

The Role of Interfacial Phenomena in the Structure of Carbon Deposits

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We have used a variety of experimental techniques, including controlled atmosphere electron microscopy, thermogravimetry, and electrical conductivity measurements to examine the structures of carbon filaments produced from the decomposition of hydrocarbons over copper-nickel and nickel catalysts. The structure of the carbon filaments formed at temperatures over the range 450 to 700°C were found to be extremely sensitive to the chemical nature of the catalyst particles. Alloy particles, particularly those rich in nickel, were found to produce much more ordered filament structures than those grown on nickel particles. This behavior is rationalized in terms of the differences in interfacial energy of the respective catalyst surfaces in contact with the carbon surface. It is speculated that metals that readily wet graphite will produce highly ordered carbon filament structures. There appears to be an upper temperature limit for filament growth from copper-nickel alloys, which is governed by the tendency of copper to preferentially segregate to the catalyst surface. Activity can be restored by subsequent reduction to the active temperature regime. © 1992 Academic Press, Inc.

INTRODUCTION

In a previous paper dealing with carbon deposition from the interaction of copper-nickel alloys with various hydrocarbons, the emphasis was placed on the events occurring at the catalyst-gas interface (1). It was shown that the distribution of the gas-phase products arising from the reaction was directly related to the structural conformation of the most favored hydrocarbon arrangement adsorbed at the alloy surface. In addition, it was found that there was an intimate link in the role of the catalyst in both carbon deposition and hydrogasification of carbon reactions. In the present study we have focused attention on the characterization of the structure of carbon filaments and how such features are controlled by the physical and chemical nature of the catalyst particle.

Other workers (2, 3) have studied the morphology and crystalline order of carbon deposits produced from the disproportionation of carbon monoxide over catalysts containing iron, nickel, and cobalt at tempera-

tures ranging from 400 to 750°C. They concluded that the structure of carbon filaments produced in these reactions was a function of both the temperature and catalyst composition. Unfortunately, no rationale was presented to account for their findings. Yang and Chen (4) have suggested that the crystallographic orientation of the catalyst surface in contact with the gas phase can be significantly different than that which exists at the catalyst/carbon filament interface. This condition was demonstrated by the use of postreaction-selected area electron diffraction measurements. Using this approach these workers were able to show the existence of (111), (311), and (220) nickel faces at the filament/metal interface. In addition to SAD data on the carbon/metal interface, extended Hückel molecular orbital (EHMO) calculations were made to provide information on (a) the epitaxial relationship between graphite and the various crystallographic faces of nickel, and (b) the relative catalytic activities of different nickel faces for decomposition of carbon-containing gases. These calculations confirmed that the most fa-

vored face for graphite precipitation was nickel (111). Based on this work, it is clear that the orientation of the catalyst particle is a key variable in its ability to decompose a hydrocarbon molecule and also to influence the structure of the carbon deposit.

It is known that the filaments produced from the catalytic decomposition of acetylene over nickel, cobalt, or iron usually have a structure containing both graphite and a more disordered carbon (5-7). The structural features found in the filaments appear to depend on a number of factors including the nature of the reactant gas phase, the particular catalyst employed, and the temperature of the reaction (8). Baird and co-workers (9, 10) reported that the morphology of carbon filaments was related to the rate of carbon deposition, graphitic structures being produced from the relatively slow reactions found from catalytic decomposition of alkanes, and less ordered structures being produced from the faster deposition rates obtained from catalyzed decomposition of unsaturated hydrocarbons. Other workers have suggested that the morphological characteristics of the filaments are dependent on the chemical composition of the catalyst (11).

The manner by which additives to the catalyst influence the growth characteristics of carbon filaments is an area that is tending to receive increased interest. Bernardo and co-workers (11, 12) have used a variety of techniques to study the formation of carbon filaments from the copper-nickel-catalyzed decomposition of methane. In addition to following the kinetics of the carbon deposition processes these workers examined the morphological characteristics of the filaments as a function of the catalyst composition. Whisker-like growths were produced from catalyst particles containing less than 80 at% copper. At higher copper concentrations, structures with at least six carbon filaments originating from a single catalyst particle were created. Similar multidirectional carbon deposits were also observed by Rostrup-Nielsen (13) in filaments produced on nickel catalysts containing a criti-

cal sulfur coverage. The symmetrical arrangement of these structures strongly suggests that the growth occurs from specific crystallographic planes of the catalyst particle. Although bidirectional growth has been observed for several binary catalyst particles, e.g., Fe-Sn (14) and Fe-Ni (15), multidirectional growth from a single catalyst particle is a rare phenomenon.

In some cases the strength of the interaction between the metal particle and the supporting media can be sufficiently strong so as to prevent catalyst particles from being lifted from the support by the whisker-like mode of filament growth. As a consequence, the only available pathway for removal of excess dissolved carbon from the particles is via an extrusion mode (16).

Recent technological advances have created the need for new materials with unique properties and in this context catalysis offers the opportunity of tailor-making some novel carbon structures. The duplex conformation of carbon filaments gives rise to a material that combines high strength, high surface area, and high electrical conductivity (17). This unusual combination of properties makes catalytically grown carbon filaments a very attractive material for both reinforcement and electrochemical applications.

In the present work, we have used a variety of techniques including controlled atmosphere electron microscopy to study the development of various carbon filament growth forms resulting from the interaction of hydrocarbons with copper-nickel catalysts. In addition, it has been possible to determine structural features of the filaments from controlled oxidation studies performed by thermogravimetric procedures and to reach independent conclusion on these properties from electrical conductivity measurements.

EXPERIMENTAL

Techniques

(a) *Controlled atmosphere electron microscopy (CAEM)*. Transitory features of systems undergoing change often remain

unobserved during conventional postreaction transmission electron microscopy examination. This restriction can be overcome by the use of controlled atmosphere electron microscopy (18). The equipment consists of a JEM 120 electron microscope fitted with a gas reaction cell, which enables the specimen to be observed continuously by electron transmission while exposed to a gas environment and heated to temperatures up to 1300°C. The changes in appearance of the specimen are recorded on video tape for subsequent detailed kinetic analysis of events of interest.

