

ARTICLES

Characteristics of Carbon Filament Formation from the Interaction of Cobalt–Tin Particles with Ethylene**T. Nemes, A. Chambers, and R. T. K. Baker****Department of Chemistry, Northeastern University, Boston, Massachusetts 02115**Received: February 26, 1998; In Final Form: June 10, 1998*

The effect of adding tin to a cobalt catalyst has been investigated using the decomposition of ethylene at 600 °C to form solid carbon, methane, and ethane as a probe reaction. These experiments have been carried out in a simple continuous flow system, where it was possible to monitor not only the gaseous product distribution but also the growth of filamentous carbon as a function of time. Particular attention was given to the modifications in the structural characteristics of the carbon filaments that accompanied the change in catalyst composition. These studies were performed using a combination of temperature-programmed oxidation, BET surface area measurements, and examination at high resolution in the transmission electron microscope. It was found that the introduction of as little as 0.5 wt % of tin into cobalt produced a dramatic increase in the catalytic activity of the bimetallic toward the formation of filamentous carbon. It is suggested that tin is responsible for inducing electronic perturbations in the surface of cobalt, and this phenomenon is reflected in a major change in the dissociative chemisorption behavior of ethylene on the mixed metal catalyst. Increasing the concentration level of tin did not lead to any further enhancement in the amount of carbon generated from the reaction; however, this procedure resulted in a significant increase in the rate of catalyst deactivation. It was also found that in the presence of tin the filamentous carbon structures acquired a high degree of crystalline order.

Introduction

It has been known for decades that when gaseous mixtures containing hydrocarbons and/or carbon monoxide are passed over selected metal surfaces, carbon filaments are one of the solid products generated during the reaction.^{1–5} While there has been considerable debate over various aspects concerning the growth mechanism of this form of carbon, there is a general consensus that diffusion of carbon species through the catalyst particles is the rate-controlling step in the process.^{6–18} In more recent years considerable efforts have been devoted to the understanding of the factors that control the structural features of the carbon filaments^{19–22} with a view to exploiting the potential of the material in various applications.^{23–31}

Although one might expect that most metals will interact with carbon-containing gases, the likelihood for such a process to occur is dependent on the arrangement of atoms at the surface of the particle, and this feature is influenced by a number of parameters including the composition of the gas environment, the reaction temperature, and the nature of the support medium. It has been found that carbon deposition from hydrocarbons can be greatly enhanced by the presence of hydrogen^{32–35} or carbon monoxide,³⁶ and this phenomenon has been interpreted as the result of either reconstruction of the metal surface or the existence of an electron-transfer process between the two components.

On the other hand, the structure of the carbon filaments is determined by a array of factors that include the crystallographic orientation of the faces of the metal catalyst particle in contact with the solid carbon and the degree of spreading of the metal on the carbon, which in turn is dictated by the interfacial energy between the two components at a given temperature. In general, metals that readily wet and spread on graphite will form filaments that are composed entirely of graphitic platelets, whereas those that do not form a strong interaction with the substrate tend to precipitate carbon in a more disordered manner.

The concept of perturbing both the chemical and physical properties of a given metal via the addition of a dopant has been exploited in the electronics industry for many years. Furthermore, this procedure has met with considerable success in a number of commercial catalytic processes where the notion of replacing pure metals with bimetallics in order to enhance both the activity and selectivity has been realized.³⁷ In the case of catalyzed carbon filament growth there is an overwhelming number of advantages that can be achieved by the addition of small amounts of a second element to the host metal catalyst. In a recent investigation from this laboratory³⁸ it was found that pure iron and copper powders exhibited very little or no activity for the growth of filaments when heated in the presence of ethylene. If, however, a very small amount (~2%) of one of these metals was added to the other, then on subsequent reaction with the olefin prolific growth of this type of carbon deposit was observed. It was suggested that the presence of “impurity” atoms at the surfaces of a metal particle will have an impact

* To whom correspondence should be addressed.

not only on the hydrocarbon dissociative chemisorption process but also on the events occurring at the metal/solid carbon interface. Major differences in the identity and the distribution of atoms at this location will affect the interstitial spacing and the strength of the interaction of the particles with carbon. Both these parameters will have direct repercussions on the degree of crystalline perfection of the precipitated solid carbon structures. Finally, when the concentration of the additive reaches proportions where there is a significant effect on the bulk properties of the catalyst, then modifications can be expected with regard to carbon diffusion characteristics through the particle and, as such, changes in carbon filament growth rates.

In the current investigation we have elected to study the manner by which the addition of tin modifies the catalytic behavior of cobalt toward carbon filament formation when the mixed metal system is reacted in the presence of ethylene and ethylene/hydrogen environments. Although tin has only met with limited use as an adatom, it has been found to exert some extremely important promotional properties on platinum for reforming reactions.^{39–41} It has been established that the addition of tin to platinum results in an enhanced catalyst stability and improved selectivity toward aromatic product formation. Liu and Chiu⁴² reported that the addition of tin to nickel produced a significant enhancement in catalytic activity for the vapor-phase carbonylation of methanol to produce acetic acid. In contrast, there is evidence that incorporation of tin into either palladium or nickel decreased the hydrogenation activity of the group VIII metals.^{43,44} It was suggested that this behavior was due to a suppression of the dissociative adsorption of hydrogen on the tin-modified metal surface. A study conducted in the controlled atmosphere electron microscope revealed the existence of an unusual type of bidirectional carbon filament growth when tin was added to iron and the bimetallic particles were heated in acetylene.⁴⁵ In this reaction the particles executed a rotational motion, and as a result of this action, the fiber limbs acquired a spiral conformation. Another peculiarity of the system was that periodically the catalyst particle was extruded from the growing filament to produce branches with identical structural features to those of the parent filament.

