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Formation of Carbonaceous Deposits from the Platinum–Iron Catalyzed Decomposition of Acetylene

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Controlled atmosphere electron microscopy has been used to study the formation of carbonaceous deposits when a platinum–iron alloy was heated in the presence of acetylene and ethylene. When Pt–Fe particles were heated in acetylene carbon filaments were produced at quite low temperatures (690 K). These deposits were formed by an entirely new mode of filament growth in which the filament was extruded from the catalyst particle, which remained in contact with the support surface. The filament growth rate was two orders of magnitude faster than with a pure iron catalyst under similar conditions. In general the diameters of filaments were less than those of the catalyst particles responsible for their growth. Oxidation studies demonstrated that metal particles were taken up in the filaments, probably in the material constituting the skin of the filaments. A possible growth mechanism for this type of extrusion filament is suggested.

When Pt–Fe particles were exposed to ethylene this type of deposit was not produced, but at 1175 K, a cluster of nodular deposit collected around the particles and this occasionally took the form of diffuse filaments. The failure to find well formed filaments is attributed to insufficient heat release at the catalyst surface from the olefin decomposition process.

INTRODUCTION

In previous publications (*1,2*) we have reported the growth of various forms of carbon from the catalyzed decomposition of acetylene by several metals. From these studies we proposed a mechanism for the growth of filamentous carbon. In the present work we have examined the catalytic effect of a platinum–iron alloy on the decomposition of both acetylene and ethylene. Studies of the acetylene interaction with this catalyst has led to the observation of an entirely new mode of filament growth in which the filament is extruded from the metal alloy particle, which remained in contact with the support surface. A possible growth mechanism for this process is suggested and the failure to find this type of deposit in the presence of ethylene is discussed.

METHODS

Technique

The experimental techniques used here were the same as those described previously (*1,2*), namely controlled atmosphere electron microscopy.

Materials

The platinum–iron alloy was deposited onto either graphite or silica supports as a thin film by rapid evaporation of a metal wire (Johnson–Matthey & Co. Ltd., stated composition platinum/46% iron) at a residual pressure of 10.0 mN m^{-2} from a tungsten filament. In some experiments the alloy was evaporated onto Pyrex slides, which had been coated with a film of detergent. The alloy film was released onto a clean water surface and small self-sup-

porting sections were used as specimens. In this way changes in the behavior of the alloy during reactions could be studied without interference from the support media.

The gases used in this work, namely acetylene, ethylene, hydrogen, argon and oxygen, had stated purities of >99% and were used directly.

RESULTS

Effective nucleation of the Pt–Fe alloy film into particles ranging in size from 30 to 120 nm diameter was accomplished by heating specimens in either 0.07 kN m^{-2} hydrogen or argon to 920 K. When hydrogen or argon was replaced by 0.07 kN m^{-2} acetylene and the temperature gradually raised from ambient several features were apparent. At 690 K some of the particles underwent a rapid change from an irregular to a more spheroidal form, and there appeared to be movement of material within these particles. This behavior immediately preceded the formation of a filamentous growth—seen as a rapid evolution of material from the particles, which in most cases remained stationary on the support surface.

A detailed examination of this process showed that the catalyst particles consisted of a dense embryo surrounded by an apron of lighter material (relative width of the embryo to the apron was about 1:7). The width of filaments was generally much less than that of the complete catalyst particle, appearing to be governed by the size of the dense embryo. There was a tendency for some filaments to become tapered, especially during the final stages of growth. In these cases it was clear that the catalyst particle became progressively smaller in size as the reaction proceeded, and eventually the dense embryo disappeared, filamentous growth ceased and often a ring of the lighter material remained on the support surface. Coiled filaments were also quite common features in this system. From Fig. 1, it can be seen that the diameter of the coil is several times that of the filament itself. It was evi-

