

# Tailoring micro-mesoporosity in activated carbon fibers to enhance SO<sub>2</sub> catalytic oxidation

Noel Diez<sup>§</sup>, Patricia Alvarez<sup>§</sup>, Marcos Granda<sup>§</sup>, Clara Blanco<sup>§</sup>, Grażyna Gryglewicz<sup>¥</sup>, Iwona Wróbel-Iwaniec<sup>¥</sup>, Agata Śliwak<sup>¥</sup>, Jacek Machnikowski<sup>¥</sup> and Rosa Menendez<sup>§\*</sup>

<sup>§</sup>Instituto Nacional del Carbon, CSIC, P. O.Box 73. 33080-Oviedo, Spain.

<sup>¥</sup>Wrocław University of Technology, Division of Polymer and Carbonaceous Materials, Gdańska 7/9, 50-344 Wrocław, Poland

**ABSTRACT.** Enhanced SO<sub>2</sub> adsorption of activated carbon fibers is obtained by tailoring a specific micro-mesoporous structure in the fibers. This architecture is obtained via metal catalytic activation of the fibers with a novel precursor, cobalt naphthenate, which contrary to other precursors, also enhances spinnability and carbon fiber yield. In the SO<sub>2</sub> oxidation, it is demonstrated that the combination of micropores and large mesopores is the main factor for an enhanced catalytic activity which is superior to that observed in other similar microporous activated carbon fibers. This provides an alternative way for the development of a new generation of catalytic material.

**KEYWORDS.** Carbon fiber, Cobalt naphthenate, mesopores, micropores, SO<sub>2</sub> adsorption.

## Corresponding Author

\* Prof. Rosa Menendez. tlf: +34 985119090. E-mail: [rosmenen@incar.csic.es](mailto:rosmenen@incar.csic.es).

## INTRODUCTION

High amounts of  $\text{SO}_2$  are nowadays released into the atmosphere, mainly from coal-fired power plants, petroleum refineries and on-road vehicles. The atmospheric oxidation of this  $\text{SO}_2$ , which preferentially occurs in liquid phase (clouds, fog) leads to the formation of acid rain that causes health problems, acidity of soil and mineral waters and the abrasion of buildings and monuments.[1-3]

In order to reduce emissions, a number of different technologies have been developed, these being mainly applied to the elimination of  $\text{SO}_2$  in the flue gases during combustion or post combustion stages. Most of the industrial methods used for the desulphurization of the flue gas involve a chemisorption process on alkaline sorbents such as  $\text{CaO}$ ,  $\text{CaCO}_3$  or  $\text{Na}_2\text{CO}_3$ . [4] However, the resultant products are non-regenerable (calcium sulfite and sulfate) and they have a low commercial value. A promising alternative to these alkaline sorbents is the use of carbon materials (activated carbons or activated carbon fibers) [5] which contribute with their adsorption capacity and also act as catalysts for the oxidation of  $\text{SO}_2$  in the presence of  $\text{O}_2$  and  $\text{H}_2\text{O}$  (which are also typically present in flue gases). In this process, adsorbed  $\text{SO}_2$  is oxidized into  $\text{SO}_3$ , which by hydration gives rise to diluted  $\text{H}_2\text{SO}_4$  solutions resulting in the regeneration of the carbon material.

Activated carbon fibers (ACF) are among the most interesting carbon materials to be used since they overcome the drawbacks derived from the high resistance to bulk gas and liquid flow characteristic of granular activated carbons. The most recent research on the preparation of such materials focused on the optimization of two main factors: i) the porous texture of the activated carbon materials, which undoubtedly plays a crucial role in the overall process and ii) the

acid/base properties on the surface of the materials. With respect to the second factor, it is generally maintained that an increase in the basicity of the surface of these materials enhances the SO<sub>2</sub> adsorption capacity and the catalytic activity of the activated carbons (AC),[6-10] although their porous texture is also modified.[11] As an example, Raymundo-Piñero et al.[6] demonstrated that an enrichment in nitrogen of the activated carbon fibers enhanced their catalytic activity from values of  $\approx 30$  to  $87 \mu\text{mol g}^{-1} \text{min}^{-1}$ .

To our knowledge, the influence of the porosity on the catalytic activity has still not been satisfactorily clarified. Some authors have associated the catalytic activity of AC towards SO<sub>2</sub> oxidation to the presence of narrow micropores ( $< 7\text{\AA}$ ).[12] On the other hand, other authors have concluded that the presence of narrow micropores binds H<sub>2</sub>SO<sub>4</sub> more strongly to the surface, making its removal almost impossible by washing.[13] As far authors are concerned, the possible influence of the mesoporosity on the adsorption and desorption kinetics of activated materials in liquid phase needs to be clarified.

This work is devoted to the preparation of activated carbon fibers (ACF) with a tailored porous texture and similar surface properties (similar basicity) for their use as active catalysts for SO<sub>2</sub> oxidation. Melt spun coal-based carbon fibers [14-16] were activated by using two different activation processes (chemical activation with KOH and physical activation with steam). We report for the first time on the preparation of microporous-mesoporous ACF using cobalt naphthenate as a catalyst precursor to develop mesoporosity and study its influence during spinning of the mixture to produce the fibers. The two ACFs displayed a good catalytic behavior for the oxidation of SO<sub>2</sub> in water and the influence of micropores-mesopores architecture in the catalytic activity was determined.

