Combined XPS and TPD study of oxygen-functionalized carbon nanofibers grown on sintered metal fibers

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ABSTRACT
A composite material consisting of carbon nanofibers (CNFs) grown on sintered metal fiber filters was modified by H2O2 or plasma-generated O3. Coupling temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) techniques in the same UHV apparatus allowed the direct correlation of the nature of the created O-functional groups and their evolution as CO and CO2 upon heating. The two oxidative treatments yielded different distributions of O-containing groups. The relative contribution of oxidized carbon was very low in the C1s region, hence the functional groups were more robustly analyzed through the O1s region. The comparison of the released oxygen by integration of the TPD CO, CO2 and H2O spectra with the intensity loss of the XPS O1s spectra showed good agreement. In order to fit the data adequately, the set of O1s spectra was deconvoluted in at least four peaks for the differently activated samples. Finally, it was shown that functional groups formed by H2O2-treatment (mostly non-phenolic OH groups) are more thermally stable than those formed by O3-treatment. The latter treatment increases the concentration of carboxylic functionalities, which decompose at temperatures < 800 K; O3-activated CNFs should therefore show a more pronounced acidic behavior.

1. Introduction
Carbon in the form of nanofilaments has been known since it was observed as an undesired product resulting from the thermal decomposition of hydrocarbons over metals [1,2]. More recently, carbon nanofibers (CNFs) have attracted scientific interest in the field of catalysis as they exhibit excellent properties as catalyst supports [3,4]. These desirable characteristics include chemical inertness under reaction conditions, good thermal and electrical conductivity, high surface area and meso-porosity. Although, like graphite, CNFs possess an inert, hydrophobic nature, for many applications it is both desirable and possible to modify their surface thereby enhancing their wettability by polar solvents. From the perspective of supporting metal-containing species on CNFs, as is the case in their application as catalyst supports, functionalization of the nanofibers is in some cases a prerequisite. Through treatment with strong oxidizing media, oxygenated groups can be introduced onto the surface of CNF [5–7]. The number and type of these oxygen-containing moieties is highly dependent on the method of preparation. A recent survey regarding the analysis of these groups is given by Boehm [8], and includes titration methods, X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and infrared (IR) spectroscopy. In the case of TPD two different interpretations of the data are to be found in the literature. Haydar et al. [9] assign different desorption temperatures to the desorption of a single-type of group but from different surface sites (i.e. carboxylic groups within the range 400-600 K). Zhou et al. [10] instead assign distinct
desorption temperatures to distinct oxygen-functional groups (i.e. 550 K for carboxylic and 670 K for anhydride groups). For XPS the situation is similar. The most straightforward O1s deconvolution model comprises only two peaks, at around 533 and 531 eV for singly and doubly bond oxygen, respectively [11]. Models based on greater differentiation use up to five or more peaks for the O1s deconvolution [10]. Interestingly, only a few studies have been reported where an examination of samples with known oxygen-functional groups have been conducted [12–14]. Considering the early studies on polymers by Clark et al. [12,13] it was shown that the binding energy range of O1s is about 2 eV, however accounting for carbonates and several, only calculated, peroxy-species it increases to ∼2.5 eV. The assignment of groups and the binding energies for these groups differ slightly within their work. For example, when comparing [12, p. 3181] and [13, p. 959f] the assignment of groups as a function of increasing binding energy is as follows:

(1) Doubly-bonded oxygen in esters, carbonates and acids (∼532.8–532.9 eV).
(2) Oxygen in isolated carbonyls, ethers and alcohols (∼533.6–533.7 eV).
(3) Singly-bonded oxygen in acids and esters (∼534.3 eV).
(4) Singly-bonded oxygen in carbonates (∼535.0–535.2 eV).

