

# Composite Carbon Nanostructures as Promising Carriers for Gaz Analysis

Laetitia Majoli\*, Alexis Evstratov\*, Jean-Michel Guillot\*, Aurélie Rouvière\*\*, Patrick Bausand\*\*

\* Ales High School of Mining, 6 Avenue de Clavières, Alès, F-30319 Cedex, France  
[alexis.evstratov@ema.fr](mailto:alexis.evstratov@ema.fr)

\*\* Research Group on Environment and Atmospheric Chemistry (GRECA), University Joseph Fourier, 39 Boulevard Gambetta, Grenoble, F-38000, France

## ABSTRACT

A lot of applications of carbon nanostructures (CNS) have been developed for the last fifteen years. Besides some particular electronic properties, such structures possess considerable adsorption capacities and so could be proposed both for gas treatment and for gas sampling and analysis. In this work, nanostructured carbon based composite samples were elaborated by the Catalytic Pyrolysis Method over the catalyst beds containing different transition metals supported by activated alumina ( $\gamma\text{-Al}_2\text{O}_3$ ). Their efficiencies for volatile organic compounds (VOC) trapping, compared with the ones of Tenax-TA as the reference material, were evaluated in dynamic conditions. The obtained results show a real interest for new active material application for VOC adsorption procedures.

**Keywords:** carbon nanostructures, volatile organic compounds, gas sampling, analytical techniques.

## 1 INTRODUCTION

Carbon nanostructures (CNS) have been widely studied for a number of advanced technical applications [1, 2], from gas storage [3, 4] to electronics [5] and bio-detection [6]. However, their important adsorption capacities allow also a probable using of the CNS based composites as alternative adsorbents for gas treatment and / or sampling [7, 8]. Unfortunately, this application axis is not yet significantly explored.

In the framework of the project ACI NPD-37 "NSC-Environment" supported by the French Ministry of Research and New Technologies, a series of composite nano- and micrometric carbon layered materials was developed in order to test them for air pollution sampling, namely for trapping of volatile organic compounds (VOC). One of widely spread commercial products for VOC sampling, Tenax-TA, had been selected as the reference material.

A development of new composite adsorbents was started from an elaboration of the material's conception. The objectives were to confer to the material prototype some special properties in order to assure its technical ability for adsorption applications.

These properties are the following:

- elevated specific surface,
- great hydrophobic capacity,
- perfect crystalline structure,
- high thermal and mechanical resistance,
- high adsorption capacity for VOC,
- easy thermal regeneration of the surface enriched with adsorption products.

It was supposed that these properties achieved in their ensemble for the same elaborated species, have to assure a good VOC sampling material quality allowing its high efficiency and intensive multi-usage for an important service period duration. In fact, an *elevated specific surface* coupled with a *great hydrophobic capacity* promotes a *high adsorption capacity* for the hydrophobic organic compounds such as many VOCs, a *perfect crystalline structure* of the nano- and micrometric carbon aggregates minimizes the surface polar site population avoiding so a negative water adsorption impact and also favoring the sample *thermal regeneration* in moderated conditions. Suitable *mechanical properties* are necessary in order both to allow material's handling and favor its lifetime.

## 2 EXPERIMENTAL

Nano-structured carbon based composite samples were elaborated by the Catalytic Pyrolysis Method over the catalyst beds being constituted from activated alumina supported transition metals (pure Fe, Ni, Co or their binary mixtures).

### 2.1 Synthesis of CNS

The catalyst samples were obtained by an impregnation of  $\gamma\text{-Al}_2\text{O}_3$  support (specific surface – 250–269  $\text{m}^2/\text{g}$ , mercury detected total pore volume – 0.683–0.684  $\text{cm}^3/\text{g}$ , fabrication – AXENS IFP Group Technologies) with nitrate salt solutions of either Ni or Fe, acetate salt solutions of Co and mixture acetate salt solutions of Ni and Fe or Co and Fe. After the impregnation step followed by the drying and calcination procedures, the samples were fulfilled in 1.5–

2.5 % ms. of pure or mixture metal oxides. The CNS elaboration was carried out at 550–850°C using a flow tubular laboratory reactor. The synthesis duration varied between 15 and 90 minutes. A synthesis gas mixture – N<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> – was used as the reaction middle. Due to the hydrogen presence, this mixture was also called to reduce, in situ, the oxide catalyst precursor to the metal one.

