

# THE ADSORPTION OF OXYGENATED HYDROCARBONS ON CARBON/CARBON COMPOSITES

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## Introduction

Carbon/Carbon composites are widely used in brushes and collectors in electrical motors. In some cases such as fuel pumps in cars, these motors are in permanent contact with hydrocarbons and an unexpected wear is observed in some cases when using bio-fuels. The objective of this work is to study the interaction of oxygenated hydrocarbons such as ethanol with C/C composites. To do this, a study of the adsorption of oxygenated hydrocarbons on these materials was done. An important difference with the numerous studies on hydrocarbon adsorption on carbon materials which have been previously done, is that no water is present. Therefore, the influence of the surface groups of the carbon material should be different from the one observed for adsorption from aqueous solutions as reported for studies of adsorption in cyclohexane [1-3].

Two kinds of carbon materials were studied: an activated carbon and C/C composites. Their textural properties were determined by gas adsorption, and their surface chemistry was studied by temperature programmed desorption with quantitative analysis by mass spectrometry. The isotherms of adsorption of ethanol in cyclohexane on these carbon materials were obtained and the results were analyzed as a function of the surface groups of the solids.

## Experimental

### *Materials*

The experiments were conducted with a HPLC grade ethanol with purity  $\geq 99.8\%$  and a Chromasolv HPLC grade cyclohexane with purity  $\geq 99.7\%$  from Sigma-Aldrich. The C/C composites are graphite/binder composites treated at different temperatures: C/B1 (binder 1) and C/B2 (binder 2, with a higher heat treatment temperature than C/B1). The steam activated carbon is a 3 mm granulated NORIT R3 extra.

### *Characterisation of materials*

Textural properties were determined by gas adsorption. The nitrogen and krypton adsorption/desorption isotherms at 77K were measured volumetrically using the ASAP 2000, Micrometrics. Prior to the experiment the adsorbents were degassed at 150°C for overnight. Structural properties were characterized by Raman spectroscopy using the microspectrometer LABRAM from Jobin Yvon (at  $\lambda = 632.8$  nm).

### *Ethanol adsorption studies*

Adsorption studies were conducted using batch mode adsorption technique by placing a known quantity of the adsorbent in glass bottles containing 10 ml of solutions (ethanol in cyclohexane) of predetermined concentrations for C/C composites. In the case of activated carbon, we used 4 ml of solution. The adsorbent dose was 4.2 g/10 ml solution for C/C composites and 0.1 g/4 ml solution. Carbons were desorbed in the oven (24h, 150°C) before adsorption experiments. The samples were placed in a thermostated shaker at 24°C and agitated at 100 rpm for 7 days.

Ethanol concentration at equilibrium was measured by GC on a HP 5890 Series II Plus model with a DB1 GW Scientific capillary column (30 m long x 32 mm i.d.) and a flame ionization detector (FID), with a detection limit of 0.001 %. Samples were analysed under a temperature programming starting at 50°C increasing to 80°C at a rate of 2°C/min. Injector and detector temperatures were 300°C.

The desorption of ethanol adsorbed on carbon materials was studied by temperature programmed desorption performed in a vacuum system equipped with a mass spectrometer at a maximum pressure of  $10^{-4}$  Pa. The sample was deposited in a fused silica tube and heat-treated with a linear heating rate of 2 °C min<sup>-1</sup>. During the experiment, the gas phase was continuously analyzed quantitatively by the mass spectrometer. Before the experiment, the mass spectrometer was calibrated using H<sub>2</sub> (m/z = 2), H<sub>2</sub>O (m/z = 10), CO (m/z = 28), N<sub>2</sub> (m/z = 28), O<sub>2</sub> (m/z = 32), CO<sub>2</sub> (m/z = 44), C<sub>2</sub>H<sub>5</sub>OH (m/z = 31) and C<sub>6</sub>H<sub>12</sub> (m/z = 56) gases. The total gas pressure evolved during the heat treatment was measured as a function of the temperature using a Bayard-Alpert gauge.

