Influence of Silver Addition on the Catalytic Behavior of Cobalt

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A variety of experimental techniques including flow reactor studies, temperature-programmed oxidation, and transmission electron microscopy have been used to investigate the manner by which silver modifies the catalytic behavior of cobalt. For this purpose the growth of filamentous carbon along with the gas phase product distribution resulting from the decomposition of ethylene over cobalt and cobalt−silver particles at 600 °C has been used as a probe reaction. It was found that the incorporation of as little as 1% of silver into cobalt caused a increase of over an order of magnitude in the amount of carbon filaments produced compared to that formed on pure cobalt under the same experimental conditions. It is suggested that some of the observed enhancement in catalytic activity could be due to the existence of electronic perturbations of cobalt induced by the presence of silver that are manifested in modifications in the adsorption and subsequent decomposition characteristics of ethylene on the bimetallic surface. Analysis of the gas phase effluent reveals that ethane is the major product with minor amounts of methane. This distribution indicates that on the cobalt−silver surface there is a strong tendency for ethylene to adsorb in a direction parallel to the surface and either is hydrogenated to ethane or undergoes carbon−carbon bond scission with resulting carbon species dissolving and diffusing through the catalyst particle to form the filamentous carbon deposit. This behavior is to be contrasted with that found for the cobalt−copper/ethylene system where a significant amount of methane is produced and believed to originate from the decomposition of an ethylidyne intermediate arising from adsorption of the olefin on the bimetallic surface in an "end-on" configuration.

Introduction

Previous work from this laboratory has focused attention on the modification of the catalytic behavior of cobalt by the addition of copper.[1,2] It was shown that incorporation of copper led to a massive increase in the catalytic activity of cobalt for the decomposition of ethylene to solid carbon and methane. These results were rationalized to a large degree by a geometric effect in which it was purported that copper ensembles effectively blocked the formation of a graphite overlayer that would otherwise have been generated on the pristine cobalt surface. It was stressed, however, that this simplified geometric approach could not account for all the data, especially the enhanced activity exhibited by the bimetallic catalyst that had a copper content of only 2%. It was suggested that there was probably also some electronic perturbation of the cobalt being induced by the presence of the adatom. The addition of copper to cobalt also had a profound effect on the chemical and physical nature of the solid carbon produced from the decomposition of ethylene.[2] It was shown that over a large temperature and catalyst composition range that the solid carbon produced was in the form of filamentous structures.

The details of the growth mechanism of filamentous carbon from the metal-catalyzed decomposition of selected carbon-containing gases is documented elsewhere,[3] and only the rudiments of the process will be given here. During the reaction, the hydrocarbon molecules are dissociatively chemisorbed on certain faces of the metal, this process being followed by the diffusion of carbon atoms through the catalyst particle to precipitate at other faces in the form of a fibrous structure. It is well established that carbon diffusion through the particle is the rate-determining step in the growth process. The degree of crystalline order of the filamentous structure is controlled by

various factors including the wetting properties of the metal with graphite and the crystallographic orientation of the metal faces in contact with the solid carbon deposit. Depending on the chemical nature of the catalyst and the conditions of the reaction, assorted filament structures with various morphologies and different degrees of crystallinity can be produced. In addition, the width of the filament formed is directly related to that of the catalyst particle, and this parameter can easily be controlled by preparation and pretreatment of the catalyst. The typical lengths of carbon filaments produced by these methods vary from 5 to 100 μm and widths of between 5 and 500 nm.

The carbon filaments generated from the interaction of cobalt with ethylene were found to be highly crystalline in nature and were produced via a bidirectional growth mechanism with two filaments being extruded from opposite faces of the metal particle. Incorporation of copper into the cobalt resulted in the formation of a more disordered structure, and multiple filament limbs were seen to emanate from a single catalyst particle. The structural characteristics of the filaments were also found to be dependent on the reaction temperature, but in contrast to the behavior exhibited by other catalyst systems, the growth characteristics of the carbon deposit appeared to be independent of the hydrogen content of the reactant gas. In the present investigation we have extended the studies performed with copper−cobalt by substituting the copper component of the catalyst with silver.

