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Catalytic Action of Iron on Graphite in a Hydrocarbon/Steam Environment

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In situ electron microscopy observations of iron particles supported on graphite have revealed some fascinating features when the system was heated in an ethane/steam (40/1) environment. At temperatures below 975°C, iron particles proceeded to attack the graphite from edges by creating channels across the basal plane. As the temperature was progressively raised to 1025°C, the rate of channeling by the large particles (>50 nm width) slowed appreciably; channeling action by particles in the size range 30 to 50 nm ceased, and the smallest particles (<30 nm width) started to move in a reverse direction and deposit carbon within the tracks they had created at lower temperatures. If the temperature was reduced to below 975°C, then gasification activity of all particles was restored. The reversible nature of these processes was demonstrated by multiple cycling between 925 and 1025°C. A rationale is presented to account for this behavior which is based on an increase in the concentration of the ethylene product in the reactant gas at the high temperatures.

INTRODUCTION

Over the past 20 years there have been numerous reports of the influence of metal and metal oxide catalysts on the gasification of graphite in various individual gases, and in a few cases, these studies have been extended to cover the situation where a specimen is reacted in either wet oxygen or wet hydrogen (*1–3*). In the present investigation we have explored the consequences of heating a metal/graphite system to high temperatures in a wet hydrocarbon environment, conditions which might be expected to produce unpredictable events.

Using controlled atmosphere electron microscopy we have been able to directly observe the behavior of iron particles supported on graphite when reacted in an ethane/steam environment. Iron was selected as the metal since it is known to be an active carbon gasification catalyst when maintained in the metallic state (*4, 5*), and also, it is one of the most active metals for catalyzing the formation of carbon when reacted in a hydrocarbon environment (*6*). During the course of these experiments we have discovered a most fascinating phenomenon associated with some of the smaller iron particles when heated in an ethane/steam mixture. This is the ability to switch their catalytic action from that of a gasifying agent to become promoters of carbon deposition at certain critical conditions, and furthermore, this action is quite reversible.

EXPERIMENTAL

The specimens used for controlled atmosphere electron microscopy experiments were prepared from single-crystal graphite (Ticonderoga) and contained sections which were between 15 and 100 nm thick. Iron was introduced onto the graphite by evaporation of the metal (99.99% purity) from a tungsten filament at a residual pressure of 5×10^{-6} Torr. The conditions were chosen so as to produce a metal film at least 1 atom in average thickness.

The reactant gases used in this work, ethane, ethane/5% hydrogen, and ethane/5% ethylene, had stated purities of 99.99% (Scientific Gas Products) and were used without further purification. Steam was

