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The Reversibility of Filamentous Carbon Growth and Gasification

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Controlled atmosphere electron microscopy observations of the nickel-catalyzed growth and gasification of carbon filaments have shown that these processes can be reversed. This supports the view that growth and gasification in either hydrogen or steam occur by similar mechanisms, where one of the steps involves the diffusion of carbon through the metal. It was observed that the small catalyst particles are the most active in filament formation and steam gasification, while the large particles are the most active for the hydrogenation reaction. This is explained in terms of different rate-controlling steps. © 1988 Academic Press, Inc.

INTRODUCTION

The gasification of carbon has been studied extensively and reviewed in some detail (*1–3*). In contrast, little effort has been devoted to the study of the gasification of filamentous carbon, a form of carbon which is produced from the interaction of certain carbon-containing gases with small catalyst particles, particularly those of the ferromagnetic metals, iron, cobalt, and nickel (*4*).

The growth of carbon filaments on nickel was first directly observed by Baker and coworkers (*5*) using controlled atmosphere electron microscopy (CAEM). The filaments were shown to consist of a duplex structure, a relatively oxidation-resistant skin surrounding a more easily oxidizable core, with a metal particle located at the growing end of the filament. Later, high-resolution transmission electron microscopy studies showed that the skin component was highly graphitic (*6–8*).

The mechanism generally accepted to account for the observed characteritics of the steady-state growth of the filaments for carbon-containing gases involves the following steps (*5, 9*):

(a) adsorption of gas at the metal surface followed by decomposition reactions leading to chemisorbed carbon species,

(b) dissolution in and diffusion of carbon species through the metal particle to active growth areas,

(c) precipitation of the carbon species to form the body of the filament, and

(d) migration of carbon species remaining on the metal surface around the particle to form the skin component of the filament. It is possible that the carbon species involved in this process are chemically different from those diffusing through the particle—step (b).

This mechanism accounts for the finding that there is no immediate deactivation of the catalyst, since carbon grows at the rear of the metal particle which is carried away from the support surface on top of the filament, with the upper surface of the catalyst remaining free to undergo continued reaction with the gas phase.

A number of kinetic studies have been reported on the gasification of carbon deposits produced on metal surfaces under conditions that favor the growth of filamentous carbon (*10–17*). Based on these studies a mechanism was postulated to ra-

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tionalize the most interesting feature of the gasification process, namely the extended periods of constant gasification rate (*12, 14*). This mechanism also included the diffusion of carbon through the metal as one of the key steps, but in the direction opposite that required for filament formation. The overall sequence of events was as follows:

(a) dissociative adsorption of the reactant gas on the metal particle surface,

(b) supply of carbon atoms from the carbonaceous solid to the catalyst surface via diffusion through the bulk or around the surface of the metal particle, and

(c) surface reaction between adsorbed gaseous species and adsorbed carbon atoms.

Unfortunately, the techniques used in these various studies, such as temperature-programmed surface reaction (TPSR) and thermogravimetric analysis (TGA), lacked the capacity to follow the gasification behavior of individual filaments. This limitation was overcome in the CAEM studies (*5*) where the gasification in oxygen of carbon filaments produced on nickel was followed continuously. It was observed that the core of the filaments oxidized first, leaving the skin behind, and, in some cases, nickel particles were seen to fall down the tubes which were created during this treatment. It is probable that under these conditions the gasification reaction proceeds by a noncatalytic route (*18*). It was, however, this observation coupled with the above-mentioned kinetic features that formed the basis for the notion that the catalytic growth and gasification of filamentous carbon could be a reversible process (*16, 19*).

The present work was undertaken to test this hypothesis, by *in situ* observation with CAEM, of the gasification of carbon filaments produced on nickel from interaction with acetylene. A further objective was to use the results of our study for comparison with a catalytic reaction model for gasification of carbon filaments proposed by Starkovich and co-workers (*20*).

EXPERIMENTAL

The experiments reported here were performed in a controlled atmosphere electron microscope system, the details of which can be found elsewhere (*21*). The sample design consisted of a nickel grid (3 mm diameter) spot-welded onto a platinum heater strip. Further coverage of nickel was introduced onto the grid by vacuum evaporation of spectrographically pure nickel wire from a heated tungsten filament at 5×10^{-6} Torr. This combination was inserted into the electron microscope and heated in 1.0 Torr hydrogen at 525°C for 1 h to ensure complete reduction of the samples and to promote nucleation of small nickel particles (25 to 200 nm diameter) along the edges of the metal grids. Following this treatment, the samples were cooled to room temperature, the hydrogen was replaced by 2.0 Torr acetylene, and the system was reheated to the stage where carbon filaments were produced. When a sufficiently large number of filaments had been formed, the samples were cooled and then gasified by reheating in 1.0 Torr hydrogen or 2.0 Torr wet argon. In this case argon was bubbled through a container of deionized water at 25°C to produce a gas stream with an argon : water ratio of 40 : 1.

