ABSTRACT

Catalytically grown carbon nanofibers (CNF) are a newly developed type of material produced from the decomposition of selected carbon-containing gases over metal particles. These materials consist of nano-sized graphite platelets separated a distance of at least 0.335 nm and stacked in various orientations with respect to the fiber axis. Such an arrangement results in a unique structure that is composed of an infinite number of extremely short and narrow pores, suitable for the sequestering of small molecules. We have attempted to capitalize on this blend of properties by using such structures for the selective removal of organic contaminants from aqueous streams. The approach is predicated on the principle that a strong interaction of the organic impurity with the non-polar basal plane regions of the graphite platelets will be established without concomitant saturation of the solid with excess water molecules. Experimental results indicate that nanofibers possessing a structure in which the graphite platelets are aligned perpendicular to the fiber axis and possessing high degree of structural perfection exhibit superior selective adsorption properties with respect to removal of alcohols from aqueous media over that displayed by active carbon. Adsorption was enhanced when the carbon nanofibers were initially subjected to a treatment in 1M hydrochloric acid. In contrast, when this step was carried out in the presence of 1M nitric acid the beneficial properties of the nanofibers were effectively suppressed. On the other hand, a similar treatment in 1M sulfuric acid produced a pattern of behavior that was, for the most part, intermediate between these cases. An analogous series of experiments carried out with nanofibers possessing a structure in which the graphite platelets were oriented at an angle with respect to the fiber axis did not result in the same degree of selective capture of the alcohols. A rationale is presented to account for this diverse pattern of behavior.

INTRODUCTION

During the production of specialty chemicals, electronic as well as pharmaceuticals, trace amounts of organic and chlorinated compounds are generated, which invariably find their way into water streams. Careful handling, disposal and/or recovery of these toxic organic compounds is one of the major environmental issues that confront such industries. The traditional methods for the elimination of effluents from the gas or liquid phase use fixed bed adsorption where the solution is passed over a solid adsorbent in an attempt to collect the impurity, and subsequently to heat the system in order to release the adsorbate. An alternative method involves the incineration of both the adsorbent and adsorbate. Granular activated carbons are usually the adsorbent of choice because of their high surface area and concomitant high adsorption capacity. In addition these solids exhibit high reactivity that allows one to modify the chemical nature of the surface by either heating or chemical treatment. Although activated carbons are extremely efficient in the adsorption of gases (1), their performance in solutions can be limited because they
indiscriminately adsorbs both the contaminant and the solvent a process that results in a quick saturation of the active sites with solvent and consequently the reduction of the efficiency of the process, which leads to a quick deactivation.

The performance of fibrous activated carbon (FAC) was found to be superior to that exhibited by powdered activated carbons possessing similar surface areas and it was argued that it was due to the small distance between the fibers that results in a much faster diffusion process (2,3). Although these results are encouraging, it is evident that one of the problems encountered with these adsorbents is the chemical structure that consists of both polar and non-polar sections. The ideal adsorbent for the removal of organic molecules is therefore an insoluble solid possessing non-polar pores that can strongly adsorb and retain non-polar adsorbates.

Carbon nanofibers (CNF), are produced from the decomposition of certain hydrocarbons and/or carbon monoxide over selected metal particles at temperatures ranging between 400 and 700°C (4). Although similar carbon conformations were reported as early as 1890, it was only in recent years, through the development of high resolution transmission electron microscopy that it was possible to observe the fine details of the various structures. The elucidation of the mechanism that later has allowed researchers to "engineer" these structures was the result of the pioneering work carried out by Baker and coworkers using controlled atmosphere transmission electron microscopy (5).

CNF consist of extremely small graphite platelets that are stacked at a distance of at least 0.335 nm. In some conformations, the graphene layers are found to be arranged perpendicular to the fiber axis and resemble an infinite stack of cards. In other configurations, the graphite layers are oriented parallel to the fiber axis and take the form of faceted tubes or in some cases open structures, designated as ribbons. The spacing between the layers is for the most part too narrow to allow the entrance of most gas or liquid adsorbates, however, very small flat or linear molecules can gain access to these normally "forbidden areas". Although these structures possess a relatively low external surface area, the void space between platelets imparts the material with an enormous surface area provided that it is accessible to an adsorbate molecule. This property makes CNF a very sophisticated type of molecular sieve, suitable for very refined separation processes. For many years the solid that we know today as carbon nanofibers was considered to be a waste product and furthermore, in many cases, a nuisance in the efficient operation of certain commercial processes (6-9). In more recent years, interest in its properties and the search for potential applications has begun to grow at a rapid rate (10). These materials can be used as reinforcing agents in conjunction with polymers to form electrodes (11-13), utilized for magnetic shielding (14), catalyst support media (15-17), selective adsorption agents (18) and more recently as a hydrogen storage agent (19-20).