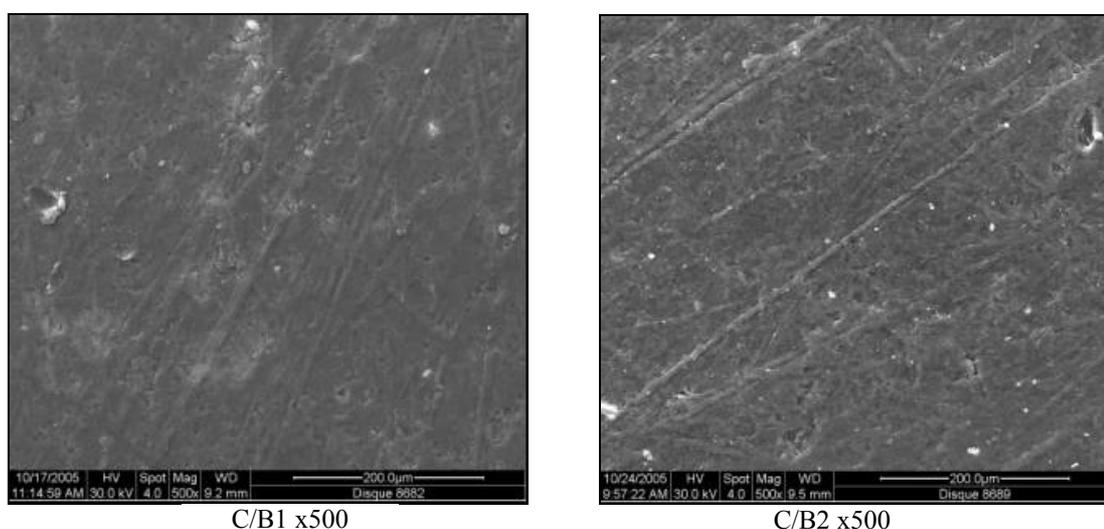
## Results and discussion

### *Textural and structural characterization*

BET surfaces (Tab. 1) of C/C composites are small compared to the activated carbon taken as a reference for adsorption experiments. The difference between C/B1 and C/B2 can be related to the morphology of the surface (Fig. 1), which is less macroporous for C/B1.

Adsorbent	S <sub>BET</sub> (m <sup>2</sup> /g)
activated carbon Norit R3 Extra	1637
C/B1	1
C/B2	43

