

Synthesis of carbon nanotubes, nanofibers and encapsulated nanoparticles by decomposition of acetylene on Ge modified Pd catalysts

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Different carbon nanostructures were synthesized by decomposition of acetylene over alumina supported palladium–germanium catalysts. The addition of small amounts of Ge to the Pd(1%)/ γ -Al₂O₃ catalyst increases the yield of carbon nanotubes among other carbon products, in the decomposition of acetylene. The use of a higher Ge concentration (0.3%) in the catalyst induces the formation of carbon nanofibers. For larger Ge concentrations (0.5%) the bimetallic catalyst particles become encapsulated in a graphitic structure.

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Among the nanostructures currently being investigated for various applications, from nanoelectronic devices to materials with novel properties, undoubtedly carbon nanotubes (CNTs) have a leading role. Hydrogen storage, reinforced polymers for lighter and stronger materials, molecular (drug) delivery and scaffolding in tissue engineering, among many other applications, require mass production of CNTs. The most commonly used catalysts, for their synthesis, are based on Fe and Ni nanoparticles. Despite the great amount of work that has been done in this area, the design of improved production methods, including the use of new catalysts, remains a current and growing field of research.

In this report we present our preliminary results from a study of the decomposition of acetylene over alumina-supported palladium–germanium catalysts, Pd–Ge/ γ -Al₂O₃. Palladium has been rarely used as a catalyst for the formation of carbon nanostructures (CNSs). We did not find any reports in the literature regarding the use of Germanium as catalyst promoter or additive in the synthesis of CNSs. Palladium have indeed been used as a catalyst, Wong et al. [1] have reported the growth of thin Pd films over silicon dioxide substrates. In a different way, Lee et al. [2] have prepared Pd particles through chemical reduction, which were subsequently supported over suitable substrates. In both reports filament-like carbon nanostructures were grown using thermal CVD. On the other hand, we have recently reported the high yield synthesis of carbon nanotubes, and carbon nanofibers of various shapes by using a catalyst consisting of Pd nanoparticles supported on γ -Al₂O₃ [3]. The addition of Germanium modifies the catalytic behavior of Palladium which, depending on the Ge load, yields different type of carbon nanostructures. Our results indicate the addition of small amounts of Ge lead to a higher efficiency toward the production of CNTs.

The catalysts for the CVD process were prepared by the Solvated Metal Atom Dispersion technique (SMAD) [4]. This procedure is carried out by simultaneous evaporation of Palladium [5] and Germanium [6] in the presence of an organic solvent (2-propanol) atmosphere. After preparation the resulting

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Table 1 Yield of carbon products as function of germanium content through the decomposition of acetylene over Pd(1%)–Ge(x%)/ γ -Al₂O₃ catalyst at 800 °C.

Ge (wt%) on Pd(1%)–Ge/ γ -Al ₂ O ₃	yield of carbon products		type of structures (diameter)
	C/Pd mass ratio	C/Pd at. ratio	
0	110	1000	MWCNTs (27 nm)
0.1	211	1870	MWCNTs (18 nm)
0.3	21	190	CNFs (38 nm)
0.5	19	170	CENPs

powder was ground before using it as a catalyst. For this study we prepared γ -Al₂O₃ catalysts with the following loads: Pd(1%), Pd(1%)–Ge(0.1%), Pd(1%)–Ge (0.3%), Pd(1%)–Ge (0.5%), and Ge (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 [7]. First, the catalyst was activated (in situ) by heating it at a rate of 20 °C/min and annealing for 10 min in an Ar/H₂ stream, at the desired synthesis temperature. For this study, we have chosen 800 °C since this temperature yielded the optimum performance of Pd/ γ -Al₂O₃ catalyst, towards the synthesis of pure carbon nanotubes [3]. After the catalyst activation, acetylene, at a rate of 25 ml/min, was accepted into the furnace and decomposed for 30 min. The mass yields of the reactions were calculated from the weight difference between the pristine catalyst and its total weight after synthesis. The structure of the products was analyzed mainly by transmission electron microscopy (TEM).

TEM measurements of fresh catalyst reveal a diameter close to 3 nm for the Pd nanoparticles and no significant changes in this size was detected when Ge was incorporated. After thermal annealing, a sintering process was detected by TEM; most Pd particles grew to sizes close to 20 nm. Selected area electron diffraction of Pd–Ge catalyst reveals the presence of alloy phases [8].

