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1 Introduction

Carbon nanostructures have reached great significance in many scientific and technological applications. Since the discovery of fullerenes, and as a wake of this development, a number of new forms of carbon have been identified in a very short period of time: carbon nanotubes, nanofibers, nano-onions and other structures. These new allotropic forms of carbon present exceptional electrical, mechanical and chemical properties. A special attention has been given to carbon nanotubes (CNTs), since they have extremely high tensile strength; they are highly flexible and can exhibit semiconducting, metallic or even superconducting behavior. In short, CNTs are the ideal building blocks for molecular nanoelectronics. Other applications currently being explored, for CNTs based materials, include hydrogen storage, reinforced polymers, molecular (drug) delivery and scaffolding in tissue engineering. Many of them require large scale production of CNTs. Hence the discovery of new catalysts and improved production methods remains a current and growing field of research. In this report we present results from a study of the decomposition of acetylene over an alumina-supported palladium catalyst. Only a few studies related to the formation of carbon nanostructures using Pd as catalyst have been reported. Wong et al. [1] have used Pd films over silicon substrates and Lee et al. [2] have prepared Pd particles through chemical reduction and subsequently dispersed them over suitable substrates. In both reports filament-like carbon nanostructures were grown using thermal CVD. In this study we describe a new way to prepare high efficiency catalysts aimed at the production of CNTs in a selected temperature range. The method to prepare the catalyst consists roughly in the formation of metallic clusters by evaporation of the metal in the presence of an organic molecular gas, this colloid is collected at liquid nitrogen temperature. When the metal clusters undergo a warm-up process they become highly reactive, anchoring to the alumina substrate, previously incorporated into the reactor. As compared with other methodologies, like reduction of metal salts [2–5]

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or the formation of nanostructured films by metal evaporation [1, 6, 7], our method is used for the first time to prepare a catalyst suitable for the synthesis of nanotubes and nanofibers.

2 Experimental procedures

The catalyst was prepared by the Solvated Metal Atom Dispersion technique (SMAD) [8]. In this procedure Palladium metal and an organic solvent, like 2-propanol, are simultaneously evaporated and condensed into a frozen matrix, on the walls of the metal atom reactor at 77 K. After warming up this matrix to room temperature, a colloid, with very small and highly reactive clusters, is obtained. These palladium clusters react with the acid sites of the high surface area γ -alumina, forming anchored nuclei. This mixture is then dried and the resulting powder ground in a mortar before using it as a catalyst. The decomposition of acetylene was carried out in a Chemical Vapour Deposition apparatus (CVD), consisting of a horizontal tube furnace and a set of gas flow lines [9]. The catalyst, Pd(1%)/ γ -Al₂O₃, was heated at a rate of 20 °C/min and annealed 10 min in an Ar/H₂ stream, at the desired synthesis temperature (500–900 °C). The acetylene (25 ml/min) was accepted into the oven and decomposed over the catalyst for 30 min. For 800 °C, a scan of the efficiency as function of synthesis time was performed. The structure of carbon products was analyzed by transmission electron microscopy (TEM).

3 Results and discussion

The decomposition of acetylene over Pd(1%)/ γ -Al₂O₃ reveals a process in which the catalyst gain mass as the synthesis temperature is increased. Auger spectroscopy of raw products reveals the deposit consists mainly of carbon. The yield of the reaction was calculated from the weight difference between the pristine catalyst and its total weight after synthesis. A more representative figure, namely the amount of C vs. the active component in the catalyst (palladium metal), is the C/Pd mass and atomic ratios. These results are presented in Table 1, together with a generic description of the dominant structures shown by our TEM analysis. The yield of carbon collected on the catalyst, due to the decomposition of acetylene, increases almost linearly when the reaction temperature is raised from 500 to 800 °C. Subsequently, there is a slight decrease in the amount of carbon collected for temperatures up to 900 °C. A photograph of the raw products has been inserted in Fig. 1a together with a graph of the yield as function of temperature for a 30 min reaction. The higher yield for carbon products occurs between 700 and 800 °C. Surprisingly this higher yield is coincident with a large increase in the volume of the products between