The promotional effects of silver have not been studied to the same extent as those of copper, and most previous work has tended to focus on the addition of silver to palladium, a system that exhibits a continuous range of solid solutions.[4−7] Wachs and co-workers[8] showed that, under Fischer−Tropsch conditions, silver did not exert any influence on the rate of carbon deposition on iron, and it was suggested that this behavior was due to poor contact between the metals. King and

Kelzeberg[9] observed that incorporation of small amounts of copper or silver into silica-supported ruthenium caused a decline in turnover frequency for the Fischer−Tropsch synthesis while at higher additive loadings no change in this parameter was detected. These workers proposed that copper and silver selectively occupied defectlike sites and that no ensemble effects were operative when these particular bimetallics were used for this reaction. More recently, Bhatia and co-workers[10] used *in situ* NMR techniques in an attempt to correlate the catalytic activity of Ru, Ru−Cu, and Ru−Ag exhibited in the Fischer−Tropsch reaction with differences in hydrogen adsorption characteristics of these systems. One of the major objectives of this work was to establish whether the promotional effect imparted by copper to various metals for catalytic carbon formation during decomposition of ethylene was unique to this element or whether other metals possessing similar electronic properties could exert the same impact.

Experimental Section

Gas Flow Experiments. Cobalt−silver bimetallic powders were prepared via a previously described coprecipitation method from silver and cobalt nitrates.[11,12] The composition of each catalyst powder was determined on an atomic ratio basis. The catalyst precursor salts were supplied by Fischer Scientific. Gas flow reactor experiments were performed in a horizontal tube furnace at 600 °C, and the catalysts were reduced at this temperature for 2 h prior to the introduction of the reactant gas, ethylene or an ethylene/hydrogen mixture. Ultrahigh-purity gases were supplied by MG Industries and used without further purification. The composition of the gas phase was monitored before and during reaction by gas chromatography using a Varian 3400 unit. In a typical experiment 50 mg of catalyst powder was used, and ethylene flow rate was 40 mL/min with varying amounts of helium also present in the gas stream to keep gas velocity constant. Gas flow rates to the reactor were regulated by mass flow controllers (MKS). Carbon and hydrogen atom mass balances in combination with the relative concentrations of the various products were used to determine the yields. The amount of solid carbon deposited was determined by careful analysis of the gas chromatography results using carbon mass balances and gravimetrically by weight difference at the conclusion of the experiment.

Characterization of Carbonaceous Deposits. A variety of techniques were used to characterize the solid carbon products, and these included temperature-programmed oxidation, N_2 surface area measurements at −196 °C, 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 gain information on the degree of crystallinity of the carbon produced. We have previously demonstrated that this is a reliable method for comparing the graphitic nature of carbon filaments.[13] The solid carbon produced from the ethylene decomposition reaction was placed in 1 N HCl for 3 days to dissolve the metal catalyst. After this demineralization procedure 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/He mixture. Sample weight loss was plotted as a function of temperature, and the curves were compared to those of active carbon and single-crystal graphite 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
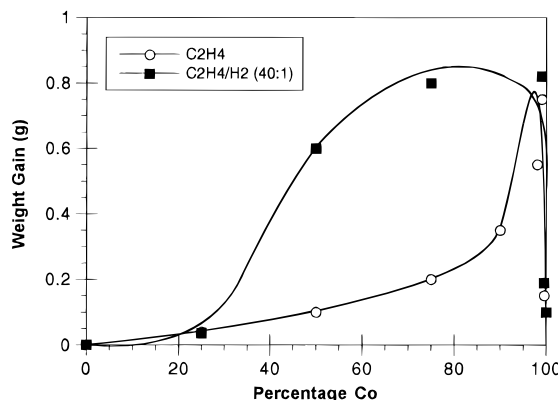

Figure 1. Solid carbon weight gain versus percentage cobalt in starting catalyst powder (50 mg) for the decomposition of ethylene and ethylene/hydrogen (40:1) at 600 °C (reaction time 90 min).

produced under various experimental conditions. High-resolution transmission electron microscopy studies were carried out in a JEOL 2000 EX11 instrument (lattice resolution 0.14 nm). 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 uninterrupted view of the detailed structural features of the catalytically formed solid carbon.

Results

Flow Reactor Studies. Initial experiments were performed using the decomposition of pure ethylene as a probe reaction to determine the effect of catalyst composition on the formation of filamentous carbon. The weight gain, attributed to solid carbon formation, as a function of the percentage cobalt present in the catalyst powder (50 mg) for the ethylene decomposition reaction at 600 °C after 90 min on stream is presented in Figure 1. We have previously shown that maximum activity for filamentous carbon formation from the interaction of bimetallic catalysts containing copper with ethylene occurs at around 600 °C,[1,14] and a similar optimum temperature was found to exist in the present system. The results given in Figure 1 show that yields of solid carbon were extremely sensitive to the composition of the catalyst and that under these reaction conditions the most active catalyst contained only 1% silver. The effect of the addition of little as 1 mL/min hydrogen to the reactant gas stream is also plotted in Figure 1, and from these data it can be seen that this operation leads to an increase in catalytic activity for all the bimetallic compositions. Furthermore, it is evident that when the reaction is performed in the presence of added hydrogen, the weight of carbon produced did not exhibit the same dependence on catalyst composition as that found with a pure ethylene feed. Indeed, large amounts of solid carbon were formed over a wide catalyst composition range.