OBJECTIVES OF THE CURRENT WORK

Carbon nanofibers possess properties that are rarely present in any other types of carbon adsorbent, including a small cross-sectional area, combined with a multitude of slit shaped nanopores that are suitable for adsorption of certain types of molecules. Because of their unique properties we plan to use these materials for the selective adsorption of organic molecules. The objectives of the current investigation are as follows:
(a) To capitalize on the unique structural arrangement of carbon nanofibers for the selective removal of organic impurities from aqueous solutions. The rationale for this approach is based on the fact that the slit-shaped nanopores existing between the two adjacent graphene layers favor the interaction with non-polar molecules and the hydrophobic nature of the material prevents these regions from becoming saturated with water molecules.

(b) To determine the influence of the degree of crystalline perfection and chemical functionality of the nanofibers on their capacity to adsorb organic molecules.

(c) To produce carbon nanofibers with a relatively small cross-sectional area in order to increase the rate of diffusion of the adsorbed species into the structure. For this purpose we endeavored to modify the structural characteristics of nanofibers via the use of supported metal catalysts for the growth process.

EXPERIMENTAL PROCEDURES

Preparation of Unsupported Metal Catalysts

Samples of powdered catalysts were prepared by co-precipitation of the respective metal nitrates mixed in the desired ratio using ammonia carbonate. The solid was filtered, washed in deionized water, dried overnight at 110°C and calcined in air at 350°C to produce the mixed metal oxide. The powders were subsequently reduced in a flowing mixture of 10% H$_2$/He for several hours at 600°C. The powders were allowed to cool to room temperature and prior to removal from the reactor were passivated in 10% CO$_2$/He mixture to produce a thin protective oxide layer. Additional details of the procedure are described in the paper by Best and Russell (21).

Preparation of Supported Metal Catalysts

In a typical procedure about 5.0 wt. % of iron, cobalt and nickel were separately introduced onto a support consisting of either silica, γ-alumina or carbon via incipient wetness impregnation in ethanol using the respective metal nitrates as precursor salts. The impregnated materials were all dried overnight in air at 110°C and then calcined at 350°C in 150 ml/min air for 4 hours. The silica and γ-alumina supported systems were reduced for 36 hours in a 10%H$_2$/He stream at 350°C, cooled to room temperature, and passivated in 2% CO$_2$/He for an hour before removal from the reactor. In the case of the carbon supported systems, the same catalyst preparation protocol was followed with the exception that calcination and reduction temperatures were limited to 300°C. This precaution was taken in order to avoid gasification of the carbon support and the reduction time limited to 24 hours in order to minimize particle sintering as the metals have significant degree of mobility on this type of carrier. The treatments described in this section and the subsequent carbon deposition reactions were performed in a horizontal flow reactor system. All gas flow rates were regulated with MKS mass flow controllers.
Preparation of Carbon Nanofibers.

Carbon nanofibers were synthesized from the interaction of ethylene/hydrogen (4:1) mixtures over powdered Cu:Ni (3:7) catalysts and carbon monoxide/hydrogen (4:1) mixtures over powdered Fe catalysts. Single metal or mixtures of metals supported on silica, graphite or carbon nanofibers were also used as catalysts. In a typical experiment, 50 mg of the metal powder was placed in a ceramic boat, positioned in the center of a quartz reactor tube heated by a Lindberg horizontal furnace. Helium was flushed through the tube for one hour in order to remove air. Prior to reaction with the carbon-containing reactant mixture, the metal particles were reduced in a 10% H₂/He mixture at 600°C for about an hour. Hydrogen was eliminated from the tube by flushing with helium, and then the carbon-containing gas/hydrogen mixture (4:1) was introduced at a total flow rate of 200 standard cm³/min (sccm). The reaction was allowed to proceed for one hour, the reactant gas flow was terminated, replaced with helium and the system allowed to cool to room temperature.