Experimental Section

Materials. The tin–cobalt powder catalysts used in this investigation varied in composition from Co–Sn 50:50 to 99.5:0.5 and were prepared by the coprecipitation of the metal carbonates from the respective nitrate solutions mixed in a ratio calculated to give the desired bimetallic composition using ammonium bicarbonate in a manner similar to that described by other workers.^{46,47} The resulting solid was violet in color and was dried in an oven overnight in air at 110 °C. Following this operation the precipitate was ground to a fine powder and then calcined in air at 400 °C for 4.0 h in order to convert the carbonates to mixed oxides. Finally, the powdered oxides were reduced in a 10% hydrogen/helium mixture at 500 °C for 20 h to form the tin–cobalt powders. Prior to removal from the furnace tube, the reduced powders were cooled to room temperature under a flow of helium and then passivated by a flow of 2% CO₂/helium for 1.0 h. The bimetallic powders were then removed from the reactor, ground, and stored in sealed containers. The BET surface area of the powders as determined by N₂ adsorption at –196 °C were in the range 1.0–2.0 m²/g, which corresponded to an average granular size of about 1.0 μm.

X-ray diffraction analysis was carried out on the bimetallic powders before and after reaction in the hydrocarbon environ-

ment using a Scintag 1 diffractometer equipped with a nickel monochromator. Diffraction was performed with Cu Kα radiation at a scan rate of 2°/min, and peaks were identified by comparison with standards in a related computer database. In the freshly prepared powders, with the exception of the sample containing only 0.5% tin, peaks corresponding to both metallic components were observed in all the patterns, and for the most part the sizes were consistent with the expected values from the various preparations. It was significant that in the starting powders there was no evidence of alloy formation at room temperature; however, following reaction in ethylene/hydrogen at 600 °C, it was possible to identify the existence of a Co₂Sn alloy phase in some of the powder patterns. The presence of the pure metallic components combined with the absence of bulk metal oxides in these samples at room temperature confirms the effectiveness of the passivation procedure in 2% CO₂/helium after reduction.

The gases used in this work, ethylene (99.99%), carbon dioxide (99.9%), helium (99.99%), and hydrogen (99.999%), were obtained from MG Industries, Inc., and were used without further purification. Reagent grade tin(II) chloride dihydrate (SnCl₂·2H₂O) and reagent grade cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O) were purchased from Aldrich Chemical Co.

Apparatus and Procedures. Carbon deposition experiments were carried out at 600 °C in a quartz reactor tube placed horizontally in a Lindberg furnace. Approximately 50 mg of a given catalyst powder was dispersed as a uniform thin bed along the base of a ceramic boat (1 cm width and 10 cm length), which was then positioned in the center of the constant heat zone of the flow reactor tube. Flow rates of gases were regulated by MKS mass flow controllers and maintained at 100 cm³/min. Initially the catalyst samples were reduced in a 10% hydrogen/helium mixture at 600 °C for 2.0 h in order to convert surface oxides into the metallic state. Following this step a predetermined feed composition consisting of ethylene/helium or ethylene/hydrogen/helium was introduced into the system and the reaction allowed to proceed for a period of 90 min. The composition of the reactant gas was analyzed at the start and at regular intervals during the reaction with a Varian 3400 gas chromatography unit using a 30 m megabore column (GS-Q). Carbon and hydrogen atom balances in conjunction with the relative concentrations of the respective components were employed to derive the various product yields, and the weight of solid carbon deposited on the catalyst was determined at the completion of a particular reaction. In all cases the computed and measured weights of the solid carbon product were within ±5%.

The identity and structural features of individual components of the solid carbon deposit were established from high-resolution transmission electron microscopy examinations performed in a JEOL 2000 EXII instrument (lattice fringe resolution = 0.14 nm). Suitable transmission specimens were prepared by ultrasonic dispersion of sections of the deposit in isobutanol and then application of a drop of the supernate to a holey carbon film. Inspection of several regions of the specimens revealed that in all cases the deposit consisted entirely of carbon filaments.

An estimation of the overall degree of crystalline order of the solid carbon was carried out using temperature-programmed oxidation in the presence of CO₂/Ar (1:1). These experiments were performed in a Cahn 2000 microbalance at a heating rate of 5 °C/min. Under these conditions the onset of gasification of amorphous carbon commences at about 550 °C, whereas the corresponding point for single-crystal graphite is 860 °C. From

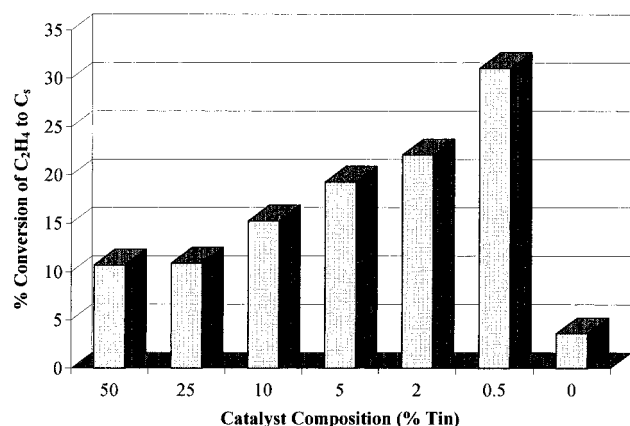


Figure 1. Percentage conversion of ethylene to solid carbon as a function of catalyst composition after 90 min reaction at 600 °C.

TABLE 1: Effect of Catalyst Composition on the Product Distribution (in %) from the Decomposition of Ethylene after 90 min Reaction at 600 °C

Co:Sn	C_s	CH_4	C_2H_6	C_2H_4
50:50	10.69	0.80	2.90	85.56
75:25	10.01	0.89	3.23	85.87
91:9	15.23	0.81	3.50	80.47
96:4	19.27	0.90	5.19	74.63
98:2	22.08	1.12	10.54	66.26
99.5:0.5	31.04	1.02	13.74	54.20
100:0	3.60	1.00	3.60	91.80

a comparison of the oxidation profiles of these two extreme structural forms of carbon with that of a noncharacterized sample, it is possible to gain an insight into the degree of crystalline perfection of the solid carbon deposit produced from a given reaction. For this type of analysis to be meaningful it is necessary to remove any metal impurities from the deposit that might otherwise exert a catalytic influence on the gasification reaction in CO_2 . This step is accomplished by repeated treatments in 1 N hydrochloric acid over a period of 3 days. Finally, BET surface area measurements of the various carbon deposits were accomplished using N_2 adsorption at -196 °C with the use of a Coulter Omnisorp 100CX unit.