## 2.2 Characterization of CNS

The CNS species morphology, crystalline structure and thermo-chemical properties were investigated by SEM, TEM, XRD, Raman spectroscopy and DTA.

The sample affinities to water (or, contra versa, hydrophobic properties) were tested by so called “drying losses method”. According to this method, the mass *Ms* of a sample saturated in water is compared with the one the same sample *Md* after its drying in air at 120°C during 3 hours. The mass difference related to the dry sample mass and expressed in percent scale corresponds to its water affinity. Subtracted from 100 %, the water affinity value yields the sample hydrophobic capacity (HC) given by the equation 1:

$$HC = 100 - [(Ms - Md) / Md] * 100, \% \quad (1)$$

## 2.3 CNS adsorption test

The VOC adsorption capacities of elaborated composite samples were evaluated in dynamic conditions at constant temperature and relative humidity (20–21°C and ≤ 20 %, respectively). The sampling flow was fixed at 0.1 L/min through the stainless steel cartridges (i.d.-5 mm) packed with 200 mg of the tested adsorbents. The selected VOCs for the test were: Toluene, Ethyl-Benzene, Xylene, Hexane, Octane, Octene, Trichloroethylene, Tetrachloroethylene, α-Pinene and Limonene. The VOC levels of a glass chamber (200 L) in the gas phase were about 1 ppm for each compound.

## 3 CHARACTERIZATION RESULTS

The specific surfaces and the pore structures of the initial alumina support and of the CNS composite samples based on 2.5 % ms. cobalt oxide / 97.5 % ms. γ-Al<sub>2</sub>O<sub>3</sub> precursor (products 1–3) are shown in the Table 1.

Sample	Specific surface, m <sup>2</sup> /g	Pore volume V, cm <sup>3</sup> /g			
		V≥37 Å	V≥100 Å	V≥0,1μ	V≥1,0 μ
Initial γ-Al <sub>2</sub> O <sub>3</sub>	250	0.684	0.341	0.009	0.003
1	170	0.263	0.084	0.024	0.007
2	205	0.444	0.247	0.009	0.002
3	211	0.596	0.309	0.016	0.003

Table 1: Structure characteristics of the alumina support and of the CNS cobalt oxide based composite samples.

The samples 2 and 3, elaborated using the optimal parameter set, manifest good structure characteristics whereas their CNS contents exceed 20 % ms.

The Table 2 contains the data on the sample hydrophobic capacities related with their CNS contents and the catalytic precursor chemical nature (samples 4, 5 – 2.5 % ms. iron oxide / 97.5 % ms. γ-Al<sub>2</sub>O<sub>3</sub>; sample 6 – 2.5 % ms. nickel oxide / 97.5 % ms. γ-Al<sub>2</sub>O<sub>3</sub>; sample 7 – 2.5 % ms. iron and cobalt oxide mixture / 97.5 % ms. γ-Al<sub>2</sub>O<sub>3</sub>).

Sample	4	5	6	7
HC, % ms.	100.00	99.99	99.96	99.97
CNS content, % ms.	29.8	25.0	34.2	33.0

Table 2: Sample hydrophobic capacities via their CNS contents and the catalytic precursor nature.

The iron based CNS samples containing less than 30 % ms. of carbon seem to have the best hydrophobic capacities which are near closed or even equal to the “ideal” (100 %) values.

Raman spectroscopy study of elaborated CNS structures clearly shows three bands from 1200 cm<sup>-1</sup> to 3500 cm<sup>-1</sup> and no signal from 100 to 500 cm<sup>-1</sup> (Figure 1). This lack of signal indicates that single wall structures are not present. In the range of 1300 to 1400 cm<sup>-1</sup>, the deformation D-band indicates carbon microcrystalline structures like disordered graphite [9, 10]. Around 1600 cm<sup>-1</sup>, the G-band confirms the presence of graphite plans.