## EXPERIMENTAL SECTION

**Synthesis of the porous fibers:** The fiber precursor used in this work (AOP) was an isotropic anthracene oil-based pitch supplied by NalonChem S.A. (Spain) with a softening point of 218 °C (Mettler, ASTM D3104). 50 g of pitch were heated to 260 °C at a heating rate of 5 °C min<sup>-1</sup> under a nitrogen flow of 20 dm<sup>3</sup> h<sup>-1</sup> in a vertical stirred reactor. Cobalt naphthenate (Sigma-Aldrich, 6.5 wt.% of Co) was slowly added to the molten pitch so that the resultant doped pitch (Co-AOP) had a composition of 1 wt. % Co. The mixture was stirred at 260 °C for 1 h. The Co-doped pitch, was melt-spun into fibers using a laboratory-scale device described in detail elsewhere.[14] 30 g of pitch were heated up to 242 °C and extruded through a stainless steel monohole spinneret (D = 500 μm) by applying a nitrogen pressure of 1 bar. The pitch filaments were collected on a spool operating at a winding speed of 250 cm s<sup>-1</sup>. For comparison purposes, carbon fibers were also obtained from the non-doped pitch by melt-spinning at 255 °C. The as-spun fibers were stabilized at 270 °C under an air flow of 20 L h<sup>-1</sup> at a heating rate of 1 °C min<sup>-1</sup>. After stabilization, the fibers were carbonized at 870 °C at a heating rate of 15 °C min<sup>-1</sup> with a soaking time of 15 min under a nitrogen flow of 40 L h<sup>-1</sup>. The Co-doped fibers were placed in a quartz crucible, which was suspended from a thermobalance and activated with steam at 850 °C until 50% burn-off was reached. Non-doped fibers were chemically activated in a horizontal furnace at 700 °C for 1 h after being impregnated with KOH (KOH/Carbon fiber (wt./wt.) = 7/1). Both activated samples were washed with diluted HCl in order to remove cobalt nanoparticles from the Co-doped fibers and to remove the chemical agent and reaction products from the undoped fibers. The total absence of cobalt in Co-ACF was confirmed by ICP (Agilent 7700x).

Characterization of the ACF: The elemental analysis of AOP, ACF and Co-ACF was performed by using a LECO-CHNS-932 micro-analyzer and a LECO-VTF-900 furnace coupled

to a microanalyzer. X-ray photoelectron spectroscopy (XPS) was carried out in a Specs spectrometer using Mg K $\alpha$  (1253.6 eV). The C1s and O1s high resolution spectra were curve-fitted using a Gaussian-Lorentzian peak shape (see Supporting Information for details). The pH of ACF and Co-ACF was measured according to the ASTM D 3838-80 standard. The textural parameters of ACF and Co-ACF were determined from the N<sub>2</sub> adsorption-desorption isotherms at 77 K (Nova 2200, Quantachrome). The samples were previously outgassed overnight at 300 °C. The specific surface area ( $S_{\text{BET}}$ ) was calculated using the BET method. The amount of nitrogen adsorbed at a relative pressure of  $p/p_0=0.96$  was used to determine the total pore volume ( $V_{\text{T}}$ ). The micropore volume ( $V_{\text{micro}}$ ) was estimated from the Dubinin-Radushkevitch equation. The BJH method was applied to the desorption branch of the N<sub>2</sub> isotherms to calculate the mesopore volume ( $V_{\text{meso}}$ ). Pore size distributions (QSDFT and BJH) were also calculated from the isotherm data. The morphology and cobalt distribution in the fibers after activation were monitored on a scanning electron microscope (SEM) using an Evo LS15 Zeiss microscope coupled to an energy-dispersive X-ray spectrometer (EDX) Brucker 29 eV and a back-scatter detector (BSE) for elemental characterization.

**Catalytic activity:** The catalytic activity towards SO<sub>2</sub> oxidation was studied by following a procedure described elsewhere.[17] A saturated solution of SO<sub>2</sub> was prepared by bubbling pure SO<sub>2</sub> through distilled water for several minutes. The saturated solution was diluted until the concentration of SO<sub>2</sub> reached a value of  $1.65 \times 10^{-3}$  M. The concentrations of the saturated and diluted solutions were determined by titration with iodine using starch as indicator. 250 mL of diluted solution was saturated in oxygen by blowing air for several minutes. The air bubbling was kept up through the whole experiment. The reaction temperature was set at 25 °C by using a thermostatic bath. Once the temperature and the conductivity were stable (25 °C,  $\sim 570 \mu\text{S cm}^{-1}$ ),

0.3 g of sample were added to the stirred solution. The oxidation reaction was followed by conductometry, by means of a high precision (Mettler Toledo) conductometer. Due to the hydrophobicity of the samples, 3 mL of distilled water was used to wet the samples for several minutes prior to their introduction into the reactor. Blank measurements in absence of fibers were also conducted.

