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Carbon Deposition on Iron–Nickel During Interaction with Ethylene–Carbon Monoxide–Hydrogen Mixtures

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We have carried out a comprehensive investigation of the decomposition of a C_2H_4/CO/H_2 reactant mixture over a series of Fe–Ni catalysts. Detailed analysis of both the gaseous products and the amount of solid carbon deposited have revealed that co-adsorption of the two carbon-containing gases produces major modifications in the behavior of the bimetallic surfaces. It was evident that the addition of CO to a C_2H_4/H_2 feed resulted in a substantial increase in the decomposition of the olefin over all the bimetallic powders with this effect being most pronounced on the iron-rich systems. The major product from this series of Fe–Ni catalysts was found to be solid carbon in the form of various filamentous structures. The possibility that adsorption of CO was responsible for inducing perturbations in the electronic properties of the bimetallic surfaces is considered to be a contributory factor to the change in the catalytic action. A reversible deactivation/reactivation phenomena was shown to exist for iron-rich bimetallic catalysts that was observed when either CO or C_2H_4 was removed and subsequently re-introduced into the reactant feed. It was interesting to find that under the same conditions this behavior did not prevail with nickel-rich bimetallic catalysts, which merely exhibited the traditional irreversible deactivation. © 2000 Academic Press

INTRODUCTION

In previous studies we have examined the behavior of Fe–Ni catalysts during the hydrogenation of both carbon monoxide and ethylene in the presence of hydrogen at moderate temperatures (1, 2). These investigations highlighted the contrasting effect that iron and nickel display under identical conditions with the different reactants. Nickel-rich catalysts were found to favor the decomposition of ethylene but only showed a limited ability to decompose CO, whereas an iron-rich catalyst exhibited completely the opposite pattern of behavior under identical conditions.

This difference in the catalytic behavior of the two metals was also reflected in the type of filamentous carbon structures that were produced from the decomposition of the respective carbon-containing gases. Carbon filaments generated from the interaction of pure iron or iron-rich bimetallics with a CO/H_2 reactant mixture tended to form via a whisker-like mode, where the catalyst particle was located at the growing tip (1, 3–5). These structures consisted of graphite platelets that were oriented in a direction parallel to the fiber axis, thereby conferring a tubular conformation on the filaments. When the same set of metal powders were reacted in a C_2H_4/H_2 mixture, under otherwise identical conditions, the carbon filaments were formed by a bi-directional mode where the catalyst particles remained embedded within the helical structures (2). Distinct differences were also observed in the structural characteristics of carbon filaments grown from the interaction of Ni-rich bimetallic powders with CO/H_2 and C_2H_4/H_2 mixtures (1, 2). Only sparing amounts of solid carbon were produced from the former reaction, and the rope-like filamentous structures were composed of highly disordered carbon. In contrast, when the same metal powders were heated in the C_2H_4/H_2 reactant mixture an abundance of carbon filaments were formed, and at nickel contents $>70\%$ the structures acquired a high degree of crystalline perfection in which the graphite platelets were stacked at an angle to the fiber axis in a so-called "herring-bone" arrangement.

Cycling of the temperature between 600 and 725°C was found to exert the opposite effect on the reaction of the Fe–Ni powders with CO/H_2 and C_2H_4/H_2 mixtures. The activity of the bimetallic catalysts decreased significantly for the decomposition of CO at the higher temperature, whereas it exhibited an expected increase when the reaction was performed in the presence of the olefin. This behavior was rationalized according to the finding that in the Fe–Ni system preferential segregation of nickel to the gas/particle interface occurs at the higher temperature, a condition that favored decomposition of ethylene, but had an adverse influence toward CO decomposition. The logical question to ask is, what sequence of events will transpire when the Fe–Ni system is treated in a reactant mixture containing both CO and ethylene?

Surface science studies conducted by Burke and Madix (6, 7) demonstrated that the hydrogenation of ethylene to ethane could be promoted by the presence of CO on an $Fe_{(100)}$ surface. In the absence of CO, hydrogenation of the olefin did not take place on this particular Fe surface. Rodriguez and co-workers (8) found that the activity of a

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powdered Fe catalyst for the decomposition of ethylene to solid carbon and ethane could be dramatically increased by combining both CO and ethylene in the reactant feed. This enhancement in the catalytic activity was shown by these authors to be entirely reversible in nature. When CO was subsequently removed from the system the catalytic activity of iron reverted back to its original low level for the hydrogenation of ethylene. This behavior was attributed to a combination of factors, a possible reconstruction of the Fe surface by CO to one that favored dissociative chemisorption of ethylene and a modification in the electronic properties of the metal surface created by the electron withdrawing capabilities of adsorbed CO molecules.

It is well documented that hydrocarbon species are extremely sensitive to the presence of CO when they are co-adsorbed on a metal surface (9–13). Somorjai and coworkers reported that the presence of CO promoted the ordering of many hydrocarbons and organic molecules on selected metal surfaces (11, 14–17). When CO and benzene were co-adsorbed on an $Rh_{(111)}$ surface the hydrocarbon molecules were found to be tightly bound to the surface before undergoing distortion and fragmentation rather than remaining intact. It was claimed that under these conditions there was an increase in the back donation of electrons from the substrate to the adsorbed CO and this in turn led to a greater donor–acceptor interaction; that is, CO promoted the scission of the C–C bonds in the benzene molecule thereby resulting in the observed fragmentation.

In the current investigation attention has been focused on the influence of both CO and ethylene on the activity of a series of Fe–Ni catalysts and the characteristics of the filamentous carbon deposited during such reactions. A further objective of the study was to establish whether the presence of both CO and ethylene in the reactant feed exerted an influence on any particular reaction pathway that was found to result in the formation of one product at the expense of another.

EXPERIMENTAL

Materials

The Fe–Ni catalyst powders used throughout this study were prepared by a standard method in which the metal carbonates were co-precipitated from the respective metal nitrate solutions using ammonium bicarbonate as described in detail by Best and Russell (18). The subsequent calcination, reduction, and passivation procedures carried out on these catalysts were outlined in detail in a previous paper (1). The gases employed in this investigation, hydrogen (99.999%), carbon monoxide (99.99%), ethylene (99.95%), and helium (99.999%), were obtained from MG Industries and were used without any further purification. Reagent-grade iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] and reagent grade nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] used for the catalyst preparation were obtained from Fisher Scientific.

Apparatus and Procedures

Flow reactor studies were performed in a horizontal tube furnace at 600°C, and the bimetallic catalysts were reduced at this temperature for 2 h in a 10% H_2/He mixture prior to introduction of the reactant gas. The gas flow to the reactor was precisely regulated by the use of mass flow controllers allowing a constant reactant composition to be delivered to the powdered catalyst. In a typical experiment passivated catalyst samples (50 mg) were placed in a ceramic boat at the center of the reactor tube in the furnace. After reduction, the system was flushed for 1 h with helium to remove any chemisorbed hydrogen from the metal surface. The desired reactant gas, CO/H_2, C_2H_4/H_2, or a $C_2H_4/CO/H_2$ mixture, was then introduced to the reduced catalyst for periods of up to 3.5 h. The ensuing reaction was carefully monitored as a function of time by sampling both the inlet and the outlet gas streams at regular intervals and analyzing the reactants and products by gas chromatography using a 30-m megabore (GS-Q) capillary in a Varian 3400 GC. Carbon and hydrogen atom mass balances in combination with the relative concentrations of the various products were used to determine the yields. The percentage of water produced in a given reaction was calculated from an oxygen balance. The total amount of carbon deposited was calculated by careful analysis of the gas chromatography data using carbon mass balances and gravimetrically by weight difference at the conclusion of each experiment. In all cases the calculated and measured weights of solid carbon were within ±5%.

The nature and characteristics of the carbon deposited during these studies was established using high-resolution transmission electron microscopy (HRTEM) and temperature-programmed oxidation (TPO) studies. The TEM investigations were performed using a JEOL 2000EXll electron microscope equipped with a high-resolution pole piece capable of giving a lattice resolution of 0.18 nm. Suitable TEM specimens were prepared by the ultrasonic dispersion of the carbon sample in isobutanol and then the addition of a drop of the suspension to a holey carbon support film.

Temperature-programmed oxidation studies were carried out using a Cahn 2000 microbalance on demineralized carbon filaments in the presence of CO_2, a mild oxidant, at a constant heating rate, as outlined in greater detail in a previous paper (8). Comparison of the oxidation profiles of the filaments produced under various conditions with those of standard materials, amorphous carbon, and single-crystal graphite allows one to gain an estimate of the degree of crystalline perfection of the deposited carbon.

