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The influence of the cooling down step in the heat treatment on the stability of activated carbons hydrophobicity

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Abstract Two samples of an activated carbon are heat treated at 500 °C for 2 h under a flow of inert gas. The only difference between the treatments of the two carbons is the cooling down step. After these treatments, the two carbons were hydrophobic and presented similar adsorption properties and an identical behavior toward water and cyclohexane uptakes. After being stored in ambient conditions for 20 months, the stability of oxygen functional groups is studied. The quantification of various oxygen groups is done by Boehm's titration and by thermogravimetry–mass spectroscopy analysis. It is found that the creation of oxygen groups, especially carboxylic acids, which are very attractive to water molecules, depends on the cooling down step. This is confirmed by both water isotherms and cyclohexane breakthrough measurements. Cyclohexane breakthrough times show that one of the heat treated carbons does not preserve its hydrophobic character compared to the other carbon, which presents a breakthrough time value close to that obtained before the storage.

Keywords Activated carbon · Hydrophobicity · Storage · Heat treatment · Surface groups

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1 Introduction

The surface groups, especially the oxygen containing ones, of activated carbon (AC) play an important role in the adsorption behavior of many species (Bandosz et al. 1996). Depending on the application, oxygen groups can have a positive or a negative influence. Therefore, a lot of researches have focused on the modification of the surface nature of carbons by adding more groups to improve the adsorption of polar molecules (Salame and Bandosz 2000), such as ammonia (e.g., Molina-Sabio et al. 2011) and methanol (e.g., Finqueneisel et al. 2005), or by removing the existing groups (Bradley and Rand 1993; Cosnier et al. 2005).

The most common process used for removing oxygen groups from the carbon surface is the heat treatment. It is used to promote the adsorption of pollutants (Feng et al. 2005; Mahajan et al. 1980) and for the reduction of oxygen groups in order to enhance the molinate herbicide adsorption capacity (Coelho et al. 2006).

The use of heat treatment is extended to the electrochemistry field. Indeed, AC is one of the most attractive materials for supercapacitors, although the presence of oxygen functional groups on the carbon surface can reduce their performance. In particular, the presence of CO evolving groups increases the pseudocapacitance (Bleda-Martinez et al. 2006; Ruiz et al. 2007). This capacitance is related to a poor life cycle due to irreversible reactions associated with the oxygenated functional groups. In this case, heat treatment increases significantly the life cycle of supercapacitors (Ruiz et al. 2008). The heat treatment is also proposed to improve the electrochemical properties of double layer capacitors (Sun et al. 2008).

The modification of the surface chemistry of ACs by heat treatment under a flow of inert gas has been a subject of intense interest for a long time. However, little is still known about the stability of the surface chemistry of the carbons after the removal of the surface functional groups during the heat treatment.

In our case, we have previously used the heat treatment to get a hydrophobic AC in order to reduce the amount of presorbed water and thus, enhance its efficacy toward organic compounds adsorption, even if the carbon is stored under ambient conditions of humidity (Tazibet et al. 2013).

The main objective of this work is to study both the post heat treatment stability of the oxygen groups, especially the carboxylic ones, and the parameters which determine their recreation. For this purpose, an AC prepared by chemical activation of olive residue was heat treated under an inert atmosphere and then subjected to two different cooling down steps. The two thermally treated carbons presented identical hydrophobicity and adsorption properties immediately after the cooling down step.

After 20 months of storage, surface characteristics of both the starting material and the heat treated ones were investigated by means of nitrogen adsorption, Boehm's titration, TPD, water isotherms and cyclohexane breakthrough time.

2 Experimental

2.1 Activated carbon preparation

The preparation of the AC is explained elsewhere (Tazibet et al. 2013). In brief, olive waste precursor was cleaned, dried and sieved to a particle diameter ranging from 0.62 to 1.2 mm, and then chemically activated by the addition of $ZnCl_2$ (purity >99 %, from Biochem Chemopharma) in the ratio of 0.49 g of Zn per gram of precursor. The mixture precursor/$ZnCl_2$ was carbonized in a tubular furnace under a controlled flow of nitrogen at 500 °C for 1 h (V = 5 °C/min). The next step consisted of washing the sample first with a HCl solution and then with distilled water until the complete removal of any residual activating agent. The obtained AC was dried overnight in air at 105 °C.