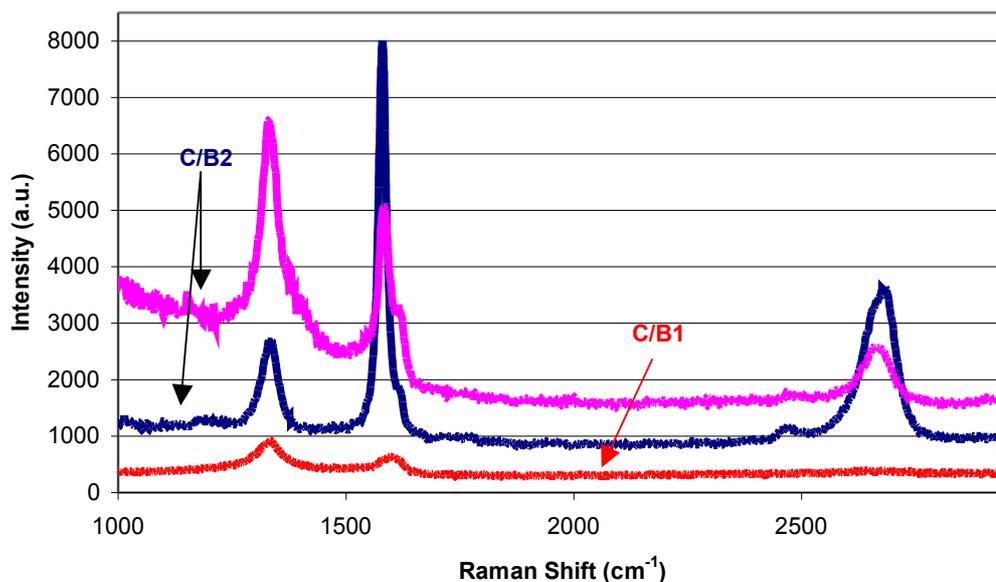
*Table 1. BET surfaces of adsorbents*



*Figure 1. MEB photos of C/C composites*

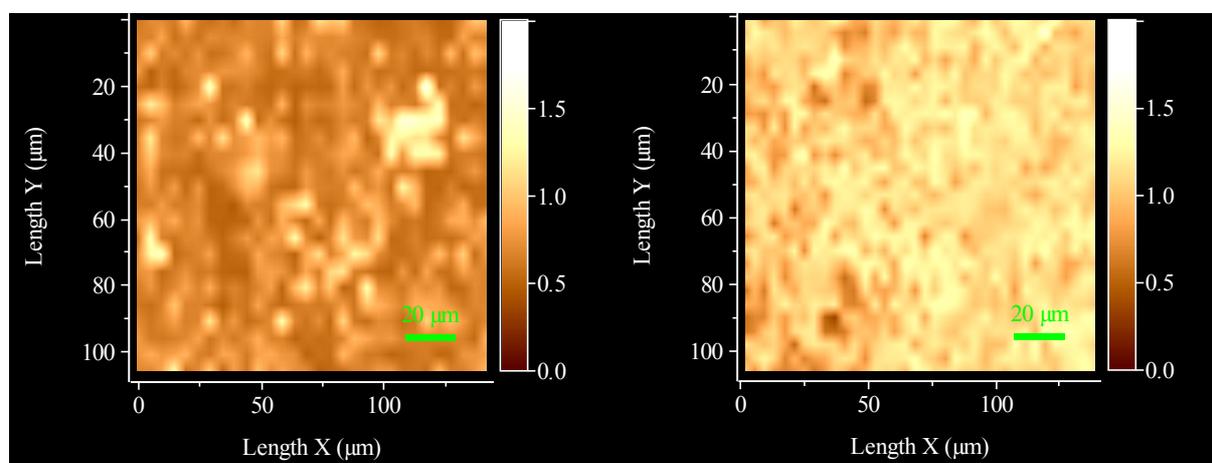
The micro-Raman spectroscopy is well adapted to the characterization of graphitic carbon materials [4]. On a single crystal of hexagonal graphite, when the graphene layers are oriented normally to the incident beam, the vibrational G mode located around 1580 cm<sup>-1</sup> is the only one observed above 100 cm<sup>-1</sup> on the first order Raman spectrum. In disordered carbons, in the absence of the long-range hexagonal symmetry, additional bands are detected : the D and D' bands located at 1350 and 1620 cm<sup>-1</sup>, respectively; and a second order Raman spectra which exhibits mainly the 2D overtone band above 2700 cm<sup>-1</sup>. The D, 2D and D' bands are assigned to defects within the carbon structure (edges, lattice defects or distorted graphene layers...). Both the band widths and band intensities can be used as structural improvement witnesses because this technique is able to follow the release of different types of defects which allows the formation of large coherent domains and possible graphitization [5-7]. It has been observed by Tuinstra and Koenig [8] that the intensity ratio between the D and G bands can be correlated to the inverse of the coherence length in the graphitic plans La, i.e. the mean coherent domains ('crystallites') size. This ratio I<sub>D</sub>/I<sub>G</sub> was therefore used as a witness of the graphitization level of the carbon material.

For the two C/C composite material C/B1 and C/B2, two types of Raman spectra can be observed locally (Fig. 2). For the two samples, well graphitized zones are observed which are related to the graphite particles. In addition, a spectrum related to each binder can be observed, which characterize less ordered zones. Hence there are two types of structures for adsorption.



*Figure 2. Raman spectra of C/B1 and C/B2*

On figure 3 are presented Raman images of the surface which shows the difference in structural ordering of the two C/C composites. Bright zones correspond to high values of the  $I_D/I_G$  ratio, and therefore to low levels of graphitization. These images also shows the heterogeneity of the surfaces, highlighting the fact there are two kind of adsorption sites at the surface of the samples.



*Figure 3. Raman spectral mapping of the surfaces of C/B1 (left) and C/B2 (right): intensity of  $I_D/I_G$*

### Adsorption isotherms

The desorption of ethanol occurred at temperature higher than 80°C under vacuum. TPD results (Fig. 4) show an important chemisorption of ethanol at the surface of the C/C composites. The desorption profile of C/B1 is very different from C/B2 and the activated carbon indicating that adsorption sites don't have the same interaction energy.

