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Effect of Copper on the Decomposition of Ethylene over an Iron Catalyst

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The catalytic properties of a series of unsupported copper–iron powders of varying composition were investigated by using a probe reaction of ethylene and hydrogen at temperatures over the range 450 to 800°C. Analysis of both the gas-phase products and the solid carbon, mainly in the form of filamentous structures, produced during the reaction provided an *in situ* method for monitoring the changes in the nature of the bimetallic surfaces under reaction conditions. Although these metals exhibit only limited miscibility in each other the reaction between ethylene and hydrogen over the bimetallic powders resulted in higher carbon yields and altered selectivities to gas-phase products compared to that observed with the single components under the same conditions. The addition of only 2 wt% copper to iron caused a 20-fold increase in the amount of carbon filaments formed compared to that produced on pure iron at 600°C. This behavior cannot be rationalized simply by an increase in metal dispersion; instead, one may speculate that the presence of a small amount of copper is capable of inducing electronic perturbations in the iron atoms, which results in a modification in the chemisorption characteristics of ethylene on such a surface. The presence of hydrogen in the gaseous reactant was found to facilitate the interaction between the olefin and the bimetallic surface, resulting in increased yields of both solid carbon and ethane. It is suggested that during the interaction of hydrocarbons with metals the particles adopt a morphology in which there are at least two distinct faces; a set which are only capable of adsorbing and decomposing hydrocarbons, and others that will precipitate dissolved carbon in the form of graphite platelets. Under such circumstances there are always a set of faces that are completely free of deposited carbon and available for continued catalytic action.

INTRODUCTION

The modification of the catalytic behavior of a metal by the addition of controlled amounts of other metals has been used extensively in order to alter both the activity and selectivity behavior as well as to control the deactivation of active surfaces with respect to poisoning and carbon deposition (1–5). It is this latter aspect that it still not well understood and presents some challenges to the various mechanisms that have been proposed to account for carbon deposition on metal catalyst particles. McCarty and co-workers (6, 7) used temperature-programmed reaction techniques to establish the existence of several forms of carbon on deactivated nickel catalysts. From these studies graphite overlayers and filamentous carbon growths were identified as being the most prevalent types associated with metals. The graphitic form of deposit tends to encapsulate the particle surface in contact with the reactant gas and thus normally results in rapid deactivation of the catalyst. In contrast, filamentous carbon is produced by a process in which carbon diffuses through the particle and precipitates at the rear faces, thereby leaving the exposed faces free to undergo continued reaction. The net result of this behavior is that the catalyst system can accumulate large amounts of carbon and maintain activity for prolonged periods of time (8).

Kim and co-workers (9) studied the interaction of selected hydrocarbons with copper–nickel and nickel catalysts and focused attention on the formation of solid carbon deposits. They found that when the alloy was reacted in pure ethylene at 600°C, prolific carbon filament growth occurred, whereas under the same conditions only trace amounts were deposited on nickel. It was suggested that on the pure nickel surface in the absence of any other gas-phase reactant, there would be a tendency for ethylene molecules to adsorb in a conformation such that the C=C bond was "parallel" to the solid surface. At saturation coverage there would be a high probability that these adsorbed species would interact with each other and eventually condense to form a graphitic overlayer. In contrast, when ethylene was adsorbed on the bimetallic surface, since copper was incapable of chemisorbing the hydrocarbon, it was proposed that other molecular arrangements could be formed. For the situation where ethylene encountered two unperturbed adjacent nickel atoms, adsorption would occur in similar fashion to that proposed for the pure metal. On the other hand, when adsorption

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took place at a nickel atom where the only unoccupied nearest neighbor was a copper atom, then it was probable that ethylene was linked to the surface in an "end-on" arrangement. Under these conditions, catalyst deactivation via the encapsulation process would be less likely and there would be a greater potential for carbon species formed on the surface to dissolve and diffuse through the particle and eventually precipitate to form a filament.

In the current investigation we have attempted to extend the concepts developed for copper–nickel, a system where the components form alloys over the whole composition range, to copper–iron, one in which the two metals exhibit only limited miscibility in each other. Over the range of temperatures used in the present investigation the solubility of copper in α-iron is 0.3 wt% and for iron in copper, 0.25 wt% (10). Recently, Wielers and co-workers (11) have reported that the amount of solid carbon produced from the interaction of a silica-supported iron–copper (4 : 1) with a CO/H_2 mixture at 400°C was about an order of magnitude higher than that of iron/silica treated under the same conditions. This behavior was rationalized according to the notion that copper enhanced the formation of an active iron face consisting of a mixture of metallic iron and iron carbide, and that carbon, in the form of filaments, was produced at the iron carbide/copper interface. Other workers (12, 13) have also examined the influence of copper addition to iron for the Fischer–Tropsch reaction and found that while copper promoted the reduction of iron oxide, it did not appear to exert any influence on the carbon deposition reaction.

Surface science studies have shown that the chemisorption characteristics of hydrocarbons on iron were extremely sensitive to small differences in geometric and electronic properties of both the hydrocarbon molecule and the pretreatment of the metal surface (14–20). Cooper and Trimm (15) found that the rate of carbon deposition from the iron-catalyzed decomposition of propylene over the range 400 to 700°C was dependent on the geometry of the metal surface; carbon formation decreasing in the order

$$\text{Fe}(100) \sim \text{polycrystalline foils} > \text{Fe}(110).$$

It was claimed that ethylene adsorption on the carbide-covered iron surface lead to the formation of a π complex, where the bonding was relatively weak but still significantly stronger than that between the olefin and a copper surface (18).

We have used the interaction of ethylene with the bimetallic system as a probe in an attempt to understand the effect of the addition of copper on the catalytic behavior of iron. Based on previous work from this laboratory it was expected that the composition of the gas-phase products formed in the reaction would be sensitive to either electronic or geometric perturbations of the copper–iron surface while the amount and characteristics of the solid carbon would depend on both bulk and surface properties of the particles (21).