Characterization of Graphite Nanofibers

Characterization studies of the CNF were conducted by a variety of techniques. The structure of individual nanofibers generated from the various catalyst systems was determined by high resolution transmission electron microscopy using a JEOL 2000 EXII TEM (resolution 0.18 nm). The degree of crystalline perfection of both individual nanofibers as well as bulk specimens was ascertained using a combination of lattice fringe image measurements, selected area electron diffraction, X-ray diffraction and temperature programmed oxidation (TPO) analysis. These studies were carried out with a Scintag XDS-2000 diffractometer using Cu Kα radiation for X-ray diffraction analysis and a Cahn 2000 vacuum microbalance for the TPO studies. Surface areas and pore size distributions were determined by standard procedures using N₂ at -196°C in an Omnisorb 100 CX unit. Temperature programmed desorption (TPD) analysis was conducted in a custom built unit operating in a range of 25 to 900°C.

Initial adsorption experiments were conducted on pristine nanofibers and their abilities to take up selected organic molecules from aqueous solutions were compared to those of active carbon under the same conditions. In further studies the effects of pre-treatments in various acid media on the subsequent adsorption characteristics of the nanofibers were investigated. For these experiments the CNF samples were allowed to soak in 1M aqueous solutions of either hydrochloric, sulfuric or nitric acids for periods of up to 1 week. The nanofibers were then thoroughly washed in deionized water before being dried overnight at 110°C and then stored in sealed vessels.

RESULTS AND DISCUSSION

Transmission Electron Microscopy

CNF from Unsupported Metal Powders. Transmission electron microscopy examination of the carbonaceous solids produced from the metal catalyzed decomposition of C₂H₄/H₂ mixtures over Cu:Ni and CO/H₂ over Fe indicated that they consisted exclusively of nanofibers, with no indication of any other forms of carbon being present. These undesirable forms of carbon are frequently found when high temperature non-catalytic methods are used for
the synthesis of the nanostructures (22). The reaction between Cu:Ni-C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} generated fibers that were very different to those obtained from the decomposition of CO/H\textsubscript{2} over Fe. The former system produced the so-called "herring-bone" type of structure where the graphene sheets are aligned at an angle with respect to the nanofiber axis, whereas the latter system yielded a "platelet" type of nanofiber in which the graphene sheets are aligned perpendicular to the nanofiber axis. Close examination of the structures indicated that under the conditions used in the experiment, the nanofibers generated from the interaction of C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} with Cu:Ni catalysts possessed significantly more structural imperfections than those synthesized from the decomposition of CO/H\textsubscript{2} over Fe powders. In both cases, however, the width of an individual nanofiber corresponded to that of the cross-sectional area of the catalyst particle responsible for its growth. It should be noted that although the initial powders consisted of granules that were ~1 \textmu m in size, those entities fragmented during the reaction to produce much smaller particles. In these unsupported systems, however, it is very difficult to exercise control over the catalyst particle size and this results in a wide size distribution. Figure 1 is a transmission electron micrograph of fibers that were produced from the interaction of carbon monoxide/hydrogen mixtures at 600°C over an iron powder. By measurement of the width of over 500 fibers it was possible to determine that the average cross-section of the fibers was ~ 100 nm.

Figure 1. Transmission electron micrograph of carbon nanofibers produced by the catalyzed decomposition of carbon monoxide/hydrogen mixtures over an unsupported iron catalyst.

The structural perfection of carbon nanofibers has been related to the ability of the metal catalysts to interact with the basal plane of graphite (23). Under such conditions, metal particles undergo rearrangement so as to generate faces in which the interstices are perfectly matched with the atomic arrangement of the carbon atoms in single crystal graphite and as a consequence, the deposited material will possess a high degree of crystalline perfection. This rearrangement occurs when Fe particles are allowed to interact with CO/H\textsubscript{2} at 600°C. At lower synthesis
temperatures it has been found that the structure of the nanofibers is less ordered. It was interesting to find that when Fe powders were reacted with C\textsubscript{2}H\textsubscript{4}/H\textsubscript{2} mixtures, very little solid carbon was obtained, an observation that is consistent with previous work reported in the literature (24).

