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The Interplay between Sulfur Adsorption and Carbon Deposition on Cobalt Catalysts

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Sulfur is present as an impurity in various industrial feedstocks and is generally regarded as a catalyst poison; however, controlled poisoning of metals by sulfur can improve both reactivity and selectivity. We have attempted to develop an understanding of the interplay between sulfur adsorption and carbon deposition reactions by monitoring not only the gas-phase products but also the amount of filamentous carbon deposited from the interaction of sulfur-contaminated cobalt particles with ethylene/hydrogen mixtures. Pretreatment of cobalt in low levels (4–100 ppm) of H_2S was found to dramatically increase the weight percentage of carbon filaments produced during the reaction, from 4.5 (without sulfur treatment) to 70%. In contrast, when the metal was pretreated at higher H_2S levels (>500 ppm) or when the sulfide was added continuously in the hydrocarbon feed at concentrations of >60 ppm the catalytic activity was completely suppressed. Carbon filaments produced on uncontaminated cobalt particles were found to be highly graphitic in nature, and this degree of structural perfection decreased as sulfur was added to the system. In addition, it was apparent that sulfur could induce fragmentation of the powdered catalyst, a feature which may provide some new insights into the understanding of redispersion phenomena of sintered metal particles.

INTRODUCTION

Sulfur poisoning of transition metal catalysts is a serious problem encountered in a number of industrial processes. Exposure to even minor concentrations of sulfur-containing compounds can drastically reduce the activity of certain supported metal catalysts (*1*). This acute sensitivity is apparently due to strong bonding between sulfur and surface metal atoms. Trace amounts of sulfur impurities (0.1–10 ppm) in the feed can decrease the methanation activity of nickel catalysts by several orders of magnitude (*2–6*). Consequently, most studies in this area have tended to focus on the deleterious effects of sulfur on catalyst performance.

On the other hand, beneficial effects on the selectivity can be obtained by a partial and well controlled poisoning of metals by sulfur, e.g., in the catalytic reforming of naphtha, partial poisoning by sulfur minimizes excessive hydrocracking (*7*). Adsorption of a small amount of sulfur was found to enhance the selective formation of heavier hydrocarbons in the Fischer–Tropsch synthesis (*1*, *8*). Rostrup-Nielsen and co-workers (*3*, *9*) reported that carbon-free steam reforming of methane could be achieved on a partially sulfur-passivated nickel catalyst under conditions which, without the presence of sulfur, would result in the formation of filamentous carbon.

Since sulfur chemisorption on metal surfaces either prevents or modifies the adsorption characteristics of other reactant molecules, in many regards it resembles the behavior of the additive in bimetallic catalysts (*6*, *9*). Sulfur adsorption on a metal surface causes two types of poisoning: blockage of catalytic sites (geometric effect) and changes in catalytic activity of the metal due to the influence of neighboring sulfur atoms (electronic effect). The geometric ef-

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fect plays an important role over the entire sulfur coverage range and dominates in high-sulfur-coverage regions (*5*, *6*, *9–11*), whereas the electronic effect is considered to be operative only at low sulfur coverages (*12*, *13*). Somorjai (*14*) proposed that facile (small ensemble) reactions such as hydrogenation and dehydrogenation should be less affected by sulfur addition than demanding (large ensemble) reactions such as hydrogenolysis. Hence, a sulfur treatment of metal catalysts may provide a sensitive tool for improving selectivity by affecting the concentration of ensembles (*15*).

Another aspect found with sulfur addition is the possibility of reconstruction or faceting of the metal surfaces. This phenomenon is important in catalysis, especially with regard to structure-sensitive reactions. Hydrogen sulfide-induced reconstruction has been rationalized in two ways (*6*): a change in the cooperative stable condition as a result of hydrogen desorption and a modification in the metal–sulfur bonding characteristics to accommodate more sulfur atoms. Presumably, a strong metal–sulfur interaction weakens the bonding between the surface and the next lower metal layers, allowing for rearrangements of the surface metal atoms to take place.

Although many investigators have studied the effect of sulfur poisoning on various catalytic reactions, there are relatively few reports on the influence of this additive on carbon deposition. Rostrup-Nielsen (*9*) studied carbon formation on supported nickel catalysts with various sulfur coverages under the reaction conditions of methane steam reforming. Sulfur was found to inhibit the rate of carbon formation to a greater extent than that of the steam-reforming reaction. The formation of filamentous carbon was prevented above a certain sulfur coverage (Θ_s = 0.7–0.8); below this level, however, inhibition of carbon was not realized. In order to account for this behavior, it was claimed that the ensembles required for the nucleation of filamentous carbon were larger than those for steam reforming (geometric effect). Swift *et al.* (*16*) also found that addition of hydrogen sulfide to the butene feed eliminated the formation of carbonaceous deposits on a nickel-based catalyst, during dehydrogenation of the olefin to butadiene.

In contrast, some studies have demonstrated that introduction of sulfur species into the reactant stream can, under certain circumstances, bring about a significant increase in the formation of carbon deposits. White (*17*) claimed that the rate of carbon deposition occurring during the thermocracking of propane to propylene was extremely sensitive to the amount of hydrogen sulfide present in the alkane feed. The carbon deposition rate increased up to a maximum when the sulfur content was about 0.001% by weight and gradually decreased with further sulfur addition. Gardner and Bartholomew (*18*) investigated carbon accumulation on presulfided alumina-supported nickel catalysts during methanation of carbon monoxide. The carbon deposition rates on sulfur-poisoned samples were less than those for uncontaminated catalysts at temperatures below 380°C. Above this temperature, however, the reverse trend was found and it was suggested that under these conditions sulfur prevented the hydrogasification of surface carbon, thereby causing a net increase in the rate of carbon deposition. Other workers (*19–21*) have found that the addition of controlled amounts of hydrogen sulfide to various hydrocarbon feeds increased the yield of vapor-grown carbon fibers produced from iron catalyst particles.