(b) *Thermogravimetric analysis.* Macroscale kinetics studies of both the growth and gasification of the filaments were performed with a Cahn 2000 microbalance reactor. The furnace was attached to a controller and was capable of operating at temperatures up to 1100°C. A small amount of alloy catalyst (~5 mg) was placed in a platinum pan hanging in the middle of the heated zone of the reactor where a constant temperature profile was maintained along its axis. Initially the reactor system was evacuated to remove residual air and then filled with an inert gas such as argon or helium. The reactor was then brought to the operating temperature in a mixture of hydrogen and inert gas and was held at that temperature until the catalyst was completely reduced, usually 1 to 2 h. Carbon deposits were produced from a selected mixture of ethylene, hydrogen, and inert gas.

Three types of gasification experiments were performed, one in which samples of carbon filaments together with the associated catalyst particles were reacted in the oxidant. These data were compared with those obtained for spectroscopic grade graphite impregnated with the same amount of the respective catalyst. In a final series of experiments the catalyst was removed from the filaments prior to the gasification step, by treatment in 1 N HCl for 3 days. The efficiency of this procedure was checked by EDX examination of selected samples. In all cases the specimen were initially heated in helium to remove adsorbed moisture from

the filaments and then carbon dioxide was introduced at a constant flow rate. The temperature of the reactor was programmed up to 1000°C at a constant heating rate of 5°C/min. The weight loss was recorded as a function of temperature and time.

(c) *Electrical conductivity measurements of carbon filaments.* The relative electrical conductivities of carbon filaments produced from the interaction of various copper-nickel alloys with ethylene were determined using a device designed for the measurement of electrical properties of powdered materials. The apparatus consisted of a brass hollow cylinder lined with a nonconducting material containing two metallic pistons, which formed a pressure chamber and were connected to a milliohmmeter. Electrical resistivities across the carbon disks were taken while the samples were kept under a constant pressure of 9000 psi and careful measurement of the thickness of the samples was made at the same time. A more detailed description of the operational procedures are described elsewhere (19).

(d) *Bulk production of carbon filaments.* In order to conduct a detailed investigation of the properties of carbon filaments and to determine the activity of a given catalyst composition as a function of temperature, a larger amount of the material was required and was produced in a horizontal flow reactor. In this procedure, 50 mg of various copper-nickel alloys (expressed as wt%) and nickel and copper powders were reacted in an ethylene-hydrogen (4 : 1) mixture at temperatures over the range 400 to 900°C for 1.5 h. The weight of the deposit was determined and samples used for the thermogravimetric studies. Finally, their morphological characteristics were examined by scanning and high-resolution transmission electron microscopy.

MATERIALS

In the CAEM experiments two procedures were used to introduce copper-nickel onto transmission specimens of various supports, including graphite and silica. In the first procedure equal amounts of copper and

nickel were sequentially deposited onto the specimens by evaporation of the respective spectrographically pure wires from a tungsten filament at 10^{-6} Torr. In the second preparation method, both components were introduced simultaneously as an atomized spray from an aqueous solution of the respective metal nitrates mixed in desired amounts. Before reaction in the hydrocarbon all samples were reduced at 400°C for 3.0 h to ensure that alloy particles were formed.

For the thermogravimetric and bulk preparation studies, samples consisted of copper–nickel alloy powders in which the metals were present in various ratios and prepared according to the method given by Best and Russell (20). The composition of the alloy powders was determined by energy dispersive X-ray spectroscopy (EDS). Surface area measurements performed by BET nitrogen adsorption at -196°C showed that all powders were about $1\text{ m}^2 \cdot \text{g}^{-1}$.

The gases used in this work, hydrogen (99.999%), acetylene (99.6%), ethylene (99.99%), helium (99.99%), and carbon dioxide (99.99%), were obtained from Alphagaz Co. and were used without further purification. Reagent grade nickel nitrate [$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$] and reagent grade cupric nitrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$] were obtained from Fisher Scientific for the catalyst preparation.

