JOURNAL OF CATALYSIS **179,** 361–374 (1998)
ARTICLE NO. CA982226

Carbon Deposition on Iron–Nickel during Interaction with Ethylene–Hydrogen Mixtures

C. Park and R. T. K. Baker[1]

Department of Chemistry, Hurtig Hall, Northeastern University, Boston, Massachusetts 02115

Received December 2, 1997; revised July 17, 1998; accepted July 17, 1998

The catalytic decomposition of ethylene over iron–nickel to produce methane, ethane, and solid carbon has been shown to be extremely sensitive to the composition of the bimetallic particles and the temperature at which the reaction is performed. The addition of an extra 5% nickel to an Fe-Ni (3 : 7) catalyst was found to result in a dramatic increase in the conversion of ethylene from 13.0 to 52.0% and a corresponding increase in the amount of solid carbon, identified as filamentous in nature, from 4.6 to 38.5%. It was also established that the graphitic content of the deposit exhibited a significant increase between the compositions Fe–Ni (3 : 7) and Fe–Ni (25 : 75). An improvement in the degree of crystalline perfection of the carbon filaments generated from the whole composition range of bimetallics was evident as the hydrogen content of the reactant mixture was raised. While increasing the temperature from 600 to 725°C enhanced the decomposition of ethylene over all the Fe–Ni powders, this effect was most striking over those bimetallic particles containing 70% or less of nickel. This behavior is to be contrasted with that found in an analogous study that demonstrated that the reverse dependence held when the same set of bimetallics was reacted in CO. The phenomenon appears to be related to preferential segregation of nickel to the gas/particle interface at higher temperatures; a condition that tends to favor the decomposition of C_2H_4, but has the opposite effect on the decomposition of CO.

INTRODUCTION

While most studies concerning the catalytic hydrogenation of ethylene and related hydrocarbons have to tended to focus on the use of noble metals, such as platinum and palladium, there has been a growing interest in the potential of the first row transition metals and, in particular, nickel for these reactions. Nickel has been found to exhibit a very high activity for the hydrogenation of ethylene, whereas metals such as copper and iron, on the other hand, are relatively inert under identical conditions (1–13). This is a finding that is in direct contrast to that encountered when carbon monoxide is used as the reactant molecule. Carbon monoxide decomposes readily on an iron catalyst in the presence of hydrogen, but it remains intact when the reaction is performed over a nickel surface (14–18).

A variety of bimetallic catalyst systems have been employed in the study of hydrogenation reactions and in some cases, the focus has centered around the concomitant growth of carbon filaments that are formed when such reactions are carried out at 450–700°C (18–28). The addition of a second metal to the catalyst system can often result in dramatic changes in both activity and selectivity when compared to that exhibited by the individual metals. The addition of as little as 2% copper to an iron catalyst, two metals which in their pure state are relatively inactive for ethylene decomposition, resulted in a significant enhancement in the conversion of the hydrocarbon to filamentous carbon (28). This type of carbonaceous solid has been shown to possess unique graphitic structures that in turn bestow the material with a set of unusual physical and chemical properties (29, 30).

Kim and coworkers (21, 22), carried out a detailed investigation of the interaction of various hydrocarbons, including ethylene, with copper–nickel and nickel catalysts. An attempt was made to take a broad view of the reactions by taking into account both the gaseous and solid products and this information was used to reconstruct the steps involved in the process. It was argued that on pure nickel and in the absence of any other reactant, ethylene bonded in such a manner that the C=C bond was "parallel" to the catalyst surface and that subsequent deactivation was due to the formation of a graphitic overlayer at saturation coverage. When this same form of interaction was carried out over a copper–nickel surface, there was a modification in the fate of the adsorbed ethylene molecule. The inability of copper to chemisorb hydrocarbons was reflected in the possibility for ethylene to adhere to the surface in a mode where the C=C bond was in an "end-on" configuration. Under such circumstances, the pathway leading to deactivation via encapsulation was effectively prevented and the system maintained its catalytic activity for prolonged periods of time.

Cooper and Trimm (31) investigated the interaction of propylene with different iron surfaces and demonstrated

---

[1] Author to whom all correspondence should be addressed.

0021-9517/98 $25.00

that in order to maintain the growth of solid carbon it was essential to add hydrogen to the propylene feed. The crystallographic arrangement of the iron surfaces was shown to play a key role in the determination of rate of carbon deposition. $Fe_{(100)}$ surfaces exhibited a higher rate of carbon deposition than $iron_{(110)}$ surfaces. A polycrystalline foil used by these authors was found to have activity similar to that of an $Fe_{(100)}$ surface, since both samples were predominantly in the same crystallographic orientation. The nature of the carbonaceous solid was not identified, but it is reasonable to assume that the majority of the deposit was composed of carbon filaments.

In a previous paper dealing with the interaction of carbon monoxide/hydrogen mixtures with iron–nickel powders, several interesting features of the reaction were discovered (18). The most notable being the sudden apparent deactivation of the bimetallic catalysts in the composition range of Fe–Ni (25 : 75) that occurred when the reaction temperature was raised above 650°C. One of the major objectives of the present study was to probe this phenomenon in greater detail in an attempt to unravel the underlying scientific issues behind this intriguing pattern of behavior. By using ethylene, a gas which is well known to preferentially interact with nickel rather iron, it was believed that more information could be obtained about the nature of the catalytic surface during this deactivation process. The natural selectivity of both ethylene and carbon monoxide to preferentially interact strongly with only one of the metals present in the catalyst in the presence of hydrogen makes the study of these various compositions of iron–nickel powders a fascinating task. The chemical nature of the active surface of the catalyst can be identified and monitored to a certain degree during the reaction by careful analysis of the gaseous and solid products.

EXPERIMENTAL

Materials

The various compositions of iron–nickel catalyst powders used in these studies were prepared by the co-precipitation of the metal carbonates from the respective metal nitrate solutions mixed in the desired ratios using ammonium bicarbonate as described in detail by Best and Russell (32). The calcination, reduction, and passivation protocol used are outlined in detail in a previous paper by this group (18). The gases used in this work, hydrogen (99.999%), ethylene (99.95%), and helium (99.999%), were obtained from MG Industries and used without any further purification. Reagent grade iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] and reagent grade nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] were obtained from Fisher Scientific for the catalyst preparation. The compositions of the passivated bimetallic powders were checked by X-ray diffraction analysis and within experimental error, were found to correspond to the desired ratios.

Apparatus and Procedures

The apparatus used for these experiments has been described in detail previously (21). The system consists of a quartz flow reactor heated by a conventional Lindberg horizontal tube furnace. The gas flow to the reactor is precisely monitored and controlled by the use of mass flow controllers allowing a constant composition of feed to be delivered. Passivated powdered catalyst samples (50 mg) were placed in a ceramic boat at the center of the reactor tube in the furnace. After reduction in a 10% H_2/He mixture for 2 h at the desired reaction temperature the system was flushed for 1 h with helium. The predetermined reactant gas, C_2H_4 or a C_2H_4/H_2 mixture, was then introduced to the reduced catalyst for periods of up to 1.5 h. The total gas velocity in all experiments reported here was 100 mL/min and, unless stated otherwise, the ethylene flow rate was maintained constant at 40 mL/min. The hydrogen flow rate was varied and helium was used to make the gas velocity up to 100 mL/min. All gas flow rates were measured at ambient conditions. The reaction was followed as a function of time by sampling both the inlet and outlet gas streams at regular intervals and analyzing the reactants and products by gas chromatography using a 30-m megabore (GS-Q) capillary column in a Varian 3400 G.C. Carbon and hydrogen atom balances, in combination with the relative concentrations of the respective components, were applied to obtain the various product yields. The total amount of carbon deposited on the catalyst during the time on stream was determined gravimetrically after the system had been cooled to ambient temperature.

Under the flow conditions utilized in this set of experiments most of the deposited carbon remained within the sample boat; however, any material that spilled out into the reactor was collected and included in the weight determinations. In this context, it was significant to observe that the walls of the reactor tube remained quite clean after a given experiment at 600°C, indicating that no other forms of carbonaceous deposit were produced. In experiments that were conducted at 725°C, evidence for the formation of small amounts of pyrolytic carbon, which was believed to originate from noncatalytic steps, accumulated on the walls of the reactor downstream at some distance from the catalyst samples. Since this type of deposit made only a minor contribution to the overall formation of solid carbon and adhered strongly to the quartz tube no quantitative assessment was made.

The nature and characteristics of the carbon deposit were established using both high resolution transmission electron microscopy (HRTEM) and CO_2 temperature-programmed oxidation (TPO) studies. The TEM investigations were performed in a JEOL 2000EXII electron microscope fitted with a high resolution pole piece capable of giving a lattice resolution of 0.14 nm. Suitable TEM specimens were prepared by ultrasonic dispersion of the carbon sample in isobutanol, followed by the application of a drop of the resultant suspension to a holey carbon support grid. From these experiments it was possible to conclude that in all cases the carbonaceous deposit was for the most part filamentous in nature. Inspection by electron diffraction showed that there were variations in the degree of crystalline perfection of these structures that was dependent on the composition of the bimetallic powders from which they were generated.