Results

1. Flow Reactor Studies. 1.1. Effect of Cobalt–Tin Ratio on Reaction Products. The influence of changing the ratio of cobalt to tin on the carbon deposition reaction was investigated in a flow reactor. This series of experiments was carried out at 600 °C for 90 min using ethylene (40 cm^3/min) diluted with helium to give an overall flow rate of 100 cm^3/min , over a constant weight of catalyst sample (50 mg). The yields of gaseous and solid carbon products from a series of cobalt–tin powders of varying composition are presented in Figure 1 and Table 1. From these data it can be seen that under the prevailing reaction conditions the amount of solid carbon formed on the bimetallic powders was significantly greater than that produced on the pure cobalt sample, reaching an optimum level for a catalyst composition of Co–Sn (99.5:0.5). It is also evident that this particular bimetallic exhibits the highest catalytic activity for the conversion of ethylene. Examination of the selectivity profile of the bimetallic powders shows that as the percentage of tin is progressively reduced from 50 to 0.5% not only is there an enhancement in the amount of solid carbon but the yield of ethane also increases. It is significant that over the same catalyst composition range, within experimental error, there is little or no change in the yield of methane.

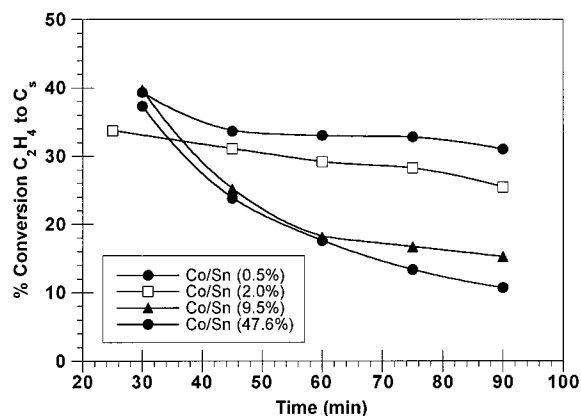


Figure 2. Percentage conversion of ethylene to solid carbon as a function of reaction time at 600 °C for a selected number of Co–Sn catalysts.

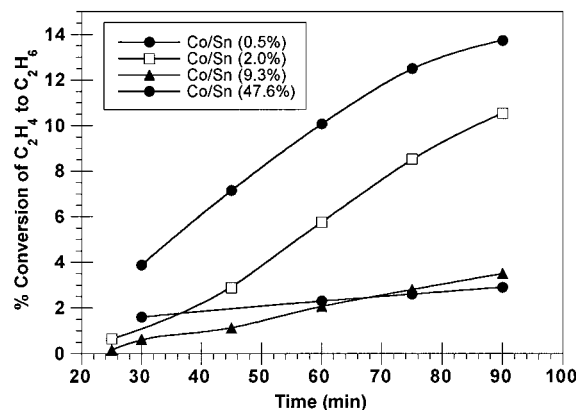


Figure 3. Percentage conversion of ethylene to ethane as a function of reaction time at 600 °C for a selected number of Co–Sn catalysts.

1.2. Influence of Reaction Time on Product Distribution. The formation of solid carbon and gas-phase products resulting from the interaction between various cobalt–tin powders and ethylene at 600 °C was studied as a function of reaction time. These experiments were undertaken in an endeavor to ascertain whether any modifications in the chemical nature of the catalyst surfaces occur during the reaction that might be reflected in a change in the activity with respect to product formation. The different activity profiles of a selected number of cobalt–tin powders for solid carbon and ethane formation are presented in Figures 2 and 3, respectively. It can be seen that all the bimetallic catalysts exhibit a relatively high initial carbon deposition activity and that powders containing the larger fraction of tin undergo rapid deactivation. In contrast, carbon deposition from bimetallic powders in which the concentration of tin is less than 2% reaches a steady state after a period of 30 min on stream and maintains this level of activity for a prolonged period of time. It was interesting to find that the activity maintenance curves for carbon deposition paralleled those for the percent decomposition of ethylene over the same catalyst systems.

Inspection of the data displayed in Figure 3 indicates that, for all the bimetallic powders, the activity for ethane formation increases uniformly as a function of reaction time, and an analogous trend was also found for the production of methane. In these cases there did not appear to be any direct relationship between the amount of gas-phase product formation and the percentage of ethylene that had decomposed. It is evident, therefore, that subtle differences may exist between the underly-

TABLE 2: Effect of Catalyst Composition on the Product Distribution (in %) from the Decomposition of Ethylene/Hydrogen (8:1) after 90 min Reaction at 600 °C

Co:Sn	C _s	CH ₄	C ₂ H ₆	C ₂ H ₄
50:50	14.21	1.18	7.95	76.66
75:25	15.06	1.29	8.40	75.25
91:9	16.68	1.37	9.71	72.24
96:4	23.78	1.16	11.19	63.86
98:2	25.45	1.18	12.64	60.73
99.5:0.5	33.15	0.95	12.09	53.80

TABLE 3: Influence of Added Hydrogen on the Product Distribution (in %) from the Interaction of Cobalt–Tin (99.5:0.5) with Ethylene after 90 min Reaction at 600 °C

hydrogen	C _s	CH ₄	C ₂ H ₆	C ₂ H ₄
0	31.04	1.02	13.74	54.20
2.5	24.57	1.06	13.27	61.11
5.0	33.15	0.95	12.09	53.80
10.0	31.04	0.97	13.78	54.22
20.0	24.96	1.33	25.07	48.64
30.0	28.79	1.43	25.58	44.20
40.0	31.60	1.57	28.33	38.49

ing factors that control the activity patterns for the gas-phase products and those responsible for the growth of solid carbon.