RESULTS

(a) *Controlled Atmosphere Electron Microscopy*

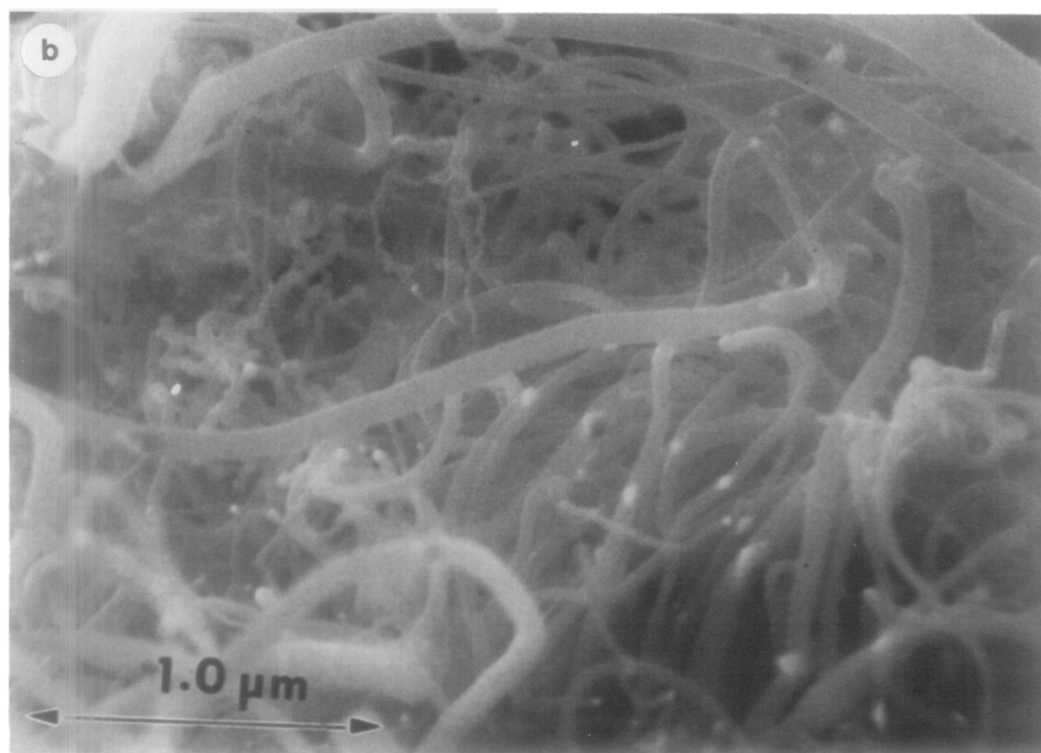
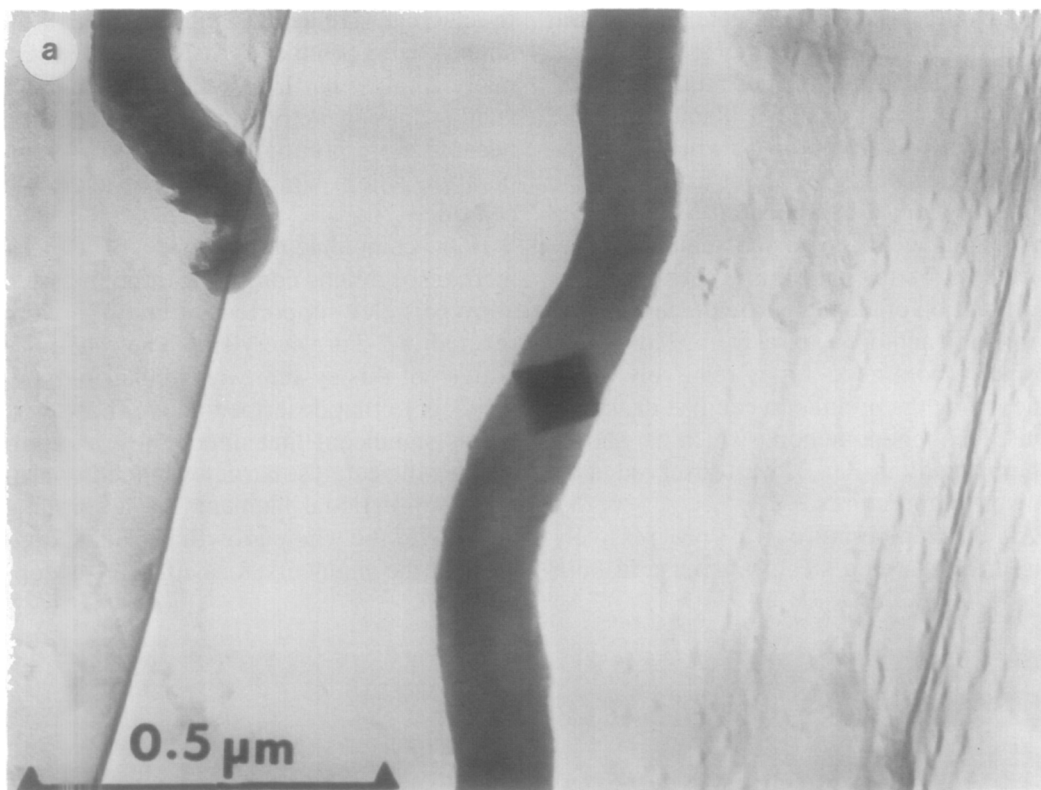
Carbon filaments were grown in the CAEM facility from the interaction of Cu–Ni particles with acetylene. The majority of experiments were conducted on particles containing the metals mixed in a 1:1 ratio; however, some studies were performed using pure copper and copper-rich

and nickel-rich catalyst particles to ascertain the influence of catalyst composition on the filament structures.

When copper–nickel particles containing 50% or more nickel, supported on either graphite or silica, were reacted in 2-Torr acetylene, carbon filaments were observed to form at 285°C . It was significant that prior to growth of filaments the alloy particles underwent a structural transformation from globular to a thin flat faceted morphology. Almost immediately following this transition carbon filaments started to grow in a bidirectional conformation with the catalyst particles being located within the body of the structure. Inspection of the catalyst particles showed that at this stage of the reaction they were diamond-shaped and the width of the filaments was controlled by that of the catalyst particles responsible for producing them, typically in the range 25 to 100 nm. These features are clearly evident in the electron micrographs, Figs. 1a and 1b. Bonnetain *et al.* have used dark-field imaging techniques to demonstrate that the catalyst particles in bidirectional filaments are polygonal in form with filaments growing around each corner and large flat facets remaining free of carbon and available for hydrocarbon adsorption (21).

The dynamics of the growth process can be appreciated from the sequence of stills taken from the TV monitor, Figs. 2a–2c, where both the location of the catalyst particle and increases in filament length as a function of reaction time are apparent. From such observations it was evident that two filaments grew from opposite faces of the catalyst particle at identical rates. Furthermore, during the major part of the growth process, the filaments were relatively smooth and tended to form into large loops. Over a period of time it became clear that many of the filaments were slowly decreas-

FIG. 1. Transmission and scanning electron micrographs of carbon filaments produced from the interaction of copper–nickel (3:7) with ethylene–hydrogen (4:1) at 600°C .



ing in width, as a result of catalyst material being dissipated within the structure and this behavior frequently resulted in the creation of secondary smaller filaments on the parent growths. Eventually, when the particles reached a size of about a third of the original value, they appeared to undergo a further change in shape and simultaneously started to rotate on an axis perpendicular to the direction of filament growth, causing the filament to acquire a spiral form. This action normally continued for a relatively short time, being the prelude to catalyst deactivation. This phenomenon, which is shown schematically in Fig. 3, was observed at all growth temperatures.

As the temperature was progressively raised there was a steady increase in both

the average size and the number of new filaments being produced. At 700°C, however, many catalyst particles tended to exhibit a sudden loss of activity and this condition became more pronounced at 740°C, a temperature where almost all filament growth ceased.

