Characterization of nanocarbons (nanotubes and nanofibers) by Inverse Gas Chromatography

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Abstract. The adsorption of different alkanes (linear and cyclic), aromatics and chlorohydrocarbons on non-microporous carbons – carbon nanotubes (CNTs) and carbon nanofibres (CNFs)– was studied in this work by inverse gas chromatography (IGC). Capacity of adsorption was derived from the isotherms of adsorption, whereas thermodynamic properties (enthalpy of adsorption, surface free energy characteristics) have been determined from chromatographic retention data. CNTs present the highest adsorption capacity. From surface free energy data, enthalpies of adsorption of polar compounds were divided into dispersive and specific contributions. The interactions of cyclic (benzene and cyclohexane) and chlorinated compounds (trichloroethylene, tetrachloroethylene and chloroform) with the surfaces are mainly dispersive over all the carbons tested, being CNTs the material with the highest dispersive contribution. Adsorption parameters were correlated with morphological and chemical properties of the materials.

1. Introduction

Carbon materials are the most promising adsorbents when adsorption of traces of gases or vapours is considered. Recently, new carbon forms like carbon nanofibers (CNFs) or nanofilaments and carbon nanotubes (CNTs) have generated a growing interest in the scientific community. The interaction of these structures with their environment, and in particular with gases, attracts attention due to the possibility of using these materials for efficient gas storage [1]. These materials are attractive because they join relatively high specific surface and uniform mesoporous diameter; these mesopores being much more accessible to adsorbates than the micropores of common activated carbons. Thus, although adsorption of gases and vapours on microporous carbons has been extensively studied, the research in this field is very active because of the discovery of these new types of carbons.

Gas adsorption, especially hydrogen adsorption capacities of CNTs and CNFs has been recently studied via theoretical calculations, experimental measurements and molecular simulations [2-4]. However, only a limited number of works have focused on adsorption of higher organic molecules on CNTs and/or CNFs [5-6]. On the other hand, the most of the published works are focused on morphological properties and capacity of adsorption derived from adsorption/desorption isotherms. Although these parameters are of great importance, thermodynamic parameters, such as enthalpy,

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entropy or free energy of adsorption and surface energies are also interesting in the characterization of the adsorption properties.

Gas calorimetry, high resolution argon adsorption and immersion calorimetry are commonly techniques employed in the determination of adsorption properties of carbon materials. Data on thermodynamic and surface energy parameters in gas phase can be determined also by inverse gas chromatography (IGC). This technique is based on the traditional gas-solid chromatography, but its goal is the characterization of the stationary phase instead of the separation of solutes in the mobile phase. Some recent applications of the IGC technique for adsorption measurements [7,8].

The scope of this work is to evaluate, by IGC, the performance of two different non-microporous carbon structures (multi-walled carbon nanotubes and nanofibers) for the adsorption of several representative volatile organic compounds (VOCs): hydrocarbons (n-pentane, n-hexane, n-heptane and n-octane), cyclic (cyclohexane), aromatic (benzene) and chlorinated compounds (chloroform, trichloroethylene and tetrachloroethylene). The evaluation is based on the isotherms of adsorption, the strength of the interaction (heat of adsorption) and the values of free energy of adsorption, considering both the dispersive component of surface energy and the specific one. By this way, pure polar or specific interactions can be obtained, which are related directly to the chemistry of the material surface.

2. Experimental

2.1. Materials
CNF (Pyrograf III, PR-24 LHT) were kindly given by Applied Sciences, whereas CNT was a generous gift of Catalytic Materials Ltd. Surface area and pore structures were determined by nitrogen physisorption: CNF (25 m²/g) and CNT (186 m²/g). The adsorbates used are n-alkanes (C5-C8), benzene, cyclohexane and chlorinated compounds (chloroform, trichloroethylene and tetrachloroethylene).

2.2. Apparatus and procedure
A conventional gas chromatograph (Varian 3800) with a thermal conductivity detector (TCD) was used for the adsorption measurements. A loading between 0.2 and 0.6 g of carbon material was placed into a stainless steel column, with passivated inner walls. Measurements were carried out in the temperature range of 200 – 250 ºC. Helium was used as carrier gas, and flow rates were measured using a calibrated soap bubble flow-meter. In order to meet the requirement of adsorption at infinite dilution, corresponding to zero coverage and GC linearity, the samples injected were in the range from 0.05-0.2 µL. The procedures used for the calculation of adsorption capacities and enthalpies from IGC experiments are described in detail in a previous work [9].

Temperature programmed desorption studies were carried out in a Micromeritics TPD-2900 apparatus connected to a Glaslab 300 mass spectrometer. For this purpose, 0.50 g carbon sample was heated from 50 to 950 ºC at 10 ºC/min in a stream of pure He with a flow rate of 50 cm³/min. Carbon structural characteristics were also determined using temperature programmed oxidation (TPO), employing the same experimental procedure, but maintaining the sample in oxygen- stream of 2 % O₂/98 % He- at 50 ºC during 30 min, and then heated from 50 to 950 ºC.