In some experiments, the samples were exposed to a further carbon deposition cycle, the temperature being reduced after the gasification treatment, hydrogen or wet argon removed from the system, and 2.0 Torr acetylene reintroduced. In all cases where gases were being replaced, extreme care was taken to prevent exposure of the samples to air.

Finally, in another type of experiment, carbon was deposited on nickel grids in a tubular reactor from an ethylene : hydrogen mixture (4 : 1) flowing at 1.7 cm^3/s at 600°C and atmospheric pressure. The grids were removed from the furnace after cooling to room temperature in an argon purge and selected samples were subsequently mounted in the environmental stage of a scanning transmission electron microscope (STEM). This technique enabled us to examine the gasification process at a higher resolution (0.8 nm) than was possible in the conventional CAEM system (2.5 nm).

The gases used in this work, acetylene, ethylene, hydrogen, and argon, were obtained from Scientific Gas Products with stated purities of 99.99% and were used without further purification.

RESULTS

(*a*) *Growth of Filaments* (*First Cycle*)

The onset of filament formation in 2.0 Torr acetylene occurred at 510°C and was associated with the smallest metal particles 95–10 nm diameter). Under these conditions the majority of filaments were formed by the conventional mode, with the catalyst particle being carried away from the support surface and remaining at the tip of the filament. Occasionally some filaments were produced by the extrusion mode, in which a stationary catalyst particle created two filaments growing in opposite directions.

Detailed kinetic measurements of several growth sequences showed that at any given temperature small particles created filaments at a faster rate than large catalyst particles. Measurements of the variation of the growth of 150-nm-wide filaments as a function of temperature yielded an apparent activation energy of 33.5 ± 4.0 kcal/mole, in good agreement with previous results (*3*).

(*b*) *Gasification of Filaments in Hydrogen*

When the filaments were heated in 1.0 Torr hydrogen gasification of the largest ones present (150–200 nm diameter) commenced at 650°C, and temperatures of >650°C were required to gasify the smallest filaments (25–50 nm diameter). Continuous observation showed that gasification was confined to the region of the filament in contact with the catalyst particle, there being no evidence for removal of carbon at the filament/support interface. The most intriguing aspect of the reaction was that the catalyst particle retraced its original path removing the core component and leaving the outer, more structurally ordered skin. Figures 1a–1d are a sequence taken from the television monitor showing the catalytic gasification of the inner core of a filament during reaction in hydrogen at 675 to 725°C. Figures 2a–2d are a sequence taken from an experiment performed in the STEM at 855°C, a temperature high enough to induce gasification of the entire filament. It was significant to find that particles which had lost their activity during the carbon deposition cycle, i.e., had been encapsulated by carbon remaining at the catalyst surface, did not appear to exhibit gasification activity when treated in hydrogen.

Rates of hydrogasification were measured over the range 645 to 860°C, and the data obtained from 150-nm-wide filaments are presented in Fig. 3. From this plot it has been possible to derive a value of 24.7 ± 3 kcal/mole for the apparent activation energy for the catalyzed hydrogenation of filaments by nickel. Unfortunately, it was not possible to obtain the precise relationship between the rate of reaction and the particle size; however, it was clear that at any given temperature large particles catalyzed removal of carbon filaments faster than small particles.

(*c*) *Growth of Filaments* (*Second Cycle*)

When hydrogen was replaced by acetylene, then on reheating to 525°C, particles which had catalyzed the removal of the inner core of the filaments reversed their direction and proceeded to fill these regions with deposited carbon. It was not possible to determine if there was any appreciable thickening of the filament skin during this second deposition cycle. An example of this behavior is presented in the sequence of Figs. 1e–1h. In addition to this behavior, secondary growth of tiny branch filaments was observed to proceed along the sides of