In the current study we have attempted to resolve the somewhat ambivalent effects of sulfur towards catalytic carbon formation by conducting a detailed investigation of the decomposition of ethylene over sulfur treated cobalt catalysts. Both the influence of sulfur pretreatment of the metal and the effect of continuously adding sulfur in the feed have been examined by monitoring not only the amount of solid carbon produced in the reaction but also the variations in the concentrations of gaseous products as a function of time. Attention has also been given to the changes in the characteristics of carbon filaments produced at the rear of catalyst particles due to modifications in the cobalt/carbon interfacial properties induced by the presence of sulfur.

EXPERIMENTAL

Materials

The cobalt powder used as catalyst in this work was prepared by precipitation of the metal carbonate from a cobalt nitrate solution using ammonium bicarbonate. The washed precipitate was filtered and dried overnight at 110°C, and then reduced at 500°C in a 20% hydrogen/helium flow for 12 h. Prior to removal from the reactor, the reduced metal granules were initially cooled to room temperature in helium and then passivated by treatment in a 2% air/helium mixture for 1 h. Finally, the metal granules were ground to make a fine powder. BET surface area measurements were carried out using nitrogen adsorption at −196°C. Values of 0.3–0.5 $m^2 g^{-1}$ were obtained for the powders. X-ray diffraction analysis showed that following this preparative procedure the powder was in the form of cubic metallic cobalt and no evidence for the existence of metal oxides was found.

Two different mixtures containing hydrogen sulfide in argon (100 ppm and 5%) were obtained from Alphagaz Co. and used for catalyst pretreatment or for addition of sulfur to the feed. Other gases used in this work, hydrogen (99.999%), ethylene (99.99%), helium (99.99%), and argon (99.99%), were obtained from the same supplier. Reagent grade cobalt nitrate was purchased from Fisher Scientific for the catalyst preparation.

The structural details of the carbon filaments produced during the treatment of cobalt under various reaction conditions were obtained from high-resolution transmission electron microscopy examinations performed in a JEOL 200CX microscope. In addition, from these experiments the average width of filaments was determined, based on measurements of over 200 filaments for each system. Representative specimens were prepared by ultrasonic dispersion of a mass of the deposit in isobutanol from which a drop of the suspension was applied to a carbon support film. The point-to-point resolution of the microscope is estimated to be 0.18 nm.

The degree of crystallinity of the carbon filament structures was estimated by comparison with the oxidation characteristics of pure graphite. Controlled oxidation studies were carried out in a 10% carbon dioxide/argon mixture using a Cahn 2000 microbalance at a heating rate of 5°C/min. Prior to oxidation, the carbon filaments were treated in 1 *N* HCl for 3 days and washed in order to remove the associated metal catalyst particles. Under these conditions the onset of oxidation of single-crystal graphite was found to occur at 850°C.

Apparatus and Procedures

Experiments were performed in a quartz flow reactor located in a Lindberg horizontal tube furnace. Flow rates were controlled with needle valves and measured with calibrated rotameters. A sample of cobalt powder (50 mg), which had been shown by X-ray diffraction analysis to be metallic in nature was dispersed uniformly in a ceramic boat. Prior to reaction the powder was treated in a 10% hydrogen/argon mixture at 535°C for 1 h to convert any surface oxide arising as a result of the passivation procedure described above and was then exposed to a desired mixture of hydrogen sulfide, hydrogen, and inert gas at a total flow rate of 200 ml/min for 30 min. It should be stressed that in these experiments our intention was to merely achieve partial sulfur coverage of the metal surface and not reach saturation, since such a condition would result in catalyst deactivation for the reactions under consideration. In many respects we were attempting to simulate the type of treatment practiced by surface scientists for the introduction of gaseous adatoms onto single-crystal metal surfaces. Following this step, the ethylene/hydrogen (1 : 1) feed gas mixture was passed over the sulfided catalyst at 535°C for extended periods of time. Experiments were also carried out on cobalt samples which were not subjected to hydrogen sulfide treatment. The compositions of the gas phase were monitored at regular intervals during the reaction from analysis with a gas chromatograph (Varian 3400) using a 30-m megabore column (GS-Q). Carbon and hydrogen atom balances in conjunction with the relative concentrations of the respective components were employed to obtain the various product yields, and the mass of carbon deposited on the catalyst also determined at the completion of a particular experiment. In all cases the calculated and measured weights of solid carbon were within ±5%. Examination of the carbonaceous deposits in the SEM showed that the major constituent was filamentous carbon.

In the case where sulfur was continuously added in the feed, the cobalt powder was treated in a selected series of mixtures containing ethylene, hydrogen, and hydrogen sulfide, in which the ethylene to hydrogen ratio was maintained at (1 : 1) and mixed with various ratios of hydrogen sulfide/argon at a total flow rate of 100 ml/min.

X-ray diffraction analyses of cobalt powders treated for various times in hydrogen sulfide/hydrogen mixtures were carried out on a Rigaku Geigerflex DMAX B diffractometer using Cu *Kα* radiation with a graphite monochromator. The scan rate of 15°/min was used for the 2Θ range of 20° to 150°. All X-ray diffraction measurements were performed on powders which had been passivated prior to exposure to air.

RESULTS

(*a*) *Presulfided Cobalt Catalyst Behavior*

Decomposition of ethylene was carried out over cobalt powder catalyst which were presulfided at various levels (0–500 ppm hydrogen sulfide). The amount of carbon deposited on the catalyst after 2 h reaction was determined and these data are presented as a function of the hydrogen sulfide concentration used in the pre-treatment step, in Fig. 1. These data indicate that cobalt samples pretreated at sulfur levels of up to 100 ppm ($H_2S/H_2 = 10^{-4}$) exhibit a remarkable enhancement in carbon deposition compared to the unadulterated samples, the amount of solid carbon increasing from 4.5 to about 70%. The maximum activity is found to occur at about 17 ppm ($H_2S/H_2 = 3.4 \times 10^{-5}$) hydrogen sulfide pretreatment, while levels of sulfur higher than about 500 ppm ($H_2S/H_2 = 10^{-3}$) tend to inhibit the accumulation of carbon.

