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The effect of copper on the structural characteristics of carbon filaments produced from iron catalyzed decomposition of ethylene

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Abstract

Carbon filaments were produced by the decomposition of ethylene over unsupported iron–copper powders in the presence of varying amounts of hydrogen at temperatures ranging from 500°C to 800°C. The structure and properties of the carbon filaments were found to be dependent on a number of parameters including the composition of the catalyst, the temperature and the percent of hydrogen in the reactant gas mixture. Temperature programmed oxidation in CO_2 of demineralized samples of carbon filaments indicated that the most stable structures were those produced from a bimetallic catalyst containing a large fraction of iron. The addition of hydrogen to the system also caused changes in the structure of the carbon filaments and this aspect was manifested by variations in the graphitic nature of the material. High resolution transmission electron microscopy examination indicated the presence of two distinct morphologies: one in which the filaments appeared to have smooth surfaces and where the graphite platelets were preferentially oriented at an angle with respect to the fiber axis; and a second type consisting of a tubular structure in which the graphite platelets were aligned in a direction parallel to the axis of the fiber. Surface areas of the carbon filaments, as determined by nitrogen adsorption at -196°C, were also found to be dependent on the catalyst composition, the reaction temperature and the fraction of hydrogen in the feed gas.

Keywords: Carbon filament; Iron–copper bimetallic catalyst; Ethylene decomposition

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1. Introduction

Although the existence of carbon filaments has been known for many years it is only recently that the potential of the material for a number of applications has been recognized. Carbon filaments are the product of the decomposition of certain carbon containing gases over hot metal surfaces and as such, are frequently found in many hydrocarbon conversion processes [1]. The structural details of this form of carbon have been studied by high resolution transmission electron microscopy and it has been reported that the material consists of a large fraction of graphite where the platelets are arranged in various orientations with respect to the fiber axis [2–4]. Audier and coworkers [3] carried out an investigation intending to correlate the effect of temperature and nature of the catalyst on the morphology of carbon deposits following the decomposition of carbon monoxide and methane. These authors used transmission electron microscopy techniques to observe the presence of tubular, solid and shell-like structures with catalyst particles enclosed within the structures. They concluded that the various morphological features encountered in the filaments were not dependent on the composition of the catalyst, but instead determined

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by the physical shape adopted by the catalyst particle that was responsible for generating them. Baird and co-workers [5,6] reported that the morphology of carbon filaments was related to the rate of carbon deposition, with the more graphitic structures being produced from the faster decomposition prevailing with unsaturated hydrocarbons.

The most comprehensive mechanistic features of carbon filament formation were put forward by Baker and co-workers [7] who used controlled atmosphere electron microscopy to directly observe the growth process. In the proposed mechanism, a hydrocarbon is dissociatively chemisorbed at the front face of a metal particle, carbon species proceed to diffuse through the bulk to precipitate at the rear of the particle to form a filamentous structure. While the total amount of carbon deposited during the formation of this type of material can be quite substantial, the growth process is such that it does not interfere with the desired reaction and as a consequence, catalytic activity of the particles is maintained for prolonged periods of time. It is apparent that when metallic particles are undergoing reaction, distinct crystallographic faces are generated, some of which are capable of chemically dissociating hydrocarbons, but they are unable to precipitate dissolved carbon atoms, and another set of faces that exhibit the reverse properties. A corollary of this phenomenon is that certain metal faces will be always free of solid carbon and therefore, available for continued decomposition of the hydrocarbon.

Over the years, additional features have been incorporated into this mechanism in an attempt to explain the various morphologies frequently encountered in this type of material [4,8,9]. The mechanism was further improved by Yang and Chen [9] who employed electron diffraction techniques combined with molecular orbital calculations to demonstrate that Ni(1 1 1) and Ni(3 1 1) would provide a better epitaxial fit with the planes of graphite than that afforded by other faces. Tubular structures were explained as the result of strained cylindrical graphite planes aligned parallel to the axis of the fiber [8]. Boellard and co-workers [4] found structures where the graphite planes were aligned at an angle with respect to the axis of the fiber and by the use of selected area electron diffraction they concluded that graphite precipitated from the particle with the planes parallel to the catalyst surface. The presence of additives to either the gas phase or the catalyst particles have also been of interest for several years. Hydrogen has been found to be an essential component in some systems, its function being not only to initiate the decomposition of carbon containing gases over certain metals systems [10–13], but also to exert an influence on the structural perfection of carbon filaments [12]. This aspect is somewhat controversial since not all metals require hydrogen to be present in order to exhibit activity for carbon filament formation [14]. A further aspect to consider is the importance of the interfacial phenomena existing at the metal–carbon interface, which has been highlighted as one of the parameters controlling the degree of perfection of the graphite platelets in carbon filaments [15]. It is believed that if the metal particle is capable of wetting and spreading on the graphite surface, then the probability of producing well ordered structures will be greatly enhanced. In this paper it is our aim to determine how the addition of copper to iron and the presence of hydrogen in the reactant gas mixtures modifies the morphology and crystallinity of carbon filaments produced by the decomposition of ethylene over the bimetallic particles. In previous work from this laboratory the decomposition of ethylene over iron–copper catalysts was studied at temperatures ranging between 450°C and 800°C in the presence of varying amounts of hydrogen [16]. In that investigation the emphasis was focused on the catalytic behavior of the bimetallic system and an attempt was made to rationalize the observed increase in carbon depositing characteristics of iron when only 2% copper was introduced into the catalyst particles. It was demonstrated that the presence of this gas was essential in order for the particles to undergo reaction with ethylene and produce significant amounts of carbon filaments.

