J. Phys. Chem. B **1997,** *101,* 1621−1630

Influence of Chlorine on the Decomposition of Ethylene over Iron and Cobalt Particles

Alan Chambers and R. Terry K. Baker*,†

*Catalytic Materials Center, Materials Research Laboratory, The Pennsylvania State University,
University Park, Pennsylvania 16802-4800*

Received: October 3, 1996; In Final Form: January 2, 1997[⊗]

The interaction of cobalt and iron powders with ethylene and ethylene/hydrogen mixtures containing trace concentrations of chlorine has been studied using a combination of flow reactor and transmission electron microscopy techniques. Detailed analysis of both the gaseous products and the amount of solid carbon (a filamentous form) deposited on the metal surfaces has permitted us to gain an insight into some of the factors surrounding the promotional effect of low concentrations of chlorine on the catalytic action of both cobalt and iron. The optimum carbon deposition activity was achieved when either of these metals was treated at 400 °C in an ethylene/hydrogen environment containing 75−100 ppm chlorine. If the halogen was removed from the reactant, then the high activity for carbon filament growth could not be sustained. Reintroduction of chlorine after a suitable period of time resulted in restoration of the carbon deposition activity to its original level, demonstrating the reversible nature of the "activation−deactivation" processes. The results of this study are rationalized according to the notion that the presence of adsorbed chlorine species is responsible for causing reconstruction of the metal surface; however, the possibility that the halogen is capable of inducing a perturbation in the electronic properties of the particles is also considered. It is possible that the charge transfer between adsorbed chlorine species and the metal surface atoms leads to a strengthening of the metal−ethylene bond and a concomitant weakening of the C−C bond in the olefin, making the latter more susceptible to decomposition and enhancing the formation of the solid carbon product.

Introduction

It is now being recognized that the incorporation of controlled amounts of certain nonmetallic atoms into metals, which have hitherto been regarded as poisons, can actually function as catalyst promoters. This approach is predicated on the assumption that the poison atoms are preferentially chemisorbed on sites that are active for undesirable reactions, while those sites that perform the desired reactions are preserved in an unadulterated state.[1,2] Previous work from this laboratory[3−5] has demonstrated that either pretreatment or the continuous addition of 5−10 ppm H_2S to iron, cobalt, or nickel undergoing reaction with ethylene had a significant impact on the catalytic activity of these metals, particularly with respect to the enhancement in the yields of solid carbon, that consisted entirely of filamentous structures. In the current investigation we have extended these studies to cover the influence of chlorine on the same reactions.

The first systematic study of the influence of chlorine on the properties of deposited carbon was carried out by Cullis and co-workers,[6] who pyrolyzed methane and the four chloromethanes at temperatures over the range 800−950 °C. They found that the substitution of hydrogen by chlorine in the reactant molecule decreased both the preferred orientation and the sizes of the carbon crystallites in the deposit. Careful poisoning with chlorine has been found to be a very effective method of altering the activity and selectivity of catalysts, and it has been suggested that such behavior could in part be attributable to induced electronic perturbations in the metal.[7] Recent studies have emphasized the critical role of chlorine in several industrial processes such as reforming, methane oxidation, oxidative coupling of methane, and hydrogenation of carbon monoxide. In catalytic reforming, the chlorine content derived from the metal precursor salt is thought to be directly related to the amount of carbon that accumulates on the catalyst.[8,9] Goodwin and co-workers[10] concluded that the observed modifications in the performance of silica-supported ruthenium for the hydrogenation of carbon monoxide resulting from the presence of chlorine species in the reactant were related to structural rearrangements in the catalyst particles, rather than either electronic effects or selective site poisoning. Peri and Lund[11] showed that in the oxidation of methane over a silica-supported palladium catalyst that prior to the attainment of steady state there was an induction period that was associated with the chloride levels in the system. These workers demonstrated that if the concentration of such species was reduced by aqueous washing, then there was a corresponding decrease in the induction time.

Burch and co-workers[12] have discussed the effect of chlorine on bismuth-based catalysts, both as a promoter for gas phase reactions and as a modifier for a range of oxychloride systems. It was stressed that although gas phase reactions may be important under certain circumstances, evidence was presented indicating that the main function of the halogen was to create new sites on the surface of the catalyst. Warren[13] demonstrated that the addition of small amounts of chlorine, in the form of ethylene chloride, significantly enhanced the rate of methane conversion during the coupling reaction and attributed this effect to an increase in the number of active sites on the catalyst. Residual chloride species derived from the metal precursor salt were found to exert a direct impact on the selectivity of the supported cobalt catalyst for the hydrogenation of crotonaldehyde.[14] Furthermore, there are a number of reports detailing the influence of chlorine on the re-dispersion phenomenon of large palladium and platinum crystallites.[15,16]

In a previous investigation[17] we conducted a series of experiments in which the conversion of ethylene to filamentous

---

* To whom all correspondence should be addressed.

† Current address: Department of Chemistry, 10 Hurtig Hall, Northeastern University, Boston, MA 02115.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

carbon was monitored during interaction with copper−cobalt bimetallics prepared from both nitrate and chloride precursors in an attempt to determine any possible changes in the catalytic activity induced by the halide. When the reaction was carried out at 600 °C, no difference in the behavior of the two sources of cobalt with respect to either the amount or characteristics of the deposited solid carbon was detected. In a further set of experiments, the reaction was performed at 500 °C, and under these conditions the activity of the bimetallic derived from chloride precursors tended to increase as the reaction proceeded, whereas the catalyst prepared from nitrates exhibited a steady decline in its ability to generate solid carbon. On the basis of these studies, it was concluded that the reaction temperature was a key factor in determining the effectiveness of a chlorine treatment on the metal catalyst. It was suggested that at 600 °C any residual chloride species were effectively desorbed and that the surfaces of the two bimetallic powders were essentially the same, in both composition and electronic character. On the other hand, at 500 °C, it was argued that although significant desorption of the halogen might have occurred, there was a sufficient residual concentration remaining at the surfaces of the copper−cobalt particles to have an impact on both the catalytic activity and the characteristics of the solid carbon structures.

In the present study, we have investigated the effect of small concentrations of chlorine on the carbon depositing characteristics of iron and cobalt when the halogen is introduced to the powdered catalyst system along with the ethylene/hydrogen reactant mixture. Ethylene does not readily undergo decomposition on the pure metal surfaces; however, the introduction of CO into the reactant gas stream or copper adatoms into the particles was found to result in a dramatic increase in the ability of iron and cobalt to convert the hydrocarbon into filamentous carbon.[18−20]

Experimental Section

Materials. Pure cobalt and iron powders used as the catalysts in this work were prepared by precipitation of the metal carbonates from the respective metal nitrate solutions using ammonium bicarbonate. The precipitates were washed, filtered, dried overnight at 110 °C, and finally calcined in air at 400 °C for 4.0 h. The powders were subsequently ground, and this step was followed by reduction in a 10% hydrogen/helium mixture at 500 °C for 20 h. Before removing the powders from the reactor, the reduced granules were initially cooled to room temperature in helium and then passivated by treatment in a 2% CO_2/helium mixture for 1.0 h. Samples of all powders were subsequently examined by X-ray diffraction using a Scintag diffractometer, and only peaks corresponding to metallic cobalt and iron were present in the patterns of the powders. BET surface area measurements were performed with a Coulter Omnisorp 100 CX unit using nitrogen adsorption at −196 °C, and values in the range 1.0−1.5 m^2/g were obtained for all the powders.

Reagent grade cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$] and iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] used in the preparation of the catalyst powders were obtained from Aldrich Chemical Co. The gases used in this work, hydrogen (99.999%), helium (99.99%), ethylene (99.95%), and a 200 ppm chlorine/helium mixture, were supplied by MG Industries and used without further purification.