1.3. Effect of Hydrogen Addition to the Reactant Mixture.

In a complementary set of experiments the effect of added hydrogen to the feed stream on the characteristics of the carbon deposition reaction was studied. These data, which were obtained for a C₂H₄/H₂ (8:1) reaction mixture and cover a somewhat more limited range of bimetallic compositions, are presented in Table 2. Comparison of these results with those shown in Table 1 reveals that when the hydrocarbon decomposition is performed in the presence of added hydrogen, there is a perceptible increase in catalytic activity for reactions over the bimetallics containing a relatively large fraction of tin; this trend declines as the concentration of the adatom is reduced. Indeed, the product yields obtained for the interaction of a cobalt–tin (99.5:0.5) powder with ethylene and ethylene/hydrogen are almost the same.

In a final series of experiments the concentration of ethylene was maintained constant at 40 cm³/min, and the effect of increasing amounts of hydrogen on the reaction product distribution was examined. The data presented in Table 3 show the change in selectivity of a cobalt–tin (99.5:0.5) catalyst as a function of added hydrogen. It is evident that while the intrinsic activity of the catalyst increases as the hydrogen content in the reactant is raised, the amount of solid carbon produced remains relatively constant. In contrast, both the yields of methane and ethane rise as hydrogen is added to the system, with the latter exhibiting a substantial increase under these conditions.

2. Characterization of the Solid Carbon Product. 2.1.

Transmission Electron Microscopy Studies. When sections of the carbon deposits were examined by transmission electron microscopy, they were found to consist exclusively of carbon filaments with no evidence for the formation of other types of deposits, such as graphitic shells. There were, however, variations in the structural characteristics of this material that were dependent on the catalyst composition and conditions of preparation. It was evident that filaments, generated from the interaction of a cobalt–tin (99.5:0.5) powder at 600 °C with ethylene containing 2.5% hydrogen, had grown via a “whiskerlike” mode. In such a sequence the metal catalyst particle remains located at the tip of the structure throughout the growth process. Furthermore, high-resolution studies showed that this material exhibited a high degree of crystalline perfection where

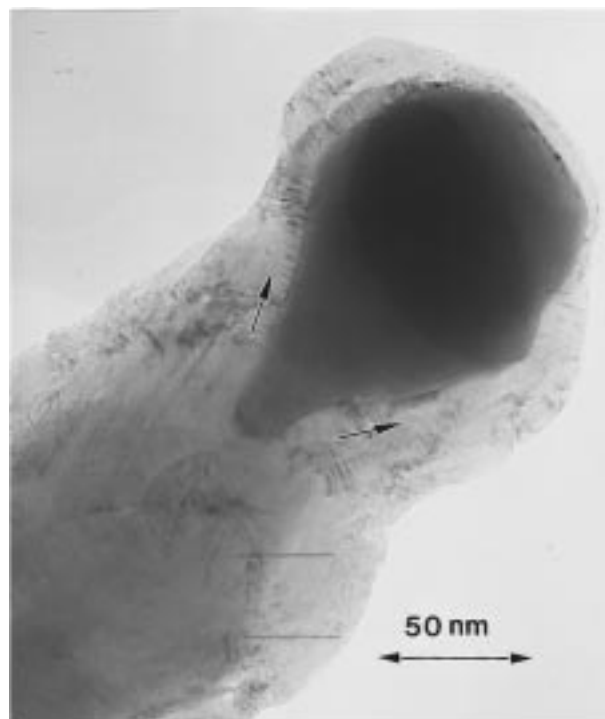


Figure 4. Transmission electron micrograph of a carbon filament generated from the interaction of a cobalt–tin (99.5:0.5) powder at 600 °C with ethylene containing 2.5% hydrogen. The arrows indicate the directions of the precipitated graphite platelets constituting the filament structure.

the graphite platelets constituting the filaments were oriented in the same directions as the faces of the metal particles in contact with the solid carbon (Figure 4). The “herringbone” arrangement of the platelets is highlighted with arrows in the micrograph.

The widths of filaments generated by the “whiskerlike” mode were similar to those of the associated catalyst particles and were typically in the range 20–100 nm, and the size distribution did not exhibit any major perturbation as the composition of the catalyst was changed. It was significant that these particles were considerably smaller than those of the original bimetallic powders (estimated to be about 1.0 μm in diameter), which indicates that during the carbon deposition reaction fragmentation of the starting material takes place. The breakup of relatively large nickel–iron particles prior to growth of carbon filaments from acetylene has been reported previously based on the direct observations obtained with controlled atmosphere electron microscopy.⁴⁸ In addition, other workers¹² have invoked the existence of such a step in order to account for the nucleation and growth of carbon filaments on metal foils.

An unexpected change in structural characteristics was observed when samples of the same bimetallic powder were heated in an ethylene stream containing 30% hydrogen under otherwise identical conditions. Under these conditions, while the catalyst maintained a well-faceted outline, the filaments tended to adopt a conformation in which several irregular-shaped limbs appeared to emanate from a single particle, in a so-called “octopus” arrangement. The typical appearance of this type of filament is presented in the electron micrograph in Figure 5. Examination of this material at high resolution failed to reveal the presence of any graphite platelet structures, and the disordered nature of these filaments was subsequently confirmed from the existence of a diffuse ring pattern by electron diffraction analysis.