EXPERIMENTAL

Materials

Copper–iron powders of different compositions were prepared by coprecipitation of the respective metal carbonates from metal nitrate solutions using ammonium bicarbonate, according to a previously outlined procedure (22). The precipitate was dried in an oven for 24 h, then ground and calcined in air for 4 h at 400°C to convert the carbonates to mixed oxides. The calcined catalyst was then ground and reduced in a 100 cc/min flow of 10% H_2/He at 500°C for 2 h. The reduced catalyst was cooled to room temperature under He and then passivated in a 2% air/He mixture for 1 h before removal from the reactor. BET surface area measurements were carried out with a Coulter Omnisorp 100CX unit using nitrogen adsorption at −196°C. Values in the range 1.0 to 2.0 m^2/g were obtained for the metal and bimetallic powders used in this work. X-ray diffraction analysis of the reduced and passivated bimetallics was performed using a Scintag diffractometer. Since the catalyst particles in this type of experiment are partially or, in some cases, completely covered by the carbon deposit at the conclusion of the reaction it is a futile exercise to attempt to determine metal surface area by chemisorption measurements. In order to overcome this dilemma we have determined the average metal size of metal particles associated with carbon filaments from transmission microscopy examinations. Particle size distributions were obtained from measurements of over 500 particles of each catalyst system.

Pure copper and iron powders were also prepared according to the above procedure. The gases used in this study, hydrogen (99.999%), helium (99.99%) and ethylene (99.5%) were obtained from MG Industries and were used without further purification. Reagent grade cupric nitrate $[Cu(NO_3) \cdot 3H_2O]$ and ferric nitrate $[Fe(NO_3)_3 \cdot 9H_2O]$ were obtained from Fischer Scientific for the catalyst preparation.

Apparatus and Procedures

Fifty milligrams of the previously reduced and passivated bimetallic copper–iron samples contained in a ceramic boat were given a further reduction treatment in a quartz reactor tube placed horizontally in a Lindberg furnace at 500°C for 2 h in a 100 cc/min flow of 10% H_2/He mixture, which was maintained by MKS mass flow controllers. The temperature was raised to the desired level and the reaction carried out for 5 h in an ethylene/hydrogen (1 : 4) mixture at a total flow rate of 100 cc/min. The effect of hydrogen on the reaction was studied using a copper–iron (3 : 7) powder and varying the hydrogen partial pressure while maintaining that of ethylene at a constant value. The total flow rate was set at 100 cc/min by using helium as a makeup gas. By using this procedure the influence of changing the ethylene to hydrogen ratio over the range 1 : 0 to 1 : 9 was investigated. The gas-phase products were analyzed at regular intervals using a gas chromatography unit (Varian 3400) equipped with a 30-m megabore column (GS-Q). Carbon and hydrogen atom balances in conjunction with the relative concentrations of the respective components were employed to obtain the various product yields, and the mass of carbon deposited on the catalyst was also determined at the completion of a particular reaction. In all cases the calculated and measured weights of solid carbon were within ±5%.

The structural characteristics of the solid carbon deposits produced on pure iron and copper–iron particles from the interaction with ethylene containing environments were established from examinations performed in a JEOL 100CX transmission electron microscope. The point to point resolution of the electron microscope was estimated to be 0.24 nm. Transmission specimens were prepared by application of a drop of an ultrasonic dispersion of the carbon deposit in iso-butanol onto a holey carbon film. In addition, when the electron microscope was operated in the diffraction mode it was possible to assess the degree of crystalline perfection of the deposited material as a function of catalyst composition.

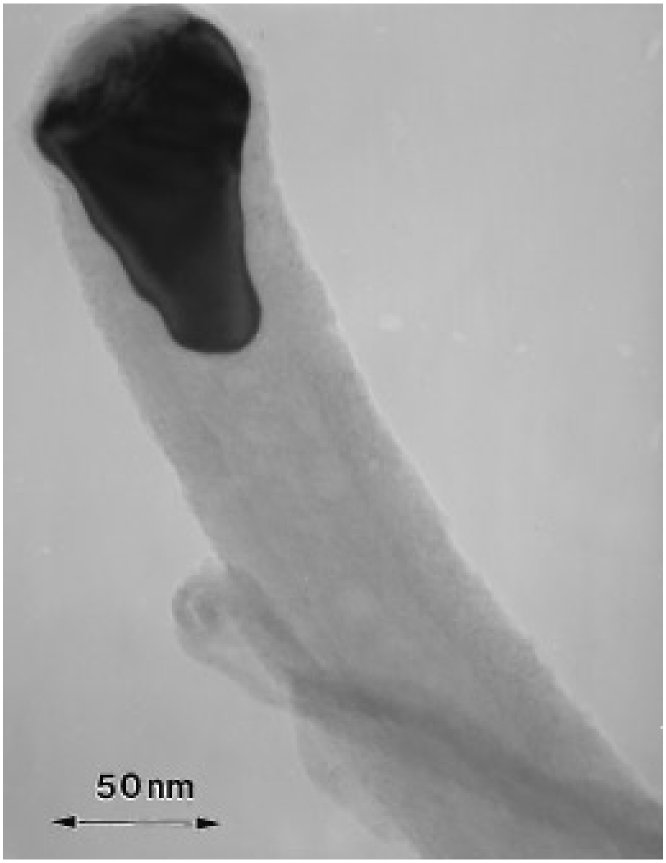

FIG. 1. Transmission electron micrograph showing the appearance of a filamentous carbon structure produced from the interaction of iron with ethylene/hydrogen (1 : 4) at 600°C.

RESULTS

1. Characterization of Bimetallic Powders

Peaks corresponding to metallic copper and metallic iron were observed in the X-ray diffraction patterns of all the bimetallic powders. No indication of bulk alloying was evident at room temperature, however, the possibility of a "strong interaction between the two metals" at the surface cannot be dismissed with samples under reaction conditions. The presence of the pure metallic components coupled with the absence of bulk metal oxides in these systems at room temperature confirms the effectiveness of the passivation procedure in 2% air after reduction.