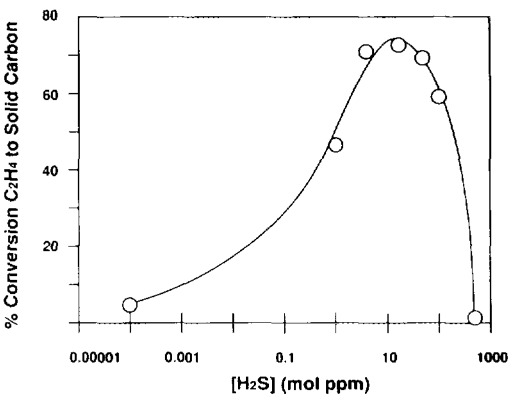

FIG. 1. Percent solid carbon formed during the cobalt catalyzed decomposition of an ethylene/hydrogen (1 : 1) mixture at 535°C as a function of the H_2S concentration in the pretreatment step.

For a more detailed understanding of the factors surrounding the carbon deposition characteristics over these metal surfaces the amount of solid carbon formed is plotted as a function of reaction time in Fig. 2 for a series of sulfur-treated cobalt catalysts. With hydrogen sulfide pretreatment levels lower than 50 ppm ($H_2S/H_2 = 5 \times 10^{-5}$) the onset of carbon deposition takes place immediately and the activities of this process are relatively high and fairly uniform, with the exception of the 1-ppm treatment. At higher sulfur concentrations then there is no carbon deposition activity for periods of up to 15 min in the case of 100 ppm,

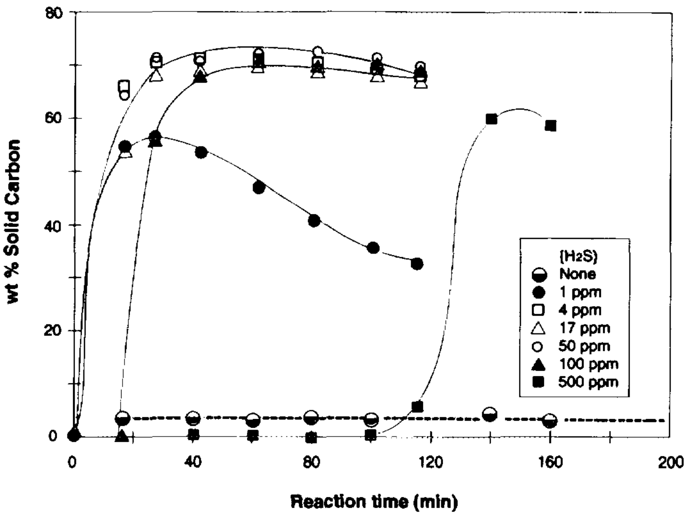

FIG. 2. Percent solid carbon formed as a function of reaction time for cobalt catalysts pretreated at various H_2S levels prior to reaction in ethylene/hydrogen (1 : 1) at 535°C.

and up to 100 min in the case of 500-ppm treatment. It is clear that although sulfur may be gradually lost from the metal surface, over the period that the current experiments were performed, carbon deposition activity did not reach the level exhibited by that of an unadulterated metal powder.

In addition to measuring the weight of solid carbon produced in these reactions, analysis of the gaseous products was carried out at various periods of time. The variation of total product distribution as a function of time for untreated cobalt is compared with samples pretreated in 4 and 100 ppm hydrogen sulfide, respectively, in Fig. 3. From these data it can be seen that methane and ethane are the major gaseous products formed in the reaction. Furthermore, the time required to reach the equilibrium levels of all products is directly related to the concentration of hydrogen sulfide used in the pretreatment step, the product distribution obtained from the higher sulfide treatment after 40 min being almost identical to that measured from the lower treatment after 25 min. Table 1 shows a compilation of the product distributions obtained from cobalt samples pretreated at various H_2S concentrations. It is apparent from examination of these results that within experimental error after a 100-min reaction in ethylene/hydrogen at 535°C all systems exhibit similar reactivity patterns.

(*b*) *Effect of Continuous Addition of Sulfur on Cobalt Activity*

In a complementary series of experiments, various amounts of hydrogen sulfide were added directly to the hydrocarbon feed stream. The various product yields were calculated as a function of time based on gas chromatographic analysis in conjunction with mass balances for carbon and hydrogen. The dependence of the amounts of solid carbon formed at various hydrogen sulfide concentrations with time is shown in Fig. 4. Other experiments revealed that when the hydrogen sulfide concentration in the feed was greater than 80 mol ppm then extensive poisoning of the catalyst occurred and no solid carbon was deposited. On the other hand, when the hydrogen sulfide concentrations was 60 mol ppm or less, then the carbon formation activities were relatively high during the early stages of the reaction, exhibiting maxima after 15 min and were even-

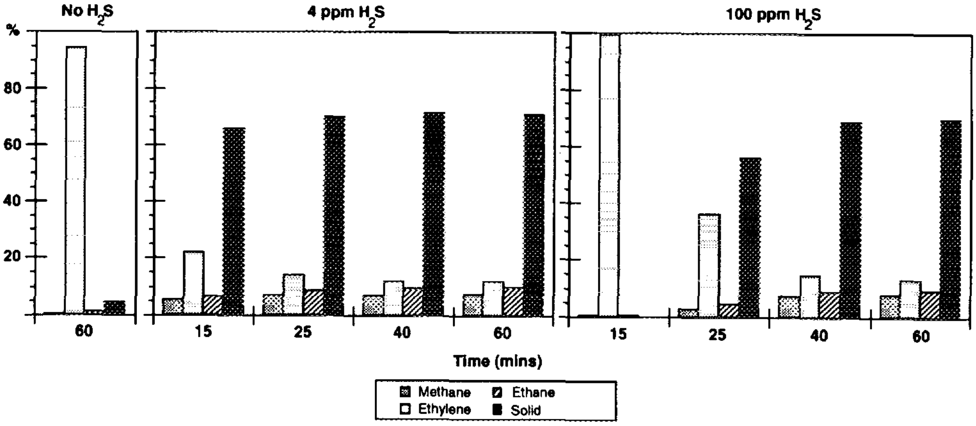

FIG. 3. Variation in product yields as a function of time for three different cobalt samples during reaction in an ethylene/hydrogen (1 : 1) mixture at 535°C.

tually observed to decline after longer periods depending on the hydrogen sulfide concentration. In experiments where the hydrogen sulfide concentration was maintained below 30 mol ppm, carbon formation activities reached a maximum at 15 min and then leveled out to a steady-state condition at between 40 and 80 min reaction time. The highest amount of solid carbon formed at steady state conditions was obtained at the lowest hydrogen sulfide concentration used in this work, 4 mol ppm.