**CNF from Supported Metal Particles.** The removal of impurities from aqueous media is generally carried out by an adsorption process in which the solution is passed over a bed containing the adsorbent. In order for the system to become commercially viable it is necessary for the removal process to be completed within a very short period of time. In the present system, adsorption of impurities is expected to occur via migration of the organic molecule from the aqueous solution to the inner regions of the nanofibers. This process involves a number of steps, one of which is diffusion of the adsorbate through the very narrow pores existing between two graphene layers. We believe that the uptake can be accelerated if a reduction in the path length traversed by the adsorbed molecule can be realized. Such a modification would result in a substantial enhancement in the efficiency of the process and should be achievable by utilizing a catalytic protocol that results in the growth of very narrow carbon nanofibers. Materials produced from the decomposition of carbon-containing gases over metal powders have a wide size distribution. This is due to inability to control the initial size of individual catalyst particles in the powders. On the other hand, the use of a supported catalyst system allows one to generate a fine dispersion of metal particles, which subsequently results in the production of nanofibers possessing narrow widths.

In this investigation we have demonstrated that major modifications in the growth characteristics of carbon nanofibers can be achieved when metals such as iron, cobalt and nickel are used in a supported form to catalyze the decomposition of ethylene at 600°C. Moreover, there were significant differences in the performance of these metals depending upon the nature of the metal-support interaction. In this respect one of the most intriguing aspects to emerge was the finding that while powdered iron samples did not generate carbon nanofibers from ethylene/hydrogen mixtures, when the metal was dispersed on either silica, graphite or carbon nanofiber supports, the growth of these structures proceeded in a very facile manner.

High resolution transmission electron microscopy studies of the solid carbon deposit formed in these reactions revealed that as with the unsupported systems, nanofibers were the exclusive product of the reaction. The most striking feature, however, was the finding that the cross-sectional area of the nanofibers was substantially smaller than those encountered when such structures were generated from powdered catalysts under otherwise identical conditions and this contrast is evident in the electron micrograph Figure 2. It can be seen that the average width of individual fibers is about 10 - 15 nm, nearly an order of magnitude smaller than those found in unsupported systems. Examination of the detailed structural characteristics of the nanofibers grown from the various supported metals indicated that the material produced from iron catalysts exhibited the highest degree of crystalline perfection. In all cases, the nanofibers derived from iron adopted a structure in which the graphite platelets were aligned in a direction parallel to the fiber axis. Close inspection showed that these nanofibers were not rounded, but instead acquired a faceted outline, where the wall thicknesses varied from a single to multiple graphite sheets. It was fascinating to find that this nanofiber geometry was maintained even when such "secondary" structures were generated from iron particles supported on "parent" carbon nanofibers where the graphite sheets were aligned in a direction perpendicular to the fiber axis.
Figure 2. Transmission electron micrograph of carbon nanofibers produced by the catalyzed decomposition of carbon monoxide/hydrogen mixtures over a silica supported iron based catalyst.

X-ray Diffraction Measurements

X-ray diffraction patterns of the two types of pristine nanofibers produced from unsupported metal catalysts showed that the "platelet" type of structure was highly graphitic in nature with a \( d \)-spacing very close to that of single crystal graphite (0.335 nm). The average stack height, \( L_c \), was determined from the broadening of the principal graphite peak (the 002 reflection) and was found to be 17.5 nm. On the other hand, the "herring-bone" material, contained more imperfections as evidenced by the wider \( d \)-spacing distribution, (0.347 nm) and a small \( L_c \) of 5.4 nm. Inspection of these data indicates that, as expected, the more disordered "herring-bone" structures have a relatively short stack height. It is interesting to find that in the "platelet" nanofibers, a significant expansion in the lattice spacing to 0.344 nm was observed following adsorption of butanol into this material, which suggests that the organic molecule "slides" between two graphene layers suggesting that perhaps following adsorption between the layers, the structure undergoes expansion.

Surface Area Determinations.

The Brunauer, Emmett and Teller (BET) method was used to determine surface area of the various carbons at –196°C in \( \text{N}_2 \) (25). The results presented in Table 1 indicate that the surface area of the "platelet CNF" was 123 m\(^2\).g\(^{-1}\), whereas that of the "herring-bone" form was 257 m\(^2\).g\(^{-1}\). In contrast, the active carbon sample exhibited a significantly higher value of 750
Subsequent treatment of both types of CNF materials in 1M hydrochloric acid resulted in a slight decrease of the respective surface areas. On the other hand, when this process was conducted in 1M nitric acid the surface areas of both nanofiber samples decreased by almost a factor of two. Loss of active sites as a result of nitric acid treatment may be due to the formation of oxygenated species that undergo cross-linking at the edge regions of the graphite sheets. Immersion of the nanofibers in 2M sulfuric acid appeared to cause an increase in the interlayer spacing of both materials and in contrast to the nitric acid treatment did exert a deleterious effect with respect to loss of active sites. It was interesting to find that no equivalent changes were apparent when the active carbon sample was subjected to the same series of acid treatments.