In order to get hydrophobic materials, two parts of the AC were heat treated at 500 °C under a flow of nitrogen for 2 h (V = 10 °C/min). One of the two samples (ACT1) was slowly cooled down with a controlled rate of 2 °C/min in the same inert atmosphere until ambient temperature. The second sample (ACT2) was removed from the furnace just after the heat treatment and immediately placed at room temperature. The ACs, AC (the non-heated initial sample), ACT1 and ACT2 were characterized just after being obtained and after storage in ambient laboratory conditions for 20 months. After storage, AC, ACT1 and ACT2 will be noted as ACS, ACT1S and ACT2S, respectively (Table 1).

Table 1 Description of activated carbon samples

Sample	Description
AC	Activated carbon without heat treatment and without storage
ACT1	Activated carbon heat treated and cooled down slowly under inert gas and without storage
ACT2	Activated carbon heat treated and cooled down immediately under ambient conditions and without storage
ACS	Activated carbon without heat treatment and stored for 20 months
ACT1S	Activated carbon heat treated and cooled down slowly under inert gas and stored 20 months
ACT2S	Activated carbon heat treated and cooled down immediately under ambient conditions and stored 20 months

2.2 Experiments

2.2.1 *Textural characterization*

The specific surface areas and the pore volumes of the samples were determined by nitrogen adsorption at −196 °C using an Autosorb Quantachrome apparatus. Before each adsorption experiment, the samples are outgassed at 120 °C under vacuum for 24 h. The surface area was determined using the Brunauer, Emmett and Teller (BET) equation, and the total volume of pores, V_t, was calculated at a relative pressure P/P_0 of 0.99. The micropore volume, V_{DR}, was determined using the Dubinin–Radushkevich (DR) method.

2.2.2 *Boehm's titration*

Boehm's method is used to evaluate the quality and the quantity of the acidic surface groups and also the amount of basic ones.

Since the selectivity of this method is based on the value of pKa of the surface species, it is assumed that sodium bicarbonate ($NaHCO_3$) neutralizes carboxylic acids, while sodium carbonate (Na_2CO_3) reacts with carboxylic acids and lactones, and sodium hydroxide (NaOH) with carboxylic acids, lactones and phenols. It is also known that hydrochloric acid neutralizes all surface basic groups.

A sample of 0.5 g of each carbon was mixed with 25 ml of the following 0.1 N solutions: $NaHCO_3$, Na_2CO_3, NaOH and HCl. The Erlenmeyer flasks were sealed and left under agitation for 48 h and then filtered. A solution of 10 ml of each filtrate was pipetted and the excess of base or acid was titrated with 0.1 N solutions of HCl and NaOH, respectively.

2.2.3 Thermogravimetry–mass spectroscopy analysis (TG/MS)

The temperature programmed desorption (TPD) analysis was performed using a TGA/SDTA 851 microbalance under argon flow (100 ml/min) with 25 mg of AC. Each sample was first heated until 100 °C, then held at this temperature for 30 min in order to remove the presorbed water, and finally subjected to TPD analysis at a linear heating rate of 10 °C/min until 900 °C. Prior to these measurements a blank was carried out by analyzing an empty cell to ensure the stability of the signal and to quantify the residual amount of each compound in the argon flow. The amounts of CO_2 ($m/e = 44$), CO ($m/e = 28$), H_2O ($m/e = 18$), and O_2 ($m/e = 32$) were determined via TPD using a Thermostar/Omnistar mass spectrometer, which was directly coupled to the microbalance.

On the other hand, the same TG/MS device was used to study the slow cooling down process of the ACT1 sample after its heat treatment at 500 °C. In this case, we were only interested in the variation of the amount of CO_2.

2.2.4 Water isotherm measurements

The water sorption isotherms were obtained at 20 °C using an Aquadyne DVS gravimetric water sorption analyzer. Before each measurement, the sample was outgassed at 120 °C under vacuum for 24 h. Thereafter, 150 mg of the sample was introduced in the apparatus, and subjected to another heating step for 1 h at 60 °C and 0 % of relative humidity in order to avoid the presence of presorbed water at the beginning of the experiment.

For each relative humidity value, the water uptake was measured after an equilibrium time corresponding to 0.0008 % of mass change per minute.