In a complementary series of experiments, specimens consisting of copper-rich alloy particles supported on graphite were reacted in 2-Torr acetylene. The reactivity pattern of this system was similar in many respects to that described above; however, it was significant that under these circumstances the catalyst particles tended to produce bidirectional filaments by a spiraling mode over the whole growth period. Examples of the filaments formed from a cop-

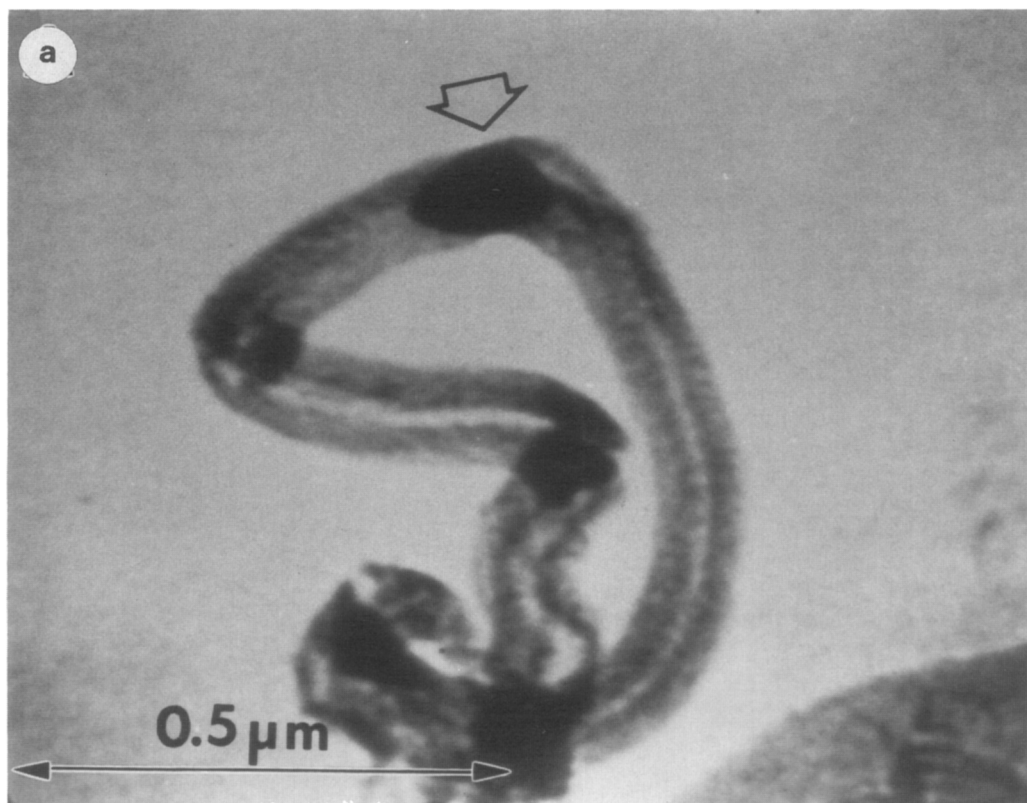


FIG. 2. Sequence showing the progressive increase in length of a carbon filament being formed by the bidirectional growth mode. These pictures are taken from the copper-nickel (1:1)-catalyzed decomposition of 2.0-Torr acetylene. The location of the catalyst particle is indicated. Time between each frame is 15 s.

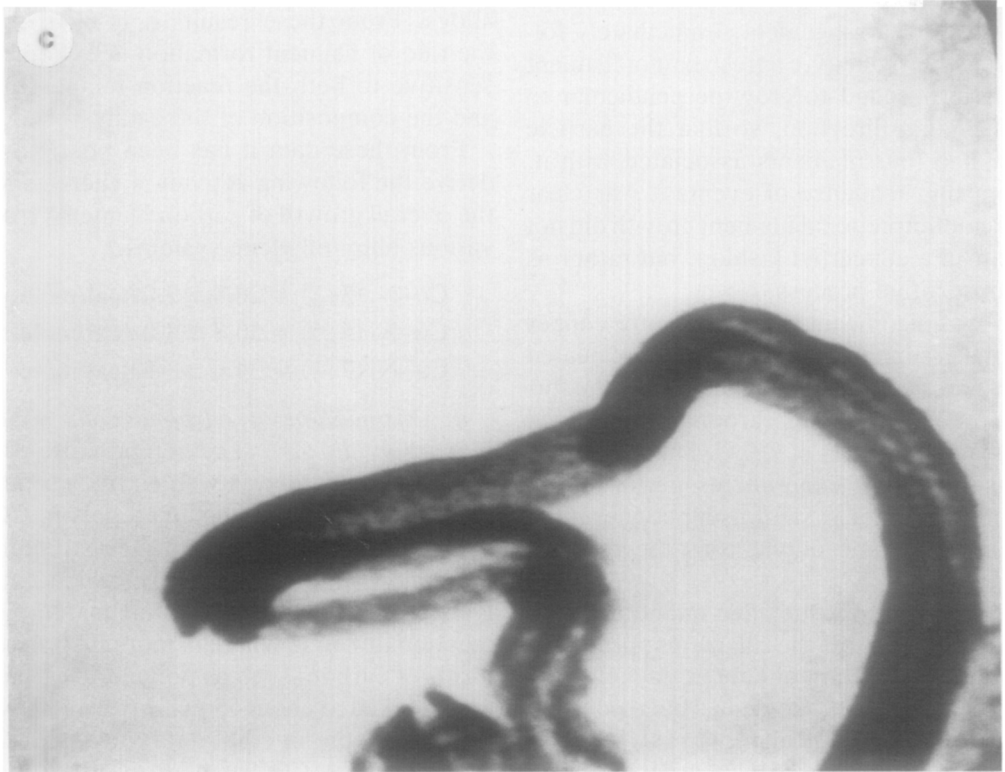


FIG. 2—Continued

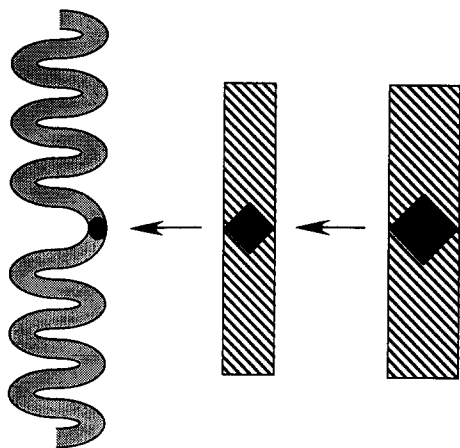


FIG. 3. Schematic representation of the change in morphology of filaments produced from copper–nickel (1 : 1)-catalyzed decomposition of acetylene at 500°C.

per–nickel (7 : 3) catalyst are presented in Figs. 4a and 4b. In some instances an active particle was observed to come to a temporary halt during the act of producing a pair of filament limbs and appeared to undergo structural rearrangement. Immediately following this manoeuvre a fresh pair of filament limbs proceeded to grow perpendicular to the original direction, so that the particle now had four filaments associated with it. From this sequence of events it was clear that multidirectional filament growth did not occur in a concerted fashion, but rather as a consecutive process.

