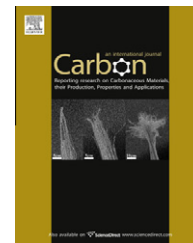


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# Krypton adsorption as a suitable tool for surface characterization of multi-walled CNTs

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## ABSTRACT

Multi-walled carbon nanotubes (CNTs), pristine and subjected to treatments, are comparatively characterized from N<sub>2</sub> and Kr (77 K) adsorption measurements. The CNTs are lab-synthesized by *in situ* chemical vapour deposition of an iron-based organometallic compound at 895 °C. The treatments applied to the CNTs include low temperature gas-phase oxidation, mild temperature annealing and ultrasonic dispersion in ethanol, in an attempt to examine possible changes in adsorption characteristics. N<sub>2</sub> and Kr adsorption measurements give rise to steadily increasing and stepped isotherms, respectively. The former are representative of a multilayer adsorption phenomenon, while the latter indicate successive monolayer condensation. The treatments affect differently gas adsorption capacities of the CNTs. Oxidation leads to CNTs with higher BET specific surface area and increased adsorption capacity, though the effect is more pronounced for Kr adsorption. Ultrasonic dispersion of the CNT brings about a significant reduction only in N<sub>2</sub> adsorption capacity. Modifications in the characteristic steps in Kr adsorption isotherms of the CNTs subjected to annealing can be appreciated, although no remarkable changes are observed in N<sub>2</sub> adsorption isotherms. Present results demonstrate that determination of Kr adsorption isotherms represents a more suitable tool to obtain a more reliable textural characterization of CNTs than does N<sub>2</sub> adsorption.

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## 1. Introduction

Physical adsorption on powdered carbon-based materials offers the opportunity of studying surface properties of a large variety of adsorbates, regardless of the different forms of these solids. Gas adsorption studies are furthermore of great interest in determining the morphology of a huge variety of industrially important porous materials. From the adsorption point of view, the possible uses of carbon nanotubes (CNTs) cover many different applications, including gas purification

and storage, heterogeneous catalysis, and nanowire manufacture [1–4]. Physisorption on CNTs corresponds to an intermediate situation between disordered substrates, such as activated carbons, and uniform surfaces approaching the ideal case of a crystalline plane without defects, such as exfoliated graphite. Since the nanotube surface is closely related to that of graphite, the adsorption properties of which have been extensively studied, it can thus be taken as a reference to determine qualitatively, from the comparison between the adsorptive properties on those two substrates, the degree

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of CNT crystallinity. Particularly, Kr adsorption isotherms measured on exfoliated graphite exhibit vertical steps, representative of successive monolayer condensation [5].

Most studies in the literature have examined gas adsorption on single-walled CNTs and only a few have been concerned with multi-walled CNTs. In particular, research concerning N<sub>2</sub> adsorption on multi-walled-CNTs (MWCNTs) has been focused on relatively thin MWCNTs produced by different synthesis methods for fixed experimental conditions and/or using commercial samples. BET specific surface areas varying between 20 and 300 m<sup>2</sup> g<sup>-1</sup> have been reported from N<sub>2</sub> adsorption measurements [6–9]. Besides, previous own results have shown that the degree of alignment of nanotubes forming the arrays of MWCNTs plays a key role in N<sub>2</sub> adsorption. A reduction in BET specific surface area of MWCNTs was achieved after the rupture of their self-aligned structure by ultrasonic dispersion [9]. On the other hand, to the best of our knowledge, only a few couple of studies have been concerned with adsorption of Kr on CNTs, exclusively examining pristine single-walled CNTs or thin multi-walled CNTs [7,10,11].

Within this context, the present work deals with N<sub>2</sub> and Kr adsorption on both as-synthesized multi-walled CNTs and further subjected to different treatments. Comparison of results enables to deepen knowledge on their textural characterization by adsorption of different gases as well as to analyze the effect of treatments on the surface properties of the CNTs.