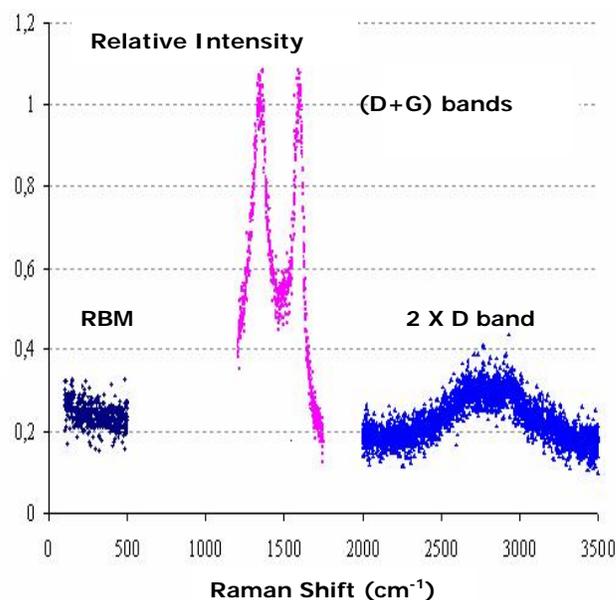


Figure 1: Raman spectra of CNS.

With XRD analyses, graphite structure development is also confirmed (Figure 2). The examined CNS structures

were obtained both with single metallic and bi-metallic catalytic supports.

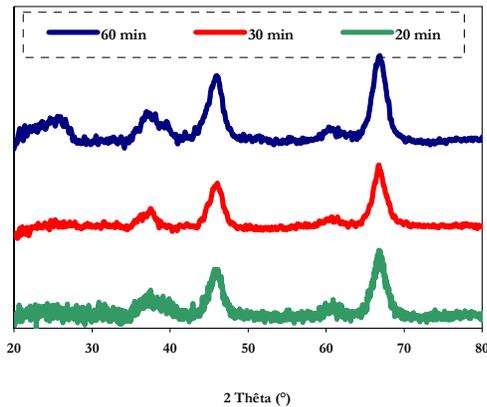


Figure 2: Synthesis duration influence on the crystalline state of CNS structures (XRD data are obtained for the samples elaborated with 2.5 % ms. iron and cobalt oxide mixture / 97.5 % ms.  $\gamma$ - $\text{Al}_2\text{O}_3$  precursor).

The CNS thermal stability was investigated by Differential Thermal Analysis (DTA) under air atmosphere. Results with bi-metallic catalyst supports are presented in Figure 3. For these CNS, no oxidative thermal degradation is observed until  $\sim 300^\circ\text{C}$ . Under reduction atmosphere, the CNS composite thermal stability will be conditioned by the support phase thermal resistance ( $600\text{--}650^\circ\text{C}$  for activated alumina).

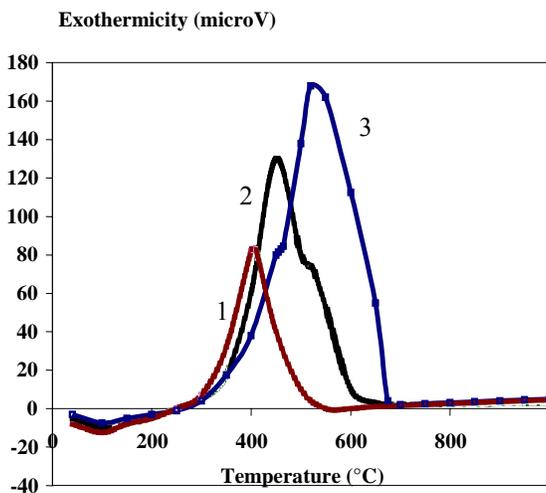


Figure 3: DTA results for 3 adsorbent with bimetallic catalysts (1-Oxides of Ni and Co; 2-Oxides of Fe and Co; 3-Oxides of Fe and Ni).

