in where the P atom is bonded to four
257 O atoms by one double bond and three single bonds, such as in C-O-PO_3 groups. These
258 authors suggested that these groups could be in the form of numerous cross-linked
259 structures attached to the carbon surface. Thus, $(C\text{-}O)_2PO_2$ and/or $(C\text{-}O)_3PO$ could also
260 be formed on the surface of the carbon. A binding energy of about 133.2 eV is
261 characteristic of C-P bonding as in C-PO_3 groups [14], where P is bonded to one C and
262 three O atoms (two single and one double bonds), and/or C_2PO_2. Lower value of
263 binding energies at 132.0 and 131 eV can be associated to C_3PO [14, 33, 34] and C_3P
264 groups [35], respectively. The XPS P_{2p} results for ACP2800 seem to indicate the
265 presence of mainly C-PO_3 (49.5 %) and C-O-PO_3 (33.3 %) type groups on the activated
266 carbon surface.

267

268

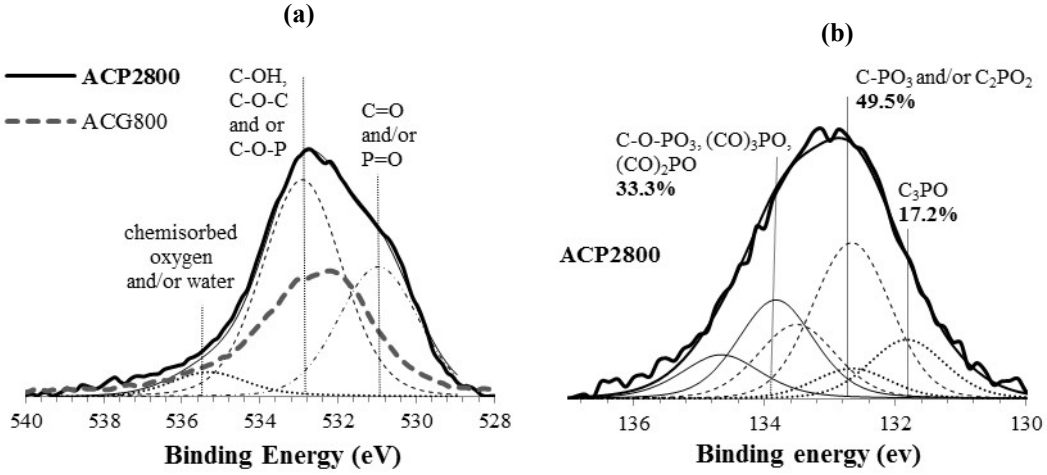


Figure 1. Representative XPS spectra for O_{1s} region of ACG800 and ACP2800 (a) and for P_{2p} region of ACP2800 (b), showing their deconvolution.

Figures 2a and 2b show the evolution of CO, CO_2, H_2O and H_2 as a function of temperature during the TPD for ACP2800 and ACG800, respectively. In addition, a second TPD experiment was performed immediately after the first one on the activated carbons, without exposure to ambient air, in order to elucidate the thermal stability of the OSG. The CO-TPD profiles during the second TPD run (CO-2nd TPD) are also presented (green line (-o-)) in Figure 2. Carbon-oxygen groups of acidic character (carboxylic, lactonic) evolve as CO_2 upon thermal decomposition in a typical TPD analysis, whereas non-acidic ones (carbonyl, ether, quinone and phenol) evolve as CO. Anydride surface groups evolve as both CO and CO_2 [36, 37]. According to previous studies, phenols evolve as CO between 600-700 ºC [36-39], ether groups at around 700 ºC, carbonyls between 800-900 ºC and more stable chromenes or pyrone groups have also been reported to evolve as CO at around 1000 ºC [40].

The TPD profile of ACP2800 (Figure 2a) shows a significant CO evolution at temperatures higher than 750 ºC that presents a maximum at 860 ºC, which has been previously assigned to the decomposition of stable C–O–P type bonds of C-O-PO_3

surface groups, producing C'-PO_3 surface groups, where C' here refers to a new surface carbon atom [8, 14]. On the other hand, the CO_2 profile shows very low desorbed amount in comparison to that of CO, indicating a lower presence of carboxyl, lactonic and anhydride groups on this sample. The washing step performed after the chemical activation process could have introduced some of these OSG of low thermal stability. The relatively higher amount of CO_2 that evolves at temperatures higher to 750 ºC, associated to the peak of CO at those temperatures, is probably due to decomposition of stable O=C–O–P surface groups [41], although secondary reactions between the CO released at these temperatures and the OSG cannot be disregarded [42].

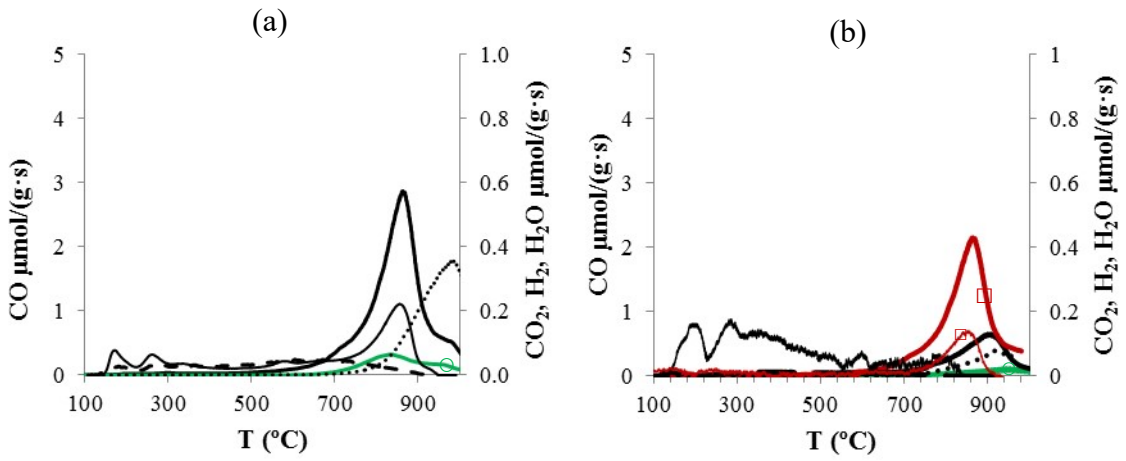


Figure 2. Amount of CO (1st TPD (—) and 2nd TPD (-o-)), CO_2 (—), H_2O (---) and H_2 (·····) evolved as a function of temperature during the TPD performed to ACP2800 (a) and ACG800 (b). Amount of CO (-■-) and CO_2 (-□-) during the TPD performed to ACG800-P2 (b).