## RESULTS AND DISCUSSIONS

**Activated carbon fibers with tailored porous textures.** Two activated carbon fibers with controlled porous texture were prepared, a microporous activated carbon fiber (ACF) and a microporous-mesoporous activated carbon fiber (Co-ACF), obtained from a coal-based carbon fiber (CF) and a Co-doped carbon fiber (Co-CF), respectively.

ACF was produced by chemical activation with KOH of a carbon fiber (diameter of 27  $\mu\text{m}$ , Figure 1a) obtained by melt spinning, stabilization and carbonization of an anthracene oil-based pitch (AOP, softening point of 218  $^{\circ}\text{C}$ ), a coal derivative obtained by pyrolysis of anthracene oil.[14-15] The KOH/fiber ratio used in the activation was 7/1.

Co-ACF was obtained by catalytic steam activation of the Co doped coal-based (from anthracene oil-based pitch) carbon fibers. This procedure required the initial Co-doping of the AOP prior to melt-spinning. Cobalt naphthenate was tested for the first time as a cobalt nanoparticle precursor. The analysis of the behavior of the mixture during spinning, stabilization and carbonization revealed several benefits to this process not observed before for other metal nanoparticle precursors under the same conditions. The softening point of the mixture decreased

from 218 to 210 °C despite the thermal treatment applied for doping (260 °C, 1 h). The large extent of this decrease suggests that it is not only the result of liquid stage of the cobalt naphthenate. Furthermore, strong interactions between the pitch components and Co naphthenate during mixing were determined by means of thermogravimetric studies. Those were evidenced by the different thermal behavior observed for the pitch-cobalt naphthenate mixture (Figure 2c) when compared to the theoretically-calculated curve (Figure 2d). In particular, a smaller weight loss of the real mixture at temperatures below 320 °C is observed, which also results in a higher yield of material at temperatures above 490 °C. This could be a consequence of hydrogen transfer reactions between the pitch components and the naphthenate (hydrogen donor).[18] As the result of that there was a decrease in the overheating required for the melt-spinning of the pitch compared to that required for the undoped one (32 °C above its softening point for Co-AOP compared to 37 °C above its softening point for AOP), effect which was not shown for other metal nanoparticle precursors.[19] After stabilization and carbonization, the as prepared doped carbon fibers showed uniform Co metallic nanoparticles distributions (Figure 1b-d, see Supporting Information for further details). Also, the fibers were obtained with an unexpectedly high spinning yield (28 % in Co-CF compared to 26 % for CF), which contrasts with the lower spinning yield obtained when other metal nanoparticle precursors were used.[19] This demonstrates that cobalt naphthenate is a more efficient alternative to other dopants currently used.

Finally, the Co-doped carbon fibers were activated in steam to 50 wt% of burn-off and subjected to acid washing until complete Co removal (less than 50 ppb residual Co, as determined by ICP-MS) to yield Co-ACF.

**Characterization of the activated carbon fibers.** The data obtained from the N<sub>2</sub> isotherm at 77 K (Table 1) show that both types of fibers, despite being obtained by different methodologies (chemical and catalytic activation), exhibit a large specific surface area ( $S_{\text{BET}}$  of 1294 and 1098 m<sup>2</sup> g<sup>-1</sup> for ACF and Co-ACF, respectively).

ACF exhibit a strictly microporous structure ( $V_{\text{micro}} = 0.56 \text{ cm}^3 \text{ g}^{-1}$ ) with a narrow pore size distribution centered at 0.6 nm (Figure 3a), which is typical of carbon fibers activated with KOH.[16] Co-ACF also exhibits high microporosity development ( $0.46 \text{ cm}^3 \text{ g}^{-1}$ ) with a micropore size distribution centered at a higher pore size, 1.2 nm (Figure 3a). This difference in micropore sizes is consistent with the findings of Maciá-Agulló et al. when activating pitch-based fibers by both chemical and physical methods.[16] Only in the Co-doped fibers the presence of mesopores is noticeable ( $V_{\text{meso}} = 0.25 \text{ cm}^3 \text{ g}^{-1}$ ). Some narrow mesopores in the range of 3 to 5 nm can be observed, which may be the result of micropores widening during activation at high burn-off values.[20] Interestingly, large mesopores show a wide size distribution covering the range of 10 to 30 nm (Figure 3b), being these values in the range of the diameter of the Co particles used as catalyst (Figure 4b).

The development of mesopores with these specific diameters is in agreement with the activation mechanism suggested by Marsh et al. whereby metal particles gasify carbon via pitting or channeling processes, leading therefore to mesopores with tailored pore diameters.[21] This was confirmed by SEM images of the fibers (Figure 4b). In contrast with the image of ACF in which an homogeneous microporous surface is observed (Figure 4a, micropores out of the detection limits of this technique), the cross-section of Co-ACF before acid washing shows the presence of mesopores. Furthermore, these mesopores appear to be the channels created during



catalytic activation of the homogeneously distributed cobalt nanoparticles, still seen within the mesoporous channels (Figure 4b, inset).