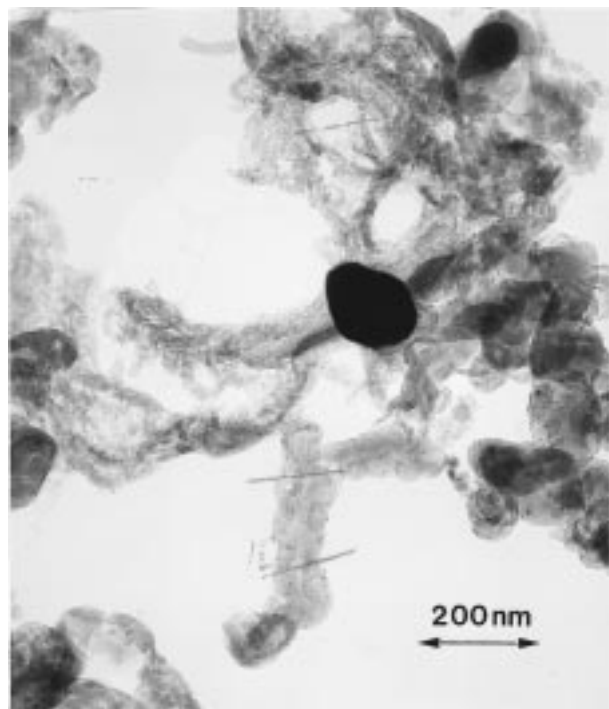


Figure 5. Transmission electron micrograph showing the multidirectional growth of several carbon filaments (octopus structure) generated from the interaction of a single particle of cobalt–tin (99.5:0.5) at 600 °C with ethylene containing 30% hydrogen.

In all cases the widths of the filaments appeared to remain constant throughout their growth period, indicating that there was no progressive loss of material from the particles during this process. This finding demonstrates that even though the reaction temperature is well above that of the melting point of tin, 232 °C, there is no preferential loss of this component that could result from a wetting action of the filamentous structures by this metal. Such a pattern of behavior is generally recognized by a tapering of the filaments as the catalyst particle gradually decreases in size. One may conclude therefore that despite the fact that the solubility of tin in cobalt is less than 2 atom % at 600 °C,⁴⁹ the strength of the interaction between the two metals is sufficient to maintain the system in a relatively stable condition.

2.2. Temperature-Programmed Oxidation Studies. The effect of adding hydrogen to ethylene on the structural characteristics of the demineralized carbon filaments can be evaluated from a comparison of the gasification profiles in CO₂ of material produced from the interaction of cobalt–tin (99.5:0.5) with several ethylene/hydrogen mixtures after a period of 90 min at 600 °C (Figure 6). Examination of these curves shows that the filaments grown from a reactant mixture containing 2.5% hydrogen display oxidation characteristics that are similar to those of single-crystal graphite. As the concentration of hydrogen in the feed was gradually increased to a level where it equaled that of ethylene, the structure of the filaments became progressively more disordered in nature. It was interesting to discover that the carbon structures generated from the interaction of the bimetallic with pure ethylene exhibited the lowest degree of crystalline perfection.

In a complementary set of experiments the oxidation profiles of carbon filaments grown from the interaction of C₂H₄/2.5% H₂ with cobalt–tin powders of varying compositions at 600 °C are presented in Figure 7. Inspection of these plots indicates that as the concentration of tin in the bimetallic is increased from 0.5 to 10%, the carbon filaments become progressively

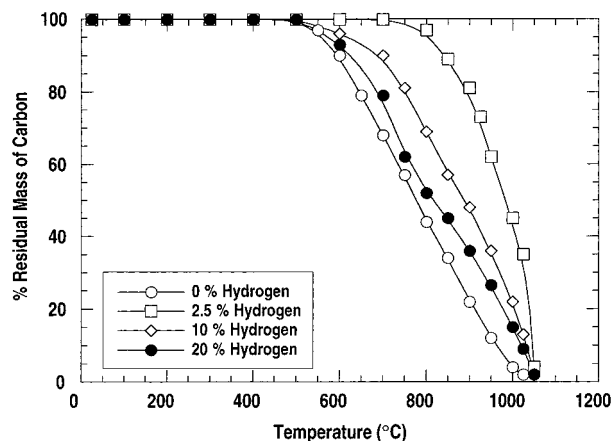


Figure 6. Temperature-programmed oxidation profiles in CO₂ of the carbon filaments produced from the interaction of cobalt–tin (99.5:0.5) with selected ethylene/hydrogen mixtures after a period of 90 min at 600 °C.

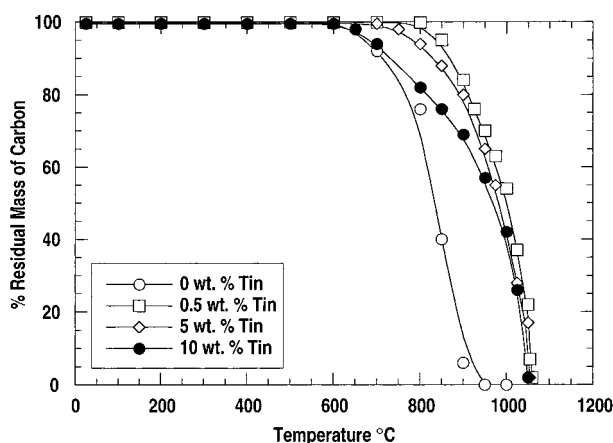


Figure 7. Temperature-programmed oxidation profiles in CO₂ of the carbon filaments produced from the decomposition of C₂H₄/2.5% H₂ at 600 °C over various Co–Sn powders.

TABLE 4: Nitrogen BET Surface Area (m²/g) of Carbon Filaments Produced from the Decomposition of a C₂H₄/2.5% H₂ Mixture at 600 °C as a Function of Catalyst Composition

% tin in cobalt	BET surf. area	% tin in cobalt	BET surf. area
0	80.4	5.0	158.7
0.50	171.0	10.0	133.8
2.0	169.3		

less graphitic in character. For comparison purposes the oxidation curves obtained from carbon filaments produced from the cobalt-catalyzed decomposition of the same reactant mixture at 600 °C have also been included in Figure 7.

The combination of these experiments has enabled us to identify the conditions that are necessary in order to produce carbon filaments possessing the highest graphitic content from the cobalt–tin-catalyzed decomposition of ethylene-containing mixtures. This objective can be achieved when powdered cobalt doped with about 0.5% tin is allowed to react with an ethylene feed containing approximately 2.5% hydrogen.