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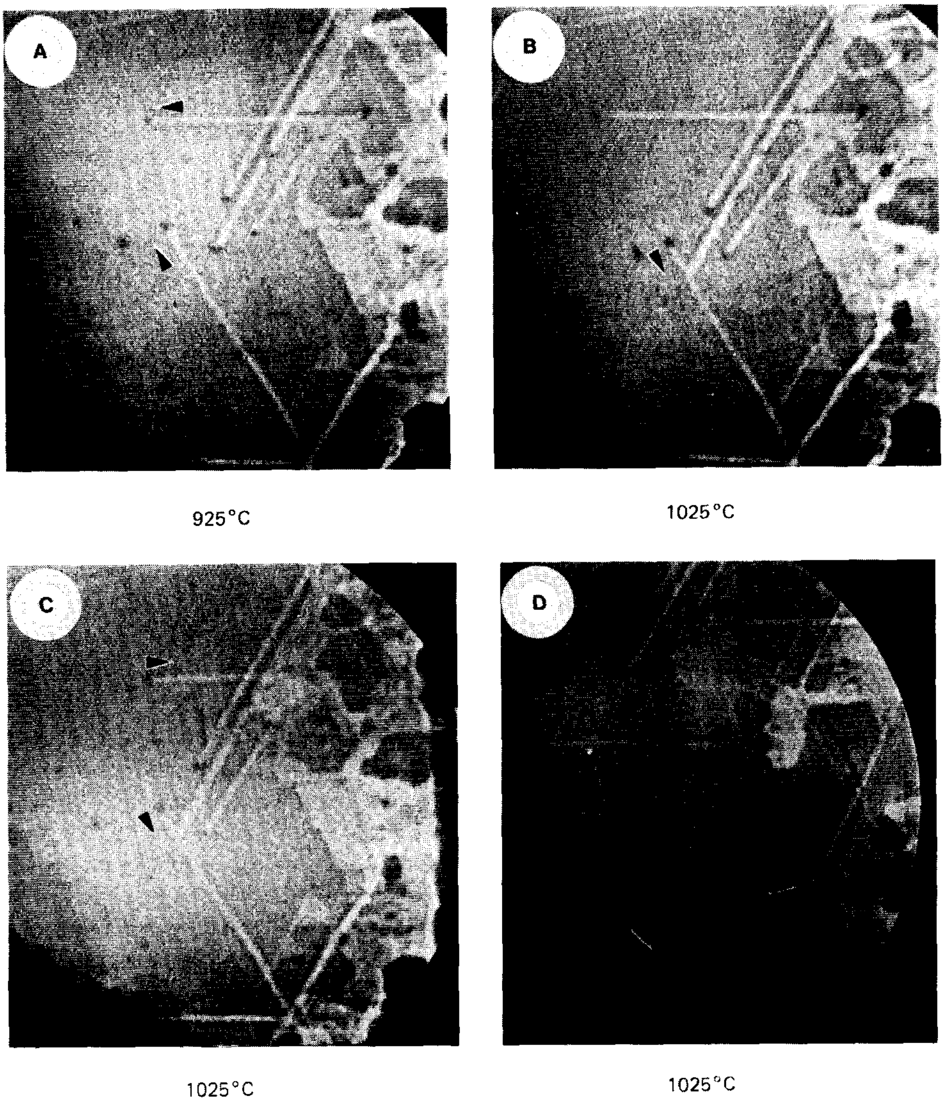
added to these gases by allowing them to flow through a bubbler containing deionized water maintained at 20°C, a procedure which created a gas/steam ratio of about 40/1.

RESULTS

When iron/graphite specimens were heated in 1.0 Torr, ethane/steam nucleation of the evaporated metal film into discrete particles was observed at 570°C. Catalytic attack of the graphite by the channeling mode commenced at 715°C and this behavior became more prolific as the temperature was progressively raised.

The propagation rate of all channels appeared to increase in a systematic manner up to 975°C and, provided that this temperature was not exceeded, subsequent temperature cycling did not produce any deviation from the expected behavior. However, at temperatures in excessof 975°C, particles



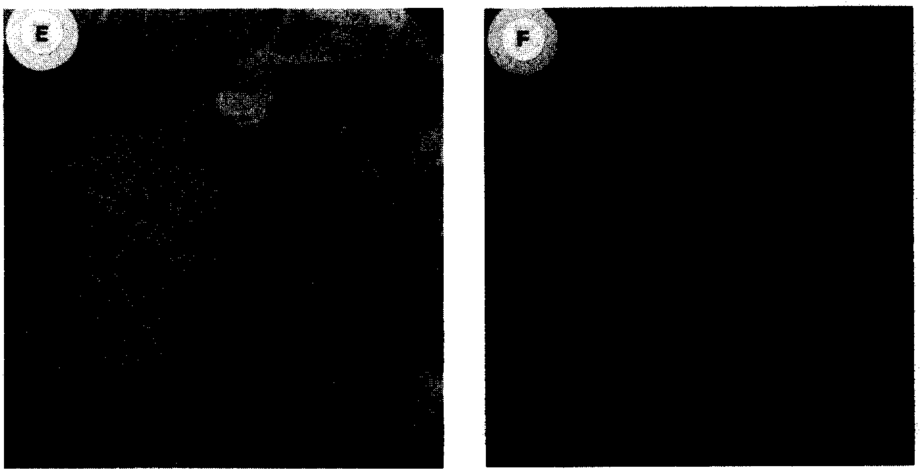
925°C

1025°C

1025°C

1025°C

FIG. 1. (A–F) Sequence showing the reversible behavior of an iron particle (arrows) when cycled between 975 and 1025°C in 1.0 Torr ethane/steam.