Temperature programmed oxidation studies were carried out using a Cahn 2000 microbalance on demineralized carbon filaments in the presence of CO_2 at a constant heating rate as outlined in a previous paper (21). This process effectively removes any metallic inclusions to provide a reproducible oxidation profile of the carbon being investigated. Comparison of the oxidation profiles derived from these experiments with those of single crystal graphite and amorphous carbon enables one to obtain an estimate of the fraction of graphite and amorphous carbon present in the deposit. X-ray diffraction analysis was performed on both the carbon deposits and the associated bimetallic particles produced from the various catalyst formulations. These examinations were carried out in a Scintag 1 diffractometer equipped with a nickel monochromater. Diffraction was performed with Cu Kα radiation at a scan rate of 2°/min, and peaks were identified by comparison with standards in a related database. The relative degree of crystalline perfection of carbonaceous materials generated from various Fe-Ni catalyst compositions was estimated from broadening of the (002) line for each sample. No major changes in the initial ratio of iron to nickel were found from experiments that were performed at 600°C.

In-situ electron diffraction analyses were performed on iron–nickel (1 : 1)/graphite specimens undergoing reaction in a 0.2 Torr ethylene/hydrogen (1 : 2) mixture at temperatures over the range 400 to 800°C, using controlled atmosphere electron microscopy (33). This procedure allows one to directly follow the changes in the chemical state of the bimetallic particles as a function of reaction conditions. As a consequence, it is a relatively simple task to identify the existence of any preferential segregation of either of the components to the graphite surface and establish the temperature at which such a phenomenon occurs. This set of reaction conditions was selected since the morphological characteristics of carbon filaments generated in analogous flow reactor experiments had demonstrated the possibility that selective removal of one of the metals could be taking place during the deposit growth process. The samples used in these experiments were prepared by introducing the bimetallic components onto transmission specimens of single crystal graphite as an atomized spray from an aqueous solution of the respective metal nitrates. Prior to reaction in the ethylene/hydrogen mixture the system was heated in oxygen at 250°C for 30 min and then reduced in hydrogen at 400°C for 2 h. This procedure resulted in the creation of small bimetallic particles ranging in size from 5 to 25 nm.

RESULTS

1. Flow Reactor Studies

1.1. Effect of the Catalyst Composition on the Gas and Solid Phase Product Distributions

The percentage product distribution obtained from the catalytic decomposition of an ethylene/hydrogen mixture (4 : 1) at 600°C over a series of iron–nickel powders of varying composition is presented in Fig. 1. This temperature was chosen as it had been shown in a previous study that these iron-nickel catalysts exhibited significant changes in activity at 600°C between catalyst compositions of Fe–Ni (3 : 7) and Fe–Ni (25 : 75) when CO/H_2 was used as the reactant feed (18). In order to obtain a direct comparison between the former and the present systems, the interaction of the bimetallic powders with a C_2H_4/H_2 mixture was carried out under as near identical conditions as possible. The reaction was allowed to proceed for a period of 1.5 h in order to ensure that the catalysts reached a steady conversion level and also to verify that the bimetallic particles did not undergo rapid deactivation as the accumulation of solid carbon became appreciable. As expected, the main gaseous products from this reaction were identified as being CH_4 and C_2H_6, along with trace amounts of C_3 and C_4 hydrocarbons, the exact concentrations of which are not reported here.

From Fig. 1 it is evident that the addition of up to and including 70% Ni to an Fe catalyst has little impact on the catalytic behavior when the hydrogenation of ethylene is studied under the stated conditions. The conversion of ethylene over Fe–Ni catalysts with a Ni content of 70% or less is extremely low, less than 10% conversion to C_2H_6 and 5% conversion to CH_4. There is, however, a significant increase

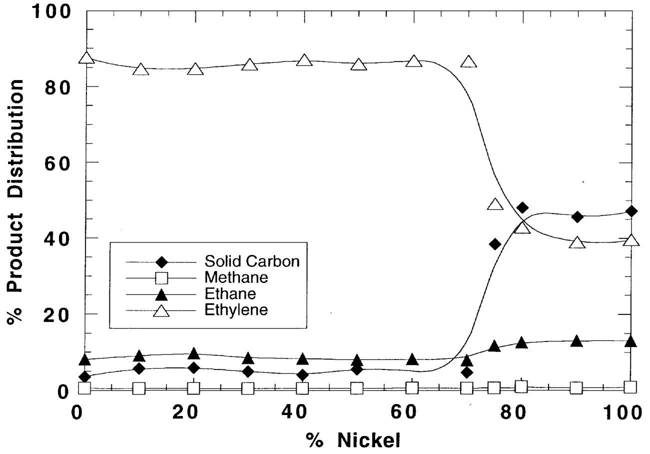

FIG. 1. The percentage product distribution from the hydrogenation of a C_2H_4/H_2 (4 : 1) mixture over various Fe-Ni powders at 600°C.

in the catalytic activity of the bimetallic for the decomposition of ethylene between the compositions Fe–Ni (3 : 7) and Fe–Ni (25 : 75). While the major increase in the conversion of ethylene results in the formation of solid carbon, there is a rise of approximately 5% in the conversion of the olefin to ethane. Quantitative measurements showed that an increase in the Ni content of the catalyst from 70 to 75% was accompanied by a corresponding increase in the amount of solid carbon deposited from 0.1 to 6.5 g, respectively. Further addition of nickel to the catalyst composition appeared to exert very little impact on either the yields of gaseous products or that of solid carbon, the product distribution being similar to that exhibited by pure nickel powder under the same conditions.

In a further series of experiments designed to determine the lifetime of a given catalyst charge during the growth of carbon filaments from the decomposition of a C_2H_4/H_2 (4 : 1) mixture at 600°C, the weight of carbon deposited on 0.050 g samples of selected bimetallic powders was measured as a function of reaction time. The data obtained from these experiments for three nickel-rich bimetallics are presented in Fig. 2. It should be pointed out that each point on these curves was obtained using a fresh sample of the respective bimetallic powder. At the termination the short and long term experiments' representative samples of the deposit were examined by TEM. These examinations showed that for the most part there was no significant difference in either the morphology or size distributions of the filaments produced from these extreme reaction periods. Based on these data it appears that:

(i) The weight of carbon deposited on a given bimetallic appears to exhibit a fairly constant growth rate over a period of 3.5 h and that any induction period is of a short duration.

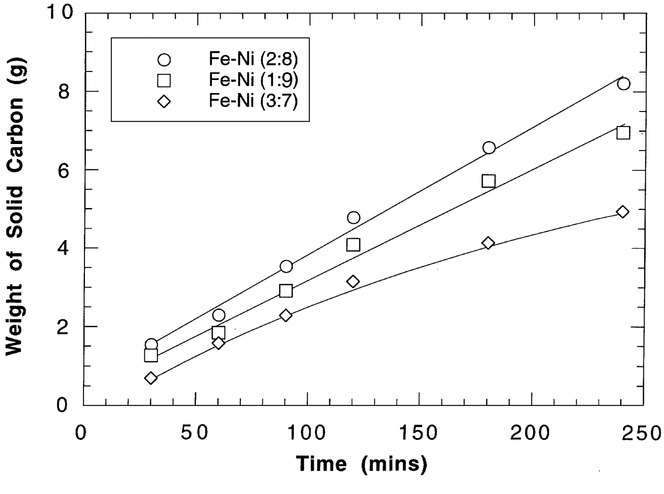

FIG. 2. Effect of reaction time on the weight of solid carbon produced from the interaction of 0.050-g quantities of selected Fe-Ni catalysts with a C_2H_4/H_2 (4 : 1) mixture at 600°C.

(ii) The size and structural characteristics of the filaments generated from a given bimetallic catalyst do not exhibit any significant changes as a function of reaction time.

1.2. Effect of Hydrogen Concentration on Product Distribution and Carbon Deposition

In an attempt to ascertain the influence of hydrogen on both the decomposition of ethylene and the growth of carbon filaments, initial experiments were conducted under conditions where the reduced catalyst powder, thoroughly flushed in He, was reacted at 600°C in the presence of pure ethylene. Under these circumstances there was very little solid carbon formed on the full composition range of Fe–Ni powders, only approximately 0.1–0.4 g deposited over a 3.5 h reaction period. Furthermore, the large variation in catalytic behavior observed between the Fe–Ni compositions (3 : 7) and (25 : 75) is not reproduced in the absence of added hydrogen.

In order to gain a clearer understanding of the role of hydrogen in these reactions experiments were undertaken in which ethylene was added immediately after the catalyst had been reduced. In this case a reduced nickel catalyst, that had not been flushed with helium, produced significant amounts of filamentous carbon, 12.2 g after 3.5 h on stream. The decomposition of ethylene was primarily to solid carbon with a small fraction being converted to both ethane and methane. The presence of hydrogen, either in a physisorbed or chemisorbed state on the metal surface after the reduction stage was evidently sufficient to initiate the hydrocarbon decomposition reaction. As this reaction proceeded hydrogen was evolved and therefore the high catalytic activity towards carbon filament growth was maintained. This experiment illustrates how small amounts of hydrogen, either sorbed on the metal surface or present in the reactant gas can have a profound effect on the behavior of these Fe-Ni catalysts, particularly with regard to the generation of filamentous carbon. This result highlights the importance of consistently flushing the catalyst after the reduction step to ensure the removal any hydrogen adsorbed on the surface if one is to avoid the extraneous accumulation of carbon deposits.