The H_2O profile of the TPD for ACP2800 sample shows a peak with a maximum at approximately 150 ºC that corresponds mainly to physisorbed water, while a second desorption peak with a maximum at 270 ºC can be associated to dehydration of two neighboring carboxylic groups. The slight H_2O evolution observed up to 800 ºC could be associated to dehydration of P-OH groups, which have been reported to be thermally stable [43]. In the last case, generation of C-O-PO_2-C and/or C-O-$PO(C)_2$ type surface

308 groups might occur, if dehydration of one and/or two –OH of the phosphate group takes
309 place, respectively, followed by the brakeage of the C–O–P bonds at higher
310 temperatures (from about 750 to 950 ºC), forming finally C'_3PO type surface groups
311 with new surface carbon atoms and gaseous CO. Similar results have been observed for
312 activated carbons obtained by chemical activation with phosphoric acid of different raw
313 materials [8, 33]. There is also some H_2 release starting at 800 ºC, probably as a
314 consequence of aromatic condensation of the carbon substrate.
315 The main peak on the CO profile for ACG800 carbon (Figure 2b) is located at
316 about 900 ºC and may be associated to carbonyl/quinone or esthers groups, given that
317 this carbon does not present any P on the surface. Besides, the shoulder at 270 ºC and
318 the large tail of the CO_2 profile between 350-650 ºC indicate the presence of anhydrides
319 and lactonic groups. The small amount of CO_2 that evolves at temperatures above 800
320 ºC is, probably, a result of secondary reactions between the CO and the OSG, as it has
321 been commented previously.
322 The amount of oxygen evolved during the first TPDs for both carbons have been
323 calculated from the total amounts of CO and CO_2 desorbed. The results are 2.6 ± 0.2
324 and 5.4 ± 0.4 wt. % of oxygen for ACG800 and ACP2800, respectively. Comparison of
325 these results with those for the elemental composition, showed in Table 2, indicates that
326 most of the oxygen on sample ACG800 has been desorbed as CO and CO_2 during the
327 first TPD up to 1000 ºC. However, ACP2800 shows a small presence of CO at high
328 temperatures (>800 °C) during a second TPD, which can be associated to
329 decomposition of C–O–P type bonds, and almost no evolution of CO_2 (>800 °C), H_2
330 and H_2O (not shown). According to the literature, remaining CO-evolving surface
331 groups of very high thermal stability may show some degree of mobility on the carbon
332 surface [39, 44]. Thus, when the temperature is dropping during the first TPD

experiment the oxygen of these CO-evolving groups may migrate to previously generated surface sites of C'–P type, in this case, producing OSG of lower thermal stability that decompose as CO during the second TPD. The amount of CO evolved for the ACP2800 carbon became negligible after a third TPD, indicating that the only oxygen source inside the oven during the thermal treatment of ACP2800 sample must be oxygen evolved from the corresponding OSG.

ACG800 carbon was impregnated with H_3PO_4 at an impregnation ratio (mass of H_3PO_4 to mass of ACG800) value of 2 and carbonized at 800 ºC. After cooling down to room temperature, this sample was washed at the same conditions as ACP2800 was prepared. The new sample thus prepared was denoted by ACG800-P2 and their textural and surface chemistry characteristics are shown in Table 1 and 2, respectively. It is interesting to point out that this sample present 2.5 ± 0.1 wt. % surface P, as measured by XPS (Table 2). The P_{2p} region of the XPS spectrum of ACG800-P2 (not shown) is very similar to that of ACP2800, indicating that ACG800-P2 presents the same P surface complexes as ACP2800. Also, the TPD profile for ACG800-P2 shows a large evolution of CO (and CO_2) at high temperatures (Fig. 2 b, red line (-⊟-)), with a peak centered at 860 ºC, not observed in the TPD profile of ACG800. These experimental evidences support the hypothesis previously exposed that the CO evolved at high temperatures (at about 860 ºC) for samples containing P surface groups result from the decomposition of these P surface complexes.

3.2. Oxidation of activated carbons

The interest on improving the oxidation resistance of carbon materials by introduction of different kinds of surface dopants (especially B and P) is clear from the large number of research papers on this subject. Nevertheless, this is a matter under

357 continuous discussion due to their inherent complexity. P shows an important oxidation
358 inhibition effect, observed in carbon treated with different P compounds, such as
359 organo-phophorus compounds [17], $POCl_3$ [45] or H_3PO_4 [41, 45, 46]. We should
360 emphasize here that in our case the surface P groups are directly generated during the
361 carbon preparation process under specific conditions and seem to be strongly bonded to
362 the carbon surface and thermally very stable. The P surface complexes could be
363 probably located at the edges of carbon crystallites, stabilizing the carbon active sites,
364 which become less reactive for the oxidation reaction, as occurs when carbon materials
365 are doped with P [14, 17, 41, 45, 47]. Nevertheless, they could also act as a physical
366 barrier, blocking the access of oxygen to the active sites.
367 To investigate the oxidation evolution of the carbon surface, the activated carbons
368 were oxidized in air at different temperatures (between 120-350 ºC) for 2 h and then
369 characterized in situ by TPD. It is interesting to mention that ACP2800 was highly
370 resistant to gasification in air, with no significant weight loss observed at 350 ºC for 2 h.
371 However, the air oxidation of ACG800 at 350 ºC for 2 h produced a carbon burn-off of
372 about 11 wt. %. Figure 3 shows the resulting CO and CO_2 evolution profiles during the
373 TPD of the oxidized samples at different temperatures. The TPD results evidence that
374 oxidation of the phosphoric acid-activated carbon (ACP2800) at temperatures lower
375 than 300 ºC increases only the amount of CO evolved at about 860 ºC, accompanied by
376 a small evolution of CO_2 at the same temperature, suggesting that oxidation of the
377 carbon surface at temperatures lower than 300 ºC takes place through the oxidation of
378 C–P surface bonds, generating C–O–P bonds that are thermally stable up to 700 ºC. At
379 higher oxidation temperatures (325 and 350 ºC), the evolution of CO (and CO_2) during
380 the TPD experiments at high temperature (860 ºC) seems to keep constant, which
381 suggests that the surface P groups are completely oxidized and other oxygen surface