925°C 1025°C

FIG. 1.—*Continued.*

in the range of 10 to 30 nm gradually lost their activity and there was a significant reduction in the forward motion of larger particles. An even more dramatic distinction in particle behavior was observed on raising the temperature to 1025°C. Under these conditions some of the smallest catalyst particles (10–15 nm diam) started to move in a reverse direction to that of their original motion and still remained within the channels they had created. This reverse motion was accompanied by deposition of material at the trailing faces of the particles so that in many cases it was difficult to discern where the tracks of the channels had been. Figure 1 (A–F) is a sequence of photographs taken from the video record showing this extraordinary phenomenon. When the temperature was raised still higher the limiting size of particles exhibiting this behavior also increased, so that at 1100°C particles up to 30 nm in size fell into this category. If the temperature was reduced to 925°C, then these particles proceeded to reverse direction once again and create channels along the original tracks, depicted schematically in Fig. 2. The time delay for a particle to switch from moving in one direction to the other once the critical temperature had been reached was of the order of a few seconds. In some experiments the extent of the reversible nature of these processes was demonstrated by switching between 925 and 1025°C for up to six cycles. At 1025°C, particles in the intermediate size range, 30 to 50 nm, came to a complete halt, and the largest particles, >50 nm diam, gradually slowed down in their forward rate, and this aspect became more apparent as the temperature was progressively raised to 1100°C.

Figure 3 shows the forward (gasification) and reverse (carbon deposition) rate measurements made from a 21-nm-sized particle which was taken through three temperature cycles between 850 and 1050°C after an initial temperature excursion from room

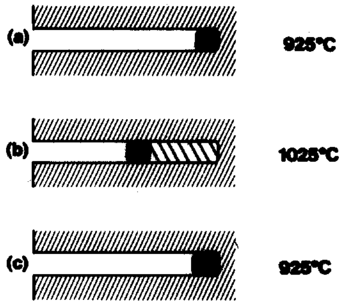


FIG. 2. Schematic representation of the catalytic reversal action of iron on graphite.

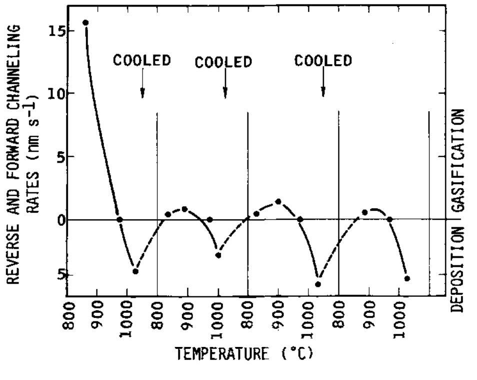


FIG. 3. Example showing the rates of gasification and deposition of a 21-nm-sized iron particle as a function of temperature in 1.0 Torr ethane/steam.

temperature up to 1050°C. Consistent with the findings from larger particles, it is found that the initial gasification rate of small particles is never reestablished; however, during subsequent temperature cycling treatments the behavior of these particles appears to be completely reversible. Examination of the rates of the forward and reverse motions as a function of particle size and temperature reveals major differences in the mechanisms of these two processes. A plot of the rate of the reverse motion at 1100°C against particle width shows that there is an inverse linear dependence, $r \propto l/d$, Fig. 4. These data were obtained from catalyst particles which had cut channels of similar depth and during the reverse process were depositing sufficient carbon to erase all traces of the previous existence of such channels. As the temperature was raised so the rate of infilling of channels increased. An Arrhenius plot of the data obtained from 14-nm-diam particles undergoing this phenomenon yielded an apparent activation energy of 32.5 ± 4 kcal mole^{-1} (Fig. 5). In contrast, during the forward motion, the rate–particle size relationship followed that previously reported for catalytic hydrogenation of graphite; i.e., $r \propto d^2$ (7), and the apparent activation energy of this process was 24.3 ± 3 kcal mole^{-1} (Fig. 5).