The internal CNS structure is visualized by means of Transmission Electronic Microscopy (TEM). Figure 4 shows that carbon filaments possess an internal channel and external walls constructed by superposed graphite plans.

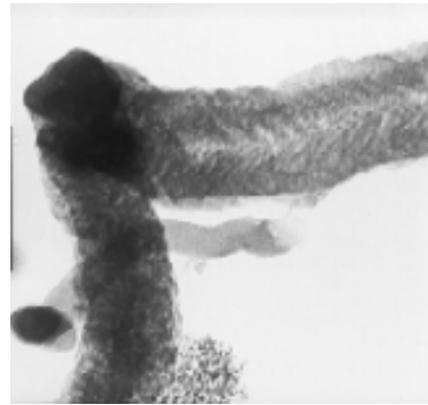


Figure 4: Internal structure with TEM analysis.

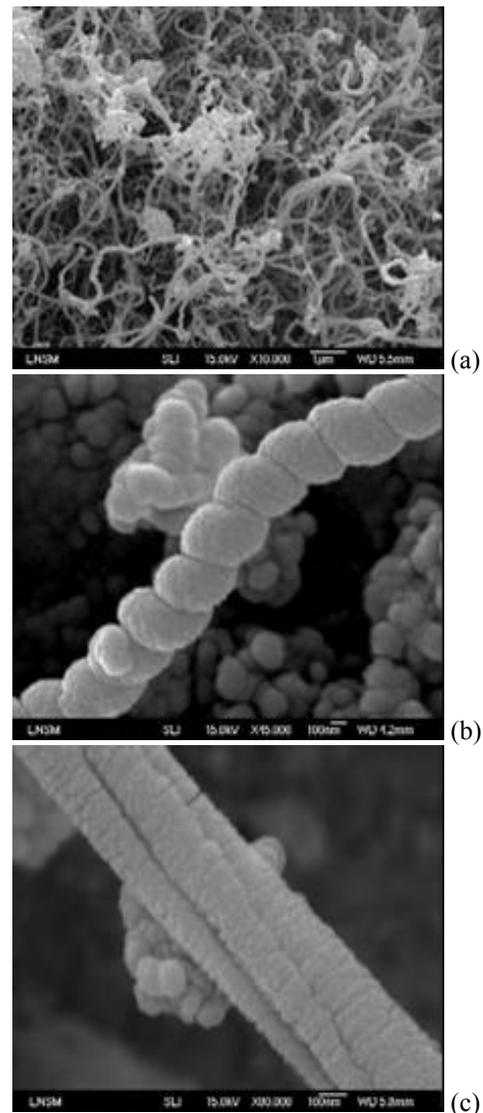


Figure 5: General view of CNS (a) and details of a nanocoil (b) and a nanofiber (c) (SEM analysis).

The CNS morphology and its details (nanocoils or nanotubes) were investigated by Scanning Electronic Microscopy (SEM). Some results are shown on the Figure 5.

All characterization results indicate that the sample properties correspond to the main objectives listed above. The elaborated CNS composites are so considered to be ready for testing as VOC trapping agents.

## 4 ADSORPTION TEST RESULTS

The adsorption test was carried out on with a mixture of selected VOCs into a glass chamber. For both cartridges packed containing Tenax-Ta and CNS, the capacities of the adsorbents were determined for each compound. An example of results obtained for a CNS sample elaborated with iron oxide – alumina catalyst is given in Table 3. The breakthrough volume (in L), as well as the adsorption capacity (mass ratio), are given. The capacity of CNS is always at least 9 times higher than for Tenax-TA and can reach to more than 20 times (cases of octane and octane). So CNS structures present a strong adsorption capacity for VOC trapping and can be used for analytical application. CNS composites with bi-metallic catalysts lead also to greater adsorption capacities than reference adsorbent. An important CNS density and their high adsorption capacity allow the packing of cartridges with very high efficiency where breakthrough probability is considerably decreased.