A recent investigation of polymers [14] provides a different picture. First of all the binding energies are in the range of 531.5–533.4 eV. If we shift the binding energy region of Clark et al. to map both regions, a carbonyl-polymer is in the lowest binding energy (531.5 eV) region similar to Clark’s et al. region 1, an ether-polymer in region 2 (532.6 eV) and alcohol-polymer (phenolic and aliphatic) are in region 3 (533.3–533.4 eV). We will therefore refer to both studies in our discussion of the XPS data below.

It appears obvious that, at present, TPD and XPS as individual methods are not capable of univocally identifying the different types of functional groups present on functionalized CNFs. A combination of both techniques is however useful as the interpretation of the data must be consistent between both methods.

The aim of this work is the characterization of oxygen-containing groups created on the surface of CNFs grown on inconel sintered metal fiber material (CNF/SMFInconel) [15–17] by two different oxidative methods. For this purpose, we have coupled a step-wise TPD with XPS in the same UHV apparatus. The paper is outlined as follows: after the experimental section the results of UHV-TPD and XPS are shown and discussed. Finally the effect of step-wise heating on TPD and XPS results is reported and both methods are correlated.

2. Experimental

2.1. Materials

Sintered metal fibers Bekipor ST 20AL3 (Bekaert Fiber Technology, Belgium) made of inconel 601 (alloy composition: Ni 58–63%; Cr 21–25%; Al 1.4%) in the form of panels (elementary filament diameter 8 μm; panel size and thickness 3×3 cm² and 0.49 mm respectively, porosity 81%, density 750 g/m²) were used as a support for CNFs. SMFInconel consists of micron-sized metallic filaments which have undergone a sintering process in order to obtain a porous mat which can be used as a filter. High purity gases (>99.995%) were purchased from Carbagas, Switzerland and were used as received. H₂O₂ aqueous solution (Fluka) was used as received. Demineralized, bidistilled, water was used throughout the study.

2.2. Preparation and surface modification of CNF/SMFInconel

Prior to the CNF synthesis, the SMFInconel panels were oxidized in air at 920 K for 3 h. Carbon nanofibers (CNFs) were grown on SMFInconel by decomposition of ethane in the presence of hydrogen. All preparation details and the characterization of the CNF/SMFInconel have been described elsewhere [17]. After the CNF synthesis, CNF/SMFInconel was treated in an ultrasonic bath to remove non-anchored carbon (<0.5 wt.%). During this study, the composite CNF/SMFInconel supports underwent one of two pre-treatments in order to functionalize the CNF surface. In the first case, the supports were functionalized in a 35% H₂O₂ boiling aqueous solution for 4 h, and then washed with water until neutral pH was attained. In the second case, the supports were treated for 30 min with plasma-generated O₃ formed in a dielectric barrier discharge plasma reactor [18]. The ozone concentration was monitored with an UV absorption monitor (API-450 NEMA): after 30 min the output value was constant at 1100 ppm.

2.3. TPD

The formed functional groups were subsequently characterized by (step-wise) TPD coupled with XPS in an UHV recipient at the FHI, Berlin. The samples of CNF/SMFInconel were mounted on a Pt foil in turn mounted on a sapphire sample-support, and inserted into the UHV recipient (base pressure <3×10⁻¹⁰ mbar). The recipient contained a manipulator with facilities for sample heating by electron-beam impact and was equipped with a differentially pumped QMS 200 quadrupole mass spectrometer (QMS, Pfeiffer Vacuum). The Pt foil prevented the direct contact of the sample with the electron-beam and protected the filament from the desorbing gases from the sample. The temperature was measured by a type-K thermocouple spot-welded onto the Pt foil. Temperature programmed desorption was performed by placing the sample ~1 mm from the entrance aperture (1 mm in diameter) of the differentially pumped QMS. The QMS signal was found to be linear with the pressure in the chamber from UHV up to the 10⁻⁶ mbar range. The contact between the sample and the Pt foil was not optimized, hence heating was not perfectly homogeneous thereby generating temperature gradients across the sample. In the high temperature region (glowing sample) the temperature difference between the TPD desorption area and the spot-welded thermocouple could feasibly reach more than 50 K, with the thermocouple at higher temperature. The temperature gradients were less severe in the area of the surface from which TPD was analyzed. Table 1 summarizes the characteristics of the samples analyzed. Firstly, surveys of TPD at heating rate of 13 K/min from samples C1, C3 (H₂O₂-treated) and D1, D3 (ozone-trea-
Results obtained at high temperatures (>1040 K) were discarded for the correlation of XPS and TPD, due to the fact that part of CNFs burns-off at such temperatures. Most probably, some residual metal oxides present on the surface of the inconel support were reduced by carbon thereby evolving CO.