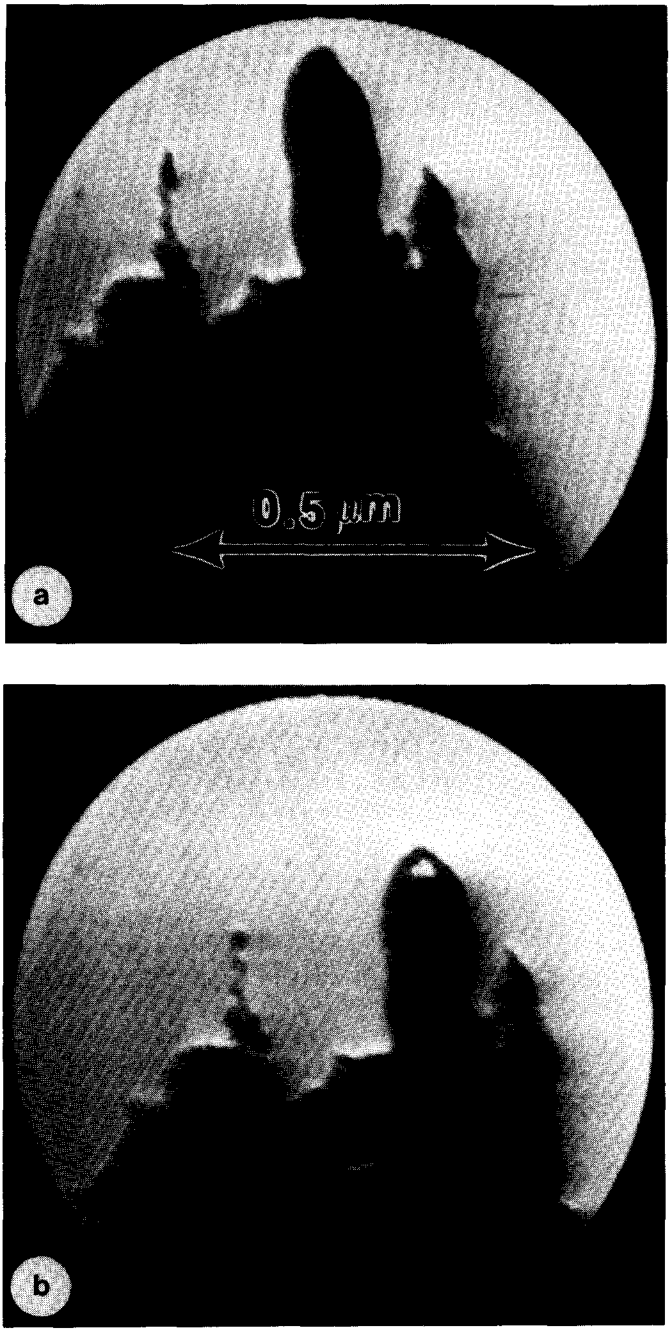

FIG. 1. Sequence (a) to (d): Gasification of a carbon filament at 657–725°C in 1.0 Torr hydrogen. Sequence (e) to (h): Growth of the same filament (second cycle) in 2.0 Torr acetylene at 525–555°C, together with formation of secondary filaments.

the parent filament. These growths probably originated from small nickel particles dispersed along the inner walls of the filament during the initial growth sequence. It was significant that no secondary growth was observed on any new filaments pro-