382 complexes, thermally less stable, are formed, decomposing as CO and CO_2 at lower
383 temperatures (~700 ºC for CO and ~500 and 700 ºC for CO_2).
384 Oxidation of ACG800 activated carbon that contains no P surface groups
385 (especially at low oxidation temperatures, <300 ºC) causes a more pronounced increase
386 in the evolution of CO (and CO_2) at lower temperatures (~700 ºC for CO and ~500 and
387 700 ºC for CO_2), compared to that of ACP2800, indicating that oxidation of this sample
388 takes place preferentially on the carbon surface, generating OSG of lower thermal
389 stability. Two broad peaks are found in the CO_2 profiles of ACG800 oxidized samples
390 (Figures 3d). The low temperature peak (c.a. 500 ºC) could be attributed to
391 decomposition of lactone groups and the higher temperature peak (c.a. 700 ºC) can be
392 originated from the more stable anhydride groups. In the case of ACP2800 oxidized
393 samples, in addition to these two broad peaks another sharp peak is observed at 860 ºC
394 that can be associated to decomposition of stable O=C–O–P surface groups, as already
395 mentioned in Section 3.1. Oxidation at low temperature seems to preferentially form
396 lactone type groups on the surface of ACG800 and anhydride ones on the surface of
397 ACP2800, increasing the amount of both surface oxygen groups with oxidation
398 temperature, especially for ACG800, which is a typical behavior, previously observed
399 for other oxidized carbon materials [48, 49].

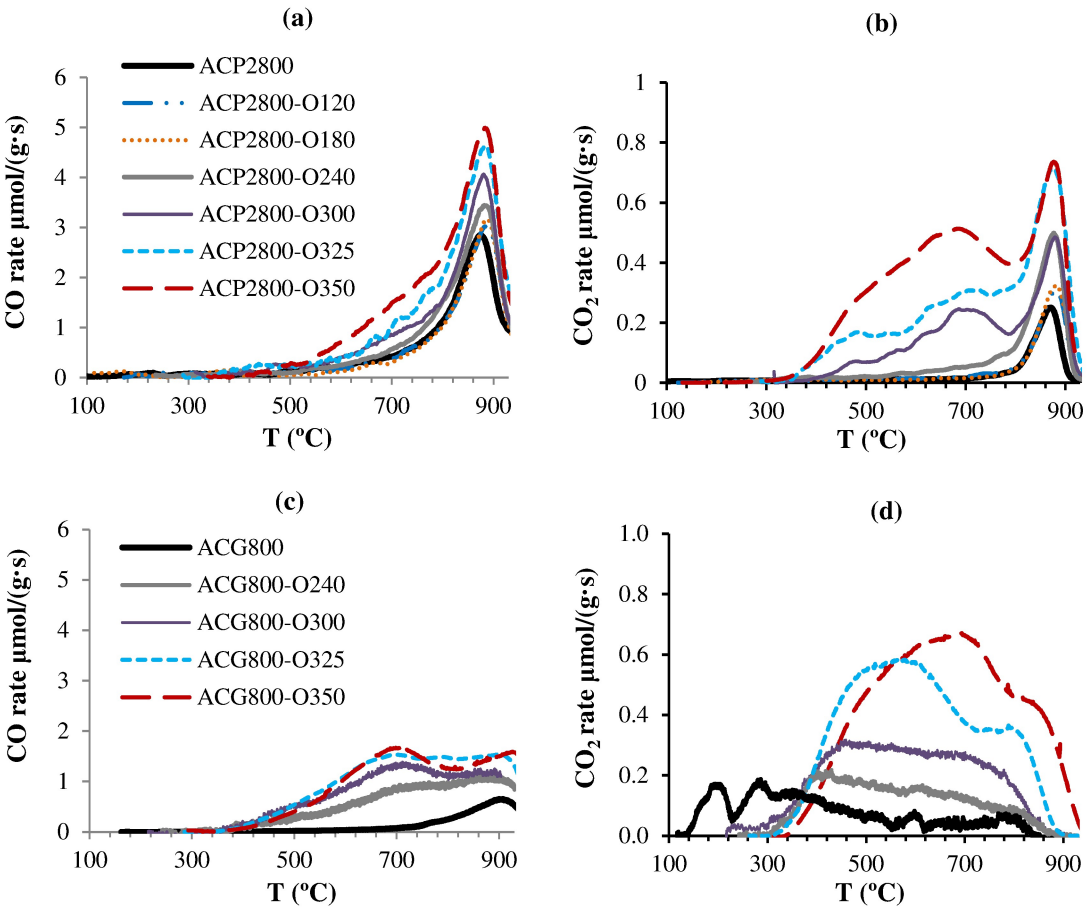


Figure 3. Amount of CO and CO_2 evolved as a function of temperature during the TPD experiments of ACP2800 (a and b, respectively) and ACG800 (c and d, respectively) after air oxidation at different temperatures (120, 180, 240, 300, 325 and 350 ºC) for 2h.

To elucidate the chemical nature and stability of P in phosphorus-containing activated carbons, reduction and re-oxidation of these (P) surface groups has been studied after subjecting ACP2800 carbon to successive thermal treatments in N_2 atmosphere up to 900 ºC (-TT) and under air oxidations at 180 and at 350 ºC for 2h (-O180 or -O350). TPD profiles of ACP2800 sample subjected to these successive treatments are shown in Figure 4. The TPD profile of the sample ACP2800 previously thermal treated in inert atmosphere up to 900 ºC, followed by in-situ oxidation in air at 180 ºC for 2 h (ACP2800-TT-O180) overlaps with that for ACP2800-O180, showing that the same OSG (decomposing as CO and CO_2) were formed (Figure 4a and b). In a