2. Experimental

2.1. *Materials*

Iron–copper powders of varying compositions were prepared by coprecipitation of the respective metal carbonates from metal nitrate solutions, $Fe(NO_3)_3$ $9H_2O$ (98%, Fisher Scientific and $Cu(NO_3)_2$ $2.5H_2O$ (99.2%, Fisher Scientific) using ammonium bicarbonate at room temperature and a pH of about 9.0, followed by oxidation to metal oxides and finally, reduction in 10% hydrogen/helium at 500°C for 20 h, as described previously [16]. The reduced catalyst was cooled to room temperature under helium, then passivated by a 2% air/helium mixture for 1.0 h and stored in sealed containers. X-ray diffraction analysis was performed on all of the bimetallic powders and only peaks corresponding to metallic iron and copper were evident. These results are consistent with the fact that the two metals exhibit only limited miscibility in each other. Pure iron and copper powders were also prepared according to the above procedure. The gases used in this study, hydrogen (99.999%), helium (99.99%) and ethylene (99.5%) were obtained from MG Industries and were used without further purification. Approximately 50 mg of each sample of all these powders were initially given a reduction treatment in 10% H_2/He at 500°C and then reacted in a horizontal flow reactor system in the presence of pure ethylene at temperatures over the range 450–800°C for a period of 2.0 h. Gas flow rates were maintained at 100 cm^3/min and regulated with MKS mass flow controllers. At the conclusion of each experiment the solid carbon product was carefully removed from the quartz reactor, weighed and then stored for subsequent structural analysis.

In a further series of experiments an iron–copper (7:3) catalyst was selected to investigate the effect of hydrogen on the structural characteristics of the solid carbon deposit. In these experiments the hydrogen partial pressure was varied while that of the olefin was maintained at a constant partial pressure. In addition, the modifications in the nature of the deposit were determined from experiments where ethylene decomposition in the presence of 80% hydrogen was carried out over the catalyst powder and the temperature progressively increased from 450°C to 800°C.

2.2. Techniques

The details of the structural characteristics of individual constituents in the various carbon deposits were obtained by examination of a number of specimens from each experiment in a JEOL 100 CX transmission electron microscope that was fitted with a high resolution pole piece. High resolution transmission electron microscopy analysis was also performed on a selected number of specimens in a JEOL 2000EX II transmission electron microscope capable of 0.14 nm lattice resolution. Suitable transmission specimens were prepared by applying a drop of an ultrasonic dispersion of the deposit in *iso*-butanol to a carbon support film. In all cases the solid carbon product was found to consist entirely of filamentous structures. Variations in the width of the filaments as a function of both catalyst composition and growth conditions were determined from the measurements of over 300 such structures in each specimen. Selected area electron diffraction studies were performed to ascertain the overall crystalline order of the carbon filaments produced from the various catalyst systems.

Temperature programmed oxidation of the carbon filaments in the presence of CO_2/Ar (1:1) was carried out in a Cahn 2000 microbalance at a heating rate of 5°C/min. Under these conditions the onset of gasification of highly amorphous active carbon was observed at 550–600°C, whereas the corresponding temperature for high purity single crystal graphite was found to be 860°C. This technique is frequently used to assess the crystallinity of carbon and is based on the concept that highly graphitic materials will be more resistant to gasification than those possessing a short range crystalline order [12]. From a comparison of the oxidation profiles of these two extreme structural forms of carbon with that of an uncharacterized sample it is possible to gain an insight into the crystalline perfection of the solid carbon deposit. In order to overcome any problems associated with the participation of metal impurities on the gasification reaction, the solid carbon products were initially demineralized by treatment in 1 M HCl for three days to remove the catalyst particles. Finally, BET surface area measurements of the various carbon deposits were performed using nitrogen adsorption at −196°C with the aid of a Coulter Omnisorp 100 CX unit.

3. Results

3.1. Temperature programmed oxidation studies

The oxidation profiles of carbon filaments produced by reaction of ethylene/hydrogen (1:4) over iron–copper catalysts at 600°C, was found to be a function of composition of the catalyst, as shown in Fig. 1. It can be seen that the carbon filaments formed over the

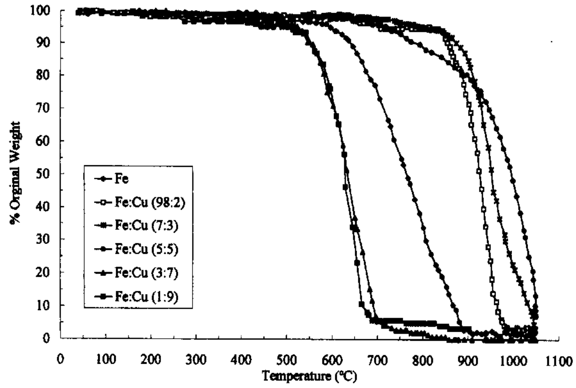

Fig. 1. Comparison of the gasification characteristics in CO_2 of carbon filaments produced from the interaction of various compositions of iron–copper powders with an ethylene/hydrogen (1:4) mixture at 600°C.

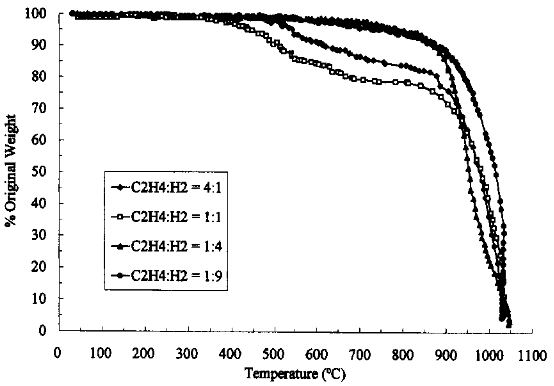

Fig. 2. Comparison of the gasification characteristics in CO_2 of carbon filaments generated from the interaction of an iron–copper (7:3) catalyst with ethylene containing various amounts of added hydrogen at 600°C.

bimetallic in the composition range 5:5 to 9:1 iron–copper were less reactive than the material produced from catalyst powders rich in copper. This trend is interpreted according to the notion that filaments generated from particles containing a large fraction of iron have a relatively high degree of structural order, i.e. are graphitic in nature. It is apparent that the carbon filaments produced from an iron–copper (7:3) catalyst exhibited the highest onset temperature for gasification and therefore one could assume that these structures possess the highest degree of crystallinity. These data indicate that by altering the bimetallic composition of the catalyst it is possible to produce a major impact on the structure of the carbon filaments formed during the interaction of such particles with ethylene.

