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Chemical and electrochemical characterization of porous carbon materials

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Abstract

Chemical and electrochemical techniques have been used in order to asses surface functionalities of porous carbon materials. An anthracite has been chemically activated using both KOH and NaOH as activating agents. As a result, activated carbons with high micropore volume (higher than 1 cm^3/g) have been obtained. These samples were oxidized with HNO_3 and thermally treated in N_2 flow at different temperatures in order to obtain porous carbon materials with different amounts of surface oxygen complexes. Thermal treatment in H_2 was also carried out. The sample treated with H_2 was subsequently treated in air flow at 450 °C. Thus, materials with very similar porous texture and widely different surface chemistry have been compared. The surface chemistry of the resulting materials was systematically characterized by TPD experiments and XPS measurements. Galvanostatic and voltammetric techniques were used to deepen into the characterization of the surface oxygen complexes. The combination of both, chemical and electrochemical methods provide unique information, regarding the key role of surface chemistry in improving carbon wettability in aqueous solution and the redox processes undergone by the surface oxygen groups. Both contributions are of relevance to understand the use of porous carbons as electrochemical capacitors.

Keywords: Activated carbon; Chemical treatment; Temperature programmed desorption; Electrochemical properties; Surface oxygen complexes

1. Introduction

Many applications of carbon materials are strongly influenced by their surface chemistry. Thus, their use in catalysis (either as catalyst or support), adsorption in solution or electrochemical processes are three examples in which the surface chemistry can have an important relevance in the materials performance [1–5]. Specially, any discussion on the electrochemical behaviour of carbon, such as its performance as double layer capacitor, which is being very much studied nowadays, should take into account the carbon electrode/electrolyte interface, where functional groups play an important role, mainly in aqueous medium [1,3–16].

The presence of surface heteroatoms, especially oxygen groups, affects the electrochemical response of the carbon materials in two different ways. On one hand oxygen groups may determine the wettability by the electrolyte solution. It is known that the micropores of carbon cannot be fully wetted in aqueous solutions because of their hydrophobic behaviour [5]. The increase in oxygen content modifies the electrostatic field in the surface, imparting certain polarity, which makes easier the interaction with water molecules [1]. On the other hand, the surface oxygen groups may experience redox reactions [4,5] that can have a significant contribution to different processes.

An interesting example of the relevance of surface oxygen groups in electrochemical processes is the capacitance

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of porous carbons, used as a component of supercapacitors. As it was shown in previous studies [5,6], the faradic current is significantly increased with the content in surface oxygen groups, while the increase in the double layer is not so important. This remarks that the enhancement in capacitance is mainly based on pseudocapacitance or redox mechanisms. Recent results showed that the promotion of capacitance with the amount of oxygen surface complexes also takes place in non-aqueous electrolyte, where wettability is not a limiting factor [7]. This idea had already been exposed by some authors [7,9–12]. Further studies in our laboratory allowed us to conclude that CO-type desorbing groups are responsible for the enhancement in capacitance [8]. The CO-type surface complexes are mainly hydroxyl, carbonyl or quinone groups which can undergo the well-known mechanism for the quinone/hydroquinone redox pair:

$$\gtrless C_xO + H^+ + e \iff \gtrless C_xOH$$

The role of CO_2-desorbing groups is still unclear and it has been rarely reported [5]. Electron delocalization, which favours electrical conductivity is enhanced by the loss of strong electron-withdrawing groups, such as CO_2-type groups [4]. In that sense, the removal of CO_2-type groups should improve capacitance. This observation was previously reported [9]: the capacitance values reached a maximum after removal of the CO_2 groups at 450 °C. Thus, it was concluded that CO_2 complexes play a negative role in electrical energy storage. However this fact should be further analysed in detail.

The above comments show that to understand the electrochemical behaviour of materials, a deep characterization of the surface chemistry is necessary, which can be carried out by spectroscopic, chemical and electrochemical techniques. The characterization of surface oxygen groups is very often done by chemical or spectroscopic methods such as TPD, XPS, acid–base titration, FTIR, ... Although the measurements are, in many cases, easy, their interpretation is not simple due to the convolution of the contribution from the different functional groups. Moreover, in spite of the fact that electrochemical methods, like cyclic voltammetry, have a high surface sensitivity and the redox reactions from surface oxygen groups can be detected, it is difficult to assign the features observed to specific types of oxygen groups due to the overlapping of the different reactions and to the difficulties in the electrochemical measurements since materials with sufficient electrical conductivity should be used.

An integration of both chemical/spectroscopic methods and electrochemical techniques to deepen into the characterization of the surface chemistry could provide unique information. Unfortunately, this is not usually encountered in the literature, although there are exceptions such as Ref. [5].

Consequently, the objective of this work is to characterize activated carbons with very similar porous texture and widely different surface chemistry by chemical and electrochemical techniques, trying to deepen into the role of surface oxygen complexes in electrochemical properties such as the capacitance of porous carbons.

2. Experimental

2.1. Activation process

Chemical activation was done using KOH and NaOH as activating agents. An anthracite was the precursor used. Details of the preparation process are available elsewhere [17,18]. The preparation conditions for each sample are included in Table 1.