second experiment, ACP2800 was previously subjected to air oxidation at 180 ºC, then, it was thermal treated in inert atmosphere at 900 ºC and, finally, it was air oxidized again at 180 ºC. The TPD profile of this sample, ACP2800-O180-TT-O180, also coincides with that of the previous ones. These results evidence that the P surface complexes of this carbon can be reduced and oxidized again and that this behavior is completely reversible, despite the fact that during the reduction/oxidation cycles slight gasification of the carbon surface takes place through the evolution of CO/CO_2 during the TPD experiments (with a total carbon burn-off of 3.1 ± 0.3 wt. %). After the thermal treatment in inert atmosphere, the new surface sites generated by CO (and CO_2) release (probably of C'–P type) seem to react with oxygen when exposed to air to (re)generate (again) the oxygen-phosphorus (C'–O–P) surface groups. This behavior indicates that oxidation takes place initially on the C–P bonds oxidizing them to C–O–P and that this system is reversible upon heat treatment to high temperature, evidencing a redox character. No loss of surface P was observed (by XPS and ICP-OES) after the different reduction/oxidation cycles. This redox character seems to affect also to the other formed oxygen surface groups, less thermally stable, in the case that the oxidation temperature is higher than 300 ºC (see Figures 4c and d for an oxidation temperature of 350 ºC). The carbon burn-off caused during the TPD experiment for ACP2800 oxidized at 350 ºC (ACP2800-O350-TT) was of 7.7 ± 0.5 wt. %.

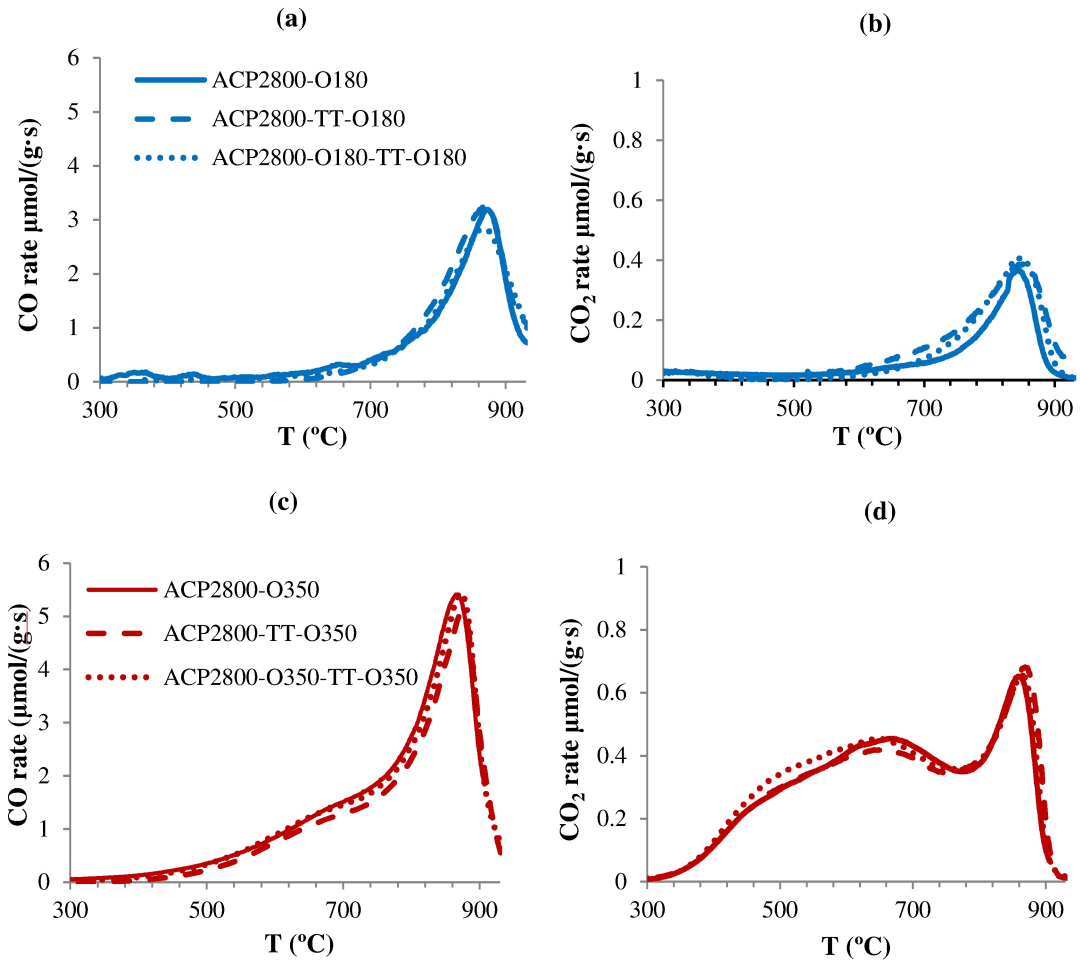


Figure 4. Amount of CO and CO_2 evolved as a function of temperature during the TPD experiment for ACP2800 subjected to oxidations in air at180 ºC (-O180ºC) (a and b, respectively) and 350 ºC (-O350C) (c and d, respectively) and thermal treatments in inert atmosphere at 900 ºC (-TT).

It is well known that the carbon surface heat treated at high temperatures in N_2 is not stable and may re-adsorb oxygen even at room temperature [50]. Re-oxidation of the phosphoric acid activated carbons at room temperature after being heat treated at high temperature (>860 ºC) may also take place during air storage taking into account the high concentration of free sites, highly reactive and susceptible to be re-oxidized. In fact, after the TPD analysis the ACP2800 carbon showed a self-heating effect upon contact with air after cooling down to room temperature, also observed by others authors [11]. Figure S2 displays a thermogravimetric and differential thermal analysis