The effect of adding hydrogen to the hydrocarbon reactant on the structure of carbon filaments can be assessed by comparison of the temperature programmed oxidation profiles of material produced from the decomposition of several ethylene/hydrogen mixtures over an iron–copper (7:3) catalyst and these data are presented in Fig. 2. It is evident that when carbon filaments were produced from ethylene containing a small amount of hydrogen (5–20%), the onset of gasification of a small amount of the sample occurs at temperatures between 550°C and 600°C whereas the major fraction starts to undergo reaction at about 850°C. This type of behavior is consistent with structures containing two components, a less ordered carbon, which is removed at low temperature, and a more highly ordered component that starts to react at higher temperatures. It is interesting to find that carbon filaments produced from reactant mixtures containing excess hydrogen exhibited a only single high temperature onset of gasification, a characteristic normally associated with single crystal graphite.

The influence of reaction temperature on the structural perfection of the filaments was investigated in a series of experiments where both the catalyst and gaseous reactant compositions were maintained constant at iron–copper (7:3) and ethylene/hydrogen (1:4), respectively. The CO_2 gasification profiles obtained from carbon filaments generated from this catalyst–reactant combination at temperatures over the range 500–800°C are presented in Fig. 3. Inspection of these data reveals some remarkable changes in the properties of the solid carbon product as the reaction temperature is progressively increased. While the filaments produced at temperatures between 500°C and 700°C exhibit gasification characteristics similar to that expected for a highly graphitic material, it is apparent that at higher preparation temperatures the carbonaceous structures become less ordered.

3.2. *Transmission electron microscopy studies*

Examination of the solid carbon samples in the transmission electron microscope indicated that the material formed under the conditions of the present study consisted primarily of filamentous structures. The carbon filaments grown from the interaction of

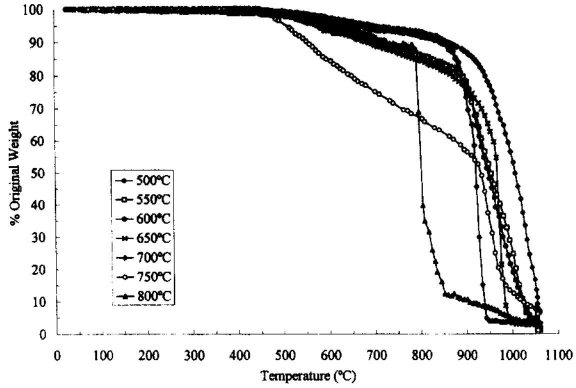

Fig. 3. Comparison of the gasification characteristics in CO_2 of carbon filaments grown from the reaction of iron–copper (7:3) powders with an ethylene/hydrogen (1:4) mixture at various temperatures.

iron powder with an ethylene/hydrogen (1:4) mixture at 600°C were of relatively short crystallographic order as indicated by the presence of diffuse rings in the selected area electron diffraction pattern. On the other hand, the carbon structures that were formed over bimetallic powders under identical conditions were found to exhibit a significantly higher degree of crystalline perfection. The morphology of these filaments, however, was found to vary as a function of the catalyst composition, and contained helical, straight whisker-like and bi-directional forms. Selected area electron diffraction patterns indicated that many of these growth forms consisted of graphitic platelets arranged in a "herring-bone" conformation with respect to the filament axis.

A wide size distribution of carbon filaments was obtained with the different iron–copper powders with cross sections ranging from 8–300 nm. For the most part the widths of the carbon filaments corresponds to that of the bimetallic particles responsible for their growth, and since the carbon structure effectively constrains the shape of the catalyst in its active state, this measurement provides an excellent method for monitoring both the size and shape of the particles under reaction conditions. Even though the surface area of the starting powder is very low (about 1 m^2/g) indicating the existence of micron-sized granules, it becomes apparent from inspection of the filament width distributions that the carbon growth process induces fragmentation of the original powders.

As mentioned previously, the carbon filaments generated from the interaction of the bimetallic catalyst systems with ethylene/hydrogen (1:4) possessed more well defined structural features than those produced from the reaction of a pure iron catalyst with the same reactant mixture. It should be stressed, however, that in the absence of added hydrogen, neither of these catalyst systems was capable of creating carbon filaments to any significant degree, and this aspect could be linked to the formation of an encapsulating layer of carbon that was responsible for deactivation of the metal particles. On the other hand, as the concentration level of hydrogen in the reactant mixture was progressively raised there was a corresponding increase in the yield of carbon filaments produced from the bimetallic catalysts, whereas the amount formed on the pure iron particles remained unchanged.

The change in the conformational characteristics of the carbon filaments produced from the interaction of various compositions of bimetallic powders with ethylene/hydrogen (1:4) at 600°C can be seen from the electron micrographs, Figs. 4–6. The filaments formed from catalysts rich in iron tended to form by the whisker-like mode, where the metal particle was located at the growing end of the carbon structure. As the percentage of copper in the catalyst was increased to about 30% the filament growth mode switched over to that of a bi-directional form, where the particle remained embedded within the structure throughout the growth process. Finally, with catalysts rich in copper, it was apparent that although the resulting carbon filaments continued to grow via a bi-directional mode, there was a subtle difference in that they acquired a helical conformation. This modification in morphology from the bi-directional linear form results from a perturbation in the diffusion characteristics of carbon species through the catalyst that introduces an element of asymmetry into the system [17,18].