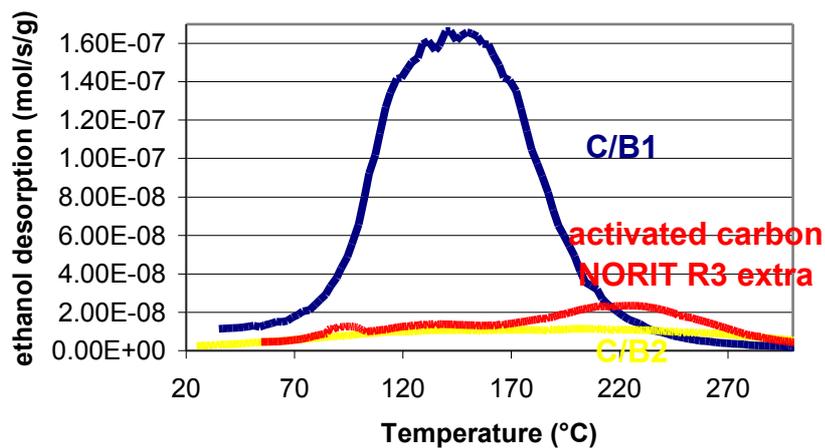


Figure 4. TPD of C/C composites after adsorption experiments (concentration of ethanol = 1.7 mol/l)

The quantity of ethanol sorbed per  $m^2$  of adsorbent is plotted versus the equilibrium concentration of ethanol in figure 4. Adsorption of ethanol on C/C composites is almost ten times higher with C/B2 and 400 times higher with C/B1 than on activated carbon, indicating a very strong interaction with ethanol. This could be explained by the fact that the activated carbon was heat treated at  $950^\circ C$  and then at  $300^\circ C$  under  $O_2$  to stabilize the functional surface groups. As a consequence it is rather hydrophobic and repulses ethanol molecules. Adsorption density seems to reach saturation for the activated carbon, not for C/B1 and C/B2.

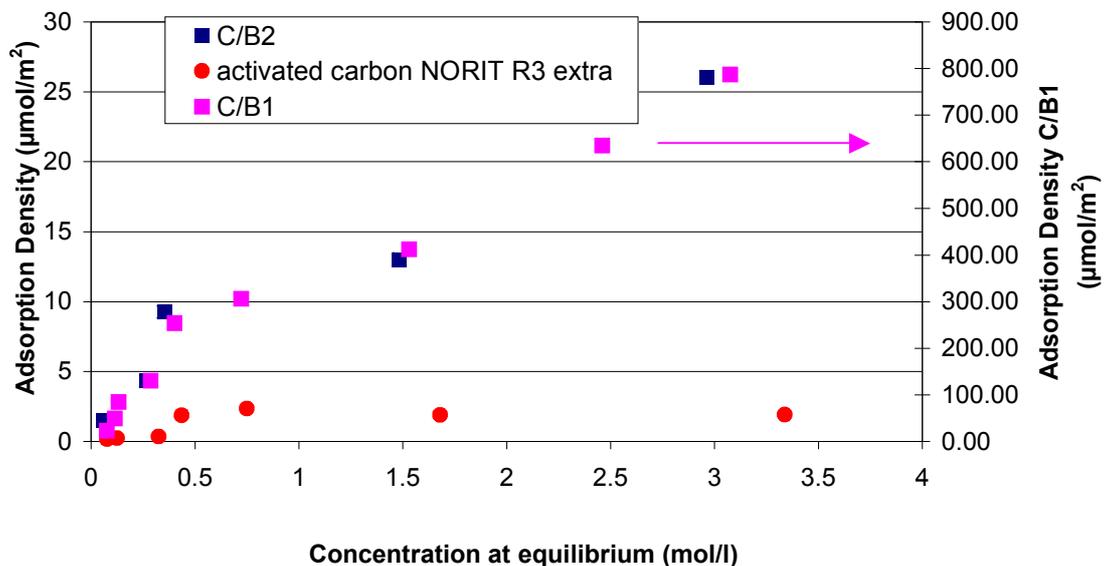
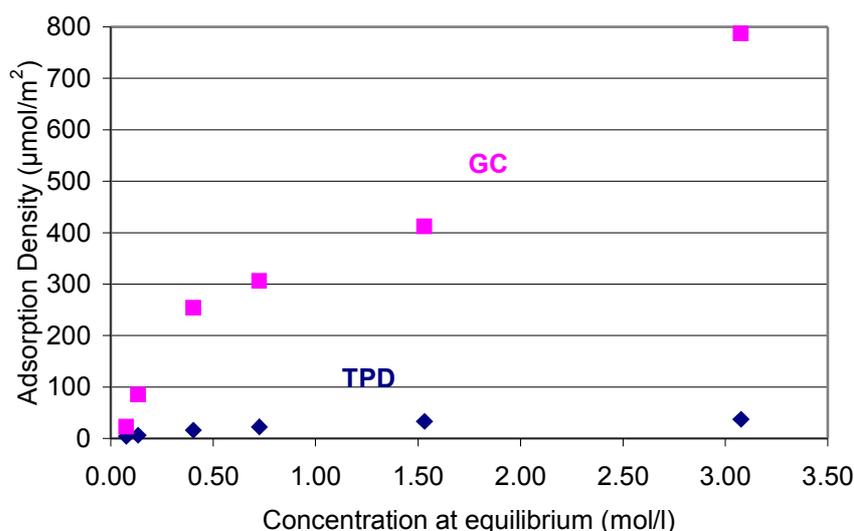