Experiments designed to determine the effect of increasing the hydrogen concentration on the product distribution and carbon filament deposition were carried out at 600°C. The results of these experiments are detailed in Table 1 for three selected catalyst compositions: Fe–Ni (7 : 3); Fe–Ni (3 : 7); Fe–Ni (2 : 8). These powders represent a cross section of all the compositions used and, more importantly, target the area where major changes in the catalytic activity for the ethylene decomposition reaction are observed. Both Fe-Ni (7 : 3) and Fe-Ni (3 : 7) compositions display limited activity for the decomposition of ethylene, however, as the hydrogen content of the reactant was raised so the overall conversion increased. This was especially noticeable for the

TABLE 1

Variation in the Percentage of Product Distribution of Selected Catalyst Compositions after 90 min Reaction at 600°C as a Function of the Percentage of Hydrogen in the Ethylene Reactant

% H_2 in reactant feed	Product	Fe : Ni (7 : 3)	Fe : Ni (3 : 7)	Fe : Ni (2 : 8)
0	CH_4	0.455	0.445	0.466
	C_2H_6	4.407	2.979	3.674
	Solid Carbon	2.466	0.036	0.255
20	CH_4	0.069	0.230	0.852
	C_2H_6	1.768	3.105	13.027
	Solid Carbon	2.796	37.263	48.141
33	CH_4	0.104	0.393	2.741
	C_2H_6	2.625	5.495	22.915
	Solid Carbon	4.022	24.175	51.658
50	CH_4	0.123	0.997	6.645
	C_2H_6	3.928	9.181	35.092
	Solid Carbon	6.759	45.232	40.944
66	CH_4	0.761	2.189	9.218
	C_2H_6	7.400	11.631	40.002
	Solid Carbon	36.508	55.106	36.773
80	CH_4	1.992	4.913	14.869
	C_2H_6	8.506	10.799	45.669
	Solid Carbon	54.810	67.859	32.541

yield of solid carbon which increased dramatically at 67% and 50% H_2 for Fe–Ni (7 : 3) and Fe–Ni (3 : 7) catalysts, respectively.

This trend does not apply to all the Fe–Ni powders used in this work as highlighted in Table 1. Inspection of the data obtained for Fe–Ni (2 : 8) catalyst, shows that while the yields of both ethane and methane climb as the hydrogen content in the feed is increased and are significantly higher than those of the other two bimetallics, the yields of solid carbon do not follow the same pattern. With an Fe–Ni (2 : 8) catalyst the conversion of ethylene to solid carbon goes through a maximum at 33% H_2 and thereafter exhibits a steady decline as the hydrogen content is progressively raised to higher levels.

1.3. Effect of Temperature on the Percentage Product Distribution

The reaction temperature was found to exert a significant impact on both carbon filament production and the conversion of ethylene over the whole composition range of Fe–Ni catalysts. In these experiments the temperature was cycled between 600 and 725°C. For the sake of brevity we have selected to present the variation of product distribution as a function of temperature for two catalyst systems, Fe–Ni (3 : 7) and Fe–Ni (2 : 8), in Figs. 3 and 4, respectively. These data have been corrected for the minor contributions to the product concentrations resulting from the uncatalyzed decomposition of a C_2H_4/H_2 (4 : 1) mixture that occurs to a small extent at 725°C. Inspection of the plots shows that at this upper temperature limit the decomposition of the olefin is relatively high for both bimetallic powders, with the nickel rich sample generating the larger amount of solid carbon. As the temperature was decreased from 725 to 600°C the catalyst activity of the Fe–Ni (3 : 7) powder decreases dramatically, whereas that of the Fe–Ni (2 : 8) sample exhibits a somewhat more moderate decline. It was significant to find that in all cases,

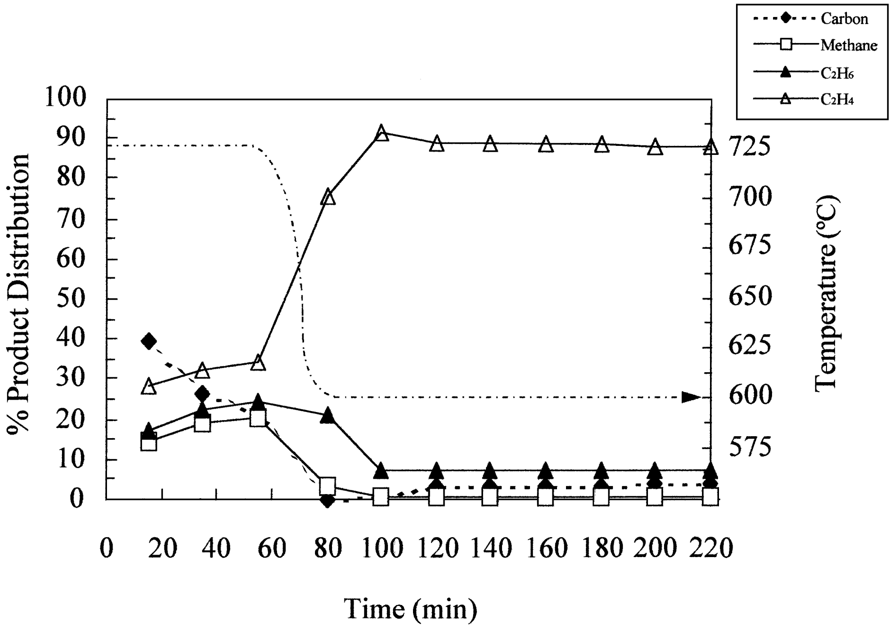

FIG. 3. Change in behavior of an Fe-Ni (3 : 7) catalyst during interaction with a C_2H_4/H_2 (4 : 1) mixture as the temperature was lowered from 725 to 600°C.

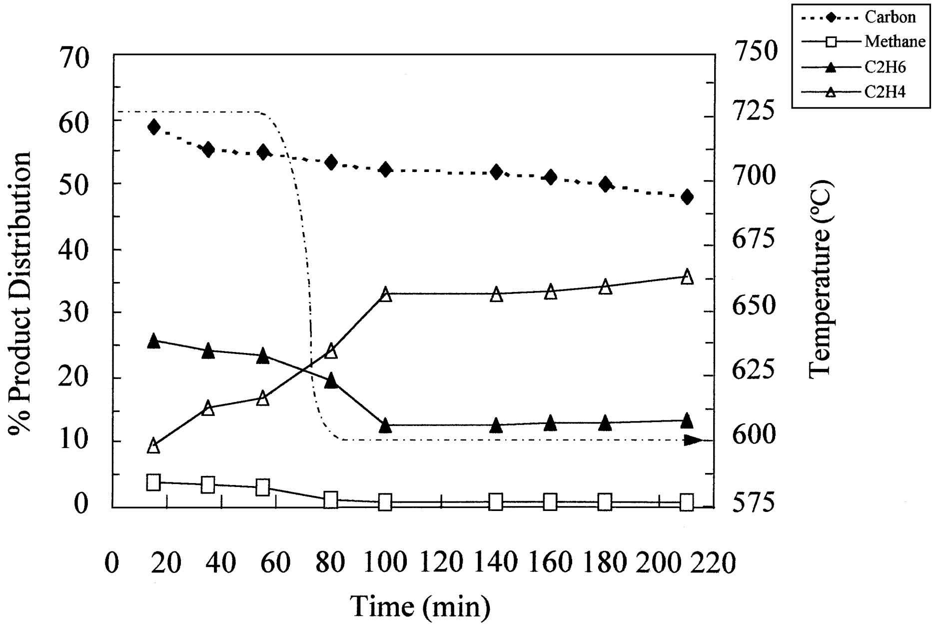

FIG. 4. Change in behavior of an Fe-Ni (2 : 8) catalyst during interaction with a C_2H_4/H_2 (4 : 1) mixture as the temperature was lowered from 725 to 600°C.

the catalytic activity could be restored to the initial high level if the temperature was increased to 725°C. Indeed, in experiments where the temperature was switched between these two limits for several temperature cycles the catalyst performance was shown to be completely reversible in nature. This pattern of behavior can seen in Fig. 5, the data obtained from an Fe–Ni (3 : 7) catalyst during interaction with an C_2H_4/H_2 (4 : 1) mixture as the temperature was cycled between 600 and 725°C. When this type of experiment was carried out with powders containing less than 70% nickel, then at 725°C the product spectrum was similar to that obtained with an Fe–Ni (3 : 7) powder when reacted under the same conditions, and quite different from the behavior displayed by the Fe–Ni (2 : 8) sample.

