

## Catalytic Gasification of Graphite by Nickel in Various Gaseous Environments

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Controlled-atmosphere electron microscopy studies of the nickel/graphite system have revealed that in a strong oxidizing environment carbon gasification occurred mainly by the uncatalyzed route. Under the milder conditions of steam, catalyzed and uncatalyzed reactions occurred at comparable rates. In contrast, the reaction proceeded exclusively via catalyzed attack when experiments were performed in a hydrogen environment. However, in this case activity ceased at temperatures of around 1000°C due to what is believed to be the formation of a strong nickel-carbon interaction resulting in the transformation of active metal particles, which formed a thin film along the edges of the catalytic channels they had produced at lower temperatures. Regeneration of particles could be achieved by heating in either oxygen at 850°C or steam at 830°C. The original activity pattern was restored if these specimens were subsequently heated in hydrogen. Although the precise cause and nature of the interaction between nickel and carbon is not fully understood, the results suggest a novel approach to redispersing large nickel particles.

### INTRODUCTION

Over the past 60 years a considerable body of information has been collected on the catalytic influence of nickel on the gasification of carbon under various conditions. Many studies have been motivated by the finding that carbon deposition is a complicating factor in the efficient operation of supported nickel catalysts in a number of commercial processes such as methanation, Fischer-Tropsch synthesis and high-temperature steam reforming of naphtha. Examination of this material leads to conflicting conclusions regarding the behavior and proposed mechanisms of nickel-catalyzed gasification of carbon.

Tamai and his co-workers have been responsible for a series of investigations of the catalytic behavior of a number of transition metals, including nickel, on the carbon-hydrogen reaction (1-4). Using optical microscopy, these workers were able to demonstrate that hydrogenation of graphite was accompanied by the forma-

tion of channels across the surface, each channel having a metal particle at its head. They concluded that the catalytic gasification of carbon occurred by dissociation of molecular hydrogen on the metal particle followed by migration of atomic hydrogen to the carbon and subsequent reaction to form methane. A similar conclusion was also reached by Figueiredo and Trimm (5) from their work on the kinetics of the reaction of hydrogen with carbon deposited on nickel foils. An alternative mechanism was proposed by Grigor'ev *et al.* (6) for the hydrogenation of carbon black in the presence of nickel. They claimed that the reaction proceeded via dissolution of carbon in the metal, followed by methane formation, according to a solid-solid-gas mechanism.

In a very recent study, Keep *et al.* (7) used controlled-atmosphere electron microscopy to investigate the effects of small nickel particles on the hydrogenation of single-crystal graphite. They also found that the particles created channels across the graphite basal planes, the ma-

jority of which were oriented parallel to the  $\langle 11\bar{2}0 \rangle$  directions. As expected, an increase in temperature was accompanied by an increase in channel propagation rate; however, at temperatures above 800°C this relationship broke down as the active nickel particles were observed to disappear. These workers attributed the disappearance as being due to diffusion of metal into the graphite structure. Quantitative analysis of the channeling sequences led them to conclude that the rate of carbon gasification was proportional to the external surface areas of individual particles rather than that of the interface between the particle and the graphite. One unifying feature which does emerge from these investigations is that the rate of the uncatalyzed reaction is virtually insignificant compared to the catalytic attack and its effect can therefore be ignored.

The effects of catalysts on the carbon-steam reaction has received very little attention. Tuddenham and Hill (8) found that nickel was effective in accelerating the gasification of graphite in steam at 1100°C. Recently it has been suggested that the rate of this reaction is controlled by the diffusion of carbon through nickel (5). Perhaps the most comprehensive study of the effect of metals on the gasification of graphite in steam and hydrogen mixtures has been reported by McKee (9). He found that the catalytic activity of nickel for graphite gasification was extremely sensitive to the oxidation state of the metal. The rate of gasification was highest in wet hydrogen, occurred less readily in dry hydrogen, and was very low in wet nitrogen, when the metal was claimed to be in the oxidized state. Hahn *et al.* (10) examined the influence of the oxidation potential of the hydrogen/steam system on the catalytic activity of several metals for gasification of carbon. They established that at 930°C nickel remained in the metallic state and that carbon conversion increased with

water vapor mole fraction. Otto and Sheref (11) derived a value of  $43.3 \pm 4.5$  kcal · mole<sup>-1</sup> for the activation energy of the nickel catalyzed gasification of graphite in steam from bulk experiments.

Thomas (12) used controlled atmosphere optical microscopy to follow the behavior of nickel particles on graphite in the presence of oxygen. At 650°C etch pits were generated in the graphite surface at every region occupied by a nickel particle, and as oxidation continued, the metal retained its catalytic activity. Thermogravimetric analysis was employed by McKee (13) to demonstrate that the catalytic action of nickel on the graphite/oxygen reaction probably involved a redox process where NiO was reduced to the metal by carbon and subsequently reoxidized back to NiO by oxygen. These observations would appear to be in conflict with the bulk data obtained by Heintz and Parker (14), who found that the gasification rate of graphite impregnated with nickel was almost the same as that of an unadulterated specimen when oxidized in air at 600 to 700°C.

In the present work, we have employed controlled-atmosphere electron microscopy to continuously follow the reactions of nickel/graphite in O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>, and H<sub>2</sub>-H<sub>2</sub>O environments. This approach has enabled us to measure the detailed kinetics of the effects of nickel on the gasification of graphite in these various environments and learn a great deal about the possible reaction mechanisms. We have also observed the mysterious disappearance of active nickel particles in the graphite-H<sub>2</sub> reaction as reported by Keep *et al.* (7) and have found that subsequent treatment in other environments can lead to a novel redispersion procedure for nickel.