Figure 5. Adsorption isotherms of ethanol on adsorbents measured by GC

After adsorption experiments, samples were analysed by TPD. Quantities of ethanol desorbed in TPD plotted in figure 5 are inferior to quantities measured by GC. This is certainly because TPD experiments are run under vacuum hereby causing a partial desorption of ethanol sorbed on the sample before measurements. This result suggests that the adsorption of ethanol can occur following two mechanisms: a physisorption with a low energy and an adsorption on some specific sites with a higher interaction energy.



*Figure 6. Adsorption isotherms of ethanol on C/B1 by GC and TPD*

## Conclusions

C/C composites for brushes and collector disks strongly interact with ethanol. Although they have a much smaller BET surface than activated carbon they adsorb much more ethanol. This could be due to a lower hydrophilicity of the activated carbon after O<sub>2</sub> adsorption. Differences observed between C/B1 and C/B2 may be explained by the differences in heat treatment temperature and in the nature of the binder.

This strong interaction of C/C composites with ethanol could be partly responsible for excessive wear of fuel pump motor parts in addition to electrical wear due to commutation.

## References

- [1] M. Franz, H. A. Arafat and N. G. Pinto, Effect of chemical surface heterogeneity on the adsorption mechanism of dissolved aromatics on activated carbon, *Carbon*, **38**, 1807-1819, 2000
- [2] P. Podkoscielny, A. Dabrowski, and M. Bulow, Heterogeneity of nanoporous solids in adsorption from solutions-evaluation of energy distribution functions for adsorption in micropores of activated carbons by a comparative method, *Applied Surface Science*, **196**, 312-321, 2002
- [3] S. Krishnakumar and P. Somasundaran, Adsorption of Aerosol-OT on graphite from aqueous and non-aqueous media, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **117**, 227-233, 1996
- [4] Holden, J. M.; Jishi, R. A. & Eklund, P. C. Vibrational modes of carbon nanotubes, spectroscopy and theory *Carbon*, 1995, 33, 959-72
- [5] Ferrari, A. C. and Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon *Phys. Rev. B*, 2000, 61, 14095-14107
- [6] Rouzaud, J.; Oberlin, A. & Beny-Bassez, C. Carbon films: Structure and microtexture (optical and electron microscopy, Raman spectroscopy) *Thin Solid Films*, 1983, 105, 75-96
- [7] Beyssac, O.; Goffe, B.; Petitet, J.; Froigneux, E.; Moreau, M. & Rouzaud, J. On the characterization of disordered and heterogeneous carbonaceous materials by Raman spectroscopy *Spectrochimica Acta A: Mol. Biomol. Spectro.*, 2003, 59, 2267-76
- [8] Tuinstra, F. & Koenig, J. L. Raman Spectrum of Graphite *J. Chem. Phys.*, 1970, 53, 1126-30