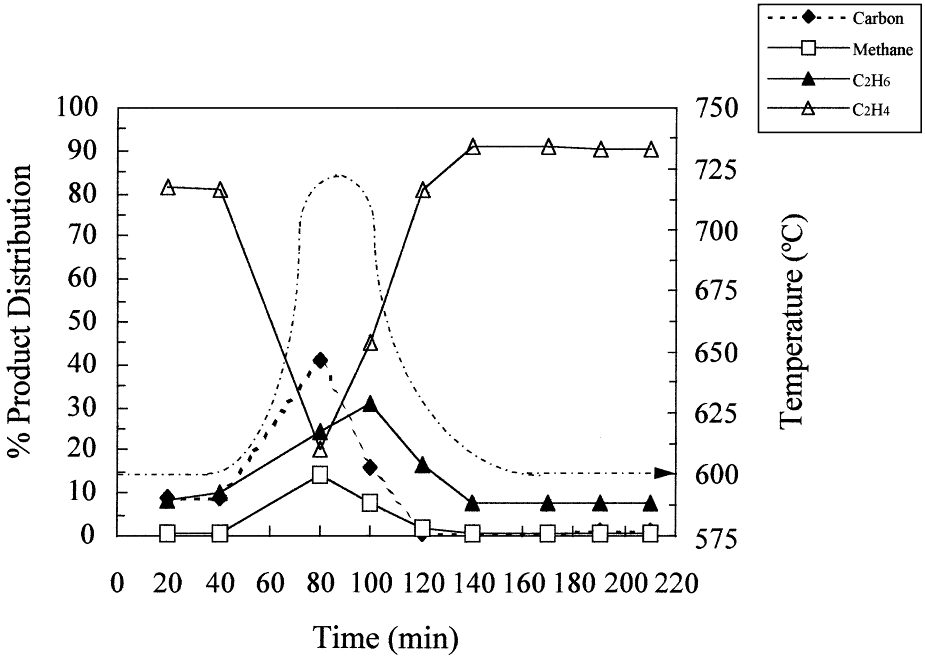

FIG. 5. Change in behavior of an Fe-Ni (3 : 7) catalyst during interaction with an C_2H_4/H_2 (4 : 1) mixture as the temperature was cycled between 600 and 725°C.

2. Characterization of the Carbon Deposits

2.1. *Transmission Electron Microscopy Studies*

Transmission electron microscopy studies of the carbon deposits grown during the decomposition of an mixture at 600°C on a range of Fe–Ni catalysts revealed that the carbon consisted almost entirely of filamentous structures. As stated above, increasing the nickel content in a series of Fe–Ni catalysts has a profound effect on the product distribution for the hydrogenation of ethylene and this aspect is particularly pronounced between the compositions Fe–Ni (3 : 7) and Fe-Ni (25 : 75). It was interesting to find that the structure of carbon filaments also exhibit a subtle change over this composition range. Carbon filaments grown from Fe-Ni powders with a high iron content tend to acquire a bidirectional helical form, as shown in the electron micrograph, Fig. 6. High resolution examinations of this material indicated that the filaments were highly crystalline in nature and that the graphitic platelets were oriented in directions either parallel or at an angle with respect to the fiber axis, Fig. 7.

As the nickel content in the catalyst powder was progressively raised so the carbon filaments generated from these particles became increasingly less twisted and the emergence of some relatively smooth-sided structures was observed. Carbon filaments produced from the decomposition of C_2H_4/H_2 (4 : 1) on Fe–Ni (3 : 7) and Fe–Ni (25 : 75) catalysts both appeared to adopt these same conformational characteristics. Detailed examination of these two materials revealed the existence of some major differences with regard to the orientation of the graphite platelets contained within the respective materials. It was evident that the majority of filaments grown from the Fe–Ni (25 : 75) composition possessed well-defined graphitic structures in which

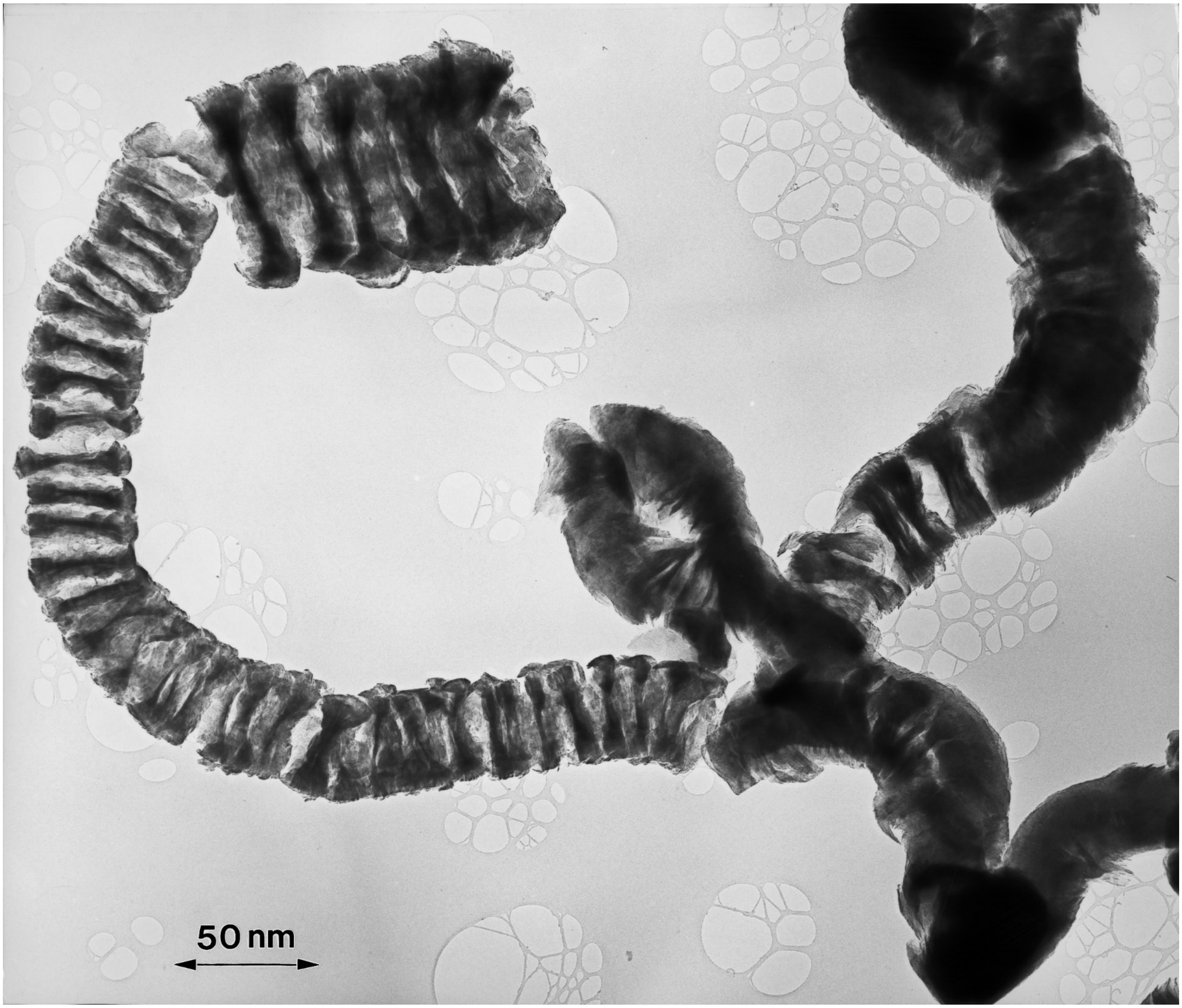

FIG. 6. Transmission electron micrograph showing the appearance of carbon filaments grown from the interaction of an Fe-Ni (7 : 3) powder with C_2H_4/H_2 (4 : 1) at 600°C.