Apparatus and Procedures. Experiments were performed in a quartz reactor tube located in a Lindberg horizontal tube furnace. The catalyst powder (50 mg) was uniformly dispersed along the bottom of a ceramic boat placed in the center of the reactor tube. Gas flow rates to the reactor were regulated by mass flow controllers (MKS), and the total gas velocity in all experiments was maintained constant at 100 mL/min. Before reaction with a hydrocarbon environment all metal powders were treated at 600 °C in 10% hydrogen/helium for 2.0 h to ensure that complete reduction of any surface oxide formed during the passivation step. Following this operation the powders were cooled to the desired reaction temperature in helium, and then the reactant gas, ethylene, ethylene/hydrogen, or these gases mixed with various ratios of chlorine/helium were introduced into the system. The composition of the gas phase before and at regular intervals throughout the reaction was monitored by gas chromatography using a Varian 3400 unit fitted with a 30 m megabore column (GS-Q). Carbon and hydrogen atom mass balances in conjunction with the relative concentrations of the respective components were employed to derive the various product yields. At the termination of a given experiment the gas flow was halted, and the reactor tube was cooled to room temperature in helium and the amount of solid carbon deposited on the catalyst powder determined by weight difference. It was subsequently established from TEM studies that filamentous carbon was the exclusive type of material that accumulated on the metal surfaces.

A variety of techniques were used to characterize the solid carbon products, and these included temperature-programmed oxidation in CO_2/argon (1:1), N_2 surface area measurements, and transmission electron microscopy. The BET surface area of selected samples was obtained from nitrogen adsorption experiments performed at −196 °C with a Coulter Omnisorp 100CX unit. Temperature-programmed oxidation in CO_2 was utilized to acquire information on the degree of crystalline perfection of the carbon deposit. We have previously demonstrated that this is a reliable method for assessing the graphitic nature of carbon filaments by comparison of the oxidation profiles with standard materials, amorphous carbon, and single crystal graphite.[21] Prior to performing this operation all the carbonaceous materials were treated in 1 N HCl for 3 days to remove any metallic inclusions that might otherwise interfere with the oxidation reaction. Following this demineralization procedure, the samples were washed and dried, and then the oxidation profiles of the carbonaceous products were determined, using a Cahn 2000 microbalance, by heating to 1100 °C at a rate of 5 °C/min in a CO_2/Ar (1:1) mixture. Sample weight loss was plotted as a function of temperature, and the curves were compared to those of the standard carbons when treated under the same conditions. Transmission electron microscopy examinations were performed in a JEOL 100CX microscope (point-to-point resolution of this instrument was 0.28 nm) in order to obtain detailed structural analysis of the individual carbon filaments produced under various experimental conditions. For this purpose suitable specimens were prepared by dispersion of a small mass of the carbon deposit in 1-butanol, and a droplet of the resulting suspension was applied to a holey carbon support film. From a careful survey of many regions of the specimen it was possible to find sections of the deposit that protruded over holes in the film, and this condition enabled one to obtain an unimpaired view of the detailed structural features of the catalytically formed solid carbon.

Finally, estimates of the chlorine content in the “as-prepared” and metal powders that had been treated at 400 °C for 3.0 h in a 200 ppm Cl_2/C_2H_4/He mixture were determined by ion chromatography. Analysis of the same weights of the metal powders indicated that the initial chloride levels were between 0.005 and 0.013 wt %, and after exposure to the halogen the values had risen to between 2.0 and 3.35 wt %, confirming that

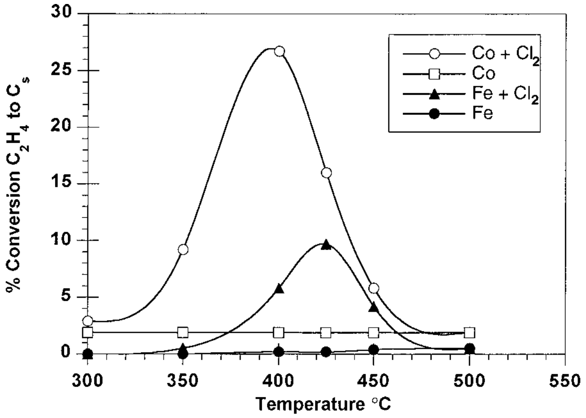

Figure 1. Percentage conversion of ethylene to solid carbon from the interaction of cobalt and iron powders with ethylene/hydrogen (4:1) in the presence of 25 ppm chlorine as a function of reaction temperature.

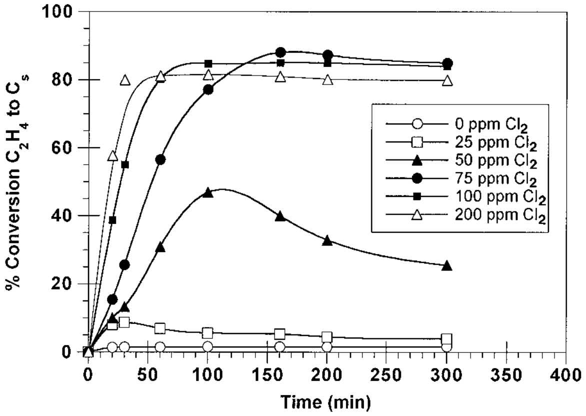

Figure 2. Percentage conversion of ethylene to solid carbon from the interaction of cobalt with ethylene in the presence of various concentrations of chlorine at 400 °C as a function of reaction time.

under these conditions halide species were indeed sticking on the catalyst surfaces.

Results

1. Flow Reactor Studies. *1.1. Effect of Temperature on the Metal Catalyzed Carbon Deposition Reaction in the Presence of Added Chlorine.* Initial experiments were performed at 500 °C, and it became evident that at this temperature the continuous addition of chlorine to the ethylene or ethylene/hydrogen reactant stream had no detectable effect on the amount of carbon deposited on either cobalt or iron. In contrast, a significant enhancement in the ability of the two metals to catalyze the growth of solid carbon was achieved when the reactions were carried out at lower temperatures, during continuous exposure to hydrocarbon mixtures containing chlorine. Earlier studies from this laboratory[3,18] showed that neither of these metals, in their unadulterated state, showed a tendency to catalyze the growth of substantial amounts of solid carbon during interaction with ethylene/hydrogen mixtures. Inspection of the data presented in Figure 1 indicates that, provided the reaction is performed at a suitable temperature, the presence of a small concentration of chlorine in the reactant gas has a profound influence on the conversion of ethylene to solid carbon. Under the prevailing conditions, a 3.0 h exposure to C_2H_4/H_2 (4:1)/25 ppm Cl_2, cobalt appears to exhibit a higher activity than iron for growth of solid carbon. For cobalt, the optimum conversion of ethylene to solid carbon occurs at 400 °C, whereas the corresponding condition for iron is achieved at 425 °C. Based on these findings all subsequent experiments with these systems were conducted at 400 °C.

TABLE 1: Total Product Distribution for Cobalt-Catalyzed Decomposition of Ethylene after 3.0 h at 400 °C with Various Concentrations of Chlorine in the Reactant Stream[a]

Cl_2 (ppm)	% solid carbon	selectivity to solid carbon	% ethane	selectivity to ethane	% methane	selectivity to methane
0	2.54	0.984	0.04	0.015	0.00	
25	7.48	0.980	0.13	0.017	0.03	0.004
50	32.95	0.977	0.71	0.021	0.07	0.002
75	87.33	0.994	3.04	0.031	7.48	0.076
100	85.12	0.983	2.54	0.026	8.89	0.092
200	80.19	0.876	2.65	0.029	8.70	0.095

[a] Selectivity defined as (% of product)/(% conversion of ethylene).

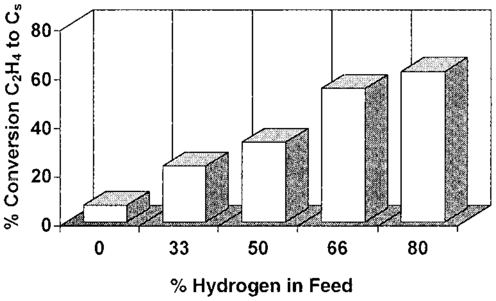

Figure 3. Influence of hydrogen on the yield of solid carbon from the interaction of cobalt with ethylene in the presence of 25 ppm chlorine at 400 °C.