In a further set of experiments it was found that the temperature at which the reaction was performed had a profound effect on both the shape of the catalyst particles and the conformational characteristics of the carbon filaments produced from a given catalyst system. The difference in the structural arrangement of carbon filaments produced from the interaction of an iron–copper (7:3) catalyst with ethylene/hydrogen (1:4) at 500°C and 700°C, respectively, is shown in

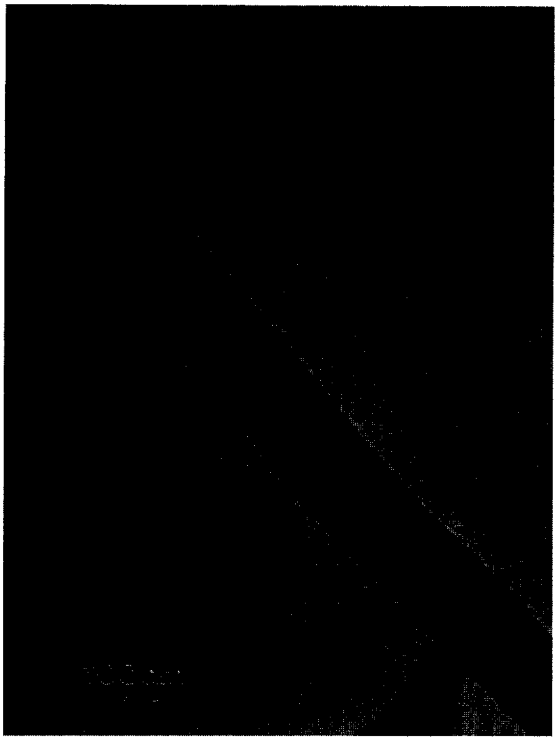

Fig. 4. Transmission electron micrograph showing the appearance of carbon filaments produced from the iron–copper (9:1) catalyzed decomposition of an ethylene/hydrogen (1:4) mixture at 600°C.

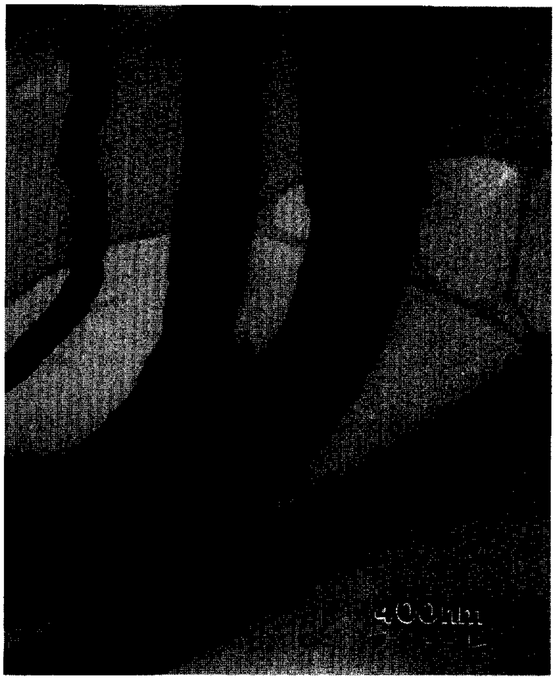

Fig. 5. Transmission electron micrograph showing the appearance of carbon filaments produced from the iron–copper (7:3) catalyzed decomposition of an ethylene/hydrogen (1:4) mixture at 600°C.

Figs. 7 and 8. It can be seen that the filaments generated at 500°C were formed by a bi-directional mode from symmetrical diamond-shaped catalyst particles. Furthermore, any kinks or imperfections created in one of the limbs were reproduced in the other in such a manner that the two sections were exact enantiomorphs. In contrast, the carbon structures produced at 700°C were multi-directional in nature where several filaments emanated from a single catalyst particle. Examination of the catalyst particles associated with these unusual "octopus" filament growth forms shows that they are highly faceted and in most cases, hexagonal in outline. Carbon filaments generated at temperatures in excess of 700°C maintained this multi-directional conformation, but tended to acquire a much more disordered structural form.

More detailed information of the micro-structural characteristics of the various types of carbon filaments was revealed from high resolution transmission electron microscopy studies. These examinations showed that the carbon filaments consisted of graphite platelets arranged in various geometric arrangements with respect to the axis of the fiber. The degree of perfection of the structures was dependent on various factors particularly the temperature of reaction and the composition of the catalyst. Figs. 9 and 10 are electron micrographs illustrating the alignments of the graphite platelets found in the major types of carbon filaments produced from the decomposition of ethylene/hydrogen mixtures over the iron–copper catalysts. These arrangements are controlled by the orientation of the precipitating faces of the metal particles [3,9,15]. In the case of a bimetallic containing a small amount of copper, the graphite was precipitated from the lateral faces of the particle and the platelets aligned in a direction parallel to the filament axis, Fig. 9. As the concentration of copper was increased to the extent where it became the major constituent in the catalyst, then the particles were observed to adopt a cubic morphology and the carbon was precipitated from a pair of opposite faces to generate a structure in which the graphite platelets were aligned at an angle to the