2.3. Nitrogen Surface Area Measurements. The influence of bimetallic composition on the surface areas of carbon filaments generated from catalyzed decomposition of an C₂H₄/2.5% H₂ mixture at 600 °C is shown in Table 4. The incorporation of tin in cobalt was found to have a significant impact on the surface area of the solid carbon structures, with the maximum value being obtained from material produced from a catalyst formulation containing 0.5% of the additive. On the other hand,

TABLE 5: Nitrogen BET Surface Area (m²/g) of Carbon Filaments as a Function of the Hydrogen Content in the Reactive Mixture for the Co–0.5% Sn-Catalyzed Decomposition of Ethylene at 600 °C

% H ₂ in C ₂ H ₄	BET surf. area	% H ₂ in C ₂ H ₄	BET surf. area
0	168.3	20.0	178.2
2.5	171.0	40.0	194.2
10.0	181.7		

unlike previous studies with other bimetallic systems,^{50,51} the addition of increasing amounts of hydrogen to the reactant stream failed to exert any profound effect on the surface area of the filaments, as evidenced from the data presented in Table 5. This trend is somewhat surprising in view of finding that the solid carbon structures were found to become progressively less graphitic in nature as the ratio of hydrogen to ethylene in the reactant was increased.

Discussion

1. Formation of Carbon Filaments from the Interaction of Cobalt–Tin with Ethylene. The most outstanding feature to emerge from this investigation is the finding that the addition of tin to cobalt results in a significant enhancement in the ability of the ferromagnetic metal to catalyze the growth of carbon filaments during interaction of the bimetallic with ethylene at 600 °C. Moreover, since the optimum carbon deposition activity is achieved with a bimetallic containing as little as 0.5% of tin, this provides some key insights with regard to the factors responsible for the promotional effect. The manner by which a given adatom alters the catalytic activity and selectivity of a host metal has been the subject of a number of comprehensive review articles.^{37,52–54} The arguments have centered around two major effects: (a) the geometric effect, where ensembles of more than one atom of a specific element are less frequently encountered in the surface of a bimetallic than in the pristine metal, and (b) the electronic structure effect, in which the properties of a given metal in the bimetallic surface are different from those of the pure metal.

While one might rationalize the observed increase in carbon filament formation obtained with bimetallic powders containing more than 5% tin according to the notion that incorporation of such a concentration of adatoms into cobalt would bring about a geometric rearrangement of the surface atoms, it is difficult to see how such an argument can account for the impact of only 0.5% of the additive on this reaction. Under such circumstances a more plausible, but speculative, reasoning may lie in the concept that the inclusion of a small amount of tin is capable of inducing electronic perturbations in the surface layers of the cobalt-rich particles.^{55,56}

2. Influence of the Catalyst Composition on the Formation of Gaseous Products. While the selectivity toward the formation of the solid carbon product remains relatively steady over the entire bimetallic composition range, inspection of the data in Table 1 shows that this is not the case with the gaseous products; the selectivity toward methane formation tended to decrease as the fraction of tin in the catalyst was gradually lowered, and that of ethane exhibited a slight upward trend over the same composition range.

In previous studies we have demonstrated that the generation of methane and ethane from the decomposition of ethylene over certain bimetallic systems occurs via two different routes that are controlled by the manner in which the olefin interacts with the catalyst surface.³⁵ It was argued that when the ethylene molecule encounters two identical metal atoms on the surface that are capable of adsorbing the hydrocarbon, the gaseous

reactant will be chemisorbed in an arrangement where the C–C is aligned in a direction “parallel” to the surface. In this configuration the adsorbed species can either interact with dissociatively adsorbed hydrogen and desorb from the surface as ethane or undergo C–C bond rupture, a step that could ultimately lead to solid carbon deposition at other faces of the catalyst particle.

In contrast, if the ethylene molecule collides with two dissimilar metal atoms in the surface, one of which does not chemisorb hydrocarbons, then the likelihood exists that the olefin will adsorb in an “end-on” configuration, in which only one carbon atom is bonded to the metal. In this arrangement there will be a strong tendency for the adsorbed molecule to undergo a rapid transformation to an “ethyldyne” intermediate that will subsequently decompose to produce methane and leave a remaining carbon atom on the surface that will eventually contribute toward the solid deposit.

Since chemisorption of hydrocarbons on tin is not a facile process, surfaces containing a large fraction of this metal will exhibit characteristics that favor adsorption of ethylene in the “end-on” configuration, and as such, there will be a corresponding tendency for methane formation. Furthermore, it is reported that dissociative adsorption of hydrogen does not readily occur on tin-modified metal surfaces,⁵⁷ and as a consequence, one would expect to find a diminution in hydrogenation activity and a lowering in the selectivity toward ethane formation. As the population of tin atoms in the surface is decreased, one would predict that the selectivity for methane production ought to drop, while that for ethane should be enhanced. In this context it is significant to find that the addition of up to 10% hydrogen to the reactant mixture appeared to exert very little influence on the decomposition behavior of ethylene over Co/Sn (99.5:0.5) powders. If, however, the level of hydrogen was raised to a maximum of 40%, the yield of ethane was substantially increased.

3. Catalyst Deactivation Phenomenon. From the data presented in Figure 2 it is apparent that all the bimetallic catalysts exhibit a significant drop in activity during the initial stages of the reaction. The subsequent extent of deactivation is clearly dependent on the fraction of tin that is in the particles; those containing <2% maintained a stable rate of carbon filament growth, while the carbon deposition activity of powders possessing a higher fraction of tin continued to steadily decline. When dealing with bimetallic systems, one is always confronted with the challenge of attempting to predict the composition of the surface at any given instant of time under reaction conditions. While there is a considerable body of information detailing the fact that the surface composition of a given bimetallic is frequently different from that of the bulk, one must also be aware that such a surface may undergo progressive changes in both composition and structural characteristics as the reaction proceeds.

