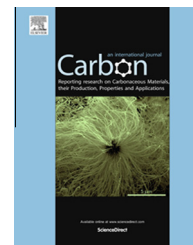


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# Infrared spectroscopy of some carbon-based materials relevant in combustion: Qualitative and quantitative analysis of hydrogen

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## ABSTRACT

A detailed procedure for the quantitative analysis of aromatic and aliphatic hydrogen based on infrared spectroscopy was set up and implemented on some carbon-based materials produced from organic precursors (naphthalene pitch) and/or relevant in combustion field (asphaltenes, carbon particulate matter, carbon black), spanning in the H/C atomic ratio range from 0.1 to 1. The quantitative FT-IR analysis involved the spectral deconvolution in the C–H vibrations regions and the calibration factors of diverse standard species having spectral characteristics suitable for the detailed peak-to-peak analysis of the C–H stretching ( $3100\text{--}2800\text{ cm}^{-1}$ ) and aromatic C–H bending ( $900\text{--}700\text{ cm}^{-1}$ ) regions. The good agreement between the H/C atomic ratio obtained by quantitative FT-IR analysis and elemental analysis showed a reasonable reliability of the procedure. The major value of the developed FT-IR quantitative technique relies also on the capacity of discriminating between the different kinds of aliphatic and aromatic hydrogen. The quantitative and detailed analysis of hydrogen in form of  $\text{CH}_3$ ,  $\text{CH}_2$  and C–H groups and in form of solo, duo and trio/quattro aromatic hydrogens showed to be useful also for inferring the structure of the aromatic moieties constituting the C–C backbone of carbon materials.

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## 1. Introduction

Carbon-based materials exhibit, in dependence on their different origin, a wide variety of chemical and physical properties that, from a structural point of view, are mainly related to the carbon hybridization state. Ranging from all- $\text{sp}^3$  hybridized 3D carbon (diamond) to all- $\text{sp}^2$  hybridized 2D carbon (graphite), a plethora of non-crystalline hydrogenated carbon materials produced from evaporation/deposition techniques (polymers, amorphous carbon, etc.), and disordered carbons derived from heating of organic precursors in pyrolysis/combustion processes (soot, chars, cokes, mesophases, etc.), can be found owing to the hybridized carbon ( $\text{sp}^2$  and/or  $\text{sp}^3$ ) character and content of incorporated hydrogen [1].

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The classification of the various kinds of solid carbons (graphite, hydrogenated and non-hydrogenated amorphous carbons, etc.) and hydrocarbons (alkanes, polycyclic aromatic hydrocarbons (PAH)) has been simply done by relating their atom density with hydrogen content [2] regardless of their hybridization state and graphitic character. The structural classification of graphitizing and non-graphitizing carbons prepared by pyrolysis of various organic precursors has been done by XRD analysis [3]. It has been found that the graphitization process is favoured by the presence of large quantities of hydrogen in the raw carbon material [3]. Recently, it has been claimed that non-graphitizing microporous carbon might have a structure related to that of the fullerenes [4,5] characterized by a mixed  $\text{sp}^2\text{--}\text{sp}^3$  hybridization state and the absence of incorporated hydrogen.

A ternary phase diagram has been used to show the composition and structural variability in terms of  $\text{sp}^2$ ,  $\text{sp}^3$  and

hydrogen content for amorphous and disordered carbons [6,7]. It has been noticed, however, that the ternary phase diagram does not include parameters important for the structural characterization of carbons, like the size of  $sp^2$  clusters [8]. In fact,  $sp^2$  sites tend to segregate into  $sp^2$  clusters of fused sixfold rings with a relatively high number of rings (graphene layers) that in turn determine the very low optical band gap of these carbon materials [1].

Overall, it appears clear that the measurement of hydrogen,  $sp^2$  and  $sp^3$  content as well as of the graphene layer size are required for the structural analysis of disordered carbon materials. It has to be also underlined that for carbon materials, as the carbon particulate matter derived from fuel rich combustion, the separation of unincorporated hydrogen, present in form of adsorbed hydrocarbons, is also required. The separation of adsorbed species, usually carried out by solvent extraction, is important both to give the complete characterization of carbon particulate matter and to define the internal structure of the solid carbon particles.

As concerns the hydrogen content of carbon materials, it is generally measured by combustion analysis. However, more details on the carbon structure are obtained by discriminating the hydrogen linked to aromatic carbon from the hydrogen linked to aliphatic carbon. To this aim, FT-IR analysis of the C–H vibrational modes has considerable value owing to the localized nature of C–H vibrations in the mid-IR range (from 4000 to 400  $cm^{-1}$ ). In particular, the typical symmetric and asymmetric C–H stretching peaks, observed in the region around 3000  $cm^{-1}$ , can be utilized to discriminate between aromatic and aliphatic hydrogen. Nevertheless, just the sensitivity of the frequency and absorption intensity of C–H vibrations to the C–C backbone causes a significant variability of response factors and a large number of suitable standard species have to be used for the quantitative FT-IR analysis of aliphatic and aromatic hydrogen.