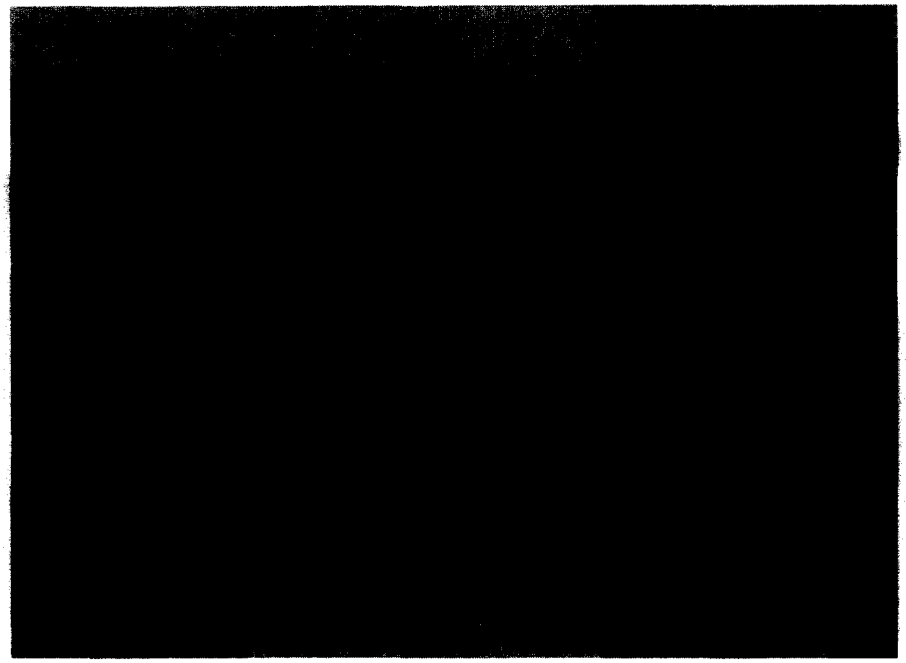

Fig. 6. Transmission electron micrograph showing the appearance of carbon filaments produced from the iron–copper (3:7) catalyzed decomposition of an ethylene/hydrogen (1:4) mixture at 600°C.

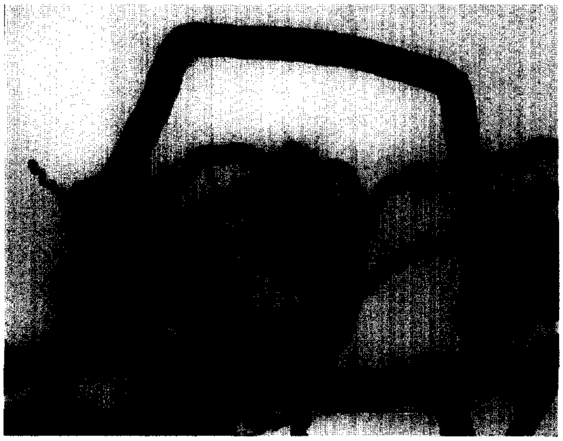

Fig. 7. Transmission electron micrograph showing the appearance of carbon filaments produced from the iron–copper (7:3) catalyzed decomposition of an ethylene/hydrogen (1:4) mixture at 500°C.

Fig. 8. Transmission electron micrograph showing the appearance of carbon filaments produced from the iron–copper (7:3) catalyzed decomposition of an ethylene/hydrogen (1:4) mixture at 700°C.

filament axis ("herring-bone" form), Fig. 10. Also included as insets in Figs. 9 and 10 are the selected area electron diffraction patterns of individual filaments, which show the existence of extremely well ordered crystalline structures as evidenced by the presence of sharp rings containing arcs. The orientation of the arcs indicates the direction of the alignment of the graphite platelets within the respective filament structures.