2.2.5 Breakthrough time determination

The cyclohexane breakthrough time was measured on a standard test rig for the estimation of the individual respirators according to the European standard EN 14387: 2004 (European Normalization 2004). The measuring and regulation equipment was metrologically confirmed according to ISO 10012 (International Organization for Standardization 1992).

Measurements were carried out using cylindrical filters (Ø 2.9 cm, H 4 cm). All breakthrough tests were done at 20 °C under constant air flow of 3.5 l/min and 70 % relative humidity with a cyclohexane concentration of 5,000 ppm. The measurement was stopped when the cyclohexane outlet concentration reached 10 ppm.

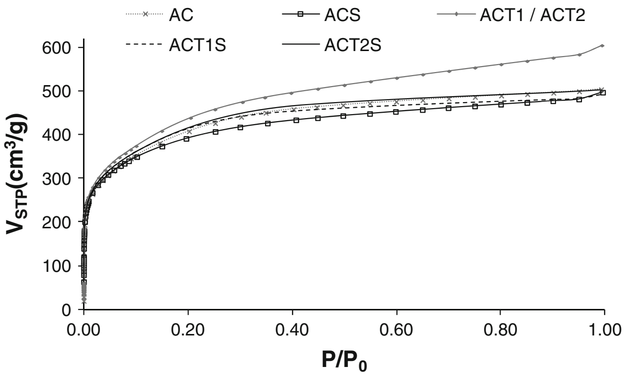

Fig. 1 Nitrogen adsorption isotherms of activated carbons at −196 °C

Table 2 BET-equivalent surface areas and adsorption capacity of nitrogen of the activated carbons

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{DR} (cm^3/g)
AC	1,490	0.78	0.45
ACT1	1,592	0.90	0.51
ACT2	1,592	0.90	0.51
ACS	1,428	0.77	0.45
ACT1S	1,508	0.76	0.51
ACT2S	1,512	0.78	0.51

3 Results and discussion

3.1 Textural characterization

The nitrogen adsorption isotherms of the samples shown in Fig. 1 are all of (type I + some type VI) according to the IUPAC classification with similar adsorptive properties as given in Table 2.

There are no differences in the values of BET-equivalent surface area (S_{BET}), V_t, and V_{DR} between AC and ACS. This indicates that the original AC preserves its textural properties at least for 20 months after its preparation. This is one of the important qualities of this material for which it is largely used in several applications.

After the heat treatment, there is a decomposition of oxygen groups (especially carboxylic groups) leading to the creation of additional porosity (Tazibet et al. 2013). Indeed, compared to the initial sample (AC), ACT1 and ACT2 present an increase of 15.4, 6.8 and 13.3 % of V_t, S_{BET} and V_{DR}, respectively.

After the storage, ACT1S and ACT2S display no differences in V_{DR} values. However, a slight decrease is noted in total pore volumes and BET-equivalent surface areas, which pass, respectively, from 0.9 to around 0.78 cm^3/g and from 1,592 to 1,512 m^2/g.

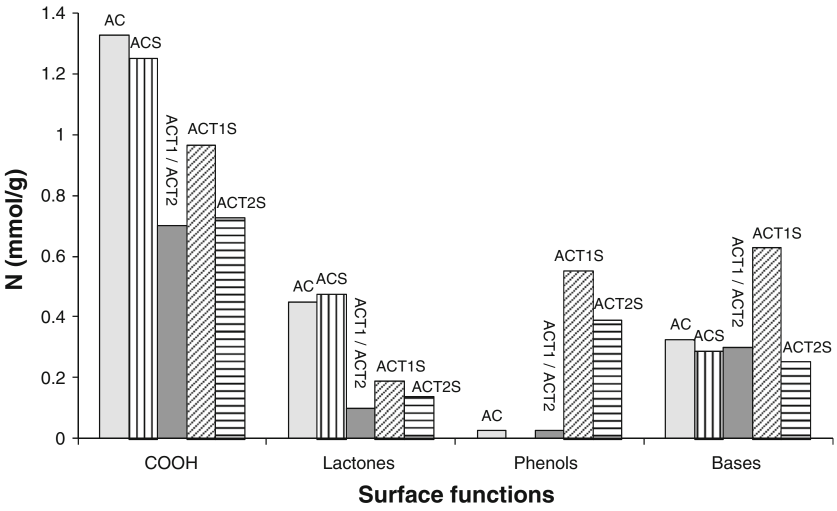

Fig. 2 Amount of surface functional groups of activated carbons after storage as determined by Boehm's titration

We notice that, in general, the three studied ACs have preserved their textural properties after 20 months.