#### EXPERIMENTAL

The details of the CAEM technique can be found elsewhere (15). Spectrographically pure nickel (99.9% pure) was depos-

ited onto transmission specimens of single-crystal graphite (Ticonderoga) by evaporation from a heated tungsten filament at a residual pressure of  $5 \times 10^{-6}$  Torr to produce a continuous film at least one-atom thick.

In some experiments the manner by which silica inclusions in the nickel particles influence the catalytic gasification reaction was investigated. The preparation of the correct form of specimen to probe this effect proved to be quite complicated. In order to meet the criterion of the silica only being present within and not on the surface of the catalyst particles or on the graphite surface, it was decided to grow carbon filaments on catalyst particles which had been treated under conditions where silica would have been incorporated in the nickel; i.e., heating silica coated nickel foils to  $>800^{\circ}\text{C}$  prior to treatment with a hydrocarbon (16). After the filaments had ceased to grow, samples were carefully removed from the bulk metal and transferred to the surfaces of graphite specimens. This combination was then heated in 5 Torr  $\text{O}_2$  at  $750^{\circ}\text{C}$  in the CAEM to gasify the filaments and leave the residual particles containing silica on the graphite surface. These specimens were subsequently reacted in hydrogen to  $600^{\circ}\text{C}$  for 1 hr to ensure that the particles were in the metallic state, and then gradually the temperature was raised to a point where catalytic attack was observed. The presence of silica in the nickel was verified using the microanalytical facility of a Philips EM 400 microscope operated in the STEM mode.

The reactant gases used in this work, hydrogen, oxygen and argon were obtained from Scientific Gas Products with stated purities of 99.99% and were used directly. Experiments where the effects of steam were being examined were accomplished by allowing the carrier gas to flow through a bubbler containing deionized water maintained at  $0^{\circ}\text{C}$ , prior to entering

the gas reaction cell, and produced a gas/water ratio of about 40/1.

## RESULTS

### (a) *Nickel/Graphite—Oxygen*

When nickel/graphite specimens were reacted in 5 Torr oxygen, nucleation of the evaporated metal film into isolated particles (5 nm diameter) was extremely sluggish, requiring a temperature of  $635^{\circ}\text{C}$  before reaching completion. With the exception of a slight increase in average particle size very little change in specimen appearance was observed until the temperature was raised to  $835^{\circ}\text{C}$ . At this stage there was some evidence of catalytic attack by the pitting mode, but the major source of carbon gasification was via the uncatalyzed route, i.e., recession of edges. It was only at very high temperatures, about  $1065^{\circ}\text{C}$ , that catalytic channeling was apparent and this action was restricted to a few particles in the size range 2.5 to 10 nm. It was interesting to find that the majority of particles, which were inactive, remained quite static on the support throughout this period. If the metal film was prenucleated in  $\text{H}_2$  and then heated in  $\text{O}_2$  some particle mobility was observed at  $640^{\circ}\text{C}$ , but this action was quickly terminated as reaction time increased. The reaction was eventually concluded at  $1150^{\circ}\text{C}$ , a condition where uncatalyzed attack had become quite vigorous and often led to specimen disintegration.

### (b) *Nickel/Graphite—Steam*

At temperatures below  $800^{\circ}\text{C}$ , the behavior of nickel/graphite specimens exposed to 1 Torr argon saturated with  $\text{H}_2\text{O}$  at  $0^{\circ}\text{C}$  was identical to that seen with  $\text{O}_2$ . The onset of gasification occurred at  $900^{\circ}\text{C}$  and this was caused by uncatalyzed attack at edges and steps on the graphite surface. Although there were some isolated examples of catalyzed attack by the pitting mode at  $915^{\circ}\text{C}$ , the

major catalytic effect did not ensue until 935°C. At this temperature particles located at edges and steps proceeded to cut channels across the graphite basal planes. The width of the channels were governed by the diameter of the particles at their leading edge, being in the range 20 to 80 nm. Although the active particles did not appear to follow any particular orientation, it was evident that at any given temperature small particles created channels at a faster rate than larger ones. This feature is seen quantitatively in Fig. 1, where the rate of channel propagation is found to vary as (particle diameter)<sup>-1/2</sup>. At 950°C it was also apparent that once formed, channels remained parallel-sided for relatively long periods, indicating that uncatalyzed attack was extremely slow. This situation changed as the temperature was gradually raised to 1100°C when channels took on a fluted appearance as the rate of uncatalyzed reaction became significant.

From an Arrhenius plot of the variation of the rate of channel propagation with temperature. Fig. 2, it has been possible to evaluate an apparent activation energy for the nickel catalyzed gasification of graphite in steam of  $33.1 \pm 3 \text{ kcal} \cdot \text{mole}^{-1}$ . This data is based on 32-nm-diameter particles cutting channels of similar depth.

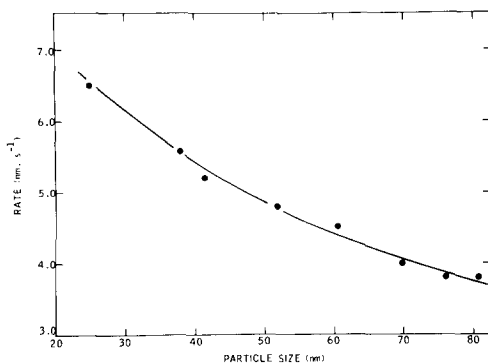


FIG. 1. Relationship between nickel particle size and channel propagation rate for particles cutting channels of similar depth on graphite in 1 Torr wet argon at 1150°C.