1.2. Effect of Reactant Gas Composition on the Gas and Solid Phase Product Distributions. The catalytic activity of both metals was found to be highly sensitive to the chlorine and hydrogen contents in the reactant gas mixture. In the case of cobalt, in order to attain the optimum yield of solid carbon from the decomposition of ethylene at 400 °C, it is necessary to have a minimum concentration of chlorine present in the reactant, as seen from the data shown in Figure 2. It is evident that when the chlorine level was raised to 75 ppm, the conversion of ethylene to solid carbon reached a maximum value after about 150 min on stream. From Table 1 it can be seen that further increases in the halogen concentration up to 200 ppm did not appear to exert any major impact on the selectivity pattern; however, the time required to reach the optimum activity level was significantly shorter when the reaction was conducted in the presence of a higher amount of chlorine.

A further feature that is apparent from Figure 2 is that when the chlorine content of the reactant was relatively low, about 25 ppm, the cobalt catalyst exhibited only a slight improvement in behavior over that observed from the interaction of the unadulterated powder with ethylene under the same conditions. If, however, hydrogen was added to the ethylene/25 ppm chlorine mixture, a dramatic increase was found in the response of the system toward solid carbon formation, with the highest activity being achieved from a C_2H_4/H_2 (1:4) reactant; see Figure 3. It should be noted that under the same conditions there was an analogous rise in the amount of solid carbon produced on the pure metal powder, from 2.54 to 24.85% as the C_2H_4/H_2 ratio was changed from 1:0 to 1:4.

In another series of experiments the C_2H_4/H_2 ratio was maintained constant at 1:4 while the concentration of chlorine in the reactant passing over the cobalt powder was progressively raised from 0 to 100 ppm. The total product distributions obtained after a 3.0 h period from following this procedure are presented in Table 2. Inspection of these data shows that while the yield of solid carbon is enhanced in the presence of added chlorine, it appears to reach a constant value over the halogen range 25−100 ppm. It should be noted, however, that at the upper level the selectivity toward the formation of solid carbon

TABLE 2: Total Product Distribution for Cobalt-Catalyzed Decomposition of Ethylene/Hydrogen (1:4) after 3.0 h at 400 °C with Various Concentrations of Chlorine in the Reactant Stream[a]

Cl_2 (ppm)	% solid carbon	selectivity to solid carbon	% ethane	selectivity to ethane	% methane	selectivity to methane
0	24.85	0.889	1.73	0.062	1.36	0.049
18	44.92	0.887	4.13	0.081	1.59	0.031
25	67.86	0.940	3.40	0.047	0.94	0.013
50	69.10	0.918	4.39	0.058	1.99	0.026
100	68.81	0.698	4.90	0.050	25.51	0.259

[a] Selectivity defined as (% of product)/(% conversion of ethylene).

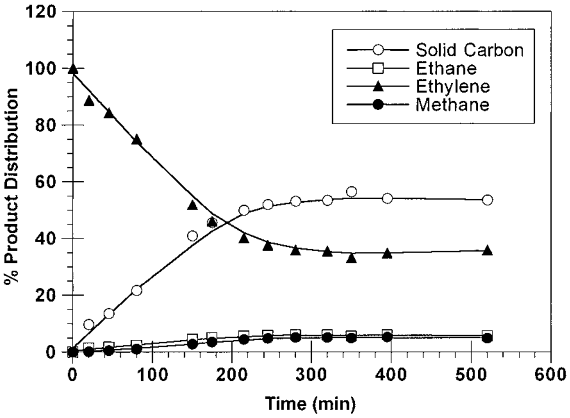

Figure 4. Total product distribution as a function of reaction time from the catalyzed decomposition of ethylene/hydrogen (1:4) in the presence of 100 ppm chlorine over iron at 400 °C.

exhibits a decline, whereas the opposite trend is observed for the formation of methane. It is interesting to compare the product selectivity data obtained for treatment of cobalt in C_2H_4/H_2 (1:4) containing 100 ppm chlorine (Table 2) with the comparable results shown in Figure 4 for the reaction of the same mixture with iron under the same conditions. In the latter system, production of methane remains at a modest level and, in this case, is comparable to that of ethane.

In contrast to the behavior observed with cobalt, it was found that in the absence of added hydrogen iron was incapable of catalyzing the decomposition of ethylene to any significant degree at 400 °C, even when up to 200 ppm chlorine was introduced into the reactant stream. If hydrogen was introduced into the ethylene/chlorine system, a distinct change in the carbon depositing characteristics of the metal was discerned, particularly when chlorine was present in the reactant mixture. The effect of progressively raising the chlorine content of a C_2H_4/H_2 (1:4) mixture on the percent conversion of the olefin to solid carbon over an iron powder at 400 °C is presented in Figure 5. While it is clear that the overall trend is similar to that observed with cobalt when treated under the same conditions, a close inspection of these data reveals some subtle differences between the two systems. In the case of the iron-catalyzed formation of solid carbon, there is an appreciable time delay before the catalyst achieves maximum activity for this reaction, typically of the order of 300 min, compared to the behavior exhibited by cobalt where the catalyst reached its optimum level after between 25–50 min on stream.

In a further set of experiments, the hydrogen content of the reactant mixture that was passed over iron was varied while that of ethylene and chlorine was maintained constant. The results of this exercise are presented in Figure 6 from which it is evident that the presence of hydrogen is not only an essential requirement to produce solid carbon, but its concentration plays a key role in the deposition process. On the one hand, excess hydrogen in the reactant appears to decrease the period of time required to attain optimum activity, whereas the highest yields of solid carbon were achieved from a mixture containing equal concentrations of ethylene and hydrogen.

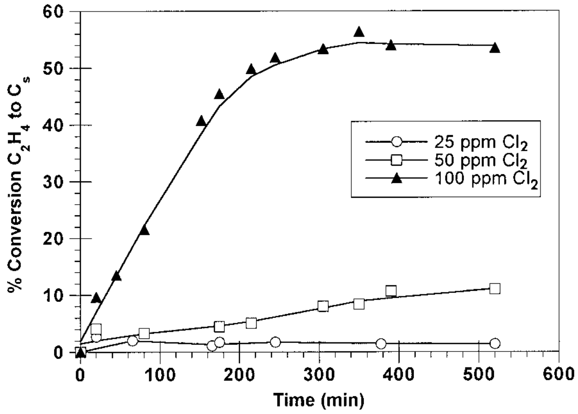

Figure 5. Yield of solid carbon as a function of chlorine concentration in the reactant feed for the iron-catalyzed decomposition of ethylene/hydrogen (1:4) at 400 °C.

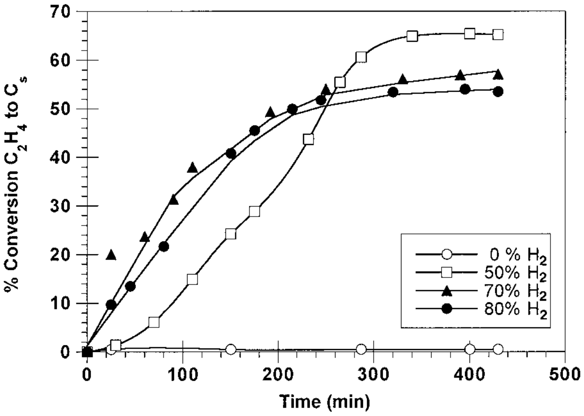

Figure 6. Influence of hydrogen on the formation of solid carbon as a function of reaction time at 400 °C from the interaction of iron with ethylene containing 100 ppm chlorine.

1.3. Pulsing Experiments. In an attempt to pinpoint the origin of the observed induction period prior to attainment of optimum solid carbon formation when the two metals were reacted in ethylene-containing environments, a number of experiments were performed in which each gaseous component was separately cycled into and out of the system. In the first approach the freshly reduced metal powders were initially pretreated for 2.0 h with a 100 ppm chlorine/hydrogen/helium mixture at 400 °C prior to exposure to the 100 ppm chlorine/ethylene/hydrogen (1:4) reactant gas at the same temperature. A comparison of the behavior of an iron powder that was subjected to a pretreatment in chlorine with one that was allowed to undergo direct reaction with the ethylene-containing mixture is presented in Figure 7, where it is apparent and that both samples exhibit identical carbon-depositing characteristics.