3. Results and discussion

3.1. Characterization
Specific surface areas, calculated according to the Brunauer, Emmett and Teller (BET) equation, total pore volume and average pore radii of the carbons are shown in table 1. The surface area recorded for CNT is significantly greater than that of CNF. Typical values of surface areas for CNT are around 200 m²/g, whereas for CNF have found to range from 10 to 200 m²/g [1], depending on the synthesis parameters and postsynthesis treatment.
Table 1. Physicochemical characterization of nanocarbons

|         | $S_{\text{BET}}$ (m$^2$/g) | $V_{\text{mesopores}}$ (BJH) (cm$^3$/g) | $V_{\text{micropores}}$ (t-Lippens) (cm$^3$/g) | Average pore radius (nm) | TPO $T_{\text{max}}$ (°C) |
|---------|-----------------------------|--------------------------------------|-----------------------------------------------|------------------------|-------------------------|
| CNT     | 186                         | 1.39                                 | 0.008                                         | 20.6                   | 550                     |
| CNF     | 25                          | 0.16                                 | 0.000                                         | 16.2                   | 700                     |

If the values of the specific surface area and the geometrical external area are compared for both CNF and CNT (using the average observed dimensions and densities reported in the literature), it is observed that the most of the surface area of the CNF is external geometrical area (more than 85 %), whereas in the case of CNT, the external area represents less than 20 % of the total surface area.

Thermal treatment of the carbon materials under an inert atmosphere (as takes place in He-TPD experiments) produces the selective decomposition of the oxygenated groups in CO and CO$_2$ [10]. Neither CO nor CO$_2$ releases were observed during the He-TPD, thus the presence of significant amounts of oxygenated groups in the surface of these materials can be discarded. TPO experiments are widely used to probe the degree of order in carbon materials. So, a shift from an amorphous to a more graphitic structure is accompanied by a rise in the temperature at which combustion takes place [11]. The characteristic $T_{\text{max}}$ values of TPO profiles are given in table 1. On the basis of TPO response, CNF substrate has significant order, whereas CNT shows a lower degree of order. These values are in agreement with those reported in the review of Serp et al. [1], where it was established the thermal stability in air of different carbons, finding that multi-walled CNT decomposes at around 650 °C and CNF at 600-900 °C.

3.2. Adsorption parameters

According to the procedure outlined in a previous paper [9], adsorption isotherms were determined in the infinite dilution region, in the so-called Henry’s law region, using the elution by characteristic point (ECP) method. Henry’s constant values, at 250 °C, for a $n$-alkane compound ($n$-hexane), cyclohexane, benzene, chloroform, trichloroethylene and tetrachloroethylene are shown in table 2.

From this figure, CNTs presents the highest adsorption capacity for all the compounds tested in this work. Regarding the chlorinated compounds, the capacity of adsorption follows the order: chloroform < trichloroethylene < tetrachloroethylene. Thus, it seems that increasing molecular sizes lead to higher adsorption capacity, this parameter being higher for cyclic forms (benzene and cyclohexane) than for aliphatic ones ($n$-hexane). The same behaviour was observed over microporous activated carbons [12]. However, over these materials, the capacity of adsorption was about 50 % higher than over the best of the adsorbents here tested.

Table 2. Henry’s constants at 250 °C and adsorption enthalpies of $n$-hexane, cyclohexane, benzene, chloroform, trichloroethylene (TCE) and tetrachloroethylene (TTCE) over CNT and CNF.

|         | Henry constant ($\mu$mol/g-mmHg) | $-\Delta H_{\text{ads}}$ (kJ/mol) | Henry constant ($\mu$mol/g-mmHg) | $-\Delta H_{\text{ads}}$ (kJ/mol) |
|---------|----------------------------------|---------------------------------|----------------------------------|---------------------------------|
| CNT     | 1.42                             | 39.5                            | 1.50                             | 40.7                            |
| CNF     | 0.82                             | 30.8                            | 0.82                             | 30.5                            |
|         | 1.56                             | 34.7                            | 0.89                             | 33.7                            |
| Chloroform | 0.81                         | 30.8                            | 0.74                             | 28.5                            |
| TCE     | 1.06                             | 34.3                            | 0.80                             | 31.6                            |
| TTCE    | 3.05                             | 40.7                            | 0.85                             | 35.6                            |

The strength of the interaction of each compound with the surface of the adsorbent is represented by the enthalpy of adsorption, $\Delta H_{\text{ads}}$. Results are summarized in table 2. Values of $\Delta H_{\text{ads}}$ for CNFs are
systematically the lowest ones for all the compounds tested, being even lower than the heats of liquefaction. The behaviour of CNTs corresponds to a process where adsorbate-adsorbent interactions are stronger than adsorbate-adsorbate ones [13]. Comparing enthalpies of adsorption of CNTs with that corresponding to activated carbons, it is remarkable that the strength of adsorption of \( n \)-alkanes and chlorinated compounds over conventional steam-activated and chemically-activated carbons is about 25 % higher than over CNTs [12], whereas for cyclohexane and benzene the difference fluctuates between 11 and 41 %.

