

# NEUTRON SPECTROSCOPIC INVESTIGATIONS ON DIFFERENT GRADES OF MODIFIED FURNACE BLACKS AND GAS BLACKS

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## Introduction

It is widely accepted that there are relationships between the nanostructure of carbonaceous materials and the amount of hydrogen engaged in various chemical bonding [1]. However, the properties of finely divided carbons such as carbon blacks severely restrict the techniques that can be useful applied for revealing the hydrogen-related aspects of the specific structure. Secondary Ion Mass Spectrometry in the dynamic mode was utilized to studying changes of the C/H-fragmentation patterns due to oxidation processes on carbon black [2].

The Inelastic Incoherent Neutron Scattering Technique (IINS or INS) is uniquely suitable to reveal and to distinguish the proton related properties of different classes of furnace blacks and of gas blacks [3]. The neutron scattering cross section of the nucleus of the hydrogen atom is more than one order of magnitude greater than those of other components of carbon black (C, O, N, S...). Therefore, for neutrons the carbon matrix is largely transparent and the proton dynamics of the small amounts of hydrogen is selectively detectable. The proton dynamics of carbon black can be utilized as a probe for the structural or microstructural properties. It is possible to investigate the degree of graphiticity of certain blacks, ranging between graphitic carbon, activated carbons and coals [3,4].

It was observed that even related ASTM grades of carbon black such as N220 and N234 show INS-spectra of different fine structure in the range of the CH bending modes of conjugated and non-conjugated structures [3]. Therefore, there is still a large potential of the INS method in revealing structural peculiarities of carbon blacks in more detail.

In the present work INS is utilized to study the micromorphological changes induced by modifying carbon blacks due to gas-phase hydrogenation, gas-phase-

deuteration, liquid-phase H/D-exchange and cofuming of Si. The neutron spectra of a typical gas black and typical furnace blacks are compared before and after introducing additional disorder into the material.

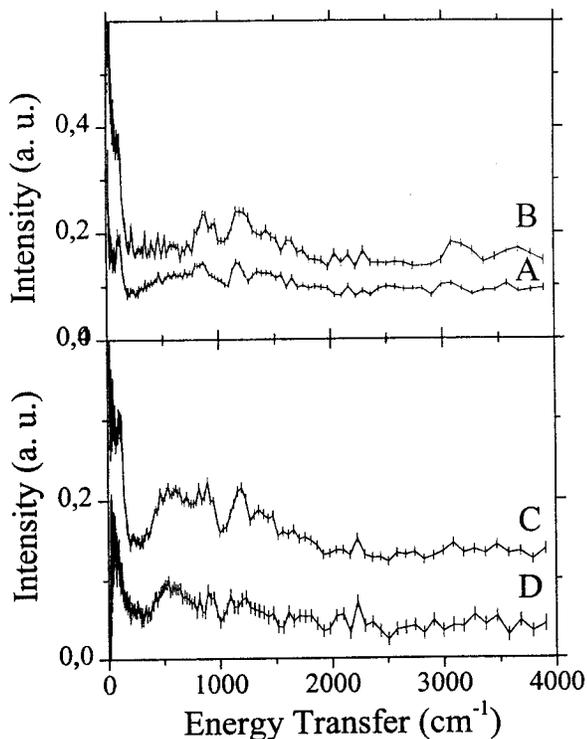
## Experimental

The INS-spectra were recorded at the TFXA-Spectrometer of the spallation neutron source ISIS (U.K.) at a sample temperature of 30K. The sample weights were in the range of 10 g to obtain results on a macroscopic amount of carbon black. The blacks were thoroughly extracted with methanol/water (24h) and, subsequently, with toluene (24h).

## Results and Discussion

Fig. 1 shows the INS-spectra of the furnace black Printex 60<sup>®</sup> before (A) and after (B) hydrogen treatment in an autoclave. The broad bands at 880 and 1170 cm<sup>-1</sup>, the dip of intensity at 1000 cm<sup>-1</sup> and the band at 100 cm<sup>-1</sup> reveal relatively large polyaromatic species with graphite-like structure. Due to partial hydrogasification new signals at 230, 350, 470 and 530 cm<sup>-1</sup> appear (B) which indicate the presence of smaller localized aromatic entities [4] whose molecular vibrations were decoupled from the lattice dynamics of the basic structural units. These aromatic entities are still connected to the carbon black structure since they could not be removed by the additional extraction procedure. Enhanced amount of disorder is indicated by changes in the low frequency region (<100 cm<sup>-1</sup>). Furthermore, increased intensity at ~ 3100 cm<sup>-1</sup> shows enhanced contributions from H-stretching modes. A significant increase of the continuum intensity due to proton recoil is observed. On the other hand no evidence for intercalated H<sub>2</sub> molecules according to a sharp rotational mode at 116 cm<sup>-1</sup> is obtained.

