

## CHEMICAL ACTIVATION OF FISH-BONE TYPE CARBON NANOFIBERS

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Carbon nanofibers (CNFs) are recognized as one of very promising materials based on its nanostructure and particular properties, being expected in various applications such as, catalysts or catalyst supports, selective adsorption agents and energy storage devices such as, lithium ion second battery or electric double layer capacitor [1].

The most principal disadvantage of CNFs is its low surface area and porosity (around 10-200 m<sup>2</sup>/g). This fact restrict the applications of these materials like hydrogen (or energy) storage or catalyst support; therefore is necessary increase the surface area to improve the yield in these materials.

The surface area can be modifying by means of activation process in which a part of structural carbon atoms are eliminated (mainly, the most reactive) by an activate agent. As consequence, the porosity and surface area increase and so, their applications as hydrogen storage or catalyst support improve.

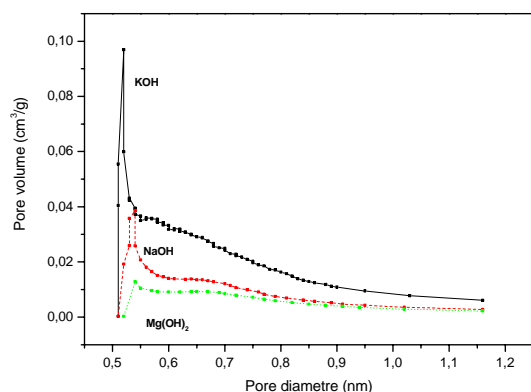
Comparatively to nanotubes, nanofibers present a nanostructure made of grapheme layer stacking which is favourable to activation. There are mainly three types of carbon nanofibers: the fishbone in which the graphene layers are stacked obliquely with respect to the fiber axis; the platelet in which the graphene layers are perpendicular to the fiber axis; and the ribbon in which the grapheme layers are parallel to the growth axis [4].

Chemical activation is an effective method to prepare activated carbon with high surface area from a wide variety of carbon precursors. Chemical activation is characterised by advantages and disadvantages when compared to physical activation by stream or carbon dioxide. To consider advantages, higher yields and more porosity are obtained, and less time is typically required to activate the samples. Key disadvantages include the corrosiveness of the activating compound and the washing stage required.

The present study was aimed to investigate the influence of different activate agents and different inert gases used in the chemistry activation process over the increase of the surface area and porosity of fishbone type CNFs. KOH, KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaOH and Mg(OH)<sub>2</sub> were the chemistry agents used and N<sub>2</sub>, Ar and He the inert gases. The structural changes of the CNFs were investigated by using BET, XRD, TGA and TEM.

Table 1 shows the surface area of the different activated CNFs using helium like inert gas. It can be observed that the KOH increase the surface of CNFs more than other agents (almost 3.3 times the initial area). Mainly, micropores are formed during the activate process. A higher increase in the surface area, lower yield is obtained, due to the collapse and rearrangement of grapheme layers (fibrous form was destroyed) during the activate process [1,2]. Figure 1 shows the micropore size distributions of the different activated CNFs (KOH, NaOH and Mg(OH)<sub>2</sub>). It can be observed that the

surface area always increase after the treatment. On the other hand, cations such as K, Na and Mg have a stronger effect on the development of the surface area because their size (K: 0.22 nm Na: 0.18 nm, Mg: 0.15) [3] permit the intercalation into the interlayer space of the carbon network structure. Finally, the basic character of the activate agents has also a great influence over the surface area increase ( $\text{pH}_{\text{KOH}}$ : 14.7,  $\text{pH}_{\text{K}_2\text{CO}_3}$ : 12.0 and  $\text{pH}_{\text{KHCO}_3}$ : 8.1).



**Table 1.** Surface area and yield to different agents with He

Activate agent <sup>a</sup>	initial CNFs	KOH	NaOH	K <sub>2</sub> CO <sub>3</sub>	KHCO <sub>3</sub>	Mg(OH) <sub>2</sub>
Surface area (m <sup>2</sup> /g)	127	407.5	177.0	261.0	233.0	173.8
Yield (%)	-	55.1	76.2	62.7	67.2	77.5

<sup>a</sup>The activate process was made to 850 °C during 1 h [4].

**Figure 1.** Micropore size distribution of the different activated CNFs

The two XRD analysis parameters, namely the average interlayer spacing  $d_{002}$  and the average stacking height of carbon planes  $L_{c(002)}$ , have been showed in Table 2. The  $d_{002}$  showed just a little change, whereas the  $L_{c(002)}$  decrease when surface area increase. It shows that the mean number of grapheme plans in the crystallites decrease with increasing activation yield [4].

**Table 2.** Surface area and XRD analysis parameters

Activate agent	initial CNFs	KOH	NaOH	K <sub>2</sub> CO <sub>3</sub>	KHCO <sub>3</sub>	Mg(OH) <sub>2</sub>
Surface area (m <sup>2</sup> /g)	127	407.5	177.0	261.0	233.0	173.8
$d_{002}$ (nm)	3.44	3.51	3.46	3.48	3.47	3.46
$L_c$ (nm)	37.25	28.70	35.13	32.59	33.60	35.41

#### References:

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