3.2 Characterization of surface oxygen groups by the Boehm method

The Boehm titration results shown in Fig. 2 highlight that, after the heat treatment of AC a noticeable decrease of the amount of carboxylic groups and lactones is observed for both ACT1 and ACT2. However a slight difference is noted for the bases and phenols. This can be explained by the fact that these functions cannot be removed during the heat treatment at 500 °C.

After the storage of AC, no major changes are noted in the amount of carboxylic acids, lactones and bases present in the sample. We notice the negligible presence of phenols in AC and their absence in ACS.

The amount of carboxylic acid groups is higher for ACT1S than for ACT2S. Given that the quantities of these functions were similar after the heat treatment, it seems that carboxylic acid groups have been created during the storage of ACT1 carbon.

After the storage of ACT1 and ACT2 the amount of lactones increases. Both ACT1S and ACT2S create these functions, being the extension of this phenomenon greater for sample ACT1S.

Both ACT1 and ACT2 contain a negligible amount of phenols. However, after the storage we notice the creation of these functions, being the effect more noticeable again for sample ACT1S.

The fact that ACT1S contains the highest amount of basic functions suggests that some of these functions are created during its storage. This result has been previously observed in the literature concerning the formation of basic groups after the heat treatment and cooling down step of the sample in an inert atmosphere, and a subsequent exposure of the carbon to oxygen (Boudou 2003). In the case of ACT2S, the quantity of these basic functions is close to that of ACT2. Therefore, it can be concluded that ACT2 does not create basic functions during its storage.

Summing up, for all surface functional groups measured by Boehm's titration, the results show that the amount of these functions is higher for ACT1S than for ACT2S. Thus ACT1S has created a higher amount of these functions than ACT2S and both of them have created phenols.

3.3 Activated carbons surface chemistry

The nature of the oxygen surface groups on the different ACs has also been studied by TPD. Figures 3, 4, and 5 report the TPD profiles of CO_2, CO, H_2O and O_2 for all the studied ACs, except for ACT2, which has the same behavior as ACT1.

The first observation is that ACS and AC TPD profiles are similar (Figs. 3, 4, 5), except for CO_2 profile, where ACS displays a relatively larger peak in the temperature region below 500 °C (Fig. 3). It is well known that CO_2 desorbed in this region comes from the decomposition of carboxylic acids (Bleda-Martinez et al. 2006). This can indicate a creation of a small amount of carboxylic groups during the storage. However, this suggestion is not confirmed by Boehm titration results.

When comparing the CO_2 desorption curves of the starting material AC and the heat treated ones, ACT1 and ACT2, it is clearly seen that there is a shift in the position of the desorption peak from 650 to 700 °C after the thermal treatment. The origin of these peaks can be due to the decomposition of the same functions but in different energetic states.

Also, whereas samples ACS and ACT1S present a noticeable CO_2 desorption peak at temperatures below 500 °C, with a relatively higher intensity for sample ACS,