It was significant that when pure copper particles supported on graphite were heated in 2-Torr acetylene, no evidence for the formation of filamentous carbon was observed up to temperatures of 950°C. This result was consistent with experiments performed in the flow reactor system using copper powder samples and ethylene as the reactant gas.

By performing a detailed quantitative kinetic analysis of the filaments produced from the interaction of copper–nickel (1 : 1) particles with acetylene it has been possible to determine the rate of growth as a function of temperature (Fig. 5). In order to overcome variations in rate due to differences in

catalyst particle size, the data presented in this plot have been normalized to a common size of 50 nm. From the slope of the line a value of 31.2 ± 3 kcal/mole has been evaluated for the apparent activation energy for the growth of carbon filaments from the copper–nickel-catalyzed decomposition of acetylene. By analogy with previous carbon filament growth studies (5) it is probable that this is the activation energy for the diffusion of carbon through copper–nickel (1 : 1) particles.

(b) Thermogravimetric Analysis

i. Filament growth. Detailed bulk kinetic studies of the formation of carbon filaments from the interaction of various copper–nickel alloys with an ethylene–hydrogen (1 : 3) mixture were carried out at temperatures over the range 350 to 800°C in a vacuum microbalance. Figure 6 shows the effect of temperature on the rate of filament formation for three different copper–nickel alloys. From these results it is clear that the rate of filament formation is extremely sensitive to both the reaction temperature and the composition of the catalyst.

From these data it has been possible to derive the following activation energies for the overall growth of carbon filaments from various alloy/ethylene systems.

$$\text{Cu-Ni (3 : 7)} = 20.8 \pm 2.0 \text{ kcal/mole}$$

$$\text{Cu-Ni (5 : 5)} = 30.8 \pm 3.0 \text{ kcal/mole}$$

$$\text{Cu-Ni (7 : 3)} = 34.6 \pm 3.5 \text{ kcal/mole}$$

ii. Gasification of carbonaceous solids in carbon dioxide. The temperature-programmed oxidation as well as the gasification rate of carbonaceous materials in CO_2 can be used as a measure of their structural perfection. In the absence of added catalysts, graphite is found to start undergoing reaction at 850°C whereas more disordered forms of carbon, such as polymeric carbon, are attacked at about 550°C. Figure 7 shows a comparison of the data obtained for gasification in CO_2 of a series of carbon filaments produced from various cop-

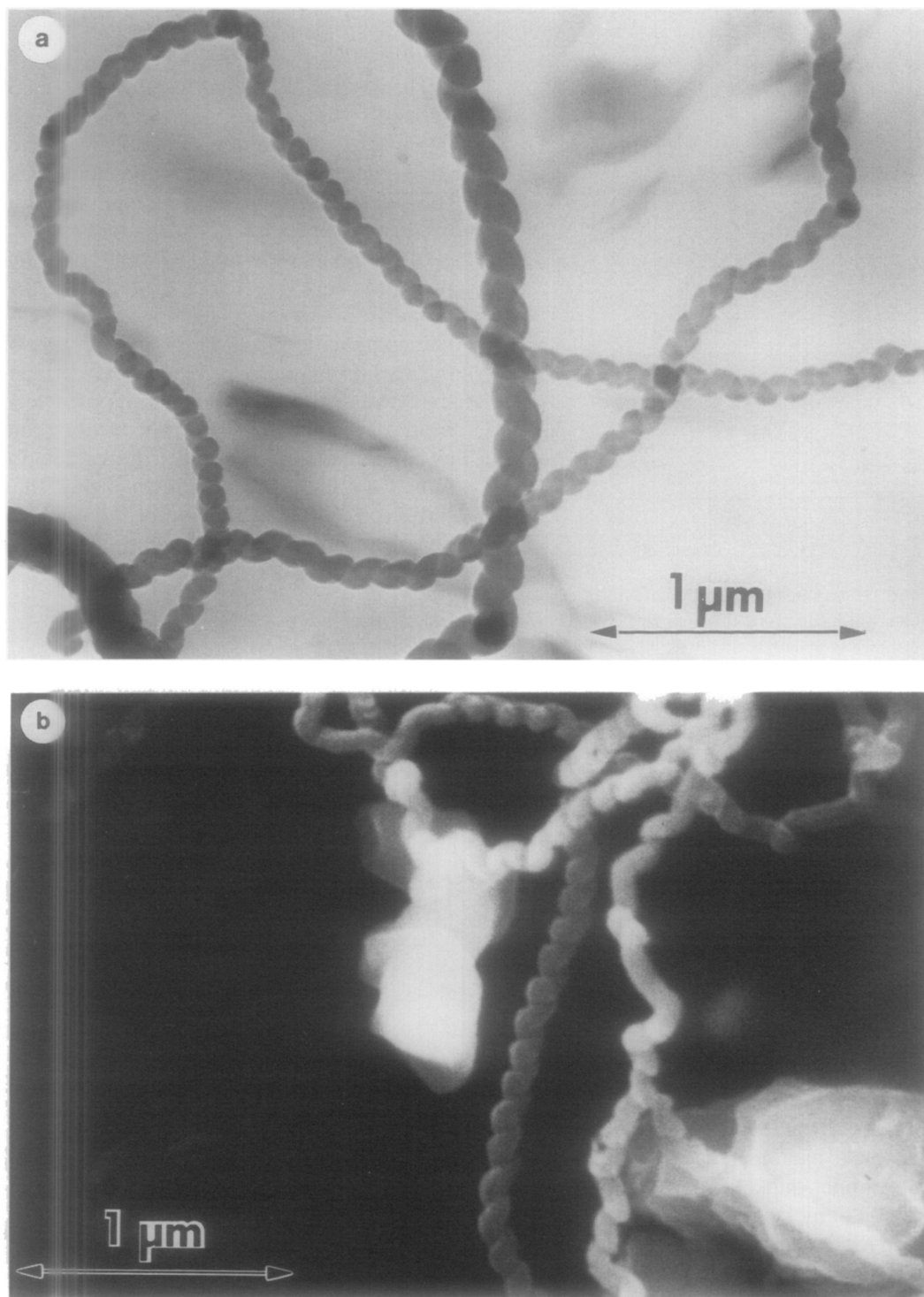


FIG. 4. Transmission and scanning electron micrographs of carbon filaments produced from the interaction of copper-nickel (7 : 3) with ethylene/hydrogen (4 : 1) at 600°C.