2.2. Chemical oxidation with HNO_3

The oxidation was carried out by mixing 1.5 g of activated carbon (AK and ANa) with 20 ml of concentrated nitric acid during 3 h at room temperature. After this treatment, the samples were washed several times with hot distilled water until the pH of the filtrate was the same as the washing water. Then, the samples were dried at 100 °C. The nomenclature includes an "N" to indicate this treatment in nitric acid (i.e., samples AKN and ANaN).

2.3. Thermal treatments in N_2

Carbons containing different amounts of surface oxygen complexes were obtained by subjecting the oxidized samples to thermal treatments at different temperatures (i.e., from 250 to 900 °C). These treatments were carried out in N_2 (200 ml/min) and using a heating rate of 3 °C/min. After reaching the heat-treatment temperature, it was kept for 1 h. Temperatures used are shown in Table 2. The nomenclature includes the treatment temperature (i.e., sample AKN-450 means sample AK treated in HNO_3 and heat-treated in N_2 up to 450 °C).

2.4. Thermal treatment in H_2

One sample (CA) was thermally treated in H_2 flow in order to remove most of the oxygen complexes. Before thermal treatment, the sample was purified (i.e., removal of inorganic impurities) by successive treatments with aqueous solutions (10 wt.%) of HCl, HNO_3 and HF, respectively, at room temperature for 48 h without stirring. After HCl and HNO_3 treatments, the sample was repeatedly washed with deionized water up to a final pH = 4.

Table 1
Preparation conditions in chemical activation

Sample	Activating agent	Activating agent/carbon ratio	Activation temperature (°C)	Activation time (h)	N_2 flow rate (ml/min)
AK	KOH	3:1	750	1	800
ANa	NaOH	3:1	750	1	800
CA	KOH	3:1	750	2	800

Table 2
Thermal treatment temperature, porous texture, quantification of oxygen surface groups in activated carbons obtained from TPD experiments and capacitance values, in all the samples studied

Sample	T (thermal treatment) (°C)	$V_{DR}(N_2)$ (cm^3/g)	Average pore size DR (N_2) (nm)	$V_{DR}(CO_2)$ (cm^3/g)	μmol CO/g	% CO	μmol CO_2/g	% CO_2	C (F/g)
AK	–	1.10	1.54	0.73	2267	80	573	20	238
AKN	–	1.05	1.72	0.68	3550	63	2059	37	254
AKN-450	450 (N_2)	1.11	1.70	0.66	3333	85	573	15	232
AKN-750	750 (N_2)	1.09	1.85	0.68	327	76	104	24	189
AKN-900	900 (N_2)	0.98	1.67	0.61	138	55	114	45	167
ANa	–	1.06	1.69	0.70	1733	76	560	24	193
ANaN	–	1.10	1.61	0.71	2380	58	1730	42	238
ANaN-250	250 (N_2)	1.09	1.64	0.69	2191	63	1312	37	242
ANaN-450	450 (N_2)	1.09	1.64	0.68	2128	77	652	23	202
ANaN-750	750 (N_2)	1.00	1.59	0.61	324	69	148	31	171
ANaN-900	900 (N_2)	0.93	1.58	0.57	68	22	240	78	148
CA	–	1.39	1.76	0.72	2817	73	1035	27	250
CAH	850 (H_2)	1.33	1.71	0.63	133	46	156	54	0.03
$CAHO_x$	450 (air)	1.22	1.75	0.56	3708	81	889	19	191

After the HF treatment, it was washed with deionized water up to the final pH of the washing water and dried at 120 °C. Then, the sample was thermally treated under a hydrogen flow of 5 ml/min g at 850 °C for 3 h. This sample is named as CAH. This procedure has been published in the literature [19].

2.5. Thermal treatment in air

The sample CAH, previously treated in H_2, was subjected to a thermal treatment in air flow in order to recover part of the surface oxygen groups. The process was carried out in a quartz tube fixed-bed reactor. The sample was heated at 10 °C/min up to 450 °C. Then, the temperature was kept for 12 h. This sample is named as $CAHO_x$.

2.6. Porous texture characterization

Porous texture of all samples was determined by physical adsorption (N_2 at 77 K and CO_2 at 273 K) using an automatic adsorption system (Autosorb-6, Quantrachrome) after samples out-gassing at 523 K under vacuum for 4 h. The total micropore volume (pore size below 2 nm) and the average pore size were calculated from the application of the Dubinin–Radushkevich equation to the N_2 adsorption at 77 K (range of relative pressures used for the DR analysis was: $0.005 < P/P_0 < 0.17$). The narrow micropore volume (pore size smaller than around 0.7 nm) has been assessed from CO_2 adsorption at 273 K using the DR equation and for relative pressures below 0.025 [20–24]. The densities of the adsorbed phases used for the calculations, were 0.808 and 1.023 g/ml for N_2 and CO_2, respectively.

2.7. Surface chemistry characterization

Temperature programmed desorption (TPD) experiments were done in a DSC–TGA equipment (TA Instruments, SDT 2960 Simultaneous) coupled to a mass spectrometer (Thermostar, Balzers, GSD 300 T3), to characterize the surface chemistry of all samples. In these experiments, 10 mg of the sample were heated up to 950 °C (heating rate 20 °C/min) under a helium flow rate of 100 ml/min.