3. Results and discussion

3.1. TPD results

During TPD experiments, hydrogen, water, carbon monoxide and carbon dioxide are the prominent desorbing gases. Since hydrogen does not influence the oxygen-functional groups it is disregarded in the analysis throughout this paper. The results of H2O, CO2 and CO desorption experiments on samples C1 (H2O2-treated) and D3 (ozone-treated) are presented in Fig. 1.

Desorption of CO2 and CO commenced at the same temperature. In comparison to TPD under flowing He which has been carried out previously [16] the peaks observed in UHV-TPD are broader. This could indicate a non-uniform temperature of the sample. However, the TPD spectra from samples treated in the same way is observed to differ only in intensity, but not in overall shape. The most remarkable differences between the two differently treated samples are related to H2O and CO2 desorption. A much greater quantity of H2O evolves from the hydrogen peroxide-treated sample up to 900 K as compared to the O3-treated sample. The origin of this could be either water trapped in micropores or the formation of water from the interaction of functional groups (e.g. adjacent aliphatic OH groups). Considering CO2 evolution, this was observed from ozone-treated sample, D3, mainly in the lower temperature range (<800 K), with a maximum at about 600 K. A broader but less intense CO2 evolution from the H2O2-treated sample, C1, is observed at low temperature, but is also observed at higher temperature (up to 1000 K). In the literature, the evolution of CO2 at low temperature is usually assigned to the carboxylic functional group, while at temperatures higher than 700 K CO2 is attributed to the decomposition of anhydride and lactone groups [21–23]. CO desorption is dominated by the CNF burn-off at higher temperatures. Additionally however, a broad CO peak at around 500–600 K can be observed for the ozone activated sample and two smaller peaks around 600 and 800 K for the H2O2 activated sample. CO formation is usually assigned to the decomposition of phenols, ethers and carbonyls/quinones at high temperature (>800 K) [14,16,17]. However, as referenced in the introduction the interpretation of TPD spectra in the literature is ambiguous. The temperatures of desorption depend on the sample properties, the oxidation conditions, the probability of secondary reactions of the evolved gases (especially in porous carbons [8]) [24], and the manner in which TPD is carried out (e.g. the heating rate).

3.2. XPS results of the oxidative treatment

Overview spectra in the range of 0–1000 eV were recorded in order to identify the surface elements present on the samples. For the samples of series C and D the major constituents identified were carbon and oxygen.

The oxygen to carbon atomic ratios are calculated through the use of the uniform distribution model [20], taking into account the transmission function and the atomic sensitivity.

| Table 1 – Samples of CNF/SMF inconel analyzed through the study. |
| --- | --- | --- |
| Sample | Oxidant | Analysis |
| A1 | – | XPS, TPD |
| C1 | H2O2 | TPD |
| C2 | H2O2 | Combined XPS–TPD |
| C3 | H2O2 | TPD |
| D1 | O2 | TPD |
| D3 | O2 | TPD |
| D4 | O2 | Combined XPS–TPD |
| SMFInconel | – | TPD |