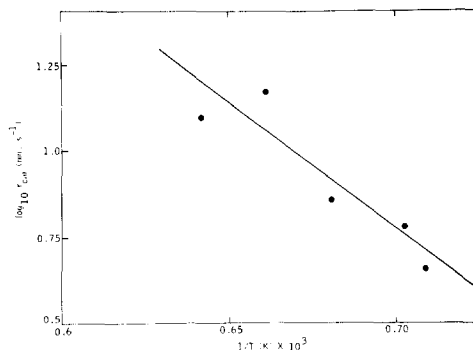


FIG. 2. Arrhenius plot of nickel-catalyzed rate of graphite gasification in 1 Torr wet argon.

From a comparison of the behavior of the nickel/graphite system in these two oxidizing environments at higher temperature it is clear that in oxygen the uncatalyzed reaction predominates, whereas in steam the catalyzed reaction accounts for a significant fraction of the carbon which is gasified.

### (c) Nickel/Graphite—Hydrogen

Treatment of nickel/graphite specimens in 1 Torr dry hydrogen resulted in particle nucleation at 755°C. Catalytic attack of the graphite commenced at 845°C and this action was seen as the development of fine channels, which emanated from edges and steps on the graphite surface. The appearance of these channels was similar in many respects to those produced under oxidizing conditions, each channel having a catalyst particle located at its leading edge. As the temperature was raised, both the size and number of particles performing this function increased. The typical appearance of channels produced after reaction of nickel/graphite with hydrogen at 950°C is shown in Fig. 3. The channels are up to 150 nm in width and have many straight sections interrupted by changes in direction of 60 or 120°, and are orientated parallel to  $\langle 11\bar{2}0 \rangle$  directions. Occasionally examples of channels moving in directions parallel to  $\langle 10\bar{1}0 \rangle$  directions were



FIG. 3. Typical appearance of channels produced after reaction of nickel/graphite in 1 Torr hydrogen at 950°C.

seen. However, even in these cases the catalyst particles possessed hexagonal facets at the graphite-particle interface which were orientated parallel to  $\langle 11\bar{2}0 \rangle$  directions. These observations are entirely consistent with the findings of other workers (3, 7, 9), but in sharp contrast to the formation of catalytic channels in some graphite-oxygen systems, which tend to be orientated exclusively in  $\langle 10\bar{1}0 \rangle$  directions (17). Extensive searches of the surfaces of a number of specimens failed to reveal the presence of any pitting attack.

Continuous observation of some of the channeling action of the larger particles ( $>100$  nm diameter) showed some fascinating behavior. As the temperature was gradually raised to  $975^\circ\text{C}$  there was a tendency for particles to undergo periodic rearrangements in shape, oscillating between a "balled-up" configuration and a flatter "spread out" form; i.e., the particles gave the appearance of "breathing." This aspect was particularly noticeable from watching the change in shape of the meniscus at the trailing edges of particles. It was significant that throughout this period, both the width of the nickel-graphite active interface and the depth of the channel remained relatively constant.

As the temperature was increased, it became quite clear that active nickel particles were wetting the graphite and either leaving material on the sides of the channels or for some reason, volatilizing. As a consequence, catalyst particles became smaller and, ultimately, when all the catalyst was depleted channeling ceased. A good example of this situation is depicted in Fig. 4, a micrograph of a specimen which had been treated up to  $1050^\circ\text{C}$ . Figure 5 is a sequence taken from the TV monitor showing the gradual depletion in catalyst material as the channel increases in length. It is apparent that the channel width is reduced in a stepwise fashion, suggesting that nickel is being lost from the particle in a gradual process and that

the particle is periodically undergoing a reorganization in its shape. Detailed examination of many experiments demonstrated that the larger the initial size of the catalyst particle the longer the period that channeling action was maintained before the particle disappeared. As an active particle approached a channel which had already been formed it tended to be deflected away from the channel rather than intersect it. Continuous observation also showed that active particles became thinner and that channel depth decreased towards the end of the track. Occasionally a small core would remain and continue to channel following an apparent random path until it eventually became completely disseminated, leaving a tail on the parent channel. The failure to observe any traces of a residual film along the edges of dormant channels indicates that either such a process does not occur or that the film thickness is less than the resolution of the CAEM, viz., 2.5 nm. This phenomenon, which started at  $980^\circ\text{C}$ , was essentially complete by the time the temperature had been raised to  $1098^\circ\text{C}$ . Continued heating in hydrogen up to  $1250^\circ\text{C}$  produced no further catalytic action or restoration of the original particles and only at the highest temperature was it possible to detect signs of uncatalyzed attack. It was significant that inactive particles remained static on the surface and showed less tendency to lose material during the reaction.