XPS on the samples were obtained by using a VG-Microtech Multilab electron spectrometer. The source employed was the MgKα (1253.6 eV) radiation of twin anode in the constant analyser energy mode. Pressure of the analysis chamber was maintained below 10^{-9} Torr. The binding energy scale was regulated by setting the C 1s transition. Peak areas were estimated by calculating the integral of each peak after subtraction of the background and fitting the experimental peak by a Gaussian curve. The binding energy values have been identified as C–C at about 284.6 eV, C–O at about 286.1 eV, C=O at about 287.3 eV and O–C=O at about 288.5 eV [25–33].

2.8. Electrochemical characterization

For the electrochemical characterization, composite electrodes were prepared from powder porous carbon material, acetylene black (Strem Chemicals) and binder (PVDC copolymer, aqueous dispersion (55% solids), Sutcliffe Speakman), in a ratio 77:10:13 wt.%, respectively. The materials were mixed and pressed up to 100 bars for 10 min. The total electrode weight used for the measurements was about 70–90 mg. After that, the composite electrode was placed in a stainless steel mesh as a current collector. In order to measure the electric double capacitance of a single porous carbon electrode, the standard three electrode cell configuration was employed. Reversible hydrogen electrode (RHE) was used as reference and a platinum wire was employed as a counterelectrode. 1 M H_2SO_4 was used as aqueous electrolyte. The galvanostatic method (at 2 mA), in a range of potentials between 0 and 1 V, has been used to measure the capacitance. The capacitance values have been calculated from the interval between 0.2 and 0.6 V, dividing the imposed current by

the slope of the lineal chronopotentiograms plot, taking the average value between charge and discharge processes. The result is then divided by the weight of porous carbon that is about 77% of the total composite.

Cyclic voltammograms have been obtained in 1 M H_2SO_4 solution in order to assess the redox behaviour of the samples, since deviations from rectangular shape resulting in reversible peaks indicate pseudocapacitance. The electrode and the electrochemical system employed were the same as those referred before. The scan rate was 0.5 mV/s.

All electrochemical measurements were carried out with an EG&G Potentionstat/Galvanostat model 273 controlled by software ECHEM M270. All the solutions were prepared with ultrapure water (Purelab ELGA).

3. Results and discussion

3.1. Porous texture characterization

The activated carbons prepared present type I isotherms, what is characteristic of microporous solids.

Table 2 contains the micropore volumes calculated from N_2 adsorption data at 77 K [$V_{DR}(N_2)$] and CO_2 adsorption data at 273 K [$V_{DR}(CO_2)$] for each sample. The comparison between the total micropore volume, $V_{DR}(N_2)$, and the narrow micropore volume, $V_{DR}(CO_2)$, gives information of the micropore size distribution [20–24]. Micropores smaller than 0.7 nm in size are measured by $V_{DR}(CO_2)$, and those smaller than 2 nm and bigger than 0.7 nm can be calculated by the difference between $V_{DR}(N_2)$ and $V_{DR}(CO_2)$. The data show that narrow micropores are 65% of the total microporosity, approximately.

Taking into account series AKN to AKN-900 and ANaN to ANaN-900, it can be seen that little changes in porosity occur when samples AK and ANa are oxidized and thermally treated at different temperatures. Nitric acid could either increase the porosity or block some micropores. According to our results, the first effect is the main one in the sample activated with NaOH, whereas the second occurs in the sample activated with KOH. The samples that have undergone the thermal treatment at higher temperatures present a slight decrease in micropore volume. This fact could be caused by certain structural rearrangement in the material [34,35]. This effect is also observed in the micropore volume reduction of sample CAH, which was strongly purified and has undergone a thermal treatment until 850 °C in H_2.

We can see that these changes in porosity caused by oxidation and thermal treatments are very slight and hence, they will not affect the electrochemical behaviour in an important way.

3.2. Surface chemistry characterization by TPD and XPS

Surface oxygen groups on carbon materials decompose upon heating producing CO and CO_2 at different temperatures. It is known that CO_2 evolves at low temperatures as a consequence of the decomposition of the acidic groups such as carboxylic groups, anhydrides or lactones [24,36–38]. The evolution of CO occurs at higher temperatures and is originated by decomposition of basic or neutral groups such as phenols, ethers and carbonyls [24,36–38].

Series AKN to AKN-900 and ANaN to ANaN-900 were characterized by TPD experiments. Figs. 1–4 show the TPD profiles corresponding to all samples.

Table 2 contains the quantification of the amount of CO and CO_2 desorbed in these experiments.

It can be observed that samples with different amounts of surface oxides have been prepared (from 68 to 3550 μmol/g of CO and from 104 to 2059 μmol/g of CO_2).