Auger spectroscopy of CVD products reveals these deposit consists mainly of carbon. The yield of these carbon products are presented as the C/Pd mass and atomic ratios, taking as a reference only the active component in the catalyst (palladium metal). These results are presented in Table 1, together with a generic description of the dominant structures shown by our TEM analysis.

When pure palladium catalyst was used, high purity Multiwall Carbon Nanotubes (MWCNTs) were obtained for a synthesis temperature of 800 °C [3]. In terms of yield, one gram of palladium produces

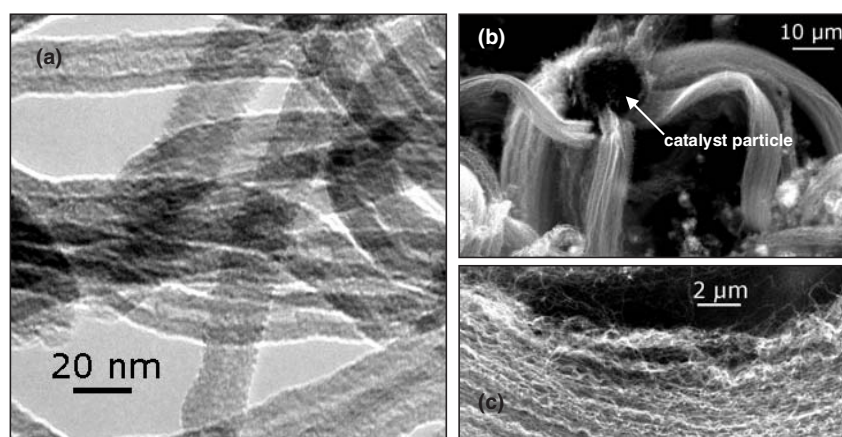


Fig. 1 Multiwall carbon nanotubes obtained by decomposition of acetylene at 800 °C in a Pd(1%)–Ge(0.1%)/ γ -Al₂O₃. (a) TEM image. Mean diameter of nanotubes is 18 nm. (b–c) SEM images. Figure (b) shows MWCNT bundles growing from a catalyst particle and figure (c) shows a magnification of a bundle.

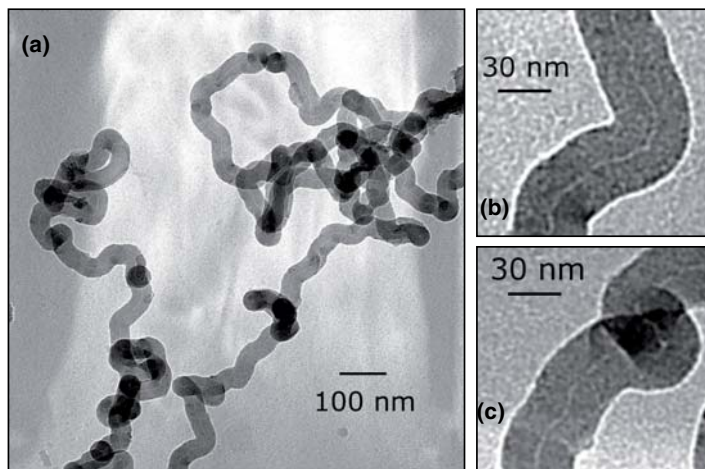


Fig. 2 TEM images of carbon nanofibers obtained by decomposition of acetylene at 800 °C in a Pd(1%)–Ge(0.3%)/ γ -Al₂O₃. The mean diameter of fibers is 38 nm.

about 110 grams of MWCNTs. When a small amount of germanium (0.1 wt%) is added to the catalyst formula, it produces around 210 grams of MWCNTs, almost twice the amount obtained from the pure Pd catalyst. Figure 1 shows TEM and SEM images of CNTs produced with this catalyst. In Fig. 1(b) it is possible to see CNT bundles emerging from catalyst particles. When 0.3% of germanium is added to the catalyst something different occurs. The yield decreases considerably, only 20 grams of carbon products per gram of palladium is produced. TEM micrographs show the formation of wire-like filament structures with an almost solid body (Fig. 2), consistent with the formation of carbon nanofibers instead of carbon nanotubes. The decrease in the product's volume provides a visual indication of this change, since a larger volume is expected, for a fixed amount of catalyst, in the case of preferential synthesis of carbon nanotubes. This is the case for Ge free samples and 0.1% Ge-modified catalysts, whereas for the addition 0.3% Ge, the volume after synthesis displays almost no significant change. Additional amounts of germanium in the catalyst formulation (0.5%), induces the formation of carbon encapsulated Pd–Ge nanoparticles (Fig. 3a–c). Similar effects were observed when only pure germanium was used as catalyst (Fig. 3d).