In a further series of experiments the effect of increasing the concentration of hydrogen in the reactant gas stream was studied for a selected number of cobalt−silver powders. The data obtained are presented in Figure 2 and show that, for all the catalyst systems studied, the yield of solid carbon produced after a 90 min reaction period was enhanced as the hydrogen partial pressure was progressively raised. The results of the gas phase analysis for the reaction of bimetallics containing 2% and 25% silver with several ethylene/hydrogen mixtures are given in Table 1. Also included in this table, for the sake of comparison, are the data obtained when the same weight of a pure cobalt
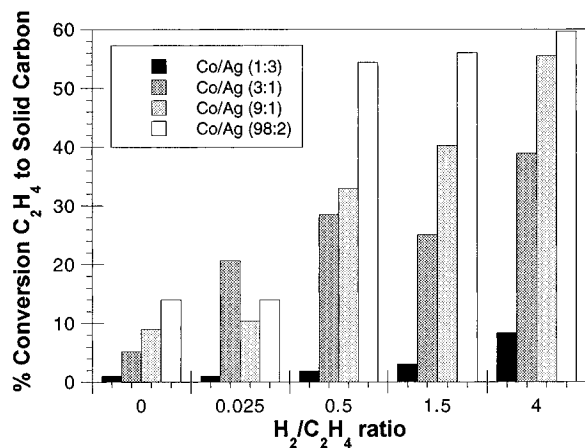
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Figure 2. Effect of increasing partial pressure of hydrogen on the conversion of ethylene to solid carbon with selected silver−cobalt powders at 600 °C.

TABLE 1: Total Product Distribution at 600 °C as a Function of Ethylene/Hydrogen Ratio after 40 min Reaction

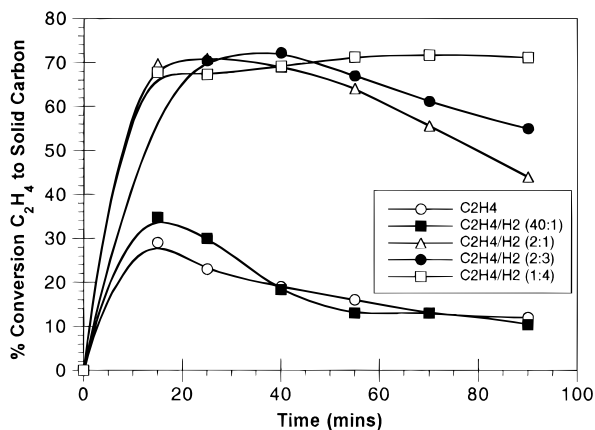| C_2H_4/H_2	% product	Co	Co/Ag (3:1)	Co/Ag (98:2)
100/0	solid carbon	3.4	11.5	26.9
	ethane	3.8	5.1	9.6
	ethylene	91.8	82.4	62.5
	methane	1.0	1.0	1.1
2/1	solid carbon	5.0	15.2	69.0
	ethane	10.3	17.9	15.0
	ethylene	83.7	65.4	15.4
	methane	1.0	1.5	0.5
1/4	solid carbon	11.8	44.2	69.2
	ethane	49.3	25.2	24.3
	ethylene	38.3	29.6	4.9
	methane	0.6	0.9	1.7

Figure 3. Effect of hydrogen on the conversion of ethylene to solid carbon over Co/Ag (98:2) at 600 °C.

powder was treated under the same conditions. The data show ethane to be the major gaseous product, and its yield exhibits a steady rise as hydrogen content in the gas stream was increased. Production of methane remains low for all the reaction conditions studied here. The reaction was also investigated over a range of temperatures; however, since optimum product yields were found to exist at 600 °C, detailed studies were restricted to this value. Finally, when samples of powdered silver were subjected to the range of reaction conditions outlined above, there was neither evidence of solid carbon formation nor a change in the composition of the gas phase.

