
Removal of Metallic and Organic Contaminants from Aqueous Streams by Novel Filtration Methods

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INTRODUCTION

Graphite nanofibers are a newly developed type of material that can be synthesized by the decomposition of selected hydrocarbons over selected metal particle surfaces ¹. The structural characteristics of the solid can be manipulated by a careful selection of parameters including the catalyst, the reaction conditions and the temperature. Both the size and the morphology of the metal particle have been found to play an important role on the cross-sectional area as well as the orientation of the graphene sheets. It is therefore possible to produce materials where the platelets are aligned either parallel, perpendicular or at an angle with respect to the fiber axis ². The consequence of the interplay between particle and morphology is that a variety of conformations are possible including tubular, ribbon-like, or structures where only edges of the basal plane are exposed. Graphite nanofibers are usually produced in bulk quantities using unsupported metal powders, having an average particle size of ~1 μm . The cross-sectional area of the resulting fibers exhibit a large range usually between 5 to 100 nm, as a result of uneven fragmentation of the original particles during the reaction ³. In our current program we have attempted to generate nanofibers of controlled dimensions in order to produce material having both a high surface area and a high electrical conductivity that results from a long range crystallographic order.

EXPERIMENTAL METHODS

Catalyst Preparation

Three silica supported nickel-iron samples were prepared: Fe-Ni (2:8), Fe-Ni (5:5), and Fe-Ni (8:2). The catalysts were prepared by incipient wetness of fumed Cab-O-Sil™ silica, using an aqueous solution of nickel and iron nitrates mixed in the desired ratio to give a 5 wt. % metal loading. The impregnate was dried overnight in air at 110°C, calcined at 400°C for 4.0 hours to convert the nitrates into mixed oxides and finally, reduced to the metallic state in a 10% hydrogen/helium mixture for 24 hours at 600°C. After the reduction step, the samples were cooled to room temperature under flowing helium and then passivated in a 2% air/helium mixture for 1.0 hour to prevent bulk oxidation of the bimetallic particles. The supported metal catalysts were then removed from the reactor and stored in sealed vessels.

Graphite Nanofiber Synthesis

The graphite nanofiber synthesis was performed according to the following protocol. Approximately 0.2 g of a given silica supported nickel-iron catalyst sample was uniformly dispersed along the base of a ceramic boat and placed in the central region of a quartz reactor tube located in a horizontal Lindberg furnace. Before treatment in a reactant environment the catalyst was reduced for 2 hours at 600°C in 10% H₂/He mixture to ensure that the passivated particles were completely converted to the metallic state. The system was maintained at 600°C, flushed with He for 1 hour, then exposed to a CO/H₂ (4:1) reactant mixture. The gaseous products were monitored with a Varian 3400 gas chromatograph, fitted with a 30m megabore (GS-Q) capillary column and thermal conductivity and flame ionization detectors. The reaction was allowed to proceed for a period of 1.5 hours and then the sample cooled to room temperature in flowing He. The amount of carbon deposited during the reaction was determined gravimetrically and the cooled samples stored in sterile glass vials under an atmosphere of N₂ for subsequent characterization studies.

Metal particle size distributions of the fresh catalyst samples and width distributions of the nanofibers grown from such systems were obtained from studies performed in a JEOL-100CX transmission electron microscope. High resolution examinations of the nanofiber structural characteristics were carried out in a JEOL 2000 EXII instrument (lattice resolution 0.18 nm) that was equipped with a closed-circuit high resolution television system. Suitable transmission specimens were prepared by ultrasonic dispersion for 2 seconds of the catalyst samples in sec-butanol and application of a drop of the suspension onto a carbon substrate film. The short dispersion treatment of the sample in the ultrasonic bath was selected so as to minimize the damage that might be done to the structure upon extended processing and to ensure that a more representative image can be obtained. The size distribution of nanofibers and catalyst particles produced from the various systems were determined in each case from measurements of over 300 particles or carbon structures from a number of diverse regions of each specimen.