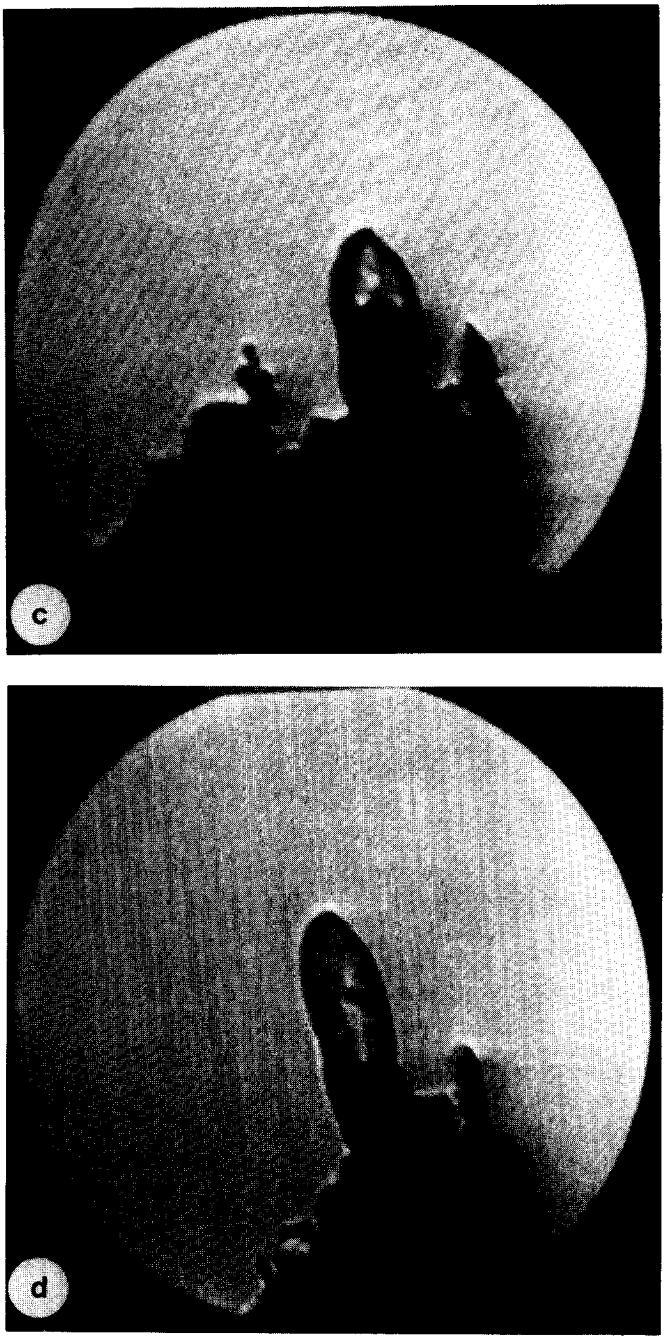

FIG. 1—*Continued.*

duced during this cycle, suggesting that accessibility of the hydrocarbon to the dispersed particles was achieved only after a gasification step.

(*d*) *Gasification of Filaments in Steam*

When the gasification step was performed in 2.0 Torr wet argon the behavioral pattern was quite different from that found

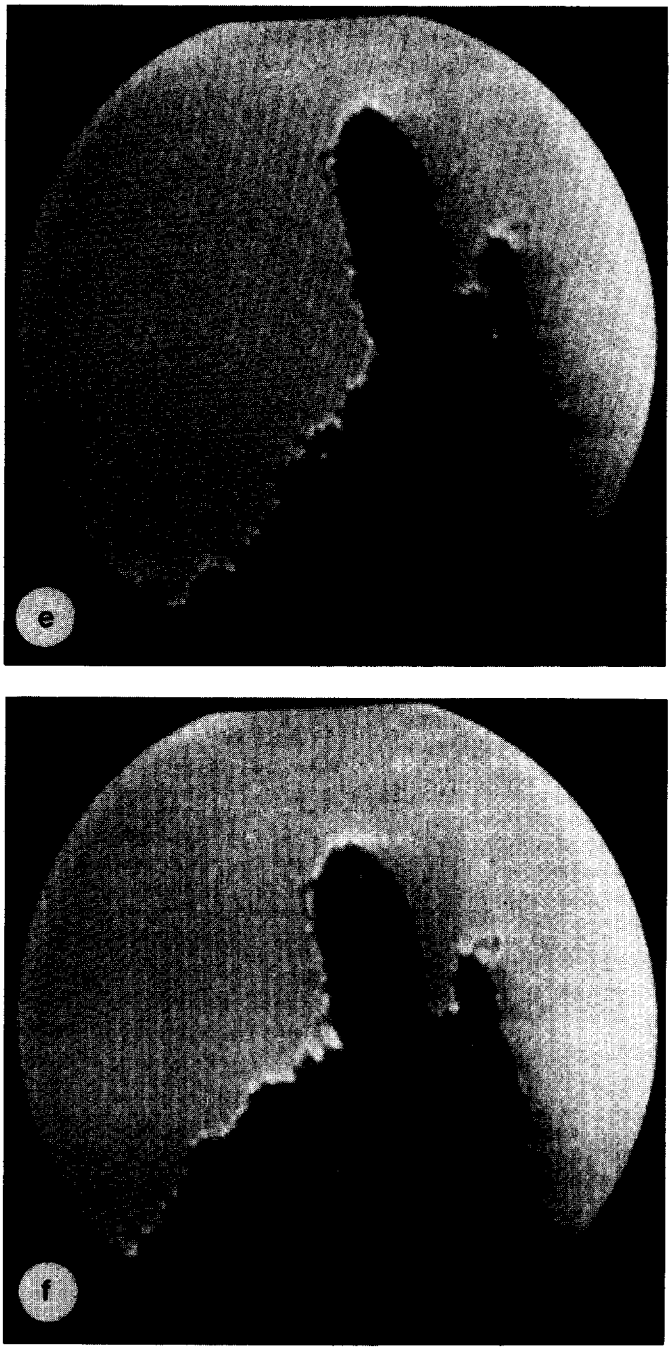

FIG. 1—*Continued.*

in hydrogen. In this case reaction started at 625°C and was characterized by attack along the sides of the filament at particular regions where small particles (3.0–5.0 nm diameter) were located, probably left as fragments during the growth process. Unfortunately it was difficult to follow the catalytic action of an individual particle for sustained periods and so it was not possible to perform quantitative kinetic analysis on