Our results clearly show that germanium modifies the catalytic properties of Pd/ γ -Al₂O₃. For low germanium content (0.1 wt%) there is a promoter effect toward MWCNT production. One reasonable explanation could be that Ge is preventing the agglomeration of Pd nanoparticles during annealing; therefore the size distribution of the Pd nanoparticles is such that their mean radius is smaller, than those without Ge, consequently there are more Pd–Ge than Pd nanoparticles for a same amount of catalyst. In fact, carbon nanotubes produced with 0.1% Ge have a mean diameter of 18 nm, smaller than those produced with the pure Pd catalyst with a mean diameter of 27 nm. Undoubtedly the added Ge modifies the electronic structure of the Pd nanoparticles, since only a slightly higher Ge concentration in the catalyst (0.3 wt%), practically eliminates the catalytic efficiency. Only a very low yield of carbon nanofibers is formed instead carbon nanotubes. These results are consistent with a lower carbon solubility and/or diffusion within the catalysts particles. For higher concentrations (0.5 wt%), the decomposition of acetylene results in the carbon encapsulation of the Pd–Ge nanoparticles. Probably Germanium is now blocking the active sites modifying drastically the catalytic properties of the Palladium particles, allowing the formation of graphitic shells around the particles, but hindering the carbon extrusion, which is the mechanism under which filament-like structures are formed.

The efficiency of this Pd–Ge catalytic system could prove useful for applications in high yield production of CNTs, since one gram of palladium, in a Pd(1%)/ γ -Al₂O₃ catalyst, can produce about 113 grams of MWCNTs at 800 °C in only 30 min. Nevertheless the Pd(1%)–Ge(0.1%)/ γ -Al₂O₃ catalyst

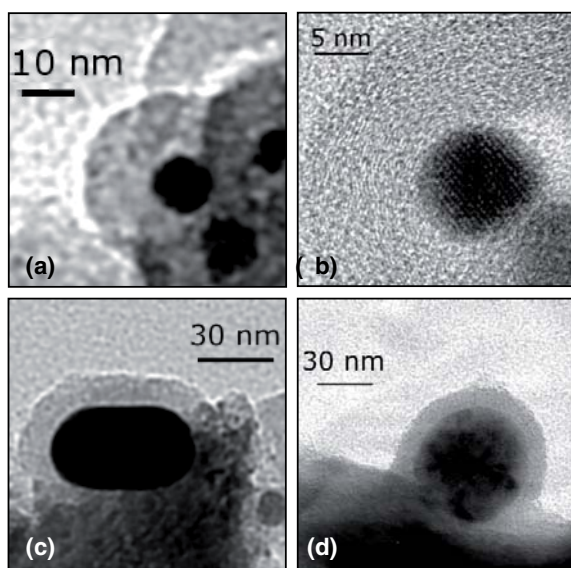


Fig. 3 (a–c) TEM images of carbon encapsulated nanoparticles obtained by decomposition of acetylene at 800 °C in a Pd(1%)–Ge(0.5%)/ γ -Al₂O₃, and (d) using Ge(1%)/ γ -Al₂O₃ catalyst.

produces twice this amount of MWCNTs, for the same synthesis conditions. These yield values compare well with previously published reports of high yield synthesis of CNTs. For example the work of Louis et al. [9] which considers the synthesis of MWCNTs over Fe(20%)/ γ -Al₂O₃ have an optimum result of 250 grams of CNTs per gram of iron per hour. Jeon et al. [10] have reported an optimum yield of 125 grams of CNTs per gram of iron per hour for a Fe(12%)/MoMgO catalyst. These numbers should be compared with ours: 210 grams of CNTs per gram of palladium per half hour.

On the other hand, this Pd–Ge catalytic system could be used to obtain different kind of C materials: nanotubes, nanofibers and encapsulated nanoparticles. Applications for carbon nanotubes and nanofibers seem to be evident but also the encapsulated nanoparticles could find interesting technological applications. For example these encapsulated nanoparticles could be used in applications where the graphite shell could be used as a chemical barrier, protecting the nanoparticle from the local environment. In this way the long range order properties of the metal core could be used without affecting the integrity of the nanoparticle. Some reports have discussed the possibility of using graphite encapsulated magnetic nanoparticles for biomedical applications [11, 12], hence variations of the method described here could be used for similar purposes or as active elements in magnetic [13, 14] or optoelectronic [14] nanodevices.

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 in CVD synthesis. The formation of carbon encapsulated Pd–Ge nanoparticles is also possible by modifying the Ge content in the catalyst.

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