## 2. Experimental section

### 2.1. Synthesis of CNTs

Self-oriented multi-walled CNTs were lab-synthesized by catalytic chemical vapour deposition under flowing Ar/H<sub>2</sub>, by using analytical grade iron (II) phthalocyanine (C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>Fe) as precursor, according to the technique described in [12]. Briefly, CNT synthesis was carried out in a semi-continuous quartz tubular reactor (20 mm-inner diameter, 1000 mm-length) of horizontal configuration under accurately controlled flow of H<sub>2</sub> and Ar. The reactor was externally heated by a two-zone furnace commanded by independent programmable temperature controllers. Experiments were carried out at a reaction temperature of 895 °C, under a total gas flow rate of 30 cm<sup>3</sup> (STP) min<sup>-1</sup>, H<sub>2</sub> molar fraction of 0.5, and total reaction time of 90 min. The CNTs were deposited on the reactor walls and on quartz substrates conveniently placed in the reactor. They were separated by scratching the surface of the walls or substrates. As reported earlier, the lab-synthesized CNTs have a length between 16 and 20 μm, and are built by individual nanotubes with inner and outer average diameters of 24 and 50 nm, respectively [9].

### 2.2. Treatments of the synthesized carbon nanotubes

Oxidation was performed according to the procedure reported earlier [12], by treating a batch of the as-synthesized CNTs (CNTs-P, P for pristine) in an O<sub>2</sub> atmosphere (O<sub>2</sub> molar fraction of 0.10) at 375 °C for 90 min, using the same set-up employed

for the synthesis. The oxidized CNTs are denoted as CNTs-O (O for oxidized). It should be emphasized that many works in the literature concerned with gas-phase oxidation of CNTs have mainly involved pure air (i.e. O<sub>2</sub> molar fraction of 0.21), as oxidation agent. These conditions, however, have led to an over-oxidation of CNTs, often causing severe damage to the CNTs, in addition to removing the amorphous carbon and other impurities, thus resulting in low yields of the oxidized CNTs [13].

Besides, a batch of the pristine CNTs was annealed at 1000 °C during 120 min under N<sub>2</sub> atmosphere in the same set-up employed for the synthesis, in order to reduce the amorphous C structures. The resulting CNTs are indicated by CNTs-A (A for annealed). On the other hand, to further compare the effect of alignment on Kr adsorption characteristics of the CNTs with previously reported own results [9], small amounts of the as-synthesized CNTs were dispersed in ethanol. The dilute dispersions were subjected to ultrasonication at room temperature for 120 min. Afterwards, ethanol was eliminated by evaporation, and the samples were dried at 100 °C overnight up to constant weight. These samples are labelled as CNTs-S (S for sonic).

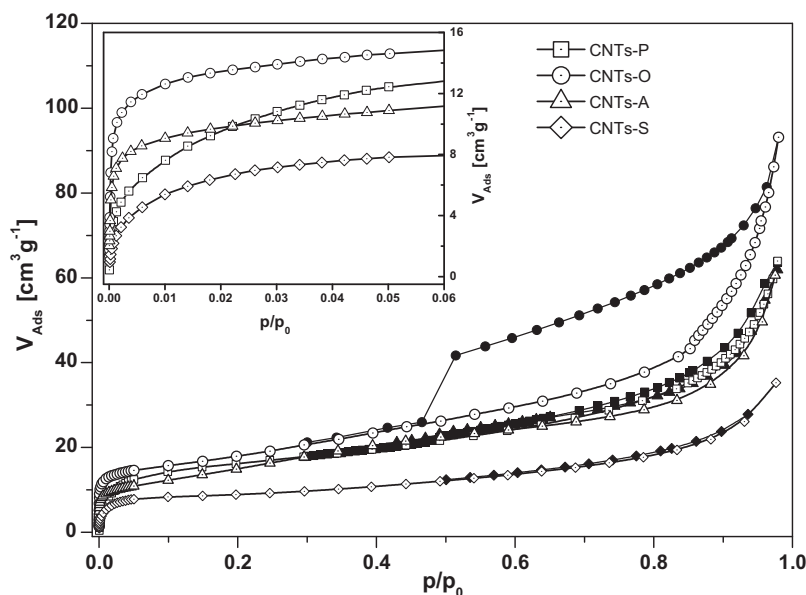
### 2.3. Characterization of the as-synthesized and post-treated carbon nanotubes

The pristine and post-treated CNTs were examined by scanning electronic microscopy using a Quanta 250 SEM instrument. N<sub>2</sub> and Kr adsorption measurements at (77 K) were conducted to determine the adsorption characteristics of the as-synthesized CNTs, without any further treatment, and the post-treated CNTs. N<sub>2</sub> adsorption-desorption isotherms were carried out using a Micromeritics ASAP 2020 HV surface analyser and Kr adsorption isotherms were determined with a CE Instruments Sorptomatic 1990 surface analyser. All the samples were overnight outgassed in vacuum at 250 °C to constant weight. Triplicate measurements were carried out for each sample and average values of the S<sub>BET</sub> specific surface are reported.