In situ electron diffraction studies were performed in the JEOL 2000EXll electron microscope when the instrument was equipped with a custom-built environmental cell. The specimens used in these experiments consisted of Fe–Ni (1 : 1) particles deposited onto transmission samples of single-crystal graphite, which were heated in a 0.2 Torr ethylene/CO/hydrogen (3 : 1 : 1) mixture over the range 500 to 775°C. Electron diffraction patterns were recorded at various stages of the reaction, and care was taken to minimize any spurious effects of the electron beam on the specimen by allowing the reaction to proceed to steady state at any given temperature with the beam switched off. Analysis of the diffraction patterns was accomplished by comparison of calculated *d*-spacings with those obtained from standard crystallographic data sources. Using this approach it is possible to ascertain the existence of any major changes in the chemical state of the bimetallic particles as a function of temperature.

RESULTS

1. *Continuous Flow Reactor Studies*

1.1. Effect of catalyst composition on the decomposition of a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture. The product distributions obtained from the decomposition of a $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant mixture over a range of Fe–Ni catalysts, measured after 2 h on stream at 600°C, are presented in Fig. 1. It is evident that increasing the nickel content of a series of the bimetallic catalysts had significant ramifications for the decomposition of the reactants, particularly that of ethylene. Furthermore, it was significant to find that the product distributions remained relatively constant even when the reaction was allowed to proceed for a further 90 min, there being no signs of catalyst deactivation for any of the samples. The first point of interest is that on a pure Fe catalyst there was a relatively high conversion of ethylene, approximately 45%, primarily to solid carbon and ethane, and approximately 30% conversion of CO to solid carbon, CO_2, and H_2O. The conversion of both CO and ethylene to methane was low and remained unchanged throughout this series of experiments. The addition of 10% nickel to a pure iron catalyst resulted in an increase in the conversion of the reactant mixture to solid carbon, which arises primarily from the decomposition of ethylene. It was interesting to find that, in general, changes in catalyst composition did not appear to exert any major influence on the yield of gaseous products produced in these reactions. Subsequent 10% increments in the nickel content of the catalyst powders resulted in significant increases in the conversion of ethylene to solid carbon. On the other hand, this change in catalyst composition was accompanied by a corresponding steady decrease in the conversion of CO to solid carbon and CO_2. With an Fe–Ni (5 : 5) catalyst, almost 80% of the ethylene was consumed in the reaction with the primary product being solid carbon. Under these same conditions there was a decrease in the conversion of CO to solid carbon and CO_2.

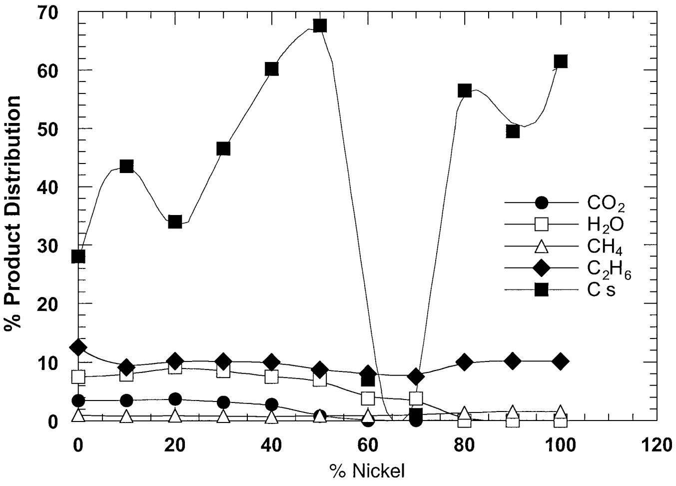

FIG. 1. The product distribution (%) from the decomposition of a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture versus the percentage of Ni in the catalyst composition at 600°C.

With bimetallic powders containing between 60 and 70% nickel, a precipitous drop in catalyst performance was observed. The conversion of ethylene exhibited a sharp decrease from 80 to 20% over an Fe–Ni (4 : 6) catalyst while that of CO decreased to 8%. When the reaction was carried out over an Fe–Ni (3 : 7) sample, a further decline in the conversion of ethylene, from 20 to 14%, took place. Indeed, over this composition range it was intriguing to find that the main product from the decomposition of ethylene was now ethane, the yield of which remained constant throughout these remarkable changes in the pattern of catalyst behavior.

On continued addition of nickel to the system the catalyst performance was almost restored to the level with an Fe–Ni (5 : 5) powder. When the gaseous reactant was passed over an Fe–Ni (2 : 8) catalyst the overall conversion to solid carbon climbed to 60%, the major contribution again being due to the decomposition of ethylene. At these high nickel contents the catalytic decomposition of the CO component in the reactant mixture was extremely low, no CO_2 or H_2O being detectable during the analysis, a finding that is consistent the results from previous Ni–CO/H_2 studies (8).

The amount of carbon deposited on the surface of the various Fe–Ni catalysts after reaction in a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture at 600°C for 3.5 h is presented in Fig. 2. The data is expressed as a percentage of the fraction of solid carbon produced from each carbon-containing gas as a function of catalyst composition. The procedure used to determine the amounts of solid carbon produced from these two sources is described in the Appendix. Inspection of these data clearly shows that carbon deposition on an Fe–Ni surface is extremely sensitive to the composition of the bimetallic catalyst.

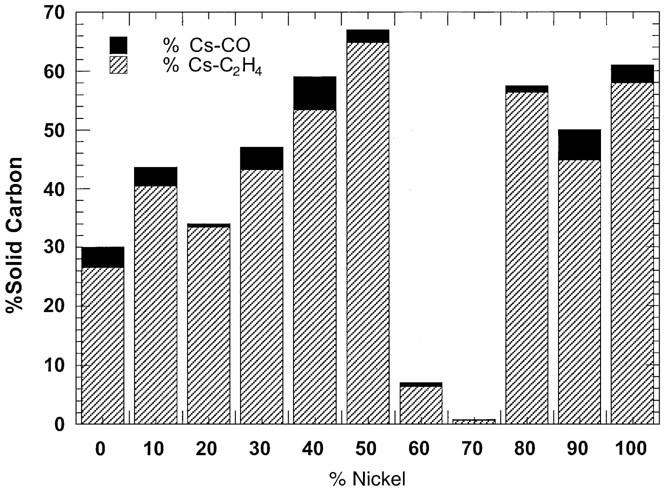

FIG. 2. The effect of the Fe–Ni catalyst composition on the percentage of solid carbon deposited on the catalyst surface during the decomposition of a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture after 3.5 h on stream.

1.2. Effect of gas composition on the product distribution from the interaction of various $C_2H_4/CO/H_2$ mixtures with iron–nickel. The effects of increasing the percentage of CO in a $C_2H_4/CO/H_2$ reactant mixutre on the product distribution of two selected catalyst compositions, Fe–Ni (6 : 4) and Fe–Ni (3 : 7), at 600°C are presented in Tables 1 and 2, respectively. The relative amounts of solid carbon produced from the ethylene and CO over these two catalyst powders as a function of the reactant gas are shown in Figs. 3 and 4, respectively. When approximately 20% CO was introduced into a C_2H_4/H_2 (4 : 1) mixture the olefin exhibited a subsequent increase in decomposition from 13 to 71% when the gaseous reactant was passed over an Fe–Ni (6 : 4) catalyst. As can be seen from Fig. 3 the increase in the decomposition of ethylene was accompanied by a corresponding enhancement in the yield of solid carbon. Under these conditions the conversion of CO was limited to 18% since most of the hydrogen was consumed in the hydrogenation of ethylene. With additional increases in the CO content of the reactant feed there was a corresponding increase in the decomposition of ethylene at 600°C. When the reactant feed contained 50% CO then about 88% of the olefin was converted, primarily to solid carbon and, to a much lesser extent, ethane. Although the overall conversion of the $C_2H_4/CO/H_2$ reactant mixture remained relatively uniform as the CO content was increased above 50%, there were significant variations in the product distributions. The overall conversion to solid carbon was observed to decrease with increasing CO content while the formation of ethane remained constant. At the same time the decomposition of CO to H_2O decreased while the formation of CO_2 increased.

The promotional effect exerted by CO on the decomposition of ethylene was not as pronounced when the reaction was carried out over an Fe–Ni (3 : 7) catalyst as seen from the data in Table 2 and Fig. 4. While the general trends were similar, in order to achieve results comparable to those observed with the Fe–Ni (6 : 4) powder, a higher CO content in the gaseous mixture was required when the reaction was performed with a nickel-rich catalyst. As the CO content in the reactant was progressively raised the overall conversion to solid carbon increased while the production of ethane exhibited an initial increase before reaching a steady level.