2. Characterization of Carbon Deposits

Examination of a number of representative catalyst samples showed that following reaction in an ethylene-containing environment at 600°C the deposits produced on iron and the copper–iron bimetallic powders were almost entirely in the form of filamentous carbon, as seen from Figs. 1 and 2. It was apparent that the structures associated with iron had grown exclusively by the "whisker-like" mode, where the catalyst particle was located at the tip of the filament. In the case of the bimetallic systems, while the aforementioned type of filaments appeared to predominant, there was evidence for the formation of bidirectional growths where the catalyst particle was embedded within the filament structure. Despite the similarity in morphological characteristics major differences in the crystalline perfection was detected in the filaments derived from the pure iron and bimetallic catalyst systems. The material produced from the interaction of copper–iron particles with ethylene at temperatures of 600°C or higher was highly graphitic in nature with the platelets aligned in a direction parallel to the fiber axis. In sharp contract, the electron diffraction patterns of filaments generated from the iron-catalyzed decomposition of the hydrocarbon gave diffuse rings, indicative of a relatively amorphous structure.

3. Catalyst Particle Size Determinations

It should be appreciated that the presence of the carbon structure provides a means of preserving the shape of the metal catalyst in the reactive state during subsequent cooling to room temperature, and therefore postreaction exam-

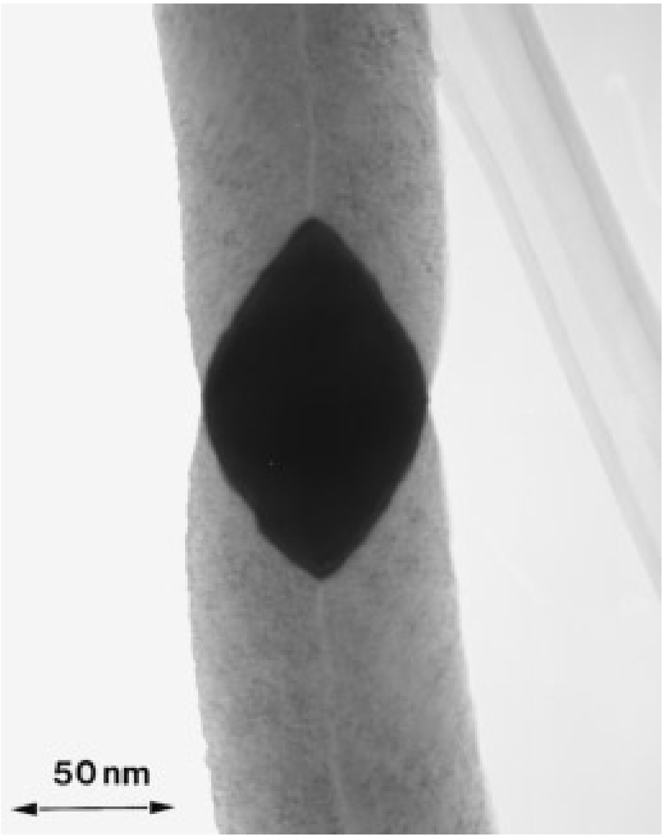

FIG. 2. Transmission electron micrograph of a filament formed by the bidirectional mode on copper-iron (3 : 7) during reaction with ethylene/hydrogen (1 : 4) at 600°C.

ination in the transmission electron microscope gives an accurate picture of the morphological characteristics of the particle. The sizes of metal particles associated with carbon filaments were determined from measurements taken from many different regions of a given sample and the values are expressed as a function of the catalyst composition in Fig. 3. The samples were all treated in an ethylene/hydrogen (1 : 4) mixture at 600°C for 5 h. Inspection of the histogram shows that while the larger average-sized particles tend to be produced from powders containing a large fraction of iron, it is difficult to discern any overall trend with respect to catalyst composition.

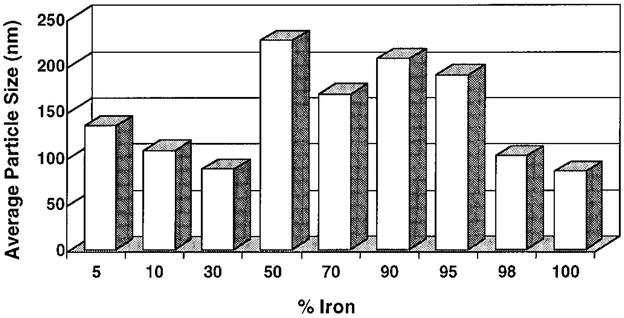

FIG. 3. Histogram showing the average metal particle size as a function of catalyst composition following reaction in an ethylene/hydrogen (1 : 4) mixture at 600°C for a period of 5.0 h.

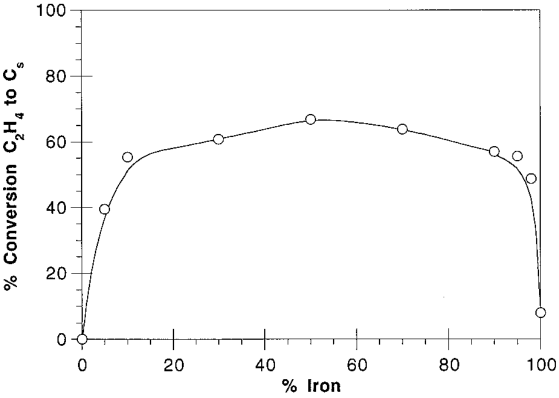

FIG. 4. Influence of catalyst composition on the amount of solid carbon produced from the decomposition of ethylene/hydrogen (1 : 4) after 1.0 h reaction at 600°C.