Apart from the textural aspects, the surface chemistry of the materials also plays an important role in the SO<sub>2</sub> adsorption process (Table 1). The elemental composition of both types of fibers was found to be fairly similar. C/O ratios of 19.7 for ACF and 19.4 for Co-ACF were calculated. Similarities were also observed in the C/O ratios calculated by means of XPS (15.9 and 14.6 for ACF and 19.4 for Co-ACF) and in their pH (6.1 for ACF and 5.8 for Co-ACF, as calculated by the ASTM standard). These results suggest that despite undergoing different activation processes, the oxygen containing moieties on the surface of both samples are similar. Evaluation of the oxygen functionalities on the surface of both activated fibers by means of deconvolution of the C1s and O1s X-ray photoelectron spectroscopy confirmed the presence of similar amounts of COH, CO and COOH species in the fibers (see Supporting Information for details).

**Catalytic oxidation of SO<sub>2</sub>.** The catalytic activity of ACF and Co-ACF towards the oxidation of SO<sub>2</sub> at room temperature in the presence of O<sub>2</sub> and H<sub>2</sub>O was measured. The samples were introduced into a batch reactor containing a diluted solution of SO<sub>2</sub> ([SO<sub>2</sub>] = 1.65x10<sup>-3</sup>) saturated in O<sub>2</sub> ([O<sub>2</sub>] > 10<sup>-3</sup>). [22] At these conditions, most of the aqueous SO<sub>2</sub> is in the form of HSO<sub>3</sub><sup>-</sup>, the concentration of SO<sub>3</sub><sup>2-</sup> being negligible. H<sub>2</sub>SO<sub>4</sub> is formed as an oxidation product and it is totally dissociated into H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup>. Thus, the overall reaction can be expressed as:



The number of ions increases with the conversion degree, and so does the conductivity. Hence, the oxidation of SO<sub>2</sub> into H<sub>2</sub>SO<sub>4</sub> can be monitored by conductivity measurements as a function of time.[17] The conductivity curves for ACF and Co-ACF, as well as the curve obtained in the absence of fiber (blank experiment), are shown in Figure 5.

For short reaction times, the conductivity decreases, probably due to the adsorption of the ionic species on the microporous carbon surface. Once steady state is reached, a linear slope was observed up to high conversion degrees. Considering that the oxygen concentration is in excess and remains constant during the experiment due to the continuous air bubbling, this observation suggests an apparent reaction order for SO<sub>2</sub> close to 0, which is in accordance with the findings of other authors.[17,23] In both curves, the conductivity reaches a final value of approx. 1050 μS cm<sup>-1</sup>, which corresponds to the total conversion of SO<sub>2</sub> to H<sub>2</sub>SO<sub>4</sub>. At low conversion values, the catalytic activity can be calculated by the equation (2):

$$\alpha = (\Delta k/\Delta t)F/m \quad (2)$$

where  $\alpha$  is the catalytic activity in μmol min<sup>-1</sup> g<sup>-1</sup>,  $\Delta k/\Delta t$  (mS cm<sup>-1</sup> min<sup>-1</sup>) is the slope of the conductivity curves, F is the relation between the initial moles of dissolved SO<sub>2</sub> and the initial conductivity in μmol cm mS<sup>-1</sup>, and m is the amount of sample used in g.

In the case of ACF, a total conversion took place after a reaction time of 28 min, and the calculated catalytic activity for this material was 52 μmol min<sup>-1</sup> g<sup>-1</sup>. Sample Co-ACF showed a remarkably higher catalytic activity of 105 μmol min<sup>-1</sup> g<sup>-1</sup>, achieving the total conversion in much shorter time, after 15 min. This catalytic activity value is greater than those found for other strictly microporous and N-enriched materials reported in the literature.[10] It should be

mentioned that Co-ACF has less micropores and a pH that is slightly lower than that of ACF, (both parameters were previously considered in the literature as negatively affecting the process) with no significant differences in their surface chemistry. However, Co-ACF combines the development of micropores and also of mesopores with a size of 10-30 nm which indicates that having a high volume of micropores is insufficient to reach high catalytic activity values. We propose that a combination of large mesopores combined with micropores facilitates diffusion during the adsorption and/or desorption of the molecules involved, leading to considerably higher oxidation rates. As result, the use of cobalt naphthenate as cobalt nanoparticle precursor does not only lead to tailored porous architectures with more effectiveness than other reactants used to this purpose, but also leads to a family of ACF with catalytic activity superior to those exhibited by similar microporous fibers or powdered activated carbons and N-enriched carbons previously described in the literature (up to  $87 \mu\text{mol g}^{-1} \text{min}^{-1}$ ),[6] representing a good starting point for the development of a new generation of catalytic materials. Further studies on the modification of the surface properties towards fibers with higher alkalinity will be undertaken to enhance the activity values we have obtained so far.

## CONCLUSIONS

Activated carbon fibers with tailored micro/mesoporous architectures can be prepared from a coal-based pitch and cobalt naphthenate as nanoparticle precursor for mesopores development during catalytic activation. This novel catalyst ensured a homogeneous distribution of metal nanoparticles during the preparation of the activated carbon fibers and, unlike other nanoparticle precursors, also acted as a coadjuvant by improving the spinnability of the Co-doped pitch, contributing to an increase in the spinning yield. The activated carbon fibers prepared were

active in the catalytic oxidation of SO<sub>2</sub>. We have also demonstrated that the presence of a combination of micropores and large mesopores is the main factor responsible for the catalytic activity in SO<sub>2</sub> oxidation and this activity is superior to the exhibited by other similar microporous activated carbon fibers including the N-enriched carbons described in the literature.