TABLE 1

Product Distributions (%) for the Decomposition of Various $C_2H_4/CO/H_2$ Mixtures over an Fe–Ni (6 : 4) Catalyst after 90 Min at 600°C

	$C_2H_4/CO/H_2$ (molar ratio)				
Product	(4 : 0 : 1)	(3 : 1 : 1)	(1 : 1 : 1)	(1 : 3 : 1)	(0 : 4 : 1)
CH_4	0.48	0.74	2.09	2.54	0.30
C_2H_6	7.77	10.18	14.06	10.96	0
CO_2	0	2.87	8.89	16.94	20.23
H_2O	0	7.90	17.36	12.19	4.92
Solid carbon	4.84	59.36	68.02	63.58	24.16

TABLE 2

Product Distributions (%) for the Decompositon of Various $C_2H_4/CO/H_2$ Mixtures over an Fe–Ni (3 : 7) Catalyst after 90 Min at 600°C

	$C_2H_4/CO/H_2$ (molar ratio)				
Product	(4 : 0 : 1)	(3 : 1 : 1)	(1 : 1 : 1)	(1 : 3 : 1)	(0 : 4 : 1)
CH_4	0.62	0.91	0.73	0.71	0.38
C_2H_6	7.85	7.78	14.02	10.53	0
CO_2	0	0	0	6.11	18.18
H_2O	0	0	3.08	5.62	3.27
Solid carbon	5.17	0.64	0.01	23.46	21.07

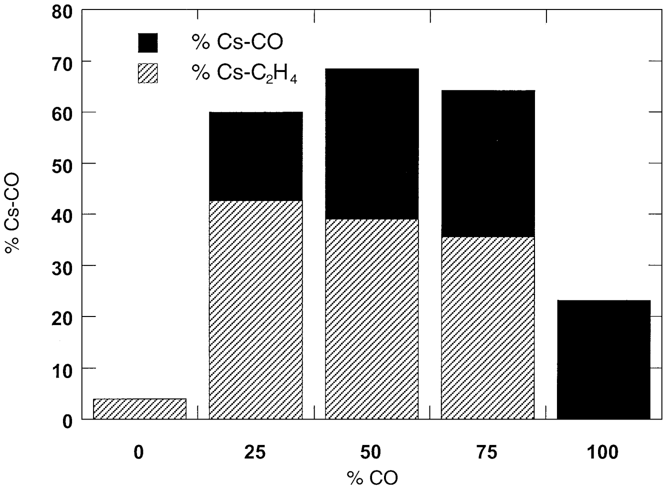

FIG. 3. Effect of increasing the CO content of a $C_2H_4/CO/H_2$ mixture on the percentage of solid carbon deposited on an Fe–Ni (6 : 4) catalyst after 90 min reaction at 600°C.

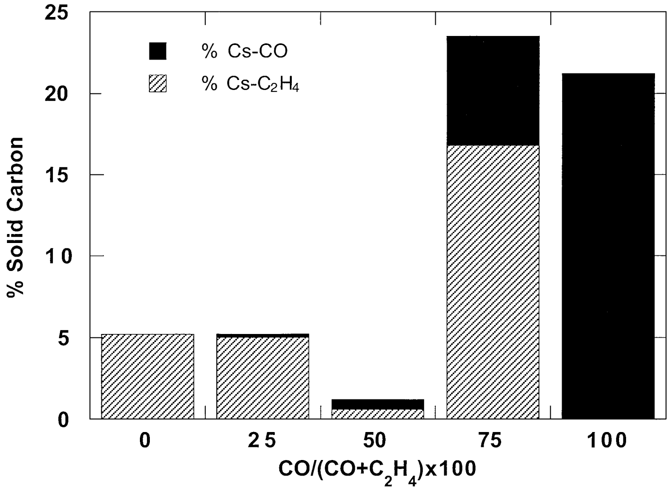

FIG. 4. Effect of increasing the CO content of a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture on the percentage of solid carbon deposited on an Fe–Ni (3 : 7) catalyst after 90 min reaction at 600°C.

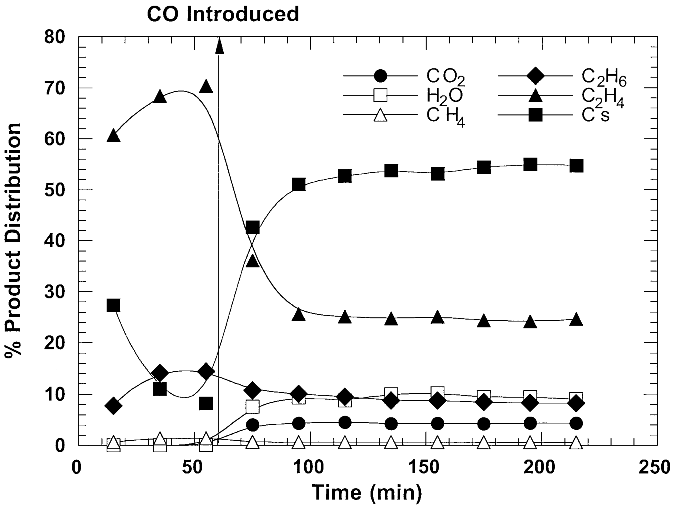

FIG. 5. Effect of the addition of 20% CO to a C_2H_4/H_2 (3 : 1) reactant feed on the product distribution (%) over an Fe–Ni (7 : 3) catalyst at 600°C.

At the same time the conversion of CO to CO_2 and H_2O exhibited an expected rise.

The contributions from each component to the total amount of solid carbon deposited on an Fe–Ni (3 : 7) catalyst during interaction with selected $C_2H_4/CO/H_2$ reactant mixtures is given in Fig. 4. As the CO content of the feed was increased, the calculated amount of carbon from the decomposition of CO increased accordingly. The ratio of the calculated amounts of carbon from the respective carbon sources did not follow the same trend as that exhibited by an Fe-rich catalyst. The optimum CO content in the reactant feed that was required to generate the maximum amount of solid carbon from the $C_2H_4/CO/H_2$ reactant feed was found to be 60% for a nickel-rich catalyst compared to 20% on an iron-rich catalyst.

1.3. Modifications in the product distribution following the injection of CO into a C_2H_4/H_2 reactant mixture. In an attempt to elucidate the role of each carbon-containing reactant gas molecule during the Fe–Ni-catalyzed decomposition of a $C_2H_4/CO/H_2$ mixture at 600°C, experiments were performed in which either CO or ethylene was systematically either injected or removed from the reactant stream. The sequence of events that transpired when CO was injected into a C_2H_4/H_2 mixture that had been undergoing reaction with an Fe–Ni (7 : 3) catalyst at 600°C for 60 min is shown graphically in Fig. 5. It can be seen that in the absence of CO the decomposition of ethylene exhibited a steady decline as a function of time and was accompanied by a concomitant decrease in the formation of solid carbon. Immediately following the introduction of CO into the system, however, there was an immediate increase in the decomposition of ethylene, primarily to solid carbon. Under these conditions an equilibrium conversion level was quickly attained, and a product selectivity pattern was established that remained constant for the duration of the experiment.

In a complimentary set of experiments the CO component of the $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant was removed and re-introduced into the mixture during interaction with an Fe–Ni (7 : 3) catalyst at 600°C. The effects of performing this series of operations on the decomposition characteristics of ethylene can be seen from the plots presented in Fig. 6. It was evident that when CO was eliminated from the reactant the initial high conversion of the olefin exhibited a dramatic drop, the yield of solid carbon decreasing correspondingly while the formation of ethane displayed a perceptible increase. Upon re-introduction of CO, the decomposition of ethylene was restored to its initial high level, and there

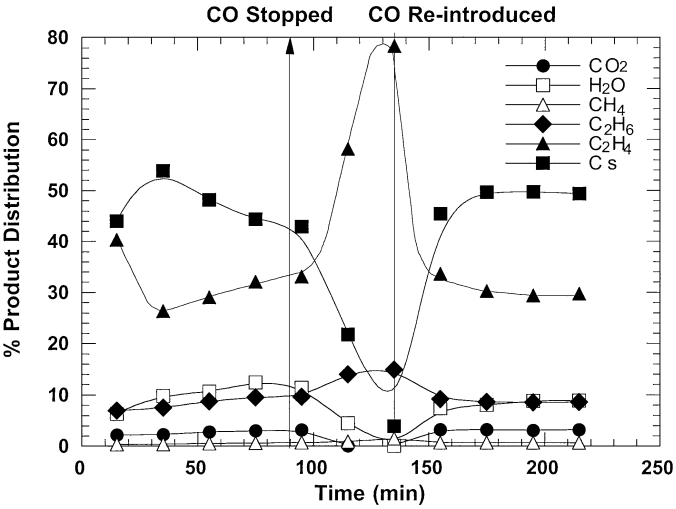

FIG. 6. Effect of eliminating and then re-introducing CO to a $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant mixture on the product distribution percentage from an Fe–Ni (7 : 3) catalyst at 600°C.