## 3. Results and discussion

Fig. 1 shows N<sub>2</sub> adsorption-desorption isotherms for the CNTs, pristine and subjected to treatments. Volumes of gas adsorbed at standard temperature and pressure conditions (STP) per sample mass unit (V<sub>ads</sub>) are represented as a function of the relative pressure ( $p/p_0$ ), where  $p$  is the equilibrium pressure and  $p_0$ , the saturation pressure of the adsorbate at 77 K. Differences in N<sub>2</sub> adsorption capacity may be noticed, depending on the treatment applied to the lab-synthesized CNTs.

The shape of the N<sub>2</sub> adsorption isotherms for the pristine CNTs, exhibits features of Type II adsorption isotherms according to IUPAC classification, with a sharp increase as the relative pressure approaches unity (Fig. 1). It agrees with some other reported results [9,14]. The gradual increasing adsorption in the relative pressure range between 0.05 and 0.80 generally takes place on solids with primarily mesoporous (2–50 nm) or macroporous (>50 nm) structures. The stea-



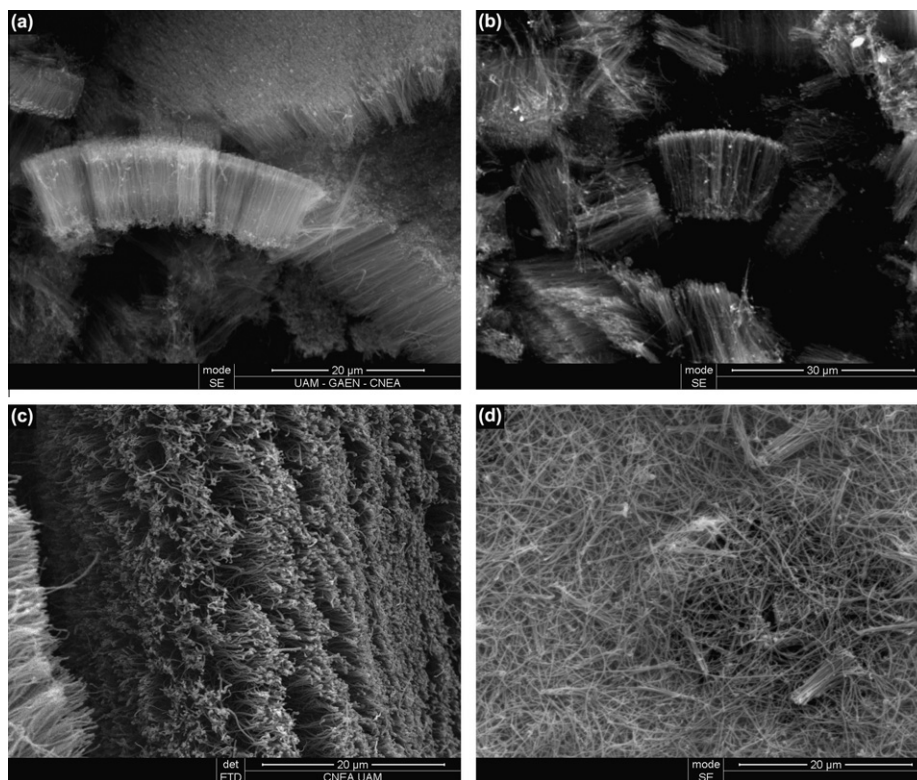
**Fig. 1** – Effect of treatments on  $N_2$  (77 K) adsorption–desorption isotherms for the lab-synthesized self-aligned CNTs (CNTs-P) and further subjected to oxidation (CNTs-O), thermal annealing (CNTs-A) and ultrasonic dispersion in ethanol (CNTs-S). The inset magnifies the low pressure range. In all cases, the size of the symbol (open symbols: adsorption, closed symbols: desorption) is representative of the size of the error bars.