In another type of experiment the reaction of iron with the ethylene/hydrogen (1:4) mixture containing 100 ppm chlorine at 400 °C was allowed to proceed for 90 min, and at this stage the reactant flow was disconnected and the system purged with chlorine/hydrogen/helium at the same temperature for 135 min. Following this hiatus the reactant was once again admitted into the system, and the carbon deposition profile that was monitored throughout the reaction sequence is also shown in Figure 7. Inspection of these data reveals that, following the intermediate purge step, the system did not immediately reach the same high carbon deposition level as was exhibited by similar iron samples

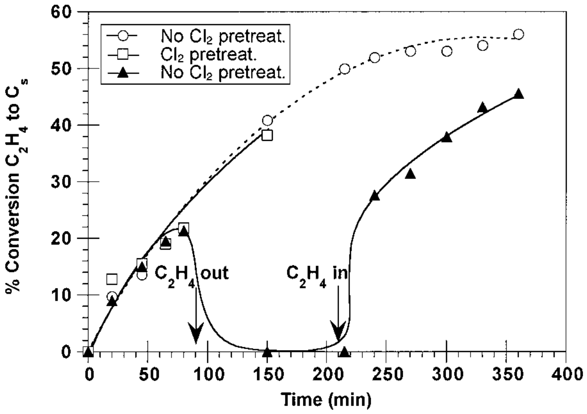

Figure 7. Influence on the yield of solid carbon as a function of time over an iron catalyst that has been subjected to (a) a chlorine treatment step prior to reaction with ethylene/hydrogen (1:4)/100 ppm chlorine at 400 °C and (b) a cycling sequence in which the ethylene component from the same mixture was removed and then reintroduced into the system after a period of 60 min.

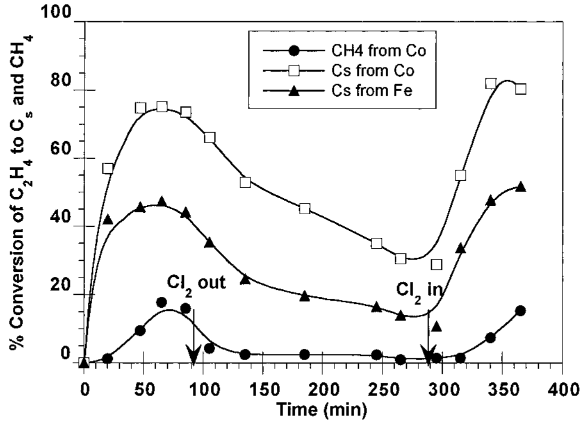

Figure 8. Effect on the carbon deposition reaction over iron and cobalt powders and also the formation of methane on cobalt at 400 °C, of pulsing 100 ppm chlorine into an ethylene/hydrogen (1:4) mixture.

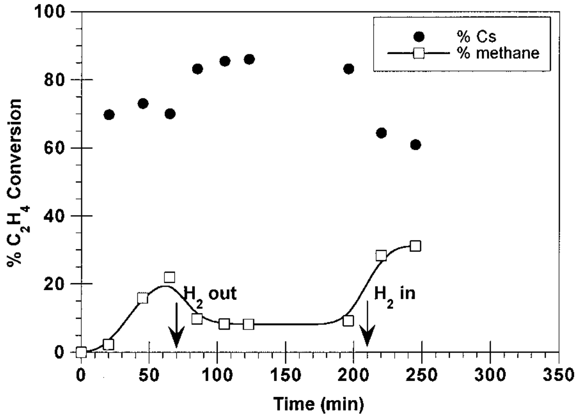

Figure 9. Effect of cycling hydrogen into an ethylene/hydrogen (1:4)/100 ppm chlorine mixture passing over a cobalt catalyst at 400 °C on the formation of solid carbon and methane.

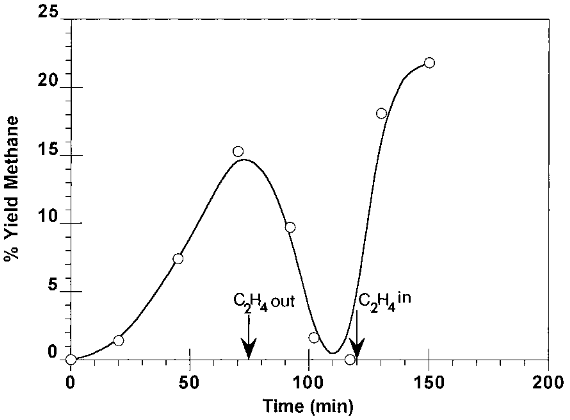

Figure 10. Change in the formation of methane resulting from the removal and subsequent reintroduction of the ethylene component in an ethylene/hydrogen (1:4)/100 ppm chlorine mixture when passed over a cobalt catalyst at 400 °C.

that were permitted to undergo uninterrupted reaction in the ethylene-containing environment. These findings imply that there is an interplay between the adsorbed chlorine and ethylene species that requires each component to be coadsorbed on the metal surface throughout the entire process in order to acquire the maximum promotional effect with regard to catalyzed carbon formation.

The effect on the yield of solid carbon of removing chlorine from the ethylene/hydrogen (1:4) reactant passing over iron and cobalt catalysts at 400 °C and reintroducing the additive after a period of about 200 min is shown in Figure 8. From these plots it is evident that in order to sustain the high growth level of solid carbon it is necessary to have a critical concentration of chlorine continuously passing over the metal surfaces. It is significant with both catalyst systems that when chlorine was withdrawn from the reactant the amount of carbon formed exhibited a steady decline, finally settling out at substantially higher levels than would be achieved from the interaction of the unadulterated metals with an ethylene/hydrogen mixture. These results indicate that while the majority of the adsorbed chlorine is only weakly bound to the metal surfaces and easily removed when the halogen supply is stopped, there is the possibility that a small fraction of strongly held chlorine species remain on the surface, which can influence the structural arrangement of the metal atoms and exert a promotional effect with regard to carbon deposition. Upon reintroduction of a suitable chlorine concentration into the reactant mixture, the amount of solid carbon product is rapidly restored to a level that is slightly higher than the original value. This pattern of behavior is consistent with the existence of a catalyst activation–deactivation process that is reversible in nature. Also presented in this plot is the change in the formation of methane from cobalt as 100 ppm chlorine is cycled into and out of the ethylene/hydrogen (1:4) mixture at 400 °C. It is significant that the profile of this latter dependence is similar to that found for the solid carbon formation under the same reaction conditions.

A final set of experiments was designed to ascertain the origin of the methane produced in the metal-catalyzed decomposition of ethylene/hydrogen in the presence of 100 ppm chlorine. Figure 9 shows the change in both the solid carbon and methane yields obtained from a cobalt catalyst at 400 °C, upon replacement of hydrogen in the reactant mixture with an equivalent amount of helium and then after a period of 120 min reintroduction of hydrogen to its original level. It is evident that when hydrogen was removed from the hydrocarbon stream the decrease in the production of methane was not accompanied by a corresponding drop in the formation of solid carbon, which indicates that the two products are formed by independent processes. The possibility of methane being formed via hydrogasification of the solid carbon deposits can be readily dismissed when one takes into consideration the data obtained from experiments in which cobalt was treated in the same reactant mixture and where the ethylene component was cycled between 20 and 0 mL/min (Figure 10). Inspection of these data reveals that during a 40 min period where the olefin flow rate was halted there was a precipitous decline in the methane yield

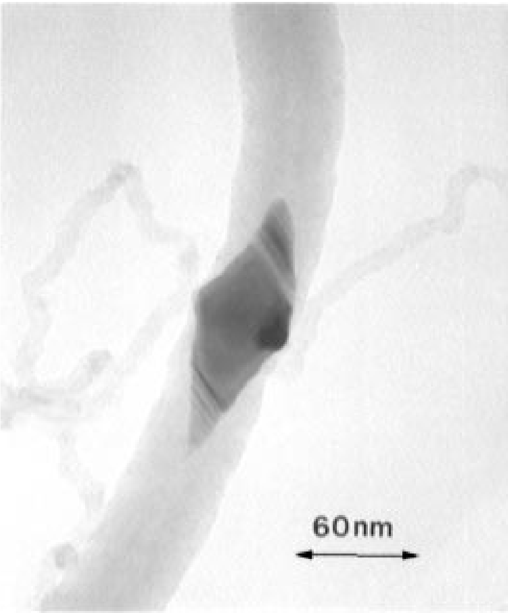

Figure 11. Transmission electron micrograph showing the appearance of carbon filaments produced from the decomposition of ethylene/hydrogen (1:4)/100 ppm chlorine over cobalt at 400 °C. The associated catalyst is seen as the diamond-shaped particle located within the carbon structure.

in spite of the fact that solid carbon and excess hydrogen were still present in the reaction system. Indeed, it is evident that when the olefin is reintroduced into the reactant mixture, the yield of methane climbs to an even higher level to that which was attained during the initial step. It is therefore reasonable to assume that the high yields of methane are derived from the catalytic decomposition of ethylene rather than hydrogasification of the solid carbon product.

