Description of chemically and thermally treated Multi-walled Carbon Nanotubes using sequential decomposition of adsorption isotherms

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The effect of wet acid oxidation by means of sulfuric/nitric mixtures, and high-temperature treatment of commercial arc-discharge synthesized multi-walled carbon nanotubes (MWCNTs) was studied. In order to analyze the adsorption capacities of differently trated MWCNTs, we employed a multistep method that considers separately different pressure ranges (zones) on the experimentally obtained isotherms. The method is based on simple gas isotherm measurements (N_2, CO_2, CH_4, etc.). Low pressure ranges can be described using Dubinins model, while high pressure regimes can be fitted using different models such as BET multilayer and Freundlich equations. This analysis allows elucidate how different substrate treatments (chemical and thermal) can affect the adsorbate-adsorbant interactions; moreover, theoretical description of adsorbate-adsorbate interactions can be improved if a combination of adsorption mechanisms are used instead of a unique model. The results hereby presented show also that, while MWCNTs are a promising material for storage applications, gas separation applications should carefully consider the effect of wide nanotube size distribution present on samples after activation procedures.

Keywords: Multi-walled carbon nanotubes; adsorption steps; isotherm decomposition; nitrogen adsorption; acid oxidation treatment; thermal treatment.

1. Introduction

Apart of great number of closed end tubes, pristine multi-walled carbon nanotubes (MWCNTs) samples contain, several kinds of heterogeneities: (i) other graphitic or carbon phases, like fullerenes, amorphous carbon, etc.; (ii) impurities such as residual metallic catalysts, often protected by more or less graphitized carbon shells; (iii) surface defects at the MWCNT surface or oxygenated grafted functions, (iv) aggregation into bundles [1,2]. These heterogeneities represent a major obstacle for both establishment of universal behavior, and development of optimized processing methods for material synthesis and purification. After synthesis, and in order to improve the MWCNTs quality, many purification procedures are usually applied, all of them having the following three main steps [3,4]. Sample is first subjected to an oxidation treatment, either wet using H_2O_2,, or dry with high temperature air, these processes remove carbon impurities and weaken carbon shells protecting residual catalytic particles that

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become then accessible for a subsequent wet treatment. The last step consists of a reflux wet acid oxidation generally carried with a nitric/sulfuric mixture, which produces a considerable amount of surface acid and carboxylic groups. A final high temperature treatment step is applied in order to remove the above mentioned surface groups and to restore the MWNT structure. Each step has its own pros and cons; e.g., among the various wet acid treatments proposed in the literature [5-9], the relatively simple and popular nitric/sulfuric acid reflux procedure above mentioned can open nanotubes closed-caps, and also remove most of the metal catalysts from the arc discharge synthesized samples. However, it is less effective with respect to the elimination of graphitic impurities, so the purity of the resulting sample after such process is still limited [10-14]. It was also reported that reflux can also induce wall damage in the tubes [15], therefore, removing the carbon-coated residual catalyst without this undesired effect remains a challenging problem. The two above described steps of purification can have opposite consequences, the wet acid treatment can obviously enhance gas uptake, while high-temperature treatment can only slightly reduce it [16,17]. As was pointed out, wet acid treatment removes impurities and open closed-caps of nanotubes; however, it also greatly increases the number of surface oxygenated groups. By studying the adsorption of simple gases in the case of MWCNTs produced by chemical vapor deposition, some authors have proposed [16], in order to complete the removal of impurities, severe heat treatments, which may slightly reduce the adsorption capacity. The adsorption of simple gases on single walled carbon nanotubes (SWCNTs) has been studied for the past several years [18,19], and applications often have involved gas storage, and purification of gas mixtures. The first linked to energetic interests, and the second related to greenhouse effect gases. In the analysis and characterization of solid adsorbents, we can mention a method developed some time ago [20], which take into account all physical processes occurring during adsorption. This procedure considers that, when pressure increases, adsorption takes place through a number of different mechanisms that can be in turn associated with a characteristic onset pressure (trigger pressure). After having determined the mechanism of adsorption corresponding to the

first pressure range studied, together with its associated (partial) isotherm, it has to be subtracted from the experimental isotherm. The next step is to use the curve obtained after subtraction, and to apply the same procedure in order to determine the adsorption mechanism corresponding to the second pressure range considered. This procedure can be sequentially repeated until a prescribed level of accuracy for isotherm description is reached for a given number of adsorption mechanism components. This method was applied to characterize carbon blacks and activated carbons by using adsorption isotherms of simple gases, and also could be applied to others solids substrates among them MWCNTs, characterized by having an heterogeneous population of adsorption site types. The paper is organized as follows; first the characteristics of samples, and the experimental methods used are described. Results for adsorption of Nitrogen over MWCNTs at 77 K are discussed in terms of a mechanism including several steps. The results are corroborated both by additional experimental information, as well as through the pore size distribution calculations. Finally, despite the use of only Nitrogen as gas probe, we can characterize the effect of different methods usually employed to open MWCNTs. For example; changes on adsorption capacity, or (supported by pore size distribution calculations) to determine if MWCNTs would be an appropriate substrate for gas mixture separation applications.