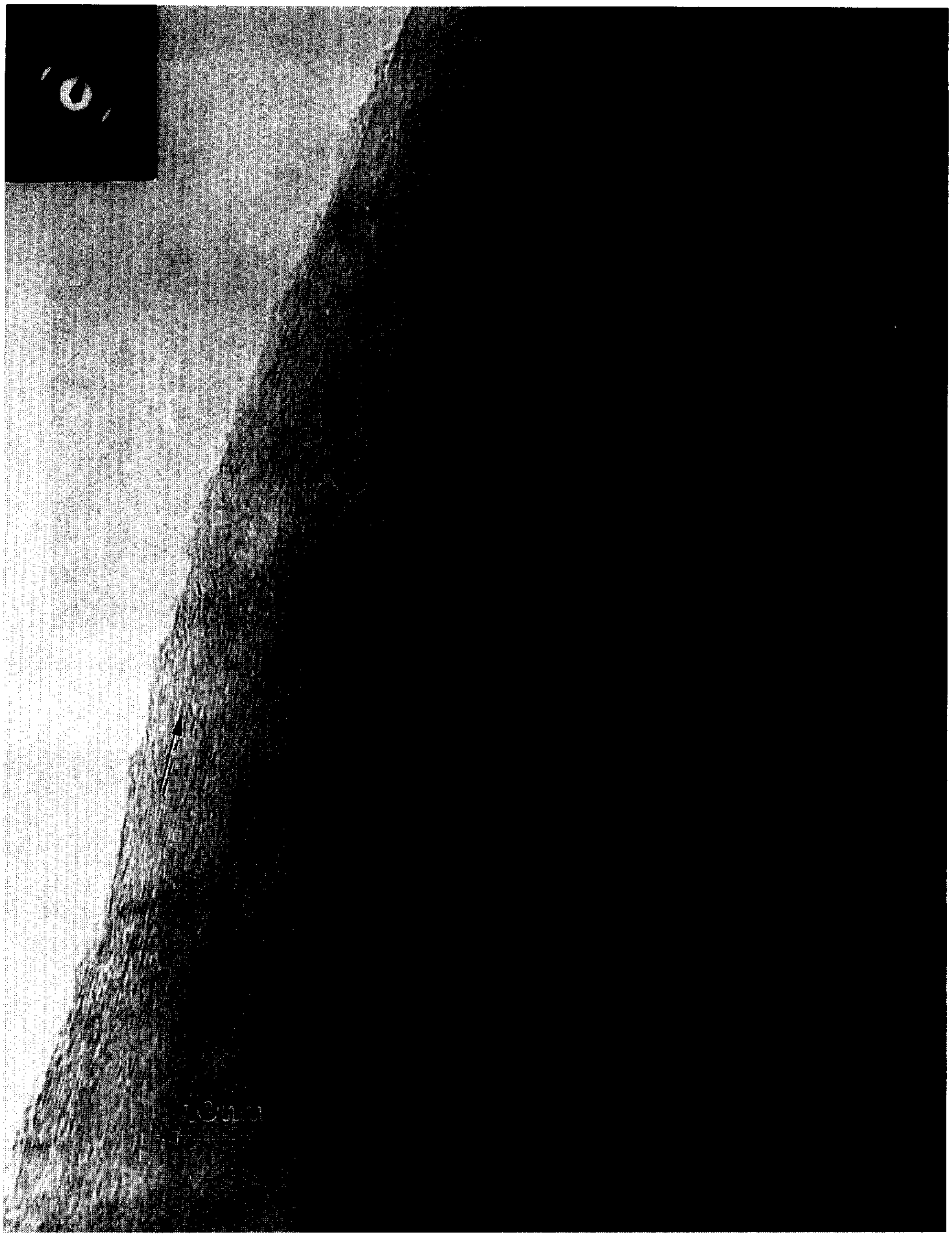

Fig. 9. High resolution transmission electron micrograph of a section of a carbon filament generated from the interaction of iron–copper (9:1) with an ethylene/hydrogen (1:4) mixture at 600°C. The inset shows the selected area electron diffraction and the alignment of the graphite platelets parallel to the fiber axis and the lateral faces of the catalyst particle is indicated.

3.3. *Surface area of carbon filaments*

The N_2 BET surface areas of the carbon filaments formed at 600°C from ethylene/hydrogen (1:4) were found to be dependent on the catalyst composition and ranged from 40 to 240 m^2/g (Table 1). The highest surface areas were observed when the Fe content in the catalyst was between 50% and 90%. The temperature

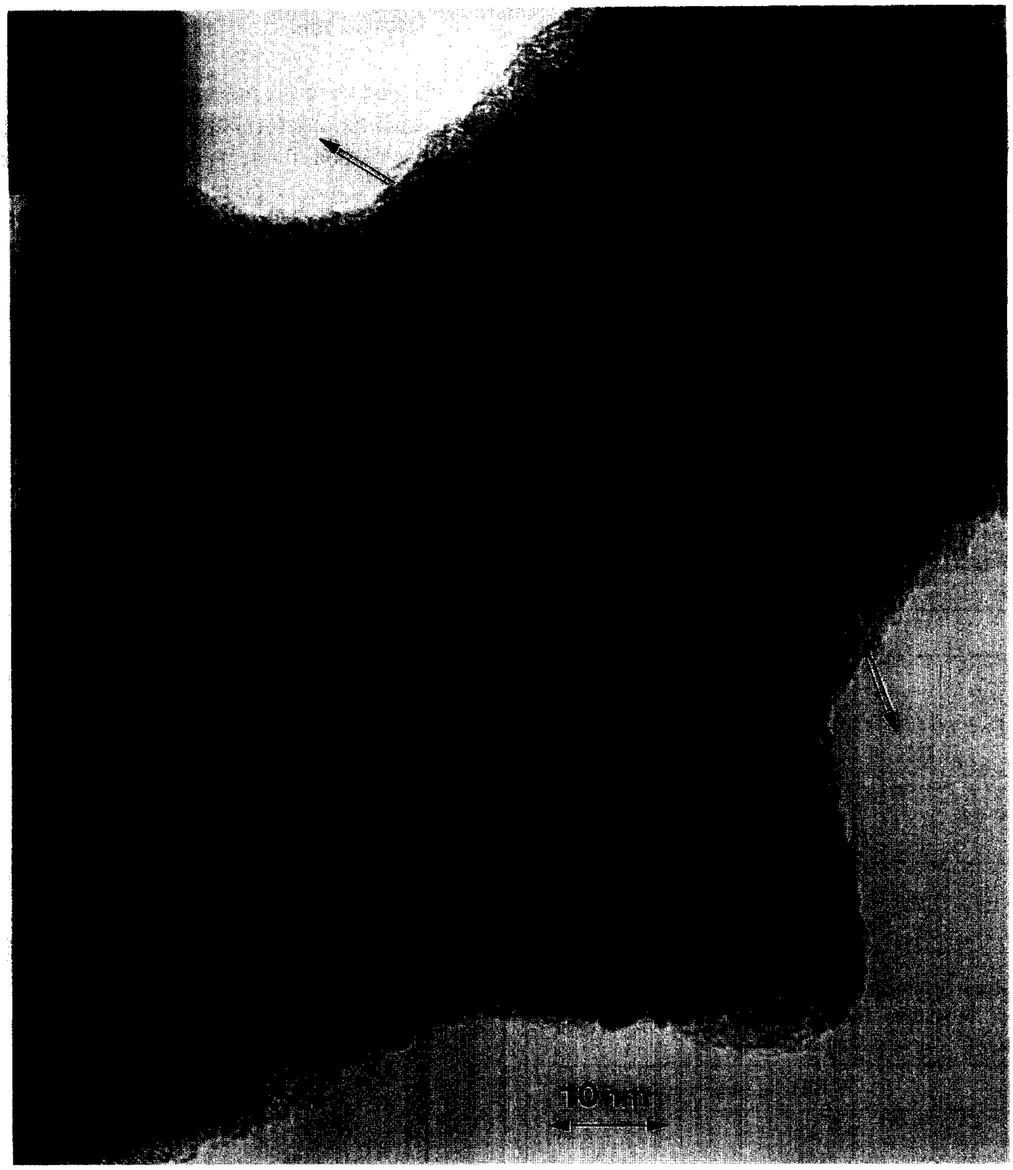

Fig. 10. High resolution transmission electron micrograph of a section of a carbon filament from the interaction of iron–copper (7:3) with an ethylene/hydrogen (1:4) mixture at 600°C. The inset shows the selected area electron diffraction and the "herring-bone" arrangement of the graphite platelets is indicated.

at which the carbon filaments were produced was found to have a significant impact on the N_2 BET surface areas of the material. An example of this dependence can be seen in data obtained from the decomposition of an ethylene/hydrogen (1:4) mixture over iron–copper (7:3) (Table 2). As the temperature was increased from 500°C to 800°C the surface areas of the filaments were found to vary from 122 to $228 m^2/g$ with the maximum value being obtained at a reaction temperature of 600°C. The presence of hydrogen in the reactant gas was also found to modify the physical characteristics of the carbon filaments (Table 3). As the percentage hydrogen in the reactant was progressively raised from 5% to 90%, the surface area of