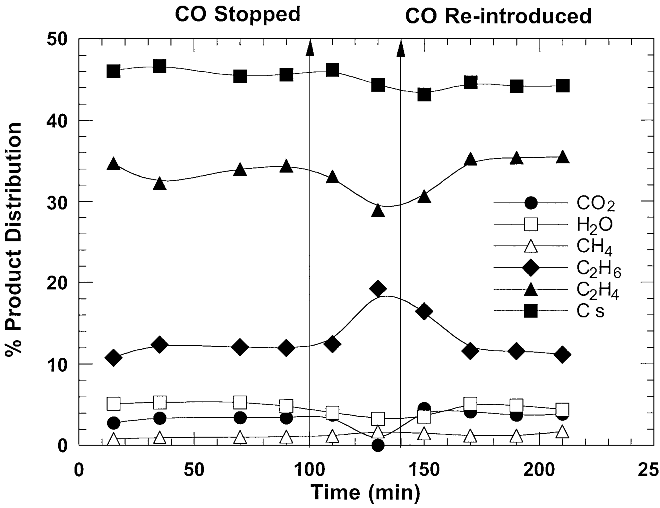

FIG. 7. Effect of eliminating and then reintroducing CO from a $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant feed on the product distribution (%) from an Fe–Ni (2 : 8) catalyst at 600°C.

was an immediate resumption of the formation of solid carbon. It was also interesting to find that the production of ethane declined to the previous value.

In order to gain further information, the sequence of experiments described above was extended to cover the behavior of a catalyst containing a higher percentage of nickel, and for this purpose an Fe–Ni (2 : 8) powder was selected. The results of switching CO into and out of the reactant gas mixture that was passed over the bimetallic catalyst at 600°C are presented in Fig. 7. From examination of these data it can seen that when CO was eliminated from the gaseous reactant, major differences in behavior were observed when compared with that exhibited by an iron-rich catalyst when reacted under the same conditions. In this case, the conversion of ethylene showed a modest increase of 5%, and the formation of ethane was enhanced by 10%. On the other hand, the yield of solid carbon tended to decrease during this period. When CO was re-introduced into the system the conversion of ethylene was restored to the initial level and a corresponding increase of about 7% in the formation of solid carbon was noted. The conversion of ethylene to ethane at this stage of the reaction decreased to a level consistent with that realized before the CO was removed from the feed.

1.4. Modifications in the product distribution following the injection of C_2H_4 into CO/H_2 reactant mixture. In a further series of experiments performed with the same two catalyst powders at 600°C the procedure was modified so that, in this case, ethylene was removed and subsequently re-introduced into the system. Examination of the data presented in Fig. 8, for the behavior of an Fe–Ni (7 : 3) catalyst, shows that at the start of the experiment the formation of solid carbon is at a relatively high value of 47%, and at the point where ethylene was eliminated from the feed, there was an initial drop in the yield of this product to 10% before it recovered to a level consistent with that produced on a CO/H_2 mixture at this temperature. The conversion of CO to CO_2 at this particular stage of the reaction increased to a level that was consistent with that produced from the interaction of a CO/H_2 reaction over this particular catalyst composition. The re-introduction of the olefin into the reactant feed after a period of 120 min had an immediate effect; the yield of solid carbon increased substantially after 5 min to a level higher than realized at the commencement of the reaction, before slowly decreasing to the initial value. This surge in carbon deposition was accompanied by a concomitant increase in the conversion of ethylene, after its re-introduction, before its activity steadily decreased in a similar fashion to a constant level.

Finally, the effect of removing the ethylene component from the gaseous reactant on the performance of an Fe–Ni (2 : 8) was investigated. Inspection of the plots presented in Fig. 9 reveals the existence of a complex pattern of behavior when the olefin was eliminated and then re-introduced into the system. The ethylene source was switched off after 40 min, and immediately the formation of solid carbon proceeded to drop by about 40%. The conversion of CO was very limited since its decomposition was not favored on a nickel-rich catalyst in the absence of ethylene. Upon re-introduction of the olefin into the reactant feed there was an unexpected outcome; instead of reverting to the original relatively high level of activity, the catalyst was found to exhibit a very poor performance for the decomposition of the olefin. This pattern of behavior was in sharp contrast to the situation encountered when a catalyst with a higher iron content was treated under the same conditions, Fig. 8.

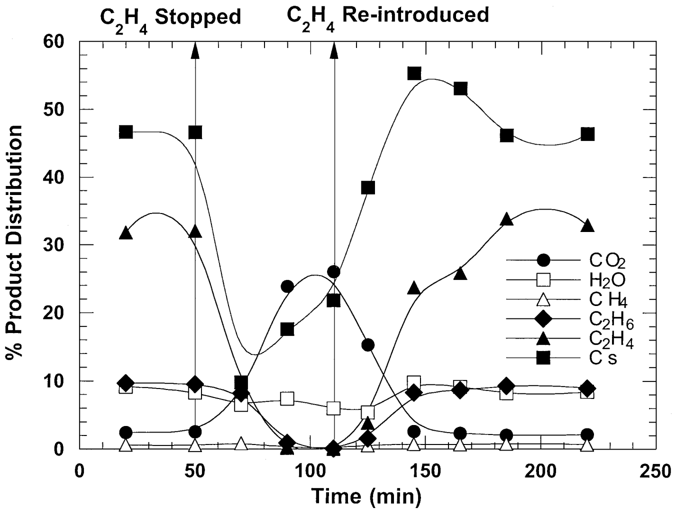

FIG. 8. Effect of removing and adding C_2H_4 to a $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant feed on the product distribution (%) from an Fe–Ni (7 : 3) catalyst at 600°C.

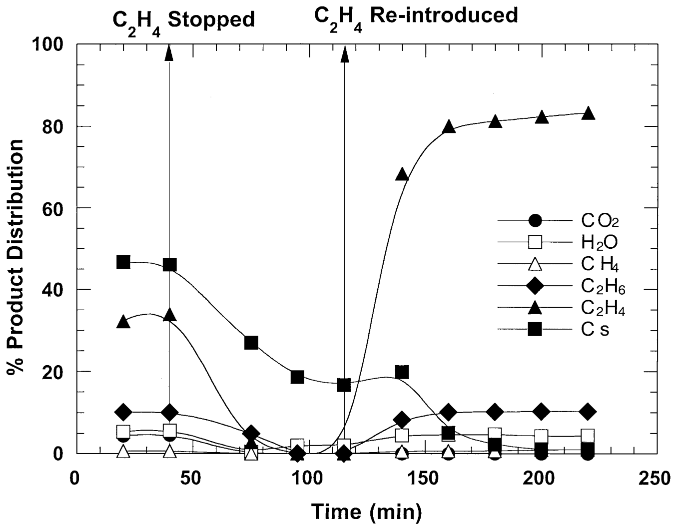

FIG. 9. Effect of eliminating and then reintroducing C_2H_4 from a $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant feed on the product distribution (%) from an Fe–Ni (2 : 8) catalyst at 600°C.

2. *Characterization of the Solid Carbon Product*

2.1. Transmission electron microscopy examinations. Previous studies have established that the conformation and degree of crystalline perfection of carbon filaments are extremely sensitive to the nature of the catalyst and its composition (19, 20). When the deposition reaction is carried out with two potential sources of carbon, CO and ethylene, one might expect to encounter unpredictable patterns of behavior with respect to the decomposition and precipitation steps occurring at the catalyst surfaces and the subsequent impact on the structure and characteristics of the carbon filaments.

The material grown from the interaction of an iron catalyst with $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture at 600°C possessed a helical conformation. Since the catalyst particles were located within the body of the filaments, it is reasonable to assume that the structures had been formed via a bidirectional mode, as seen in the micrograph in Fig. 10. It was interesting to find that the appearance of these filaments was very similar to those produced from the interaction of Fe–Ni (7 : 3) with a C_2H_4/H_2 mixture at the same temperature (2). A further feature to emerge from these examinations was the finding that the metal particles associated with the filaments tended to acquire a smooth globular morphology. This observation should be contrasted with the structures produced from the interaction of iron with CO/H_2 mixtures, where the filaments tended to be relatively straight and the catalyst particles adopted highly faceted shapes (1).