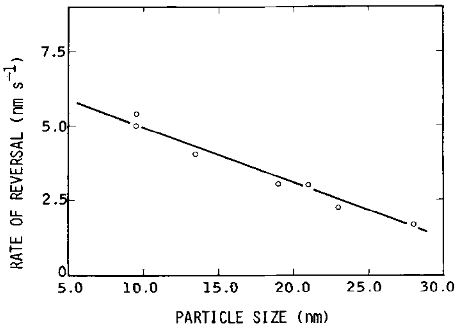


FIG. 4. Relationship between the reverse motion and particle width at 1000°C.

In a second series of experiments iron/graphite specimens were reacted in 1.0 Torr ethane/steam containing 5% added hydrogen. In this case, the smaller particles up to 30 nm diam continued to exhibit the forward and reverse motion but at a significantly higher temperature than the conditions stated for ethane/steam; channeling action persisted up to 975°C and evidence of reverse motion of some of these particles was observed at 1075°C.

Finally, the action of iron on graphite was studied in the presence of 1.0 Torr ethane/steam containing 5% added ethylene. Although particle nucleation was once again achieved at 570°C, on continued reaction it became evident that the behavior of iron in these experiments was quite differ-

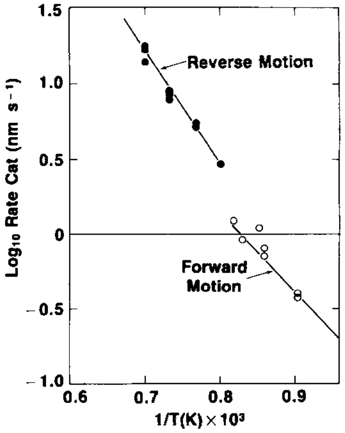


FIG. 5. Arrhenius plots of catalyzed gasification (forward motion) and catalyzed deposition (reverse motion) from 14-nm iron particles/graphite heated in 1.0 Torr ethane/steam.

ent from that found in the previous systems. At 680°C, particles located at the graphite edge sites transformed from a nonwetting to a wetting condition and then slowly proceeded to spread along the edges and form a thin coating. These regions started to undergo recession at about 700°C in a very orderly manner, which resulted in the edges acquiring a hexagonal faceted profile. The rate of edge recession increased systematically as the temperature was progressively raised to 925°C when an unexpected decrease in catalytic gasification was observed and at 945°C complete suppression of edge movement occurred. Increasing the temperature did not lead to reformation of the gasified edges; however, it was evident that a carbon overlayer was being produced over the entire specimen surface, indicating that at these elevated temperatures carbon deposition was the prevailing reaction. Provided that the specimen was not held at temperatures in excess of 945°C for extended periods of time, then lowering the temperature to about 875°C resulted in the restoration of the catalytic gasification activity.

DISCUSSION

The results of this investigation provide an excellent example of how catalyst particle size can have a profound effect on the selectivity of a reaction. When iron/graphite specimens were heated in ethane/steam to temperatures of 1025°C or higher, a range of catalyst particle characteristics was observed. Large particles (>50 nm diam) slowed down in their foward channeling motion, a feature which became more pronounced as the temperature was raised to 1100°C; intermediate-sized particles (30 to 50 nm diam) lost their catalytic activity; and small particles (<30 nm diam) exhibited a reversal in catalytic action, becoming catalysts for carbon deposition. In order to understand these features we must first consider the chemical state of the catalyst and that of the ambient gas.

At 900°C, the partial pressure of H_2 created in an ethane/steam (40/1) environment is sufficient to make H_2/H_2O greater than 2, and under these conditions γ-Fe is the stable thermodynamic phase. In the present work the iron is supported on graphite, which itself is a strong reducing agent which makes the conditions even more favorable toward γ-Fe formation. Finally, Mössbauer spectroscopic studies of iron/graphite samples, treated in 1 atm of flowing ethane/steam (40/1) at 900°C, indicate that under these conditions iron is present as γ-Fe (*8*), and this phase remains thermodynamically stable up to the highest temperature used in the present study (*9*). It is, therefore, extremely doubtful that phase changes in the catalyst account for the various observed modifications in particle behavior. It is more likely that these various events are the result of a competition between two catalytic mechanisms; hydrogenation of graphite and carbon deposition.

