

NANOSTRUCTURED CARBON FROM CHLORINATION OF METALLOCENES.

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Nanostructured carbon has attracted very much attention in recent years not only to scientists from Solid State Physics and Chemistry but also to the industrial engineers due to several applications [1,2]. In particular, carbon nanotubes (CNTs) and fullerene-related materials have become very popular nowadays [3,4]. Recently, we have carried out some experiments concerning the chlorination of some metal carbides and metallocenes in order to obtain nanostructured carbon, with promising applications as hydrogen storage and transport materials. In this work we present our electron microscopy observations from the direct reaction of ferrocene (FeCp_2) and cobaltocene (CoCp_2) [$\text{Cp}=(\text{C}_5\text{H}_5)^-$] with chlorine gas, producing carbon materials and volatile metal halides. Nanoporous amorphous carbon materials with variable morphologies, such as nanotubes, elliptical nanobags-branches and hollow nanospheres, will be described.

Experimental: 1. Sample preparation: FeCp_2 , placed in silica boats, was treated with a flow of Cl_2 gas in a tubular furnace at 100, 150, 200, 300 and 900 °C, for 30 minutes. The reaction time was extended to 180 minutes at 200 and 900 °C. More details are given in [5]. 2. Electron Microscopy: SEM observations were carried out in a JSM 6335F microscope; TEM studies were carried out in a CM200 FEG (fitted with a GIF 200 and an EDAX DX4 spectrometer) and in a JEM 3000 F (HRTEM) electron microscopes.

Results and discussion: Fig. 1 shows a SEM micrograph of several carbon nanotubes, with a external diameter (ϕ_e) of 500 nm and an internal one (ϕ_i) of 80 nm, obtained at 150 °C. Fig. 2 corresponds to a TEM image of two types of amorphous CNTs (see the SAED pattern in the upper left corner), obtained at 200 °C (30 minutes). The one on the right, with thicker walls, is more common in the sample than the tube shown on the left, with a larger diameter. The XEDS analyses indicate that the tubes consist on ~90% of carbon, with remains of Fe and Cl. In addition to the amorphous CNTs, amorphous carbon nanobags and open-end branches were also found. In order to study the influence of the reaction time on the formation of these carbon nanostructures, the reaction time was extended to 180 minutes at 200°C. Amorphous CNTs were not observed and, instead, elliptical nanobags were found, see Figure 3. They are ~100 nm long, with a wall-thickness of ~20 nm. Notice the high curvature of the nanobags marked with an arrow. The Fe and Cl remains, measured with XEDS, are lower because a higher quantity of metal chloride is eliminated during the reaction process. When the reaction temperature is increased to 900 °C (30 minutes) the carbon nanobags are almost spherical and very homogeneous, as it can be seen in the TEM image at low magnification of Figure 4a. The wall thickness is ~12-20 nm and $\phi_e \sim 150$ nm. A HRTEM image of one of this carbon spheres is included in fig. 4b, where single wave-like graphene layers are observed at the walls. XEDS analyses (fig. 4c) indicate that they consist on ~100% of carbon; Fe and Cl are eliminated due to the high reaction temperature. The carbon nanobags obtained when the reaction of FeCp_2 with Cl_2 is maintained at 900 °C for 180 minutes keep the same dimensions as the previously described ones (fig. 5a), but the graphene layers are more ordered (see the HRTEM micrograph of fig.5b). Besides, the longer reaction time increases the sinterization process of the spheres. EELS spectra taken from these carbon nanostructures show the typical ELNES features in the carbon K absorption edge of a disordered array of graphene-like sheets. Therefore, a sharp π^* and a broad σ^* peaks are observed in the spectra, as it can be seen in figure 5c (the spectrum was obtained from the sample treated at 900 °C for 180 minutes). In the case of CoCp_2 , open and closed nanospheres with $\phi_e = 70 - 300$ nm were observed. Besides, amorphous carbon filaments up to 500 nm long and up to 25 nm thick were also found in this case.

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References

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