When the same reactant mixture was passed over a bimetallic powder containing an equal or larger amount of iron than nickel then the carbon filaments tended to be relatively straight and were formed via a whisker-like mode in which the catalyst particle responsible for the growth remained at the tip of the structure; see Fig. 11. Under these circumstances high-resolution examination showed that the material was highly crystalline in nature and consisted of

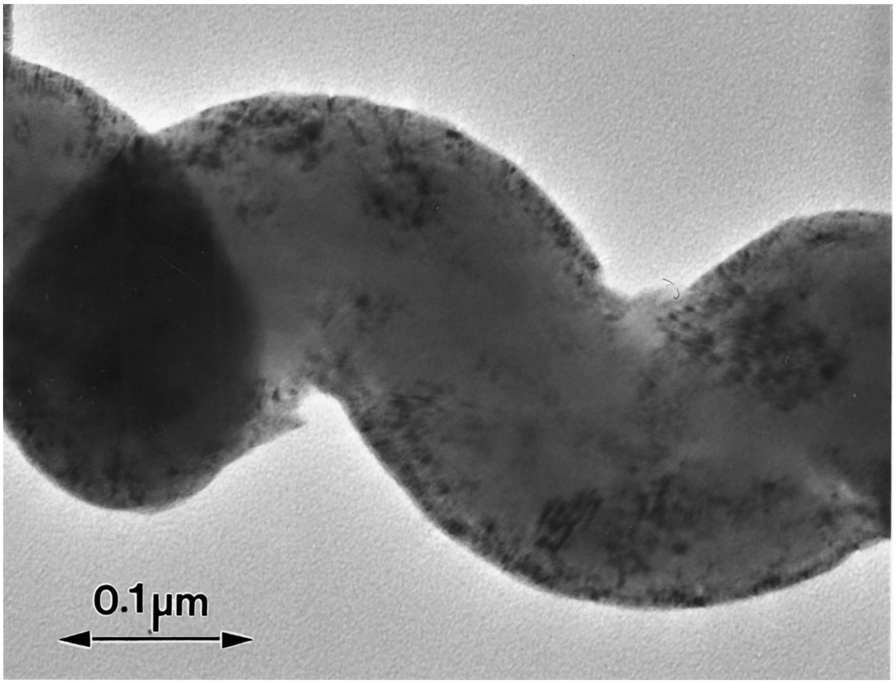

FIG. 10. Transmission electron micrograph of a helical carbon filament produced from the interaction of an Fe catalyst with a $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant mixture at 600°C.

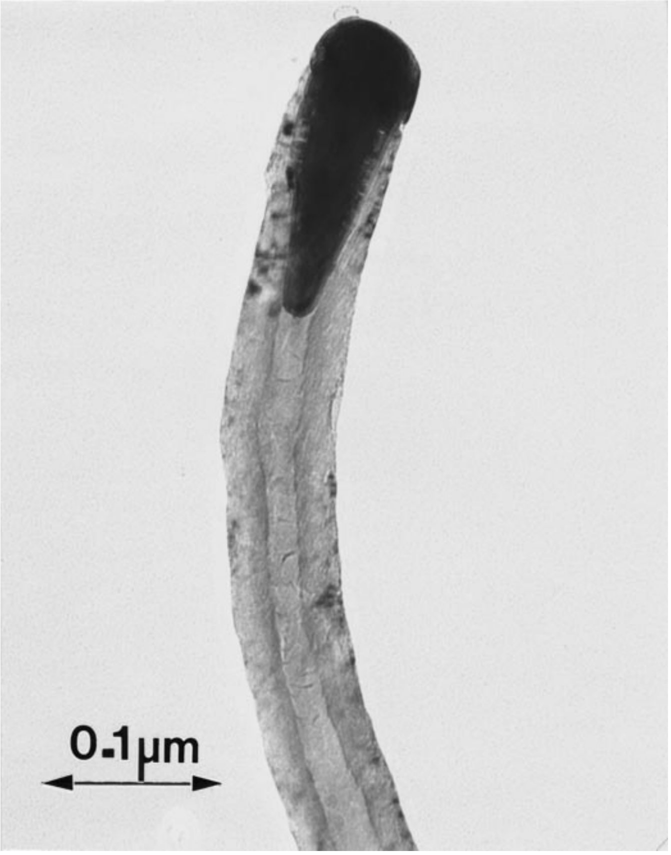

FIG. 11. Transmission electron micrograph showing the appearance of a "whisker-like" carbon filament produced from the interaction of an Fe–Ni (6 : 4) catalyst with $C_2H_4/CO/H_2$ (3 : 1 : 1) at 600°C.

graphite platelets that were aligned in a direction parallel to the fiber axis. Figure 12 is a high-resolution micrograph of a filament that had been generated from the interaction of an Fe–Ni (6 : 4) catalyst with a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture at 600°C. The interlayer spacing between the graphite platelets in these "ribbon-like" structures was found to be 0.335 nm from both electron microscopy studies and XRD analysis.

The introduction of increasing amounts of nickel into the bimetallic particles was found to result in a distinct change in the filamentous structures. Carbon filament growth proceeded by a bi-directional mode, and in this case it was evident that the helical structures were more tightly coiled in nature, see Fig. 13. Close examination of the filaments revealed that they consisted of a mixture of highly ordered graphite platelets and regions of more disordered carbon, where the degree of structural perfection increased as the nickel content in the catalyst was progressively raised to 80%.

Although the amounts of carbon filaments produced on samples of the bimetallic powders containing between 60 and 70% nickel were quite sparse, it was interesting to find that the dimensions of such structures were comparable to those generated from systems containing 80% nickel. This finding indicates that there were no unusual growth characteristics associated with the bimetallic particles in the 60 to 70% nickel composition range, and as a consequence, one can dismiss sintering phenomena as being responsible for the observed low activity of these particular systems.

2.2. Temperature-programmed oxidation studies of the carbon filaments. The CO_2 temperature-programmed oxidation profiles of demineralized carbon filaments grown from the decomposition of a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture over selected Fe–Ni catalysts at 600°C are given in Fig. 14. While there was no clear uniform trend observable from the oxidation profiles of these carbon filaments, it was apparent the material produced from catalyst particles containing a relatively large amount of iron tended to exhibit a higher oxidation resistance than those generated from powders where nickel was the major component. These findings are completely in accord with the information obtained for individual filaments from the transmission electron microscopy studies and X-ray diffraction analysis of bulk samples of the solid carbon deposits.

2.3. In situ electron diffraction studies. The identities of possible chemical species present when an Fe–Ni (1 : 1)/graphite specimen was heated in a 0.2 Torr $C_2H_4/CO/H_2$ (3 : 1 : 1) mxiture at temperatures over the range 500 to 775°C are given in Table 3. The specimen was held at each temperature for a minimum period of 30 min before the diffraction pattern was taken. Inspection of these data shows that for the most part there is no major change in the bulk composition of the bimetallic particles when treated under these conditions. It should be appreciated, however, that changes in the chemical state of the particle surfaces would not be detected by this technique, and therefore one must exercise caution with regard to the possible existence of preferential surface segregation of one of the components.

DISCUSSION

1. *Effect of Catalyst Composition on the Product Distribution*

It has been shown that the composition of an Fe–Ni catalyst has a pronounced effect on both the gaseous product distribution and the amount of filamentous carbon that is generated from the decomposition of a $C_2H_4/CO/H_2$ (3 : 1 : 1) reactant mixture at 600°C. One of the most remarkable features to emerge from this investigation was the finding that bimetallic powders with a nickel content of between 60 and 80% displayed a very low and quite different activity pattern than any other Fe–Ni catalyst composition for this reaction. Previous studies of Fe–Ni catalysts have demonstrated that dramatic changes in the behavior of the system occurred between the compositions Fe–Ni (3 : 7) and Fe–Ni (25 : 75), (1, 2, 21–23). This unusual behavior was