(*c*) *X-Ray Diffraction Analysis*

The X-ray diffraction patterns of cobalt powders which had been heated in 500 ppm H_2S ($H_2S/H_2 = 10^{-3}$) and 2000 ppm H_2S ($H_2S/H_2 = 4 \times 10^{-3}$) for 30 min at 535°C, respectively, are shown in Fig. 5. It is apparent that under these conditions at the lower sulfur concentration the bulk of the material remains in the metallic state, whereas at the higher sulfur level the principal component of the sample is cobalt sulfide, Co_9S_8. From these results it is concluded that for the most part only the surface layers of the cobalt are affected following treatment in mixtures of $H_2S/H_2 = 1 \times 10^{-3}$ or less.

TABLE 1

Product Distribution for the Decomposition of Ethylene after 100 min Reaction for Various Sulfur-Treated Cobalt Powders

$[H_2S]$ pretreatment	Carbon products				
	CH_4	C_2H_4	C_2H_6	C_s	$C_2H_6 + C_s$
4	5.54	16.36	8.84	69.0	77.84
17	5.80	13.65	9.51	70.8	80.31
50	5.29	18.10	8.59	67.8	76.39
100	6.35	14.47	10.14	68.7	78.84

(*d*) *Structural Characteristics of Carbon Filaments*

Three types of carbon filaments were selected for this series of examinations;

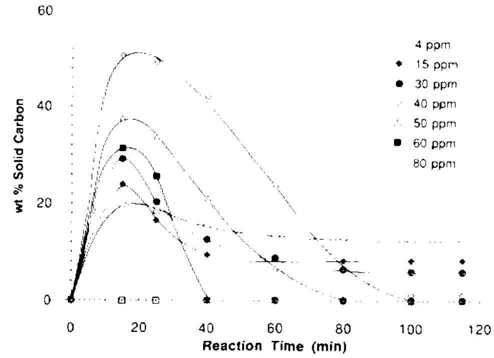

FIG. 4. Percent solid carbon formed as a function of reaction time for cobalt catalysts reacted in ethylene/hydrogen (1 : 1) containing various amounts of H_2S at 535°C.

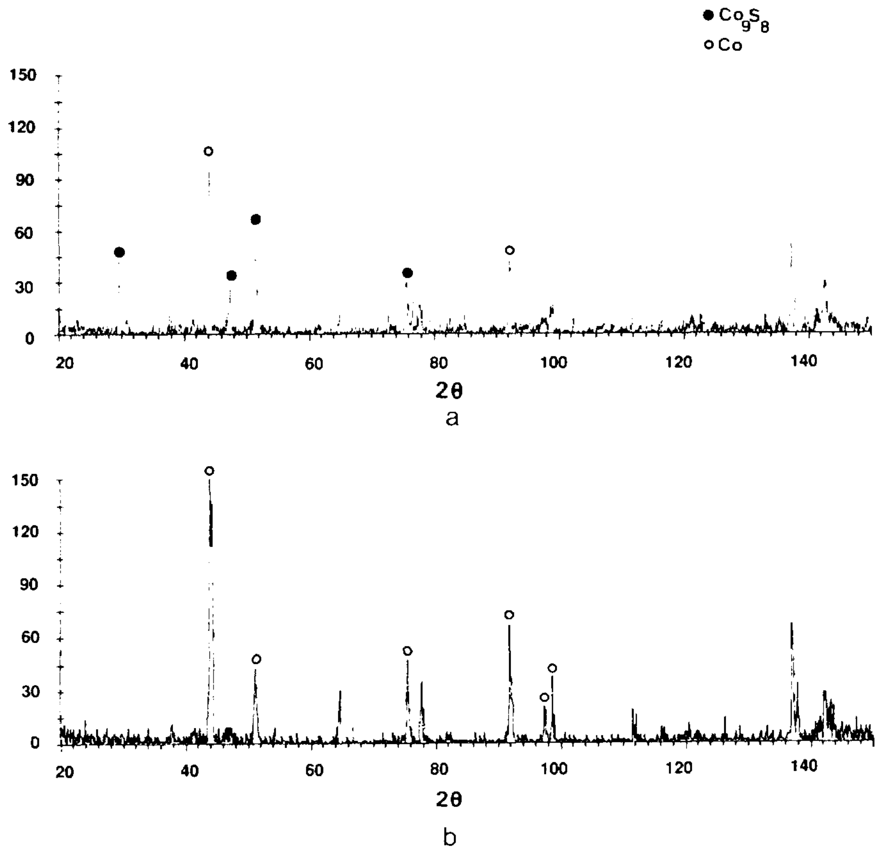

FIG. 5. X-ray diffraction patterns of powdered cobalt catalysts which have been treated in (a) 2000 ppm and (b) 500 ppm H_2S, respectively, for 30 min at 535°C.

(1) A sample produced from the interaction of cobalt with ethylene/hydrogen at 535°C for 2 h.

(2) A sample produced from cobalt which had been pretreated in 1 ppm H_2S at 535°C for 30 min and then reacted in the same manner as (1).

(3) A sample produced from cobalt which had been pretreated in 100 ppm H_2S at 535°C for 30 min and then reacted in the same manner as (1).

Examination of representative specimens of these three samples of filaments in the transmission electron microscope showed that they possessed many common characteristics and in particular they all appeared to have been formed via a bidirectional mode, where the catalyst particle remained embedded within the structure throughout the growth process. A typical example of this type of deposit is presented in the electron micrograph, Fig. 6. Close inspection of individual filaments revealed a number of morphological features:

(i) The width of a given filament and its associated metal particle remained constant throughout the growth period, there being no evidence for dispersion of catalyst material within the deposit.