From the standard free energy of adsorption at infinite dilution, obtained from chromatographic data, both the dispersive and specific components of the surface energy are calculated [9]. The dispersive component, intrinsic and unspecific for all molecules, is due to London forces, and it is obtained from the \( n \)-alkanes adsorption data. Figure 1 shows the dispersive component of the surface energy, \( \gamma_D \), within the range of temperature studied.

![Figure 1. Dispersive component of surface energy over CNT (black) and CNF (dark grey)](image)

The dispersive component of the surface energy follows the same trend that the surface area, this explains the high values of \( \gamma_D \) obtained for CNTs.

Whereas adsorption of \( n \)-alkanes takes place through dispersive interactions, rendering information related to carbon structure, polar probes are needed to determine the acid-base character of the surfaces. The adsorption of these molecules on the stationary phase involves, add to the dispersive interactions, specific contributions. Thus, two main components can be considered to contribute to the standard enthalpy of adsorption of polar probes, namely the specific contribution and the dispersive contribution. Results obtained, according to the procedure showed in the literature [14], are shown in table 3. It is worth noting that benzene exhibits the highest values of specific interaction over all the materials tested and its percentage is very close for the four materials. Following benzene, tetrachloroethylene and trichloroethylene exhibit also important relative values of the specific interaction, being the contribution of chloroform considerably less important. Thus, the dipolar moment is not decisive in the specific interaction, since the highest one corresponds to chloroform (1.01 debye), whereas benzene presents null dipolar moment. This fact is in agreement with the absence of oxygenated surface groups in the four materials tested, as it was deduced from He-TPD experiments. Regarding cyclohexane, its specific interaction is considerably lower than that of benzene over all materials, being its percentage similar to chlorinated compounds.
Table 3. Specific contribution to the enthalpy of adsorption, (kJ/mol), of several polar adsorbates. In parentheses the percentage of the specific contribution respect the total enthalpy of adsorption.

|                  | CNTs     | CNFs     |
|------------------|----------|----------|
| Cyclohexane      | -7.4 (18 %) | -5.0 (16 %) |
| Benzene          | -15.3 (44 %) | -12.6 (37 %) |
| Chloroform       | -2.1 (7 %) | -4.6 (16 %) |
| Trichloroethylene| -6.7 (19 %) | -11.4 (36 %) |
| Tetrachloroethylene| -13.5 (33 %) | -12.5 (35 %) |

Benzene specific interaction could be explained attending to the donor-acceptor interaction through the π system, more favoured than the dipole-dipole interaction of chloroform. The closer specific interaction of trichloroethylene and tetrachloroethylene to benzene than to chloroform (the other chlorinated compound), could suggest that the specific interaction of the three molecules has the same origin, i.e. the π carbon-carbon bond, instead of dipole-dipole interaction.

4. Summary
Inverse gas chromatography has been used to study the adsorption of n-alkanes and other polar probes on nanotubes and nanofibers. Moreover, properties such as enthalpy of adsorption, free energy of adsorption and surface free energy as well as the dispersive and specific component are also reported. It is shown that the capacity of adsorption of CNTs is higher than that of CNFs, following the enthalpy of adsorption the same trend. The dispersive contribution of the enthalpy of adsorption is more important than the specific one as expected for the non polar surface of mesoporous carbons, being remarkable that there is no influence of dipolar moments of polar molecules to this parameter.

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References
[1] Serp P, Corrias M and Kalck P 2003 Appl. Catal. A 253 337
[2] Liu C, Fan YY, Liu M, Cong HT, Cheng HM and Dresselhaus MS 1999 Science 286 1127
[3] Takagi H, Hatori H, Yamada Y, Matsuo S and Shiraishi M 2004 J. Alloy Compd. 385 257
[4] Kojima Y, Kawai Y, Koiwai A, Suzuki N, Haga T, Hioki T, Tange K 2006 J. Alloy Compd. in press
[5] Gauden PA, Terzyk AP, Rychlicki G, Kowalczyk P, Lota K, Raymundo-Pinero E, Frackowiak E, Béguin F 2006 Chem. Phys. Lett. 421 409
[6] Nuriel S, Liu L, Barber AH and Wagner HD 2005 Chem. Phys. Lett. 404 263
[7] Xie J, Bousmina M, Xu G and Kaliaguine S 1998 J. Mol. Catal. 135 187
[8] Papirer E, Brendle E, Ozil F and Balard H 1999 Carbon 37 1265
[9] Diaz E, Ordóñez S, Vega A and Coca J 2004 Micropor. Mesopor. Mater. 70 109
[10] Rodriguez-Reinoso F and Molina-Sabio M 1998 Adv. Colloid Interface Sci. 76-77 271
[11] Amorim C, Yuan G, Patterson PM and Keane MA 2005 J. Catal. 234 268
[12] Diaz E, Ordóñez S, Vega A and Coca J 2005 Micropor. Mesopor. Mater. 82 173
[13] Montes-Morán MA, Paredes JI, Martínez-Alonso A and Tascón JMD 2002 Macromolecules 35 5085
[14] Donnet JB, Park SJ and Balard H 1991 Chromatographia 31 434