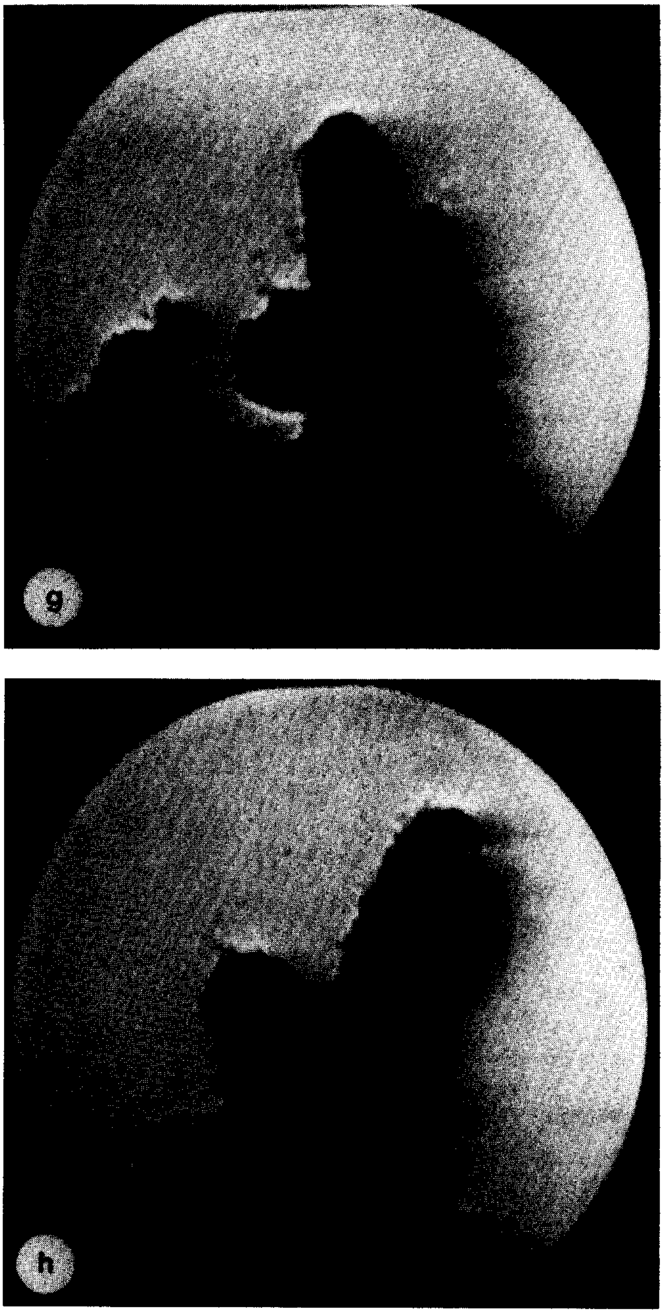

FIG. 1—*Continued.*

this reaction. No evidence was found under these conditions for the catalyst particles located at the tips of the filaments to exhibit the type of reversal behavior observed in the presence of hydrogen. When these specimens were subsequently reexposed to 2.0 Torr acetylene then secondary branched filaments were observed to grow on the sides of most of the original filaments when the temperature was raised to 525°C.