TPD experiments contain different peaks in the CO and CO_2 profiles, what indicates the presence of different types of surface oxygen groups. In the CO spectra, several peaks can be distinguished that come from the decomposition of

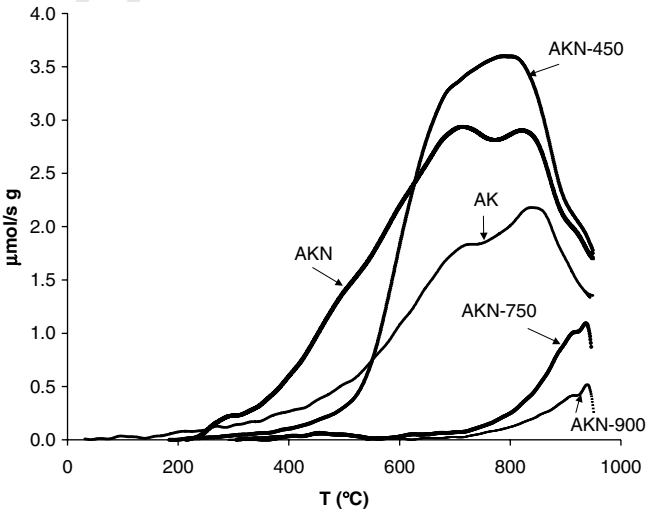

Fig. 1. TPD curves corresponding to CO desorption in AK samples.

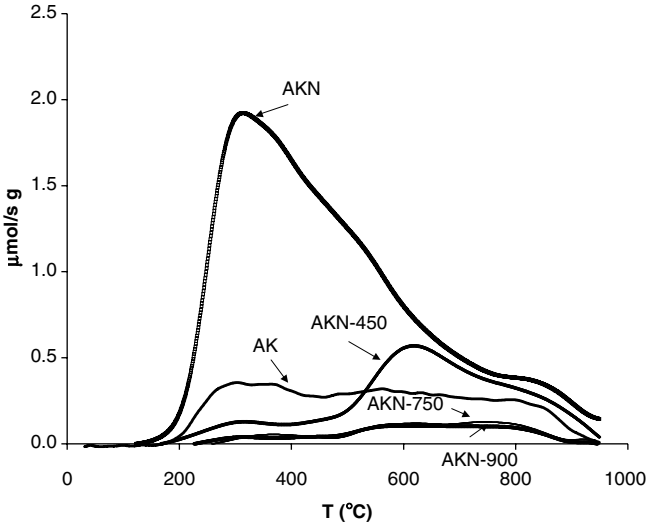

Fig. 2. TPD curves corresponding to CO_2 desorption in AK samples.

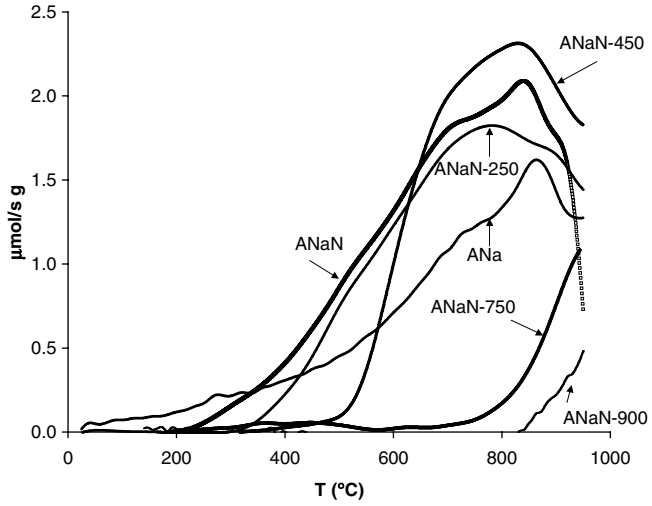

Fig. 3. TPD curves corresponding to CO desorption in ANa samples.

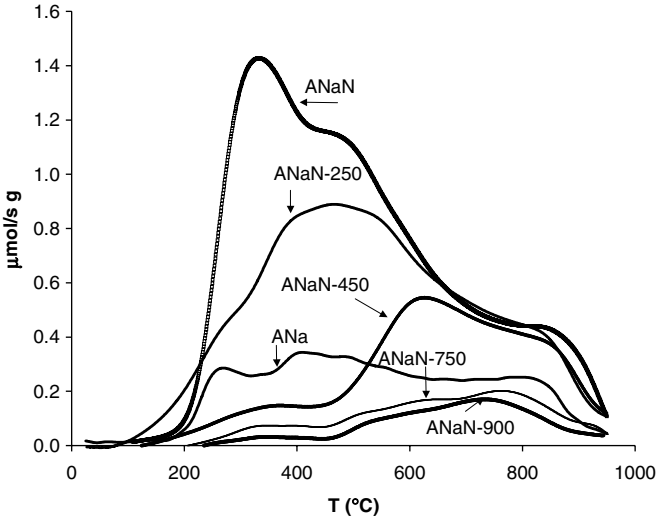

Fig. 4. TPD curves corresponding to CO_2 desorption in ANa sample.

carboxylic anhydrides (at about 500 °C) [24,37–40] and phenol, carbonyl, quinone and ether groups (at higher temperatures) [24,37–40]. In the CO_2 spectra, three peaks appear. The peak at 300 °C is usually associated to carboxyl groups, the one at 500 °C is related to carboxylic anhydrides and the desorption above this temperature could be caused by lactone groups decomposition or CO_2 coming from secondary reactions as these are substantially enhanced with porous carbon [5,37–39].