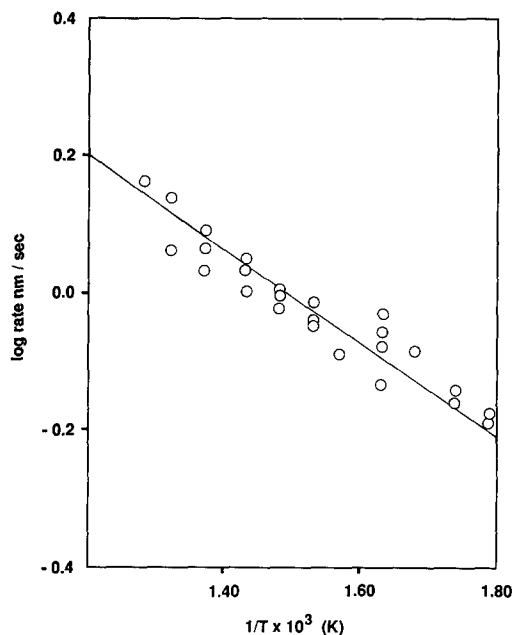


FIG. 5. Arrhenius plot of the growth of carbon filaments produced from the copper-nickel (1:1)-catalyzed decomposition of acetylene obtained from CAEM studies.

per-nickel compositions with that observed for graphite specimens loaded with the same amount of the corresponding catalysts. Inspection of these curves indicates that filaments produced from nickel rich alloy catalysts exhibit gasification characteristics similar to those of graphite. When a similar procedure was repeated for filaments from which the catalyst particles had been removed before treatment in CO_2 , it can be seen from Fig. 8 that both the onset temperature and the reactivity of filaments are extremely sensitive to the nature of the catalyst. Based on these experiments it is possible to establish that filaments produced from copper-nickel alloys containing a large fraction of nickel tend to exhibit gasification behavior that is very similar to that of graphite. In contrast, filaments produced from a pure nickel catalyst and from alloys rich in copper appear to possess a more disordered structure.

(c) Electrical Conductivity of Carbon Filaments

The electrical conductivity of a series of filament batches was measured and compared with the values obtained for other well-characterized carbonaceous materials. In all cases the samples were maintained at a constant pressure of 9000 psi while the measurements were taken. From the results presented in Table 1 it is evident that this property is extremely sensitive to the catalyst composition used in the preparation of the carbon filaments. The highest conductivity was exhibited by filaments produced from a copper : nickel (20 : 80) catalyst and as can be seen from Table 1 the values obtained for filaments are much higher than those for active carbon and of the same order as that determined for graphite under these conditions.

(d) Flow Reactor Studies

The influence of reaction temperature on the formation of carbon filaments from the

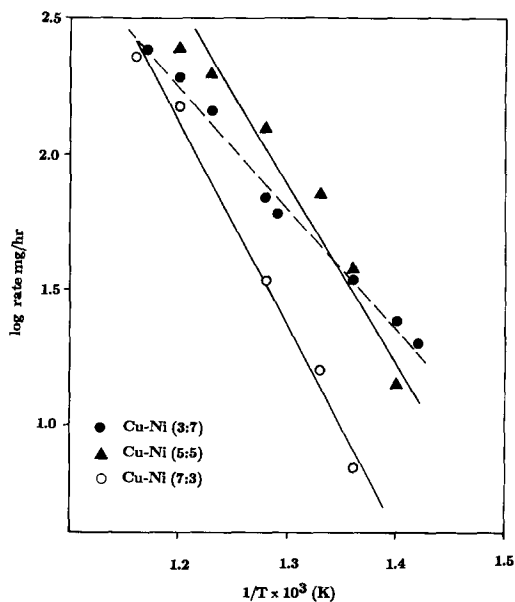


FIG. 6. Arrhenius plot of bulk kinetic data of the deposition of carbon from the decomposition of ethylene by various copper-nickel alloy catalysts.

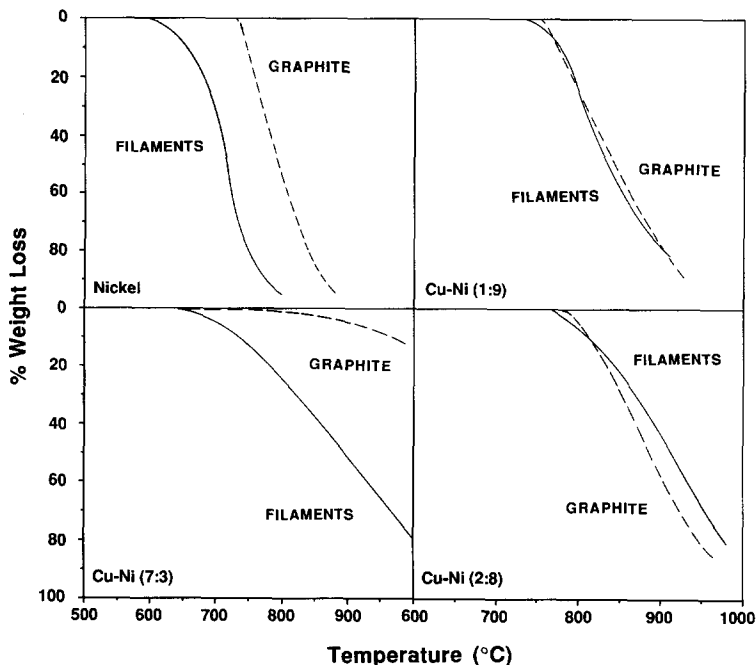


FIG. 7. Comparison of gasification characteristics in CO_2 of filaments produced from various catalyst compositions with those of graphite loaded with similar amount of the respective catalysts.