Using the criteria established by Chelikowsky⁵⁸ to determine surface segregation in bimetallic systems in a reducing environment, one can predict that under such conditions tin will tend to segregate to the exposed surfaces of cobalt–tin particles. Although there does not appear to have been any experimental studies conducted on the segregation phenomena in the cobalt–tin system, there are a number of papers detailing the behavior of tin in nickel and iron bimetallics.^{59–61} In all cases the data point to the fact that tin readily segregates to the surfaces of the mixed metal systems. One of the most prominent aspects revealed by such studies is the surface segregation behavior of

tin compared to that exhibited by other elements. It is well established from surface science studies that additives such as sulfur and phosphorus achieve optimum coverages of about half a monolayer,^{62,63} on the other hand, much higher coverages are attained with tin. On the basis of these findings, it is therefore tempting to correlate the observed deactivation of cobalt–tin particles with the propensity of the latter element to selectively diffuse to the metal/gas interface. A consequence of this action would be that catalysts containing a relatively high concentration of tin would be expected to undergo deactivation at a faster rate than those where the metal was a minor constituent. This pattern of behavior was indeed observed experimentally.

4. Effect of Tin on the Structural Characteristics of Carbon Filaments Produced from the Cobalt-Catalyzed Decomposition of Ethylene. A comparison of the appearance of carbon filaments derived from the interaction of cobalt and cobalt–tin with ethylene/hydrogen mixtures revealed that the presence of a small quantity of the additive produced substantial modifications in the crystalline perfection of the deposited material. High-resolution transmission electron microscopy examination showed that the structure of filaments generated from pure cobalt tended to be of relatively short-range order and exhibited oxidation characteristics that were close to that of amorphous carbon.⁶³ In contrast, those generated under the same experimental conditions with cobalt containing only 0.5% tin were highly crystalline in nature and adopted a structure where the graphitic platelets were oriented in a “herringbone” arrangement.

Previous studies²² have established that the atomic arrangement that exists at the carbon-depositing faces of the metal catalyst particle is the key factor in determining the degree of crystalline perfection of the filamentous structure. If the spacing of the metal atoms at this interface is in accordance with that of the carbon atoms in graphite, then one would expect the filamentous structures that are produced to be highly crystalline in nature. On the basis of this criterion, one may conclude that in the present bimetallic system the presence of a small amount of tin is sufficient to bring about a modification in the structural arrangement of cobalt atoms to a condition that favors precipitation of carbon in the form of graphite.

Summary. It has been found that the introduction of a mere 0.5 wt % of tin into cobalt produces a dramatic effect on the catalytic activity of the ferromagnetic metal toward the formation of filamentous carbon when the bimetallic powder is treated in ethylene at 600 °C. It is believed that the enhancement in solid carbon formation is due to electronic perturbations in the surface of the host metal resulting from the presence of a critical number of tin atoms. It should be stressed that definitive evidence to support this postulate has not been obtained. A further increase in the concentration level of tin in the system did not exert any major impact on the amount of carbon generated from the hydrocarbon decomposition reaction; however, it was observed that under these circumstances there was a significant increase in the rate of catalyst deactivation. Finally, characterization studies of the solid carbon product revealed that in the presence of tin the catalytically grown filamentous structures acquired a high degree of crystalline order.

Acknowledgment. The authors would like to thank Dr. Nelly Rodriguez for her help with the high-resolution electron microscopy studies. Financial support for this project was provided by the United States Department of Energy, Basic Energy Sciences, Grant DE-FG02-97ER14741.