Results obtained at high temperatures (>1040 K) were discarded for the correlation of XPS and TPD, due to the fact that...
factors [20], and are presented in Table 2. This model overestimates the oxygen content if one assumes the more likely case that oxygen is predominately located at the outer surface. For several carbon samples the difference between the uniform distribution and a surface layer model could be up to a factor of 30 [19]. Thus, the very high amount of oxygen in the H2O2-treated sample C2 points to more aliphatic carbon on the surface accompanied by a loss of the graphitic character. No oxygen peak was observed in the spectra of sample A1, demonstrating that the surface oxygen content of untreated CNF/SMFInconel is negligible. Fig. 2 presents the superposition of the XP spectra in the C1s region for non-heated samples A1 (untreated), C2 (H2O2-treated), D4 (ozone-treated) and additionally for sample C2 heated to 1043 K. The difference spectra between oxidized and non-activated samples (D4 and A1) and oxidized C2 (RT) and heated samples C2 (840 K) are shown at the bottom. The observation of the changes in the C1s spectra allows us to elucidate the presence of defect sites in the CNF and thus the degree of graphitization [19,25,26]. In the case of the ozone-treated sample, D4, the intensity of the peak associated with graphitic carbon (284.5 eV) decreases slightly upon going from the untreated sample to the oxygen-functionalized sample.

In contrast, the loss of intensity for the H2O2-treated sample, C2, is remarkable: the main signal is much broader and lower than for the untreated sample, A1. It regains some intensity however after heating to >1000 K. Additionally, the π→π* loss feature around 291 eV is almost non-existent after functionalization, regaining some intensity after heating. These results indicate the partial loss of graphitic character, as already alluded above. The contribution of oxidized carbon to the XPS C1s signal can be observed through deconvolution or through analyzing the difference spectra as previously described by Proctor and Sherwood [27]. Both methods have their advantages and drawbacks. Regardless, the analysis is hindered by the stark changes in the carbon signal unrelated to oxygen-functionalities, e.g. the loss of graphitic character. One often underestimated drawback of the deconvolution is that the C1s intensity of the carbon in oxygen-containing functional groups is very low as compared to the whole C1s signal. In particular, clean graphitic carbon also shows some intensity in the region of interest (286–289 eV [12,28]), therefore the carbon in oxygen-functional groups is often overestimated. It is a good validation to calculate the overall stoichiometric ratio of oxygen to carbon – it should be within the range of 0.5–2 (for ethers to carboxylic acids). If the shape of the C1s signals vary only slightly the difference method is a good choice. This is the case for the ozone-treated sample (D4). The difference spectrum of untreated and ozone-treated samples is shown at the bottom of Fig. 2. By contrast, for the H2O2-treated sample C2 it was impossible to calculate meaningful difference spectra with the untreated sample A1. Only

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxygen</th>
<th>Carbon</th>
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<tr>
<td>A1</td>
<td>–</td>
<td>100%</td>
</tr>
<tr>
<td>C2*</td>
<td>18%</td>
<td>80%</td>
</tr>
<tr>
<td>D4</td>
<td>6.6%</td>
<td>93.4%</td>
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Following heat treatment, the surface of the CNFs loses a fraction of the functional groups created by the oxidative treatments. From the analysis of the TPD profiles shown in Fig. 1, the heating steps for the XPS analysis were chosen in order to analyze the surface composition corresponding to maxima and shoulders in the TPD spectra. The TPD spectra of the step-wise heating of samples C2 and D4 are presented in Fig. 5. They show a good agreement with the complete TPD spectra in Fig. 1; after addition of all spectra the overall shape is the same. Note that the desorption of water is shown in Fig. 5 for the ozone-treated sample D4.

The step-wise heating procedure is justified and does not yield artefacts due to interruption of heating and cooling procedures. Furthermore, in particular for the H2O2-treated sample the TPD raises doubts that the origin of most of the desorbing water signal is adsorbed or trapped water as it would be expected that this would equilibrate over the prolonged heating time. However, we cannot rule out adsorbed water in micro-channels. Another origin could also be the reactive decomposition of oxygen-functional groups (for example \( \alpha, \beta \) diol groups leaving a ketone group). This is an example where oxygen-functional groups are converted into others releasing an oxygen-containing molecule. Amongst others, esters could be converted into ethers.