Table 1
Characterization of carbon filaments formed by reaction of ethylene and hydrogen (1:4) at 600°C over iron–copper systems for a period of 5 h

% Fe in catalyst powder	BET N_2 surface area
5	91
10	82
30	40
50	240
70	228
90	199
95	113
98	61
100	32

Table 2
Characterization of carbon filaments formed by reaction of ethylene/hydrogen (1:4) at different temperatures over iron–copper (7:3) powders

Temp (°C)	BET N_2 surface area
500	135
550	177
600	228
650	181
700	166
750	139
800	122

Table 3
Effect of percent hydrogen in the gas phase on the physical characteristics of carbon filaments formed from reaction of ethylene at 600°C over iron–copper (7:3) powder

% Hydrogen	BET N_2 surface area
5	15
20	142
80	228
90	110

filaments produced from iron–copper (7:3) particles increased from 15 to 110 m^2/g with the highest value being attained for this system at 80% hydrogen. It is therefore possible to control the surface area of the solid carbon product from a given catalyst composition by modulation of either the reaction temperature or the composition of the reactant gas.

4. Discussion

The results of the present investigation indicate that the structure, conformation and degree of crystalline order of carbon filaments is dependent on a number of parameters that include the nature of the catalyst particle, the composition of the reactant gas and the temperature. In order to understand some of the morphological features associated with the material it is necessary to consider the various steps involved in its growth. Carbon filaments can be produced when conditions are reached whereby a hydrocarbon can dissociatively chemisorb over particular faces of a metal particle. Carbon species then proceed to diffuse through the bulk of the particle to precipitate at certain faces leading to the formation of a carbon deposit. A schematic representation of the process is presented in Fig. 11. Although the adsorption of the hydrocarbon is a crucial step in the formation of the filaments, it is the geometrical shape of the metal particle and the number of precipitating faces that ultimately will determine the morphology of the filament and the orientation of the graphite platelets. It is therefore

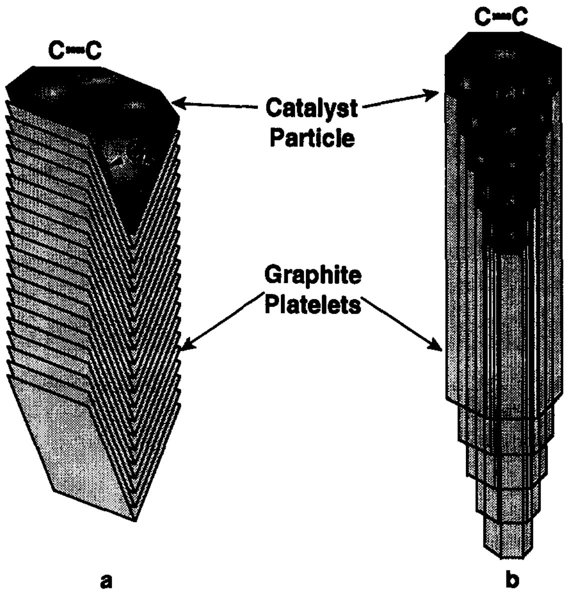

Fig. 11. Schematic diagram highlighting the essential steps involved in the catalytic growth of carbon filaments from decomposition of a hydrocarbon and the alignment of graphite platelets in the filament structures, (a) herring-bone and (b) tubular arrangements.

possible to have several faces that simultaneously precipitate carbon giving rise to variations in the conformation of the fibrous structure. A further aspect of importance in this process is the match between the interstices of the metal precipitating face and the C–C bond distance of graphite; a perfect spacing will undoubtedly lead to the formation of flawless graphite platelets. This aspect has been presented by Yang and Chen [9] who demonstrated by the use of selected area electron diffraction and HOMO calculations that certain faces in nickel will favor the precipitation of graphite.

The extent of crystalline order of carbon filaments produced from the decomposition of ethylene over iron–copper powders is dependent on the composition of the metal catalyst as revealed by the temperature programmed oxidation studies, Fig. 1. Carbon structures formed from the decomposition of ethylene over pure iron and bimetallic powders containing a substantial amount of copper, exhibited very little degree of crystalline order as indicated by the onset of temperature of oxidation, approx. 550°C, and these samples were rapidly consumed at low temperatures, well below the onset of gasification of graphite. On the other hand, the solid carbon product generated during the decomposition of ethylene over bimetallic powders containing at least 50% iron, exhibited a much higher onset temperature for gasification, that was quite close to that displayed by graphite when reacted under the same conditions. The extreme variations found in the crystalline character of the filaments resulting from a change in the composition of the metal catalyst can be attributed to variations in the strength of the interaction of the metal particle with carbon at the catalyst–carbon interface. It is not unreasonable to assume that major differences in both the identity and the distribution of atoms at the surface of the particle in contact with the deposited carbon is a variable that is dependent on the initial chemical composition of the particle. Ordered carbon structures are expected to form when two conditions are satisfied: (i) the interstitial spaces in the carbon precipitating faces of the metal match the bonding of carbon atoms in graphite and (ii) the number of metal atoms at the catalyst–solid carbon interface is substantial thereby allowing for the generation of relatively large-sized crystallites.

The effect of hydrogen on the structure of carbon filaments is clearly observed in the temperature programmed oxidation curve, Fig. 2. It is evident that the degree of crystallographic order in the carbon structures is enhanced by addition of increasing amounts of hydrogen. Although the reasons for this behavior are not completely understood, it is possible that the presence of hydrogen either induces reconstruction of the particle to generate faces that are more favorable towards the formation of graphite and/or that hydrogen also enhances the wetting of carbon by the metal particle thereby generating a structure with a more extended crystallographic order. The morphological changes accompanying the interaction of metal particles over carbon and graphite have been directly observed by in situ electron microscopy [19–21], and it has been observed that the presence of hydrogen in the reactant gas stimulates the formation of a strong interaction between the two components, i.e. promotes a spreading action of metal along the graphite edge regions.