Cu-Ni (3 : 7)-catalyzed decomposition of an ethylene-hydrogen (4 : 1) mixture is presented in Fig. 9. The weight gains resulting from carbon deposition on 50 mg of catalyst powder after 1.5-h reaction time were measured as a function of temperature. Inspection of these data shows that the maximum yield of filaments is obtained at temperatures between 600 and 700°C and that at temperatures greater than 740°C the catalyst undergoes rapid deactivation. In a further series of experiments the upper temperature was raised to 900°C and as expected no evidence for carbon filament growth was observed. If, however, the specimen was held in the reactor and the temperature reduced to 700°C, then catalytic activity was restored. Moreover, the rate of reaction measured under these circumstances appeared to be identical to that obtained when a fresh sample was reacted at 700°C. The reversible nature of this unusual deactivation phenomenon was demonstrated in a very definitive

manner by multiple cycling between 900 and 700°C, the data points obtained after this procedure being shown in Fig. 9 as open circles.

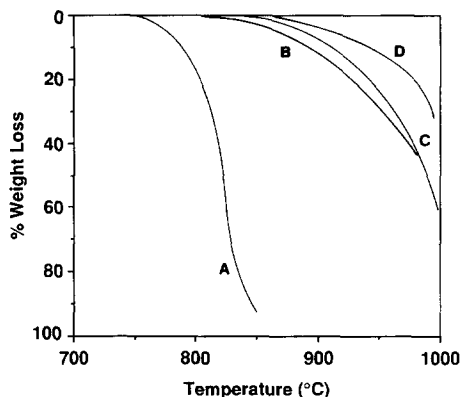


FIG. 8. Gasification characteristics in CO_2 of filaments produced from various copper-nickel compositions, where the catalyst has been removed prior to gasification. Filaments produced from A, Ni; B, Cu-Ni (7 : 3); C, Cu-Ni (1 : 9); D, Cu-Ni (2 : 8).

TABLE 1

Comparison of the Relative Electrical Conductivities of Carbon Filaments from Copper-Nickel and Nickel with Other Forms of Carbon

Alloy composition Cu-Ni	Relative electrical conductivity $\text{ohm}^{-1} \cdot \text{cm}^{-1}$
0:100	0.226
10:90	0.274
20:80	0.306
70:30	0.230
Graphite	0.568
Active carbon	0.307×10^{-3}

DISCUSSION

Chemical Structure of Carbon Filaments

It is apparent that controlled gasification of carbonaceous solids in a mild oxidizing agent such as carbon dioxide can reveal a great deal of information relating to the structure of the material. The presence of catalytic impurity particles, however, can have a dramatic effect on the gasification behavior of a carbonaceous solid and as a consequence one must exercise extreme caution for this type of experiment to pro-

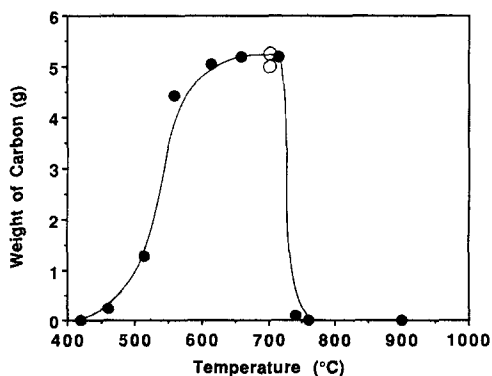


FIG. 9. Influence of temperature on the weight of solid carbon produced from the decomposition of ethylene over copper-nickel (3:7), after 1.5 h reaction. Points shown as open circles represent experiments where the catalyst was initially heated to 900°C and subsequently reacted at 700°C.

vide meaningful data on the characteristics of the carbon structure. It is imperative for one to either compare the behavior of the "contaminated" specimen with a standard material impregnated with the same amount of the particular impurity or ensure that all such inclusions are removed before performing the gasification step. An example of this condition can be seen from the present study where it was found that nickel is an extremely active catalyst for the gasification of graphite in carbon dioxide and even more active for the gasification of carbon filaments. The finding that filaments produced from a reaction using nickel as catalyst react at a much lower temperature than graphite indicates that in this case the filaments possess a relatively high fraction of disordered carbon. In contrast, filaments produced from copper-nickel alloys containing a high fraction of nickel exhibit gasification characteristics, which are similar to that found when graphite is treated with the same catalyst composition. As the amount of the copper component in the catalyst particle is increased, there is a corresponding decrease in the oxidation resistance of the filaments. Furthermore, prolonged treatment in acid media to remove the associated catalyst particles does not appear to have had any deleterious effect on the carbon filaments since the gasification characteristics follow the same pattern as that displayed in experiments where the metal remained in contact with the carbonaceous solids.

It is also evident from the electrical conductivity measurements presented in Table 1 that this property is also dependent on the nature of the catalyst used for the preparation of the filaments. Walker *et al.* (22) measured the electrical conductivity of carbon filaments produced from the iron-catalyzed decomposition of carbon monoxide-hydrogen mixtures. Although it is difficult to compare their results with the present values since the filament preparation conditions were completely different, they did report that the conductivity of their filaments was

considerably higher than that of most common forms of amorphous carbon. It is significant to find that the filaments produced from the copper–nickel (2:8) catalyst that exhibits the highest electrical conductivity also contain the highest fraction of graphite as determined from the gasification experiments. This is an extremely important finding since it enables one to design the structural features of carbon filaments for a particular application and also to understand some of the factors controlling the types of carbon deposit that accumulate on metal catalyst surfaces. We are able to control the ratio of graphitic to amorphous carbon components in carbon filaments by judicious choice of the specific catalyst composition. As a consequence, it follows that one might also control the mechanical or electrical properties of the material.

Dependence of Filament Structure on Metal/Carbon Interfacial Energy

In order to understand the ability of certain copper–nickel alloy catalysts to promote the formation of highly graphitic filaments, it is necessary to focus on the events that occur at the metal/carbon interface during the growth process. It is well known that dissolved carbon will precipitate in the form of graphite at certain faces of metals, which are favorable toward an epitaxial fit between the two components. Yang and Chen (4) have shown that for the case of carbon filaments produced from the interaction of hydrocarbons with nickel it is the (111) face of the metal that favors the precipitation of graphite.