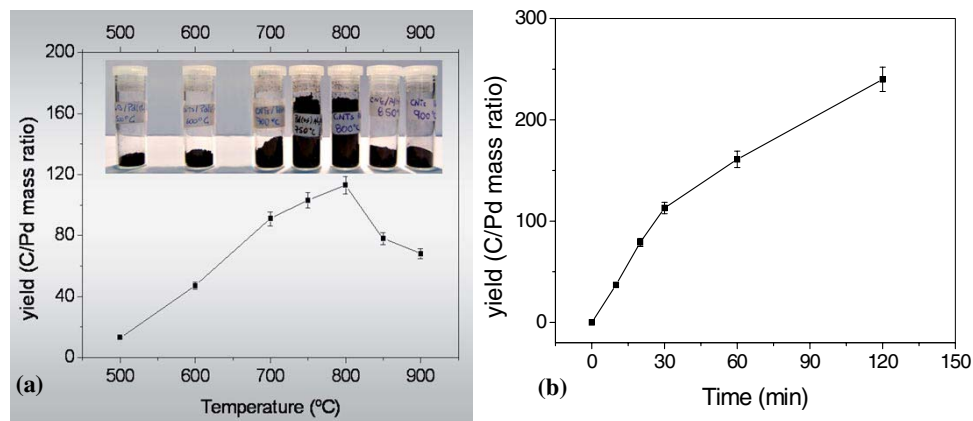


Fig. 1 (online colour at: www.pss-a.com) Yield of carbon products as a function of (a) temperature and (b) time for 800 °C synthesis. The insert in Fig. 1(a) shows a photograph of the vials containing the raw products.

Table 1 Carbon products as function of synthesis parameters for the decomposition of acetylene over Pd(1%)/ γ -Al₂O₃ catalyst. The yield is presented as the mass and atomic ratios between total amount of carbon collected and the amount of Pd present in the catalyst.

| synthesis parameters | | yield of carbon products | | type of structures (diameter in nm) |
|----------------------|----------------|--------------------------|-------------------|---|
| <i>T</i> (°C) | <i>t</i> (min) | C/Pd mass ratio | C/Pd atomic ratio | |
| 500 | 30 | 13 | 112 | CNFs (20–70) |
| 600 | 30 | 47 | 416 | MWCNTs (8–25), c-CNFs (50–70) |
| 700 | 30 | 91 | 803 | MWCNTs(8–25), c-CNFs(55), s-CNFs(60–100) |
| 750 | 30 | 103 | 915 | MWCNTs (18) |
| 800 | 10 | 37 | 326 | MWCNTs (27) |
| | 20 | 79 | 695 | |
| | 30 | 113 | 1000 | |
| | 60 | 161 | 1426 | |
| | 120 | 240 | 2129 | |
| 850 | 30 | 78 | 694 | MWCNTs, sl-MWCNTs, s μ -MWCNTs – (40–60) |
| 900 | 30 | 68 | 600 | s μ -MWCNTs (40–70), s μ -CNFs (>100) |

750 and 800 °C. This volume raise is consistent with the formation of hollow structures, such as carbon nanotubes. Figure 1b shows the yield as function of time for a synthesis temperature of 800 °C.

Figures 2 and 3 shows several TEM micrographs of the synthesized products. The carbon products consist mainly of filament-like (high aspect ratio) nanostructures. Between 500 and 700 °C (Fig. 2) the predominant structures were carbon nanofibers (CNFs) with different shapes: with submicrometric lengths (s μ -CNFs), coiled (c-CNFs) and straight fibers (s-CNFs). Multiwall Carbon Nanotubes (MWCNTs) were also observed between 600 and 700 °C, but in a lower proportion. Instead, between 750 and 800 °C pure and high quality MWCNTs were observed (Fig. 3). This result is consistent with the large volume increase displayed by the reaction products. If CNTs are compared with carbon nanofibers, which have solid inner structure or a small cavity surrounded by stacked graphite sheets, a larger volume is expected for the tubular structures. At higher temperatures only CNTs with different shapes

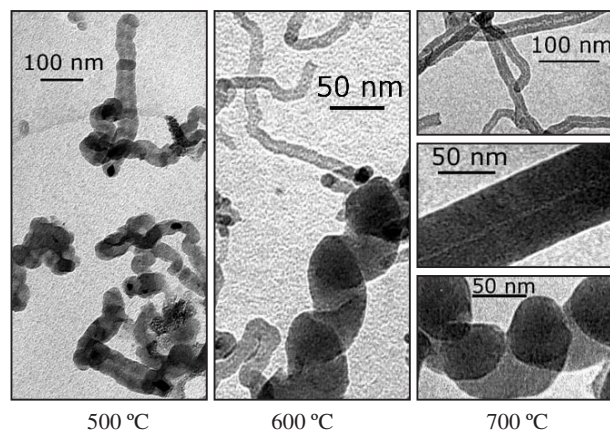


Fig. 2 TEM images of carbon nanostructures synthesized by decomposition of acetylene over Pd(1%)/ γ -Al₂O₃ in the range 500–700 °C.