dily increased adsorption of  $N_2$  is related to the multilayer adsorption phenomenon on the surface of an adsorbent, i.e. the gradually increased film thickness of  $N_2$  and likely capillary condensation in some mesopores [15]. Adsorption and condensation of  $N_2$  occur in the relative pressure range of 0.95–0.98, that correspond to the largest pores. As seen in Fig. 1, even though the treatments may affect the volumes of  $N_2$  adsorbed, the shape of the isotherms remains similar to that determined for the pristine CNTs. The  $N_2$  volumes adsorbed on the ultrasonicated samples significantly decrease over all the range of relative pressures, attributable to the pronounced loss of alignment of the CNTs. The loss of alignment results in a reduction of the number of interstices between the individual nanotubes; moreover, it has also to be stressed that the outer surface of non-touching nanotubes has a positive curvature, which is very unfavourable for adsorption [9,16]. The loss of alignment of the individual nanotubes forming the arrays of CNTs can be appreciated in Fig. 2(a) and (d). On the contrary, oxidation of the CNTs leads to slightly enhance  $N_2$  adsorption capacity over the whole range of relative pressures. In view of the fact that the degree of alignment of the individual CNTs forming the arrays is the key factor in  $N_2$  adsorption [9] and that, for the oxidized sample, it remains similar to that for the pristine CNTs (Fig. 2(b)), the slight increase in  $N_2$  volume adsorbed would be related to the creation of new adsorption sites accessible to  $N_2$  and/or to the opening of previously closed CNTs.  $N_2$  adsorption occurs mainly by capillary condensation in the interstitial spaces between individual neighbouring carbon nanotubes. Hence, despite intratube spaces become available to adsorb  $N_2$  after oxidation, the amount of  $N_2$  adsorbed at the low pressure range does not vary considerable due to their relatively large size compared to interstitial spaces. Comparing the  $N_2$  adsorption isotherm obtained for the CNTs subjected to the

annealing treatment with the one for the pristine samples, no significant differences can be appreciated (Fig. 1). As seen, both adsorption isotherms show similar shapes and volumes adsorbed, indicating that  $N_2$  adsorption would not be a completely reliable tool in order to characterize the surface of the individual nanotubes making up highly-ordered CNTs (Fig. 2(a) and (c)).

The specific surface areas were evaluated applying the BET model and considering that the area occupied by a nitrogen molecule is  $0.162 \text{ nm}^2$ . Straight lines over the range of relative pressures 0.03–0.20 with high correlation coefficients ( $r^2 \geq 0.99$ ) for which the BET model is valid were obtained in all cases. Estimated values of  $S_{\text{BET}}(N_2)$  are listed in Table 1. The standard error was less than 5% in all cases.

Furthermore, the Kr adsorption isotherms of the pristine and post-treated CNTs are shown in Fig. 3. All isotherms exhibit two steps, and correspond to Type VI according to IUPAC classification. Nevertheless, the treatments applied to the pristine CNTs lead to appreciable modifications in the Kr adsorption capacity. The Type VI adsorption isotherms correspond to the successive formation of monolayers on uniform or quasi-uniform (Q-U) surface patches as when the pressure is progressively increased. Interestingly, the monolayer condensation phenomenon occurs only on surfaces that are smooth at the atomic level. The influence of surface smoothness has been demonstrated by studying annealed graphitic samples [17], and this has also been recently analyzed theoretically by non-local density theory [18]. In the case of multi-walled carbon nanotubes, the uniform surface is thought to be the crystalline outer surface of the tubes, as opposed to the amorphous impurities that may also be present in the samples. The shape of the steps and the slope of the plateaux between them are related with the extent of non-crystalline-like (NCL) regions in the sample; the more rounded are the



**Fig. 2 – Effect of treatments on morphological characteristics of lab synthesized CNTs at 895 °C. SEM images of: (a) pristine CNTs (CNTs-P), (b) CNTs-P after being subjected to low temperature oxidation (CNTs-O), (c) CNTs-P after applying a mild temperature annealing (CNTs-A) and (d) loss of alignment in CNTs-P after ultrasonic dispersion in ethanol (CNTs-S).**

steps and the more increased is the slope, the larger the extent is [19]. These steps are neither vertical nor are the plateaux between the steps completely horizontal, pointing to the existence of some NCL regions in the CNTs. Accordingly, it is apparent that the physical constitution of the surface of the CNTs may be considered as composed by two different kinds of structures. In Q-U patches, the Kr adsorption phenomenon would occur as monolayer condensation at certain pressure (resulting in stepped adsorption isotherms with quasi-vertical steps and horizontal plateau between them), whereas in the NCL regions, it would occur as a multilayer adsorption phenomenon on the surface as the pressure is increased (resulting in steadily increased adsorption isotherms).