For Printex 60<sup>®</sup> which was cofumed with Si changes of the vibrational band at  $\sim 600\text{ cm}^{-1}$  (Fig.1, C, D) indicate the presence of enhanced amounts of highly disordered, presumably amorphous domains enriched in  $sp^3$  entities.



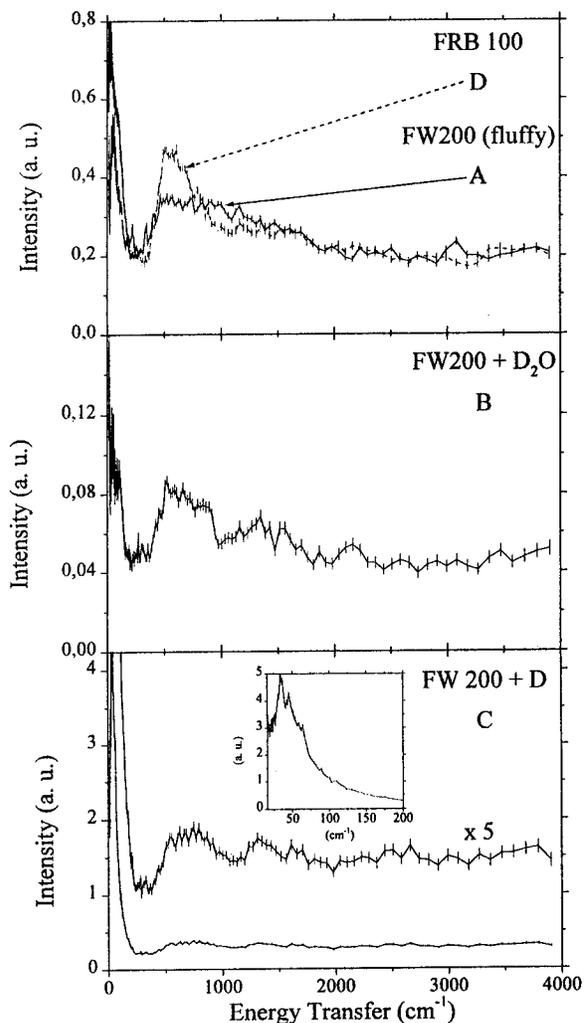
**Figure 1.** INS spectra of furnace blacks. A: Printex 60<sup>®</sup>; B: Printex 60<sup>®</sup> after hydrogenation under 350 bar at 350°C; C: Si-modified Printex 60<sup>®</sup>; D: difference spectrum C-A.

The postoxidized, finely divided gas black FW200 shows completely different INS spectra (Fig. 2, A-C) than typical furnace blacks. A broad vibrational band between 500 and 2000  $\text{cm}^{-1}$  seems to be indicative for the presence of protons trapped in a broad distribution of potential wells of small carbonaceous entities of this highly disordered material.

A wet-chemical H/D-exchange (B) as well as a treatment with gaseous  $D_2$  (C) led to significant changes of the spectra. The neutron cross section of D is about 40 times smaller than for H. This effect is exploited to indicate the part of the spectrum which represents chemically active hydrogen or the vibrational contributions of C-H structures which are sensitive to deuteration. Bands due to exchangeable H disappear. The INS-spectra (Fig.2, A-C) suggest that this technique can be employed in the identification of reactive sites on carbons in more detail.

The spectrum of a finely divided black derived from furnace technology (Fig.2, D) in principle is similar to the spectrum of the gas black (Fig.2, A). The dip of intensity at 1000  $\text{cm}^{-1}$  is missing indicating a high degree of disorder. The particle size of both, postoxidized, blacks is

in the range of 10-12 nm. However, in spite of previous extraction procedures significant amounts of water were retained on this furnace black. This suggests an enhanced interaction of this sample with  $H_2O$ . The vibrational bands of the adsorbed water molecules at about 600  $\text{cm}^{-1}$  are quite similar to the results on wet activated carbon [3].



**Figure 2.** INS spectra of finely divided gas black and furnace black. A: FW200<sup>®</sup>; B: FW200<sup>®</sup> after deuteration under 90 bar at 350°C; C: FW200<sup>®</sup> after H/D-exchange in  $D_2O$ ; D: furnace black.

## References

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