4. *Flow Reactor Studies*

4.1. Effect of copper–iron ratio on carbon deposition. The yields of gaseous and solid carbon products from the interaction of a series of copper–iron powders of varying composition with ethylene/hydrogen (1 : 4) after 1.0 h at 600°C are presented in Fig. 4 and Table 1. From these data it can be seen that under the prevailing reaction conditions no solid carbon was deposited on the pure copper powder and only 0.18 g was produced on the pure iron powder. The addition of only 5% iron to copper and at the other extreme 2% copper to iron resulted in a dramatic

TABLE 1

Comparison of Carbon Distribution from Ethylene/Hydrogen (1 : 4) over Copper–Iron, Copper, and Iron after 1.0 h at 600°C

Sample Cu : Fe ratio	% CH_4	% C_2H_4	% C_2H_6	% solid carbon
1 : 0	0.30	68.1	31.6	0.0
19 : 1	1.23	24.9	21.3	52.6
9 : 1	0.98	24.9	18.8	55.3
7 : 3	0.94	22.1	16.2	60.8
5 : 5	3.97	11.4	19.8	66.8
3 : 7	1.96	13.3	20.9	63.8
1 : 9	2.69	17.9	22.5	56.9
19 : 1	1.64	22.8	22.8	59.6
49 : 1	0.94	25.2	25.2	54.8
0 : 1	0.53	61.3	30.2	8.0

increase in the yields of carbon, compared to those observed with the single metals, the carbon yields from the bimetallics being 20 to 60 times greater than those obtained from the pure iron powder. The yield of carbon exhibited a steady rise as the fraction of iron in the bimetallics was increased, reaching a maximum value with a copper–iron (1 : 9) catalyst.

The selectivity profile of the bimetallic powders is quite different from that of either of the pure metals. Ethylene exhibits a 40% conversion over pure copper powder with 30% going to C_2H_6, 0.3% to CH_4, and 9.7% going to higher hydrocarbons (0.75 selectivity to C_2H_6). The pure iron surface is very selective toward C_2H_6 formation even though the ethylene conversion level rapidly drops off to 30%; of this amount 27.3% goes to the formation of C_2H_6, while 2% goes to solid carbon and 0.7% to CH_4 (selectivity to C_2H_6 is 0.91). These behavioral patterns are to be contrasted with those of the copper–iron systems where the ethylene conversions are significantly higher (75–90%), but the selectivity is altered: about 50–70% forms solid carbon, 1–4% is converted into CH_4, and 16–25% goes to C_2H_6 (selectivity to C_2H_6 is only 0.2–0.3).

4.2. Effect of copper–iron ratio on activity maintenance. The interaction between a series of copper–iron powders and ethylene/hydrogen (1 : 4) was conducted at 600°C over a prolonged period of time, 5 h, in order to monitor possible modifications in the nature of the bimetallic surfaces and to gain an insight into the chemical state of the surface under reaction conditions. The different activity maintenance profiles of a selected number of copper–iron catalysts for carbon deposition are shown in Fig. 5, while those of the same catalysts for C_2H_6 formation are presented in Fig. 6. The pure iron powder initially exhibited a high solid carbon yield of about 60%, and after a short time on stream the metal underwent rapid deactivation, causing the deposit formation to diminish to less than 10%. Addition of only 2% copper to iron (1 : 49 Cu–Fe) resulted in a substantial improvement in catalyst lifetime, and as the level of copper in the bimetallic was progressively raised, the activity toward carbon formation began to reach steady state (1 : 19 Cu–Fe) and even increase with time (1 : 9 and 3 : 7 Cu–Fe). At copper contents of 50% and higher a decrease in carbon deposition activity with time was once again observed, culminating in a state where no solid carbon was formed when the powder consisted of pure copper. For certain compositions, the bimetallic is still active at the end of 5 h of reaction.

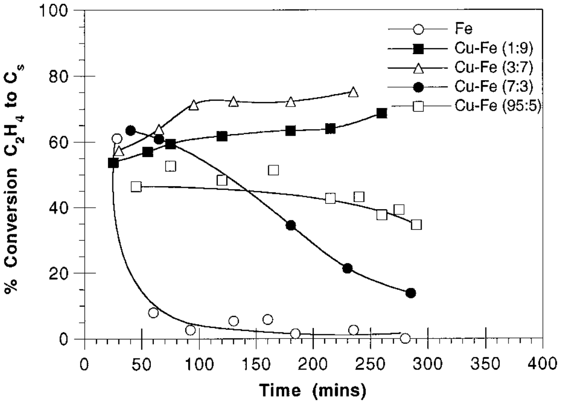

FIG. 5. Amount of solid carbon formed from the decomposition of ethylene/hydrogen (1 : 4) at 600°C over various copper-iron catalysts as a function of reaction time.

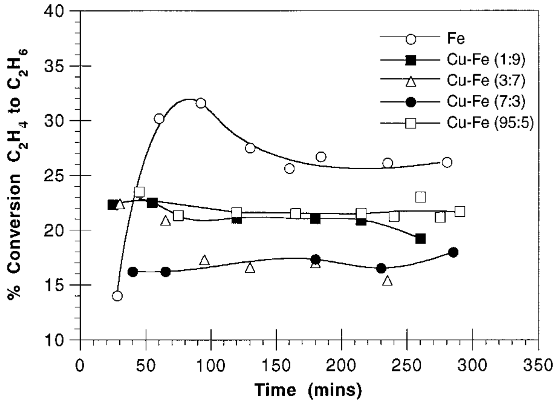

FIG. 6. Amount of ethane produced from the decomposition of ethylene/hydrogen (1 : 4) at 600°C over various copper-iron catalysts as a function of reaction time.

Inspection of the data presented in Fig. 6 shows that the activity for C_2H_6 formation decreased slowly with time, and moreover, similar dependencies were found for pure iron and the bimetallic systems. It is clear, therefore, that the activity maintenance profiles for the gas-phase products are quite different from those observed for the growth of solid carbon.