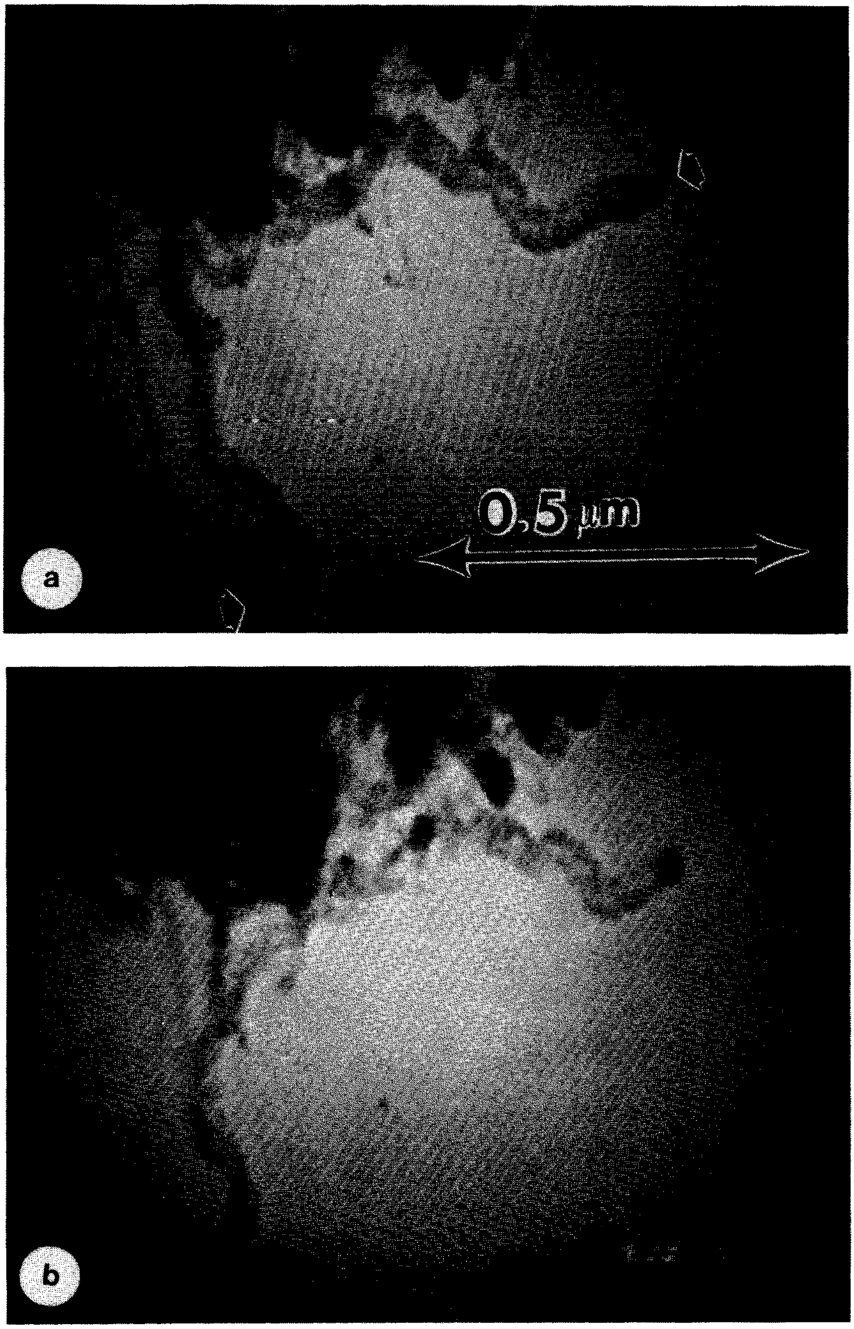

FIG. 2. Sequence (a) to (d) shows the gasification of two filaments in 1.0 Torr hydrogen at 855°C. Note that at this temperature the entire filament is gasified.

DISCUSSION

This study has shown that the nickel-catalyzed formation of carbon filaments from acetylene and gasification of the structures in hydrogen are reversible processes. It is generally agreed that diffusion of carbon through the catalyst particle is the rate-con-