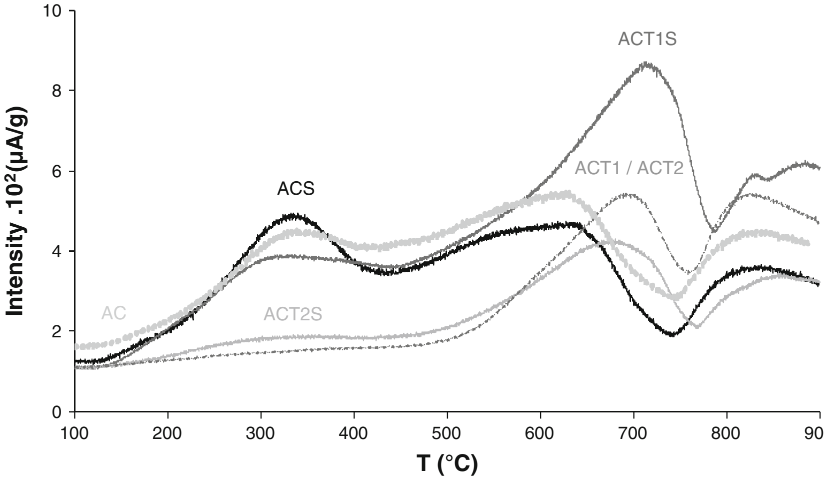

Fig. 3 CO_2 TPD profiles obtained by mass spectrometry

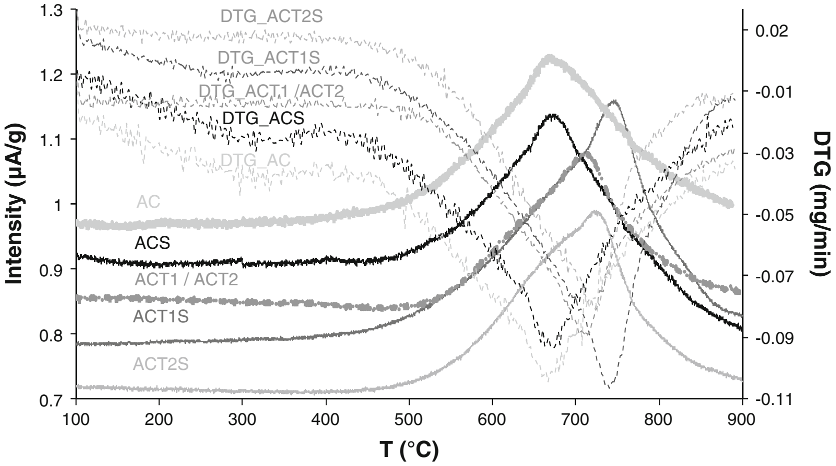

Fig. 4 CO TPD profiles and DTG curves of the activated carbons

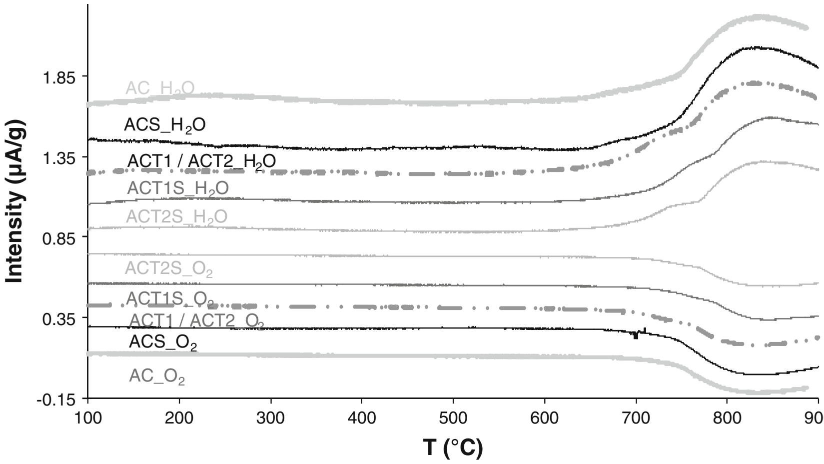

Fig. 5 H_2O and O_2 TPD profiles obtained by mass spectrometry

this phenomenon is less marked in the case of ACT2S (Fig. 3).

Desorption of CO_2 from ACT1S in the same region confirms that this carbon created carboxylic acid groups during the storage after its heat treatment. This can be observed at the CO_2 profile curve of ACT1 obtained just after the heat treatment of AC. Indeed, there is no CO_2 peak below 500 °C, indicating the complete absence of carboxylic groups.

CO_2 peaks with different intensities are observed between 500 °C and around 750 °C for the different carbons (ACT1S displays the highest one). In each case, the release of CO_2 is accompanied by desorption of CO as shown in Fig. 4. In this region, CO_2 and CO desorption can be attributed to the decomposition of carboxylic anhydrides, lactones and carbonyls (Bleda-Martinez et al. 2006; Fletcher et al. 2007). We also noticed that CO_2 and CO desorption around 700 °C is more pronounced for ACT1S than for the other samples. This may be due to the presence of a higher amount of these functions in ACTS1 in comparison with the other carbons. Around 700 °C phenols decompose and condense in the case of AC, ACT1, ACT2, ACT1S and ACT2S. This can be demonstrated by the appearance of a weak peak (shoulder) of water in these cases (Fig. 5), in agreement with the literature (Velasco and Ania 2011). We observe that, even in the case of ACS, a shoulder corresponding to H_2O appears in this region, suggesting that a small amount of phenols is present in ACS, but too negligible to be detected by Boehm's titration. In this regard, it was noticed that the H_2O desorption in this region is not proportional to the amount of phenols in each sample according to Boehm's titration.