**Table I. Physical Properties of Carbon Materials**

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Surface Area $A_{BET}/N_2$ m$^2$/g</th>
<th>X-ray $d_{200}$ nm</th>
<th>$L_e$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit</td>
<td>750</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Platelet CNF</td>
<td>123</td>
<td>0.335</td>
<td>17.5</td>
</tr>
<tr>
<td>Herringbone CNF</td>
<td>257</td>
<td>0.347</td>
<td>5.4</td>
</tr>
</tbody>
</table>

**Adsorption Studies**

**Adsorption of Organic Molecules on "Platelet" CNF.** In this series of experiments, the adsorption of ethanol on active carbon and "platelet" CNF was examined. The results (Figure 3) show that the ability of the nanofibers to adsorb the alcohol far exceeds that of active carbon. After a period of about 60 hours the uptake of ethanol on active carbon was only 6%, but was 38% on the nanofibers. Although active carbon has a much larger surface area, it is apparent that with this material adsorption of the organic from an aqueous solution is non-selective in nature; i.e. pores in active carbon are quickly saturated with water thus preventing the alcohol from being adsorbed into these regions. On the other hand, due to the chemical character of CNF, which consists entirely of graphite platelets, we believe that it is possible for relatively narrow molecules to "slide" between the layers where they interact with the basal plane regions of the material. Indeed, although ethanol has some polarity, the molecule is known to be capable of wetting graphite due to such interactions. In contrast, water molecules are expected to have negligible affinity for the basal plane of graphite, and so do not gain access to the inner structure.

**Adsorption of Organic Molecules on "Herring-Bone" CNF.** When "herringbone" type nanofibers were used for the same set of adsorption experiments, the results were somewhat disappointing as evidenced by the finding that the performance of these materials was very similar to that exhibited by activated carbon. We believe that due to the lower degree of crystalline character exhibited by these materials, abundant oxygenated groups are present at the edge regions, which in turn, will directly affect the adsorption properties of the material. These results demonstrate that while the molecular structure of the adsorbate is an important feature, the degree of crystalline perfection of the solid carbon must also be taken into consideration when designing a material for selective adsorption. A combination of these two factors would therefore provide the best adsorption performance in novel filtration devices.
FUTURE WORK

The outstanding performance exhibited by highly crystalline carbon nanofibers for the removal of ethanol and alcohol opens up the potential for the selective adsorption of a variety of adsorbate molecules. It should be appreciated that in the present study although the alcohols were not flat molecules, this geometrical arrangement did not prevent their removal from aqueous solution by certain types of CNF. It is our belief that other molecules such as toluene, phenol and aniline, compounds that exhibit a planar structure could be easily extracted from aqueous mixtures. This task will be the subject of a future series of experiments. Perhaps one of the most attractive applications of these materials in the near future would be in the removal of oil-spills from the ocean.
Figure 4. (a) TEM micrograph of "platelet" CNF; (b) Schematic representation of CNF illustrated in (a); and (c) details of the proposed model of adsorption of organic molecules in CNF.

PROSPECTS FOR THIS TECHNOLOGY

The synthesis of carbon nanofibers possessing uniform structures and well defined properties has been optimized in our laboratory. Using unsupported catalyst powders that are commercially available we are in a position to produce around 30 different types of material all of which have potential for different applications. These include, filtration devices, catalyst supports, rubber reinforcement, fuel cells and hydrogen storage. The manufacturing of this type of materials can be rapidly moved into the industrial sector. To this end, negotiations with various companies, including Corning Inc. and General Motors, have taken place, which will lead to possible licensing of some of the technology. Research is being conducted in order to improve the yield of fibers produced using supported systems and this can lead to process that will allow one to produce large quantities of extremely fine materials having excellent thermal and electrical conductivity.

ACKNOWLEDGMENT

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