The percentage conversion of ethylene to solid carbon as a function of reaction time is plotted in Figure 3. These data were obtained for the decomposition of various ethylene/hydrogen mixtures over a Co−Ag (98:2) catalyst at 600 °C.
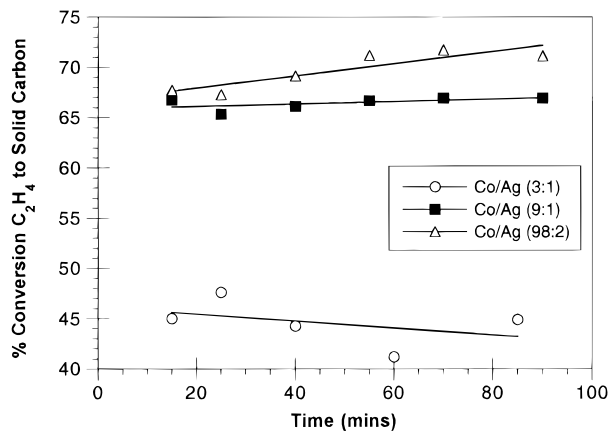

Figure 4. Percentage conversion to solid carbon as a function of reaction time for the decomposition of ethylene/hydrogen (1:4) at 600 °C with selected Co/Ag catalysts.

From the plots it is apparent that deactivation characteristics of the bimetallic powder are directly related to the nature of the reactant gas. Similar trends were found for bimetallic powders containing different ratios of the two components. It is clear that the catalysts become resistant to deactivation as hydrogen content in the reactant gas is increased. The maximum conversion of ethylene to solid carbon is attained with an ethylene/hydrogen ratio of 1:4. In a complementary set of experiments the reactant gas composition was maintained constant at C_2H_4/H_2 (1:4) while that of the catalyst powder varied. A comparison of the amount of solid carbon produced the from the interaction of catalysts containing 2%, 10%, and 25% silver with the hydrocarbon mixture as a function of time is shown in Figure 4. Inspection of these plots indicates that the lower yields of solid carbon produced from the powders containing a relatively high fraction of silver are not due to the premature catalyst deactivation since the steady state activity is maintained for prolonged periods of time. Instead, it is probable that these data reflect the fact that under these conditions the catalyst powders containing 2% silver exhibit the highest intrinsic activity for growth of filamentous carbon from ethylene.

Characterization of the Solid Carbon Deposit. Transmission electron microscopy examinations of the deposits produced from the various reactions revealed that the major constituent in all samples was filamentous carbon. The physical and chemical characteristics of the material, however, were found to be dependent on the catalyst composition and the nature of the reactant gas. The geometry of the catalyst particle itself also appeared to be sensitive to reaction conditions and composition of the bimetallic. Carbon filaments produced from the decomposition of pure ethylene over catalysts containing a large percentage of cobalt were formed via a bidirectional growth mode from cuboidal-shaped metallic particles (Figure 5). When the silver content in the starting powder was increased, the catalyst particle adopted a multifaceted morphology, as shown in Figure 6.

In order to obtain a clearer understanding of the role of hydrogen in these types of reactions, the filaments produced from the interaction of Co−Ag (3:1) particles with selected ethylene/hydrogen mixtures (C_2H_4/H_2 = 40:1, 1:1, and 1:4) were characterized in more detail. It was found that as hydrogen level was increased in the reactant gas, the catalyst particles acquired shapes similar to that of the multifaceted particle shown in Figure 6 as compared to the more frequently encountered diamond-like morphology that is presented in Figure 7.

Figure 5. Typical appearance of carbon filaments produced from the decomposition of ethylene at 600 °C with Co/Ag catalyst having a high cobalt content.
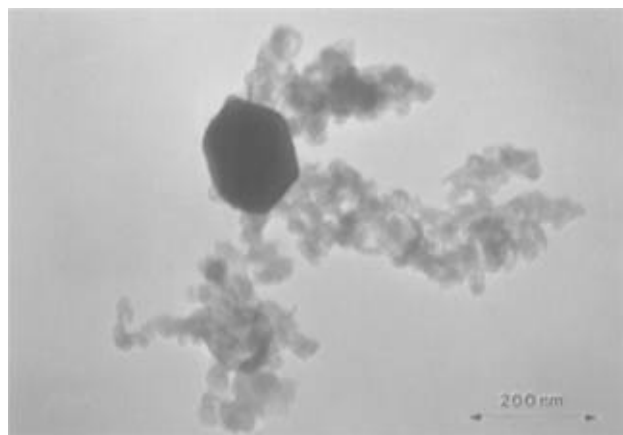