446 (TG-DTA) of ACP2800 subjected firstly to a thermal treatment in N_2 up to 900 ºC and
447 later, once the sample is cooling down to room temperature under N_2 flow, to an air-
448 oxidation step at 25 ºC for 120 min. During the thermal treatment, the TGA curve
449 exhibits two distinct weight loss steps and the DTA curve shows two endothermic
450 peaks. The first weight loss step in the temperature range of 25-100 ºC, which was
451 accompanied by an endothermic peak in the DTA curve, is due to the loss of residual
452 water in the carbon. The second weight loss step in the temperature range of 700-800
453 ºC, which was accompanied by an endothermic peak around 800 ºC in the DTA curve,
454 corresponds to the decomposition of C–O–P type bonds in agreement with the TPD
455 results (Figure 2a). The introduction of air at 25ºC, in the last step of the experiment,
456 leads to a sharp exothermic peak in the DTA curve (+6 ºC) and a weight increment of
457 3.0 % in the TGA curve. Thus, it is suggested that new C'-O-PO_3 groups could be
458 generated on heat-treated samples in inert atmosphere after exposure to air and storage
459 at room temperature. For this reason, ACP2800 subjected to a thermal treatment in
460 nitrogen at 900 ºC was exposed to air flow at 20 ºC for 2h. This sample was denoted as
461 ACP2800-TT-O20. Figure 5 shows the CO and CO_2 TPD profiles for ACP2800-TT-
462 O20. As a baseline, the TPD for ACP2800-TT without exposure to air flow is also
463 presented. The TPD results for ACP2800-TT-O20 evidence mainly desorption of CO at
464 high temperatures in the same temperature range as that observed for the original
465 activated carbon and for the oxidized sample at temperatures lower than 300 ºC,
466 confirming the oxidation of the C'-P type groups to C'–O–P ones (their (re)generation),
467 even by oxidation at room temperature. The weight gain observed in the initial step of
468 the oxidation profile of ACP2800-TT (Figure S2, TG-DTA curve) correlates quite well
469 with the total amount of oxygen gained by ACP2800-TT-O20, 3.1 wt. %, calculated
470 from the total CO and CO_2 evolved during the TPD (Figure 5).

3.3. Characterization of the treated activated carbons

P_{2p} spectra of ACP2800 and the corresponding treated samples are presented in Figure S3. As a general observation, it can be stated that there are not big differences among the P_{2p} spectra for the different samples, despite the fact that ACP2800 has been treated in very drastic different ways (air oxidation at 350 ºC for 2 hours and thermal treatment in inert atmosphere at 900 ºC). After oxidation of ACP2800 at 350 ºC for 2 h (ACP2800-O350) the P_{2p} peak shows a slight displacement to higher binding energies, which can be associated to the presence of few more polyphosphates groups, of C-O-PO_3, $(CO)_2PO_2$ and $(CO)_3PO$ types, on the surface of the carbon. On the other hand, the thermally treated samples in inert atmosphere (-TT) should present a shift of the binding energy of the maximum of the P_{2p} peak to lower binding energies compared to that for ACP2800 (and for that of ACP2800-TT-O350), showing a reduction of the most oxygenated P groups (C–O–P type) to C-PO_3 ,C_2PO_2 and/or C_3PO type. However, the peaks are positioned at the same binding energies as that of the fresh activated carbon, confirming that re-oxidation of the C-PO_3 type groups takes place once the samples are exposed to ambient air, before XPS analysis.

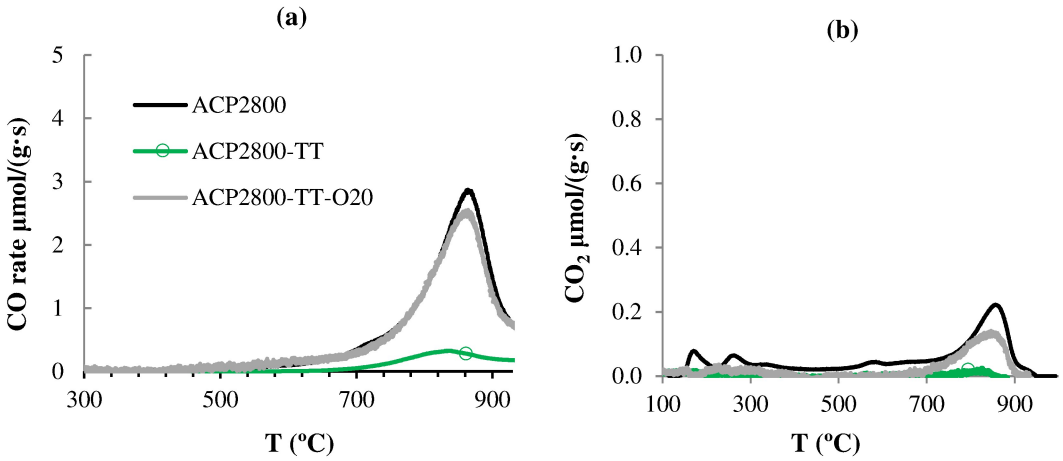


Figure 5. Amount of CO (a) and CO_2 (b) evolved as a function of temperature during the TPD of ACP2800 and ACP2800-TT without exposure to air and that of ACP2800 submitted to a thermal treatment at 900º C, followed by oxidation in air at 20 ºC for 1 h (ACP2800-TT-O20).

These results would explain the unexpectedly and large amount of oxygen left in all phosphoric acid activated carbons prepared or heated at high temperatures in inert atmosphere reported in the literature [8, 11, 12, 14]. In those cases, the oxygen content measurement was carried out by elemental analysis, FTIR, XPS, etc., in which the samples had been exposed to ambient air before the analysis. These results also support that the more thermally stable groups seem to be C-PO_3 ones, which are very reactive and can be re-oxidized to C-O-PO_3 type groups, even at room temperature, upon contact with air. Therefore, the surface chemistry of these thermally treated carbons could change during different storage conditions.

Table 3 presents the total amounts of CO and CO_2 released from the carbon samples during the TPD experiments, obtained by integration the areas under the TPD peaks, and the C, O, and P surface concentrations measured by XPS for the treated samples with their uncertainties (see Figure S3). The results obtained for ACP2800 and the derived carbons reveal very similar surface P content that is even slightly higher after the different treatments, confirming the high stability of these surface P complexes generated after the chemical activation of olive stone with H_3PO_4 at 800 ºC. It has to be mentioned that the N_2 adsorption-desorption and the CO_2 adsorption results (Table S1) do not show relevant differences in the porous texture of the treated samples when they are compared to those of the fresh activated carbon, indicating that the slight partial gasification of the ACP2800 carbon during the different oxidation/reduction treatment did not modify the porous texture and specific surface area of this carbon.

513 **Table 3.** Amount of CO and CO_2 evolved from the original and treated activated carbons and
514 the surface chemistry characterization (XPS): total and surface oxygen concentrations. The
515 uncertainties are discussed in the text and are provided in parentheses.