4.3. Effect of hydrogen on carbon deposition and catalyst selectivity. The effect of adding increasing amounts of hydrogen to the ethylene feed on the formation of solid carbon over a copper–iron (3 : 7) catalyst at 600°C is shown in Fig. 7. For comparison purposes we have also included on this plot the corresponding data for copper–nickel (3 : 7) obtained in a previous study (9). From these plots it is apparent that for most of the reactant composition range, hydrogen has a diametrically opposite effect on the carbon deposition characteristics of the two bimetallic systems. As the hydrogen content of the gas is increased, there is a gradual decrease in the amount of solid carbon formed in the copper–nickel system. In contrast, when a corresponding series of experiments were performed with the copper–iron powders the fraction of ethylene converted to solid carbon exhibited a progressive rise, reaching a maximum

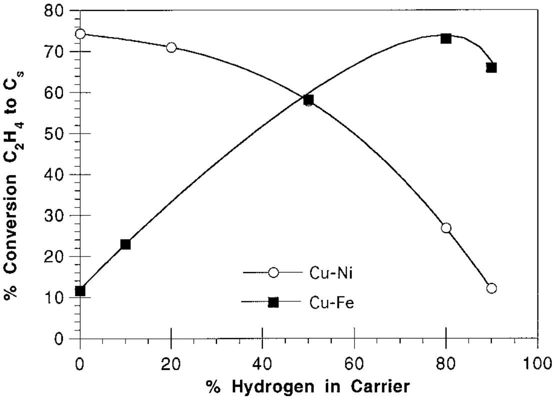

FIG. 7. Effect of hydrogen on the amount of solid carbon produced from copper-nickel (3 : 7) and copper-iron (3 : 7) catalyzed decomposition of ethylene at 600°C (reaction time 1.5 h).

level from a mixture containing 80% hydrogen and then decreasing at higher concentrations. It was also demonstrated that in order to sustain the optimum catalytic carbon deposition activity it was necessary to maintain the level of hydrogen at 80% throughout the reaction period. In experiments where hydrogen was removed from the system after a few hours of reaction it was observed that the carbon filament formation decreased dramatically.

An analogous set of experiments were performed with pure iron and the observed dependence of solid carbon formation on the percent of hydrogen in the hydrocarbon reactant is compared in Fig. 8 with that found previously for pure nickel when treated under the same experimental conditions (9). It is apparent that while the amount of solid carbon deposited on a nickel catalyst is extremely sensitive to the presence of hydrogen in the reactant mixture, it has no effect on the amount of this material that accumulates on an iron sample. In both metal/ethylene systems, however, the presence of added hydrogen may exert a significant impact on the morphological characteristics and the degree of crystalline perfection of the carbonaceous structures. It should also be noted that the introduction of hydrogen into the reactant did not induce the growth of solid carbon structures on a powdered copper specimen.

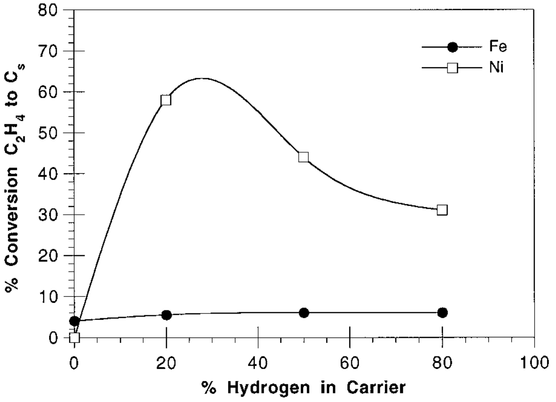

FIG. 8. Effect of hydrogen on the amount of solid carbon produced from the nickel and iron catalyzed decomposition of ethylene at 600°C (reaction time 1.5 h).

Inspection of the data presented in Table 2 shows that ethane is the major gas-phase product from both the copper–iron (3 : 7) and iron-catalyzed decomposition of ethylene, along with minor amounts of methane. This finding is to be contrasted with that found when copper–nickel (3 : 7) particles were reacted under identical conditions and where methane was the predominant gas-phase product (9). It is also apparent from Table 2 that as the percentage of hydrogen in the reactant is increased, the yields of both methane and ethane exhibit a progressive rise. When one compares the behavior of copper–iron with that of pure iron it is interesting to find that the gas product distribution is almost the same from reactant gas mixtures where the hydrogen content ranges from 0 to 50 mole%. The major difference in the two systems is seen in the percent conversion of ethylene and this feature is reflected in the lower amount of solid carbon produced over a pure iron catalyst.

4.4 Effect of temperature on the carbon deposition reaction. These experiments were designed to establish the reaction conditions necessary to obtain the maximum growth of the solid carbon structures. For this purpose we elected to investigate the interaction between a copper–iron (3 : 7) catalyst and an ethylene/hydrogen (1 : 4) reactant gas mixture at temperatures over the range 450 to

TABLE 2

Percentage Carbon Distribution at 600°C as a Function of Ethylene/Hydrogen Ratio

$C_2H_4 : H_2$	% product	Cu–Fe (3 : 7)	Fe
100 : 0	CH_4	0.11	0.10
	C_2H_4	86.1	95.4
	C_2H_6	0.9	0.5
	Solid carbon	11.64	4.01
4 : 1	CH_4	0.14	0.17
	C_2H_4	73.7	90.2
	C_2H_6	2.4	3.1
	Solid carbon	22.9	6.57
1 : 1	CH_4	0.22	0.23
	C_2H_4	35.5	85.0
	C_2H_6	7.1	8.8
	Solid carbon	57.1	6.0
1 : 4	CH_4	1.64	0.70
	C_2H_4	9.1	66.4
	C_2H_6	16.6	27.5
	Solid carbon	72.3	5.4

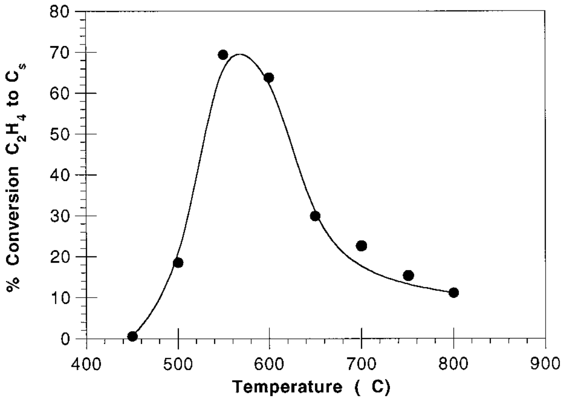

FIG. 9. Effect of reaction temperature on the amount of solid carbon produced from the decomposition of ethylene/hydrogen (1 : 4) over copper-iron (3 : 7) (reaction time 1 h).