Figure 6. Typical appearance of carbon filaments produced from the decomposition of ethylene at 600 °C with Co/Ag catalyst having a relatively high silver content.
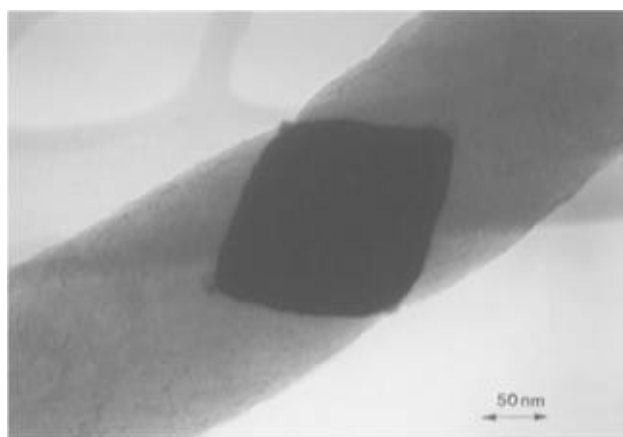

Figure 7. Typical appearance of carbon filaments produced from the decomposition of pure ethylene with Co/Ag 3:1 at 600 °C.

A comparison of the metal particle size distributions obtained after the reaction of a Co−Ag (3:1) catalyst with selected C_2H_4/H_2 mixtures at 600 °C is given in Figure 8. These measurements were taken of several hundred metal particles from each system. Inspection of the data reveals that the sizes of the majority of the catalyst particles are in the range 25−350 nm, values that are considerably smaller than those of the starting catalyst powders, which were approximately 1.0 μm. Furthermore, it is apparent that the average metal particle width during the growth of filamentous carbon was larger when an excess of hydrogen was present in the reactant gas.
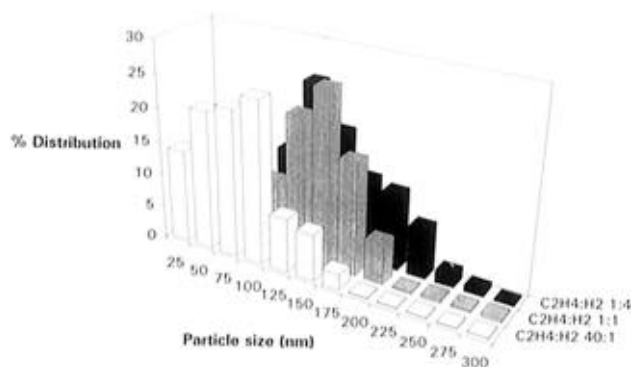

Figure 8. Metal particle size distribution as a function of hydrogen content in the reactant gas from the Co/Ag (3:1) catalyzed decomposition of ethylene at 600 °C.
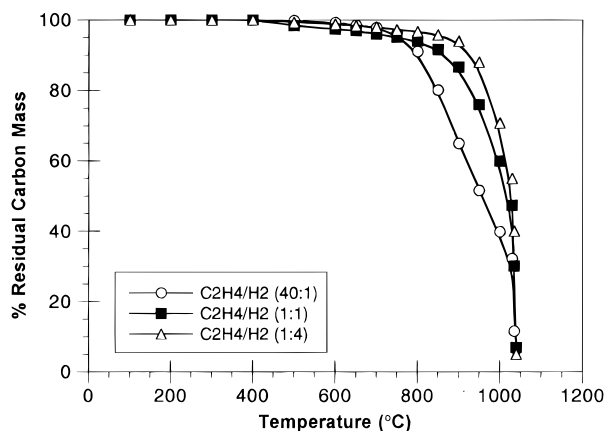

Figure 9. Temperature-programmed oxidation of the carbon filaments produced from the interaction of Co/Ag (3:1) with selected ethylene/hydrogen mixtures at 600 °C.

Temperature-programmed oxidation profiles of the demineralized carbon filaments produced from the interaction of a Co−Ag (3:1) catalyst with various C_2H_4/H_2 mixtures, (Figure 9) indicate that deposits produced in a hydrogen-rich environment had a greater resistance to gasification than those produced from a hydrogen-lean reactant. This finding is consistent with the notion that the material generated from a C_2H_4/H_2 (1:4) mixture possesses a greater degree of long-range crystalline order. In another set of thermogravimetric experiments the oxidation characteristics of carbon filaments produced from various Co−Ag powders were compared with those generated from pure cobalt following interaction of the catalysts with a C_2H_4/H_2 (40:1) mixture, and these curves are presented in Figure 10. It is evident that the carbon filaments formed from a bimetallic powder having a high silver content appeared to exhibit the greatest degree of graphitic character. It is interesting to find that these results correlate with those reported previously for copper−cobalt catalysts.[2]

The nitrogen BET surface areas of the carbon filaments produced from the reaction of C_2H_4/H_2 mixtures containing different partial pressures of hydrogen with Co−Ag (3:1) at 600 °C are shown in Table 2. The results show that as the hydrogen concentration in the reactant gas is raised, the surface area of the resulting carbonaceous deposit was found to increase.