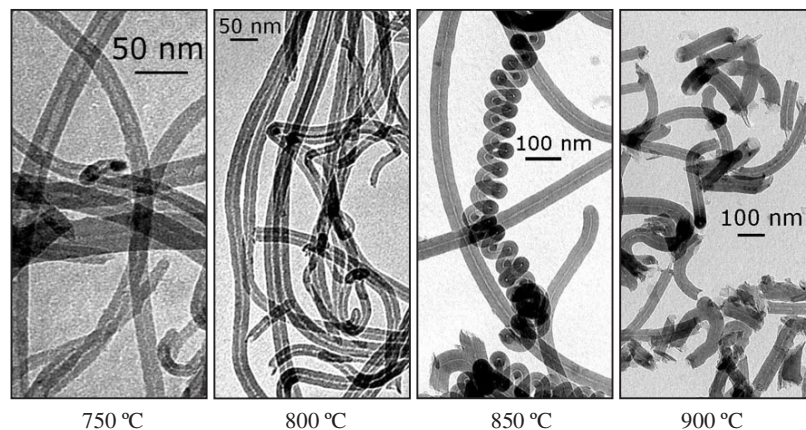


Fig. 3 TEM images of carbon nanotubes synthesized by decomposition of acetylene over Pd(1%)/ γ - Al_2O_3 in the temperature range 750–900 °C.

were observed. In the case of 850 °C some spring-like nanotubes (sl-MWCNTs) were present in the samples. For 900 °C, CNTs with submicrometric lengths (μ -MWCNTs) were the predominant structure (Fig. 3).

The difference in the structure of the products as function of temperature could be related, in principle, to the state and size of the catalytic metal particle. At lower temperatures, a solid bulk diffusion mechanism or surface nucleation, seems to govern the growth process in which carbon atoms precipitate in the form of stacked graphene platelets into unidirectional carbon fibers. At higher temperatures the metal nanoparticles have an almost-melted surface, which allows a higher solubility and a faster surface diffusion of the carbon atoms as compared to the solid metal core. Once the first few layers of graphite have precipitated, forming a cap around the particle free surface, this cap is extruded out and the subsequent diffusion and incorporation of carbon atoms take place in a ring like section surrounding the metal particle, thus forming the nanotube. This mechanism explains, in part, the formation of tubes instead a solid fiber at higher temperatures. It should be noted that the formation of stacked graphene platelets implies the existence of dangling bonds at the edges of the fiber. From a thermodynamic point of view these graphene sheets have a higher surface energy than the nanotubes. Therefore at high temperatures the tubular structures are energetically favourable since no dangling bonds are formed in their growth [10].

For lower temperatures the surface pre-melting of the catalytic particles is less dominant. Hence very few tubes should be expected in the products. In the case of a catalyst with a rather broad metal particle size distribution, the formation of CNFs, which grow over larger particles, would be the preferred nucleation mechanism. The larger particles sizes are thermodynamically selected since they allow the growth of wider graphite platelets; hence, inducing a smaller number of dangling bonds per carbon atoms in the products.

Consistently, we observe (see Table 1) that CNFs of relatively large diameters grow predominantly at low temperatures, while CNTs of small diameters, is the favoured growth mode at the higher temperature range. In part the high yield of CNTs as compared with CNFs, is due to the effectively smaller number of palladium particles available to catalyze the growth of CNFs.

For this particular report we have centered our attention in the 750–800 °C temperature range, where high quality MWCNTs were obtained. The efficiency of the catalyst could prove useful for its application in high yield production of CNTs. In terms of yield, one gram of palladium produces about 103 grams of MWCNTs at 750 °C and 113 grams at 800 °C in only 30 min. If we were to continue the 800 °C reaction (Fig. 1b) it is possible to obtain more than 240 grams of MWCNTs (per gram of Pd) after two hours of synthesis. These results compare well with previously published reports of high yield synthesis, for example Louis et al. [11] which considers the synthesis of MWCNTs over Fe(20%)/

γ -Al₂O₃ with an optimum result of 50 grams of nanotubes per gram of catalyst per hour or 250 grams of CNTs per gram of iron per hour. Jeon et al. [12] have reported an optimum yield of 125 grams of CNTs per gram of iron per hour for a Fe(12%)/MoMgO catalyst. As a concluding remark, the Pd-catalyst, prepared by our method, can catalyze different kinds of high aspect ratio carbon nanostructures and it is very selective for MWCNT production in a narrow temperature range (750–800 °C). The yield obtained by using the Pd/ γ -Al₂O₃ catalyst is comparable with other “high yield methods” and could be an option for a scaled-up fabrication process.

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