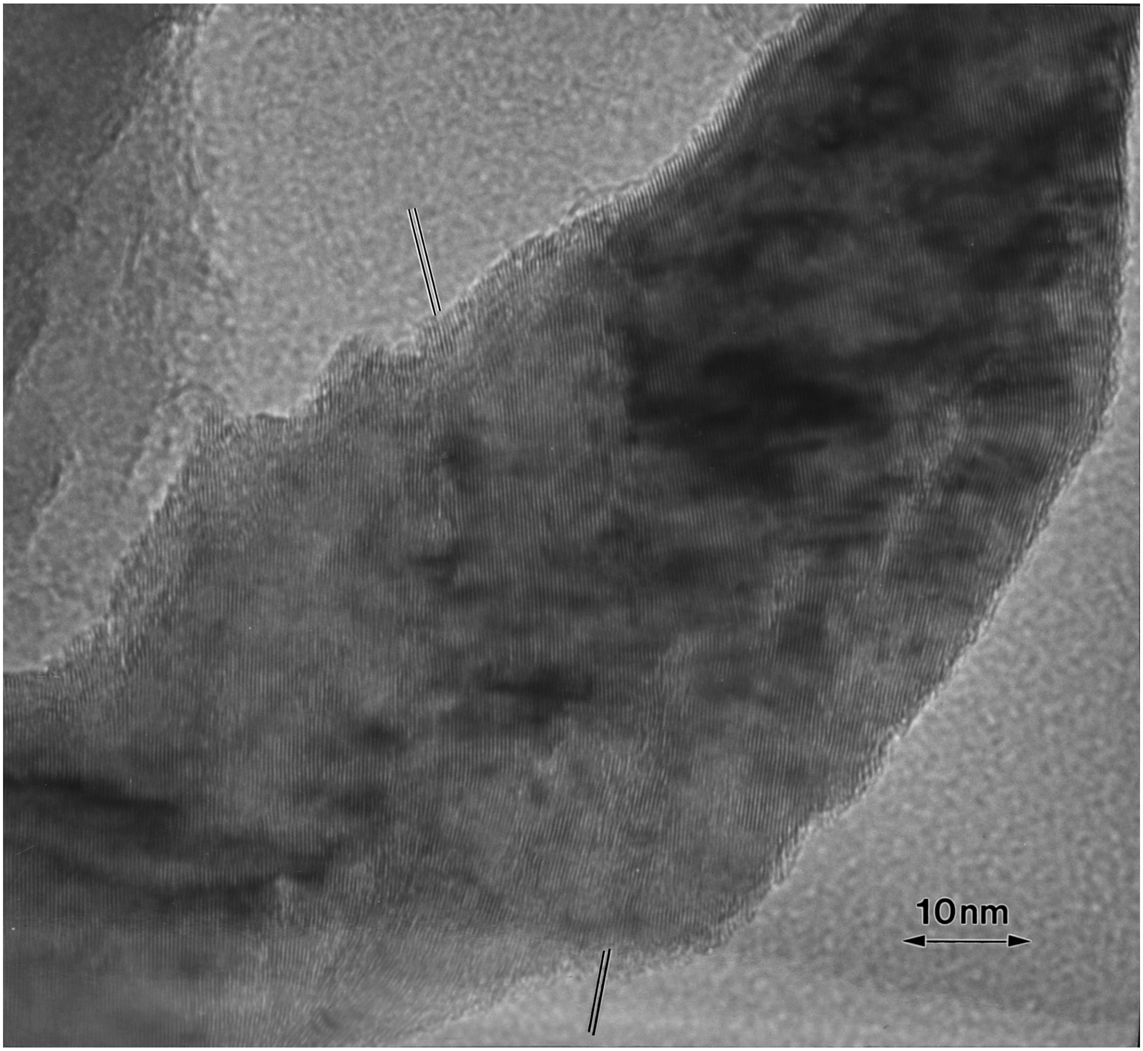

FIG. 7. High resolution transmission electron micrograph of a section of a carbon filament generated from the interaction of an Fe-Ni (7 : 3) powder with C_2H_4/H_2 (1 : 1) at 600°C showing the arrangement of graphitic platelets in the structure.

the platelets were preferentially stacked at an angle to the fiber axis in a so-called "herring-bone" arrangement. In contrast, the number of filaments grown from the Fe–Ni (3 : 7) powder possessing these particular structural characteristics was very small.

The ratio of the hydrogen to ethylene in the reactant was also found to have a pronounced effect on the nature and growth of the carbon filaments from these Fe–Ni catalysts. As the concentration of hydrogen was progressively raised it was evident the carbon filaments grown from a given bimetallic formulation became increasingly more graphitic in nature. Electron diffraction studies of individual filaments combined with XRD analysis of bulk samples produced from a C_2H_4/H_2 (1 : 1) reactant stream indicated that the interlayer spacing between the graphite platelets of such materials was 0.335 nm, identical to that of graphite (34). In contrast, carbon filaments grown from the interaction of a C_2H_4/H_2 (4 : 1) mixture with the same bimetallic powder did not possess the same degree of crystalline perfection. A further notable feature was the observation that as hydrogen content in the reactant was increased the metal particles responsible for generating the filaments lost their rounded corners and adopted a more distinctive faceted shape.

A fascinating phenomenon that was evident during the examinations of some of the carbon filaments formed from the reactant mixtures containing a large hydrogen content was the presence of metal particles that appeared to be entrained within the body structure, an example of which is shown in the micrograph, Fig. 8. This behavior is believed to be caused by the periodic loss of metallic fragments from the parent particle that remained at the growing tip of the filament. This behavior, which was first observed during controlled atmosphere electron microscopy experiments, eventually results in a gradual decrease in the width of the

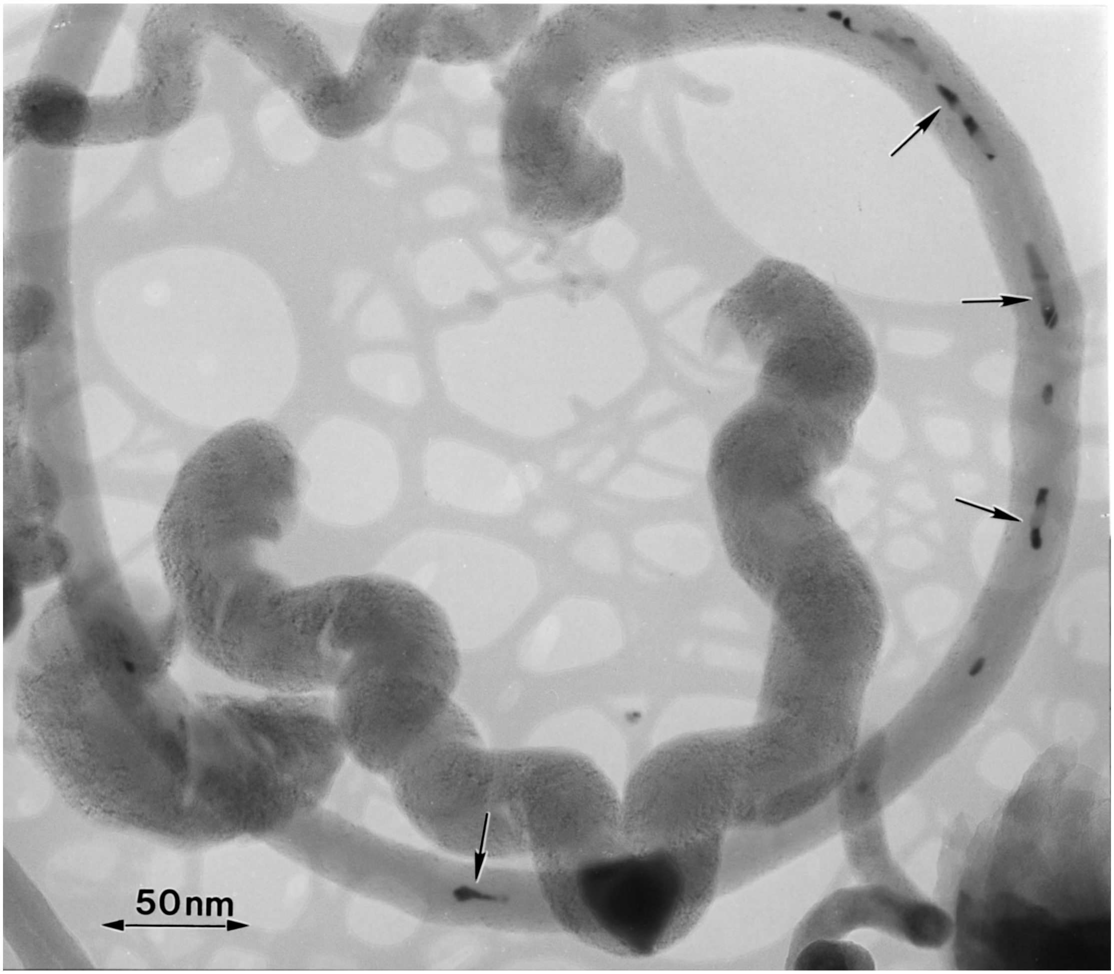

FIG. 8. Transmission electron micrograph showing the deposition of metal particles (indicated by arrows) in the central region of a carbon filament grown from interaction of an Fe-Ni (3 : 7) powder with an C_2H_4/H_2 (1 : 2) mixture at 600°C.

filament, giving rise to a tapered form (35), losing small sections of the tail piece as the filament grows. Whether the fragmentary metal particles are indeed inside the filament or merely located on the outside surface of the carbon structure is still to be ascertained in future studies.

2.2. *Temperature-Programmed Oxidation Studies*

Temperature-programmed oxidation profiles of demineralized carbon filaments grown from the interaction of a series of Fe–Ni catalyst powders with C_2H_4/H_2 (4 : 1) mixture at 600°C are presented in Fig. 9. One striking feature to emerge from these oxidation profiles is the apparent separation in the oxidation characteristics of these carbon filaments into two distinct classes between the compositions Fe–Ni (3 : 7) and Fe–Ni (25 : 75). Initially as the amount of nickel in the catalyst formulation is increased there is a concomitant drop in the onset temperature for oxidation, indicative of a progressive decrease in the graphitic nature of the carbon filaments. An extraordinary change in this sequence of structural characteristics occurs when the nickel content of the catalyst particles reaches a level of 75%. Under these circumstances, the graphitic nature of the filaments increases dramatically when compared to those produced from catalyst formulations containing 70% or less nickel. As the amount of nickel in the bimetallic is further increased above 75% there is a corresponding increase in the degree of crystalline perfection of the filamentous deposit. It is clear therefore, that as the nickel content in the catalyst is increased from 70 to 75%, an extraordinary change takes place, not only in the amount of carbon filaments generated, but also in the structural characteristics of the material.