(ii) Examination of many regions of the specimens showed that branched filaments were not formed in any of these systems. This type of structural

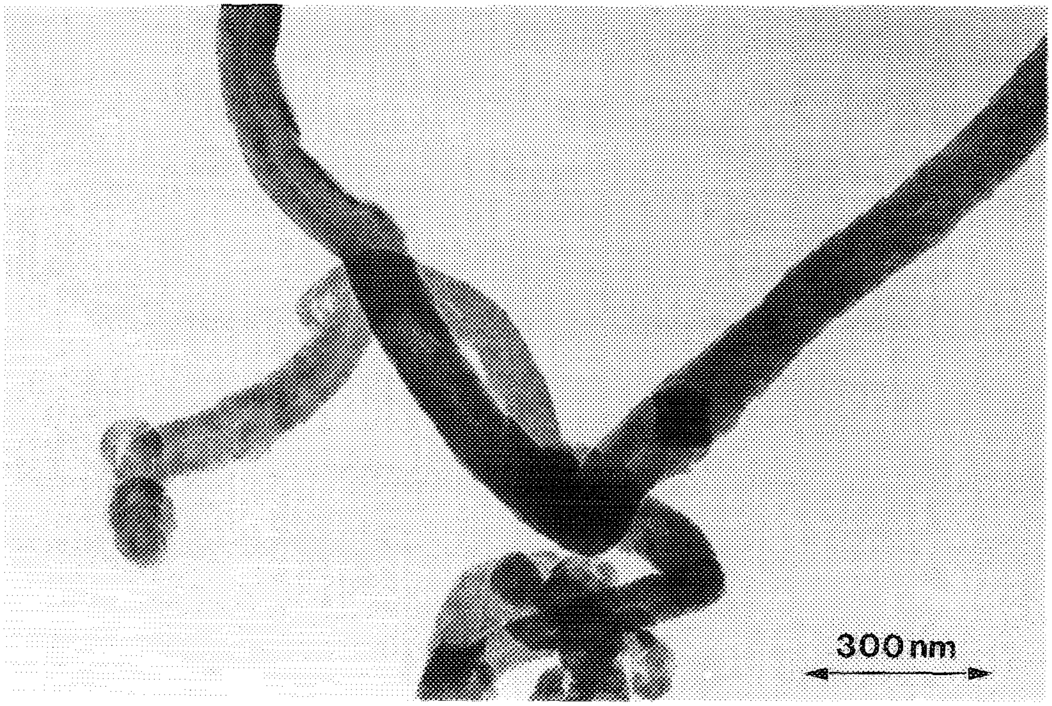

FIG. 6. Transmission electron micrograph showing the typical appearance of a carbon filament and its associated catalyst particle following reaction in ethylene/hydrogen (1 : 1) at 535°C for 60 min.

conformation results from fragmentation of a relatively large particle during the deposition process into a number of smaller entities which then proceed to create secondary growths emanating from the parent filament.

(iii) Comparison of the dimensions of filaments in the three samples demonstrated the existence of a significant change in average width and this aspect appeared to be related to the pretreatment conditions of the catalyst. Measurements of many filaments confirmed this observation, and from the detailed width distributions shown in Figs. 7a–7c, it was possible to estimate the average width associated with the three treatments. These data are presented in Table 2.

Although the electron microscopy examination failed to indicate the existence of any differences in the crystalline perfection between the three samples, it was clear from controlled oxidation studies in CO_2 that pretreatment in H_2S, particularly at the higher level, tended to produce a more disordered carbon structure, as evidenced from the difference in the onset of temperature of oxidation of filaments produced from the various treatments, Fig. 8 and Table 2. Also from this table it is evident that there is a steady increase in filament surface area as the level of sulfur pretreatment is raised. This trend is consistent with a progressive decrease in the structural perfection of the filaments, which will tend to give rise to a more porous deposit. In contrast, when batches of different sized carbon filaments, grown from metal particles which had not been exposed to H_2S, were reacted in CO_2 then all samples exhibited identical oxidation profiles, suggesting that for the most part dimensional features were not critical factors in de-

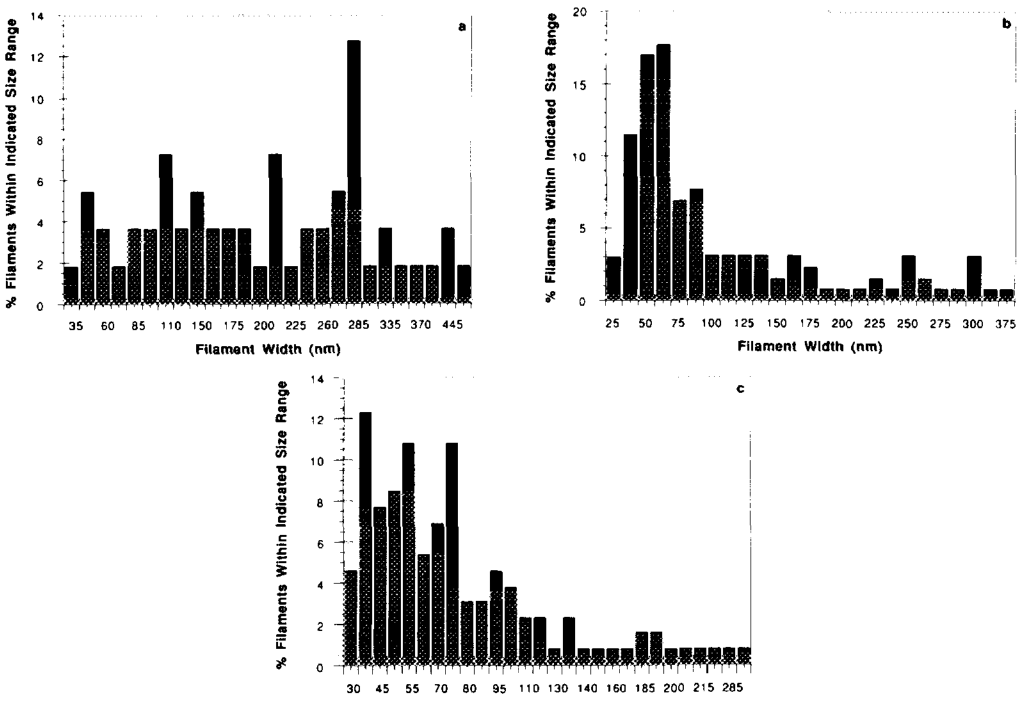

FIG. 7. Filament width distributions obtained from reaction of (a) pure cobalt, (b) cobalt pretreated in 1 ppm H_2S, and (c) cobalt pretreated in 100 ppm H_2S, prior to reaction in ethylene/hydrogen (1 : 1) at 535°C for 2 h.