Subsequent cooling and reheating produced no change in specimen appearance, indicating that the proposed metal-support interaction was very strong. If hydrogen was replaced by oxygen and the specimen reheated, then at  $850^\circ\text{C}$  small particles, 2.5 nm diameter, started to reform along the edges of the original channels, which were in the process of undergoing expansion due to uncatalyzed oxidation. These observations would seem to imply that particle shrinkage in hydrogen was due to film formation along

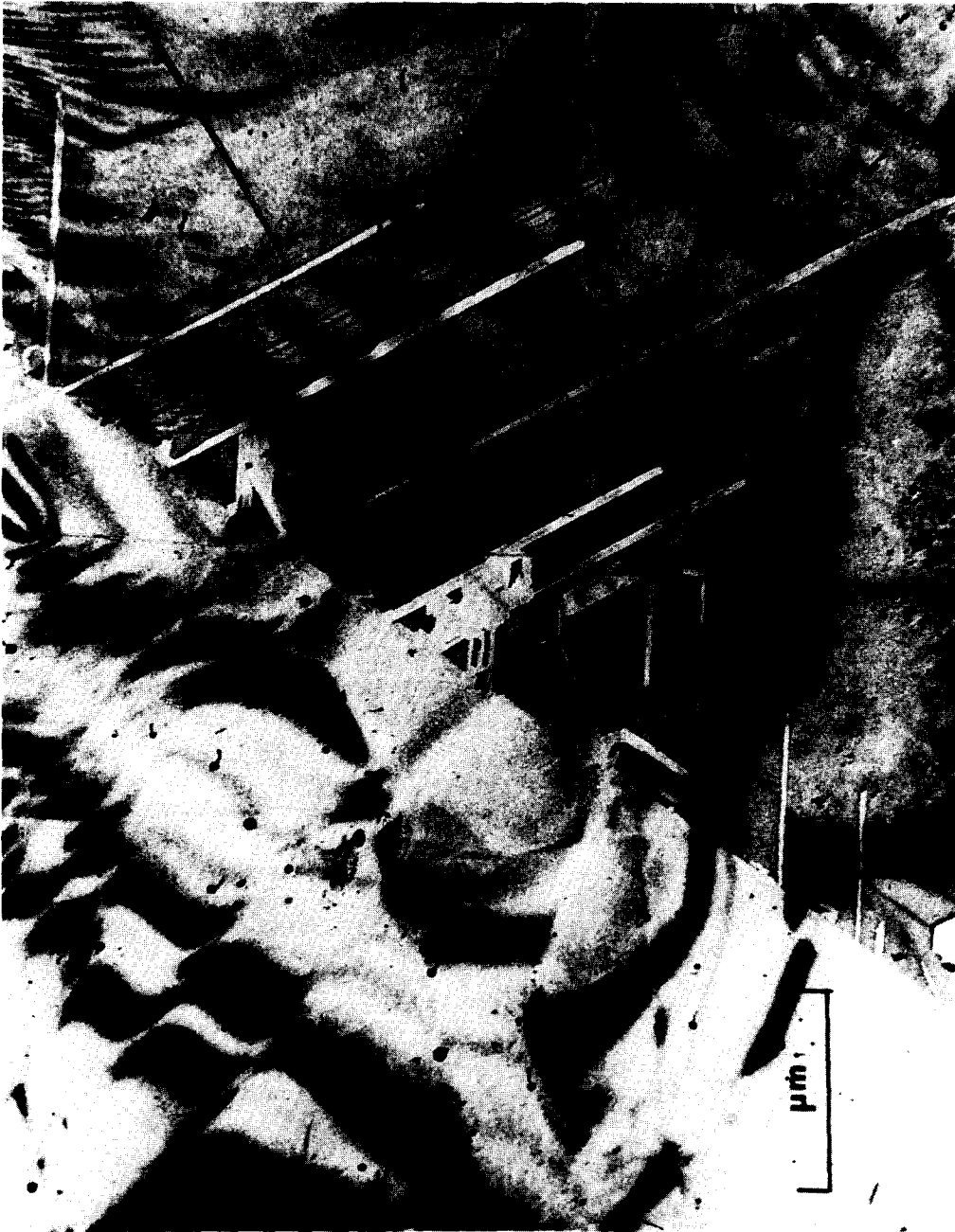


FIG. 4. Transmission micrograph showing loss of material from the ends of channels after treatment in 1 Torr hydrogen at 1050°C.