Discussion

Influence of Silver Addition on the Growth of Carbon Filaments from the Cobalt-Catalyzed Decomposition of Ethylene. The results presented here show without any doubt that the incorporation of silver into cobalt has a dramatic effect on the catalytic activity of the host metal toward formation
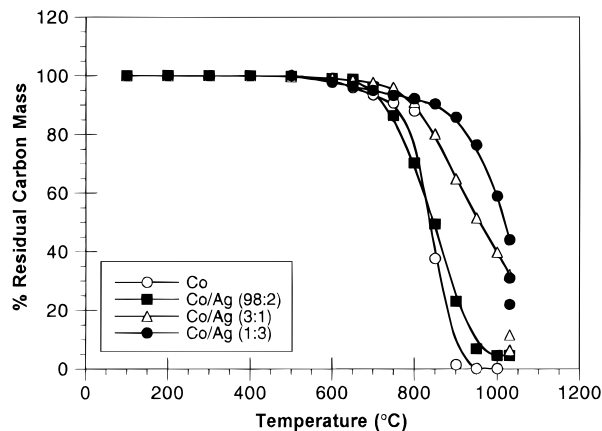
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Figure 10. Temperature-programmed oxidation of the carbon filaments produced from the decomposition of ethylene/hydrogen (40:1) at 600 °C over selected Co/Ag catalysts.

TABLE 2: Nitrogen BET Surface Area as a Function of Hydrogen Content in the Reactive Gas Mixture for the Co−Ag (3:1)-Catalyzed Decomposition of Ethylene at 600 °C

ethylene/hydrogen	BET surface area, $m^2\ g^{-1}$
40:1	157
1:1	199
1:4	236

of filamentous carbon during the decomposition of ethylene. Silver and cobalt have been reported to be completely insoluble in each other;[15] however, we have demonstrated that the addition of as little as 1% silver to the cobalt can induce a significant increase in the activity of the system for this reaction. A 10-fold increase in the amount of carbon filaments was formed from the bimetallic after 90 min reaction with ethylene at 600 °C compared to that produced on pure cobalt under the same conditions. This is further evidence in support of the theory developed by Sinfelt that, in the dispersed state, interaction between two metals does not necessarily require that they form an alloy.[16] The finding that relatively high catalytic activity was obtained with a bimetallic containing only 1% silver tends to lend support to the notion that incorporation of a small concentration of a second metal into cobalt can modify the catalytic behavior of the host metal by some mechanism other than merely that of a geometric reorganization of surface atoms. The decomposition of ethylene over a catalyst surface giving rise to the growth of carbon filaments requires the establishment of an interaction between the hydrocarbon and the metal that leads to dissociative chemisorption. In order to achieve such a condition, a suitable atomic arrangement in the metal as well as the formation of a strong metal−carbon bond is necessary. It is not unreasonable to consider the possibility that electronic perturbations of cobalt induced by the presence of silver are having an impact on the manner by which ethylene is adsorbed and subsequently decomposed on the bimetallic surface. At higher adatom concentrations it is feasible to argue that a geometric effect is the dominant factor and may well override or superimpose the influence of an electronic contribution at the catalyst surface as was previously suggested for copper−cobalt, copper−iron, and copper−nickel systems.[1,17,18]

Silver has a significantly lower heat of sublimation than that of cobalt (68 and 102 kcal/mol, respectively[19]) and the relatively low conversion of pure ethylene to solid carbon exhibited by bimetallic particles containing a large fraction of silver may be due, in part, to the thermodynamic tendency of silver to enrich the catalyst surface, thereby rendering the particles less active for filamentous carbon formation. Another factor that must be taken into consideration in this regard is the potential for

chemisorption-induced surface segregation of cobalt by ethylene and hydrogen. Finally, a further complication that could have a great deal of impact on the segregation phenomenon is the events that take place during the interaction of the bimetallic with the carbon deposit. If a strong wetting behavior exists between one of the metals and graphite, then preferential enrichment of this component at the particle/solid carbon interface will occur and under certain conditions could override the effects of chemisorption-induced segregation at the particle/gas interface.[14]