In this framework, this paper reports a procedure for the quantitative FT-IR analysis of aromatic and aliphatic hydrogen that has been set up by using standard species having different kinds of aliphatic and aromatic hydrogen. The procedure has been implemented on carbon materials having H/C atomic ratio from 0.1 to 1. Carbon materials produced from organic precursors and/or relevant in the combustion field as naphthalene pitch, fuel oil asphaltenes and the extractable fraction of fuel-rich flame-formed carbon particulate matter have been analyzed as hydrogen-rich carbon materials (H/C atomic ratio from 0.4 to 1). Carbon black and flame-formed soot (the insoluble fraction of fuel rich flame-formed carbon particulate matter) have been considered as representative of hydrogen-poor carbon materials (H/C atomic ratio from 0.1 to 0.3). On the same carbon materials UV-visible spectroscopic properties (absorption coefficient, optical band gap) measured by optical methodologies [9–12], are currently under study [12–14] to verify the correlation between the hydrogen content and spectral absorption features, in turn related to the  $sp^2$ – $sp^3$  character. In previous work, CHN micro-combustion analysis of matrix-isolated single and clustered nano-sized (hydrogenated) carbon grains prepared by condensation of resistively vaporized graphite gave significantly higher hydrogen contents in comparison to those ob-

tained by integrated strength of the C–H bands in the infrared spectra [15]. The absolute intensity of the C–H stretching peaks due to aromatic and aliphatic hydrogen has been measured to follow the dehydrogenation and growth of carbon nanoparticles [16]. FT-IR analysis has been also used to follow the evolution of aromatic and aliphatic hydrogen along the soot formation region of premixed and inverse diffusion flames [17,18].

The procedure reported in this work aims to give a quantitative evaluation of aliphatic and aromatic hydrogen of carbon materials of different origin through the use of aliphatic C–H stretching peaks in the 3100–2800  $cm^{-1}$  and of the peaks due to aromatic C–H out-of-plane bending modes located in the 900–700  $cm^{-1}$  region. The value of total hydrogen obtained by means of the quantitative FT-IR procedure has been compared with elemental analysis of the same samples to verify the reliability of the FT-IR procedure.

## 2. Experimental

### 2.1. Samples and materials

Standard aromatic compounds were purchased from Sigma-Aldrich.

Hydrogen-rich carbons as naphthalene pitch and asphaltenes, having H/C atomic ratio of 0.53 and 0.95, respectively were used. Naphthalene pitch (Mitsubishi Gas-Chemical Company) is a carbon solid prepared by pyrolysis of naphthalene at 600 °C, using HF/BF<sub>3</sub> as catalyst [19]. It is considered to be constituted of aromatic units carrying some alkyl and naphthenic groups and linked by phenyl–phenyl or methylene bridges to give a molecular weight (MW) in the  $m/z$  400–1000 range as measured by mass spectrometry [19,20]. Asphaltenes were obtained by heptane insolubilization of a commercial heavy fuel oil. They are considered to consist of small fused-ring systems with aliphatic chains [21,22].

Carbon black (Phillips Petroleum) having a very low H/C atomic ratio (<0.1) was classified on the basis of ASTM classification as N110 (10–20 nm) carbon black.

Carbon particulates were sampled at short (SRT) and long residence times (LRT) in a fuel-rich (C/O = 0.8,  $v = 3$  cm/s) atmospheric-pressure ethylene premixed flame [12]. The particulate matter was extracted with dichloromethane to separate the soluble condensed species (CS) avoiding their interference in the FT-IR analysis of soot [18,23]. CS generally exhibit a H/C atomic ratio varying in a small range (from 0.4 to 0.6) [24] and are representative of tar-like carbon material mainly constituted of small unsubstituted PAH (200–400 u) [20]. In this work a CS sample having a H/C atomic ratio of 0.49, obtained by extraction of carbon particulate matter sampled at long residence time, was analyzed.

### 2.2. Sample characterization

Quantitative analysis of hydrogen and carbon content of carbon samples was performed by microcombustion analysis on a Perkin-Elmer 2400 CHNSO elemental analyzer.

FT-IR analysis was performed on a Perkin-Elmer 1600 FT-IR spectrophotometer to quantify the hydrogen content in car-

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