termining the degree of structural perfection of this material.

DISCUSSION

The Gas/Metal Interface

It is abundantly clear from this study that a very sensitive relationship exists between the level of sulfur pretreatment of a cobalt catalyst and the amount of solid carbon produced when the modified system is reacted in an ethylene/hydrogen mixture. Pretreatment of cobalt under mild H_2S conditions (4–100 ppm) results in a tremendous increase in the amount of carbon filaments

TABLE 2

Physical Properties of Carbon Filaments as a Function of the Catalyst Pretreatment

Property	Sample[a]	Sample[b]	Sample[c]
Average filament width from TEM (nm)	288	62	50
Onset of oxidation (°C)	835	800	720
Surface area (m^2/g)	56	110	137

[a] Filaments from untreated cobalt powder.
[b] Filaments from cobalt pretreated in 1 ppm H_2S.
[c] Filaments from cobalt pretreated in 100 ppm H_2S.

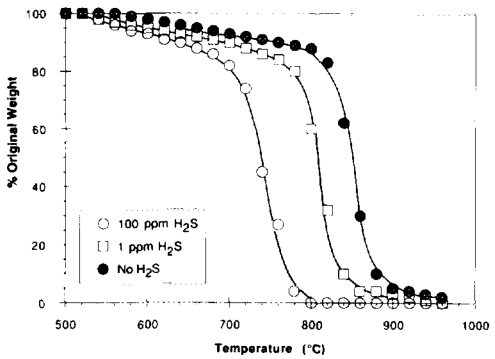

FIG. 8. Comparison of gasification characteristics in CO_2 of filaments produced from pure cobalt and sulfur-contaminated cobalt particles.

produced during interaction with ethylene, from 4.5 (without sulfur treatment) to 70%. On the other hand, pretreatment in 500 ppm H_2S effectively suppresses carbon deposition, however, after 100 min of exposure to the hydrocarbon containing environment the ability of cobalt to catalyze the growth of filaments is restored to a similar level to that exhibited by a catalyst pre-treated under milder conditions.

The argument that the enhancement in carbon deposition following treatment in H_2S is due to the stronger reducing capabilities of the sulfide compared to that of hydrogen can be dismissed in the present study since:

(a) Prior to reaction, X-ray diffraction analysis of samples which had been heated in 20% hydrogen/helium at 500°C for 12 h showed that the bulk cobalt powder was in the fully reduced state.

(b) It is expected that following a careful passivation procedure a monolayer of oxide will be present on the metallic particles, however, this monolayer will easily be removed during exposure to hydrogen at 535°C for 1 h.

(c) In a previous study (*22*) it was found that following H_2S pretreatment of an alumina supported cobalt catalyst, enhancement in carbon deposition arising from the interaction with ethylene occurred. The high yield of solid carbon could be decreased if the H_2S step was followed by an additional H_2 treatment prior to interaction with the hydrocarbon. Finally, if the latter pretreatment procedure (H_2–H_2S–H_2) was modified to include a further treatment in H_2S, then the optimum yield of solid carbon was restored to its initial high level when the system was reacted in ethylene.

There have been a considerable number of investigations performed on the physical and chemical aspects of sulfur adsorption on single-crystal metal surfaces using a variety of surface science techniques, and although studies of cobalt interactions with sulfur are limited, there is an extensive literature dealing with the effects of sulfur on nickel surfaces (*12*, *13*, *23–27*). Wise *et al.* (*28*, *29*) found that there was a significant decrease in the binding energy of sulfur on $Ni_{(111)}$ at 375°C, as the fractional saturation coverage was increased from 0.05 to 0.84. Introduction of sulfur atoms is known to increase the surface diffusion rates of metal atoms and as a consequence surface reconstruction is facilitated, which results in faceting of the metal crystallites (*30*, *31*). A systematic study of faceting induced by sulfur on nickel has been undertaken by Delescluse and Masson (*27*), who reported that when certain crystalline planes of nickel were covered with an almost complete layer of sulfur they underwent reconstruction, e.g., $Ni_{(810)}$ decomposed into facets of $Ni_{(410)}$ and $Ni_{(100)}$. As sulfur was gradually removed from the system the nickel surface recovered its original orientation. It is also known that in this system, sulfur atoms initially adsorb on sites of maximum symmetry—the atomic hollows of the nickel surface. When the adatom coverage was increased above 0.25 on $Ni_{(100)}$ surface, the sulfur configuration changed from a $p(2 \times 2)$ where each nickel atom was bonded to four sulfur atoms, to a $c(2 \times 2)$ arrangement, in which each nickel atom was bonded to only two sulfur atoms (*12*, *23*, *24*). It is therefore not unreasonable to expect that these surface transformations could also occur when sulfur atoms are incorporated into cobalt and as a consequence would have dramatic effects on the catalytic activity of the metal.

