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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_2 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_2 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_2 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_2 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_2 adsorption.

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_2 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 $m^2 g^{-1}$ have been reported from N_2 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_2 adsorption. A reduction in BET specific surface area of MWCNTs was achieved after the rupture of the 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_2 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_2, by using analytical grade iron (II) phthalocyanine ($C_{32}H_{16}N_8Fe$) 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_2 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^3 (STP) min^{-1}, H_2 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_2 atmosphere (O_2 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_2 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_2 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_2 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_2 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_{BET} specific surface are reported.

3. Results and discussion

Fig. 1 shows N_2 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_{ads}) 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_2 adsorption capacity may be noticed, depending on the treatment applied to the lab-synthesized CNTs.

The shape of the N_2 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-