2. Characterization of the Solid Carbon Deposit. *2.1. Transmission Electron Microscopy Examinations.* In both cases the solid carbon deposit was found to be comprised completely of filamentous structures that had been generated via a bidirectional growth mechanism, and as a consequence the catalyst particle was located within the body of the material. Close inspection of the detailed features of the filaments produced from cobalt and iron revealed that in all other aspects there were major differences between the two systems. Comparison of the appearance of the catalyst particles associated with the filaments shows that while cobalt acquires a diamond-shaped morphology (Figure 11), iron tends to adopt a “pill box” form (Figure 12). The average sizes of the metal particles associated with the carbon filaments were determined from measurements taken from different regions of a given specimen and are based on over 300 determinations in each system. The value for cobalt was found to be 55 nm, whereas that for iron was 68 nm. It should be emphasized that these values were determined from samples that had been reacted in an ethylene/hydrogen (1:4) mixture containing 100 ppm chlorine after a reaction time of 3.0 h and, as consequence, do not represent the average metal particle size at any given instant during the reaction. One cannot state whether there is a gradual change in this parameter as the reaction proceeds. It is apparent, however, that since the original metal powders had average sizes of between 1.0 and 1.5 μm, fragmentation of the parent granules takes place during the filament growth sequence.

The impact of these different catalyst particle shapes on the alignment and crystalline perfection of graphite platelets that constitute the filament structure can be ascertained from the corresponding lattice fringe images obtained by high-resolution transmission electron microscopy. It is evident from Figure 13 that the filaments produced from the interaction of cobalt with an ethylene/hydrogen (1:4) mixture containing 100 ppm chlorine at 400 °C possess a structure in which the graphite platelets are oriented at an angle to the fiber axis in a “herringbone” form. In contrast, when the same reactant mixture is passed over a powdered iron catalyst, examination of the carbon filaments shows that in this case the graphite platelets are stacked in a direction parallel to the base of the particle and perpendicular to the fiber axis (Figure 14). The details surrounding the generation of these two different graphite platelet arrangements have been given in a previous publication.[22]

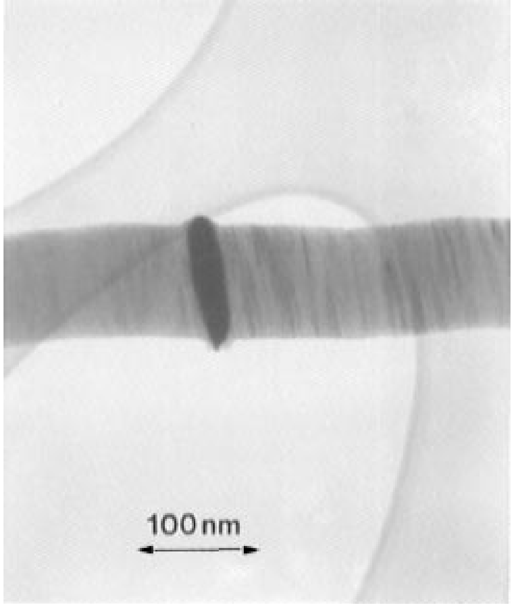

Figure 12. Typical appearance of carbon filaments generated from the iron-catalyzed decomposition of ethylene/hydrogen (1:4)/100 ppm chlorine at 400 °C. In this system the catalyst particle adopts a “pill boxed”-shaped morphology.

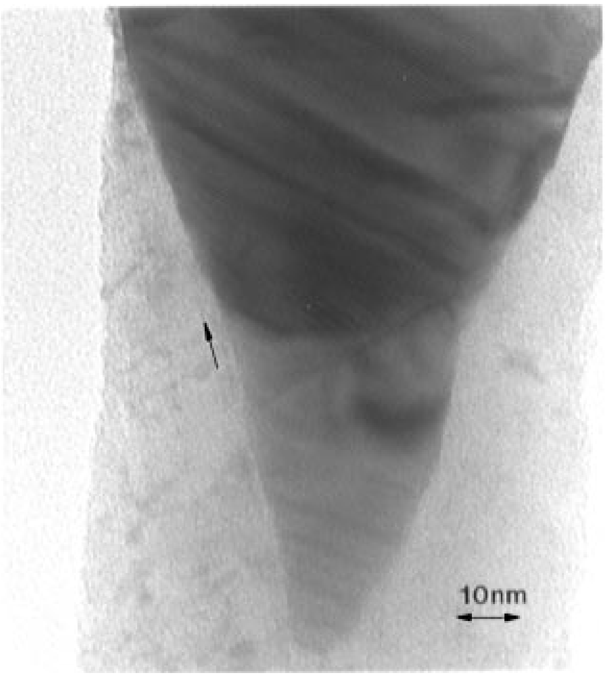

Figure 13. High-resolution transmission electron micrograph of a section of a carbon filament generated from the cobalt-catalyzed decomposition of ethylene/hydrogen (1:4)/100 ppm chlorine at 400 °C where the direction of the graphite platelets, parallel to the carbon precipitating face of the metal particle, is indicated by the arrow.

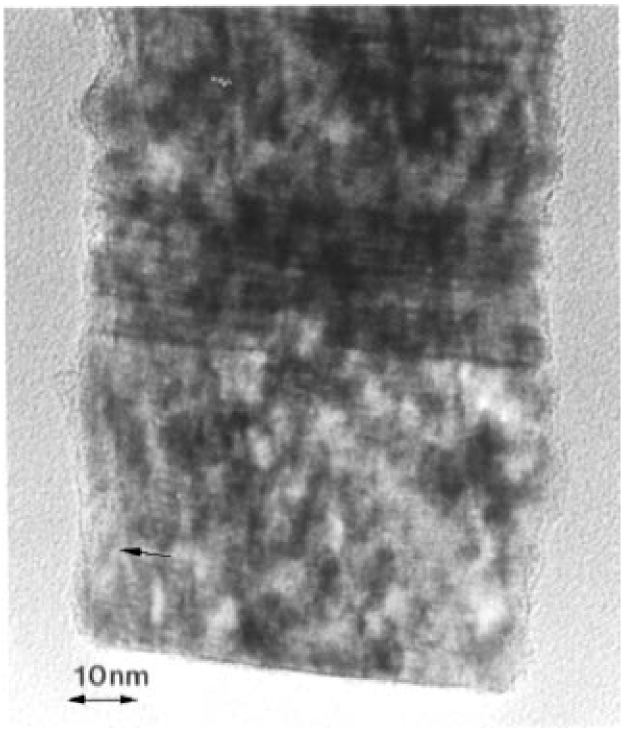

Figure 14. High-resolution transmission electron micrograph of a section of a carbon filament generated from the iron-catalyzed decomposition of ethylene/hydrogen (1:4)/100 ppm chlorine at 400 °C where the direction of the graphite platelets, perpendicular to the fiber axis, is indicated by the arrow.

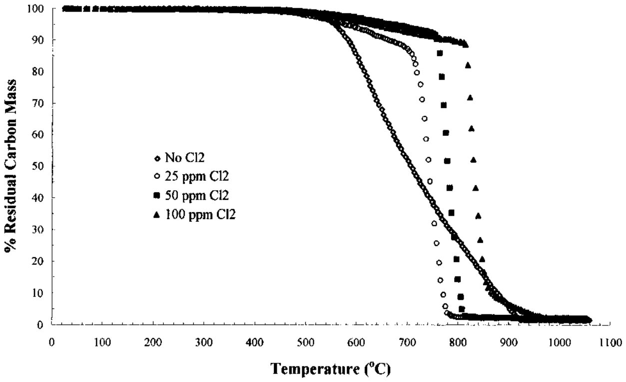

Figure 15. Comparison of the gasification characteristics in CO_2 of carbon filaments produced from the interaction of cobalt with ethylene/hydrogen (1:4) at 400 °C in the presence of various concentrations of chlorine.