Effect of Hydrogen Addition to the Reactant Mixture. The introduction of hydrogen into the reactant stream was observed to have a profound effect on the ability of the bimetallic to catalytically decompose ethylene to form carbon filaments. For all the catalyst compositions studied here an increase in solid carbon formation was observed when various amounts of hydrogen were added to the hydrocarbon stream (Figure 2). On the basis of the data presented in Figures 3 and 4, it is also evident that a high partial pressure of hydrogen is required to maintain all the bimetallic catalysts in their most active state. Since cobalt has a strong tendency to interact with ethylene, diffusion of this component to the particle surface will be facilitated in a hydrocarbon-rich environment. As a consequence, as the reaction proceeds it is expected that the system would exhibit carbon deposition characteristics comparable to those found for pure cobalt, i.e., relatively low activity. Furthermore, previous studies have demonstrated that the presence of hydrogen in the reactant has little effect on the ability of cobalt to produce carbon filaments from ethylene.[1] In the cobalt−silver systems it is likely that coadsorbed hydrogen generates a surface where dissociative chemisorption of ethylene is promoted, in the presence of silver. It is apparent that coadsorption of hydrogen is necessary in order for the catalyst to remain in a highly active state.

A further aspect that can play a major role in the modification of the catalytic activity of the bimetallic particles is surface reconstruction induced by adsorbed hydrogen species. The details and ramifications of this phenomenon and its implications on the catalytic behavior of metal surfaces have been well documented in the surface science literature.[20−23] If such an effect was operative in the current system, then one would expect to observe changes in both the gas and solid phase product distribution, since restructuring of the crystallographic faces involved in both hydrocarbon decomposition and carbon precipitation would occur. Inspection of the data presented in Table 1 indicates that, in addition to the enhancement in the formation of solid carbon, there is also a progressive increase in the yield of ethane as the partial pressure of hydrogen in the reactant is raised. It is significant that the formation of methane is relatively low and appears to be insensitive to the presence of hydrogen.

We have previously proposed for other bimetallic systems that the origin of the methane was from the decomposition of an ethylidyne intermediate on the catalyst surface.[1,17,18] Carbon−carbon bond scission of ethylidyne on the surface not only would give rise to methane, but the residual carbon fragment would eventually contribute toward the yield of solid carbon. It was suggested that ethylidyne formation was preceded by the propensity of the reactant ethylene molecule to adsorb perpendicular to the surface in an "end-on" geometry when the hydrocarbon encountered a cobalt atom located next to a copper atom. It follows that if this was the case the majority of ethylene adsorbing on the surface of the silver−cobalt bimetallic is adsorbing parallel to the surface and is subsequently hydrogenated to ethane or undergoes carbon−carbon bond scission with

the resulting surface carbon species dissolving and diffusing through the catalyst particle to constitute the carbon filament structure.

The Metal−Carbon Interface. Transmission electron microscopy examinations show that while carbon filaments are the exclusive type of deposit in all the catalytic systems studied in this work, there is a distinct change in the conformation of these structures upon the addition of silver to the cobalt particles from a bidirectional to multidirectional form. These filament growth characteristics can be correlated with a change in the crystallographic orientation of the associated catalyst particles. We have recently discussed the relationship between catalyst particle geometry and the growth characteristics of carbon filaments.[24] It was demonstrated that the bidirectional type of filaments were prevalent when the metal particles adopt a rhombic morphology in which two crystal faces were available for adsorption and decomposition of the hydrocarbon and four faces available for precipitation of carbon. On the other hand, when the catalyst particles acquire a multifaceted geometry where there are four to eight faces possessing carbon depositing properties, then multidirectional filament growth forms will be generated. One may rationalize the observed change in the structural characteristics of filaments when hydrogen was added to the cobalt−silver/ethylene system according to the notion that the bimetallic particles undergo a reorganization in shape, without a concomitant change in volume, that results in an increase in the area of the faces on which hydrocarbon dissociation occurs. This geometric transformation would account for not only the enhancement in the conversion of ethylene to solid carbon but also the apparent increase in metal particle size that is found when hydrogen is present in the reactant (Figure 8).

It is also interesting to note that hydrogen plays a critical role in determining the chemical and physical characteristics of the carbon filaments. The increase in the degree of crystallinity of the carbonaceous product in the presence of hydrogen, as witnessed from the temperature-programmed oxidation profiles, is an indication that the phenomenon occurring at the metal/solid carbon interface is influenced by this gas. It would appear that hydrogen not only induces reconstruction of the crystallographic faces of the catalyst available for hydrocarbon decomposition but also is capable of generating an arrangement of metal atoms at the precipitating faces of the particle, where the interatomic spacing matches that of carbon−carbon in graphite.[25] The higher surface area of the filaments produced from reactants containing excess hydrogen (Table 2) suggests that the structures formed under these circumstances possess a larger number of graphite edge sites accessible for adsorption of nitrogen than those formed from ethylene-rich mixtures. Such a condition could be achieved from the catalyst morphologies depicted in Figure 11, where in one case (a) the particle precipitates carbon in a manner such that the graphite platelets are in intimate contact in the middle of the structure and do not allow access to a gaseous adsorbent and (b) following reaction in excess hydrogen the particles adopt a crystallographic arrangement in which one of the faces does not favor carbon precipitation and, as a consequence, the pairs of graphite platelets are separated from each other and the number of edge sites exposed to a gas is increased. Examples of these two types of carbon filament structures are presented in the high-resolution electron micrographs (Figure 12a,b).