800°C. Inspection of the data presented in Fig. 9 shows that the onset of catalyzed carbon formation occurs at about 450°C and exhibits a maximum yield at about 575°C. On increasing the temperature to higher levels there is a sharp decrease in the ability of the catalyst to generate this form of carbonaceous material.

The change in the total product distribution as a function of reaction temperature is given in Table 3. Inspection of these data shows that as the temperature is progressively raised from 450 to 700°C ethane becomes the dominant gas-phase product. When the reaction is performed at 750°C, it is apparent that the amounts of methane and ethane are virtually the same and the former becomes the major product when the temperature is finally increased to 800°C. It was not possible to investigate the behavior at more extreme conditions since ethylene exhibits a strong tendency to undergo polymerization reactions, which interferes with the function of the catalyst.

Finally, in an attempt to establish whether the high yield of methane produced from the copper–iron/ethylene–hydrogen reaction at 800°C originated from hydrogasification of solid carbon, the following experiment was conducted. Initially the copper–iron (3 : 7) powder was reacted in C_2H_4/H_2 (1 : 4) at 800°C and the amount of methane formed was determined at regular intervals. After a period of 60 mins the ethylene was replaced with helium and the reaction continued at the same temperature. Almost immediately following this operation the amount of methane produced decreased to about 1% of that formed in the presence of ethylene. On replacing the helium with ethylene the concentration of methane was gradually restored to a value close to its original high level. This sequence of events indicates that methane is not being formed as a result of hydrogasification of carbon, but rather due to rearrangements in the structure of the catalyst surface that favor hydrogenolysis of the ethylene.

TABLE 3

Effect of Temperature on Carbon Distribution after 1.0 h Reaction between Iron–Copper (7 : 3) and Ethylene/Hydrogen (1 : 4)

Temperature (°C)	% CH_4	% C_2H_4	% C_2H_6	% solid carbon
450	1.4	96.5	1.5	0.6
500	1.5	73.0	7.0	18.5
550	2.8	17.1	10.7	69.4
600	2.0	13.3	20.9	63.8
650	1.6	6.9	61.6	29.9
700	9.0	9.2	55.4	26.3
750	37.2	9.5	33.7	19.7
800	69.5	6.0	13.3	11.1

DISCUSSION

Comparison of the Carbon Deposition Characteristics of Iron and Copper–Iron

Although carbon deposition is a phenomenon that occurs in many catalytic systems, the formation of a highly ordered filamentous structure is a very demanding reaction. In order for a metal to function as a catalyst for the growth of this form of carbon certain criteria must be satisfied. Initially, it is necessary for the carbon-containing reactant gas molecules to undergo dissociative chemisorption at particular metal surfaces to produce a significant number of atomic carbon species. Dissolution and subsequent diffusion of the carbon atoms will occur at a particular temperature that is dependent on the nature and structure of the metal. The range of crystalline order of the carbon deposit generated at the rear faces of the particle is controlled to a large degree by the wetting characteristics exhibited between the metal and graphite. However, the geometric alignment of the precipitated graphite platelets in the filament structure as well as their crystalline perfection is ultimately determined by the crystallographic orientation of the metal faces in contact with the solid carbon deposit (23). In many cases the deposited carbon constrains the particle in such a manner that the shape in the reactive state is maintained on subsequent cooling to room temperature. This aspect enables one to develop more accurate descriptions of the events taking place at the various interfaces.

One of the most dramatic features to emerge from this investigation is the finding that while the pure metals, iron and copper, show very little activity toward the formation of filamentous carbon deposits when reacted in the presence of ethylene containing environments, mixtures of these metals show extremely high activity for the growth of this form of carbon, particularly when hydrogen is present in the hydrocarbon reactant stream. It is significant that this promotional effect occurs despite the fact that the two metals only exhibit limited miscibility in each other. The inability of copper to catalyze the formation of solid carbon can be attributed to its low activity towards dissociative chemisorption of hydrocarbons (24, 25).

On the other hand, iron initially exhibits a high activity for the growth of carbon filaments from the decomposition of an ethylene/hydrogen (1 : 4) mixture at 600°C, but after a short period of time undergoes a rapid deactivation. In this regard it is interesting to take into consideration recent *in situ* electron diffraction data obtained from specimens of supported iron particles undergoing reaction with an ethylene/hydrogen environment, where the formation of iron carbide (Fe_3C) was found to occur at 420°C and persist up to temperatures in excess of 750°C (26). Based on this information one may confidently conclude that the deactivated state is directly related to bulk carbide formation, a finding consistent with previous studies (27–30). One might also argue that, since the addition of carbon monoxide to the ethylene/hydrogen mixture results in a restoration of the activity of the spent iron catalyst (31), Fe_3C is transformed back to the metallic state under these conditions.

The results of the present study show that the product selectivities in the reaction of ethylene and hydrogen at temperatures around 600°C are drastically altered by the addition of either small amounts of iron to copper or vice versa. While no significant degree of bulk alloying is expected between these metals (10), it is evident that intimate contact of the metals is achieved in the preparation of the bimetallic powders. Taking into consideration that copper has no activity toward the decomposition of ethylene to produce solid carbon, it is surprising to find that particles containing as little as 5% iron exhibit such a high reactivity. On the other hand, iron has a strong affinity for hydrocarbons, which will result in chemisorption-induced segregation of this element to the particle surface. Furthermore, this phenomenon could have been initiated during the preparation step (32). One could therefore assume that modifications in the behavior of a copper-rich powder are due to geometric effects resulting in a reduction of the copper atom ensemble size (2, 3, 33–35). This explanation, however, cannot account for the influence of small amounts of copper (as little as 2%) on the catalytic behavior of iron as most of the adatoms would be present within the bulk of the bimetallic particles. Moreover, based on particle size measurements performed at the conclusion of the experiment, it is evident that the enhancement in activity cannot be rationalized simply on an increase in metal surface area. Under these circumstances it is tempting to speculate that the presence of a small concentration of copper atoms is capable of inducing significant electronic perturbations in the iron atoms, which could have a direct impact on the mode of adsorption and decomposition of ethylene on such surfaces. Dowden and Reynolds (36, 37) were first to recognize the importance of the electronic effect on the chemisorption characteristics of bimetallic systems and the concept has been invoked to account for the observed behavior of various systems (38–43).