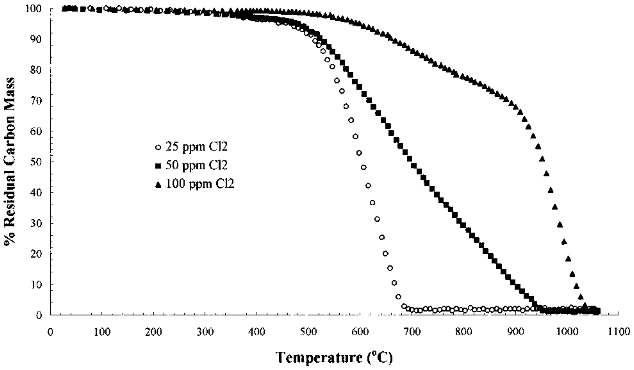

Figure 16. Comparison of the gasification characteristics in CO_2 of carbon filaments produced from the interaction of iron with ethylene/hydrogen (1:4) at 400 °C in the presence of various concentrations of chlorine.

In a separate series of experiments the influence of increasing amounts of chlorine in the reactant gas on the structural characteristics of the individual carbon filaments was studied. While an increase in the chlorine concentration up to a maximum level of 100 ppm did not appear to induce any major modifications in the conformation or physical dimensions of the carbon filaments, it was evident from high-resolution examinations that there was a progressive change in the degree of structural perfection of the material produced from both metal catalyst/hydrocarbon systems. The filaments formed from the interaction of cobalt with an ethylene/hydrogen (1:4) mixture containing 25 ppm chlorine at 400 °C exhibited a somewhat disordered structure that was comparable to that observed from the decomposition of the same reactant over an unadulterated metal powder.[3] As the fraction of halogen in the reactant was raised to 100 ppm, the crystalline perfection of the filaments improved significantly. Since pure iron did not catalyze the growth of filamentous carbon when heated in the presence of ethylene/hydrogen (1:4), it was not possible to make the same comparative study as was carried out for cobalt; however, the high-resolution electron microscopy examinations clearly demonstrated that as the chlorine level was raised from 25 to 100 ppm there was a perceptible enhancement in the crystalline character of the deposited structures.

Finally, examination of carbon filaments that had been formed during long-term experiments, where the chlorine component had been removed and after a period of time reintroduced into the reactant stream, showed some interesting features. In general, all the filaments were relatively long, about 100 μm, and their widths remained constant over the entire length. A detailed inspection of the graphite platelet arrangements within the filaments was conducted at various regions and revealed that, for the most part, the initial crystallite orientation, either “herringbone” or perpendicular to the fiber axis, was maintained throughout the structure with no evidence of any major discontinuities.

2.2. Temperature-Programmed Oxidation Studies. These experiments provided a measure of the overall degree of crystallinity of the carbon filaments from the various preparative procedures. The oxidation profiles of batches of carbon filaments produced by reaction of ethylene/hydrogen (1:4) over cobalt at 400 °C were found to be a strong function of the concentration of added chlorine, as shown in Figure 15. It is evident that in the absence of chlorine the onset of gasification of the solid carbon occurs at 560 °C, and the majority of the sample has been removed when the temperature reaches 850 °C. These are gasification characteristics that are generally associated with amorphous carbon.[21] There is a gradual increase in the oxidation resistance of the filaments as chlorine is introduced into the gaseous reactant mixture, which implies that the samples containing the largest fraction of highly crystalline material are being formed in the presence of 100 ppm of the halogen. Examination of the corresponding data obtained for carbon filaments produced from the interaction of iron with ethylene/hydrogen (1:4) containing chlorine at 400 °C is presented in Figure 16. In this case, one can see a dramatic change in the characteristics of the filaments as the chlorine content is progressively increased from 25 to 100 ppm. In contrast, the materials produced from the reaction mixture containing the lower concentration of chlorine would appear to be quite amorphous in nature.

2.3. Surface Area of Carbon Filaments. The N_2 BET surface areas of carbon filaments formed at 400 °C from the interaction of cobalt and iron powders with ethylene/hydrogen (1:4) containing various concentrations of chlorine are presented in

TABLE 3: N_2 BET Surface Areas of Carbon Filaments Produced from the Interaction of Cobalt with Ethylene/Hydrogen (1:4) in the Presence of Added Chlorine at 400 °C

Cl_2 (ppm)	BET surface area (m^2/g)
25	118.2
50	177.4
100	182.0
200	261.8

TABLE 4: N_2 BET Surface Areas of Carbon Filaments Produced from the Interaction of Iron with Ethylene/Hydrogen (1:4) in the Presence of Added Chlorine at 400 °C

Cl_2 (ppm)	BET surface area (m^2/g)
25	28.4
50	51.3
100	341.3
200	382.9

Tables 3 and 4, respectively. Inspection of these data shows that the surface areas of the filaments produced on both metal catalysts increases as the halogen concentration in the reactant gas is progressively raised, reaching the highest value at 200 ppm chlorine. It should be appreciated, however, that at this concentration the yield of carbon filaments formed during both these reactions is not at the optimum value.

Discussion

1. Interplay between Chlorine Adsorption and Carbon Deposition on Cobalt and Iron. The results of the present investigation clearly demonstrate that at temperatures in the vicinity of 400 °C the catalytic activity of cobalt towards decomposition of ethylene is significantly enhanced when such particles are reacted in an environment containing ppm levels of chlorine. This result suggests that a critical amount of chlorine is retained on the surfaces of the metal particles when the system is treated in a reaction stream containing a small concentration of the halogen. Under these circumstances it is evident from the data presented in Tables 1 and 2 that coadsorption of chlorine on cobalt facilitates the dissociative chemisorption of ethylene in both the absence and presence of added hydrogen. It is interesting to find that chlorine only exerted a promotional effect on the decomposition of ethylene over iron when hydrogen was present in the reactant mixture. While the precise reasons for this behavior are not clear at this time, we believe a contributing factor is that the coadsorption of hydrogen is an essential requirement for the reconstruction of the iron surface.

In many regards the influence of chlorine on these two metals with respect to the enhancement of filamentous carbon growth parallels the observed behavior of CO on iron,[18] and S and Cu on both iron and cobalt[3,5,19,20] when these respective systems were heated in an ethylene/hydrogen environment. It should be stressed, however, that while these trends are similar from a qualitative standpoint, the promotional behavior may be the result of different operative modes in each system. It was argued that geometric effects were largely responsible for the observed changes in the behavior of the ferromagnetic metals when copper was introduced into the particles. On the other hand, when ethylene was coadsorbed in the presence of either H_2S or CO, the gaseous additives were believed to induce electronic perturbations in the metal surface layers that resulted in a weakening of the C−C bond of the olefin that lead to an enhancement in decomposition.

Carbon filaments are the product of the decomposition of selected hydrocarbons or carbon monoxide over hot metal surfaces.[23] It has been proposed that prior to carbon deposition the particles undergo reconstruction and adopt well-defined geometric shapes where two distinct sets of faces are formed[22] as depicted schematically in Figure 17. Initially, the gaseous reactant is adsorbed and decomposed on the type A faces, this process being followed by the diffusion of carbon species through the catalyst particle to precipitate at type B faces, in the form of a fibrous structure. It is generally agreed that carbon diffusion through the particle is the rate-determining step in the growth process. From the present investigation it is evident that the presence of chlorine not only enhances the decomposition of ethylene but also modifies the product distribution. Furthermore, the degree of crystalline perfection of the solid carbon is increased as chlorine is added to the system; i.e., the halogen exerts an influence on both types of faces, A and B.

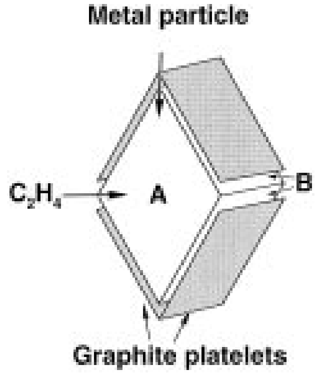

Figure 17. Schematic rendition of the essential steps involved in the catalytic growth of carbon filaments from the decomposition of a hydrocarbon. Ethylene undergoes dissociative chemisorption on face A; carbon species produced from this reaction diffuse through the metal catalyst particle and precipitate in the form of graphite platelets at faces B.