By taking into consideration the information generated from surface science studies of the influence of sulfur on various metals, it is possible to develop a model which accounts for the manner by which sulfur modifies the catalytic activity of cobalt towards carbon filament formation during interaction with ethylene. At low coverage, sulfur is strongly bound to the metal and this action may facilitate reconstruction of the surface layers, a step which may favor carbon–carbon bond rupture in the adsorbed ethylene molecule producing species which dissolve and diffuse through the metal particles and ultimately precipitate at the rear faces in the form of a carbon filament. Exposure of the metal particles to higher levels of H_2S appears to result in complete coverage of the surface leading to the loss of catalytic activity when the metal is subsequently treated in an ethylene/hydrogen environment. During prolonged reaction, however, a large fraction of relatively weakly bound sulfur is progressively lost from the surface so that a critical coverage is achieved and the catalyst surface once again exhibits a high activity for carbon deposition. When the metal is treated under more severe sulfiding conditions X-ray diffraction analysis demonstrates that a three-dimensional sulfide is formed and under these circumstances the catalytic activity of the metal particles towards the decomposition of ethylene is totally suppressed.

Methane is a major gaseous product produced from the interaction of ethylene/hydrogen with the sulfur modified cobalt catalyst and at its formation might be thought to arise from hydrogenation of solid carbon. Previous studies performed in our laboratory, however, have demonstrated that following treatment in H_2S the catalytic action of cobalt in the graphite/hydrogen reaction is effectively inhibited (*22*). Methane formation in the present system cannot be accounted for by hydrogasification of carbon and therefore must arise from other reactions. In this context it is worthwhile to consider the data obtained from the interaction of ethylene with copper–nickel catalyst particles where anomalously high yields of methane were also produced and was believed to result from the formation of an "ethylidyne" intermediate (*32*).

Incorporation of sulfur atoms into cobalt is likely to induce major perturbations in the adsorption characteristics of the surface. In the absence of added sulfur, the ethylene molecule will probably adsorb in a configuration where the C=C is aligned "parallel" to the metal surface, and in such an arrangement there is a high probability that the adsorbed molecules will undergo polymerization and eventually condense to form a graphitic overlayer resulting in rapid catalyst deactivation. On the other hand, when sulfur is present in the surface, catalytic activity is sustained for relatively long periods of time and there is a considerable increase in the yield of solid carbon. In this case there is a possibility that when the ethylene molecule encounters a cobalt atom whose nearest neighbor is a sulfur atom the hydrocarbon will be adsorbed in an "end-on" configuration, adopting the "ethylidyne" intermediate structure in which one carbon atom is attached to three metal surface atoms. The subsequent rupture of the C–C bond will lead to methane formation and the residual carbon atom will subsequently precipitate as part of a filament structure at the rear of the particle. In contrast, when the ethylene molecule contacts two unperturbed adjacent cobalt atoms then the hydrocarbon will probably be adsorbed in the "parallel" configuration, and since the route for surface graphite formation is now blocked due to the presence of sulfur adatoms, it may subsequently undergo C=C bond rupture to form a carbon species which ultimately contribute to the solid carbon deposit or interact with hydrogen and desorb as ethane. The argument that controlled addition of sulfur to the cobalt surface inhibits the formation of a graphitic overlayer is consistent with the model proposed by Sachtler and co-workers (*33*, *34*) for the observed enhancement in activity of a Pt–Re hydrocarbon conversion catalyst when treated in 1 ppm H_2S. These workers suggested that sulfur atoms were strongly adsorbed on exposed rhenium atoms and this arrangement was responsible for obstructing the formation of a continuous graphite encapsulating layer.

In a previous study, we used the adsorption and decomposition of ethylene as a probe to monitor the composition of a sur-

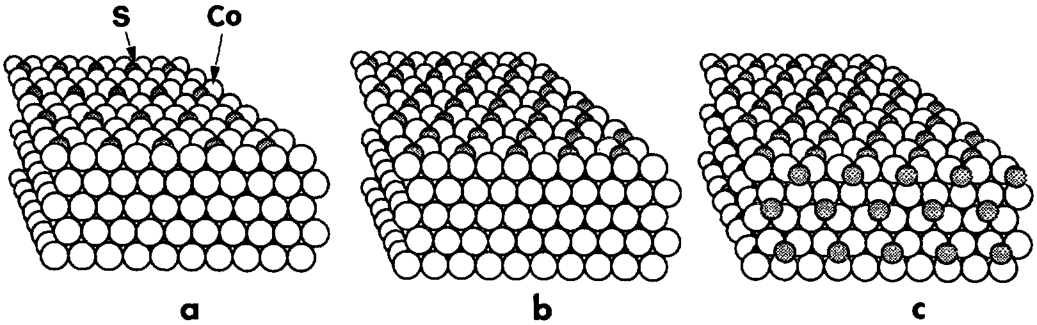

FIG. 9. Postulated arrangements of cobalt and sulfur atoms following various presulfiding treatments (a) H_2S/H_2 = ~2 × 10^{-6} (S coverage below saturation—instantaneous reaction with C_2H_4); (b) H_2S/H_2 = ~2 × 10^{-4} (2-D surface sulfide formation—short induction period prior to reaction with C_2H_4); and (c) H_2S/H_2 > 1 × 10^{-3} (3-D bulk sulfide formation—suppression of reaction with C_2H_4).

face consisting of two elements with widely differing hydrocarbon adsorption characteristics (*35*). In the proposed model, it was assumed that the ethylene only underwent catalyzed decomposition and the fraction of metal atoms capable of adsorbing the olefin was shown to be equal to the sum of the solid carbon and ethane yields. If we apply the same concept to the current system, utilizing the data presented in Table 1, then it is apparent that the surface of the catalyst in its most active state approximates to about 78% cobalt atoms, with the remaining fraction being sulfur, occupying about 0.25 of a monolayer, and this composition is eventually attained in spite of the wide variation in sulfur pre-treatment levels.