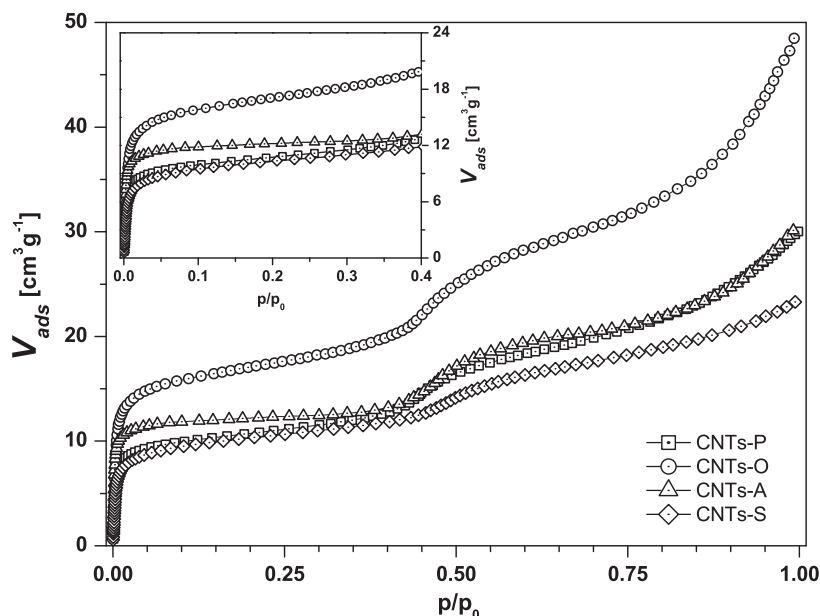
Considering the effect of the treatments over the adsorption capacity of the CNTs, the Kr volumes adsorbed on the ultrasonicated samples slightly decrease over all the range of relative pressures, suggesting that no capillary condensation takes place in the interstitial volumes present in the CNTs. This should imply that the degree of alignment of the

individual nanotubes in the multi-walled CNTs is not the key factor in Kr adsorption, as it is in N<sub>2</sub> adsorption [9]. Furthermore, the oxidized samples exhibit a noticeable increase in Kr adsorption capacity over all the range of relative pressures in comparison with the pristine CNTs. As shown in Fig. 4, the volume of Kr adsorbed by the oxidized sample at each relative pressure tends to be proportional to that adsorbed by the pristine CNTs at the same relative pressure. This indicates that the gain in the Kr adsorption capacity would be related to an increase in the available surface that maintains similar surface characteristics to that of the pristine CNTs, thus meaning a similar ratio between the extents of Q-U patches and NCL regions. The opening of the CNTs is produced by the oxidation treatment and the inner surfaces of the hollow nanotubes, which have the same surface characteristics than the outer ones, are exposed. Besides, as mentioned above, the degree of alignment of the individual nanotubes on the oxidized arrays remains similar to that of the pristine ones (Fig. 2(b)). Therefore, the inner surfaces of the partially opened CNTs should be the main cause of the increase in the Kr volumes adsorbed over all the range of relative pressures. An improvement of the adsorption capacity of the original surfaces by reduction of the extent of NCL regions would result in a reduction of the multilayer adsorption phenomenon, leading to the loss of proportionality between the volumes of Kr adsorbed by the two samples.

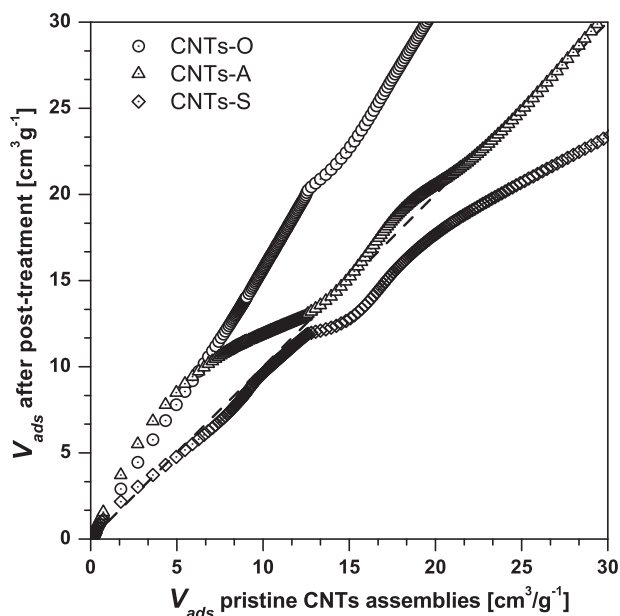
In the case of the Kr adsorption isotherms of the annealed CNTs, the slope of the plateau between the steps differs from the one of the pristine sample. In Fig. 3, it can be appreciated

**Table 1 – Specific surface area estimated values for the pristine and post-treated CNTs.**

Sample (m <sup>2</sup> g <sup>-1</sup> )	CNTs-P	CNTs-O	CNTs-A	CNTs-S
S <sub>BET</sub> (N <sub>2</sub> )	56.4	62.3	55.2	32.0
S <sub>Kr</sub>	35.4	55.4	41.8	35.0



**Fig. 3** – Effect of treatments on Kr (77 K) adsorption isotherms for the lab-synthesized self-aligned CNTs (CNTs-P) and further subjected to oxidation (CNTs-O), thermal annealing (CNTs-A) and ultrasonic dispersion in ethanol (CNTs-S). The inset magnifies the low pressure range. In all cases, the size of the symbol is representative of the size of the error bars.