In experiments where the reaction temperature was raised to 500 °C the promotional effect of chlorine did not appear to be maintained, and one might therefore conclude that under these circumstances the halogen is readily desorbed from the metal surfaces. In this context mention should be made of the work of Dowben and Jones,[24] who used a combination of surface science techniques to study the sticking probability of chlorine on iron single crystals. They reported that there was almost no loss of adsorbed chlorine from the surface at 170 °C, but as the temperature was gradually increased to 460 °C the rate of loss of the halogen became quite substantial, causing the coverage to decrease by 50%. Other workers[25] investigated the interaction of chlorine with Ni(100) surfaces and found that in this system no changes in the halogen coverage were detectable at temperatures up to 325 °C. A thorough search of the literature has failed to reveal the existence of any similar studies devoted to the interaction of chlorine with cobalt surfaces, however, there is no reason to believe that this system will exhibit any major differences in halogen adsorption characteristics to that displayed by either iron or nickel.

While there are several examples of the use of trace quantities of halogens as promoters in metal-catalyzed reactions and it is well recognized that this behavior is related to their strong electron-accepting properties, the details of the manner by such additives function are still not well understood.[26] A further factor that must be taken into consideration is the potential for adsorbed chlorine species to induce reconstruction of the metal crystallites, and this phenomenon opens up the possibility that the newly created faces present an atomic arrangement that favors dissociative chemisorption of the gaseous reactant molecules, thereby leading to an enhancement in a desired reaction pathway. Although there has only been a limited research effort devoted to investigations of the nature of the structural impact of chlorine on ferromagnetic metal surfaces,[24−29] there is a substantial literature detailing the sulfur-induced reconstruction of these metals.[30−32] By analogy it can be argued that the formation of a strong metal−chlorine interaction weakens the bonding between the surface and the next lower metal layers, allowing for rearrangements of the surface metal atoms to take place.

2. Influence of Chlorine on the Metal Activation−Deactivation Phenomena. Perhaps one of the most outstanding features to emerge from this investigation is the requirement to maintain a critical concentration of chlorine in the gas phase in order to achieve optimum catalytic activity of either cobalt or iron. An unexpected finding is that pretreatment of the metal surfaces with chlorine does not appear to inhibit the subsequent chemisorption behavior of ethylene. This conclusion is based on the data presented in Figure 7 where identical reactivity patterns were obtained for two systems: one that had been pretreated in 100 ppm chlorine for 90 min, prior to reaction in the hydrocarbon/chlorine mixture, and the other where the reactant mixture was introduced directly. Two possible explanations can be considered: (a) the halogen is adsorbed on a different face to that of the olefin and modifies the crystalline orientation of this latter face by inducing an overall reconstruction of the particle, and (b) the majority of adsorbed chlorine species tend to diffuse into the surface sublayers of the cobalt particles and exert an influence on the ethylene adsorption characteristics by inducing electronic perturbations in the metal atoms. Inspection of the data presented in Figure 8 indicates that the effect of chlorine is evident even after the halogen flow had been terminated for 200 min, and this observation is consistent with the notion that desorbed surface species are being continuously replenished by bulk sources, until a state of complete exhaustion is attained.

If the halogen was removed from the reactant, then the high activity for the carbon deposition reaction could not be sustained. Reintroduction of chlorine after a suitable period of time resulted in restoration of the carbon deposition activity to its original level, indicating that the “activation−deactivation” processes were completely reversible in nature (Figure 7). Since the response in the behavior of the metals to the change in the gas phase composition was almost instantaneous, as far as the regeneration step was concerned, one can dismiss the normal causes of catalyst deactivation, such as the collection of carbonaceous residues on the surfaces in contact with the gas phase reactants or particle sintering, as playing a role in these systems. These factors would tend to exert a permanent effect on the performance of the catalyst and unlikely to be influenced by the injection of a small concentration of chlorine into the reactant. It is logical to assume, therefore, that other more subtle effects are responsible for this dramatic reversal in catalytic activity.

In order to gain a clearer insight into this phenomenon, it is necessary to focus attention on the events that might be operative under these conditions. In this context two different scenarios should be considered: (a) upon reintroduction of chlorine into the system, fresh catalyst particles are created from any residual metal powder and proceed to generate the growth of new carbon filaments in the same manner as that by accomplished other particles in the initial stages of the reaction; (b) during this step, reactivation of the faces of existing particles that dissociate ethylene occurs, and as a consequence the growth of carbon filaments is reinitiated with no apparent change in the structural characteristics of the material. The weight of experimental evidence would tend to favor the latter explanation since it is highly unlikely that any of the original metal powder exists after the first 3.0 h carbon deposition cycle. It is significant that the type of activation−deactivation behavior envisaged in scenario (b) has been observed in previous controlled atmosphere electron microscopy experiments.[33] In this case it was found that the introduction of chlorine into an oxygen environment resulted in the cessation of the channeling action of platinum particles across the basal plane surfaces of graphite. When the halogen was removed from the system, the metal particles were observed to resume their catalytic channeling behavior.

If, indeed, the presence of chlorine is responsible for restoring the activity of a catalyst associated with carbon filaments, then on the basis of the detailed electron microscopic studies of the deposit formed during these types of experiments, one can draw some further conclusions with regard to the function of the halogen in these reactions. The observation that there were no obvious alterations in the structural characteristics of particularly long filaments after the regeneration step would tend to argue against the possibility that the additive was responsible for bringing about particle reconstruction, since such a process results in a change in catalyst morphology, and this behavior would be manifested in a corresponding modification in the orientation of the precipitated graphite platelets constituting the filaments. We therefore favor a rationale in which the presence of adsorbed chlorine species are responsible for inducing a perturbation in the electronic properties of the surface layers of the metal particles. It is possible that the charge transfer between adsorbed chlorine molecules and the metal surface atoms leads to a strengthening of the metal−ethylene bond and a concomitant weakening of the C−C bond in the olefin, making the latter more susceptible to decomposition and enhancing the formation of the solid carbon product. A similar argument was put forward by Martin[34] to account for the influence of chlorine on the catalytic behavior of iron for the CO/H_2 reaction.

3. Gas Phase Product Analysis. Comparison of the behavior of unsupported cobalt−ethylene/hydrogen (1:4) in the absence of added chlorine at 400 °C with that reported previously for the same reaction performed at 600 °C[3,19] shows a significant difference in the respective reactivity patterns. At the higher temperature it was found that cobalt did not exhibit any appreciable activity toward decomposition of ethylene, and this behavior persisted even when the reactant contained a large fraction of added hydrogen. From Table 2 it is apparent that when the same reaction was carried out at 400 °C, approximately 26% of the ethylene was decomposed, with solid carbon being the dominant product. It is possible that this variation in catalytic performance is related to the cobalt phase transformation, α (hcp) to β (fcc), that is known to occur at around 400 °C.

A further feature that is evident from the gas phase product distributions is the finding of a considerable increase in the selectivity toward methane formation when cobalt particles were reacted in either ethylene or ethylene/hydrogen (1:4) in the presence of >75 ppm chlorine. Examination of the data in Figure 8 shows the dramatic change in methane yield when the flow of chlorine is deliberately interrupted for a period of 200 min and then subsequently reinjected. In contrast, the selectivity to the other major gaseous product, ethane, appeared to be relatively insensitive to the presence chlorine. It was also interesting to discover that this same trend was not observed when iron particles were reacted under the same conditions. In this case, the yields of methane and ethane were quite similar and did not exhibit any significant major changes in selectivity as the concentration of chlorine was progressively raised to 100 ppm.

At first sight one might rationalize the anomalously high yields of methane according to the notion that this product is formed via hydrogasification of the solid carbon. While *in-situ* electron microscopy experiments have demonstrated that the onset of cobalt-catalyzed hydrogenation of graphite commences at 450 °C,[35] studies with this technique revealed that the introduction of a small amount of chlorine into the system resulted in the complete suppression of this particular type of reaction.[33] Moreover, the results of current studies where the yield of methane exhibited a precipitous drop when ethylene was removed from a reactant stream also containing an excess of hydrogen together with 100 ppm chlorine is consistent with the conclusion that in this system methane does not arise from hydrogasification of carbon.