**Supporting Information.** X-ray diffraction of Co-containing anthracene oil based carbon fibers and XPS C1S curves and corresponding deconvolution curves of ACF and Co-ACF are supplied as Supporting Information.

#### ACKNOWLEDGMENT

The research leading to these results has received funding from the European Union's Research Fund for Coal and Steel research program under Grant Agreement number RFCR-CT-2009-00004. Assistance from the Spanish Science and Innovation Ministry (CONSOLIDER INGENIO 2010, MAT2010-16194 and Ramon y Cajal research contract of Dr. P. Álvarez) is also acknowledged.

#### REFERENCES

- (1) Baird, C.; Cann, M. *Environmental Chemistry*; 5th Edition, W.H. Freeman and Company: New York, 2012.
- (2) Bosh, H.; Janssen, J. NO<sub>x</sub> removal processes. *Catalysis today* **1988**, 2 (4), 369-531.
- (3) Harter, P. Sulphates in the Atmosphere. *IEA Coal Research*, London, U.K., 1985.

- (4) Couch, G. R. Advanced coal cleaning technology. *IEA Coal Research*, London, U.K., 1991.
- (5) Wakabayashi, A.; Umehara, Y.; Sonehara, H.; Kimura, T. Method for desulphurizing sulphur dioxide containing gas as gas to be treated. Patent JP07241441, **1995**.
- (6) Raymundo-Piñero, E.; Cazorla-Amorós, D.; Linares-Solano, A. The role of different nitrogen functional groups on the removal of SO<sub>2</sub> from flue gases by N-doped activated carbon powders and fibres. *Carbon* **2003**, 41 (10), 1925-1932.
- (7) Davini, P. Adsorption and desorption of SO<sub>2</sub> on active carbon: The effect of surface basic groups. *Carbon* **1990**, 28 (4), 565-571.
- (8) Anurov, S. A.; Keltsev, N.V.; Smola, V.I.; Torocheshnikov, N. S. The Mechanism of the Adsorption of Sulphur Dioxide on Carbonaceous Adsorbents. *Russ. Chem. Reviews (Usp. Khim.)* **1977**, 46, 16-33.
- (9) Li, K.; Ling, L.; Lu, Ch.; Qiao, W.; Liu, Z.; Liu, L.; Mochida, I. Catalytic removal of SO<sub>2</sub> over ammonia-activated carbon fibers. *Carbon* **2001**, 39 (12), 1803-1808.
- (10) Boudou, J.P.; Chehimi, M.; Broniek, E.; Siemieniowska T.; Bimer, J. Adsorption of H<sub>2</sub>S or SO<sub>2</sub> on an activated carbon cloth modified by ammonia treatment. *Carbon* **2003**, 41 (10), 1999-2007.
- (11) Bimer, J.; Salbut, P.D.; Berlozecki S.; Boudou, J.P.; Boniek, E.; Siemieniowska T. Modified active carbons from precursors enriched with nitrogen functions: Sulfur removal capabilities. *Fuel* **1998**, 77(6), 519-525.

(12) Raymundo-Piñero, E.; Cazorla-Amorós, D.; Salinas-Martinez de Lecea, C.; Linares-Solano, A. Factors controlling the SO<sub>2</sub> removal by porous carbons: relevance of the SO<sub>2</sub> oxidation step. *Carbon* **2000**, 38 (3), 335-344.

(13) Bagreev, A.; Rahman, H.; Bandosz, T.J. Study of H<sub>2</sub>S Adsorption and Water Regeneration of Spent Coconut-Based Activated Carbon. *Environm, Sci. Technol.* **2000**, 34 (21), 4587-4592.

(14) Díez, N.; Álvarez, P.; Santamaría, R.; Blanco, C.; Menéndez, R.; Granda, M. Optimization of the melt-spinning of anthracene oil-based pitch for isotropic carbon fibre preparation. *Fuel Processing Technology* **2012**, 93 (1), 99-104.

(15) Berrueco, C.; Álvarez, P.; Díez, N.; Granda, M.; Menéndez, R.; Blanco, C.; Santamaria, R.; Millan, M. Characterization and feasibility as carbon fibre precursors of isotropic pitches derived from anthracene oil. *Fuel* **2012**, 101, 9-15.

(16) Maciá-Agulló, J.A.; Moore, B.C.; Cazorla-Amorós D.; Linares-Solano, A. Activation of coal tar pitch carbon fibres: Physical activation vs. chemical activation. *Carbon* **2004**, 42 (7), 1367-1370.

(17) Raymundo-Piñero, E.; Cazorla-Amorós, D.; Morallón, E. Catalytic oxidation of sulfur dioxide by activated carbon. *Journal of Chemical Education* **1999**, 76, 958-961.

(18) Yokono, T.; Marsh, H.; Yokono, M. Hydrogen donor and acceptor abilities of pitch: <sup>1</sup>H n.m.r. study of hydrogen transfer to anthracene. *Fuel* **1981**, 60 (7), 607-611.