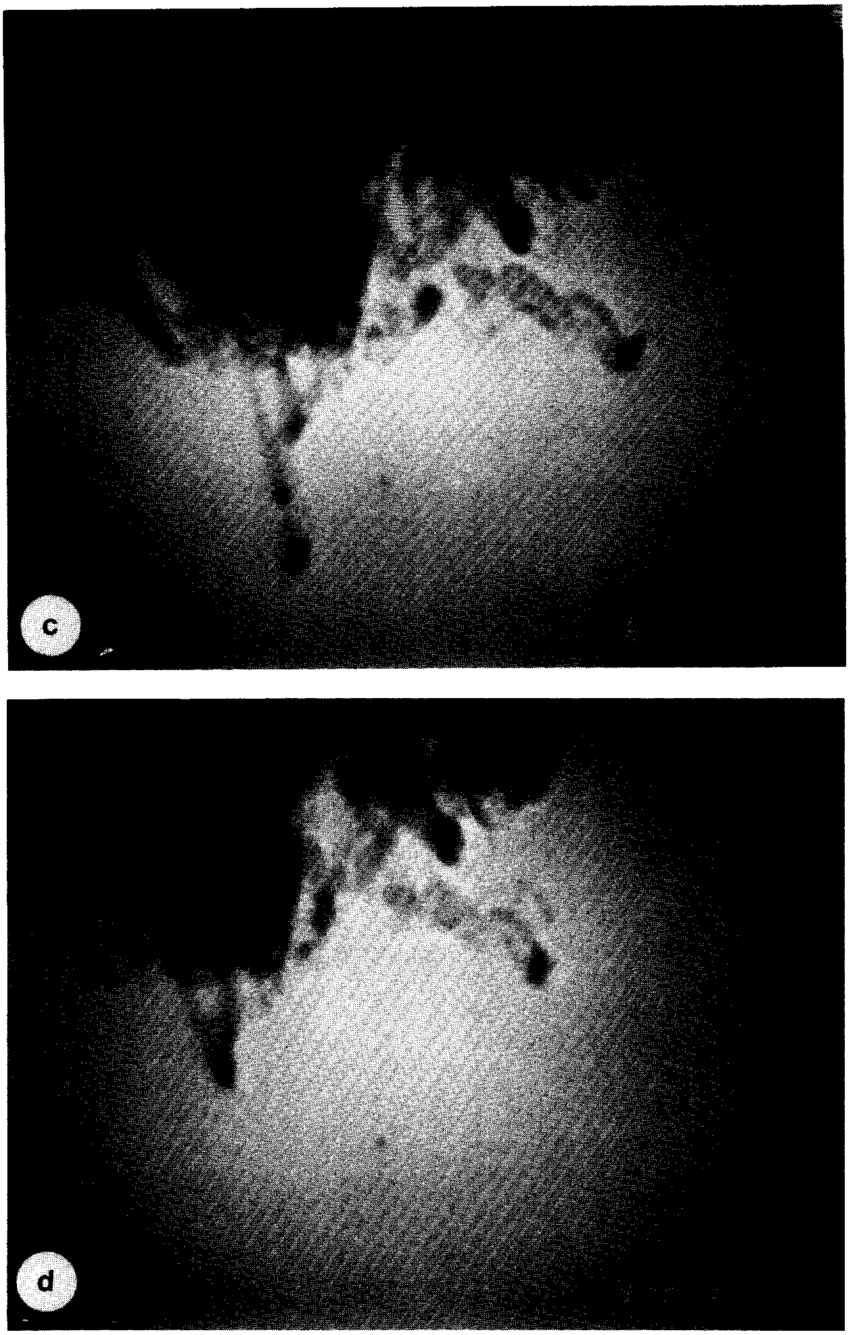

FIG. 2—*Continued.*

trolling step in filament growth (*5*, *9*). Continuous observation of the events occurring during the gasification of filaments in hydrogen suggests that carbon diffusion through the catalyst may be a step involved in this process. This notion is based on the following considerations. Catalytic gasification was *not* observed in cases where the metal particle had been deactivated during filament growth. This would imply that hy-

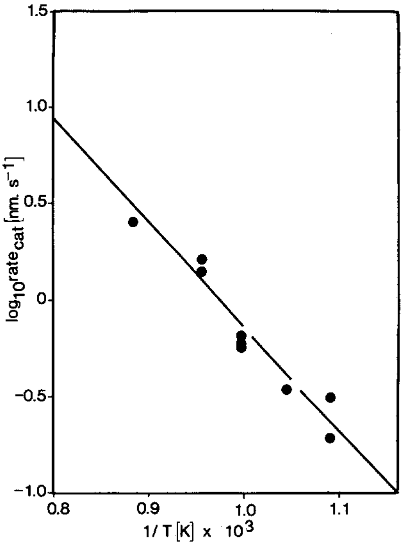

FIG. 3. Arrhenius plot for the rate of gasification of 150-nm-diameter filaments in 1.0 Torr hydrogen.

drogen cannot readily gain access to the inner core carbon by diffusion through the skin of the filament. In contrast, when the catalyst had maintained its activity during the carbon deposition reaction (i.e., the upper surface of the particle was exposed to the gas) then, in the subsequent gasification cycle, hydrogen could undergo dissociative adsorption on the metal surface. The final step is the formation of methane by reaction of atomic hydrogen with carbidic carbon, which is formed on the metal surface by diffusion of carbon species from the filament core. As this reaction proceeds the direction of movement of the catalyst particle is reversed and the core of the filament is gradually removed.

Examination of the rates of the filament formation and hydrogasification reactions as a function of particle size and temperature shows that major differences exist in the mechanisms of the two processes. For a given temperature, small particles form filaments at a faster rate than large particles, and previous studies (*22*) have indicated that the filament growth rate was proportional to (particle diameter)$^{-1/2}$. The value of the apparent activation energy obtained here of 35.5 kcal/mole is consistent with that found earlier for the same system (*5*) and in close agreement with the value for the diffusion of carbon through nickel (*23*).