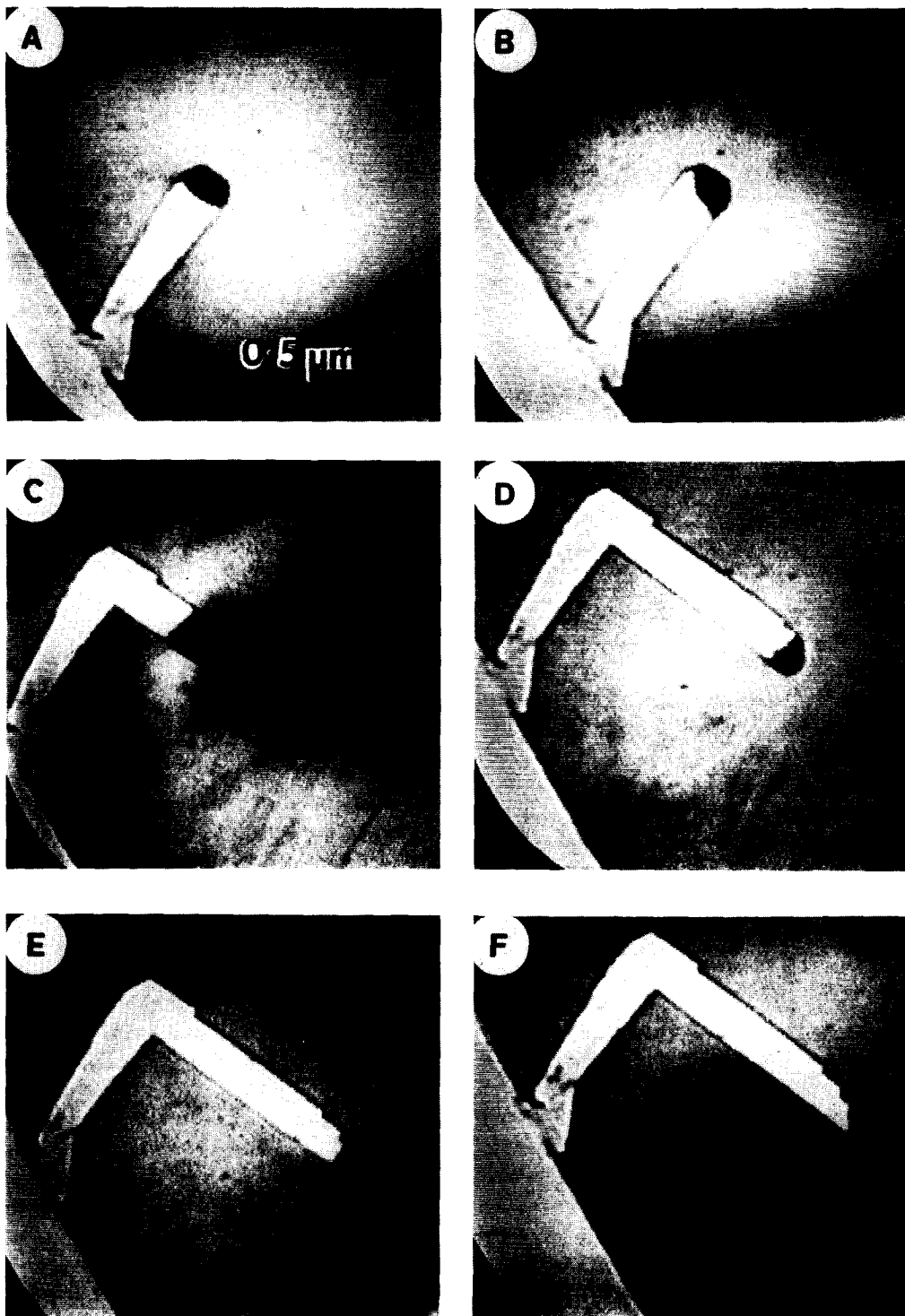


FIG. 5. Sequence (A to D) showing the gradual depletion in catalyst material as the channel increases in length (time between each frame is about 10 sec).



channel edges rather than volatilization. Eventually at 1065°C these particles proceeded to cut very fine channels emanating from the edges of the original channels, Fig. 6. This behavior paralleled that found for Ni/graphite heated directly in oxygen. Substitution of oxygen by hydrogen at this stage resulted in a temporary loss of activity, which was restored after a period of 20 min at 900°C in the form of straight channels with similar characteristics to those found during the initial hydrogen step.

In a second series of experiments the oxygen cycle was replaced by a steam treatment. Introduction of steam (1 Torr argon saturated with water at 0°C) resulted in "breakup" of the wetted nickel film at 830°C and on continued reaction fresh channels were propagated from the edges of the original ones (i.e., those produced after the first hydrogen treatment) and this behavior became more pronounced at 935°C. It was evident that in this case the rate of the uncatalyzed reaction was insignificant and as a consequence all channels remained parallel-sided throughout the reaction. The reintroduction of 1.0 Torr hydrogen resulted in the continued formation of channels which were created almost instantly when the temperature was raised to 850°C.

Finally, the behavior in 1 Torr of either argon or helium was studied using a fresh batch of specimens which had been heated to 1000°C in hydrogen so that some particles still remained at the leading edge of the channels. Under these ostensibly inert conditions the previously active particles were observed to undergo a rearrangement in shape at 725°C and there was a tendency for areas of the graphite adjacent to the channels to undergo what appeared to be behavior typical of uncatalyzed gasification (edge recession); however, this action was not vigorous enough to completely erase the outline of the channels. This reaction

seemed to predominate in the vicinity of the catalyst particle which after a period of time lost contact with the graphite edges and consequently became isolated. During this time the nickel particles remained stationary on the surface and gradually lost most of the viscous nature, which had been observed in the hydrogen environment. Figure 7 shows the typical appearance of channels after a H<sub>2</sub>-He treatment. It is significant to note that this behavior also occurred if specimens were held *in vacuo* at 1000°C after the initial H<sub>2</sub> treatment. As the temperature was raised to 915°C all activity subsided, indicating that the supply of active species in the graphite had been consumed. Even at 960°C, there was no evidence of particle motion or nucleation of fresh particles from the metal film located along the channel walls. Introduction of steam into the system produced some dramatic changes in the appearance of the specimens and provided the answers to many of the anomalies seen in the inert environments. At 830°C small metal particles started to nucleate at the site of the original channel edges and not at those edges caused by uncatalyzed gasification of the graphite, suggesting that the nickel particles were not directly responsible for this erosion of the graphite surface. A more likely explanation for this action is that H<sub>2</sub> or H atoms, which had diffused into the graphite structure during the reduction cycle were released on heating in inert gas or *in vacuo* and available to attack graphite edges to produce methane (18). This interpretation is also consistent with the observation that during this cycle, uncatalyzed gasification was a temporary effect, persisting for as long as H<sub>2</sub> or H atoms were present.

Quantitative analysis of the channels produced by catalytic hydrogenation revealed a number of interesting features. Perhaps the most startling difference between this system and catalyzed oxidation of graphite was the dependence of



FIG. 6. Transmission micrograph showing both channel broadening by uncatalyzed attack and reformation of nickel particles on a sample which has been heated in 1 Torr hydrogen at 1200°C and then exposed to 5 Torr oxygen at 1065°C.