Following step-wise heating, XPS analysis of the surface was carried out. Although the shape of the spectra changes dramatically for the ozone-treated sample, all spectra could be deconvoluted with the set of functions described in Section 3.2, first suggested by Clark et al. [12,13]. The development of the intensity of each O1s peak in the deconvoluted O1s spectra was calculated and is shown in Fig. 6. This allows for the correlation of the CO and CO2 desorption with the relative decrease in intensity of the peaks in the O1s region. Within the decomposition model of Clark et al. the parallel decreasing signals A at 531.3 eV and C at 533.3 eV of the ozone-treated sample D4 should be assigned to carboxylic functional groups. The signal at B at 532.2 eV must then be assigned to water and CO according to the TPD results. Haydar et al. [9] suggested aldehydes or ketones as the origin of CO evolution at low temperature. These are isolated carbonyls and hence indeed fall in region 2 in the model of Clark. Water can originate either from adsorbed water or from a chemically bound form of aliphatic alcohol (in accordance with the model of Clark). We are aware that this assignment of water is in contrast to Marchon et al. [21] who indicated a binding energy of approximately 533 eV for water “wetting” graphite, with successively lower binding energies for higher heating temperatures (532.5 eV after flashing to 593 K).

With reference to Fig. 6 it is seen that significant spectral intensity remains in the high temperature range (900–1000 K) in regions A and C, indicating the presence of very thermally stable functional groups. In contrast, the intensity in region B is much lower. These very stable groups are usually assigned to phenols, ethers and carbonyls directly attached to the \( \pi \)-system, e.g. in the form of quinones [9]. It should be noted here that these groups are only stable if no additional source of oxygen such as from gasification reactions is present [31]. In our samples such additional oxygen could arise from the oxidized inconel. Significantly, according to the model of Clark [13] one would assign phenols and ethers to region B, which is in contrast to the results of XPS analysis. To the best of our knowledge carboxyls directly attached to the \( \pi \)-system, e.g. quinones, have not previously been investigated by XPS.

A more recent investigation of polymers by Langley et al. [14] provides differing assignments from those of Clark et al.
Specifically, a carbonyl-polymer is located in region A, an ether-polymer in region B and alcohol-polymers in region C. According to this assignment the highly stable groups observed by XPS would be phenols and carbonyls. Such contrasting conclusions identify the need for further investigation in this area.

Interpretation of the present results is more straightforward in the case of the H$_2$O$_2$-treated sample. In general, the loss of oxygen-functional groups as compared to the remaining groups is considerably lower than for the ozone-treated sample. Here a loss in intensity at low temperature occurs only in regions B (532.2 eV) and C (533.3 eV) and leads to a overall shift to lower binding energy. From our employed deconvolution model this excludes the existence of carboxylic groups, as no signal loss is observed in region A. This conclusion is further supported by the absence of a pronounced TPD-CO$_2$ desorption signal. The small decrease in O1s intensity at low temperature is in clear contrast to the large water desorption signal in TPD. Therefore it is evident from the TPD of the H$_2$O$_2$-treated sample C1 (Fig. 1), which is dominated by water, that the majority of the desorbed water is invisible to the XPS analysis. A possible explanation is (as already discussed in Section 3.1) the presence of condensed water in micro-channels or the formation of a sp$^3$ layer with OH groups mainly beyond of the XPS probing depth. The latter hypothesis is supported by the loss of the graphitic character after H$_2$O$_2$-treatment, its restoration upon heating to ~1000 K (Fig. 2) and the accompanying loss of water (TPD,}

Fig. 3 – Development of the XPS O1s spectra of the samples D4 (O$_3$, left) and C2 (H$_2$O$_2$, right) during step-wise heating until 1040 K. The spectra are unrefined, but aligned at the minimum of the intensity between the O1s and its Mg satellites.

Fig. 4 – Superposition of O1s spectra of the samples differently activated before heating in UHV. The H$_2$O$_2$ activated sample C2 is offset by 700 kcps for clarity.