References and Notes

- (1) Hofer, L. J. E. In *Catalysis*; Emmett, P. H., Ed.; Reinhold Publishing Co.: New York, 1956; Vol. 4, p 373.
- (2) Palmer, H. B.; Cullis, C. F. In *Chemistry and Physics of Carbon*; Walker, Jr., P. L., Ed.; Marcel Dekker: New York, 1965; Vol. 1, p 265.
- (3) Baker, R. T. K.; Harris, P. S. In *Chemistry and Physics of Carbon*; Walker, Jr., P. L.; Thrower, P. A., Eds.; Marcel Dekker: New York, 1978; Vol. 14, p 83.
- (4) Trimm, D. L. *Catal. Rev.—Sci. Eng.* **1977**, *24*, 67.
- (5) Rodriguez, N. M. *J. Mater. Res.* **1993**, *8*, 3233.
- (6) Ruston, W. R.; Warzee, M. J.; Hennaut, J.; Waty, J. *Carbon* **1969**, *7*, 47.
- (7) Baker, R. T. K.; Barber, M. A.; Harris, P. S.; Feates F. S.; Waite, R. J. *J. Catal.* **1972**, *26*, 51.
- (8) Boehm, H. P. *Carbon* **1973**, *11*, 583.
- (9) Bernardo, C. A.; Lobo, L. S. *J. Catal.* **1975**, *37*, 267.
- (10) Oberlin, A.; Endo, M.; Koyama, T. *J. Cryst. Growth* **1976**, *32*, 335.
- (11) Rostrup-Nielsen J. R.; Trimm, D. L. *J. Catal.* **1977**, *48*, 155.
- (12) Sacco, A. Jr.; Thacker, P.; Chang, T. N.; Chiang, A. T. S. *J. Catal.* **1984**, *85*, 224.
- (13) Yang R. T.; Yang, K. L. *J. Catal.* **1985**, *93*, 182.
- (14) Kock, A. J. H. M.; de Bokx, P. K.; Boellard, E.; Klop, W.; Geus, J. W. *J. Catal.* **1985**, *96*, 468.
- (15) Tibbetts, G. G.; Devour, M. G.; Rodda, E. J. *Carbon* **1987**, *25*, 367.
- (16) Alstrup, I. *J. Catal.* **1988**, *109*, 241.
- (17) Chitrapu, P.; Lund, C. R. F.; Tsamopoulos, J. A. *Carbon* **1992**, *30*, 285.
- (18) McAllister, P.; Wolf, E. E. *J. Catal.* **1992**, *138*, 129.
- (19) Audier, M.; Oberlin, A.; Oberlin, M.; Coulon, M.; Bonnetain, L. *Carbon* **1981**, *19*, 217.
- (20) Yang, R. T.; Chen, J. P. *J. Catal.* **1989**, *115*, 52.
- (21) Kim, M. S.; Rodriguez, N. M.; Baker, R. T. K. *J. Catal.* **1992**, *134*, 253.
- (22) Rodriguez, N. M.; Chambers, A.; Baker, R. T. K. *Langmuir* **1995**, *11*, 3862.
- (23) Rodriguez, N. M.; Kim, M. S.; Downs, W. B.; Baker, R. T. K. In *Carbon Fibers, Filaments and Composites*; Figueiredo, J. L.; Bernardo, C. A.; Baker, R. T. K.; Huttering, K. J., Eds.; NATO ASI Series; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1987; Vol. 177, p 541.
- (24) Downs, W. B.; Baker, R. T. K. *Carbon* **1991**, *29*, 1173.
- (25) Downs, W. B.; Baker, R. T. K. *J. Mater. Res.* **1995**, *10*, 625.
- (26) Fenelonov, V. B.; Avdeeva, L. B.; Zheivot, V. I.; Okkel, L. G.; Goncharova, G.; Pimneva, L. G. *Kinet. Catal.* **1993**, *34*, 483.
- (27) Kim, M. S.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem.* **1994**, *98*, 13108.
- (28) Shaikhutdinov, S. K. *Kinet. Catal.* **1995**, *36*, 549.
- (29) Hoogenraad, M. S.; van Leeuwarden, R. A. G. M. M.; van Breda, G. J. B.; Vriesman, B.; Broersma, A.; van Dillen, A. J.; Geus, J. W. *Stud. Surf. Sci. Catal.* **1995**, 263.
- (30) Likholobov, V. A.; Fenelonov, V. B.; Okkel, L. G.; Goncharova, O. V.; Avdeeva, L. B.; Zaikovskii, V. I.; Kuvshinov, G. G.; Semikolenov, V. A.; Duplyakin, V. K.; Baklanova, O. N.; Plaksin, G. V. *React. Kinet. Catal. Lett.* **1995**, *54*, 381.
- (31) Chambers, A.; Nemes, T.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem. B* **1998**, *102*, 2251.
- (32) Walker, P. L., Jr.; Raksawski, J. F.; Imperial, G. R. *J. Phys. Chem.* **1959**, *63*, 140.
- (33) Nishiyama, Y.; Tamai, Y. *J. Catal.* **1976**, *45*, 1.
- (34) Yang, K. L.; Yang, R. T. *Carbon* **1986**, *24*, 687.
- (35) Kim, M. S.; Rodriguez, N. M.; Baker, R. T. K. *J. Catal.* **1991**, *131*, 60.
- (36) Rodriguez, N. M.; Kim, M. S.; Baker, R. T. K. *J. Catal.* **1993**, *144*, 93.
- (37) Sinfelt, J. H. *Bimetallic Catalysts*; Exxon Monograph; John Wiley and Sons: New York, 1983.
- (38) Krishnakutty, N.; Rodriguez, N. M.; Baker, R. T. K. *J. Catal.* **1996**, *158*, 217.
- (39) Dautzenberg, F. M.; Helle, J. N.; Bileon, P.; Sachtler, W. M. H. *J. Catal.* **1980**, *63*, 119.
- (40) Burch, R.; Garla, L. C. *J. Catal.* **1981**, *71*, 360.
- (41) Lieske, H.; Volter, J. *J. Catal.* **1984**, *90*, 96.
- (42) Liu, T.-C.; Chiu, S.-J. *Ind. Eng. Chem. Res.* **1994**, *33*, 488.
- (43) Masai, M.; Honda, K.; Kubota, A.; Ohnaka, S.; Nishikawa, Y.; Nakahara, K.; Kishi, K.; Ikeda, S. *J. Catal.* **1977**, *50*, 419.
- (44) Masai, M.; Honda, K.; Ohnaka, S.; Ando, T.; Maeda, Y.; Kishi, K.; Ikeda, S. *Nippon Kagaku Kaishi* **1979**, 1153.
- (45) Baker, R. T. K.; Terry, S.; Harris, P. S. *Nature* **1975**, *253*, 37.
- (46) Best, R. J.; Russell, W. W. *J. Am. Chem. Soc.* **1954**, *76*, 838.
- (47) Sinfelt, J. H.; Carter, J. L.; Yates, D. J. C. *J. Catal.* **1972**, *24*, 283.
- (48) Baker, R. T. K.; Chludzinski, J. J. *J. Catal.* **1980**, *64*, 464.

- (49) Hansen, M. *Constitution of Binary Alloys*; McGraw-Hill Book Company: New York, 1958; p 506.
- (50) Chambers, A.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem.* **1996**, *100*, 4229.
- (51) Krishnankutty, N.; Park, C.; Rodriguez, N. M.; Baker, R. T. K. *Catal. Today* **1997**, *37*, 295.
- (52) Sachtler, W. M. H. *Faraday Discuss. Chem. Soc.* **1981**, *72*, 7.
- (53) Rodriguez, J. A.; Goodman, D. W. *J. Phys. Chem.* **1991**, *95*, 4196.
- (54) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.
- (55) Solymosi, F. *Catal. Rev.—Sci. Eng.* **1967**, *1*, 233.
- (56) Kuhn, W. K.; Campbell, R. A.; Goodman, D. W. In *The Chemical Physics of Solid Surfaces*; Elsevier: Amsterdam, 1993; p 157.
- (57) Masai, M.; Noma, K.; Miyamoto, H.; Kaibara, H.; Tsuruya, S. *Appl. Catal.* **1982**, *4*, 83.
- (58) Chelikowsky, J. R. *Surf. Sci. Lett.* **1984**, *139*, 1197.
- (59) Xu, C.; Koel, B. E. *Surf. Sci.* **1995**, *327*, 38.
- (60) Seah, M. P.; Hondros, E. D. *Proc. R. Soc. London* **1973**, *A335*, 191.
- (61) Zhou, Y. X.; Hsiao, R.; McMahon, C. J., Jr.; Plummer, E. W. *Surf. Sci.* **1987**, *179*, 209.
- (62) Berthier, Y.; Oudar, J. *C. R. Acad. Sci.* **1961**, 269, 1149.
- (63) Grabke, H. J.; Petersen, E. M.; Srinivasan, S. R. *Surf. Sci.* **1977**, *67*, 501.