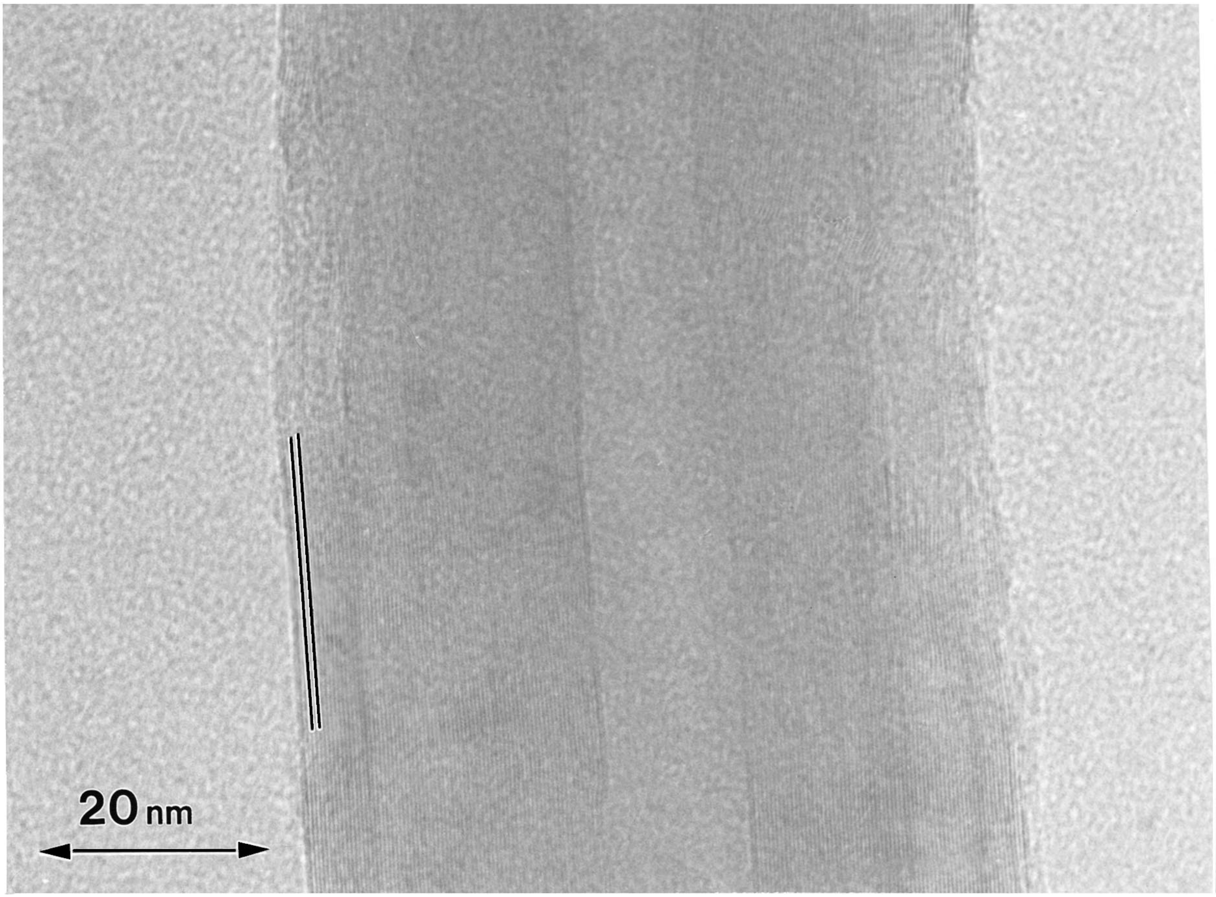

FIG. 12. High-resolution electron micrograph of a section of a carbon filament generated from the decomposition of $C_2H_4/CO/H_2$ (3 : 1 : 1) over an Fe–Ni (6 : 4) catalyst at 600°C. The markers highlight the direction of the graphite platelets stacked parallel to the fiber axis.

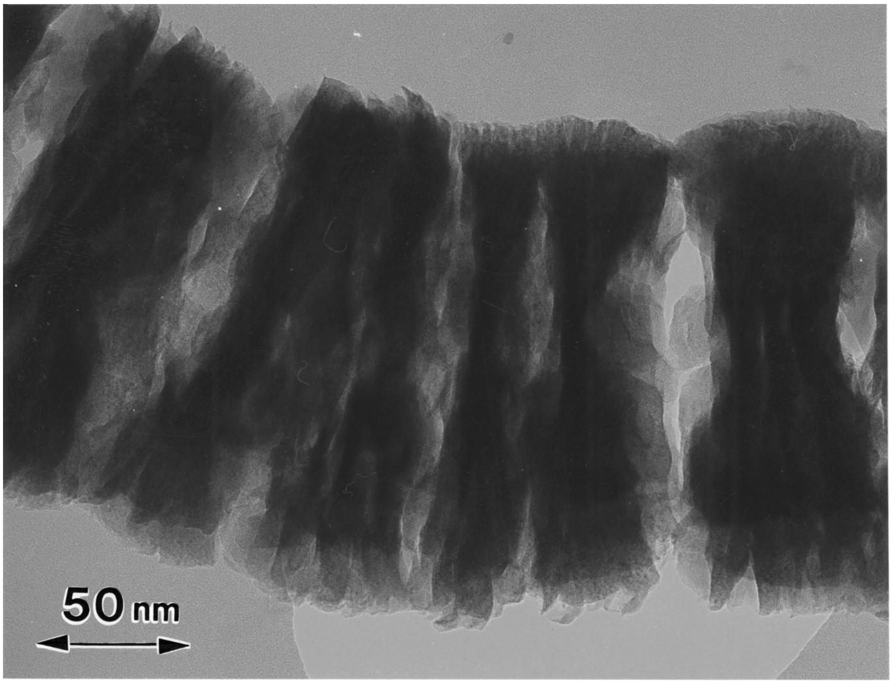

FIG. 13. Transmission electron micrograph illustrating the tightly coiled nature of a carbon filament grown from the interaction of an Fe–Ni (2 : 8) catalyst with $C_2H_4/CO/H_2$ (3 : 1 : 1) at 600°C.

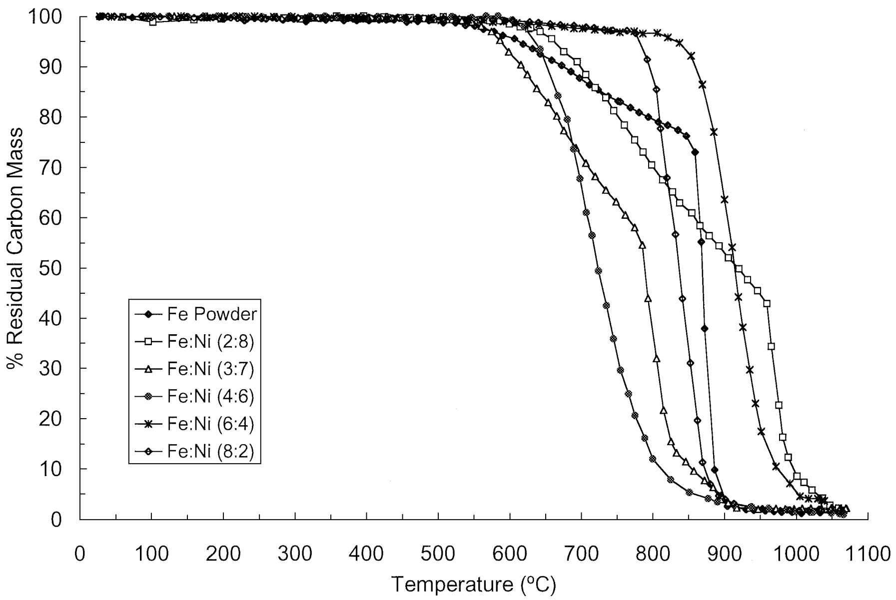

FIG. 14. Temperature-programmed oxidation profiles of demineralized carbon filaments grown from the decomposition of a C_2H_4/CO/H_2 (3 : 1 : 1) mixture over selected Fe–Ni powdered catalysts at 600°C.

explained in terms of a surface reconstruction of the catalyst particles leading to a decrease in the likelihood of iron atoms being nearest neighbors. It was claimed that it was necessary for the bulk composition to exceed 70% nickel in order to ensure that the above condition relating to the arrangement of iron atoms in the surface was achieved, and under these circumstances there were significant changes in the properties of the alloy (24–26). Wandelt and Ertl

TABLE 3

Electron Diffraction Pattern Analysis of an Fe–Ni/Graphite Specimen as a Function of Temperature in 0.2 Torr Ethylene/CO/Hydrogen (3 : 1 : 1) Mixture

Temperature (°C)	Calculated *d*-spacings (nm)	*d*-Spacings (nm)				
		Fe–Ni (1 : 1)	Fe–Ni (7 : 3)	Fe–Ni (3 : 7)	Fe	Ni
500	0.2068	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1788	$0.1800_{(200)}$	$0.1784_{(400)}$			
	0.1260	$0.1270_{(220)}$	$0.1260_{(110)}$			
	0.1026	$0.1037_{(222)}$				
600	0.2073	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1801	$0.1800_{(200)}$				
	0.1266	$0.1270_{(220)}$	$0.1260_{(110)}$	$0.1253_{(222)}$		
	0.1084	$0.1083_{(311)}$				
	0.1034	$0.1037_{(222)}$				
650	0.2051	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1776	$0.1800_{(200)}$	$0.1784_{(400)}$			
	0.1253	$0.1270_{(220)}$	$0.1260_{(110)}$			
	0.1074	$0.1083_{(311)}$				
	0.1034	$0.1037_{(222)}$				
700	0.2062	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1784	$0.1800_{(200)}$	$0.1784_{(400)}$	$0.1772_{(200)}$		
	0.1290	$0.1270_{(220)}$				
	0.1039	$0.1037_{(222)}$				
775	0.2068	$0.2080_{(111)}$	$0.2070_{(222)}$			
	0.1788	$0.1800_{(200)}$	$0.1784_{(400)}$	$0.1772_{(200)}$		
	0.1264	$0.1270_{(220)}$	$0.1260_{(110)}$			
	0.1070	$0.1083_{(311)}$				
	0.1038	$0.1037_{(222)}$				