FIG. 7. Appearance of catalytic channels produced on Ni/graphite after heating in 1.0 Torr  $H_2$  at  $950^\circ C$  followed by exposure to 1.0 Torr He at  $725^\circ C$ .

gasification rate on particle size. Here, at a given temperature, large particles propagated channels at a faster rate than small ones. A plot of channel propagation rate against particle width at the reaction temperature of 1000°C is presented in Fig. 8 and indicates that the catalytic rate is proportional to (particle diameter)<sup>2</sup>. At temperatures above 975°C the linear rate of channel propagation for a given-sized particle was not constant with time. As material was left on the walls of the channel, the particle decreased in size with a concomitant decrease in channeling rate. In order to compensate for this effect in subsequent kinetic evaluations, the rates were normalized to that of the initial sized particle by reference to curves such as that presented in Fig. 8. An Arrhenius plot of the data obtained from 56-nm-diameter particles cutting channels of similar depth yielded an ap-

parent activation energy of  $23.6 \pm 3$  kcal · mole<sup>-1</sup>, Fig. 9, Plot B.

When nickel particles containing silica were reacted with graphite in the presence of H<sub>2</sub>, the catalytic behavior was identical to that seen when ostensibly pure nickel particles on graphite were exposed to this environment. Quantitative measurements of the rates of channel formation, shown on Plot B, Fig. 9, confirm the claim that the silica inclusions in nickel do not impair the catalytic action of these particles towards carbon gasification in a reducing environment.

(d) *Nickel/Graphite—Hydrogen/Steam*

For the most part the behavior of nickel/graphite in wet hydrogen (H<sub>2</sub>/H<sub>2</sub>O 40:1) was identical to that described above for the dry system. The only major qualitative differences were the observations of channel activity at 780°C and iso-

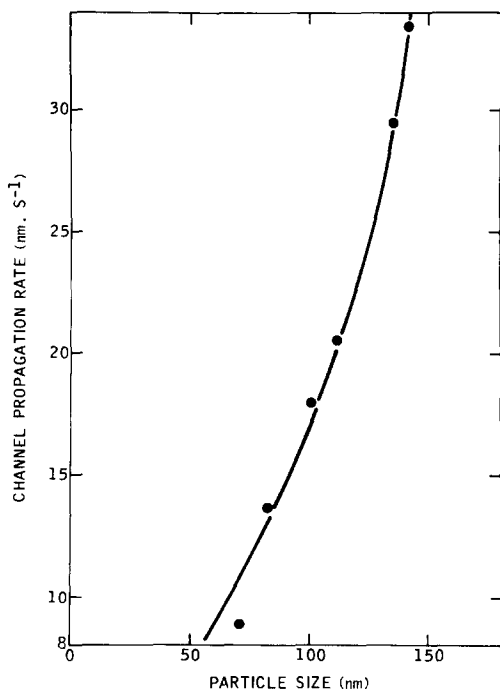


FIG. 8. Relationship between nickel particle size and channel propagation rate at 1000°C in 1 Torr hydrogen.

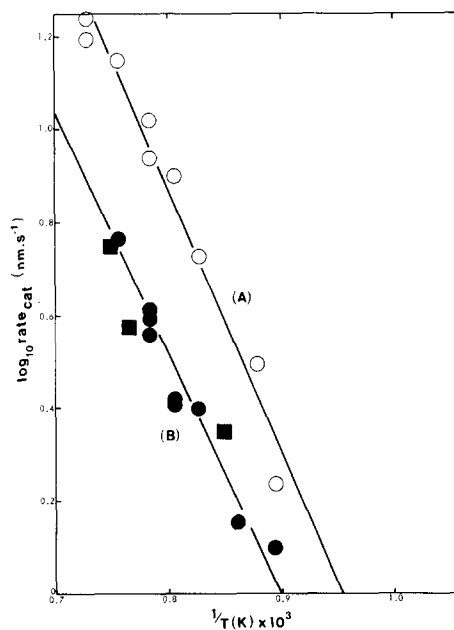


FIG. 9. Arrhenius plots of (A) nickel-catalyzed rate in 1 Torr hydrogen/steam and (B) nickel-catalyzed rate in 1 Torr dry hydrogen, ■ represents those experiments where Si was incorporated in the Ni.

lated examples of particle mobility at about 850°C and participation of uncatalyzed attack at a temperature of 1150°C.

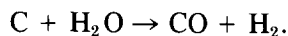
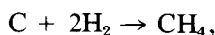
Quantitative kinetic analysis of reaction sequences showed that the apparent activation energy for the catalyzed reaction was  $26.2 \pm 3$  kcal · mole<sup>-1</sup>, i.e., identical to that obtained in the dry system, Fig. 9, Curve A. A comparison of these plots demonstrates, however, that the presence of water increases the catalyzed rate by a factor of 2 at all temperatures. These measurements are all based on similar-sized catalyst particles (56 nm diameter) cutting channels of about the same depth. The points presented in Fig. 9 are the average of at least ten different particles at each temperature.

#### DISCUSSION

This CAEM investigation has revealed several significant facts regarding the catalytic influence of nickel on graphite gasification. In a strongly oxidizing environment, such as oxygen, the major source of carbon gasification is due to uncatalyzed attack. Under such conditions nickel would be present as NiO and one must conclude that this species is not a very effective catalyst for oxidation of carbon. Although some catalytic activity was observed in the presence of steam, a milder oxidizing environment, temperatures of 935°C were required to promote such attack and even in this case the rate was only slightly faster than that of the uncatalyzed reaction. Here the precise nature of the catalytic entity is somewhat less certain, but it is possible that the particles consist of a metallic core surrounded by a thin oxide skin.