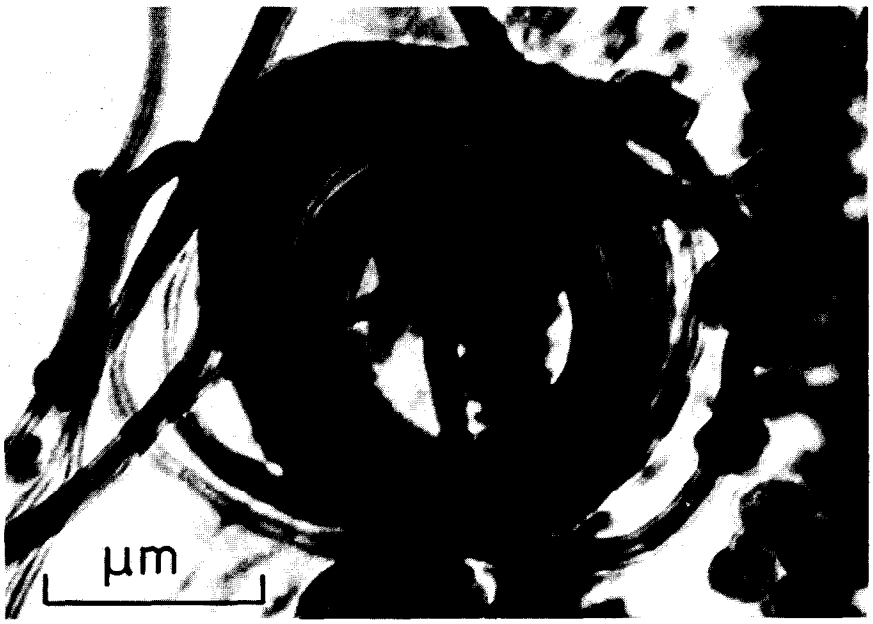

FIG. 1. Transmission electron micrograph of a coiled filament growth form (×28,280).

dent that once formed the coils remained quite rigid and self-supporting indicating that even though these structures had been produced by a rapid process, they nevertheless possessed considerable strength.

Filaments continued to grow at temperatures up to 990 K, but ceased to form as the amount of amorphous carbon deposit collecting on the surface became appreciable. In some experiments where temperatures of 990 K had not been exceeded and filamentous growth had terminated, the hydrocarbon was replaced by 0.07 kN m^{-2} hydrogen and the specimen heated at 950 K for 1 h. On re-introducing the acetylene many of the existing filaments were observed to start growing again.

Quantitative analysis of filament growth sequences indicated that a rapid constant growth rate region was preceded by a very short initial growth period of <0.1 s. Linear filament growth rates were measured over the range 690 K to 990 K, and from the values obtained for filaments of 45 nm diameter a plot of log rate against $1/T$ yielded an activation energy of 79.3 ± 6.0 kJ $mole^{-1}$. A comparison of the rates of filament formation in the present system with those obtained for a pure iron catalyst under similar conditions shows the dramatic effect of adding platinum to iron, e.g., at 990 K, filament growth rate from Pt/Fe catalyst was 2880 nm s^{-1} and for a similar size Fe catalyst particle, 20.6 nm s^{-1} (in each case the filaments were of similar width).

From measurements of over two hundred filaments the filament lengths when growth ceased were between 10 to 40 μm with a few exceptional filaments of up to 200 μm in length.

When specimens were exposed to 0.3 kN m^{-2} oxygen, the inner portions of the filaments started to oxidize at 845 K

