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Synthesis and study of carbon nanotubes and carbon spheres

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ABSTRACT

The synthesis of multi-walled carbon nanotubes (MWCNTs) and carbon spheres (CSs) was achieved using catalytic and non-catalytic chemical vapour deposition processes (CVD) respectively. Fe-Co bimetallic catalysts supported on $CaCO_3$ were prepared by a wet impregnation (IMP), a deposition-precipitation (DP) and a reverse micelle method (RM). The sizes of the Fe and Co particles were not affected by the Fe and Co sources (nitrate, acetate) when the wet impregnation and deposition-precipitation methods were used. High quality 'clean' multi-walled carbon nanotubes (MWCNTs) were obtained from all three Fe-Co synthesis procedures under optimized reaction conditions. The CNTs produced gave yields ranging from 623% - 1215% in 1 h under the optimum conditions, with similar outer diameters (o.d.) of 20 - 30 nm and inner diameters (i.d.) ~ 10 nm. The Fe-Co catalyst formed in the wet impregnation method revealed that the *yield, outer diameter* and *purity* of the CNTs were influenced by C_2H_2/N_2 *ratios, time* and *temperature*. All the methods gave high quality CNTs after short reaction times but the quality deteriorated as the synthesis time was increased from 5 - 360 min. Indeed, the influential parameter in controlling CNT purity, length and outer diameter was found to be the synthesis time.

In order to control the i.d. of the CNTs, the three methods of catalyst preparation were employed with the aim of controlling the Fe-Co catalyst particle sizes. It was observed that the IMP and DP methods were less effective in controlling the size of the metal particles. A reverse micelle process was used to synthesize Fe-Co nanoparticles that were highly crystalline and uniform in size. The reverse micelle technique displayed the ability to prepare nanoparticles of controlled size (3, 6 and 13 nm) obtained by varying the concentrations of Fe and Co in the micelle. By using the RM method, smaller diameter CNTs could be obtained compared with the IMP and DP methods. The CNT i.d. was found to correlate with the size of the catalyst particle used.

The effect of synthesis time on *CNT widths* was investigated for the first time. In this study the issue of carbon build up on the CNTs as a function of time was investigated. It

was observed that both the CNT yield and the outer diameters increased with time. With increase in synthesis time, the tubes *broke* into small *fragments*. The use of excess C_2H_2 resulted in the deposition of carbon on the already formed CNTs and it is this deposited carbon that caused tube fragmentation.

MWCNTs with unusual rough surfaces (including pits) were synthesized by the CVD of acetylene using a novel $Ca_3(PO_4)_2$-$CaCO_3$ support mixture. Mixtures of $Ca_3(PO_4)_2$-$CaCO_3$ (0/100 to 100/0) yielded tubes with *very rough surfaces* and the CNT yield increased as the amount of $CaCO_3$ in the support mixture was increased. The inner walls of the CNTs possessed a regular orientation of crystalline graphite sheets (3 - 5 nm) while the outer surface of the CNTs had a thick, rough, compact layer (~ 30 nm) of carbon with a random orientation of graphite sheets.

The production of pure carbon spheres (CSs) was achieved in the absence of a catalyst through the direct pyrolysis of acetylene and ethylene in a horizontal CVD reactor. The detailed experiments conducted with acetylene as a precursor indicated that the diameters of the CSs could be controlled by varying the pyrolysis conditions (e.g. temperature and synthesis time) and that the process could readily be scaled up for commercial production. This process thus provides a variant of the carbon black synthesis procedure. The effect of using oxygenates (alcohol C:O ratio dependence) on the CS morphology was also investigated.

CSs were also synthesized in a vertical swirled floating catalytic chemical vapour deposition (SFCCVD) reactor for the first time. This process allowed for continuous and large scale production of these materials. The CSs were obtained by the direct pyrolysis of acetylene in an inert atmosphere without the use of a catalyst. The effect of pyrolysis temperatures and the flow rate of argon carrier gas on the size, quality and quantity of the synthesized carbon spheres were investigated. TEM analysis of the carbon materials revealed graphitic spheres with a smooth surface and uniform diameter that could be controlled by varying reaction conditions (size: 50 - 250 nm). The materials were spongy and very light. It was established that under controlled experimental parameters, sphere

size is also regulated by the structural and bonding properties of a hydrocarbon source such as *carbon/hydrogen (C:H) content, hybridization* and *isomerism*.