Selected VOCs For the test	Tenax TA (reference)		CNS (Oxides of Fe)	
	V (L)	m <sub>c</sub> /m <sub>a</sub> (µg/g)	V (L)	m <sub>c</sub> /m <sub>a</sub> (µg/g)
Toluene	0.85	27.6	11.2	364.1
Ethylbenzene	1.00	32.6	11.2	365.4
o-Xylene	1.20	39.5	11	362.2
Hexane	0.30	7.4	4.9	121.3
Octane	0.50	13.3	10.5	278.8
Trichloroethylene	0.50	27.4	4.6	252.2
Tetrachloroethylene	0.60	36.5	7	425.3
α-Pinene	0.80	25.7	10.9	350.5
D-Limonene	> 20	n.m.	> 17	n.m
Octene	0.50	13.4	10.6	284.2

Table 3: Comparison of adsorption capacities between Tenax-TA and CNS adsorbent for several VOCs (m<sub>c</sub>: compound mass, m<sub>a</sub>: adsorbent mass, n.m.: not measured).

## 5 CONCLUSION

This study has shown the characterization results and the application field for new composite adsorbents based on carbon nanostructures. These supports present the specific surface similar to the initial support (alumina) with values

close to 200 m<sup>2</sup>/g. The carbon level is in the range 25–35 % ms. The structure is perfectly crystalline (graphite type). This fact permits to confer to elaborated composites not only suitable mechanical hardness and thermal resistance (until 280–300°C under air atmosphere) but also hydrophobic behaviour. A comparative test, based on breakthrough volume, between CNS and Tenax-TA has shown that CNS composites manifest high adsorption efficiency. Comparatively to Tenax-TA, adsorption capacities of CNS are 10 times higher than capacities of the reference adsorbent. This fact opens a real application field for CNS as potential adsorbent in analytical chemistry. The adsorption capacity gives also the possibility to use these adsorbent for some treatment steps (VOC removal) especially for confined atmospheres or all applications where material resistance criteria are determinant for the adsorbent choice.

## 6 ACKNOWLEDGEMENTS

The authors thank the French Ministry of Research and New Technologies for financial support of this project called NPD-37 “NSC-Environment” in ACI program. Some characterization have been carried out with the help of other French research teams: J.F. Chapat and J.L. Le Loarer (Axens-IFP Group Technologies), B. Ducourant and J.L. Sauvajol (University of Montpellier II) and A. Frazckiewicz and P. Jouffrey (Saint-Etienne High School of Mining).

## REFERENCES

- [1] J.C. Charlier and J. P. Issy, *J. Phys. Chem. Solids*, **57**, 957-965, 1996.
- [2] L.P. Biro, G.I. Mark, J. Gyulai and P.A. Thiry, *Mater. Struct.*, **6**, 104-108, 1999.
- [3] M. Yumura, S. Ohshima, K. Uchida, Y. Tasaka, Y. Kuriki, F. Ikazaki, Y. Saito and S. Uemura, *Diam. Relat. Mater.*, **8**, 785-791, 1999.
- [4] E. Frackowiak and F. Béguin, *Carbon*, **40**, 1775-1787, 2002.
- [5] A. Minett, J. Fraysse, G. Gang, G.-T. Kim and S. Roth, *Curr. Appl. Phys.*, **2**, 61-64, 2002.
- [6] S. Carrara, V. Bavastrello, D. Ricci, E. Stura, C. Nicolini, *Sensor.Actuat. B-Chem.*, **109**, 221-226, 2005.
- [7] L. Majoli, A. Evstratov and J.M. Guillot, *6<sup>th</sup> International Conférence on Nanotechnology in Carbon, Nanotec'04*, Batz-sur-Mer, France, 2004.
- [8] L. Majoli, A. Evstratov, and J.M. Guillot, *Colloque du Groupe Français d'Etudes des Carbones*, Saint Agnan-en-Morvan, France, 2005.
- [9] T. Luo, J. Liu, L. Chen, S. Zeng and Y. Qian L., *Carbon*, **43**, 755-759, 2005.
- [10] A. Maroto Valiente, P. Navarro López, I. Rodríguez Ramos, A. Guerrero Ruiz, Can Lin and Qin Xin, *Carbon*, **38**, 2003-2006, 2000.