A Cahn 2000 microbalance was used to monitor the weight loss of a sample as a function of temperature in an atmosphere of CO₂/He (4:1). This type of analysis is routinely used to assess the degree of crystallinity of carbons and is based on the principle that less ordered structures will react with an oxidant and lose weight due to gasification at a much lower temperature than that exhibited by more highly crystalline materials⁴. As a consequence, the onset temperature for the gasification of amorphous carbon is considerably lower than that of graphitic carbon. From a comparison of the oxidation profiles of the carbon nanofiber samples with those of two standards, amorphous carbon and single crystal graphite, it was possible to gain an assessment of the degree of crystallinity of the material. Under these conditions, Temperature Programmed Oxidation (TPO), profiles indicate that amorphous carbon started to undergo gasification at 690°C, whereas single crystal graphite started to gasify at about 900°C. Prior to performing the oxidation step all samples were soaked in 1M HCl for 7 days in order to remove any associated metal inclusions. Subsequent examination of the acid-treated nanofibers in the TEM showed that no metal residues

were present after the completion of the demineralization process. Such a step is absolutely necessary before any oxidation studies are carried out because both nickel and iron are efficient catalysts for the gasification of carbon and graphite, and as a consequence, could alter the onset temperature of sample weight loss in the CO₂ environment and therefore interfere with the analytical method.

RESULTS AND CONCLUSIONS

The graphitic nanostructures produced from the reaction of CO and hydrogen over silica supported Fe-Ni particles have been examined by a number of techniques. Transmission electron microscopy studies of the solid carbon deposit formed in these reactions revealed that nanofibers were the exclusive product with no other forms of carbon being present. The morphologies of the products ranged from nanofibers to nanotubes to faceted chain-like tubes, depending upon the catalyst composition used in the reaction. An example of one of the tubular structures can be seen in [Figure 1](#). A high resolution TEM of a section of a graphite nanofiber, where the perfectly aligned graphitic layers that are oriented parallel to the fiber axis of the structure is shown in [Figure 2](#).

[Table I](#) shows the increase in amount of solid carbon produced from the disproportionation of CO as the nickel content of the catalyst particles was progressively raised. Examination of samples after reaction revealed that in all cases, a considerable amount of carbonaceous deposit had collected on the surface. In the case of the silica supported Fe-Ni (2:8) system, there was such a significant amount of growth that the catalyst bed was matted together and the deposit had grown to such an extent that some material was pushed over the ends of the boat. This type of “overflowing” behavior was not observed in the other systems as the product yields were smaller.

Table I. Effect of Bimetallic Composition on the Yield of Graphite Nanofibers from the Decomposition of CO/H₂ (4:1) over Fe-Ni Catalysts at 600°C that were reacted for 90 minutes.

Catalyst System	Carbon Deposited (g C/g Metal)
Fe-Ni (2:8)	21.16
Fe-Ni (5:5)	12.04
Fe-Ni (8:2)	4.80

[Table II](#) summarizes an attempt to quantify the fraction of amorphous and graphitic character of the nanofibers obtained with the three catalyst systems. The temperatures at the points of inflection in each peak in the differential TPO curves were used to determine the weight change exhibited during these intervals. The low temperature weight change was used as the percentage of amorphous carbon whereas

the high temperature was used to determine the percent of graphitic carbon. Using this approach it becomes apparent that the Fe-Ni (8:2) system produced the most oxidation resistant nanofibers, which we interpret as those with the most graphitic character. The weight of carbon deposit is a percentage with respect to the total weight of catalyst (metal and support).

Table II. Composition of Carbonaceous Deposits as Calculated from Temperature Programmed Oxidation Experiments in a CO₂/He (4:1) Mixture.