	TPD				XPS (%wt)			
Sample	**CO** (μmol/g)	**CO_2** (μmol/g)	**O(TPD)[a] % wt**	**O-P(TPD)[b] % wt**	**C_{1s}**	**P_{2p}**	**O_{1s}(XPS)[c]**	**O-P(XPS)[d]**
AG800	305 (6)	652 (5)	2.6 (0.2)	n.a.	96.8 (0.8)	0.0 (0.1)	3.2 (0.2)	n.a.
ACG800-O350	3179 (8)	1455 (8)	9.7 (0.6)	n.a	89.7 (0.7)	0.0 (0.1)	9.9 (0.4)	n.a
ACG800-TT	164 (3)	22 (1)	0.3[e] (0.1)	n.a.	95.6 (0.8)	0.3 (0.1)	3.5 (0.3)	n.a.
ACP2800	2735 (7)	305 (3)	5.4 (0.4)	4.1 (0.4)	87.3 (0.6)	3.5 (0.2)	9.2 (0.3)	5.0 (0.3)
ACP2800-O350	5139 (9)	1321 (7)	12.5 (0.7)	5.6 (0.7)	82.8 (0.6)	3.8 (0.3)	12.8 (0.4)	5.8 (0.3)
ACP2800-TT	507 (6)	112 (2)	1.2[e] (0.2)	1.1[e] (0.2)	89.6 (0.6)	3.6 (0.2)	6.5 (0.3)	4.6 (0.2)
ACP2800-TT-O20	2450 (7)	111 (3)	4.3 (0.2)	3.1 (0.2)	89.4 (0.7)	3.7 (0.3)	6.6 (0.3)	4.7 (0.2)
ACP2800-TT-O350	5107 (8)	1182 (8)	12.0 (0.7)	5.8 (0.7)	85.3 (0.6)	4.0 (0.3)	10.4 (0.4)	6.0 (0.3)

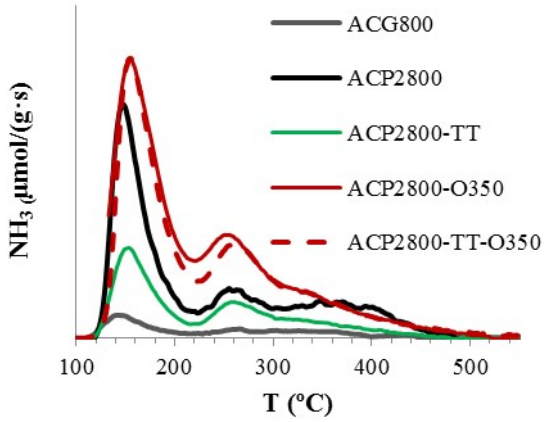
516 [a] Total oxygen from the total amounts of CO and CO_2 evolved
517 [b] Total oxygen bonded to P (as C-O-P) from the amounts of CO and CO_2 evolved at 860 ºC.
518 [c] Surface oxygen content from XPS measurements. The samples were exposed to ambient air.
519 [d] Surface oxygen bonded to P from XPS = $P\cdot(4\cdot COPO_3+3\cdot CPO_3+C_3PO)$
520 [e] not exposed to ambient air
521 n.a.: not applicable

522 From the amount of CO and CO_2 evolved during the TPD experiments, the total
523 oxygen content, O(TPD), was calculated and compared to the surface oxygen content
524 obtained from XPS analysis, O(XPS) (Table 3). Papier *et al.* [51] indicated that the 80-
525 90 % peak area of the O1s peak represents the contribution of surface atoms, or atoms
526 of the 3.5-4 nm thick outer shell of the particle. However, TPD results reveal also
527 oxygen-containing groups located on the surface of meso- or/and micropores, deeper in
528 the carbon particle. The amount of oxygen bonded to P on the activated carbon prepared
529 by chemical activation and the corresponding derived carbons has also been calculated
530 taking into account both characterization techniques: i) from deconvolution of the TPD
531 profile, quantifying the peak evolved at 860 ºC (O-P(TPD)) and ii) from the amount of
532 the different surface P species obtained from deconvolution of the P2p spectra (O-
533 P(XPS)). From the TPD results, the total amount of oxygen (from total CO and CO_2
534 evolved) and that bonded to a P group (C-O-P) can be quantified, since the P type
535 groups seem to decompose to CO (and CO_2) at 860 ºC, as it was previously indicated. It

536 is remarkable to note the low uncertainties obtained which represent the 95 %
537 confidence interval calculated from three replicate measurements, evidencing the
538 reproducibility of the TPD and XPS measurements.
539 The observed general trend for oxygen surface content on ACG800 and ACP2800
540 and their corresponding derived carbons was predictable, being lower after the thermal
541 treatment and higher after the oxidation process. However, certain differences can be
542 appreciated between these two carbons. Similar values of O(XPS) and O(TPD) for the
543 fresh ACG800 activated carbon can be observed, indicating a homogeneous distribution
544 of oxygen surface groups on the whole particle surface. On the other hand, the high
545 value of O(XPS) compared to that obtained from TPD, O(TPD), for ACP2800 could
546 indicate that a higher proportion of oxygen groups could be concentrated on the external
547 surface of the carbon particles. However, it has to be pointed out that (and contrary to
548 ACG800 sample) not all the oxygen surface content of this sample is being taking into
549 account during the first TPD experiment, as was shown in Figures 3a. In this sense, the
550 O(TPD) value observed for ACP2800 after the thermal treatment (ACP2800-TT) of 1.2
551 ± 0.2 wt.% represents about 22 % of that for the fresh carbon (O(TPD) = 5.4 ± 0.4
552 wt.%) and this surface oxygen seems to be attached to surface P, given that the value of
553 1.1 wt. % of O-P(TPD) for this sample represent about 90 % of the O(TPD) value.
554 Furthermore, the high values of O-P(XPS) and O-P(TPD) observed for ACP2800 and
555 its derived carbons prepared by oxidation at temperatures lower than 300 ºC, very
556 similar to their respective total XPS and TPD oxygen amount, indicate that most of the
557 oxygen present in the carbon particles seems to be bonded to surface P. Once ACP2800
558 is oxidized at higher temperature (350 ºC) the total amount is much higher than that
559 referred to O-P because, apart from oxidation of C-P to C-O-P bonds, oxidation of the