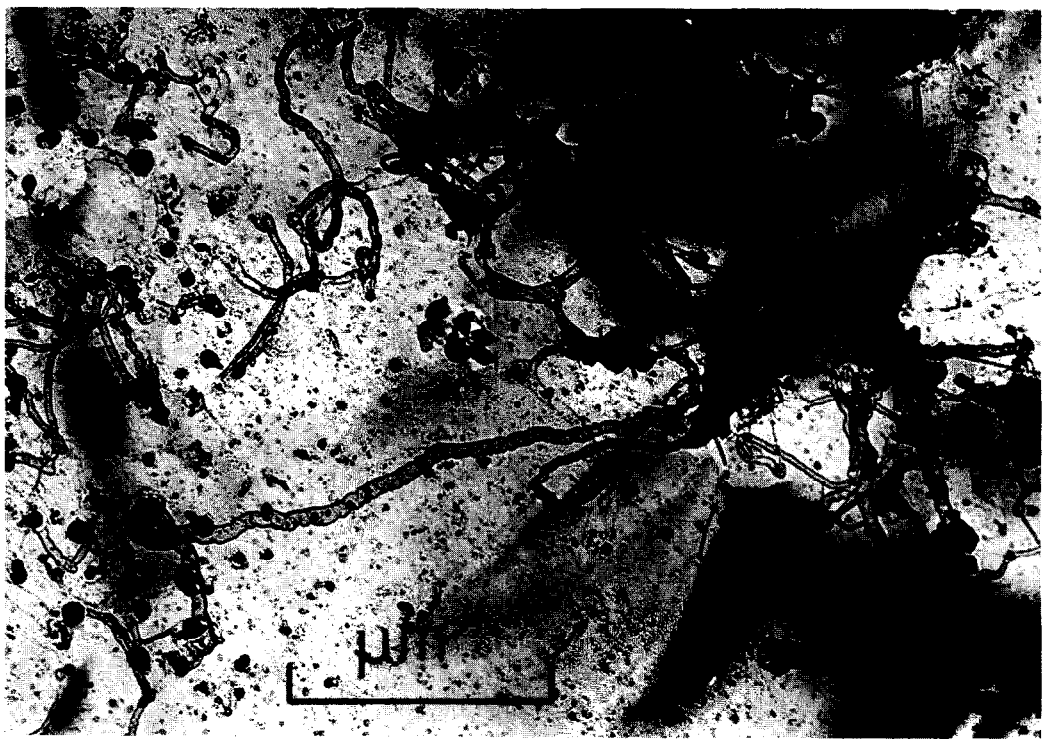

FIG. 2. Transmission electron micrograph of partially oxidized filaments (note the appearance of small metal particle inclusions in some of the filaments) (×33,750).

leaving behind a relatively oxidation resistant skin. This stage in the reaction is shown in Fig. 2. As the inner portions were removed metal particles (2–20 nm diameter) were clearly visible as inclusions in the filament skin, and were distinguishable from those particles remaining on the support as the inclusions moved with the oscillating motion of the filaments in which they were embedded. If the reaction were continued, then at 1000 K the skin of the filaments was observed to oxidize leaving a skeletal arrangement of small metal particles.

In experiments where the alloy catalyst was exposed to ethylene at pressures over the range 0.07–0.7 kN m^{-2} the alloy particles showed the same behavioral pattern as in acetylene, but formation of the type of filamentous carbon produced from acetylene was not observed at temperatures up to 1175 K. At this temperature a deposit did start to grow around the alloy particles and in some cases took the form of ill-defined filaments.

In a final series of experiments a self-supporting film of the alloy was heated in 0.07 kN m^{-2} acetylene and besides observing changes in the transmission image, changes in structure were monitored from electron diffraction examination as the reaction proceeded. From these experiments it was quite clear that separation of the alloy components was occurring at 700 K.

DISCUSSION

Observations indicate that before filamentous growth proceeds in the Pt–Fe/C_2H_2 system there is a separation of the two metals constituting the alloy catalyst particle. If Pt preferentially diffuses to the outer regions of the particle during this period to form an apron around a core of Fe, the situation depicted in Fig. 3a will be achieved. At 690 K it is probable that decomposition of adsorbed acetylene will only occur on those surfaces of the particle

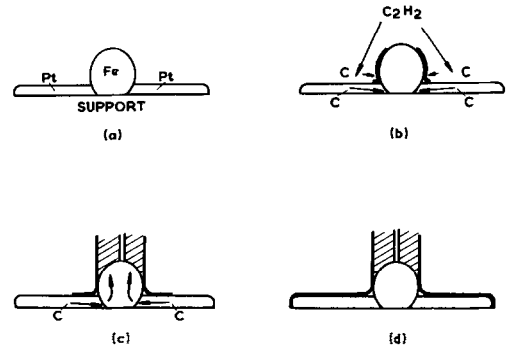

FIG. 3. Stages in the growth of filaments.

containing Pt, since previous work (*2*) has shown that temperatures of 925 K are necessary to produce filaments from the Fe/C_2H_2 system. This implies that decomposition of acetylene to produce carbon on the Fe core will be insignificant at 690 K and heat due to the exothermic decomposition of acetylene will only be generated initially at the exposed Pt surfaces of the particle.