A dramatic difference was found in the case of the reducing environments, dry and wet hydrogen. Here the rate of carbon gasification was entirely dependent on the presence of the nickel catalyst, there being virtually no contribution from the uncatalyzed reaction. There is little doubt that in both these systems the cata-

lyst is in the metallic state as McKee (8) has calculated the minimum H<sub>2</sub>/H<sub>2</sub>O ratio required to convert NiO → Ni at 1000°C to be  $1 \times 10^{-2}$  and with the present mixture being 40, nickel will exist as the metal. There is no simple explanation for the finding that the rate of catalyzed gasification was enhanced in the presence of steam. It is possible that in this system carbon removal occurs by two parallel pathways, viz.,



In the presence of excess hydrogen the catalyst will be maintained in the metallic state, the most active catalytic form for the dissociation of water. Further, since the addition of a small amount of water to the hydrogen causes no change in the apparent activation energy for catalyzed carbon gasification one may conclude that the latter reaction is not overall rate determining.

The major distinction between catalyzed reduction and catalyzed oxidation of graphite was the dependence of gasification rate on particle size. The discovery that for a given temperature, under oxidizing conditions the rate of channel propagation varied as the inverse square root of particle width, whereas in reducing conditions the rate had a square dependence with particle size implies that there is a fundamental difference in the mechanisms of these two processes. A similar conclusion was reached in earlier studies from this laboratory, (19, 20) and by Keep *et al.* (7).

It is suggested that in strong oxidizing conditions, carbon at the graphite-catalyst interface is dissolved in the particle and diffuses through a viscous outer layer of the particle and at the cooler face is converted to CO<sub>2</sub>/CO by reaction with atomic or molecular oxygen, thereby creating a carbon concentration gradient in the particle. In reality this process is

probably quite complex, consisting of a number of steps, any of which could be rate determining depending on the nature of the catalyst material. In many respects this mechanism resembles that proposed for the formation of filamentous carbon from nickel-catalyzed decomposition of acetylene (21). The major difference being the fate of the transferred carbon; in filament growth it is deposited, here it is gasified.

Keep *et al.* (7) have presented a lengthy discussion of the possible mechanisms operative in catalytic reduction of graphite. They outlined two basic models, one termed "Mechanism A," which is based largely on the ideas of Rewick *et al.* (22) and Robell *et al.* (23). These workers envisage the role of the metal catalyst as being the dissociation center for hydrogen, producing atoms which diffuse across the metal/carbon interface and react with the carbon to produce methane. A corollary of such a mechanism is that the rate of reaction should increase with increasing surface area of the particles.

An alternative model, which Keep *et al.* (7) refer to as "Mechanism B," involves the dissolution of carbon in the nickel, followed by diffusion to the exposed particle surfaces and eventual reaction with hydrogen to produce methane. This is the mechanism suggested by Grigor'ev *et al.* (6). Although no definite conclusions were reached, the arguments put forth by the Harwell workers (7) tended to favor "Mechanism A" as being the more probable route.

In a previous investigation (16) we demonstrated that silica inclusions in small nickel particles not only reduced carbon solubility in the metal, but also inhibited its diffusion through the catalyst particles. The finding in the present investigation that silica inclusions had no observable influence on the nickel catalyzed hydrogenation of graphite is therefore highly significant in terms of which

mechanism is operative. Based on this result it is clear that "Mechanism B" cannot account for the observed behavior, and as such we believe "Mechanism A" provides the more rational explanation.

It is possible that under the milder oxidizing conditions of steam gasification of graphite the catalytic reaction involves aspects of both the oxidation and reduction mechanisms; i.e., there is a step involving the dissociation of water molecules on the catalyst surface and another where carbon diffusion through the catalyst particle takes place. The question of which of these steps is rate determining will depend on the characteristic properties of a given catalyst system. It should be possible to determine which step is predominating from the dependence of channeling rate with particle size. In the nickel-catalyzed steam gasification reaction the inverse square root dependence of channel formation rate with particle width is suggestive of a diffusion-controlled mechanism. Further support for this conclusion is seen from the excellent agreement between the measured activation energy of  $33.1 \pm 3 \text{ kcal} \cdot \text{mole}^{-1}$  and the literature values for carbon diffusion through nickel, 33.0–34.8  $\text{kcal} \cdot \text{mole}^{-1}$ , listed in Ref. (24). A similar mechanism was also proposed by Figueiredo and Trimm (5) to account for carbon removal from a coked nickel surface in steam.