560 carbon surface takes place, generating oxygen surface groups of lower thermal stability
561 that decompose as CO at lower temperatures in the DTP.
562 The NH_3-TPD profiles for ACG800, ACP2800, ACP2800-TT, ACP2800-O350 and
563 ACP2800-TT-O350 samples after adsorption and desorption of NH_3 at 100 ºC are
564 compared in Figure 6. ACG800 sample presents an almost negligible desorption of
565 NH_3. On the other hand, the NH_3 desorption profile of ACP2800 shows two maxima, at
566 around 150 and 250 ºC. The first one is known to arise from desorption of weakly
567 adsorbed NH_3 molecules (probably by hydrogen-bonded), identified on zeolite supports
568 [52]. However, it can also be related to weak acidic groups of C-O-PO_3 type on these
569 carbon materials since ACP2800, which desorbs a higher amount of NH_3 at this
570 temperatures compared to that of ACP2800-TT, presented a higher amount of oxygen-
571 containing P groups of C-O-PO_3 type, as was showed in Figure 2a. ACP2800-TT was
572 not exposed to ambient air before the adsorption of NH_3. This sample desorbed a small
573 amount of CO (and CO_2) at high temperatures in the TPDs experiments (Figures 2a),
574 associated to decomposition of C-O-PO_3 groups, which suggest the presence of a
575 relatively high amount of surface groups of C_2PO_2 and/or C_3PO type, instead of C-
576 OPO_3 one, that may contribute to the low acidity of this sample. On the other hand, the
577 shoulder at 250 ºC and the large tail at higher temperatures may originate from NH_3
578 adsorbed on strong Brönsted acid sites [33]. The acidity of this type is related mainly to
579 the high amount of P retained on the carbon surface and probably associated to OH in
580 the phosphates groups. The total surface acidity for ACP2800 increases after air
581 oxidation at 350 ºC, given that a high amount of oxygen-containing P groups of C-O-
582 PO_3 type are formed, as was deduced from results reported in Figures 3a and b and in
583 Table 3. Finally, the similar NH_3-TPD profiles obtained for ACP2800-O350 and
584 ACP2800-TT-O350 samples also confirm the (re-)oxidation of the P surface groups (C-

585 P to C-O-P types) after the thermal treatment in inert atmosphere and the acid character
586 of these oxygen-containing P groups.



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588 **Figure 6.** NH_3-TPD profiles of the activated carbons ACG800, ACP2800, ACP2800-TT,
589 ACP2800-O350 and ACP2800-TT-O350 after NH_3 adsorption/desorption at 100 ºC.