An analogous set of TPO experiments were carried out on demineralized carbon filaments produced from systems where selected Fe–Ni catalysts were exposed at 600°C to reactant mixtures containing various concentration levels of hydrogen. An example of the influence of hydrogen on the structural characteristics of the filaments can be seen in the series of oxidation profiles shown in Fig. 10, where the data have been obtained from carbon filaments generated from

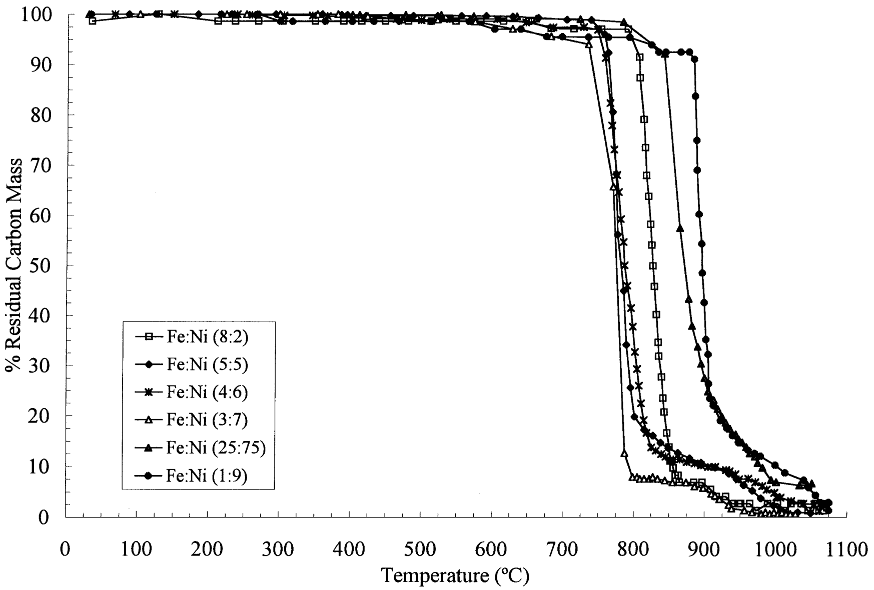

FIG. 9. Comparison of the gasification characteristics in CO_2 of carbon filaments formed during the interaction of selected Fe-Ni catalysts with C_2H_4/H_2 (4 : 1) mixtures at 600°C.

the reaction of a Fe–Ni (7 : 3) catalyst with various C_2H_4/H_2 mixtures at 600°C. It is evident from this set of oxidation profiles that the reactant feed composition has a significant impact on the graphitic nature of the filamentous carbon deposited on the bimetallic catalyst. For all the bimetallic compositions studied it was found that as the hydrogen content of the feed was increased so was the resistance to oxidation in a CO_2 atmosphere and, therefore, the graphitic nature of the filamentous carbon deposited increased.

2.3. In-Situ Electron Diffraction Studies

The distribution of chemical species present when Fe–Ni (1 : 1)/graphite specimens were heated in a 0.2 Torr ethylene/hydrogen (1 : 2) mixture at temperatures over the range 400 to 800°C and then finally cooled to room temperature is presented in Table 2. In all cases the specimen was held at a given temperature for 30 min before the electron diffraction pattern was taken. Examination of these

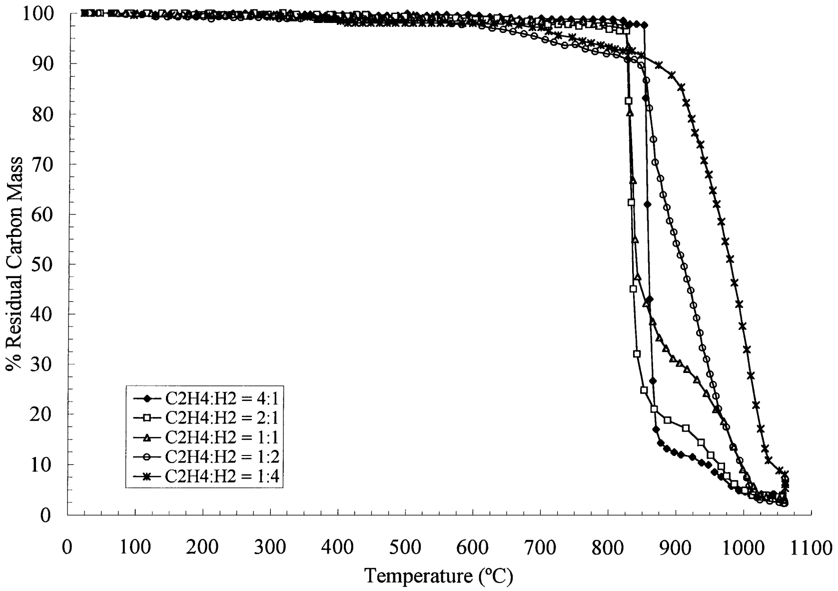

FIG. 10. Comparison of the gasification characteristics in CO_2 of carbon filaments grown from the interaction of an Fe-Ni (7 : 3) powder with ethylene containing various amounts of added hydrogen at 600°C.

TABLE 2

Electron Diffraction Pattern Analysis of a Fe–Ni/Graphite Specimen as a Function of Temperature in 0.2 Torr Ethylene/Hydrogen (1 : 2)

Temperature (°C)	Calculated *d*-spacings (nm)	*d*-spacings (nm)				
		Fe–Ni (1 : 1)	Fe–Ni (7 : 3)	Fe–Ni (3 : 7)	Fe	Ni
400	0.2096	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1619		$0.1614_{(420)}$			
	0.1274	$0.1270_{(220)}$	$0.1260_{(110)}$			
	0.1048	$0.1037_{(222)}$		$0.1047_{(631)}$		
600	0.2353		$0.2398_{(221)}$			
	0.2083	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1660		$0.1673_{(330)}$			
	0.1578		$0.1572_{(421)}$			
	0.1278	$0.1270_{(220)}$	$0.1260_{(110)}$	$0.1253_{(222)}$		
650	0.2442		$0.2398_{(221)}$			
	0.2073	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1605		$0.1614_{(420)}$			
	0.1278	$0.1270_{(220)}$	$0.1260_{(110)}$			
700	0.1801	$0.1800_{(200)}$	$0.1784_{(400)}$	$0.1772_{(200)}$		
	0.1540		$0.1542_{(110)}$			
	0.1257	$0.1270_{(220)}$	$0.1260_{(110)}$	$0.1253_{(222)}$		
	0.1083	$0.1083_{(311)}$				
750	0.2515		$0.2526_{(222)}$			
	0.2069	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1701		$0.1673_{(330)}$			
	0.1276	$0.1270_{(220)}$	$0.1260_{(110)}$			
	0.1094	$0.1083_{(311)}$				
800	0.2090	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1287	$0.1270_{(220)}$				
	0.1083	$0.1083_{(311)}$				
Cooled to 25°C	0.2084	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1270	$0.1270_{(220)}$	$0.1260_{(110)}$			
	0.1086	$0.1083_{(311)}$				
	0.1045	$0.1037_{(222)}$		$0.1047_{(631)}$		

data reveals some interesting aspects. It is evident that while equimolar amounts of iron and nickel were introduced onto the graphite support, the nucleated particles do not all have this composition. The most significant finding is that once formed, the alloy particles maintain their original overall composition up to 800°C and on subsequent cooling to room temperature, there being no evidence for the formation of the separate metals. It should be stressed that the technique provides only information with respect to the bulk composition and does not give one an insight into the existence of possible surface segregation phenomena.

DISCUSSION

The results of this study demonstrate that the characteristics of the carbonaceous deposit formed on Fe–Ni catalyst during the decomposition of C_2H_4/H_2 are highly dependent on the interplay of a number of factors. Such variables include the ratio of the bimetallic components, the composition of the gaseous reactant, and the temperature at which the reaction is performed.

Effect of Catalyst Composition on Carbon Deposition

The composition of the Fe–Ni catalyst has been found to exert a profound effect, not only on the catalyst activity, but also on the nature and amount of the solid carbon product formed under the conditions used in this study. The observed low activity of iron and iron-rich bimetallic catalysts for the hydrogenation of ethylene, when compared with a nickel-rich catalyst, is consistent with the findings of other workers (1, 16, 31, 36) and is associated with the inability of iron to dissociatively chemisorb ethylene (11). It is intriguing to find that the addition of a further 5% nickel to a Fe–Ni (3 : 7) powder can bring about a dramatic change in the ability of the bimetallic system to catalyze the growth of filamentous carbon from ethylene at 600°C. This result is consistent with the notion that the 5% increment in the nickel content of the bimetallic is responsible for inducing a change the arrangement of atoms in the particle surfaces at which ethylene adsorption occurs. Furthermore, since there is a significant increase in the graphitic character of the carbon filaments generated from this particular bimetallic, it would appear that this modification in crystallographic properties extends to those faces of the particles at which precipitation of carbon takes place. This conclusion is based on previous arguments, suggesting that the degree of crystalline perfection of carbon filaments is intimately related to the nature of the interfacial phenomena that exist at the metal–solid carbon boundary (37, 38). In order for dissolved carbon to be precipitated in a highly crystalline form, there must be a registry between the atomic spacing of the metal atoms in the depositing face and the atoms constituting the graphite basal plane structure. Yang and Chen (39) used a combination of HOMO calculations and selected area electron diffraction to show that the precipitation of graphite is limited to particular nickel faces. It is also found that these conditions match those where the metal particles undergo a wetting and spreading action with graphite, i.e. form a strong metal–substrate interaction (40).