Comparison of the values of the apparent activation energies obtained here for the nickel catalyzed gasification in dry and wet hydrogen of 23.6 and 26.2  $\text{kcal} \cdot \text{mole}^{-1}$ , respectively, shows close agreement with that reported by Tomita *et al.* (2) of 25  $\text{kcal} \cdot \text{mole}^{-1}$  for the bulk system. It is also interesting to note that the present values are similar to that derived for the removal of surface carbon formed on a single crystal nickel surface during CO hydrogenation of between 22 to 25  $\text{kcal} \cdot \text{mole}^{-1}$  (25). There is some deviation from the figure quoted by Fi-

gueiredo and Trimm (5) of 31–32 kcal · mole<sup>-1</sup> and a major disagreement from that obtained by Keep *et al.* (7) of 52.6 kcal · mole<sup>-1</sup>. This latter discrepancy is difficult to rationalize since their reaction conditions and observed qualitative observations of the nickel/graphite–hydrogen system were similar to those reported here, with the exception of the temperatures at which various events were reported to occur. It should be appreciated that they based their Arrhenius plot on a relatively narrow temperature range of 75°C (975 to 1050 K) and calculated their rate measurements in terms of area of graphite removed per unit time. In the present study the rate is expressed as the linear increase in length of a given channel with time. In an attempt to relate the value of 52.6 kcal · mole<sup>-1</sup> to that of the possible rate-determining step in the reaction, the catalytic dissociation of molecular hydrogen, they drew a comparison of their value with those reported by Brennan and Fletcher (26, 27) for the production of atomic hydrogen from the reaction of molecular hydrogen with platinum, gold, and tungsten, which were between 50.7 to 51.9 kcal · mole<sup>-1</sup>. We see no a priori reason to expect that nickel would behave the same as these three metals, and therefore a comparison of such activation energies is meaningless. In this context it is worthwhile mentioning that using an identical approach to that described here we derived an apparent activation energy for the platinum catalyzed hydrogenation of graphite of 49.3 kcal · mole<sup>-1</sup> (20).

Many of the channeling characteristics of the nickel can be best understood from a consideration of the theoretical aspects. Using the available surface tension data for graphite (28) and nickel (29) one finds the following sequence:

$$\gamma_c^{\text{zigzag}} > \gamma_{\text{Ni}} > \gamma_c^{\text{basal}},$$

where  $\gamma$  is the surface (interfacial) tension. This indicates (a) that nickel will

wet the zigzag face ( $\langle 11\bar{2}0 \rangle$  directions) and the metal particles will move in such a manner to maintain contact with these faces, and (b) the metal should not wet the basal plane of graphite unless it contains defects, steps, etc.

A particle which encounters a channel will rebound since it is approaching a low-surface-tension region. Small particles are expected to become activated first as they attain a higher temperature relatively quicker (their surface/volume is higher than large particles), while large particles, once activated, will move faster than small particles because they have an extensive interface with the graphite.

One of the most important aspects to emerge from this investigation is the identification of the nickel–graphite wetting phenomena. Based on the accumulated data one can formulate some tentative explanations to account for this behavior. At elevated temperatures active nickel particles appear to have liquidlike characteristics and as a consequence surface tension forces are expected to play an important role in the metal–carbon interaction. If the metal–support interaction is stronger than that of the metal–metal bond, then the preferred configuration of the metal will be that of a thin film on the support rather than a discrete particle. It seems that nickel particles sustain their activity for as long as the source of metal atoms is available to generate a very thin coherent layer along the faces of the channels they are creating. In the initial stages of the reaction the particle will assume an equilibrium shape (tending to be hemispherical) and as it loses material, it will approach a limiting shape (disklike). At some point where the cohesive forces of the metal exceed those of surface tension between the particle and the support, the particle will rapidly contract to restore the equilibrium shape and as a consequence the width of the channel will decrease. Ultimately the particle will become completely dissipated and channel

propagation will cease. This interpretation is consistent with the observation that large particles maintain their activity for the longest periods. Clearly, in this case, a larger number of reactive carbon atoms need to be exposed to satisfy the requirements of the nickel particle. It is evident that the interaction is limited to those particles in contact with reactive carbon atoms, i.e., these exposed at edges and steps, there being little change in shape of inactive nickel particles located on perfect regions of the graphite basal planes.

There is little doubt that in the spent condition nickel remains as a thin film along the walls of the channels. Evidence for this conclusion is seen in observations that during regeneration in either oxygen or steam the nickel always nucleated to re-form particles at the site of the initial channel edge. If diffusion of metal into the graphite structure had taken place, as suggested by Keep *et al.* (7), then it is difficult to see how re-formation of particles could occur in such an ordered fashion. A similar conclusion was also reached from Ferromagnetic Resonance studies of the nickel/graphite-hydrogen system (30).

It is clear that the behavior of nickel on graphite can be reversed by cycling in either hydrogen-oxygen or hydrogen-steam. In the former case, the delay in onset of activity in the final hydrogen treatment is probably due to the time required to reduce nickel oxide back to the metallic state. In contrast, in the presence of steam the bulk of the particle probably remains in the metallic state while the surface may be covered with a thin layer of oxide. Under such circumstances complete reduction of the particle would be expected to occur quite readily during the final hydrogen treatment and catalytic channeling activity maintained in an interrupted fashion as was observed.

A more detailed discussion of the precise cause and nature of the interaction between nickel and graphite will be given

in subsequent publications (30, 31). In the meantime it is of interest to note that the morphological behavior of the system bears many similarities to that associated with a strong metal-support interaction (32, 33). This behavior is typified by the metal particles assuming a thin pillbox structure in hydrogen and reverting to the more energetically favored configuration of a hemisphere when the metal-support interaction is severed upon treatment with oxygen or steam.

#### SUMMARY

Controlled-atmosphere electron microscopy studies of the nickel/graphite system have revealed that in a strong oxidizing environment carbon gasification occurred mainly by the uncatalyzed route. Under the milder condition of steam, catalyzed and uncatalyzed reactions occurred at comparable rates. In contrast, the reaction proceeded exclusively via catalyzed attack when experiments were performed in a reducing environment. However, in this case, activity ceased at temperatures of around 1000°C due to what is believed to be the formation of a strong nickel-carbon interaction resulting in the loss of active metal particles.

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