Ethylene adsorbs strongly on clean iron surfaces at low temperatures (−150°C) and decomposes at room temperature to form acetylene or adsorbed C atoms and H_2 (14, 16, 17), possibly via a methylidyne intermediate resulting in the formation of a carbide layer on the iron surface. The mode of ethylene adsorption on iron is altered by the presence of other adatoms. The adsorption of carbon or oxygen species on iron was found to prevent the dissociative chemisorption of ethylene (14, 18). On iron surfaces presaturated with hydrogen, ethylene was found to adsorb reversibly without decomposition or reaction to form ethane. It was argued that under these circumstances H atoms effectively "passified" the iron surface and decreased the binding energy of ethylene to the metal (19, 20).

Adsorption of ethylene on transition metals usually results in a decrease of the work function, indicating the existence of electron transfer between the reactant gas molecules and the surface atoms in the catalyst particles (44). Such electronic modifications have been proposed for a variety of systems by other workers (42), with the transfer taking place from the electron-rich to the electron-poor element. Goodman and co-workers (45) have recently developed a model, based on data from surface science experiments, that addresses the direction of the electron transfer resulting from the mixing of two metals. Using the criteria of the model we may conclude that for the copper–iron system, where copper is in contact with a metal that has more than a half-filled valence band, iron is the electron-rich component and donates charge to the copper. It is probable, therefore, that the electronic perturbations occurring in iron resulting from the addition of copper would also cause changes in the strength of the hydrocarbon/metal interaction and this phenomenon might be responsible for the observed increase in activity exhibited by the bimetallic toward the conversion of ethylene into both gaseous and solid carbon products.

It is interesting to compare the effect of copper on the carbon depositing characteristics of iron when reacted in ethylene/hydrogen with that found previously when carbon monoxide was added to the same reaction system (31). In the latter case, the carbon monoxide was believed to perform two functions, assisting in the reconstruction of the exposed iron surfaces to create various faces with differing reactivity characteristics and facilitating the rupture of the $C=C$ bonds in adsorbed ethylene molecules by generating electronic perturbations at the surface atoms of iron particles. It was found that upon the addition of a small amount of carbon monoxide to the ethylene/hydrogen mixture there was a dramatic increase in the formation of filamentous carbon, of which the major fraction could be attributed to decomposition of the olefin. The striking similarity of these two sets of results indicates that it is possible to enhance the reactivity of iron toward dissociative chemisorption of ethylene by either the addition of adatoms or coadsorption of certain gases that can induce charge transfer to or from the metal.

In addition it is anticipated that changes in surface composition will occur upon increasing the reaction temperature. In most bimetallic systems two forces are operative, thermally induced segregation, where the component possessing the lower heat of sublimation will preferentially enrich the surface, and chemisorption-induced segregation. This latter phenomenon is further complicated by the presence of a solid carbon residue that competes with the reactive gas phase for one of the metallic components (46). The results of the present investigation suggest that the observed changes in catalytic activity and selectivity accompanying an increase in temperature (Fig. 9 and Table 3) are probably due to major alterations in the distribution of atoms at the metal/gas interface.

Role of Hydrogen in the Carbon Deposition Reaction

It is significant that in the present investigation while the addition of hydrogen to the ethylene feed did not appear to exert any influence on the amount of filamentous carbon produced over a pure iron surface, it had an appreciable effect when the reaction was conducted over the bimetallic system. Incorporation of copper into iron might be expected to weaken the strength of the interaction with ethylene, however, in this case the presence of hydrogen was found to stimulate the growth of carbon filaments, reaching a maximum level for a reaction mixture containing 80% hydrogen. Under these conditions it would appear that the rate of ethylene decomposition at the bimetallic surface is comparable to that for diffusion of carbon through the catalyst particle, enabling a sustained carbon filament growth to be achieved.

The promotional effect of hydrogen on carbon filament formation from the metal catalyzed decomposition of carbon-containing gas molecules has been attributed to its ability to convert inactive metal carbides into the catalytically active metallic state (30, 47) as well as to prevent the formation of graphitic overlayers on the particle surfaces (48). While these explanations may have some validity, it is doubtful whether they can account for the pattern of behavior observed with the current systems, since iron and copper–iron do not respond to the presence of hydrogen in the reactant gas in a comparable manner. It is therefore probable that other factors are operative and in this regard it is important to take into consideration the transformations in particle morphology and concomitant changes in atomic arrangement of the reactive faces arising from the participation of hydrogen in the reaction. We believe that during the interaction of hydrocarbons with metals the particles adopt a morphology in which there are at least two distinct faces: (i) those which are only capable of adsorbing and decomposing hydrocarbons, and (ii) others that will precipitate dissolved carbon in the form of graphite platelets. As a consequence, regardless of the existence and amount of solid carbon present on a given particle there will always be a set of faces that are completely free of deposited carbon and are available for continued catalytic action (49). In this context the presence of hydrogen might be a much more active participant than has hitherto been recognized as it could facilitate the generation of these required atomic arrangements.

Hydrogen is known to induce reconstruction of certain metal faces (50, 51) and some attention has been given to the displacement of atoms in the Fe(110) and Fe(211) faces and the modifications in chemisorption characteristics resulting from such a treatment (52, 53). Studies performed in the controlled atmosphere electron microscope of the behavior of certain metal/graphite-hydrogen systems have demonstrated that when copper is added to a host metal there is an increase in the interfacial energy between such particles and graphite, which results in a spreading action of the bimetallic on the support (54). In contrast, when iron/graphite specimens were treated in hydrogen the metal particles did not show a tendency to exhibit a strong interaction with the support (55).