Fig. 5 – Step-wise TPD profiles of CO (black line) and CO$_2$ (red line) evolution from the samples D4 (ozone activated, left) and C2 (hydrogen peroxide activated, right). For sample D4 also the traces of water without background subtraction are shown.
The restoration of the graphitic character could be accomplished through either desorption of aliphatic OH groups and accompanying formation of a C=C bond, or more generally through burning-off of the aliphatic carbon.

The remaining strong O1s signal in region A (531.3 eV) at higher temperature could be explained by the formation of very thermally stable carbonyl or ether groups. Nevertheless, both hypotheses are in contrast to the employed model whereby in region A (531.3 eV) only C=O groups from esters and acids are expected. It is more likely that the assignment of Langley et al. [14] of region A to carbonyls is correct. Further investigations are therefore required in order to improve the XPS deconvolution model.

The integral TPD intensities are compared with the XPS O1s intensity loss in Fig. 7. A direct comparison of the amount of oxygen is not possible since the probing depth of both methods is very different and quantification of our TPD data is hampered by the need to estimate the carbon content of the composite samples. Therefore, the curves are adjusted in the high temperature range (800–900 K) of the integrated TPD profile without water, although here the influence of CO released by carbon burn-off is remarkable. A further caveat is the presence of temperature gradients across the sample and its heterogeneous surface. Despite this, a good correlation is observed between XPS and integral TPD data, particularly for the ozone-treated sample D4. Note that adsorbed water contributes to the XPS O1s region, but is ignored in the adjusted TPD integrals. Adsorbed water will contribute in both techniques and therefore may be responsible for the discrepancy at lower temperature. If we add water at low temperature (<700 K) to the integrated TPD data the correlation becomes even better. The consequence of this is again that the water desorbing at higher temperatures is invisible for XPS, regardless if the origin is water trapped in micro-porosity or chemisorbed in water releasing functional groups.

4. Conclusions

Samples of CNF/SMF Inconel, functionalized with O-containing groups by two different methods (boiling H2O2 or plasma-gen-
erated O$_3$, were successfully characterized by TPD coupled with XPS in the same UHV chamber. This technique was found to be useful in directly linking the release of oxygen-containing molecules from the samples at different temperatures with the decomposition of oxygen-functional groups present on the CNF surface. The TPD analysis provided evidence that the two oxidative treatments yielded different distributions of O-containing groups: O$_3$-functionalized samples contained a relatively higher amount of groups releasing CO$_2$ in the lower temperature range as compared to H$_2$O$_2$-functionalized samples. The release of significant H$_2$O is a good indicator that the initial aim to create a surface wetable by polar solvents has been fulfilled through both oxidation procedures. Step-wise heating with subsequent XPS analysis provided insights into the nature of these CO$_2$ releasing groups. Based on the deconvolution of O1s spectra, it could be shown that they most likely correspond to carboxylic functionalities which tend to decompose at temperatures < 800 K. Following the change in the peak areas after each heating step, it was found that most of the O-groups formed by H$_2$O$_2$-treatment were more thermally stable than those formed by O$_3$-treatment. The nearly complete loss of intensities which tend to decompose at temperatures < 800 K. Following the change in the peak areas after each heating step, it was found that most of the O-groups formed by H$_2$O$_2$-treatment were more thermally stable than those formed by O$_3$-treatment. The nearly complete loss of intensity in the π-π* loss feature shows that the H$_2$O$_2$-treatment heavily disrupts the π-system of the outer surface of CNFs as probed by XPS (10 nm). Since H$_2$O$_2$ forms OH radicals it is very likely that a large amount of non-phenolic OH groups are formed. Temperatures of 1000 K are necessary to start removing these OH functional groups again resorting the π-system. Finally, the overall integral intensities of TPD and XPS during step-wise heating are found to be comparable. The aim of linking TPD desorption signals and XPS signals with specific oxygen–carbon functional groups should therefore be achievable with a more sophisticated XPS deconvolution model.

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