In addition, it was also found that the weight losses obtained by TGA analysis are unexpectedly high around 700 °C: the values varied between 4.8 and 12.5 %. We have to remark that these values were obtained after the complete removal of the humidity content by heating the samples at 100 °C for 30 min. Another fact to be highlighted is the presence of minimums in the DTG profile (Fig. 4) that correspond perfectly to the maximum of each CO desorption peak. This means that the CO desorbed in the considered region cannot be assigned only to the decomposition of surface functional groups, but also to the conversion of residual lignin to CO around 700 °C as reported in the literature (Boonpoke et al. 2011). This phenomenon is very probable considering the lignocellulosic nature of the ACS precursor. The shift in the CO profiles of the three carbons may be due to the presence of the same kind of oxygen groups on energetically different sites (Moreno-Castilla et al. 1998).

The last CO_2 peak appears for all carbons at temperatures higher than 750 °C (Fig. 3) and it is accompanied by a H_2O peak (following the one that appeared due to phenols condensation). We suspect that a small amount of CO appears in this range of temperature but it is probably masked by the slow disappearance of the peak until 900 °C. Therefore, the desorption of CO_2, H_2O and probably CO around 800 °C can be attributed to two different phenomena. The first one is due to the decomposition of stronger functional groups such as carbonyl and bases, and the second one is related to the liberation of H_2 from the carbon surface, which combines with the residual oxygen to form water molecules. This explains the fact that at these temperatures the residual oxygen is consumed and its disappearance follows perfectly the H_2O profile (Fig. 5). It has also been reported that at this high temperature range, CO_2 can result from the occurrence of secondary reactions, as these are substantially enhanced in the presence of porous carbons (Bleda-Martinez et al. 2006).

The most important result shown in this section is that ACT1S recreated several oxygen surface groups, especially carboxylic acids, whereas ACT2S could only recreate a small amount of these functions. These two carbons have the same origin and were treated at the same time and stored under the same conditions, being the only difference between them the cooling down procedure followed after their thermal treatment. It is reported that heat treatment of carbons followed by a cooling down step under a flow of inert gas and then exposure to air leads to the fixation of oxygen on the carbon surface resulting on the formation of functional groups, particularly basic ones, in the form of pyrone (Boudou 2003).

In order to understand the phenomena occurring during the slow cooling down of ACT1S, we monitored this step of the treatment by TG/MS. For this purpose, the heat treatment of the AC is followed with both cooling down rates of 2 °C/min (as during the preparation of ACT1) and 20 °C/min. After the AC heat treatment, which is held for 2 h at 500 °C (Fig. 6), the CO_2 signal was perfectly stable and no variations were noticed. When the heating is stopped and the cooling down starts, the residual CO_2 is consumed as shown in Fig. 6. It seemed that the amount of CO_2 consumed is proportional to the cooling down rate.

Many facts reported in the literature are very interesting and may be used to explain our results. For instance, AC samples were heat treated by Moreno-Castilla et al. (1998) at different temperatures in an inert atmosphere without any exposure to air during all of the experiment, and then cooled down at room temperature. Thereafter, TPD profiles were obtained for the heat treated carbons and the non-treated one in order to determine the amount of CO and CO_2 released from their surface. These authors found that for all treated carbons there is a desorption of CO which starts at temperatures below the maximum temperature of the heat treatment. One of the suggestions given is that heat treated carbons readsorbed CO from the gas phase. However, they declined this suggestion after finding out that the addition of the amount of CO released during the heat treatment of the AC and its subsequent TPD analysis was almost the same than the amount of CO evolved during the TPD of the original sample. Notwithstanding, the corresponding CO_2 results show that for all temperature treatments the amount of CO_2 evolved in the case of the treated carbons is lower than that evolved by the original carbon. This suggests a very probable readsorption of CO_2.