(19) Lee , Y.; Basova , Y.V.; Edie , D.D.; Reid , L. K.; Newcombe , S.R.; Ryu S. P reparation and characterization of trilobal activated carbon fibers. *Carbon* **2003**, 41, 2573-2584.

(20) Vilaplana-Ortego, E.; Maciá-agulló, J.A.; Alcañiz-Monge, J.; Cazorla-Amorós, D.; Linares-Solano, A. Comparative study of the micropore development on physical activation of carbon fibers from coal tar and petroleum pitches. *Micropor. Mesopor. Mater.* **2008**, 112, 125-132.

(21) Marsh, H.; Diez, M.A.; Kuo, K. *Fundamental issues in control of carbon gasification reactivity*, Kluwer Academic Publishers: Dordrecht, Netherlands, 1991.

(22) Beyer, W. H.; Weast, R. C.; Astle, M. J., Eds. *Handbook of Chemistry and Physics* 69th ed.; CRC Press: Boca Raton, Florida, 1992.

(23) Mochida, I.; Kuroda, K.; Kawano, Sh.; Matsumura, Y.; Yo-shikawa, M. Kinetic study of the continuous removal of SO<sub>x</sub> on polyacrylonitrile-based activated carbon fibers. *Fuel* **1997**, 76 (6), 533-536.

**Figure Captions:**

**Figure 1.** (A) SEM images corresponding to the ACF precursor. (B) SEM, (C) BSE and (D) EDX-Co mapping of B, corresponding to the Co-ACF precursor.

**Figure 2.** TG curves of a) cobalt naphthenate, b) parent pitch, c) mixture of pitch containing a 1 wt.% of Co, d) theoretically determined from the cobalt naphthenate and parent pitch curves for a 1 wt.% of Co.

**Figure 3.** (a) QSDFT pore size distributions in ACF and Co-ACF and (b) BJH pore size distribution in Co-ACF.

**Figure 4.** SEM images of (A) ACF and (B) Co-ACF (before removal of cobalt nanoparticles. Inset: amplification).

**Figure 5.** Conductivity as a function of time for the activated samples.



**Table 1.** Chemical composition and surface characteristics of the parent pitch (AOP) as well as undoped (ACF) and doped (Co-ACF) activated carbon fibers.

Sample	Elemental Analysis [wt.%]					pH	Textural Properties				
	C	H	N	S	O		burn-off [%]	S <sub>BET</sub> [m <sup>2</sup> g <sup>-1</sup> ]	V <sub>T</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	V <sub>micro</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	V <sub>meso</sub> [cm <sup>3</sup> g <sup>-1</sup> ]
AOP	92.1	4.2	1.4	0.4	1.9	-	-	-	-	-	-
ACF	93.3	0.4	0.0	0.0	6.3	6.1	36	1294	0.60	0.56	0.00
Co-ACF	93.2	0.4	0.0	0.0	6.4	5.8	50	1098	0.62	0.46	0.25

## SUPPORTING INFORMATION

# Tailoring micro-mesoporosity in activated carbon fibers to enhance SO<sub>2</sub> catalytic oxidation.

*Noel Diez<sup>§</sup>, Patricia Alvarez<sup>§</sup>, Marcos Granda<sup>§</sup>, Clara Blanco<sup>§</sup>, Grażyna Gryglewicz<sup>¥</sup>, Iwona Wróbel-Iwaniec<sup>¥</sup>, Agata Śliwak<sup>¥</sup>, Jacek Machnikowski<sup>¥</sup> and Rosa Menendez<sup>§\*</sup>.*

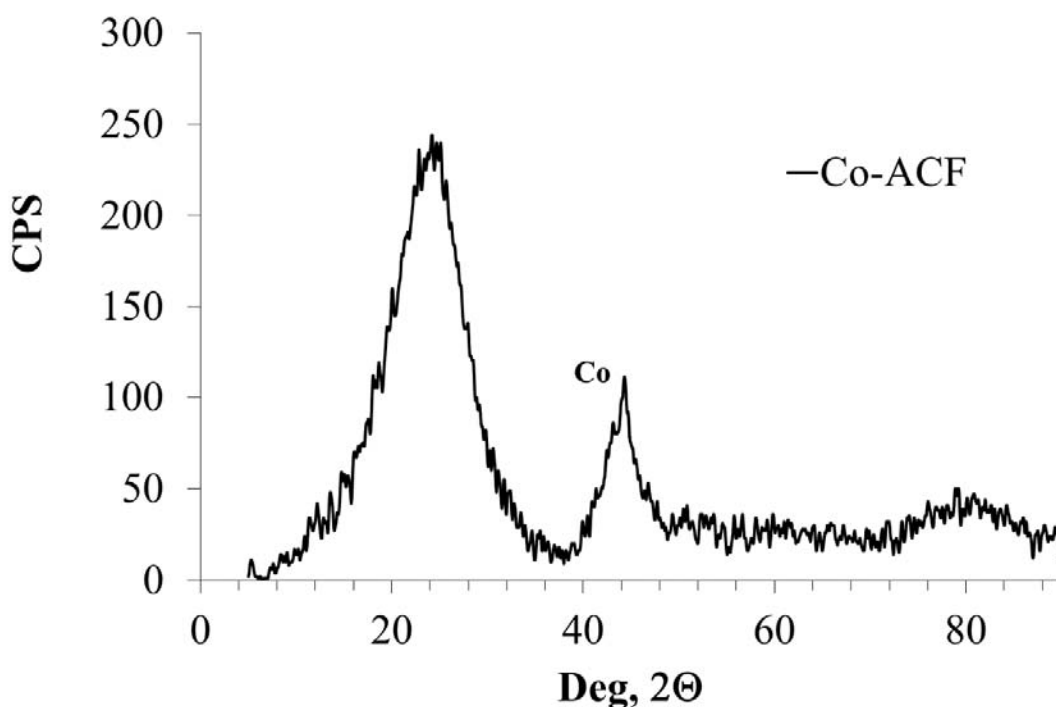
<sup>§</sup>Instituto Nacional del Carbon, CSIC, P. O.Box 73. 33080-Oviedo, Spain.