GNF System	% Weight of C Deposited	% Amorphous Component	% Graphitic Component
Fe-Ni (2:8)	60	58	42
Fe-Ni (5:5)	45	22	78
Fe-Ni (8:2)	25	--	100

Provided that suitable procedures are utilized to remove the support material, catalytic production of nanostructures does not require any further purification steps and is significantly more efficient than the current high energy methods employed in the production of nanoscale products. It is therefore imperative to gain further insight into the factors controlling the catalytic behavior if one is to optimize the procedures needed to fully exploit the technological benefits afforded by these nanostructured materials. The results of this investigation have confirmed that the composition of a bimetallic catalyst plays a key role in determining the degree of crystalline perfection of carbon nanofibers. The most important aspect is the finding that the use of a supporting medium for the metal particles introduces a further contributing factor to the structural characteristics of the final product. It is shown that the ability to manipulate the arrangement of the graphite platelets constituting the nanofiber structure is a direct consequence of the nature of the strength of the metal-support interaction, that in turn is responsible for dictating the crystallographic features of the catalyst particles.

PUBLICATIONS GENERATED FROM THIS GRANT

- "Growth of Graphite Nanofibers from the Decomposition of CO/H₂ over Silica Supported Iron-Nickel Particles" P. E. Anderson and N. M. Rodriguez, J. Materials Research, in press.
- Influence of the Support on the Structural Characteristics of Carbon Nanofibers Produced from the Metal Catalyzed Decomposition of Ethylene", P. E. Anderson and N. M. Rodriguez, submitted to J. of Materials Chemistry

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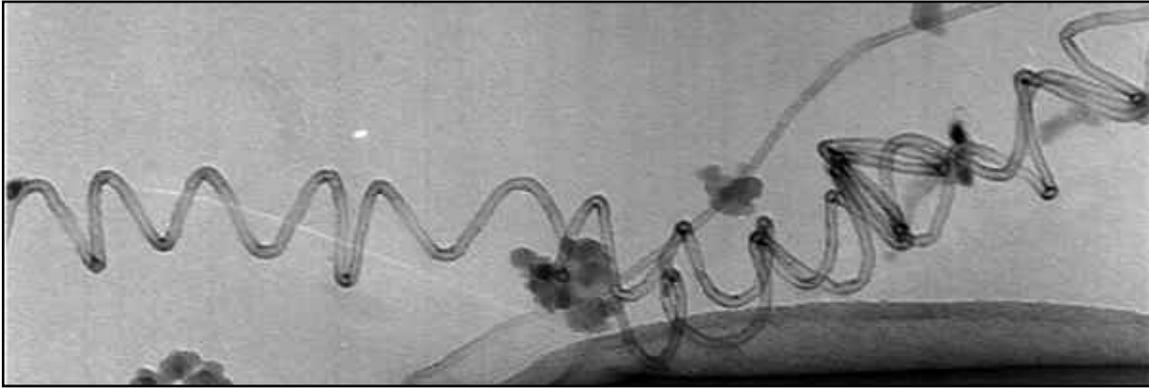


Figure 1. Transmission electron₂ with silica supported Fe-Ni catalyst

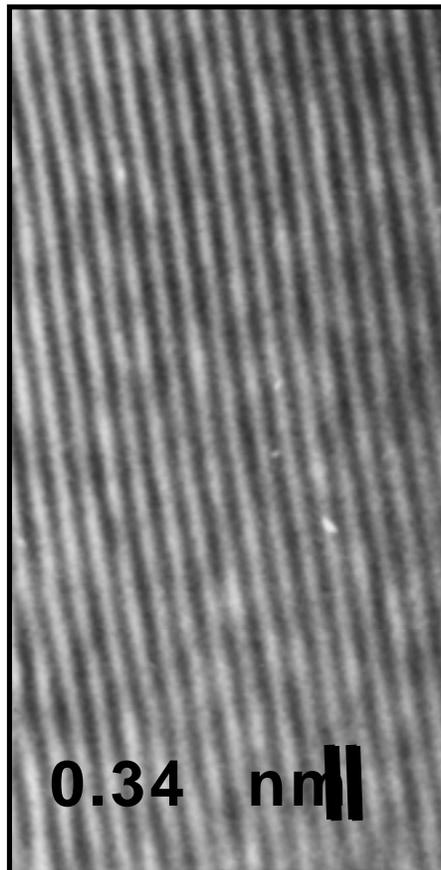


Figure 2. High resolution transmission electron micrograph of section of nanofiber where the graphene sheets are aligned parallel to the fiber axis.