2. Experimental Part

All reagents used for oxidation treatment were of analytical grade. MWCNTs, produced by arc discharge, were provided by Nano Craft Inc (about 30 - 40% purity, with onion-like and polygonal nanoparticles, with 5-20 nm diameter and 300-2000 nm length). A process of three-stage acid oxidation and thermal treatment, was applied to the MWCNT sample. It can be summarized as follows: i) 4 hours room temperature sonication in 6 M HNO_3. Filtration with 0.22 mm polycarbonate Millipore membrane with distilled water until neutral pH, and dried under vacuum. ii) 4 hours reflux at 120 C in a mixture (3:1) H_2SO_4/HNO_3; followed by filtration and drying as described above. iii) 6 hours of thermal treatment. The samples were heated up to 500 C slowly in 240 min and maintained for

6 h, and then cooled down to room temperature. This procedure constitutes a pre-treatment process, since it can only remove unreacted metal catalyst (in case MWCNT were produced using chemical vapor deposition (CVD) [17]), and temperatures reached are below values required to eliminate completely the amorphous carbon present. MWCNTs used in this study do not contain such amorphous carbon impurities (as confirmed by thermogravimetric analysis (TGA) experiments), but in order to compare present results with previous reports, the complete three-step process was applied. The efficiency of the entire operation was ≈15-20 % mass loss. The goal of purification of the MWCNTs is removal of all the impurities present (i.e., amorphous carbon, multi shell carbon, and metal catalyst). Ideally, this should not cause significant damage to the nanotubes. TGA experiments carried previously for identical samples demonstrate the absence of amorphous carbon for the untreated MWCNTs; but after purification treatment, results indicate the appearance of surface defects and/or amorphous carbon as demonstrated by the weight loss corresponding to temperature ranges of 200 - 600 C. The gas phase isotherms were volumetrically determined employing Pyrex conventional equipment. Equilibrium isotherms for the adsorption/desorption of nitrogen, were measured at 77 K, on as-produced, and both chemically and thermally treated MWCNT samples.

3. Multi-stage adsorption process on aggregated MWCNTs

In order to describe the adsorption process on highly heterogeneous substrates one has two basic problems. First, the complexity of the substrate does not allow the use of a single theory, i.e. choosing between two models, such as BET or Dubinin, makes no sense, because an approach may be appropriate just for certain parts of the adsorption process. For instance, each CNT class has a wide variety of adsorption sites and therefore there will be multiple adsorption mechanisms that should be considered in particular [21-24]. Second, the growing interest in studying the adsorption at high-pressures makes it necessary to search for new tools for a theoretical description in a wider pressure range. Some time ago it was proposed an alternative method that allows one to describe and analyze the characteristics of

many solid adsorbents, based on a phenomenological point of view [20]. While the original proposal was limited to carbon blacks and activated carbons, as examples of homogeneous and heterogeneous solids respectively, it was also considered that carbon nanotubes could be suitable adsorbents to apply this technique. The description of isotherms, instead of being associated with parameters obtained from theoretical models established a priori, is based on the physical processes that really take place throughout the adsorption. Each of these processes corresponds to an adsorption mechanism that starts at a certain pressure, in other words each process has an associated trigger pressure. So after having determined the first adsorption mechanism, with this trigger pressure, it has to be subtracted from the original isotherm. Then the same task is repeated with the isotherm that was left from the previous subtraction, and so on. From this multi-step adsorption description the resulting decomposition equation is:

$$V(p,T) = \sum_{i=1}^{n} V_i(x,T,C_{i,k}) \qquad (1)$$

where $V(p,T)$ is the volume occupied by the adsorbate on the surface at a pressure p and temperature T, and x is the relative pressure ($x = p/p_0$, where p_0 is the pressure when the bulk vapor is saturated). The parameters $C_{i,k}$ can be associated with the substrate geometry (i.e., related to the V_i scale) or with the interaction energy of adsorbed molecules (i.e., related to the $RT \log p$ scale); in other words, the parameters $C_{i,k}$ tell us not only about the surface structure but about the adsorption mechanism. Ambiguities may occur; e.g., some $C_{i,k}$ can depend on the temperature, but comparing the different values obtained from isotherms at different temperatures provide additional information on the adsorption mechanism and the surface structure itself. The nitrogen adsorption isotherm for MWCNTs can be divided into four different stages [16,20], as shown in Figure 1.
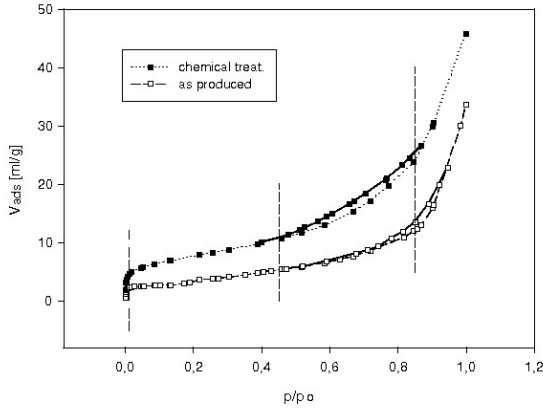
Fig. 1.   Adsorption-desorption isotherm of Nitrogen at 77 K of both as-produced and treated MWCNT samples, show different hysteretic behavior.
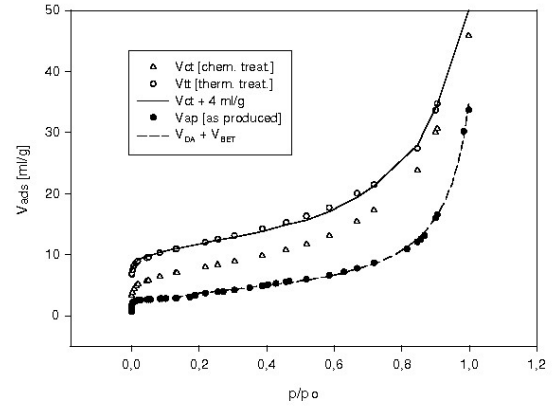

Fig. 2.   Nitrogen adsorption isotherms over MWCNT as produced and chemically, and chemically plus thermally treated. Treated MWCNT isotherms differ by a constant shift ($\approx 4 \, ml/g$), but showing same behavior. Untreated MWCNT isotherm is adjusted by adding Dubinin-Astakhov and BET equations, at low and high pressure respectively.

Part I ($p/p_0 < 0.01$) is the typical type I isotherm, characterized by a rapid increase in ultra low pressure ranges. This process occurs in pores of molecular dimensions, so it confirms the presence of these pores in the samples of MWCNTs. Nitrogen molecules with diameter of about 0.364 nm, can fill these pores at ultra-low pressures. In Figure 2, the isotherms of as-produced, chemically treated, and chemically followed of thermally treated MWCNTs samples are compared; at very low pressures ($p/p_0 < 0.01$), MWCNTs have the same qualitative behavior differing only in a constant shift. Considering that ultra-low pressures characterize the filling process of molecular dimensions pores; the isotherm reflects that, thermal treatment MWCNTs, basically improves the adsorption capacity of very small pores. When the adsorption, at ultra-low pressures, is in fact a micropore-filling process, isotherms can be described by Dubinin-Astakhov equation (DA);

$$V_I(x, T, C_{i,k}) = C_{11} \exp\left(-RT/C_{12} \ln(1/x)^{1/C_{13}}\right)$$
$$(2)$$

Two of Dubinin-Astakhov parameters, i.e., the characteristic adsorption energy $E_0 = C_{12}/\beta$ (the affinity coefficient β depends on the adsorptive, $\beta = 0.33$ for N_2; $\beta = 0.35$ for CH_4), and the heterogeneity factor C_{13}, have almost the same value, $E_0 = 16 \, kJ/mol$ and $C_{13} = 3.53$, but the micropore volume, C_{11}, are 2.69, 4.36 and 8.33 ml/g, corresponding to untreated MWCNTs, and after chemical and thermal treatments, respectively. Considering the Weibull statistical function, associated to the DA isotherm, the heterogeneity factor $C_{13} = 3.53$ gives the energy distribution as a well defined Gaussian curve, indicating the homogeneous nature of these nanotubes adsorbants. Micropore volumes show an increase of 60% after chemical treatment and a further 90% after heating process. These results not only confirm that purification process removes some of the end caps of the nanotubes of very small dimensions, with diameters lower than 10 nm (which confirms the results obtained from isotherms, see comparison of MWCNT TEM images presented in Fig. 3; but also allows for a quantification of the effectiveness of both treatments. It is well known [5] that raw materials generated by the developed methods to obtain MWCNTs, produce a large amount of amorphous carbon as well as carbon nanotubes. In addition, after the first purification processes (by acid