It is an interesting exercise to compare the present results with those of an earlier study (18), where it was shown that for the decomposition of a CO/H_2 (4 : 1) mixture at 600°C the activity of Fe–Ni catalysts exhibited a significant decrease in activity as the fraction of nickel in the bimetallic was raised above 70%. Since there are no predicted or observed changes in the bulk structure of the alloy over the composition range 70 to 75% nickel, one might attribute the variations in catalytic activity to surface modifications of the bimetallic particles. The sudden increase in activity for C_2H_4 decomposition and the corresponding decrease for CO decomposition resulting from the addition of a mere 5% nickel to an Fe–Ni (3 : 7) powder is in all probability due to the reconstruction of the bimetallic particle surfaces.

It is possible that this behavior results in the creation of a surface where iron atoms are randomly dispersed, a condition that, on the one hand, favors dissociative chemisorption of C_2H_4, but functions in the opposite with respect to CO.

While the structural characteristics of the carbon filaments grown from both C_2H_4/H_2 and CO/H_2 mixtures at 600°C were substantially different when examined in the TEM some similarities were observed upon increasing the nickel content of the catalyst. High resolution studies revealed that filaments grown from the interaction of CO/H_2 mixtures with iron-rich powders were in general, relatively straight, highly crystalline in nature, and possessed structures in which the graphite platelets were aligned at an angle to the fiber axis in a "herring-bone" arrangement. The material grown from C_2H_4/H_2 mixtures on the same iron-rich catalyst powders adopted helical conformations and tended to consist of a less ordered structure than those generated from CO. In contrast, the morphological characteristics of carbon filaments produced from the interaction of these two reactant mixtures with nickel-rich bimetallic powders were similar, both being helical in form. It was, however, evident that in this case, the material generated from a C_2H_4/H_2 mixture was significantly more highly ordered in nature than that grown a CO/H_2 mixture. These observations highlight the difference in the strengths of interaction between CO and C_2H_4 and the bimetallic catalyst surface. On an iron-rich surface the interaction of CO is much stronger than that of C_2H_4, whereas the opposite relationship is found to exist on the nickel-rich surface.

The existence of a direct correlation between the electronic structure of Fe–Ni alloys and the electronic specific heat has been proposed by Lawniczak-Jablonska and Auleytner (41, 42). Studies carried out by these authors indicated that an Fe–Ni (25 : 75) alloy displays unique properties due to the formation of $FeNi_3$. They claimed that the formation of this intermetallic species was responsible for an ordering that in turn lead to changes in the electronic structure of the Fe–Ni alloy. This particular alloy composition was reported by Chourasia and Chopra (43) to undergo a charge transfer from Fe to Ni. This unusual behavior is not only limited to unsupported Fe–Ni alloys, since there are comparable examples observed when mixtures of iron and nickel particles have been supported on traditional carrier materials, such as alumina and silica. Yadav and coworkers (44) found that an Fe–Ni (1 : 3)/SiO_2 catalyst displayed an improved selectivity for the hydrogenation of benzonitrile and butyronitrile but did not exhibit the same benefits for the hydrogenation of crotonitrile. These authors rationalized the increased activity on the basis of a charge transfer from Fe to Ni. Rao and co-workers (45) investigated the hydrogenation of benzophenone over Fe–Ni and demonstrated that an Fe–Ni (1 : 3) catalyst exhibited the highest activity for this reaction and attributed this finding to the formation of a superparamagnetic alloy at this particular composition.

Influence of Hydrogen on Carbon Deposition

We have found that a reduced nickel powder, thoroughly flushed with helium, displayed very little catalytic activity for the decomposition of ethylene, in the absence of hydrogen, to either ethane or solid carbon. On the other hand, if the helium flushing step was omitted, following the reduction of the metal or hydrogen introduced into the ethylene stream then significant quantities of ethane and, in particular, carbon were produced. Under these conditions the decomposition of ethylene occurred rapidly with approximately 70% being converted to either ethane or solid carbon. These findings are in agreement with previous studies by Zaera (46), who reported that ethylene would only decompose to form ethane on nickel in appreciable quantities if hydrogen had been preadsorbed or co-adsorbed onto the metal surface.

It was interesting to find that, while the addition of hydrogen had a promotional effect on the ethylene decomposition reaction over all the Fe–Ni powders, the precise concentration that was required to achieve optimum performance was dependent on the composition of the bimetallic powder. Those powders containing less than 75% nickel exhibited a steady rise in catalytic activity as the level of hydrogen in the reactant was progressively increased. As the nickel content in the bimetallic was increased so the amount of hydrogen in the reactant feed necessary to reach the maximum deposition of carbon at 600°C decreased as detailed in Table 3. This aspect is consistent with the inability of iron to readily decompose or hydrogenate ethylene, a large fraction of hydrogen being needed to facilitate this reaction as the amount of iron in the catalyst was progressively raised.

The enhancement in the degree of crystalline perfection of the carbon filaments formed during the interaction of mixtures of ethylene containing increasing amounts of hydrogen with a given Fe–Ni powder is consistent with result obtained for the growth of this type of carbon when the

TABLE 3

Percentage of Hydrogen in the Ethylene Reactant Required to Achieve the Maximum Growth of Filamentous Carbon from Fe–Ni Powders at 600°C for 90 min

Catalyst composition	% H_2 in feed to achieve maximum carbon deposition
Ni	33
Fe : Ni (2 : 8)	33
Fe : Ni (3 : 7)	50
Fe : Ni (7 : 3)	67
Fe	80

corresponding reactant compositions were passed over other bimetallics (18, 21, 22, 28). The presence of added hydrogen in the reactant is believed to be responsible for inducing reconstruction of the metal particle surfaces to generate a set of faces that favor the precipitation of carbon in the form of graphite. This aspect was highlighted from examinations performed by TEM of carbon filaments generated from a series of reactant mixtures, which indicated that the associated metal catalyst particles tended to become progressively more faceted as the hydrogen content of the reactant gas was increased.

A further contributing factor to modification in crystalline structure of carbon filaments is the observation from controlled atmosphere electron microscopy studies that in the presence of hydrogen, Fe–Ni particles tend to undergo a wetting and spreading action on graphite at temperatures of around 600°C, features that are consistent with the establishment of a strong metal–support interaction (47). While the addition of other gases to the reactant may exert an impact on this type of action, the presence of small amounts of hydrocarbons do not appear to modify such behavior. This phenomenon is most certainly responsible for the sporadic loss of small amounts of metal from the active particles, the fragments of which were subsequently found as inclusions at the center of filaments generated from systems where the reactant gas had a high hydrogen content Fig. 8.

In-situ electron diffraction analysis of a model catalyst system provides important information pertaining to any chemical changes that might be occurring in individual bimetallic particles as a function of temperature and gas environment. It should be appreciated that, although these experiments were carried out with a model system, the chemical behavior exhibited by such a sample should parallel those of the powdered catalysts used in the flow reactor studies. It is evident that while nickel-rich bimetallic particles tend to undergo a wetting and spreading action on graphite the particles do not exhibit any major perturbations in their chemical composition during the interaction with a C_2H_4/H_2 (1 : 2) mixture at temperatures up to 800°C. One may conclude therefore, that during this process there is no separation of the bimetallic into its separate components or preferential removal of one of the metals during the catalyst fragmentation step described above. While this behavior does not appear to exert any influence on the structural characteristics of the filaments it does make the determination of turnover frequencies (TOF) a futile operation, since one cannot make an accurate determination of the active area of the catalyst particle at any given point in time.

Effect of Temperature on Carbon Deposition

The decomposition of ethylene over selected Fe–Ni catalysts was found to be highly dependent upon the reaction temperature. At 725°C the conversion of ethylene is similar over all Fe–Ni catalysts tested; however, upon decreasing the temperature to 600°C significant differences were observed between the Fe–Ni (3 : 7) and Fe–Ni (2 : 8) compositions. Indeed, for all bimetallic powders having a nickel content of below 80% a very pronounced drop in activity was observed upon decreasing the temperature from 725 to 600°C. It was interesting to find that reproducible activity levels were attained if the temperature was cycled between these two limits. In contrast, the catalytic activity of the Fe–Ni (2 : 8) powder did exhibit the same sharp decrease over this temperature range. It is possible that at the higher temperatures preferential segregation of nickel to the surface of the bimetallic occurs and, as the temperature is lowered, the composition of this region is restored to that of the bulk. It would appear that the presence of a significant amount of iron in the surface of the bimetallic effectively inhibits the decomposition of ethylene. In powders containing 80% nickel and higher, this effect does not exert the same degree of influence and, as a consequence, there is little change in catalytic behavior as the temperature is changed over this range.