Figure 9 is an idealized schematic representation of the possible surface arrangements of cobalt and sulfur atoms during reaction with ethylene/hydrogen mixtures. These structures were developed following treatment in various levels of H_2S and are proposed on the basis of the present experimental results. At low sulfur levels (4–50 ppm), the surface would adopt a $p(2 \times 2)$ configuration where each sulfur atom is surrounded by four metal atoms (Fig. 9a). It is significant that by analogy with the nickel/sulfur system this surface composition is close to that where sulfur might be expected to induce modifications in the surface structure and also where a major change in the binding energy of sulfur to the metal could occur (*12*, *23*, *24*). If pretreatment conditions are somewhat more drastic (100–500 ppm), then the surface would assume the $c(2 \times 2)$ conformation depicted in Fig. 9b, which appears to be unreactive for the decomposition of ethylene. After a certain induction time, however, the surface will lose some of the sulfur atoms to the extent where it once more becomes reactive towards hydrocarbon decomposition. Higher levels of sulfur will produce the bulk sulfide (Fig. 9c), a state which is completely inactive for the reaction.

Inspection of the data obtained from experiments where H_2S was continuously added to the ethylene/hydrogen feed shows a somewhat more complex pattern of behavior. In this case we are dealing with a system where there is a competition between ethylene and H_2S adsorption, and while there is an enhancement in carbon deposition at H_2S levels up to 60 ppm, this activity is not as high as that achieved by a pretreatment operation nor is it sustained over long periods of time. Indeed, complete deactivation of the catalyst occurs at sulfur levels >30 ppm within a 2-h period and no activity is observed for H_2S levels of 80 ppm or greater. One may conclude therefore that with this type of sulfur treatment the most active catalyst surface state is never realized.

The Metal/Solid Carbon Interface

It has been demonstrated that the crystalline structure of carbon filaments is dependent not only on the chemical properties of the metal used as the catalyst but also on the nature of the interaction at the catalyst/solid carbon interface (*36*). It was suggested that metals which exhibit a strong interaction with graphite and as a consequence tend to spread in the form of a thin film when heated in a reducing atmosphere will produce highly ordered carbon structures when reacted in a hydrocarbon environment. In this context, it is significant to find that cobalt particles readily undergo a spreading action along graphite edges when heated in hydrogen at between 400 and 650°C (*37*). When cobalt/graphite specimens were reacted hydrogen containing a small amount of H_2S then there was a dramatic change in the reactivity pattern which included the observation of particle mobility on the graphite basal plane regions at about 600°C, a feature generally indicative of a weak metal/support interaction. Based on these findings, one would expect that filaments produced from cobalt catalyzed decomposition of ethylene would be highly graphitic in nature, and that as the concentration of H_2S in the pretreatment step was increased they would progressively acquire a more disordered structure. As can be seen from the physical properties of the three samples presented in Table 2, this predicted trend in structural characteristics of filaments was observed experimentally.

Sulfur-Induced Metal Particle Fragmentation

Finally, a further point which is apparent from the characterization studies of the solid deposit is the finding that as sulfur is added to the system the carbon filaments produced during the subsequent hydrocarbon decomposition step exhibit a systematic decrease in width. Since the same batch of cobalt powder was used for all these experiments and no evidence for particle fragmentation was found during the carbon deposition step, one may presume that pretreatment in sulfur is responsible for the observed enhancement in splitting of the relatively large granules of the starting catalyst powder. The topic of particle redispersion or fragmentation, is of major concern as it is the process whereby sintered catalyst particles are rejuvenated.

Traditional mechanisms which have been advanced to explain redispersion phenomena in heterogeneous catalyst systems have usually invoked the participation of a support media in the process. Morphological changes in the metal particles have been attributed to a modification in their wetting properties with the support induced by the chemical nature of the gas phase (*38*). The wetting angle of the crystallites on an oxide support such as alumina or silica is greater in a reducing than in an oxidizing environment. As a consequence the particles will tend to spread on the support and expose a large surface area under oxidizing conditions (*39*). In the current investigation particle fragmentation occurred during the presulfiding step without the aid of a catalyst support, which suggests that sulfur species are capable of performing this function directly. Other workers (*40*) found that sulfiding of supported noble metal catalysts also resulted in major transformations in both the size and shape of the crystallites. In addition, evidence of particle fragmentation could be seen in electron micrographs taken of samples which had been heated in H_2S between 500 and 600°C, and this behavior was rationalized in terms of the degree of crystallinity of the various faces which were present.

It is probable that the sulfur induced fragmentation of the powdered catalyst results in an enhancement in the number of active catalyst particles and as such this phenomenon contributes to an increase in the amount of filamentous carbon which is produced during subsequent reaction in the hydrocarbon environment. Indeed, such an argument was invoked previously to account for the observed increase in the formation of this type of carbon on iron which had been pretreated in steam under conditions where FeO formation was favored (*41*). It is doubtful, however, whether this effect can account for the entire increase, and we believe other factors, particularly sulfur-induced surface reconstruction are operative in the system.

We plan to extend these studies to include the effect of sulfur on other metals in order to establish whether the trends observed with cobalt are more general in nature. It is also our intention to examine the interplay between sulfur adsorption and carbon deposition on supported cobalt catalysts, where the particle sizes are typically 5–10 nm, considerably smaller than those obtained from a powdered catalyst system.

SUMMARY

It has been demonstrated that pretreatment of cobalt in low levels (4–100 ppm) of H_2S has a dramatic effect on the ability of the metal to produce filamentous carbon during the catalytic decomposition of ethylene. In contrast, when the metal was pretreated at higher H_2S levels (>500 ppm) or when H_2S was added continuously in the hydrocarbon feed at concentrations of >60 ppm, the catalytic action was suppressed. It is suggested that enhancement in carbon deposition following treatment at low levels of H_2S is related to a reconstruction of the metal surface coupled with the blocking action of surface sulfur atoms towards the formation of a graphitic overlayer. The inhibition of activity following more severe treatment in H_2S is believed to be associated with the formation of a 2-D or 3-D bulk sulfide. In some cases the gradual loss of sulfur results in the eventual attainment of the active surface state and restoration of carbon filament growth.

The presence of sulfur species in the catalyst was found to produce significant changes in the structural perfection of the filaments, which can be correlated with a decrease in the wetting properties of the modified cobalt particle surfaces in contact with the solid carbon deposit. Furthermore, there is evidence that sulfur adatoms appear to induce fragmentation of the powdered cobalt catalyst, and this finding may have important ramifications on redispersion of sintered metal particles.

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