(27) summarized much of the early work on Fe–Ni catalysts by concluding that a narrow region in the composition range existed where a significant change in the electronic structure of the alloy took place. It is therefore intriguing to find that the Fe–Ni composition range where significant changes in the catalytic activity for the decomposition of a $C_2H_4/CO/H_2$ (3 : 1 : 1) mixture are found coincides with that where major perturbations in the electronic structure of the alloy have been reported. It is therefore possible that the observed decrease in the catalytic performance of these particular Fe–Ni formulations might be related to a combination of both a change in the electronic structure and a reorganization of the particle surfaces.

Another aspect that was revealed in this study was the promotion of ethylene decomposition to form solid carbon resulting from the co-adsorption of CO on catalysts that would not normally dissociate the olefin to any significant degree under the prevailing conditions. For example, when a C_2H_4/H_2 (4 : 1) mixture was passed over an Fe–Ni (9 : 1) catalyst at 600°C, approximately 15% of the olefin was observed to undergo decomposition. On the other hand, when 20% CO was introduced into the reactant, the conversion of ethylene increased to 58%. This promotional effect of CO on iron and iron-rich bimetallic catalysts has been attributed to a combination of factors, including surface reconstruction and perturbation of the electronic properties of the metal particles.

The ability of CO to facilitate reconstruction of iron surfaces to generate a set of crystallographic faces that favor the dissociative chemisorption of ethylene has been invoked in previous investigations (7, 8). Furthermore, Cooper and Trimm (28) demonstrated that the rates of carbon deposition on iron surfaces arising from the decomposition of C_3H_6/H_2 mixtures were extremely sensitive to the orientation of the metal crystallites. $Fe_{(100)}$ faces were found to favor the decomposition of propylene, giving rise to a concomitant high yield of solid carbon, while $Fe_{(110)}$ were relatively inactive toward this reaction. Therefore in the presence of CO it is conceivable that Fe particles may undergo reconstruction to an orientation that facilitates the decomposition of ethylene.

The promotion of ethylene decomposition on the modified iron surface might also be expected to be accompanied by a concomitant change in the decomposition behavior of CO in the three-component gas mixture compared to that observed when CO/H_2 was passed over the metal under similar reaction conditions. Examination of the pertinent data shows that this is indeed the case. A decrease of approximately 15% in the conversion level of CO was found when iron and iron-rich powders was treated in a $C_2H_4/CO/H_2$ mixture compared to when the metal catalysts were exposed to a CO/H_2 reactant. One may conclude therefore that the co-adsorption of the two carbon-containing gases on such metal surfaces results in a diverse pattern of behavior, promotion of C_2H_4 decomposition at the expense of a lowering of the conversion of CO.

In contrast, on a nickel-rich surface the extent of CO decomposition in the three-component mixture was found to be extremely limited, with no CO_2 being detected when the nickel content in the bimetallic exceeded 50%. Clearly, the presence of co-adsorbed ethylene exerted an inhibiting effect on the decomposition of CO on all of these Fe–Ni compositions. On the other hand, it was fascinating to find that on nickel-rich surfaces the decomposition of ethylene was enhanced, albeit to a lesser degree than on iron-rich surfaces, by the presence of CO in the reactant feed. Particles containing a high nickel content are known to function as active catalysts toward the decomposition of ethylene under conditions used for the current experiments (2, 29, 30); however, *a priori* one would not predict that the addition of CO to the reactant feed would necessarily result in an enhancement in carbon filament formation. Based on the current results it would appear that the presence of CO played a pivotal role when co-adsorbed on nickel or nickel-rich surfaces with ethylene. The promotional effect created by the presence of co-adsorbed CO might be achieved by either a reconstruction of the bimetallic surface to a generate a set of crystallographic faces that favor the dissociative chemisorption of ethylene or a modification of the electronic properties of the surface induced by the electron withdrawing properties of adsorbed CO molecules.

It is appropriate to also consider the data obtained by other workers on the co-adsorption of CO and ethylene on iron surfaces at lower temperatures (31, 32). Under such conditions hydrocarbon fragments were shown to be incorporated into growing chains, sections of which could readsorb on the catalyst surface. In the current investigation it is doubtful whether such a mechanism could be operative, since it would take place at the metal/gas interface and, as a consequence, would result in premature irreversible catalyst deactivation. Carbon filament growth ensues from a different set of crystallographic planes, thus leaving the exposed metal surfaces available for continued dissociative chemisorption of the reactant molecules.

When either the CO or the ethylene component was removed from the $C_2H_4/CO/H_2$ reactant feed, the catalytic activity of an Fe–Ni (7 : 3) powder was observed to exhibit a substantial decrease, reaching levels similar to those achieved with CO/H_2 and C_2H_4/H_2 reactants, respectively (1, 2). Upon the re-introduction of either CO or C_2H_4 to the feed a significant enhancement in the decomposition of the olefin was observed compared to that attained during the initial stages of the reaction with a fresh catalyst. This deactivation/reactivation process was found to be completely reversible when this type of pulsing experiment was performed on an iron-rich bimetallic catalyst system. The co-adsorption of CO and ethylene would appear to bring about a reconstruction of the iron-rich bimetallic surface to one that favored the formation of filamentous carbon.

An entirely different scenario was realized when the same set of experiments was carried out over a nickel-rich bimetallic system. For example, when ethylene was removed from the three-component gas mixture the catalytic activity of an Fe–Ni (2 : 8) powder decreased to a level consistent with that obtained when the bimetallic was treated with a CO/H_2 feed. In this case, however, the reintroduction of ethylene to the feed did not bring any change in the subsequent catalytic behavior of the system; i.e., the initial catalytic activity associated with a C_2H_4/CO/H_2 reactant was not re-established on such catalyst powders. On the other hand, upon removal and subsequent reintroduction of CO from the reactant feed over this set of bimetallic catalysts, a comparable deactivation and reactivation of the activity level was observed.

Nickel is known to a relatively poor catalyst for the hydrogenation of CO (33), thereby allowing for the possibility of the buildup of a CO layer on the metal surface. This behavior would tend to inhibit the adsorption of ethylene when the olefin was re-introduced into the reactant stream. Another explanation that should be given serious consideration is the possibility that in the absence of ethylene, CO reconstructed the enriched nickel surface to a such an extent that the exposed crystallographic faces were no longer suitable for olefin decomposition to solid carbon. This situation was not encountered with an iron-rich bimetallic as this metal is known to be a very good hydrogenation catalyst for CO (1, 34, 35). Therefore any adsorbed CO species that remained on the iron surface would be readily hydrogenated, thereby overcoming any potential blocking action toward the subsequent adsorption of ethylene molecules. These results show the sensitivity of the catalytic surface to the composition of the reactant feed and the contrasting effects created by the exposure to certain reactants.

2. *Effect of Reactant Composition on the Product Distribution*

Diverse patterns of behavior were observed when iron-rich and nickel-rich bimetallic powders were reacted in gaseous mixtures in which the CO content was progressively increased. A comparison of the data presented in Tables 1 and 2 shows that the addition of 20% CO to the C_2H_4/H_2 feed produced an enhancement in overall activity when the reactant was passed over an Fe–Ni (6 : 4) catalyst from 13.1 to 81.05%. When the same experiment was conducted with an Fe–Ni (3 : 7) catalyst the overall activity was observed to decrease from 13.6 to 9.3%, and even when the CO content in the reactant stream was raised to 60% the increase in activity was limited to 46.4%.