It is known that the thermal decomposition of each carboxylic anhydride produces one CO molecule and one CO_2 molecule at close temperatures [37–39]. In order to assess the amount of CO and CO_2 associated to different functional groups, the deconvolution of the CO and CO_2 spectra was made using a multi-Gaussian function. Table 3 contains the results for the anhydride peak from the CO and CO_2-profiles deconvolution, respectively, since this specific information will be later used.

As it can be observed, the CO_2 peak tends to appear just a little before than CO peak. The reason why we observed this difference is that the decomposition of carboxylic anhydrides is not a simultaneous process. A CO_2 molecule desorbs first and then the CO one. However, these desorptions are very close and it is usually considered that they take place simultaneously.

XPS was employed for the analysis of the surface oxygen groups in the samples AKN and ANaN, since these ones have the highest amounts of surface oxygen groups. The distribution of oxygen complexes of each sample has been calculated by deconvolution of the XPS spectra, fixing the binding energy in the values presented in the experimental section. The results are included in Table 4.

It can be observed that the percentage of O–C=O species measured from XPS is of the same order of magnitude (but smaller) to the percentage of CO_2-type groups obtained from the TPD experiments (Table 2). Unambiguous interpretation of XPS spectra is difficult: the external and the internal composition of a solid carbon sample may differ and, additionally, carbon external voids can artificially lower the measured concentration of surface species [4]. Taking into account that these two techniques are not quantitatively comparable, we can conclude that the results obtained by TPD and XPS are relatively consistent with each other.

Samples CA, CAH and $CAHO_x$ were also subjected to TPD experiments. The TPD profiles are shown in Figs. 5 and 6 and the quantifications are included in Table 2.

It is important to note the differences existing between the samples. The main difference between sample CA and

Table 4
Distribution of oxygen complexes from the XPS spectra

Sample	C–O (%)	C=O (%)	CO_2 (%)
AKN	22	47	30
ANaN	51	19	30

Table 3
CO and CO_2 contribution to the TPD from carboxylic anhydride decomposition

Sample	CO data from anhydrides			CO_2 data from anhydrides		
	µmol/g	Peak temperature (°C)	Width (°C)	µmol/g	Peak temperature (°C)	Width (°C)
AKN	810	505	198	843	487	161
ANaN	525	505	198	531	433	103
ANaN-250	513	545	176	507	499	200

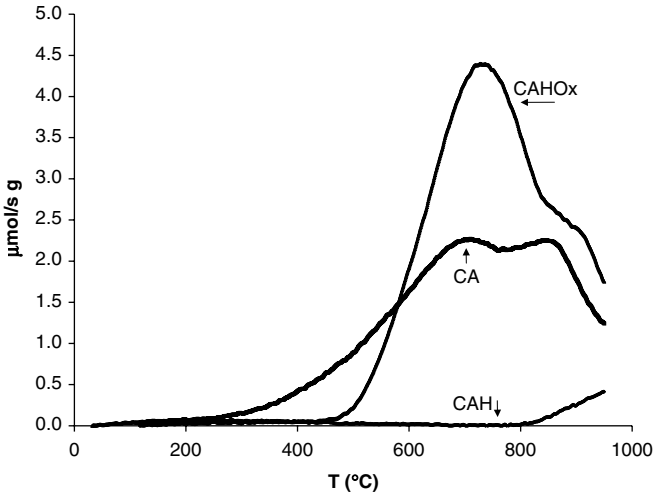

Fig. 5. TPD curves corresponding to CO desorption in CA samples.

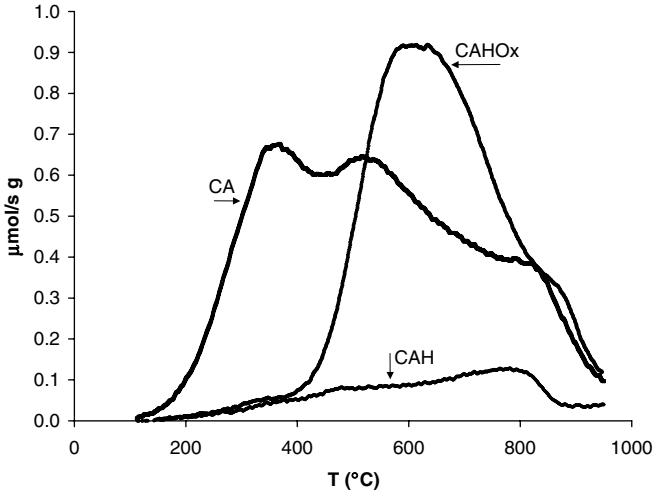

Fig. 6. TPD curves corresponding to CO_2 desorption in CA samples.

CAH is that the latter does not contain surface oxygen groups in a significant amount. In addition, sample CAH is different from AKN-900 and ANaN-900 from the point of view of thermal treatment although TPD profiles are similar: this happens because the treatment in H_2 has saturated carbon bonds, its reactivity towards oxygen is the lowest and it is the most hydrophobic. Then, this sample is very useful to test the role of surface chemistry in the wettability of the carbon material. Sample $CAHO_x$ has a high amount of CO and CO_2 desorbing groups because the treatment in air at 450 °C has generated an important number of surface oxygen groups. However, it is important to note that the peaks corresponding to carboxylic acids and anhydrides do not appear in the CO_2 spectrum, being the lactone peak, at temperatures above 500 °C, the only one remaining. The CO spectrum has also changed considerably since the peak at 500 °C (anhydrides) has almost completely disappeared as expected because the heat treatment temperature is very close to the temperature of anhydrides decomposition.