In a previous investigation dealing with the interaction of copper−nickel and ethylene/hydrogen,[36] the unexpected high yields of methane were accounted for in terms of a change in the mode of adsorption of the olefin when such a molecule encounters a nickel atom whose nearest neighbor is a copper atom. It was postulated that since copper does not readily chemisorb hydrocarbons, the ethylene would bond to the surface in an “end-on” arrangement. In this conformation the adsorbed molecule would rapidly rearrange to form an “ethylidyne” intermediate, which would subsequently undergo C−C bond scission to produce a methane molecule, leaving a residual carbon atom on the metal surface, that would eventually contribute toward the growth of a carbon filament. If, however, this was the major route for methane formation, one would expect to find a corresponding decrease in the amount of solid carbon formation. Inspection of the data presented in Tables 1 and 2 shows that the observed enhancement in methane formation is not accompanied by a corresponding decrease in magnitude of solid carbon deposition, and therefore one is forced to conclude that some other mechanism must be operative in the formation of the paraffinic product.

4. Influence of Chlorine on the Structural Characteristics of Carbon Filaments. Finally, the presence of foreign atoms is likely to have a direct impact on the wetting characteristics of the metal with respect to solid carbon, and as a consequence, both the degree of crystallinity and morphology of the carbon deposit are expected to be subject to major modifications. In previous studies we have shown 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.[4,37] 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. These conditions are generally achieved when the modified metal faces undergo a wetting and spreading action with graphite, i.e., form a strong metal−support interaction.[38]

The introduction of a small concentration of chlorine into either the cobalt or iron−ethylene/hydrogen systems was found to produce a significant improvement in the degree of crystalline perfection of the precipitated carbon filament structures, but did not appear to exert any modifications on the morphological characteristics of the deposit. This behavior is to be contrasted with the changes that were observed in the conformation of carbon filaments when small amounts of either sulfur[3−5,39] or phosphorus[40] were added to a hydrocarbon feed undergoing reaction with cobalt, nickel, and iron powders. In these cases the filaments were generated in the form of regularly coiled structures that exhibited a somewhat lower degree of crystalline perfection than the material formed under the same conditions on the respective unadulterated metal powders. Despite the difference in the influence of the these additives on the growth characteristics of carbon filaments to that observed with chlorine, one may conclude that in all cases the adatom is capable of exerting an effect on all the faces of the metal particles and inducing changes in the nature of the metal−metal bonding at the carbon-depositing regions.

Acknowledgment. Financial support for this work was provided by the United States Department of Energy, Basic Energy Sciences, Grant DE-FG02-93ER14358.

References and Notes

(1) Rostrup-Nielsen, J. R. In *Catalyst Deactivation*, Bartholomew, C. H., Butt, J. B., Eds.; Elsevier Science: Amsterdam, 1991; p 85.
(2) Rostrup-Nielsen, J. R. *J. Catal.* **1984**, *85*, 31.
(3) Kim, M. S.; Rodriguez, N. M.; Baker, R. T. K. *J. Catal.* **1993**, *143*, 449.
(4) Owens, W. T.; Rodriguez, N. M.; Baker, R. T. K. *Catal. Today* **1994**, *21*, 3.
(5) Owens, W. T.; Kim, M. S.; Rodriguez, N. M.; Baker, R. T. K. In *Catalyst Deactivation 1994*; Delmon, B., Froment, G. F., Eds.; Elsevier Science: Amsterdam, 1994; p 191.
(6) Cullis, C. F.; Manton, J. E.; Thomas, G. B.; Wilman, H. *Acta Cryst.* **1959**, *12*, 382.
(7) Wu, X.; Gerstein, B. C.; King, T. S. *J. Catal.* **1992**, *135*, 68.
(8) Verderone, R. J.; Pieck, C. L.; Sad, M. R.; Parera, J. M. *Appl. Catal.* **1986**, *21*, 239.
(9) Pieck, C. L.; Marecot, P.; Parera, J. M.; Barbier, J. *Appl. Catal.* **1990**, *126*, 235.
(10) Iyagba, E. T.; Hoost, T. E.; Nwalor, J. U.; Goodwin, J. G. *J. Catal.* **1990**, *123*, 1.
(11) Peri, S. S.; Lund, C. R. F. *J. Catal.* **1995**, *152*, 410.
(12) Burch, R.; Chalker, S.; Loader, P.; Thomas, J. M.; Ueda, W. *Appl. Catal.* **1992**, *82*, 77.
(13) Warren, B. K. *Catal. Today* **1992**, *13*, 311.
(14) Nitta, Y.; Hiramatsu, Y.; Imanaka, T. *J. Catal.* **1990**, *126*, 235.
(15) Foger, K.; Jaeger, H. *Appl. Catal.* **1989**, *56*, 137.
(16) Feeley, O. C.; Sachtler, W. M. H. *Appl. Catal.***1991**, *75*, 93.
(17) Chambers, A.; Baker, R. T. K. *J. Catal.* **1996**, *158*, 356.
(18) Rodriguez, N. M.; Kim, M. S.; Baker, R. T. K. *J. Catal.* **1993**, *144*, 93.
(19) Chambers, A.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem.* **1995**, *99*, 10581.
(20) Krishnankutty, N.; Rodriguez, N. M.; Baker, R. T. K. *J. Catal.* **1996**, *158*, 217.
(21) Owens, W. T.; Rodriguez, N. M.; Baker, R. T. K. *J. Phys. Chem.* **1992**, *96*, 5048.
(22) Rodriguez, N. M.; Chambers, A.; Baker, R. T. K. *Langmuir* **1995**, *11*, 3862.
(23) Rodriguez, N. M. *J. Mater. Res.* **1993**, *8*, 3233.
(24) Dowben, P. A.; Jones, R. G. *Surf. Sci.* **1979**, *84*, 449.
(25) Kiskinova, M.; Goodman, D. W. *Surf. Sci.* **1981**, *108*, 64.
(26) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley & Sons: New York, 1994.
(27) Erley, W. *Surf. Sci.* **1982**, *114*, 47.
(28) Gudde, N. J.; Lambert, R. M. *Surf. Sci.* **1983**, *134*, 703.
(29) Mueller, D. R.; Rhodin, T. N.; Sakisaka, Y.; Dowben, P. A. *Surf. Sci.* **1991**, *250*, 185.
(30) Shih, H. D.; Jona, F.; Jepson, D. W.; Marcus, P. M. *Phys. Rev. Lett.* **1981**, *46*, 731.
(31) Cabane-Brouty, F.; Oudar, J.; Bernard, J. *Acta. Metall.* **1962**, *10*, 901.
(32) Oudar, J.; Barbouth, N.; Bernard, J. *Mem. Sci. Rev. Metall.* **1975**, *72*, 649.
(33) Baker, R. T. K.; Lund, C. R. F.; Dumesic, J. A. *Carbon* **1983**, *21*, 469.
(34) Martin, G. A. In *Studies in Surface Science and Catalysis*; Imelik, B., et al., Eds.; Elsevier Science: Amsterdam, 1982, Vol. 11, p 315.
(35) Oh, S. G.; Baker, R. T. K. *J. Catal.* **1993**, *143*, 449.
(36) Kim, M. S.; Rodriguez, N. M.; Baker, R. T. K. *J. Catal.* **1991**, *131*, 60.
(37) Kim, M. S.; Rodriguez, N. M.; and Baker, R. T. K. *J. Catal.* **1992**, *134*, 253.
(38) Angermann, H. H.; Horz, G. *Appl. Surf. Sci.* **1993**, *70*, 163.
(39) Kawaguchi, M.; Nozaki, K.;Motojima, S.; Iwanaga, H. *J. Crystal Growth* **1992**, *118*, 309.
(40) Motojima, S.; Hasegana, I.; Kagiya, S.; Momiyama, M.; Kawaguchi, M.; Iwanaga, H. *Appl. Phys. Lett.* **1993**, *62*, 2322.