The presence of CO in the reactant feed did not appear to exert any pronounced effect on the hydrogenation of ethylene to ethane, but it did promote the formation of solid carbon on all the Fe–Ni catalysts used in this investigation. These findings are consistent with the notion that the coadsorption of CO on the catalytic surface with ethylene caused significant changes in the stabilization of certain C_2 species, favoring the formation of specific products or reconstructing the surface to one that favored the formation of carbon filaments. It has been reported by Akhter and White (12) that on an $Ni_{(100)}$ surface the presence of CO in an acetylene feed stabilized both vinyl and vinylidine species, but not acetylide species. These authors attributed the stabilization effect to the physical blocking of the dissociation sites on the nickel surface by CO near the C_2 species and a repulsion between CO and C_2 causing a lowering of the binding strength of Ni–C_2. In contrast, it was demonstrated that when an iron catalyst was used, the yield of ethane could be enhanced upon the addition of a small amount of CO to a C_2H_4/H_2 feed (6–8).

In the decomposition of C_2H_4/CO/H_2 (3 : 1 : 1) mixtures the yield of methane was extremely low, <1.0%, over all the Fe–Ni powders. In a previous study dealing with the Cu–Ni-catalyzed decomposition of ethylene, Kim and coworkers (36) suggested that for the most part methane was generated via the formation of an ethylidyne intermediate. If one assumes that this situation is applicable to this current bimetallic system, it may be concluded that when both ethylene and CO are present in the feed the decomposition of the olefin to ethylidyne is not favored on the reconstructed surface.

While it would be desirable to express the relative activities of the various bimetallic catalyst systems in terms of turnover frequencies (TOF) there is an inherent difficulty in attempting to perform this task. It is well established that during carbon filament growth, dissociative chemisorption of the carbon-containing gases takes place on specific faces of the catalyst, and the carbon species created at this interface proceed to dissolve and diffuse through the particle, eventually precipitating at a different set of crystal faces (20). If one is to calculate a meaningful value for TOF it is essential to determine the active area of the catalyst particle during the growth of the filaments. The problem is further compounded by the fact that the structures of the carbon filaments exhibit significant differences depending upon the composition of the catalyst, which makes this endeavor a fruitless operation.

3. *Structural Characteristics of Carbon Filaments*

It was evident from the TEM examinations of carbon filaments grown from the interaction of iron-rich bimetallic particles with a C_2H_4/CO/H_2 mixture that the characteristics of the material had all the hallmarks of that were produced when the same powders were reacted in a C_2H_4/H_2 mixture at the same temperature. In the main, these structures acquired a helical conformation and were quite different from the highly crystalline filaments generated from iron-rich powders with CO/H_2 in which the graphite platelets were aligned in directions perpendicular to the fiber axis. Differences were detected in both the structural and conformational characteristics of carbon filaments formed during the reactions of $C_2H_4/CO/H_2$ and C_2H_4/H_2 mixtures over nickel-rich bimetallic powders. In the former system, a multitude of tightly coiled filaments were generated, whereas when the same catalysts were treated in the absence of added CO, the structures tended to be smooth-sided and relatively straight.

It has been determined that the structure, conformation, and degree of crystalline perfection of carbon filaments is dictated by various factors, including the composition of the reactant gas, the chemical nature of the catalyst particles, and the temperature at which the reaction is performed. In order for dissolved carbon species to precipitate from the catalyst particle in a highly crystalline form there must be a correspondence between the spacing of the metal atom interstices at the interface and the C–C bond distance of graphite (20). The geometric shape of the metal particle in concert with the number and orientation of precipitating faces is responsible for determining the morphology and alignment of the graphite platelets. In addition, symmetrical diffusion of carbon species through the catalyst particle will give rise to a relatively straight structure. In contrast, when certain additives are present in the metal particle the diffusion characteristics are modified, and this factor causes a nonbalanced process that results in the formation of helical structures. Examples of this behavior can be seen in studies where either sulfur or phosphorus species have been introduced into the system (37–39). In these particular cases the generation of coiled filamentous structures was attributed to the preferential adsorption of the additive molecules at particular faces at the rear of the particle that interfered with the carbon precipitation step to such an extent so as to create an anisotropic growth pattern.

Addition of CO to a C_2H_4/H_2 mixture did not appear to change either the structural or the morphological properties of the carbon filaments produced during the reaction with iron-rich powders. This observation implies that the CO did not exert any substantial influence on the atomic arrangement of the metal atoms at the carbon precipitating faces of bimetallic particles with this elemental composition. It was clear, however, that with nickel-rich particles major modifications in the filament characteristics were found when CO was present in the gaseous reactant. Under these circumstances it would appear that CO was having a significant impact on the events that occurred at the metal/solid carbon interface.

The analysis of *in situ* electron diffraction experiments on the Fe–Ni (1 : 1)/graphite specimens undergoing reaction in an $C_2H_4/CO/H_2$ (3 : 1 : 1) environment shows that while equal amounts of the two metals were introduced onto the support not all the alloy particles consisted of this ratio. Nevertheless, it was significant to find that as the temperature was progressively raised there were no major modifications in the composition of the particles. One may therefore conclude that while surface enrichment in one component may occur, there is no evidence for separation of the two metals. This condition is to be contrasted with that encountered in the Cu-Ni/graphite–C_2H_4/H_2 system, where the strong interaction of nickel with graphite resulted in preferential spreading of this metal, so that at high temperatures only copper was detected in the electron diffraction pattern (40). It would appear that in the case of the Fe–Ni system the work of cohesion between the two metals is greater than the work of adhesion with the graphite support.

SUMMARY

The decomposition of a $C_2H_4/CO/H_2$ reactant mixture over a series of Fe–Ni catalysts has raised some very interesting issues with respect to the impact of co-adsorption of the two carbon-containing gases on the bimetallic surfaces. It was evident that the addition of CO to a C_2H_4/H_2 feed resulted in a substantial increase in the decomposition of the olefin over all the bimetallic powders, with this effect being most pronounced on the iron-rich systems. The major product from this series of Fe–Ni catalysts was found to be solid carbon in the form of various filamentous structures, and this material was produced in significantly higher amounts than when grown from the interaction of the same bimetallics with either CO/H_2 or C_2H_4/H_2 mixtures. Analysis of all the reaction products indicated that the enhancement in the decomposition of ethylene occurred at the expense of the CO conversion, with the latter playing a key role in the reconstruction of the bimetallic surface to one that favored decomposition of the olefin. A further feature of this reaction was the finding that the conversion of ethylene to ethane was inhibited by the addition of CO on all Fe–Ni catalysts. The improvement in the catalytic performance realized from the introduction of CO to the C_2H_4/H_2 mixture was not limited to the interactions with iron-rich powders but was also seen to a somewhat lesser degree on the corresponding nickel-rich catalyst systems. This behavior was rationalized according to the notion that the co-adsorption of CO and ethylene led to a reconstruction of the catalytic surface to an orientation that favored the decomposition of the reactant to solid carbon. The possibility that adsorption of CO was responsible for inducing perturbations in the electronic properties of the bimetallic surfaces should also be considered as a contributory factor to the change in the catalytic action.

Finally, a reversible deactivation/reactivation phenomena was shown to exist for iron-rich bimetallic catalysts and was observed when either CO or C_2H_4 was removed and subsequently re-introduced into the reactant feed. When the same procedure was undertaken with nickel-rich bimetallic catalysts the reversible behavior was once again observed with the CO component, but pulsing with C_2H_4 merely resulted in the establishment of an irreversible deactivation process. This pattern of behavior highlighted the sensitivity of the catalytic surface to the nature of the reactant feed and illustrated the ramifications of a CO treatment on a catalyst system that did not readily hydrogenate this component.

APPENDIX

The relative amounts of solid carbon generated from the decomposition of ethylene and carbon monoxide as a function of the reactant gas composition, presented in Figs. 2 to 4, were calculated according to the following protocol.

Consider the carbon atom balances in the two deposition systems:

(a) Solid carbon yield from CO disproportionation can be expressed as

$$\frac{\mathrm{CO}_{\mathrm{input}} - (\mathrm{CO} + \mathrm{CO}_2)_{\mathrm{output}}}{\mathrm{CO}_{\mathrm{input}}},$$

which is

$$\{\mathrm{CO}_{\mathrm{conversion}} - \mathrm{CO}_{2\ \mathrm{yield}}\}\chi_{\mathrm{C\ atoms}},$$

where $\chi_{\mathrm{C\ atoms}}$ is the fraction of carbon atoms per mole.

(b) Solid carbon yield from C_2H_4 decomposition can be written as

$$\frac{\mathrm{C_2H_4}_{\mathrm{input}} - (\mathrm{CH_4}/2 + \mathrm{C_2H_6} + \mathrm{C_2H_4})_{\mathrm{output}}}{\mathrm{C_2H_4}_{\mathrm{input}}},$$

which is

$$\{\mathrm{C_2H_4}_{\mathrm{conversion}} - (\mathrm{CH_4} + \mathrm{C_2H_6})_{\mathrm{yield}}\}\chi_{\mathrm{C\ atoms}}.$$

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