From a combination of these factors it is possible to speculate on the sequence of changes that might occur in the morphology and carbon deposition characteristics of iron–copper particles as the concentration of hydrogen in the reactant is progressively increased. These features are depicted in the schematic rendition, Fig. 10, where the particles have two faces capable of dissociatively chemisorbing hydrocarbon molecules and four faces that simultaneously precipitate dissolved carbon as graphite platelets. The orientation of the graphite platelets is consistent with lattice fringe analysis performed by high-resolution transmission electron microscopy (49). The observed increase in reactivity of ethylene in the presence of a large amount of hydrogen is rationalized in terms of a stretching of the metal particle without concomitant change in volume, which results in an enlargement of those faces where hydrocarbon dissociation takes place. The net result of this modification in particle geometry is that the rate of ethylene decomposition and the growth of filamentous carbon will be enhanced as shown in Fig. 6.

Comparison of the Behavior of Copper–Iron and Copper–Nickel Systems

A comparison of the key features of the catalytic behavior of copper–iron and copper–nickel systems in the forma-

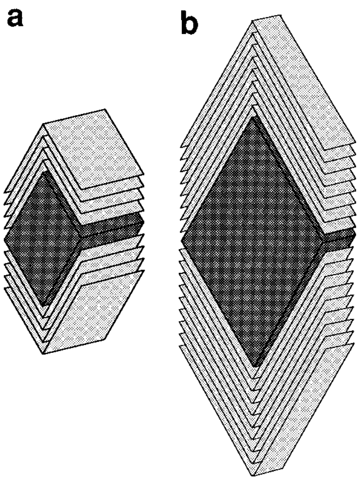

FIG. 10. Schematic representation of the changes in the carbon deposition phenomenon as a function of the reactant gas composition: (a) $C_2H_4:H_2$ (1:1), and (b) $C_2H_4:H_2$ (1:4). Note that the volume of the catalyst particles remains constant, however, the area of the faces on which dissociative chemisorption of C_2H_4 occurs increases in (b).

tion of carbon filaments from ethylene/hydrogen (1:4) is presented in Table 4. It can be seen that the product selectivities are strikingly different, suggesting that fundamental differences exist in the elementary steps taking place on the two surfaces. It was suggested that most of the methane produced from the interaction of copper–nickel with ethylene and ethylene/hydrogen mixtures could be attributed to the decomposition of an "ethylidyne" intermediate (9). It was claimed that this structure was formed when the ethylene molecule encountered a nickel atom whose nearest neighbor was a copper atom, which did not chemisorb the hydrocarbon. Under these circumstances the ethylene would bond to the surface in a manner such that the C–C bond was in an "end-on" configuration. In this arrangement one of the carbon atoms in the adsorbate is attached to three metal atoms. The subsequent decomposition of this intermediate will give rise to a methyl radical, which readily abstracts hydrogen from other molecules to form methane. The carbon atom that remains on the surface will dissolve in the metal and eventually become part of the filamentous carbon structure created at the rear of the particle. In this system the modifications in catalytic behavior of nickel brought about by the introduction of copper were rationalized in terms of a geometric effect.

TABLE 4

Comparison of the Percentage Carbon Distribution from the Interaction of Copper–Nickel (3:7) and Copper–Iron (3:7) with Ethylene/Hydrogen after 1.0 h at 600°C

Product	Cu–Ni (3:7) (Ref [9])	Cu–Fe (3:7)
CH_4	35.7	1.96
C_2H_4	8.4	13.3
C_2H_6	29.6	20.9
Solid carbon	26.8	63.84

The small amounts of methane formed and the large yields of solid carbon provide some insights into the reaction mechanism over the copper–iron particles. In this case one might argue that since the formation of the major fraction of methane is controlled by the concentration of copper atoms present in the particle surface that in this bimetallic system the reactive faces consist essentially of iron atoms. As a consequence it is expected that the ethylene molecules will be adsorbed in a configuration where the C–C bond is aligned "parallel" to the surface with little probability in this case for the concomitant formation of an "ethylidyne" intermediate. As stated previously, we believe that in this system the addition of copper produces an electron deficiency in the iron and this effect will tend to increase the strength of the interaction between the metal surface atoms and the π electrons in the ethylene molecule. This phenomenon will facilitate the rupture of the C=C bond, which in turn will lead to the formation of a large amount of filamentous carbon.

Finally, the difference in carbon deposition behavior of the two bimetallics as a function of increasing hydrogen content in the reactive gas mixture (Fig. 7) is an important point to emerge from this investigation. As stated previously hydrogen can induce preferential segregation of one of the components to the metal/gas interface, which will have a direct impact on the catalytic activity. If the chemisorption-induced segregation phenomenon generates a surface that favors decompositon of ethylene, the net result will be an increase in carbon filament formation. On the other hand, if the process results in the formation of a less reactive surface then the amount of solid carbon growth will be decreased. In addition, one must also take into consideration the potential for hydrogen-induced surface reconstruction to produce surfaces with differing reactivity. Clearly a number of factors are contributing to the reactivity patterns exhibited by these two bimetallic systems and the data obtained in this study do not enable us to reach definite conclusions as to dominant cause.

SUMMARY

When iron or copper powders were heated in the presence of ethylene or ethylene/hydrogen mixtures the metals exhibited little or no ability to catalyze the growth of filamentous carbon structures. In sharp contrast, when a very small amount of one of these metals was added to the other, on subsequent reaction in an ethylene/hydrogen environment prolific growth of this form of carbon was observed. For the dilute copper bimetallic systems this behavior is accounted for in terms of an electronic perturbation of the iron atoms created by the presence of a small amount of adatoms, which results in a facilitation of dissociative chemisorption of ethylene on such a modified surface. The presence of hydrogen in the reactant gas is also found to enhance the growth of filamentous carbon on the bimetallic catalyst particles. It is suggested this aspect is due to a combination of hydrogen reconstruction and a concomitant change in the shape of the particles to create an enlargement in the area of the faces on which hydrocarbon adsorption and decompositon take place.

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