In contrast, during the hydrogasification cycle at any given temperature, large particles removed carbon at a faster rate than small ones. This finding is in general agreement with the results of Baker and Sherwood (*24*) for the nickel/graphite system, where the gasification rates in hydrogen were proportional to (particle diameter)^2 (i.e., proportional to the surface areas of the particles). Although the geometry of the nickel/filament–hydrogen system is different from that of the channeling action produced in the nickel/graphite–hydrogen system (see the schematic representation, Fig. 4), the ratio of rates of two particles with different sizes should be the same in both systems.

The apparent activation energies determined for the hydrogasification of carbon filaments (24.7 kcal/mole) and graphite (23.6 kcal/mole (*24*)) are similar (thus independent of the substrate) and different from

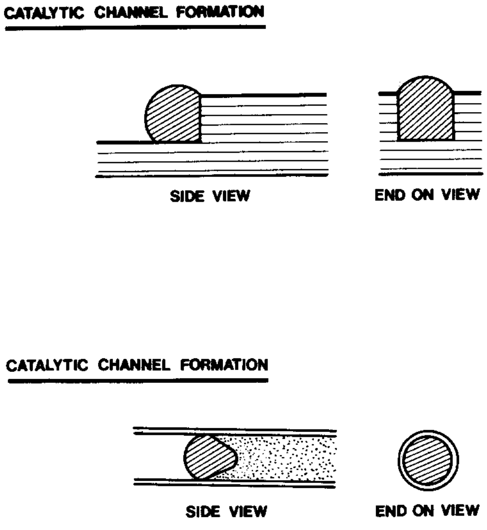

FIG. 4. Schematic representation highlighting the difference in catalyst action during channel propagation and filament gasification. In the latter situation, the particle can be considered as operating in a tunnel.

the value for the carbon diffusion through nickel. This suggests that the rate-determining step in the nickel-catalyzed gasification of carbon filaments in hydrogen is also the reaction between surface carbon and adsorbed hydrogen (*25*).

The disparity between the value of 24.7 kcal/mole obtained here and those reported from microbalance/flow reactor reaction studies of 32 to 36 kcal/mole (*16*) is readily understood from a consideration of the techniques. Using CAEM one can follow the catalytic gasification of individual filaments, whereas with the bulk experiments one measures the overall rate (catalytic and noncatalytic) of the total deposit, which may consist of other forms of carbon in addition to carbon filaments.

The differences in gasification characteristics of filaments shown in Figs. 1 and 2 are probably attributable to differences in the reaction temperatures. In the case of the specimen behavior presented in Fig. 2 the temperature is sufficiently high for the gasification of the graphitic skin of the filament to proceed at an appreciable rate.

Gasification of the filaments in steam does not follow the same pattern of behavior as that found in hydrogen. In this case, the catalytic action was caused by the small particles which had been left as fragments in the filament skin during the initial growth cycle. For the most part, the larger particles located at the filament tips tended to remain immobile and did not participate in the reaction. This behavior can be readily understood from a consideration of the mechanism of nickel-catalyzed steam gasification of carbon (*10, 16*). It has been shown that carbon diffusion through the catalyst particle is the rate-determining step and, as a consequence, at any given temperature small particles (with shorter diffusion paths) would be expected to be more active than large particles (*24*).

It is important to examine the model proposed for filamentous carbon gasification by Starkovich and co-workers (*20*) in light of the present results. The reported features and kinetic data are in line with earlier studies of the metal-catalyzed hydrogenation of carbons (*11*). The model (termed ASF—axially shrinking filament) assumes that during steady-state gasification, the filaments shrink without changing their cross section. The present work indicates that the model may be applicable in the case of hydrogen, but with more reactive gases such as steam, radial attack is significant and it can no longer be used.

Finally, in addition to providing some fundamental information on the catalytic gasification of carbon filaments, this work has also provided the key to an improved regeneration procedure for nickel catalysts. At present, the decoking step is performed in air at about 500°C and under these conditions the nickel will have little influence on the carbon filament removal process (*26*). As a consequence, there is a high probability that nickel particles will lose contact with the carbon filaments during gasification and be swept out of the reactor by the gas stream. In contrast, if the system is reacted in hydrogen prior to treatment in air the majority of the nickel particles will return to the support.

SUMMARY

The results presented in this paper show that catalytic formation of carbon filaments and gasification under mild conditions (by hydrogen at low temperature) are reversible processes. Furthermore, carbon diffusion through the catalyst particle appears to be a common step in these processes. In filament growth, carbon diffusion is followed by precipitation at the rear of the particle to form the body of the filament. In the presence of hydrogen, carbon diffusion occurs in the opposite direction and the deposited carbon is subsequently converted to methane by interaction with adsorbed hydrogen at the front face of the particle.

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