treatments), to remove most of the present impurities, it is required a burning process, to eliminate the rest of the remaining non-nanotube materials. The aim of burning acid-treated materials is to purify MWCNTs based on the difference of oxidation temperature between CNTs and non-nanotubes. Because atom sheets in CNT are formed by sp2,6 bond, the oxidation temperature is higher [25] than that of amorphous carbon. Therefore, to purify MWCNTs with high quality and no damage, a burning temperature in air around 500 C, was found experimentally [26].
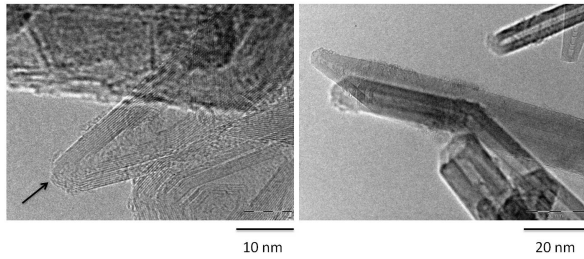

Fig. 3. TEM image of synthesized MWCNT (right), where a variety of nanotube sizes can be observed, and also shows MWCNT with closed ends; and the respective image to sample after acid treatment (left) with an example of the opened ends as is indicated with a black arrow.

A closer inspection of TEM images of as-produced sample reveals that the carbon nanotubes dimensions are roughly, 5 20 nm diameter and 100 2000 nm long; while a great majority shows capped ends. A careful comparison with as-produced sample reveals partial opening of the originally closed ends.

Part II pressure range of the isotherm ($0.01 < p/p_0 < 0.45$) shows a process of surface adsorption (monolayer formation), in which the amount of adsorbed nitrogen grows slowly. From Figure 2 we note that, beyond very low pressures, the isotherms resulting from both treatments differ only in a shift of approximately 4 ml/g, which tell us that the heat treatment does not cause ulterior damages in MWCNTs, and 4 ml/g can be nicely correlated to the difference between the C_{11} parameters for each setting; i.e., $8.33 - 4.36 \approx 4$ ml/g. Although isotherms appear very similar, in this middle range of pressures, we also analyze the plots obtained by subtracting the DA to experimental data. We find, that in the case of untreated MWCNTs there is a good agreement

with the BET curves (dashed line in Fig. 2, not only in this range of pressures, but for all relative values greater than 0.01. We employ the BET equation.

$$V_{II}(x,T,C_{i,k}) = C_{21}C_{22}x/((1-x)(1+(C_{22}-1)x)) \tag{3}$$

The empirical constants obtained from fitting experimental data are as follows: $C_{21} = 2.512$ ml/g, $C_{22} = 84.41$, and a surface area of $10.9 m^2/g$. Nevertheless, it can be observed a small hysteresis loop in the isotherm, for values of p/p_0 above 0.6. Although BET curves describe the adsorption on surfaces, pores corresponding to these pressures are so large that there are no nanotubes within these diameter range. This pores should correspond to the confined space on aggregates of MWCNT bundles with the internal surfaces corresponding to the outer surfaces of several MWCNTs. This interpretation would allow to explain the observed hysteresis mechanism. For the treated MWCNTs, we find that Freundlich approximation gives better adjustment than other models (Langmuir, BET, etc.), only in the pressure range corresponding to Part II, as expected according to this type of approximation (Freundlich).