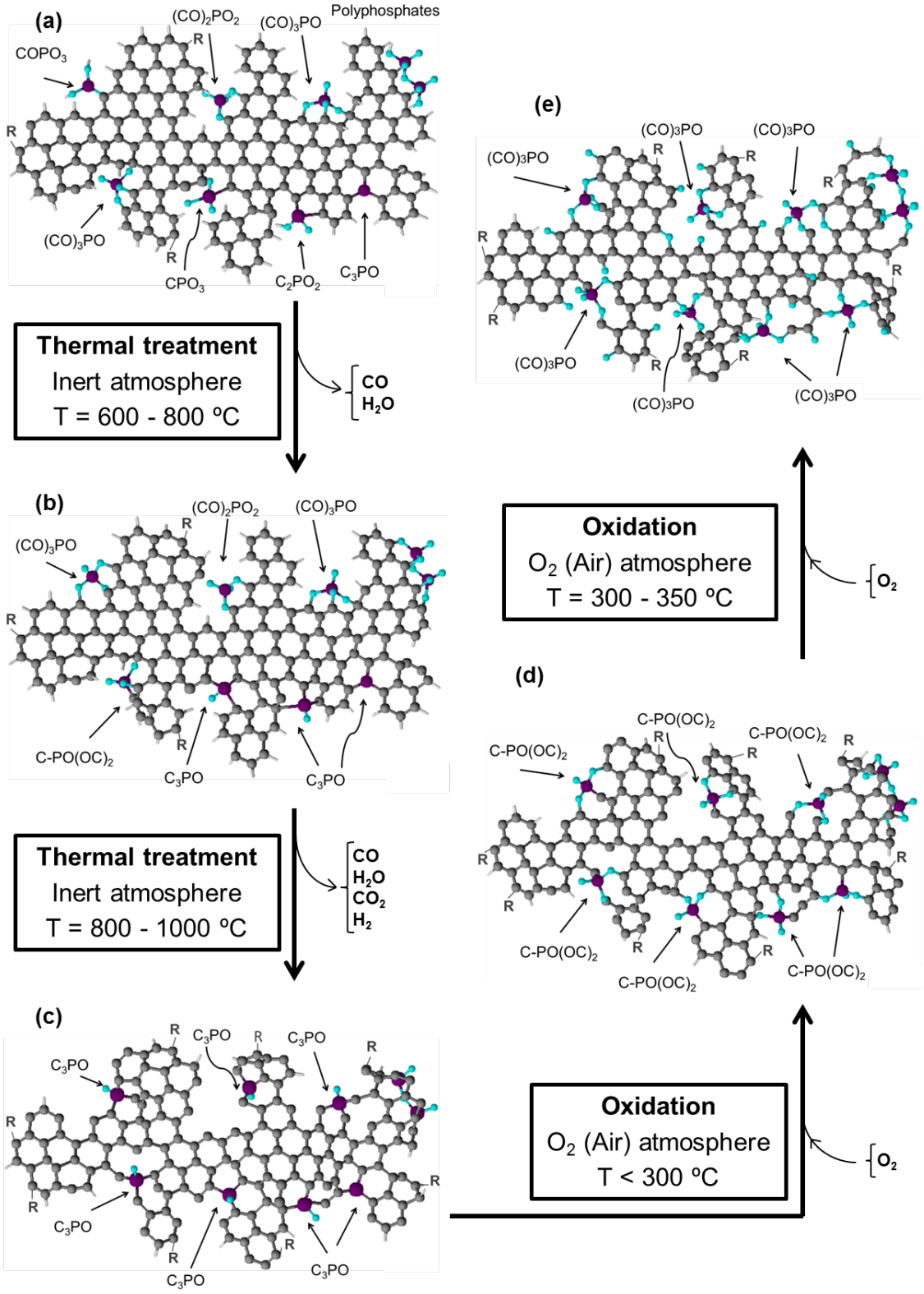
590

591 Scheme 1 represents some of the possible P surface groups formed during
592 phosphoric acid activated carbons surface reduction and oxidation reactions. Activated
593 carbons prepared by chemical activation of lignocellulosic materials with phosphoric
594 acid at temperatures below 600 ºC have been reported to present mainly oxygen-
595 containing P surface groups of type C-O-PO_3 (Scheme 1a) [7, 8, 19, 33]. Dehydration of
596 P-OH groups of these surface P complexes (from 600 to 750º C) and aromatic
597 condensation of the carbon substrate at higher temperatures seem to be responsible of
598 the formation of H_2O and H_2, respectively, in the gas phase and new C-P bonds on the
599 carbon surface. The C-O-P bonds are thermally very stable and decompose only at
600 temperatures higher than 700 ºC, producing CO (and CO_2) in the gas phase and C'-P
601 bonds (that may include C'PO_3, C'$_2PO_2$ (Scheme 1b) and C'$_3$PO (Scheme 1c) surface
602 groups, depending on the activation/oxidation treatment and temperature). The C_3PO
603 groups seem to be very stable even at 1000 ºC, given that the P content on the surface of
604 these carbons remains constant or slightly increases after the thermal treatment at this

605 temperature (see Table 3). Oxidation of the carbon surface after being treated in N_2 at
606 1000º C (i.e., with all the P-surface group being converted in C_3PO) with molecular
607 oxygen at temperatures lower than 300 ºC seems to take place only through the C–P
608 bond producing C–O–P ones; i.e., regenerating C-O-P type surface groups that may
609 include C_2PO-O-C, C-$PO(OC)_2$ (Scheme 1d) and $(CO)_3PO$ (Scheme 1e)), depending on
610 the intensity of the oxidation treatment (oxidation time and/or temperature). Only after
611 oxidation at temperatures higher than 300 ºC, these C–O–P bonds become saturated (all
612 of them of $(CO)_3PO$ type groups) and oxidation of the carbonaceous substrate seems to
613 be possible, with production of oxygen surface groups that although are less stable than
614 those of P type, still present a relatively high thermal stability, decomposing at
615 moderated temperatures (between 500 and 800 ºC; see Fig. 2a). Formation of
616 polyphosphate type groups cannot be disregarded on the surface of these carbons.
617 The surface of these activated carbons with oxygen-containing P groups should be a
618 strong acceptor of spill-over oxygen [53, 54]. The formation of these oxygen surface
619 groups on the carbonaceous substrate that decompose at lower temperatures might be
620 explained by a spill-over mechanism, involving adsorbed oxygen on the P surface
621 groups and migration of activated oxygen species from these P surface complexes to the
622 carbonaceous substrate [54], increasing the rate of formation of these oxygen surface
623 groups of lower stability with oxidation temperature (>300 ºC).
624 These results may explain the effect of P surface groups on the enhancement of
625 carbon oxidation resistance observed for many carbon-containing P materials (fibers,
626 composites, etc) [9, 14, 17, 41, 45-47]. ACP2800 carbon, despite having similar BET
627 surface area and higher mesopore volume than ACG800, is resistant to air oxidation up
628 to 550 ºC, whereas ACG800 carbon starts to lose weight at about 350 ºC (see the
629 thermogravimetric analysis profiles in air for these two activated carbons in Figure S4).

630 Thus, the presence of O bonded to both a carbon site and a P group seems to be the
631 critical factor for maintaining the carbon oxidation inhibition effect (by site blockage)
632 [14], given that although the C-P bond is very reactive to oxygen, even at room
633 temperature, the C-O-P group is thermally very stable and appears to be the preferential
634 (and the only) surface product upon oxidation of carbons with P surface groups, at least
635 until saturation of these P-surface group with oxygen. The loss of such oxygen (or its
636 connecting bond) seems to be very difficult at typical O_2 gasification/combustion
637 temperatures (300-700 ºC), given that the C-O-P group does not decompose at
638 temperatures lower than 700 ºC (and the high thermal stability of the C-P bond). A
639 possible oxygen spill-over mechanism, given rise to other C-oxygen groups of lower
640 stability on the surface of the carbonaceous substrate, once the oxidation of the P groups
641 is completed, may play an important role in reducing the oxidation inhibition at higher
642 temperatures. Polyphosphates surface groups (also possible on the surface of these
643 carbons) may function as both physical barrier and site blockers.

644 On the other hand, the fact that the C'-P bond generated at high temperature
645 treatment is easily oxidized to C'-O-P ones, even at 20 ºC, would explain the high
646 oxygen content observed for activated carbons prepared by chemical activation of
647 lignocellulosic materials with H_3PO_4 at high temperatures (>700 ºC). Moreover, the low
648 enough uncertainties obtained suggest that these results would also be applied to those
649 carbons prepared by the same experimental procedure at lower activation temperatures
650 and/or to those post-heat treated at high temperature in inert atmosphere and exposed to
651 ambient air [8, 11, 12, 14, 19, 46].



652

653 **Scheme 1**. Possible P surface groups formed during phosphoric acid activated carbons surface
654 oxidation and reduction reactions. (Greys: C, purple: P, blue: O, silver: H; R represents other
655 similar carbonaceous matrix structures).

5. Conclusions

Chemical activation of olive stone with phosphoric acid produces activated carbons with high BET surface areas, compared to those of olive stone chars carbonized at similar temperatures that are usually below 200 m^2/g, and a relatively high content of P surface groups that remain very stable on the carbon surface at high temperatures. TPD and XPS results point out that these P surface groups preferentially reacts with oxygen, prior to carbon gasification, through the oxidation of C–P bond, forming C–O–P ones, which are thermally stable at temperatures lower than 700 ºC. Thermal treatments at higher temperature (about 860 ºC) decompose the C-O-P type surface groups to less oxygenated P groups on the carbon surface (of C-P type) generating CO (and CO_2) in the gas phase. These C-P groups seem to be very reactive and are (re)oxidized upon contact with air, even at room temperature, forming again C-O-P type groups. Thus, the presence of these oxygen-containing P surface groups with an interesting redox functionality of high chemical and thermal stability seems to be responsible of the high oxygen content (once exposed to ambient air) and high oxidation resistance of this kind of porous carbons.

Acknowledgments

We gratefully thank Spanish Ministry of Economy and Competitiveness (MINECO) and FEDER (Projects CTQ2015-68654-R) for financial support. M.J.V.R. gratefully thanks MINECO for a FPI fellowship (BES-2010-032213).

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