During the filament growth process it was established that the entire catalyst particle remained on the support surface and that the width of the extruded filament was similar to that of the dense embryo (i.e., the iron core). From the oxidation behaviour of the filaments it was evident that their structures consisted of an easily oxidizable core of disordered carbon surrounded by a more resistant skin in which metal particles were often embedded. The following proposed filament growth process is consistent with these facts.

Some of the carbon produced from the hydrocarbon decomposition will be taken into solution by Pt and diffuse down the temperature gradient created in this metal by the acetylene decomposition. The carbon will move to the cooler regions (i.e., the Pt–Fe interface) furthest from the exposed Pt surfaces of the particle. Carbon remaining at the surface will tend to move towards the cooler Fe surfaces, Fig. 3b. Although carbon solubility in Pt is low, its diffusion rate through Pt is

extremely high (*3*), and therefore it is doubtful whether this step will be a rate determining factor in the process. Carbon will build up at the Pt–Fe interface and be steadily transferred into the Fe (a slightly exothermic process). The diffusion process will increase in rate as heat is imparted to the Fe surfaces in contact with Pt and, more particularly, as the upper surface of the iron core is cooled when carbon is endothermically precipitated to form the inner portions of the filament, Fig 3c. It is the direction of this initial carbon flow path that is responsible for maintaining contact between particle and support. If diffusion of carbon through the Fe is the rate determining step in the process carbon will accumulate at the Pt surface. It would be expected that during this rapid growth process fragments of Pt and Fe could be carried away from the particle and eventually become embedded in the structure. The ultimate filament growth rate is expected to be very high in such a process because the Fe core has an effective surface collection area for carbon provided by the Pt apron of approximately 25 times its own exposed surface area. It is also quite likely that the Pt component is a more efficient catalyst for acetylene decomposition than is the Fe. The measured activation energy for filaments produced in this system of 79.3 ± 6.0 kJ mole^{-1} is close to that for diffusion of carbon through Fe (see values given in Ref. (*2*)) and appears to support the postulate that diffusion of carbon through the Fe is the rate determining step in this process as it was in the growth process involving pure iron (*2*).

Attrition of Fe from the catalyst particle would be expected to result in a decrease in filament width and is consistent with the observed tapering of some filaments in the final stages of growth. Indeed, one way in which filaments could be terminated is when all the Fe had been consumed, so that only the Pt apron remained on the support surface.

It was found that deactivated catalyst particles could sometimes be regenerated by reaction in H_2, followed by re-introduction of acetylene. This observation indicates that the termination step in these cases was interference with reactions at the exposed surface of the catalyst particle, i.e., the Pt surface, with the gas phase. If carbon at the particle surface is not removed to form the filament skin fast enough, then the Pt surface will rapidly become blocked, the source of the temperature gradient in the Pt will be removed, and the passage of carbon through the particle will cease abruptly (Fig. 3d). Regeneration of catalyst activity would be accomplished by removal of this carbon coating, and reaction with H_2 would be an effective treatment (*1*).

The failure to find carbon filaments of this type when ethylene was used as the hydrocarbon source instead of acetylene is not completely understood but it is possible that the heat released by ethylene decomposition (ΔH_f for $C_2H_4 = -39.5$ kJ mole^{-1} (*4*)) is not sufficient to create the necessary temperature gradient in the particle when compared to the amount generated by decomposition of acetylene ($-\Delta H_f$ for $C_2H_2 = -223.6$ kJ mole^{-1}).

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