This sequence of events is to be compared with that found when the same set of Fe–Ni powders were reacted in CO and the opposite trend in catalytic behavior was observed as a function of nickel content (18). At temperatures of about 550°C, even powders containing excess nickel exhibited relatively high activity towards the decomposition of CO, indicating that the amount of iron present in the surface was sufficient to catalyze this reaction. On the other hand, as the temperature was raised to 725°C the decomposition of CO was suppressed, a condition consistent with surface enrichment in nickel.

Support for the notion that nickel preferentially segregates to the surface of Fe–Ni powders is found from the work of Wandelt and Ertl (48) who used soft X-ray spectroscopy to examine the effect of heating alloys of these two metals and reported that under these conditions there was an increase in the apparent potential of nickel while that of iron remained unchanged. This result was interpreted in terms of a model in which nickel was purported to enrich the alloy surface. Chelikowsky (49) using a modified theoretical model proposed by Miedema (50) predicted that, under reducing conditions, nickel would preferentially segregate to the surface of Fe-Ni alloys.

CONCLUSIONS

The composition of Fe–Ni catalysts has been shown to exert a profound influence on both the crystalline nature and structure of carbon filaments produced during the reaction with C_2H_4/H_2 mixtures. The addition of 5% nickel to a Fe–Ni (3 : 7) catalyst resulted in a dramatic increase in the conversion of ethylene from 13.0 to 52.0% and a corresponding increase in the amount of solid carbon from 4.6 to 38.5%. The graphitic content, as determined by TPO and TEM studies, of the carbon filaments produced from the interaction of the bimetallic powders with ethylene exhibited a significant increase between the compositions of Fe–Ni (3 : 7) and Fe–Ni (25 : 75). It is suggested that this abrupt change in structural characteristics of the filaments is directly related to a transformation in the crystallographic features of the catalyst particles over this composition range.

The extent of the influence of added hydrogen on the decomposition of ethylene was extremely sensitive to the composition of the Fe–Ni powder. Iron-rich bimetallic powders did not exhibit any substantial change in performance until the level of hydrogen in the reactant reached about 66%. On the other hand, the catalytic behavior of bimetallic powders containing 70% or more of nickel, showed a significant improvement at relatively low concentrations of hydrogen. It was evident that, as the hydrogen content of the reactant was raised, modifications in the structural conformations and an enhancement in the degree of crystalline perfection of the carbon filaments produced from all the bimetallic powders were observed.

Finally, it was found that increasing the temperature from 600 to 725°C favored the decomposition of ethylene over all Fe–Ni powders, this effect being most marked over those bimetallic particles containing 70% or less nickel. This behavior is to be contrasted with that found in an earlier study that demonstrated that the reverse dependence held when the same set of bimetallics was reacted in CO. The phenomenon appears to be related to preferential segregation of nickel to the gas/particle interface at higher temperatures; a condition that favors decomposition of C_2H_4, but opposes the decomposition of CO.

ACKNOWLEDGMENT

Financial support for this work was provided by the U. S. Department of Energy, Basic Energy Sciences, Grant DE-FG02-93ER14358. The authors thank Professor N. M. Rodriguez for stimulating discussions doing the course of this investigation.

REFERENCES

1. Brucker, C., and Rhodin, T., *J. Catal.* **47**, 214 (1977).
2. Erley, W., Baro, A. M., and Ibach, H., *Surf. Sci.* **120**, 273 (1982).
3. Seip, U., Tsai, M. C., Küppers, J., and Ertl, G., *Surf. Sci.* **147**, 65 (1984).
4. Stoscio, J. A., Bare, S. R., and Ho, W., *Surf. Sci.* **148**, 499 (1984).
5. Bhattacharya, A. K., and Chesters, M. A., *Surf. Sci.* **186**, 279 (1987).
6. Zaera, F., and Hall, R. B., *Surf. Sci.* **180**, 1 (1987).
7. Rye, R. R., Greenlief, L. M., Goodman, D. W., Hardegree, E. L., and White, J. M., *Surf. Sci.* **203**, 101 (1988).
8. Zhu, X. Y., Castro, M. E., Akhter, S., White, J. M., and Houston, J. E., *Surf. Sci.* **207**, 1 (1988).
9. Morgante, A., Modesti, S., Bertolo, M., Rudolf, P., and Rosrei, R., *Surf. Sci.* **212**, 829 (1989).
10. Zhu, X. Y., and White, J. M., *Surf. Sci.* **214**, 240 (1989).
11. Burke, M. L., and Madix, R. J., *J. Am. Chem. Soc.* **113**, 4151 (1991).
12. Daley, S. P., Utz, A. L., and Trautman, T. R., *J. Am. Chem. Soc.* **116**, 6001 (1994).
13. Vorburger, T. V., Sandstrom, D. R., and Waclawski, B. J., *Surf. Sci.* **60**, 211 (1976).
14. Textor, M., Gay, I. D., and Mason, R., *Proc. Roy. Soc. A* **356**, 37 (1977).
15. Goodman, D. W., Madey, T. E., and Yates, Jr., J. T., *J. Catal.* **50**, 279 (1977).
16. Rodriguez, N. M., Kim, M. S., and Baker, R. T. K., *J. Catal.* **144**, 93 (1993).
17. Hung, W. H., and Bernasek, S. L., *Surf. Sci.* **339**, 272 (1995).
18. Park, C., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **169**, 212 (1997).
19. Dowden, D. A., and Reynolds, P., *Discuss. Faraday Soc.* **8**, 184 (1950).
20. Dowden, D. A., *J. Chem. Soc.*, 242 (1950).
21. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **131**, 60 (1990).
22. Rodriguez, N. M., Kim, M. S., and Baker, R. T. K., *J. Catal.* **140**, 16 (1993).
23. Audier, M., Guinot, J., Coulon, M., and Bonnetain, L., *Carbon* **19**, 99 (1981).
24. Audier, M., Oberlin, A., Oberlin, M., Coulon, M., and Bonnetain, L., *Carbon* **19**, 217 (1981).
25. Audier, M., and Coulon, M., *Carbon* **23**, 317 (1985).
26. Wachs, I. E., Dwyer, D. J., and Iglesia, E., *Appl. Catal.* **12**, 201 (1984).
27. Wielders, A. F. H., Koebrugge, G. W., and Geus, J. W., *J. Catal.* **121**, 375 (1990).
28. Krishnankutty, N., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **158**, 217 (1996).
29. Rodriguez, N. M., *J. Mater. Res.* **8**, 3233 (1993).
30. Rodriguez, N. M., Chambers, A., and Baker, R. T. K., *Langmuir* **11**, 3862 (1995).
31. Cooper, B. J., and Trimm, D. L., *J. Catal.* **62**, 35 (1980).
32. Best, R. J., and Russell, W. W., *J. Am. Chem. Soc.* **76**, 838 (1954).
33. Oh, S. G., and Baker, R. T. K., *J. Catal.* **128**, 137 (1991).
34. Marsh, H., *in* "Carbon and Coal Gasification" (J. L. Figueiredo and J. L. Moulijn, Eds.), p. 29. NATO ASI Series, Kluwer, Dordrecht, 1986.
35. Baker, R. T. K., and Waite, R. J., *J. Catal.* **37**, 17 (1975).
36. Sacco, A., *in* "Carbon Fibres Filaments and Composites" (J. L. Figueiredo *et al.*, Eds.), p. 459. Kluwer Academic, Amsterdam, 1990.
37. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **134**, 253 (1992).
38. Owens, W. T., Rodriguez, N. M., and Baker, R. T. K., *Catal. Today* **21**, 3 (1994).
39. Yang, R. T., and Chen, J. P., *J. Catal.* **113**, 52 (1989).
40. Angermann, H. H., and Horz, G., *Appl. Surf. Sci.* **70**, 163 (1993).
41. Lawniczak-Jablonska, K., and Auleytner, J., *J. Phys. F: Met. Phys.* **12**, 2523 (1982).
42. Lawniczak-Jablonska, K., and Auleytner, J., *J. Phys. F: Met. Phys.* **12**, 2729 (1982).
43. Chourasia, A. R., and Chopra, D. R., *Surf. Sci.* **206**, 484 (1988).
44. Yadav, G. D., and Kharkara, M. R., *Appl. Catal.* **126**, 115 (1995).
45. Rao, C. N. R., Kulkarni, G. U., Kannan, K. R., and Chaturvedi, S., *J. Phys. Chem.* **96**, 7379 (1992).
46. Zaera, F., *J. Catal.* **121**, 318 (1990).
47. Baker, R. T. K., Chludzinski, J. J., and Sherwood, R. D., *Carbon* **23**, 245 (1985).
48. Wandelt, K., and Ertl, G., *J. Phys. F: Met. Phys.* **6**, 1607 (1976).
49. Chelikowsky, J. R., *Surf. Sci.* **139**, 1197 (1984).
50. Miedema, A. R., *Z. Metallkde* **69**, 455 (1978).