<sup>¥</sup> Wrocław University of Technology, Division of Polymer and Carbonaceous Materials, Gdańska 7/9, 50-344 Wrocław, Poland

### **1. X-ray diffraction of Co-containing anthracene oil based carbon fibers.**

XRD analyses of pitches and fibers were performed using a Bruker D8 Advance diffractometer. The radiation frequency used was the K $\alpha$ 1 line from Cu (1.5406 Å), with a power supply of 40 KV and 40 mA. The XRD patterns were recorded at steps of 0.02° and intervals of 1 s per step. The XRD patterns obtained for green, stabilized and carbonized fibers containing 1% Co are summarized in Figure S1. The spectra show a peak at around 26° corresponding to the 002 plane of graphite. The band at 42-45° is also ascribed to 110 and 101 planes of graphite. The

peaks corresponding to elemental Co are only visible in the carbonized sample and confirm that the reduction of cobalt naphthenate to elemental Co was achieved at temperatures above those of stabilization.

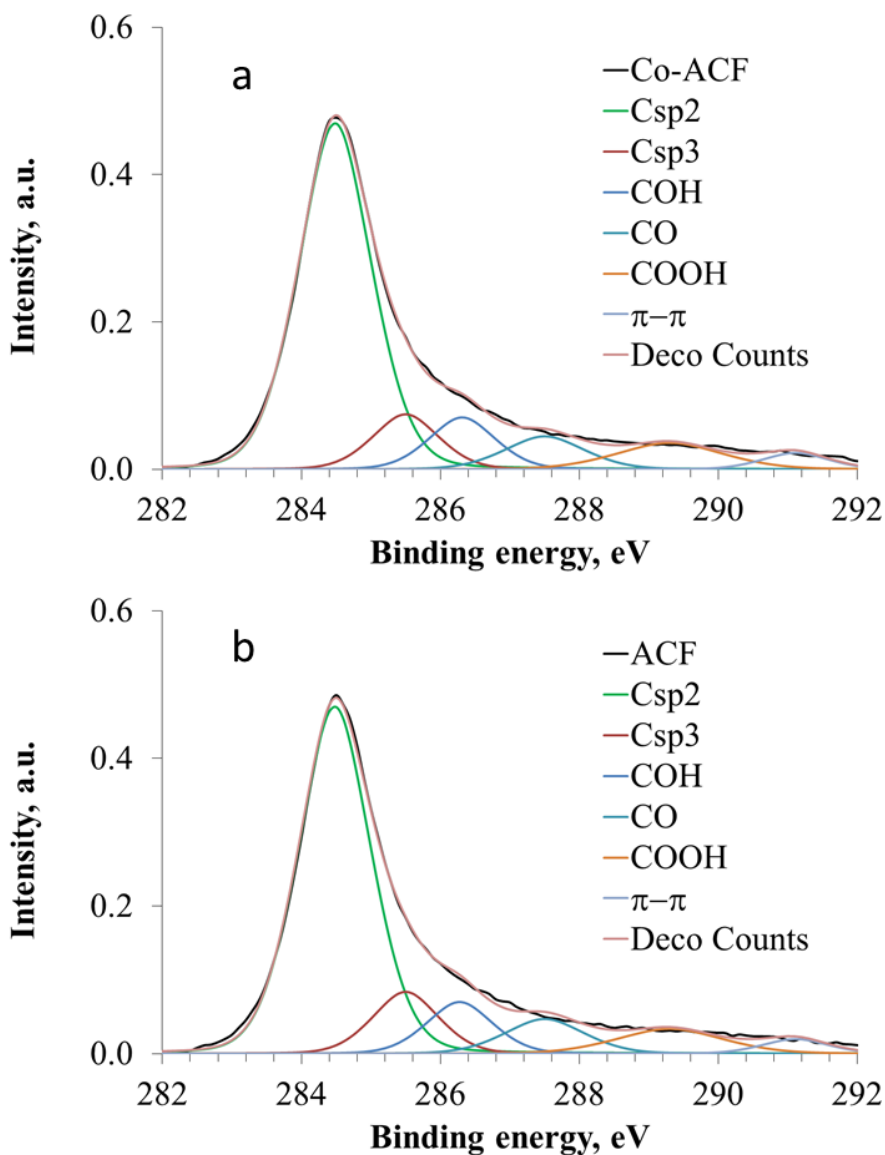


**Figure S1:** X-ray diffraction patterns Co-ACF

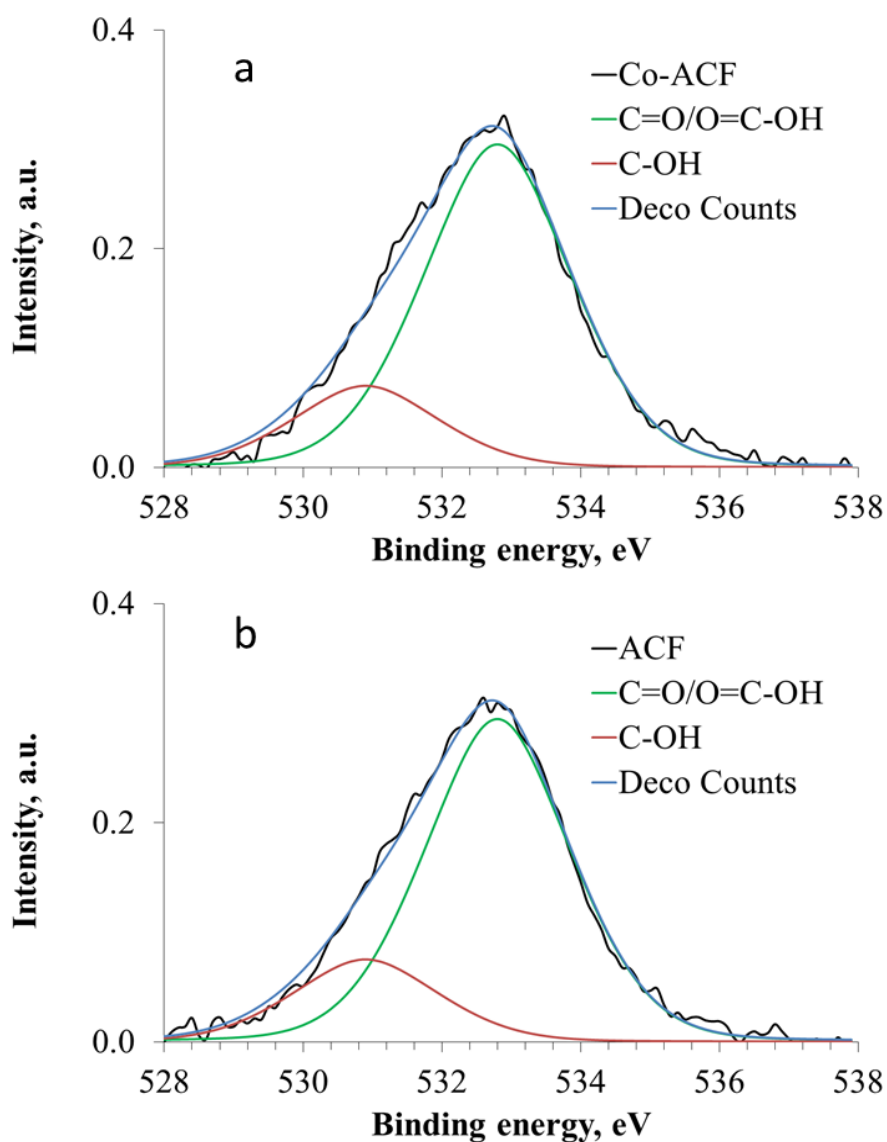