**Fig. 4** – Representation of the volume of Kr adsorbed at each relative pressure by oxidized (CNTs-O), thermal annealed (CNTs-A) and ultrasonic dispersed in ethanol (CNTs-S) CNTs in comparison with that adsorbed by the as-synthesized sample. The slope of the dash line is equal to 1.

that the slope of the plateau is lower than the one associated with the pristine sample, with a better approach to a horizontal line. The annealing at 1000 °C would reduce the extent of the NCL regions of the CNTs, changing the shape of the steps and the slope of the plateau between them in the Kr adsorption stepped isotherms. Since the ratio between the Q-U patches and the NCL regions on the surface of the annealed

CNTs is apparently different from that of the pristine sample, there is no longer a proportional relation between the volumes of Kr adsorbed by the annealed and pristine samples at each relative pressure, as observed in Fig. 4.

The Kr specific surface areas ( $S_{Kr}$ ) were evaluated by means of the volume of the monolayer of Kr adsorbed ( $v_m$ ) [17]. As mentioned before, it can be considered that Kr adsorption isotherms arise from the contribution of two different types of isotherms: a stepped adsorption isotherm with horizontal plateaux between steps, and a steadily increased adsorption isotherm. Therefore, the first step of the Kr adsorption isotherms, in the range of relative pressures below 0.35 ( $p/p_0 < 0.35$ ) (inset of Fig. 3), was fitted with a two terms mathematical expression, one related with the layer by layer adsorption phenomenon, and the second with the multilayer phenomenon. The following mathematical expression was used:

$$V_{ads} = v_m \cdot f_1(p/p_0) + f_2(p/p_0) \quad (1)$$

where  $f_1(p/p_0)$  represents a normalized step function, and  $f_2(p/p_0)$ , a growth exponential expression [17]. The Kr specific surface areas were then evaluated by considering the values of  $v_m$  obtained as a parameter from (1), and that the area occupied by a krypton molecule is 0.147 nm<sup>2</sup>. Estimated values of  $S_{Kr}$  are also listed in Table 1. The standard error was less than 5% in all cases. As seen in Table 1, lower  $S_{Kr}$  values than those of  $S_{BET}(N_2)$  are estimated in all cases.

#### 4. Conclusions

Adsorption of N<sub>2</sub> and Kr on lab-synthesized highly oriented CNTs, pristine and subjected to different thermal and/or dispersive treatments, has been comparatively examined. According to IUPAC classification, N<sub>2</sub> adsorption isotherms

are Type-II and Kr adsorption ones are Type-VI (stepped isotherms), the shapes being held even after applying the treatments to the pristine CNTs. N<sub>2</sub> and Kr gases exhibit a remarkably different interaction with the CNTs. While the degree of alignment of the individual CNTs, namely the outer interspaces between neighbouring nanotubes, plays a key role in N<sub>2</sub> adsorption, the characteristics inherent to the surface of the CNTs are crucial in Kr adsorption.

Present results show that N<sub>2</sub> adsorption isotherms are slightly modified after applying the thermal treatments, while a pronounced decrease of the volume of N<sub>2</sub> adsorbed all over the range of relative pressures is achieved after the dispersion of the as-synthesized CNTs. On the other hand, the Kr adsorption isotherms corresponding to both, the as-synthesized and the dispersed CNTs, are rather similar, although appreciable differences are observed after the pristine CNTs are subjected to the thermal treatments. Low temperature oxidation leads to an opening of the individual CNT increasing the volume of Kr adsorbed in the hollow surface, maintaining the shape of the steps and the plateaux between them. In opposition, the mild temperature annealing introduces surface modifications that lead to changes in the shape of the steps and the slope of the plateaux between them. Overall, the present work demonstrates that Kr adsorption isotherms represent a more complete tool to perform surface characterization of multi-walled CNTs than N<sub>2</sub> adsorption ones.

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