More explanation about the reactivity of AC in the presence of CO_2 at high temperature is given in the work of Kapteijn et al. (1991). The authors studied the gasification

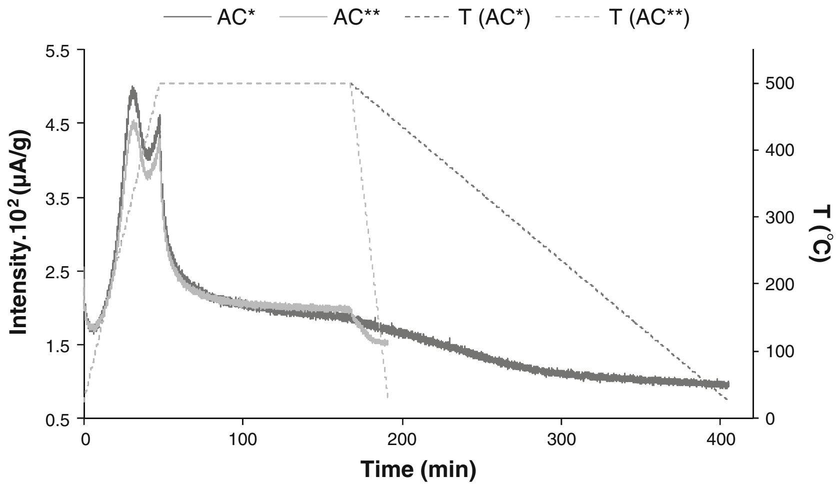

Fig. 6 Effect of the cooling down step on the CO_2 TPD profile during the heat treatment of AC: (*) cooling down at 2 °C/min, (**) cooling down at 20 °C/min

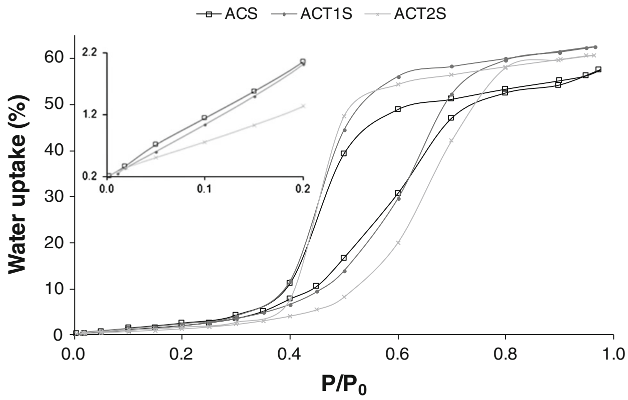

Fig. 7 Water isotherms of stored activated carbons at 20 °C

of an AC in various CO_2/Ar mixtures. TPD analysis is then performed on the obtained carbons. Results show that in all cases the total amount of CO desorbed during TPD up to 1,000 °C exceeds the amount of CO produced after the carbon gasification in an inert atmosphere. Therefore, the authors conclude that CO_2 interacts with active sites and yields semiquinone structures (Kapteijn et al. 1991).

In addition, it is reported that carbons activated in an atmosphere of pure CO_2, or in vacuum, react with molecular oxygen at room temperature and below (Mattson et al. 1970).

Taking into account these results, we suggest that the small amount of groups formed during the slow cooling down step in an inert atmosphere, react with O_2 molecules to create other surface functional groups at room temperature.

3.4 Water isotherms

Water adsorption–desorption isotherms of the three carbons shown in Fig. 7 exhibit a type V isotherm.

At very low relative humidity up to 0.02, a small and equal amount of water is adsorbed for the three carbons. This is certainly due to the fact that in this region water molecules are not adsorbed on the carbon, but a small quantity of molecules can be inserted into the pores (Kimura et al. 2004).

The oxygen functional groups play an important role at low relative humidity (0.02–0.4) (Thommes et al. 2011). In fact, the water molecules are first adsorbed on these active sites of micropores resulting on the formation of small clusters growing to bridges between pore walls with the increase in relative humidity (Lodewyckx 2010; McCallum et al. 1999; Muller et al. 1996). In this relative humidity range, the surface oxygen acts depending on the surface functional group nature and amount. Based on Boehm and TPD results, ACT2S displays the lower amount of oxygen groups, especially acidic ones. This explains the lower slope of the ACT2S curve compared to the ACS and ACT1S curves (Fig. 7). It is well known that carboxylic acids act primarily as hydrogen bond donors with high interaction energy and other oxygen functional groups gave lower interaction energy. Based on Boehm and TPD results, ACS contains more COOH than ACT1S; however ACT1S exhibits more phenols and carbonyls. Therefore, we suppose that this surface composition compensates the difference found in COOH content (Fletcher et al. 2007), which would explain the superposition of ACS and ACT1S adsorption isotherms in this pressure range.