3.3. Electrochemical characterization: galvanostatic and voltammetric experiments

Table 2 contains the specific capacitance values for all the samples measured for a constant current intensity of 2 mA (this corresponds to a current of about 30 mA/g). Samples from AKN to AKN-900 and from ANaN to ANaN-900 show that, as previously reported [8], the higher the amount of surface oxygen groups, the higher the capacitance.

Figs. 7 and 8 show the cyclic voltmmograms for AKN to AKN-900 and ANaN to ANaN-900 samples.

An ideal double layer capacitance behaviour of an electrode material should consist of a rectangular shape of the cyclic voltammogram. The phenomenon, then, is purely electrostatic. On the other hand, materials with pseudocapacitance show redox peaks related to electron transfer reactions. Such redox processes can be observed in the voltammograms included in Figs. 7 and 8, especially for samples AKN, AKN-450 (Fig. 7) and ANaN and ANaN-450 (Fig. 8). If the voltammograms are observed carefully, several overlapping peaks from 0.5 to 0.65 V can be distinguished, being the main features an oxidation peak at 0.5 V and a second one at 0.63 V, approximately. The reduction peaks are less defined. The existence of this broad peak shows that different redox processes are involved. The peak at 0.63 V is more intense for the most oxidized samples (AKN, ANaN). In addition, it disappears almost completely after thermal treatment at 450 °C. Moreover, after thermal treatments at 750 °C or 900 °C, all the peaks seem to disappear, obtaining a quasi-rectangular shape in the voltammograms, indicating again that surface oxygen groups are contributing to capacitance by redox reactions.

In a previous work, an excellent correlation between CO-desorbing groups and capacitance (both referred to the porosity of the material) was observed [8]. The corresponding plot (capacitance vs. CO-type groups) was made

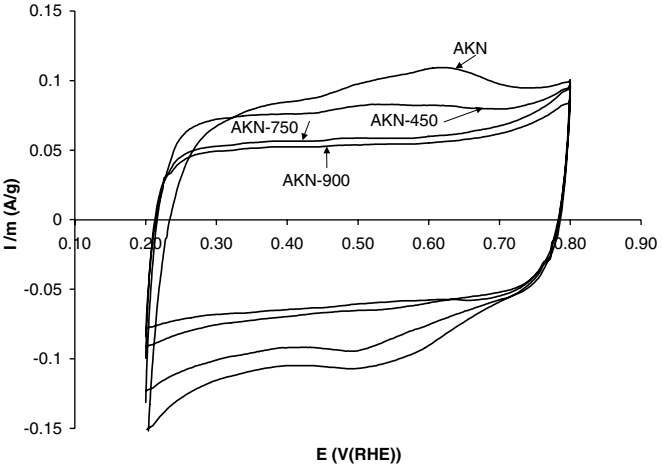

Fig. 7. Steady cyclic voltammograms of AK series. 1 M H_2SO_4, $V = 0.5$ mV/s.

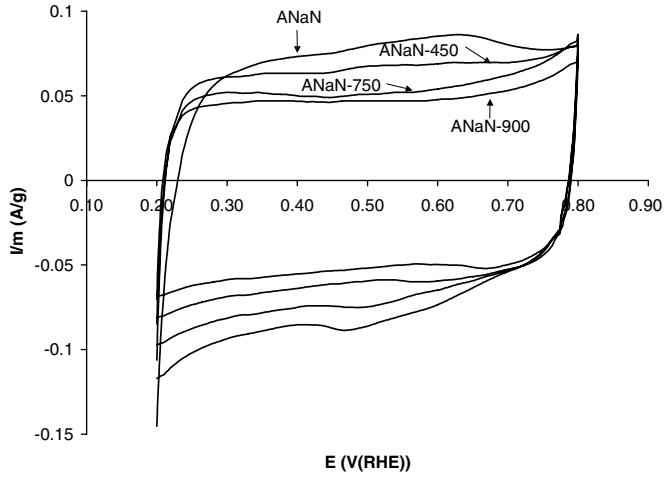

Fig. 8. Steady cyclic voltammograms of ANa series. 1 M H_2SO_4, $V = 0.5$ mV/s.

with these series of samples (Fig. 9). Let us note that in this case the plot has been done without dividing by the porosity of the materials, due to the very similar porous texture of these samples; however, if this parameter is taken into account (for example, by dividing by the VDR(N_2) in Table 2), a better correlation is obtained. In any case, a clear correlation between capacitance and the CO-type groups exists. The samples heat-treated at 450 °C or higher temperatures, follow a linear trend (except for sample ANaN-900 due to its lower porosity – Table 2), but the rest of the samples exhibit an upwards deviation. The main difference between these two groups of samples is that those treated above 450 °C do not contain a significant amount of carboxyl groups and anhydrides. Then, either both type of surface oxygen groups or one of them is the responsible for the additional contribution to the capacitance.

