GAS ADSORPTION BY CATALYTIC CARBON NANOTUBES

*H .Gaucher, R.J.M. Pellenq, *Y .Grillet, S. Bonnamy and F. Béguin*
CRMD, CNRS-University, 1B, Rue de la Férollerie, 45071 Orléans Cedex 02, France
**CTM, CNRS, 26, Rue du 141e R.I.A., 13003 Marseille, France*

Introduction

Since they were discovered in 1991 as by-product in the synthesis of fullerenes [1], carbon nanotubes are a source of tremendous work. Even if they are expected to have exceptional properties, one of the main problems for future applications is their production at a large scale. Using an electric arc between two graphite rods, they are produced together with nanoparticles and microporous carbon [2], and purification is not easy. In 1993, it was claimed that they could also be synthesized by the catalytic decomposition of hydocarbons, using a supported transition metal [3]. This process allowed us to produce large amounts of carbon nanotubes [4]. Gas adsorption has been used for their characterization, and the pores characteristics are compared to the information given by T.E.M.

Experimental

A catalyst precursor was prepared by stirring silica gel (90 Å, Janssen) with an aqueous cobalt nitrate solution and subsequent drying under vacuum at 100°C (the proportions were selected for getting 10wt % of cobalt in the catalyst). Then it was reduced at 400°C by a 10%/90% hydrogen/nitrogen mixture in a vertical flow furnace. The temperature of the reduced material was rapidly raised to 900°C and a 10%/90% acetylene/nitrogen mixture was introduced in order to produce nanotubes. After half an hour decomposition time of acetylene, the system was cooled down under nitrogen. Nanotubes were purified by dissolving silica and cobalt respectively with hydrofluoric acid (73%) and diluted nitric acid. In some cases, the purified carbon material was heat-treated under argon at 2800°C. Prior to gas adsorption, samples were outgassed (10^{-2} bar) at 200°C during 12h. Nitrogen or argon adsorption was performed at 77K on a Sorptomatic 1900 (Carlo Erba). Alcoholic suspensions of the nanotubes were dispersed on the grids for Transmission Electron Microscopy (Philips EM400) characterization.

Results and discussion

Carbon nanotubes, produced in high yield, are associated to some concentric carbon shells surrounding metallic cobalt (3wt %). They are sinuous and entangled; their tips are never closed and they are always free of metal in the canal [4]. The conic shape of some tips suggests that the catalyst particle from which the decomposition of hydrocarbon occured has been expelled. The carbon layers appear as almost continuous and slightly wrinkled, and the nanotubes are always free of any amorphous carbon coating. The outer diameter is homogeneous, ranging from 20 to 40 nm, and the diameter of the hollow core is about 4 nm.

Heat-treatment at 2800°C allows complete vaporization of cobalt. Simultaneously the nanotubes are transformed, becoming comparable to those prepared by the electric arc process. The aromatic carbon layers are perfectly straight and the tips of these tubes are closed. A number of « elbows » are observed; they correspond to the accumulation of defects at grain boundaries [4].

Nitrogen and argon adsorption isotherms are presented on figures 1 and 2 respectively for as-received (900°C) and heat-treated (2800°C) nanotubes. Whatever the temperature, the isotherms are of type IV, characteristic of a mesoporous adsorbent. They are very comparable to the curve which is observed for clays [5]. Such an analogy could be attributed to swelling of the nanotubes or to adsorption on the external surface. The first interpretation goes against the « Russian doll » model which is accepted for carbon nanotubes.

The B.J.H. method was used to determine the mesopores characteristics [5]. As seen on figures 3 and 4, a maximum in the pores size distribution appears at a radius of about 2 nm, in good agreement with the dimensions which were measured for the canal of the nanotubes. Due to the fact that nanotubes formed at 900°C are opened, this canal is easily accessible for nitrogen or argon. Table 1 shows that the mesopore volume drastically decreases from 900 to 2800°C. As mentioned above the tips are closed after heating at 2800°C, therefore gas can hardly penetrate in the canal. The micropores volume was calculated by using the t-plot method [6]. At 900°C, it is rather small, and it only slightly decreases with heating at 2800°C (table 1). In fact, in our TEM images, we did not detect a number of intervals with one carbon layer missing which could be responsible for some microporosity. This explain why there is not a drastic change with temperature, even if TEM observations show perfect carbon layers at

2800°C. It means that even the nanotubes prepared at 900°C present a limited number of defects.

Conclusion

There is an interesting correlation between the nanotextural observations given by TEM and the data which are deduced from gas adsorption. The nanotubes are mainly mesoporous materials, however the pores are not accessible after 2800°C heat treatment.

Acknowledgements

This work was supported by European Community through as TMR program (under network contract: **NAMITECH,** ERBFMRX-CT96 (DG12-MITH).