All carbons display DR micropore volumes around 0.5 cm^3/g. This may explain the almost identical water isotherm segment at medium relative humidity (0.4–0.7).

The maximum values of water adsorption exceed the DR micropore volumes, and are probably attributable to the capillary condensation in wide micropores and small mesopores (Mahle and Friday 1989; Marban and Fuertes 2004; Matsuoka et al. 2004).

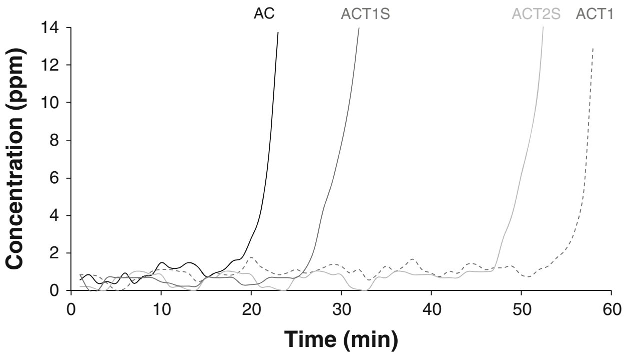

Fig. 8 Cyclohexane breakthrough curves of the activated carbons

Table 3 Cyclohexane breakthrough time of activated carbons

Sample	AC	ACT1	ACT2	ACS	ACT1S	ACT2S
t_b (min)	22	57	57	22	30	51

3.5 The breakthrough time

The dynamic cyclohexane breakthrough plots for the three carbons are shown in Fig. 8. ACT1 and ACT2 have a similar breakthrough time (57 min) (Table 3). This breakthrough time is close to that of the same samples tested after being dried at 105 °C for 24 h. However, AC exhibits a significantly shorter breakthrough time when tested without drying (22 min). After 20 months of storage ACS breakthrough time has not changed. This fact is due to the presence of a high amount of humidity in the AC from the time it was prepared.

After the heat treatment and storage, the breakthrough times become very different: 51 and 30 min respectively for ACT2S and ACT1S. Indeed, ACT1S is much closer to AC than to ACT1. The ACT2S breakthrough time is 51 min, being this value very close to the one of ACT2. Since there are no significant changes in the adsorptive properties for the three carbons, the decrease of breakthrough time must be due to the influence of the ambient humidity. It is clear that water occupies more micropore volume in ACT1S than in the case of ACT2S (Cho 1995; Cosnier et al. 2006; Lodewyckx 2010; Lodewyckx and Vansant 2000).

4 Conclusion

This work has studied the stability of the surface chemistry of an AC after the removal of oxygen groups from its surface by a thermal treatment followed by different cooling down procedures and after being stored in ambient conditions for 20 months.

The storage does not have a significant influence on the textural properties. Indeed, the BET surface area and DR micropore volume did not change after the preparation of the samples.

However, the surface functional groups change after the storage of the heat treated carbons. The extent of the change depends considerably on the cooling down step, which follows the heat treatment. The results obtained show that after the heat treatment at 500 °C, carbons became hydrophobic due to the removal of, essentially, carboxylic acid groups. After the storage, the carbon which was cooled down under ambient conditions is still hydrophobic because it contains a small amount of carboxylic groups. However, the carbon which was cooled down slowly in an inert atmosphere became less hydrophobic after storage. In fact, the removal of the carboxylic acidic groups by heat treatment at 500 °C under a flow of inert atmosphere will leave a number of reactive carbon atoms on the surface of the carbon. These can react with the residual CO_2 during the cooling down step under the same inert atmosphere, creating sites which can react with oxygen when the material is later put in contact with air. The carbon does not only recreate the removed carboxylic groups, but also other functions such as phenols and bases.

It is found that after the storage, the amount of water adsorbed is higher in the case of the sample which was cooled down slowly in an inert atmosphere. As a consequence, the cyclohexane breakthrough time is shorter than that of the other sample, which presents a value close to the breakthrough time obtained immediately after the heat treatment.

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