SYNTHESIS OF CARBON NANOTUBES, NANOFIBERS AND CARBON ENCAPSULATED NANOPARTICLES BY DECOMPOSITION OF ACETYLENE OVER PD AND Pd-Ge CATALYSTS

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Since their discovery, the design and study of Carbon nanotubes (CNTs), nanotubes-based materials and devices have become topics of great interest in material science. CNTs have been used as building blocks in the design of molecular electronic devices of great technological interest, as field emitters, in diodes, transistors, flat-panel displays, scanning probe microscopy tips and many others. Potential applications currently being investigated include hydrogen storage, reinforced polymers, molecular (drug) delivery and scaffolding in tissue engineering. For these applications, mass production of nanotubes play an important role. Due to this reason the discovery of new catalysts for an efficient production, remains a current topic of investigation. In this line we present results from a study of the decomposition of acetylene over alumina-supported palladium and palladium-germanium catalysts.

The catalysts were prepared by the Solvated Metal Atom Dispersion technique (SMAD).[1] This procedure is carried out by simultaneous evaporation of Palladium and/or Germanium and an organic solvent like 2-propanol to generate a frozen matrix on the walls of the metal atom reactor at 77K. After warming this matrix to room temperature, a colloid with very small and highly reactive clusters is obtained. These clusters react with acid sites of the high surface area γ-alumina, forming anchored nucleus of Pd, Ge and Pd-Ge alloys. This mixture was subsequently dried and the powder ground in a mortar before their use as catalyst. For this study we prepared γ-alumina catalysts with the following loads: Pd(1%), Pd(1%)-Ge (0.1%), Pd(1%)-Ge (0.3%), Pd(1%)-Ge (0.5%), and Ge (0.1%).

The decomposition of acetylene was carried out in a Chemical Vapor Deposition apparatus (CVD) composed of a horizontal tube furnace and gas flow lines.[2] The catalyst, was loaded in a quartz boat inside the tube reactor, heated at a rate of 20ºC/min and annealed 10 min in a Ar/H_2 stream at 800 ºC. Then, acetylene (25 ml/min) was decomposed over the catalyst for 30 min. We have chosen 800 ºC because this is the optimum temperature for synthesis of pure carbon nanotubes with the Pd(1%)/γ-Al_2O_3 catalyst.[3] The effects of Germanium loading in the final nanocarbon products were analyzed by Transmission Electron Microscopy.

When pure palladium catalyst is used carbon products consist predominantly of Multiwall Carbon Nanotubes (MWCNTs). In terms of yield, one gram of palladium produces about 110 grams of MWCNTs. When a small amount of germanium (0.1%) is added to the catalyst formula, it produces around 210 grams of MWCNTs (see Figure 1). The change in the yield could be attributed to modifications in the electronic structure of the palladium nanoparticles, which preferentially induces the production of tubular structures. When 0.3% of Germanium is added to the catalyst something different occurs. Carbon products decrease close to 20 grams per gram of palladium. TEM micrographs show the formation of carbon fibers (Figure 2). Additional amounts of germanium in the catalyst formulation (0.5%), induces the formation of carbon encapsulated Pd-Ge nanoparticles (Figure 3). Probably germanium, in this case, is blocking the active sites or producing drastic changes in the electronic structure of palladium particles, thus hindering the formation of filamentous structures. Similar effects were observed when pure germanium was used as catalyst (figure 4).

As final remarks we can conclude that adding small amounts of germanium to the palladium catalyst can improve considerably the yield toward the formation of carbon nanotubes. The formation of carbon encapsulated Pd-Ge nanoparticles by this method could also have technological interest.

1. G. Cárdenas, R. A. Segura, J. Reyes, *Colloid Polym. Sci*. **2004**, 282, 1206.
2. R. A. Segura, W. Ibáñez, R. Soto, S. Hevia, P. Häberle, *J. Nanosc. Nanotech.* **2006** (in press)
3. R. A. Segura, A. Tello, G. Cardenas, P. Häberle (unpublished)

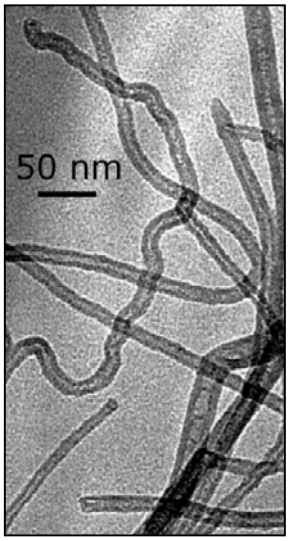

Figure 1. Multiwall Carbon Nanotubes obtained by decomposition of acetylene at 800 ºC in a Pd(1%)-Ge(0.1%)/γ-Al_2O_3. The mean diameter of nanotubes is 18 nm.

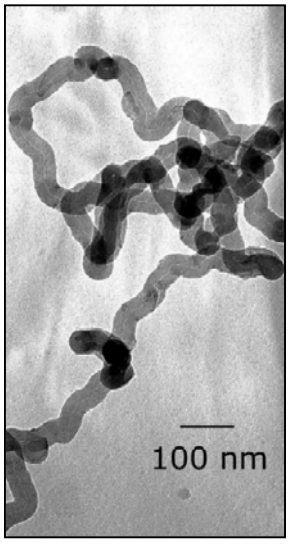

Figure 2. Carbon Nanofibers obtained by decomposition of acetylene at 800 ºC in a Pd(1%)-Ge(0.3%)/γ-Al_2O_3. The mean diameter of fibers is 38 nm.

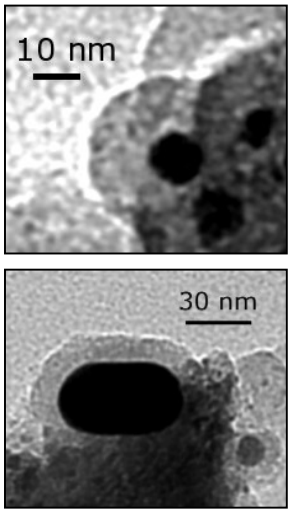

Figure 3. Carbon encapsulated nanoparticles obtained by decomposition of acetylene at 800 ºC in a Pd(1%)-Ge(0.5%)/γ-Al_2O_3.

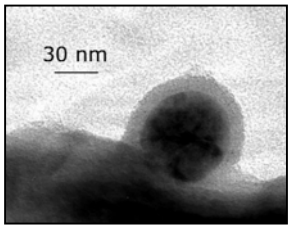

Figure 4. Carbon encapsulated germanium nanoparticle obtained by decomposition of acetylene at 800 ºC in Ge(1%)/γ-Al_2O_3 catalyst.