In this context it is an enlightening exercise to consider a reaction in which the reverse process is a key step, i.e., the dissolution of carbon atoms from a graphite substrate by the action of a metal catalyst during hydrogasification. It has been established that one of the requirements for a metal particle to react with graphite is that it must first undergo a wetting action with the reactive edge carbon atoms (23). This

condition is achieved when the interfacial energy of the support exceeds the cohesive forces existing within the metal and causes the particle to acquire a hemispherical (cap-shaped) geometry. Direct observation of this phenomenon has revealed that copper–nickel alloy particles, rich in nickel, exhibit this behavior much more readily than either of the single components at temperatures of about 425°C (24). Indeed, these characteristics were not exhibited by similar sized nickel particles until the temperature was increased to 850°C and the activity of such particles was curtailed at about 1000°C as a result of graphite precipitation at the metal–gas interface (25).

In order to test this wetting hypothesis we have attempted to grow carbon filaments from the nickel-catalyzed decomposition of ethylene/hydrogen mixtures at temperatures between 800 and 900°C. Unfortunately, under these conditions the hydrocarbon undergoes uncatalyzed thermal decomposition leading to polymer formation, and this reaction interferes with the catalytic production of filaments. As a consequence it was not possible to compare the properties with filaments produced at lower temperatures. It should, however, be appreciated that the ability of nickel to precipitate graphite from dissolved carbon at 1000°C had been established earlier from studies designed to follow the diffusion of carbon produced from the decomposition of methane, through the walls of a thin nickel tube (26).

The reversible gasification/deposition behavior postulated for the case of nickel was demonstrated in a very definitive manner by Baker and Sherwood (27) who used *in situ* electron microscopy to follow the behavior of iron particles supported on graphite when heated in an ethane/steam environment. They reported that at temperatures of about 975°C iron particles proceeded to attack the graphite from edges by creating channels across the basal plane and argued that under these conditions the prevailing gasification reaction was hydrogenation of graphite due

to the buildup of hydrogen in the system. As the temperature was progressively raised to 1025°C small iron particles started to move in a reverse direction and precipitate carbon within the tracks they had created at lower temperatures. Furthermore, it was difficult to discern where the tracks of the original channels had been suggesting that the deposited carbon had a structure similar to that of the substrate, i.e., it was graphitic. Subsequent cycling between 925 and 1025°C showed that the rates of gasification and deposition steps were completely reproducible.

It would appear that metals that are capable of dissolving carbon atoms from graphite in the presence of hydrogen are also likely to precipitate the dissolved carbon atoms in the form of graphite when the system is heated in a hydrocarbon environment. Based on these arguments it is not unreasonable to expect that carbon filaments produced from nickel-rich copper-nickel alloys at temperatures of around 600°C will be highly graphitic in nature, whereas those produced on nickel or copper-rich alloy particles at these temperatures will be more disordered.

Filament Growth Characteristics

The spontaneous wetting action of copper-nickel particles on graphite may also account for the unusual filament growth characteristics observed from these particles. The diamond-shaped catalyst particles have been shown by dark-field electron microscopy techniques to consist of symmetrical twinned crystals (28, 29), which will give rise to two identical carbon diffusion pathways within the particle leading to the formation of filaments via a bidirectional growth mode. The observed progressive decrease in width of such filaments after a certain period of time is probably associated with loss of material from the catalyst particle caused by dispersion along the filament itself. If this process results in the removal of a higher fraction of nickel than copper

then over a period of time the residual catalyst particle will tend to become enriched in copper causing the filament to acquire the spiral form characteristic of high copper alloys, and ultimately, when a critical amount of nickel has been dissipated, the particle will lose its catalytic activity.

Catalyst Deactivation

The loss of catalytic activity exhibited by copper-nickel (3:7) particles when heated in ethylene/hydrogen (4:1) to temperatures in excess of 740°C does not follow conventional deactivation behavior associated with metal catalysts, such as formation of a graphitic overlayer, adsorption of a poison, or loss of active metal surface area due to sintering. On the contrary, the finding that catalytic activity could be recovered when specimens were cooled from high temperature back to 700°C points to the existence of some transitory change in the chemical nature of the catalyst surface at high temperatures. It is probable that as the temperature is increased copper tends to segregate at the metal-gas interface and since this component was found to be incapable of decomposing the hydrocarbon, the particle is no longer able to catalyze the growth of filamentous carbon. On cooling to a lower temperature regime, the alloy composition at the surface is once again restored to about its original value and the reaction proceeds in a relatively smooth fashion. A review of the pertinent literature shows that there is abundant experimental and theoretical evidence to support the claim that copper preferentially segregates to the alloy surface (30-35). This phenomenon adds another aspect to the list of causes that can account for catalyst deactivation. This aspect is currently being further investigated.

CONCLUSIONS

1. We have found that the structural characteristics of carbon filaments are a strong function of the nature of the catalyst parti-

cles from which they are produced. Nickel-rich alloy particles tend to form smooth filaments via a bidirectional mode, whereas those obtained from copper-rich particles grow in a spiral conformation. A combination of controlled gasification studies and conductivity measurements indicates that filaments formed from alloy particles, particularly those rich in nickel, are highly graphitic, whereas those produced on nickel contain a large fraction of disordered carbon.

2. The differences in both the structural and chemical nature of the filaments can be understood by consideration of the respective wetting characteristics of the catalyst particles on a graphite surface. The interfacial phenomenon occurring at the metal/graphite boundary has been directly observed by *in situ* electron microscopy studies during metal-catalyzed graphite-hydrogen reactions. It was found that the wetting behavior of the metal on graphite was extremely sensitive to both the chemical nature of the particles and the reaction temperature. At 600°C nickel-rich alloy particles exhibit superior wetting properties on graphite compared to those found with either nickel or copper.

3. A unique form of catalyst deactivation has been encountered in the copper-nickel/ethylene-hydrogen system, which is believed to arise from preferential segregation of copper at high temperatures. Under these circumstances, the catalyst particles lose their ability to dissociate hydrocarbons and filamentous carbon growth is arrested. On cooling the specimen, however, catalytic activity is regenerated and it is suggested that an equilibrium composition of both nickel and copper is once again produced at the surface. The reversible nature of this deactivation step has been shown by multiple cycling between the active temperature (700°C) and deactivating condition (900°C).

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