At temperatures below 975°C it is probable that under the present conditions the prevailing carbon/gas reaction is steam gasification. Above 975°C, the composition of the gas phase undergoes a significant change due to the increase in the rate of ethane decomposition:

$$C_2H_6 \rightarrow C_2H_4 + H_2. \qquad (1)$$

As a consequence, sufficient ethylene and hydrogen are produced so that the gasification reaction is now controlled by catalytic hydrogenation and the concentration of unsaturated hydrocarbons is raised to a level where a potentially carbon-depositing environment is created with respect to small iron particles. Support for the notion that gasification at this stage is occurring by catalytic hydrogenation rather than by catalyzed steam gasification is seen from the agreement between the value for the apparent activation energy of the former reaction of 23.6 kcal mole^{-1} (*5*) and that reported here of 24.3 kcal mole^{-1}, which is quite different from the value of 40.8 kcal mole^{-1} found for the Fe/graphite–steam reaction (*5*).

The ramifications of this situation can best be understood from a consideration of the manner by which the kinetics of catalytic hydrogenation of graphite and catalytic carbon formation vary with metal particle size. The rate of the catalytic hydrogenation reaction increases with the square of the particle size, which points to a surface-controlled process (*7*). In contrast, the rate of the catalytic carbon formation reaction is inversely proportional to the particle size (Fig. 4), suggesting that diffusion of carbon through the particle is the rate-limiting step (*10*). Consistent with this notion is the fact that the measured activation energy for channel reversal, 32.5 kcal mole^{-1}, is in close agreement with the value for diffusion fo carbon through γ-Fe (*11*).

An overlay of these two curve forms, shown for a hypothetical situation (Fig. 6), provides the key to this whole enigma. At the point where the two curves intersect, the rate of carbon removal and carbon formation are equal, and as a consequence, one would expect to find a narrow size range of particles which gradually lose their activity and come to a standstill. At the large-particle size range the hydrogenation reaction is favored, albeit at a reduced rate compared to that found in a H_2/H_2O environment (*5*), and at the small-particle regime, carbon formation predominates. The dotted curves depict the expected shift in the reactivity pattern that would accompany an increase in temperature. From such a rationale one would predict that the rate of catalytic hydrogenation from a given-sized large particle would decrease, whereas the rate of carbon formation from a given-sized small particle would increase, and furthermore, the limiting size of particles exhibiting this latter behavior should increase with increasing temperature. All of these features were observed experimentally.

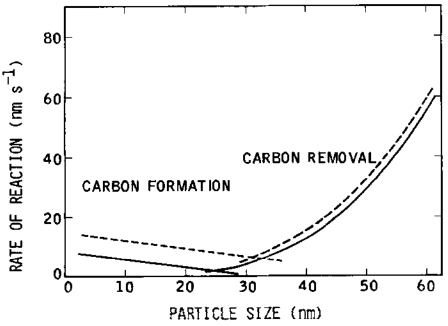


FIG. 6. Overlay of the particle size dependence for carbon deposition and carbon gasification in a reducing environment at 1000°C. Dotted lines indicate the expected shift with an increase in temperature.

Addition of a small amount of H_2 to the C_2H_6/H_2O mixture would be expected to enhance the rate of the catalytic hydrogenation of graphite at the expense of the carbon-formation process. Consistent with these arguments was the finding that in a (95% C_2H_6–5% H_2)/H_2O (40/1) environment higher temperatures were required to induce the onset of the channel reversal phenomenon.

In contrast, one would predict that adding a small amount of C_2H_4 to the C_2H_6/H_2O mixture would result in a lowering of the onset temperature for carbon deposition. Unfortunately, catalytic attack did not occur by the channeling mode when iron/graphite samples were reacted in (95% C_2H_6–5% C_2H_4)/H_2O (40 : 1), so this postulate could not be tested. Nevertheless, it is significant that catalyzed gasification by the edge recession mode was terminated at a relatively low temperature in this system and could only be restored by reducing the temperature.

SUMMARY

This study has revealed some fascinating behavior of small iron particles supported on graphite when heated in a hydrocarbon/steam environment. Furthermore, the observations highlight the manner by which catalytic action can be modified by the participation of gas-phase products.

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