NICKEL AND COPPER CATALYSED SYNTHESIS OF CARBON FIBERS

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Abstract

Structured carbon nanomaterials have attracted considerable interest because of their unique structures and outstanding properties. Among other structured carbon nanomaterials, carbon nanofibers (CNFs) have been the subject of study for several decades with particular interest having been paid towards their synthesis and application. However, control over the size and shape of these materials still remains a challenge. Three main components necessary for the synthesis of CNFs are the catalyst or template, the carbon source and the source of energy/power. It has been noted that catalyst morphology and the carbon source plays an important role in controlling CNF growth and morphology. As such one of the main challenges is to produce the catalyst particles that would yield the desired CNF morphology.

In this study, we investigated methods for controlling the size and morphology of CNFs by synthesizing Ni and Cu catalysts of particular morphology, while using C_2H_2 and trichloroethylene (TCE) as a carbon source for the synthesis of CNFs. A mixture of TCE/C_2H_2 was also employed as a carbon source for comparison. The catalysts and synthesized CNFs were characterized by different techniques such as TEM, XRD, TPR, TGA, Raman spectroscopy, IR spectroscopy, etc.

The synthesis of Ni nanoparticles (NPs) was achieved by reduction of Ni(acetate)$_2$ with hydrazine (35%). CNFs were synthesized by deposition of TCE, C_2H_2 and their mixtures using a chemical vapor deposition technique (CVD) in the temperature range 400-800 ^oC. N_2 and CO_2 were used as carrier gases. TEM analysis of the Ni particles as a function of time revealed that the Ni underwent a morphological change with time. Further, as the temperature of the reaction changed, so did the shape of the carbon materials. The shapes changed from structures showing bilateral growth at T = 400 ^oC to tripod-like structures and multipod-like structures at T = 450 ^oC and T = 500 ^oC respectively. Irregular shaped materials were observed at T > 500 ^oC. It was also found that when acetylene or an acetylene/trichloroethylene mixture was used at T = 450 ^oC, helical (> 80%) and linear fibers were produced respectively. It was also demonstrated that the flow rate of H_2, N_2 and CO_2 had a dramatic influence on the morphology of CNFs. CO_2/TCE was found to produce linear fibers with controlled sizes at 800 ^oC. The results demonstrated that the formation of tripod CNFs only occurs in a very narrow parameter regime.

The preheating of the TCE prior to its deposition over a Ni particle catalyst was achieved using a double stage CVD reactor. TCE was subjected to high temperatures prior to its deposition at low temperatures. Results showed that the decomposition temperature was the key parameter in the synthesis of CNFs. It was found that during the decomposition, TCE breaks down into different species/radicals which then adsorb onto the catalyst particle to give CNFs of different morphology. Raman studies revealed that the synthesized CNFs showed an increase in graphitic nature when the temperature in the first reactor of a two stage reactor was increased.

Decomposition of C_2H_2 was also performed over Cu NPs, and Cu modified catalysts ($Cu@SiO_2$ and Cu/SiO_2) with different silica coatings at 300 ^oC. These catalysts were prepared by reduction of $Cu(acac)_2$ with hydrazine (35%). TEM images revealed that coiled CNFs were only produced from Cu/SiO_2 grown in the presence of H_2 (> 90 %; d = 60-70 nm). IR spectra of all the CNFs indicated the presence of surface C=C, C=O, CH_3 and CH_2 moieties, and that the ratios of peak intensities of $C=O/CH_x$ and $C=C/CH_x$ species indicated the variable CNF surface that was produced by the gases and the Cu particles used. It was thus revealed that the CNFs produced by different Cu catalysts have different chemical and physical properties and that these properties correlate with catalyst particle size and the gas mixtures used.

CuO and SrO modified Cu catalysts (with different Cu/Sr ratios) were also employed using the CVD method for the synthesis of CNFs at 300 ^oC. These catalysts were prepared by a co-precipitation method. The TEM images of the CNFs revealed a mixture of straight and coiled CNFs with a broad diameter distribution (50-400 nm) dependent on the Cu/Sr ratio of the catalyst used. IR and TGA analysis revealed that the chemical composition of the CNFs changed as the SrO content changed. The SrO content also affected the Cu particle size and influenced the morphology of the Cu particles from which the CNFs grew.