To check this point, sample ANaN-250 was obtained by heat treatment up to 250 °C, in order to remove most of the carboxylic groups without decomposing the anhydrides. Interestingly, the capacitance of sample ANaN-250 is slightly better than that of sample ANaN. This suggests that carboxylic groups do not play an important role in the promotion of capacitance, although it seems that their contribution to this property is not positive, as previously proposed [4,9].

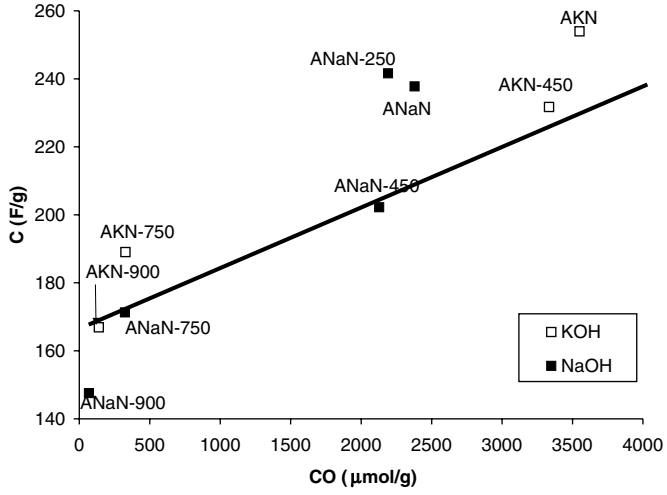

Fig. 9. Capacitance vs. CO content.

From the previous comments, it can be concluded that carboxylic anhydrides could be the responsible for the enhancement in capacitance, since these kinds of groups only exist in the samples not treated above 400–550 °C, which is the desorption temperature interval of anhydrides.

Taking into account that a redox peak at 0.63 V appears in cyclic voltammograms for samples treated at lower temperatures than 450 °C and that it almost disappears after treatment at 450 °C, it can be suggested that anhydrides undergo a redox reaction at this potential. This reaction should be somehow different from that occurring in carbonyls or quinone groups, which redox process should occur at lower potentials. According to our experiments they are mainly associated to the first peak in cyclic voltammograms. It is known that the reduction potential of the pair quinone/hydroquinone is located at, approximately, 0.7 V vs. NHE. However, as it has been previously published, an increase in the number of aromatic rings causes the formal potential to decrease [5] and can reach values close to 0.5 V [1]. Taking into account that the basic structure of activated carbons is based on graphene layers, the decrease in the expected potential could be logical and the process located below 0.6 V presumably proceeds through a one electron transfer quinone/hydroquinone mechanism [4]:

$$\rangle C_xO + H^+ + e^- \iff \rangle C_xOH \qquad (444)$$

The reaction mechanism for the oxidation/reduction of anhydrides (at about 0.63 V) is not very clear. Many electrochemistry textbooks indicate that carboxyl groups are inactive electrochemically. However, it must be considered that, on carbon materials, the nature of the substrate can have a substantial effect on the electrochemical behaviour of the available functional groups; for instance, large aromatic substrates and activating functional neighbours can facilitate their reduction [4]. In organic chemistry literature, studies related to oxidation and reduction of anhydrides in organic medium can be found [41,42] and the following mechanism is proposed:

$$A\,(\text{anhydride}) + e^- \iff A^{\cdot -} \qquad (458)$$

$$A^{\cdot -} + e^- \iff A^{2-} \qquad (460)$$

Despite the fact that anhydrides could be hydrolysed in aqueous medium, the thermodynamic and kinetic stability of these functional groups can be enhanced by electron delocalization in the ππ orbitals of the graphene layers. An experimental observation of this effect can be found in Ref. [38]. A sample oxidized in air which contained a large number of anhydrides was put in contact with a wet atmosphere for a long period of time, and after drying at low temperatures, the TPD experiment still revealed the presence of an important amount of this type of groups.

Thus, the hydrolysis of these groups linked to graphene layers, seems to be slow.

According to the redox scheme presented above, each anhydride group will contribute with two electrons in the redox process. If we consider this aspect in the capacitance vs. CO-type groups plot presented in Fig. 9 (that is, to take into account that one anhydride contributes with two electrons in the redox process), we will have to change the plot for samples treated under 450 °C. Each carboxylic anhydride contributes to capacitance with two electrons, so the amount of anhydrides should be taken into account twice when the plot is done vs. CO. The amount of CO desorbing groups in the corrected plot, corresponds to the CO desorbed in TPD experiments plus the part corresponding to anhydrides (obtained from the deconvolution). Then Fig. 10 is obtained in which all the samples fit much better to the linear trend.

This result could indicate that anhydrides play a special role in the redox contribution of the surface oxygen complexes in the capacitance. In our previous work [8], we did not observe this contribution as we used the activated carbons without any treatment after activation. Because the activation temperature is usually higher than 700 °C, anhydrides groups will not remain in the carbon material. Then, to observe this effect it is necessary the selection of samples with appropriate surface chemistry as we did in this study.