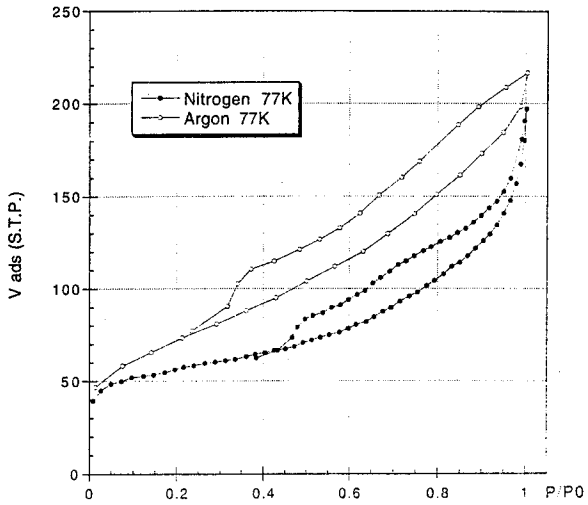

Figure 1. Adsorption-desorption isotherms 900°C.

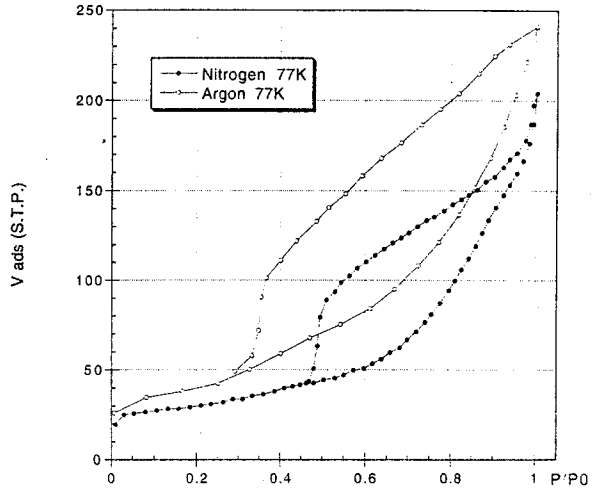

Figure 2. Adsorption-desorption isotherms 2800°C.

Références

1. Iijima S., *Nature*, 1991, 354, 56.
2. Clinard C., Rouzaud J.N., Delpeux S., Béguin F. and Conard J., *J.Phys.Chem.Solids*, 1994, 55, 651.
3. José-Yacaman M., Miki-Yoshida M., Rendon L. and Santiesteban J.G., *Appl. Phys. Lett.*, 1993, 62, 202.
4. Gaucher H., Bonnamy S. and Béguin F., submitted to *Carbon*.
5. Gregg S.J. and Sing K.W.S., in *Adsorption, surface area and porosity*, Academic Press, London, 1967, p.174, *ibid.* p.160.
6. Molina-Sabio M., Rodriguez-Reinoso F., Valladares D. and Zgrablich G., *Studies in surface science and catalysis*, 1994, 87, p.573.

Heat treatment temperature	BET Surface area $m^2.g^{-1}$	Microporous volume $cm^3.g^{-1}$	Mesoporous volume $cm^3.g^{-1}$
900°C	204	0.038	0.040
2800°C	109	0.027	0.012

Table 1. Data of nitrogen adsorption at 77K.

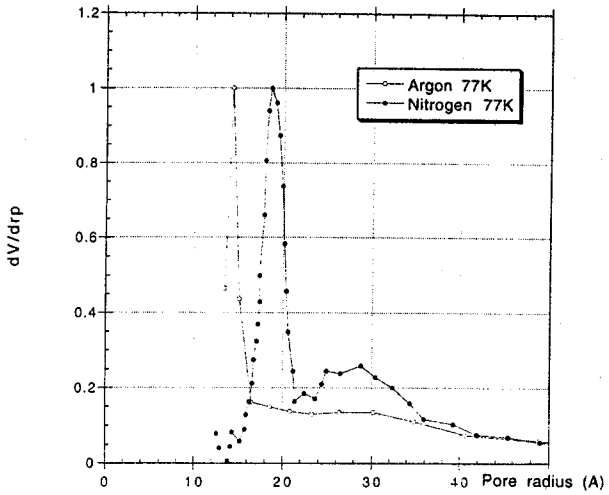

Figure 3. Pore size distribution 900°C.

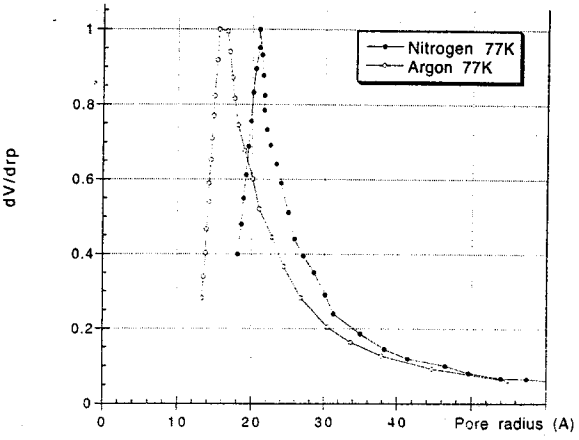

Figure 4. Pore size distribution 2800°C.