## ***2. XPS C1s curves and corresponding deconvolution curves of ACF and Co-ACF.***

To calculate the functional groups of the samples by means of XPS analysis, the XPS C1s peaks were curve-fitted by combining the components and by minimizing the total square-error fit. Curve fitting of the C1s spectra was performed using a Gaussian–Lorentzian peak shape after performing a Shirley background correction. The resulting spectra show the binding energy of

the C ( $sp^2$ ) at 284.5 eV. The chemical shifts of +1.0, +2.1, +3.0, +4.5 and +5.5 eV were assigned to the C ( $sp^3$ ) hybridisation, COH, CO and COOH functional groups and  $\pi$ - $\pi$  transitions, respectively. [S1,S2] The O1s spectra were curve fitted assuming the peaks at 533eV to be those of C-OH and 530 eV to be those of C=O/O=C-OH. The results are displayed in Figures S2 and S3.



**Figure S2:** C1S Core level high resolution spectra of (a) Co-ACF and (b) ACF.



**Figure S3:** O1S Core level high resolution spectra of (a) Co-ACF and (b) ACF.

[S1] Deng, D.; Pan, X.; Yu, L.; Cui, Y.; Jiang, Y.; Qi, J.; Li, W.X.; Fu, Q.; Ma, X.; Xue, Q.; Sun, G.; Bao, X. Toward N-doped graphene via solvothermal synthesis. *Chem. Mater.* **2011**, *23*, 1188–1193.

[S2] Botas, C.; Álvarez, P.; Blanco, C.; Gutiérrez, M.D.; Ares, P.; Zamani, R.; Arbiol, J.; Morante, J.R.; Menéndez, R. Tailored graphene materials by chemical reduction of graphene oxides of different atomic structure. *RSC Adv.* **2012**, 2, 9643-9650.