$$V_{II}(x,T,C_{2,k}) = C_{21}(p_0 x)^{1/C_{22}} \tag{4}$$

The empirical constants obtained from experimental fitting of data using Freundlich isotherm are almost equal, $C_{22} = 1.25, 1.24$, and $C_{21} \approx 0.05, 0.06$, for chemical and thermal treated MWCNTs, respectively, as could be expected because, as was mentioned, both isotherms behave similar in a qualitative way. These numerical values obtained suggest the existence of important lateral interactions, which gives low adsorption energies on both studied surfaces. These results indicate different surface adsorption processes occurring on MWCNTs sample before and after modification via chemical and thermal treatment. All MWCNTs untreated surfaces appear to be soft enough to allow the adsorption to be appropriately described with BET mechanism. However, after acid treatment heterogeneities on the surface begin to develop and cannot be removed with the heat treatment applied (500 C). Heterogeneities present are so abundant that the adsorption process has to be described using Freundlich approach. These conclusions are supported by TGA results pointing

that, unlike as-produced MWCNTs, treated samples have defects and/or amorphous carbon on the surface, at least if the heat treatment is carried below 600 C. Hysteresis loop is clearly observed in Parts III and IV of the isotherm for treated MWCNTs and relative pressures greater than 0.5 a (see Fig. 2), this behavior can be associated with capillary condensation on mesopores [20]. Both routes are characteristic of type IV isotherms. Part III corresponds to the capillary condensation that occurs in the mid range pressures ($0.45 < p/p_0 < 0.85$). Part IV of the isotherm, in the pressure range ($0.85 < p/p_0 < 0.99$) features hysteresis. The amount of adsorbed nitrogen grows rapidly, from 10 to 50 ml/g. According to the Kelvin equation, the radius of the respective pores is above 10 nm (large pores distribution), where contribution of pores within aggregates (pores confined to the structure of the aggregates), as was mentioned in case of untreated MWCNTs, taking into account that there are no nanotubes with such large diameters, porosity accessible within this pressure range has to be determined by internal cavities. Insulated nanotubes, of different diameters and orientations, interact by molecular forces and form aggregated structures, between these aggregates of nanotubes there are isolated spaces that constitutes relatively stable pores (see Fig. 3). Due to its wide distribution and its large volume, the pores in MWCNTs aggregates have greater contribution to the capillary condensation of the internal cavities. Therefore, it can be concluded that the hollow cavities inside of the MWCNTs are responsible for capillary adsorption at intermediate pressure. Adsorption-desorption isotherms of nitrogen of the MWCNTs samples, original and treated, exhibit two different hysteresis behaviors. Untreated MWCNTs isotherms (closed ends) show weak hysteresis loops, and purified MWCNTs (open ends) show clear hysteresis loops, indicative of strong capillary adsorption. At least two causes may be attributed to this different behavior, first the increase of the above-mentioned interaction between the various tubes after treatment (which increases the number of aggregates of pores), and secondly the heterogeneous structure of surfaces of these pores, which makes them much more active.

What we should stand out is that after thermal treatment (see Fig. 2), there are almost no changes in the behavior of larger pores of the aggregate structure and, according to the isotherm shape (without steps) no graphitization is observed as a consequence that heating process, because it is below the threshold to reach perfect crystalline surfaces. In short, the large aggregates and distribution of pores in the original sample was preserved without reducing or improving the adsorption capacity at medium or high pressures.

Hysteresis loops, associated with capillary condensation in mesopores, at relative pressures greater than 0.45, are observed in both isotherms, but pressure range and strength are quite different between treated and untreated MWCNTs (see Fig. 2). After treatment the MWCNTs isotherms show apparent hysteresis in the medium relative pressure range ($0.45 < p/p_0 < 0.85$), resulted from larger inner cavities ($3.0 - 4.0$ nm), and when the pressure nears to the saturation value, the adsorption amount shows a great increase, bounded up with a large hysteresis loop, indicative of ultra-strong capillarity in larger mesopores (aggregated pore diameters of $10-50$ nm), this type of capillarity corresponds to condensation in large pores, which agree with larger pores in the aggregated structure. On the other hand, in the case of untreated MWCNTs, the isotherm shows only a weak hysteresis loop at high pressures, which means that condensation occurs only in larger aggregated pores.
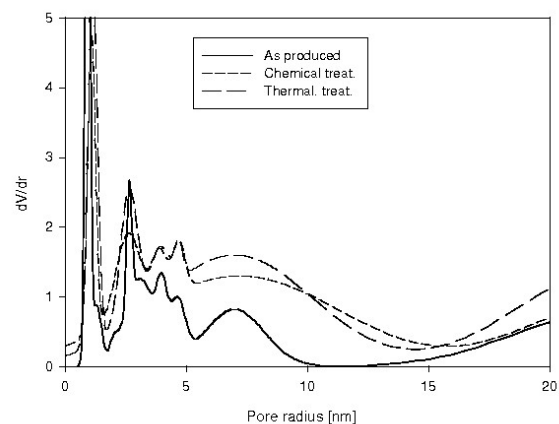

Fig. 4.   Pore sizes distribution of untreated (solid line), chemically (short dashed line), and thermally treated (long dashed line) sample of MWCNTs. It is observed the same pore sizes and an increase in volume and distribution (radius 1.2, 2.5, 3.0, 4.0, 4.5, 7.0 nm).