On the other hand, CA series evidences that surface chemistry has also a key role in improving carbon wettability. As it can be observed, sample CAH, the most hydrophobic one, presents a negligible value of capacitance (Table 2) in agreement with results obtained with graphite fibers [43]. When this sample is reoxidized in air flow, it practically recovers the capacitance value of the original sample (Table 2). The capacitance value of $CAHO_x$ sample is smaller than that of sample CA, but this can be understood taking into account that this sample has lost some surface area and some structural order due to the aggressive procedure carried out before H_2 thermal treatment. Fig. 11 contains the cyclic voltammograms for samples CA, CAH and $CAHO_x$.

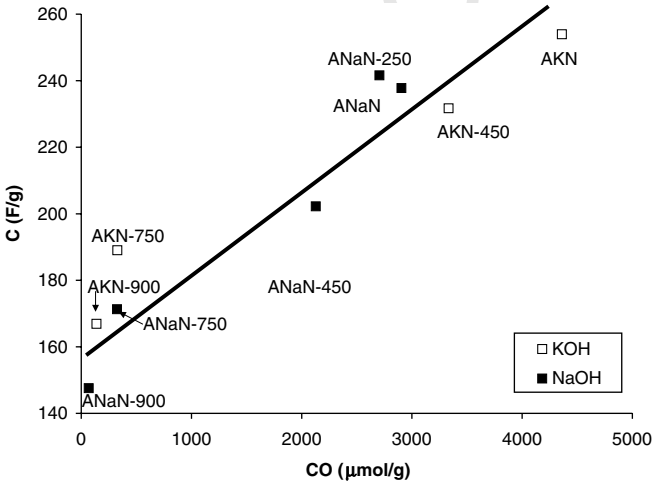

Fig. 10. Capacitance vs. CO content. Corrected values to take into account the contribution of anhydrides.

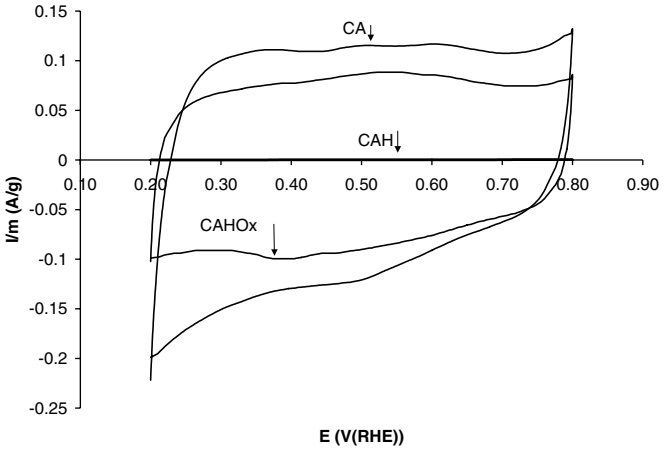

Fig. 11. Steady cyclic voltammograms of CA series. 1 M H_2SO_4, $V = 0.5$ mV/s.

Interestingly, we can deduce that only the heat treatment in hydrogen produces such a decrease in wettability, because the surface oxygen-containing samples and those heat-treated in inert atmosphere (i.e., AKN-900 and ANaN-900 samples), still have enough wettability to create most of the double layer, showing the role of dangling bonds in this property.

It can be observed that in CA sample a broad peak appears as it happened in the AKN and ANaN samples. However, the intensity of the peak at 0.63 V is lower because the content in carboxylic anhydrides is smaller than in the samples oxidized by HNO_3. In the voltammogram of sample $CAHO_x$, the redox process below 0.6 V, related to quinone/hydroquinone redox pair, has the highest intensity. It is important to note that this sample has a low content in carboxylic anhydrides as it can be seen in the TPD spectra (Figs. 5 and 6).

Finally, it should be noted that the presence of surface oxides also has an influence in the formation and structure of the double layer, as a consequence of the ion–ion interactions between surface oxygen groups and electrolyte ions (H^+ and HSO_4^- in this case). This type of interactions might have an influence on the kinetics of the charge–discharge process and on the effective pore dimensions. These questions need to be studied in future work.

4. Conclusions

Activated carbons with similar porosity but different surface chemistry have been studied by chemical and electrochemical methods to characterize their surface chemistry. The combination of both techniques has allowed us to deepen into the surface electrochemical properties of porous carbon materials. Thus, the features observed in the steady cyclic voltammograms have been tentatively assigned to redox processes associated to CO-type groups

(broad peak below 0.6 V RHE) and carboxylic anhydrides (peak at about 0.63 V RHE). The surface oxygen groups have, at least, a twofold relevant contribution to the total capacitance of porous carbons. On one hand, the surface oxygen groups have an important contribution to the capacitance through faradic processes which involve one or two electron transfer reactions. On the other hand, the surface oxygen groups (or the dangling bonds created after decomposition in inert atmosphere), determine the wettability of aqueous electrolyte; thus, their presence on the carbon surface is essential to take profit of the large double layer contribution to the capacitance of the porous carbons which is associated to their high porosity. Further studies in organic medium will be done to understand the role of these functionalities in the capacitance.

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Appendix A. Supplementary data

N_2 and CO_2 adsorption isotherms and their DR plots are available as supplementary material on the web. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbon.2006.04.017.

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