High resolution transmission electron microscopy of individual filaments confirmed the existence of structures containing various degrees of crystalline order as well as variations in the orientation of the graphite platelets with respect to the fiber axis in the various growth conformations. These aspects are clearly evident from inspection of the micrographs, Figs. 9 and 10. The existence of such micro-structural arrangements can in turn have a direct influence on some of the physical properties of the carbonaceous materials. Indeed, the results of a number of studies have demonstrated that properties such as the surface area, degree of crystalline perfection and conformational form of carbon filaments grown from decomposition of a given carbon-containing gas depend on the nature of the catalyst used, the temperature of the reaction and the gas phase reactant composition.

When one is dealing with a bimetallic catalyst system, however, the interplay between these various factors becomes somewhat more complex. Under these circumstances it is essential to take into consideration how the reaction temperature coupled with the nature of the gas phase affect the surface composition of the metal particle due to the preferential segregation behavior of one of the components. This is a critical feature that dictates not only the mode of adsorption, but also the subsequent decomposition behavior of the hydrocarbon reactant molecule. The characteristics of hydrocarbon adsorption is dependent on the arrangement of atoms at the exposed crystallographic face of the metal and also, the chemical identity of the surface atoms that come into contact with the gas phase.

Previous studies from this laboratory have demonstrated that in the case of nickel–copper undergoing reaction with ethylene and ethylene/hydrogen mixtures, there was an upper temperature limit above which the catalyst lost its activity with respect to growth of carbon filaments and this behavior, which was reversible in nature, was attributed to the accumulation of high concentrations of copper at the particle/gas interface [22]. The overriding factor in the separation phenomenon of the two components was believed to be the tendency of nickel to form a strong interaction with the graphite platelets in the filamentous structure and as a consequence, preferentially segregate to the particle/solid carbon interface. In contrast to nickel, iron does not exhibit the same affinity to spread on a graphite surface under these conditions [23] and therefore, the driving force for complete separation of the two components and concomitant catalyst deactivation should not be as intense in this system. Nevertheless, it is expected that at high temperatures the composition of the interfacial regions of the catalyst particles will be appreciably different to that of the bulk and as such, structural changes in the deposited carbon structures are anticipated.

This phenomenon may also be affected in a very dramatic fashion by the presence of certain gas phase additives. In this context, it has recently been demonstrated that while iron exhibits very little tendency to undergo interaction with ethylene/hydrogen, the introduction of carbon monoxide into the reactant mixture brought about a promotion of the adsorption and decomposition of the hydrocarbon [24,25]. This behavior was rationalized in terms of either a reconstruction of the metal surface in the presence of coadsorbed carbon monoxide which resulted in the formation of various faces with differing reactivity characteristics, or as an alternative, the ability of CO to extract electrons from the metal and consequently alter the electronic configuration of the iron surface. Other workers [26,27] have reported that the presence of carbon monoxide in the gaseous reactant causes an enrichment of the iron–copper surface by the ferromagnetic metal. Geus and co-workers [28,29] showed that it was necessary for iron to be present in the surface in order for iron–copper particles to produce filamentous carbon from the disproportionation of carbon monoxide.

Perhaps one of the most dramatic features to emerge from this investigation is the finding that by merely changing the concentration of copper in the catalyst particles it is possible to manipulate the orientation of the graphite platelets in the filament structures. From an examination of the high resolution electron micrographs, Figs. 9 and 10, it is evident that as the copper content in the particles is increased from 2% to 30% the graphite structures switch from a state where the platelets are aligned parallel to the filament axis to that of a "herring-bone" arrangement. In a previous investigation [30] it was demonstrated that the alignment of the graphite platelets is associated with major differences in the overall 3D conformation. This aspect can be more easily appreciated by reference to the schematic diagrams depicted in Fig. 11, where it can be seen that in the "herring-bone" structure (Fig. 11a) a large number of edge sites are exposed, whereas in the "tubular" configuration (Fig. 11b) a limited number of such sites are presented to the reactant environment. While this transformation in growth characteristics is not expected to produce any major overall modification in the graphitic content of the filaments, it is anticipated that there would be significant differences in the surface areas of the two structures, with the former exhibiting the lower value, as was observed experimentally.

Furthermore, this distinction in geometric arrangement of the graphite platelets bestows some interesting differences in properties of the respective types of filaments, which have a significant impact on their potential applications. Carbon filaments produced in a structural ordering where the platelets are in a "herring-bone" stacking will possess an extensive number of edge sites, that can be modified by the addition of various functional groups, and therefore be capable of selectively interacting with either acidic or basic compounds. These regions will also be the preferred locations for the accumulation of metal and metal oxide particles when introduced into the system by either gas or liquid phase deposition techniques [31]. Conversely, filaments that are formed with the platelets aligned in a parallel manner to the axis and tend to present graphite basal plane regions to the reactive phase will have a reactivity pattern limited to groups of species that have an affinity for delocalized p-electrons. This latter structural arrangement should, however, confer higher electrical conducting properties on the solid carbon product and also have an impact on the rate of gasification.

5. Summary

The results of this investigation have shown that iron–copper particles are very active catalysts for the formation of carbon filaments when samples of the bimetallic powders are reacted in the presence of ethylene at temperatures over the range 500–800°C. It was found that for catalysts containing a large fraction of iron the filaments were produced in a highly crystalline form at temperatures up to 700°C and above this level they tended to acquire a more disordered structure. The addition of hydrogen to the reactant gas mixture was also shown to increase the degree of crystalline perfection of the solid carbon structures. High resolution transmission electron microscopic examinations revealed that by merely changing the fraction of iron in the catalyst from 70% to 90% it was possible to modify the stacking arrangement of the graphite platelets constituting the filaments from a "herring-bone" to tubular alignment with respect to the growth axis.

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