Unlike the single-walled nanotubes, showing in general a well defined internal diameter in micropore sizes (about 1 nm), multi-walled nanotubes are characterized in general by a distribution of diameters, which can reach mesopores ranges. Figure 4 shows the pore size distributions obtained using the BJH equation [27], for pristine, and treated (chemically and thermally) MWCNTs. All samples show the same peaks corresponding to the diameters 2.2, 5.0, 8.0, 9.0, 14.0 and 44.0 nm. These peaks, consistently with TEM observations, can be divided into the diameters smaller than 6.0 nm, all narrowly distributed, that can be associated with inner hollow cavities; and the diameters greater than 7.0 nm, widely distributed, corresponding to aggregated pores of greater radii. In the microporous region, we can say that beyond the increase of pore capacities, different treatments not affect relative adsorption amounts for each kind of pores. In inner hollow cavities the situation is different, because the treatments not only change the spread of each distribution, but also the relative capacities of pores. According to what has been mentioned with reference to the phenomenon of capillarity, we can say that this occurs in pores with radius above 1.5 nm, however the significantly higher abundance of pores in the MWCNTs after treatment, causes the loop hysteresis is perceptible only in those pores, whereas in the untreated MWCNTs, a small hysteresis loop, only can be seen, at relative pressures above about 0.7.

Summarizing we can say that the mixed characteristics of nitrogen adsorption isotherm is a consequence of the different types of porosity present in MWCNTs: inner cavities in micropores range (diameters less than 6.0 nm), and aggregated pores (diameters over 7.0 nm) in mesopores ranges. Moreover, capillary phenomena are observed in the aggregates pores, and nanotubes of larger diameters. This distribution of pore size does not suggest that these samples are suitable to be used in processes of separation of gases, at least from a geometric approach; however before making a final judgment further analysis should be carried from the energetic point of view; i.e, to develop a study of the adsorption energy.

4. Conclusions and perspectives

One way to optimize purification procedures that are carried out on MWCNTs, commercially produced by arc discharge, is to establish conditions so that the effects produced by acid treatment, to open the nanotubes, and heat treatment to remove the carbon impurities, whose counterparts are: producing damage to the walls of the nanotubes and generating organic functions by the former, while the latter reduces the storage capacity by graphitization, and both causing mass loss. Since most mass loss in the heat treatment occurs above 500 C, we have adopted this value as a threshold for such treatment, given that in this range also an acceptable degree of purification is achieved.

To determine the capacity of MWCNTs we measured N2 adsorption at 77 K on samples, as produced, and after each treatment (with acid and heat, that we call chemical and thermal). As this is a clear case of multilayer adsorption, we describe the isotherms as the sum of fitting curves, each of which represents a different process to be triggering with increasing pressure, as had been proposed in the literature [20]. At low pressures, a single type of nanotube size is detected (DA fit curve), and at higher pressures adsorption on surfaces is evidenced (BET fit curve), this may correspond either to wider nanotubes, or the outer faces of them. In turn, at low pressures, MWCNTs after treatments, chemical and thermal, have the same behavior (a single nanotube size detection), where the only change is the increases of the adsorbed volumes, corresponding to a largest number of open nanotubes after treatments. At higher pressures, the increase in the adsorbed amount is greater after treatment, going from a BET curve to a Freundlich, and most notably, both isotherms have same shapes and differ only by a constant, which is equal to the difference between the volumes of nanotubes, after each treatment (C_{11} parameters, in the notation employed). The determined pore size distribution allow us to check a variety of sizes of nanotubes, especially for small diameters apart from that was detected in the adsorption of N2 at low pressure. Besides the distribution suggests that there is greater nanotubes ratio (broader distributions) as they increase their diameters. The final conclusion is that, according to the adsorption of nitrogen performed, the proposed treatment allows

to achieve good adsorption capacity, a rise of about 80% of the volume adsorbed, with a low loss material, not exceed 20%, for the MWCNTs produced by arch discharge. Therefore the MWCNTs that are obtained, after standard purification processes are promising for storing gases of energetic interest, inasmuch as they are very good adsorbents, but on the other hand, and because its complex structure, we can't be so optimistic about their capacity to purify gasses, i.e. be able to separate efficiently, gases with similar features.

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