Many of the deductions in this paper relating to the catalyst characteristics are based on postreaction transmission electron microscopy examinations of the metal particles and the associated carbon filament. The presence of the solid carbon structure
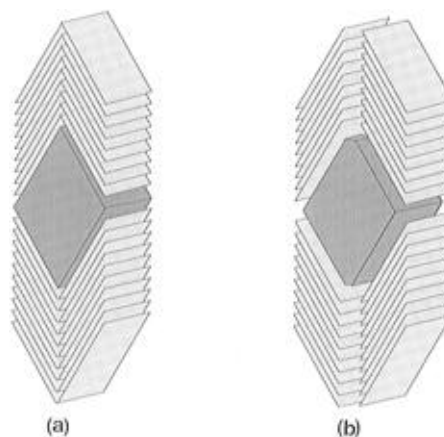

Figure 11. Schematic representation of the influence of catalyst particle morphology on the "herringbone" arrangement of graphite platelets in carbon filaments (a) platelets connected at central region and (b) platelets separated at central region.
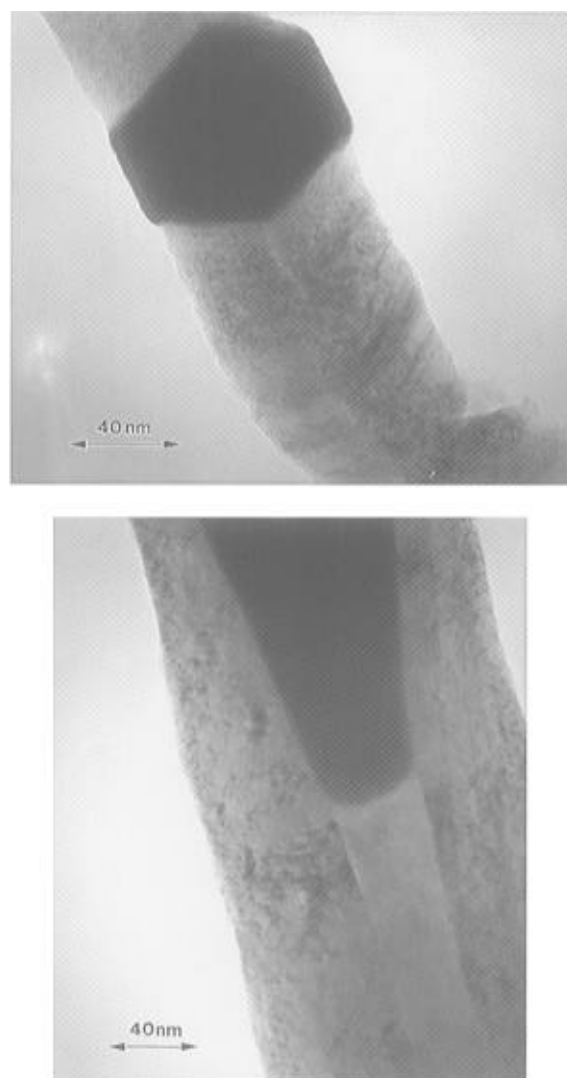

Figure 12. (a, top) Electron micrograph showing an example of a carbon filament structure where the platelets are connected at the central region. (b, bottom) A filament with a hollow central region where the platelets are separated.

provides a means of preserving the shape of the metal catalyst in the reactive state during the subsequent cooling step, and it can therefore be argued that the electron microscopy studies give an accurate picture of the morphology of the catalyst particles under reaction conditions. It should be stressed,

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however, that the images obtained from this technique are only 2-dimensional in nature. Despite this limitation, it is possible to monitor the modifications in metal particle morphology as a function of the nature of the gas environment, and this operation emphasizes the difficulties that one can encounter in attempting to determine the characteristics of such particles by traditional chemisorption methods. It is also apparent that the morphology and adsorption properties of the catalyst particle when heated in the presence of a reactant gas are going to be vastly different than those in the presence of pure hydrogen at room temperature, conditions where most chemisorption experiments are performed. A further shortcoming of the chemisorption method is that one assumes that the gaseous molecule adsorbs uniformly on all the exposed surfaces of the metal particle. Lin and Somorjai[26] have shown from surface science studies that distinct crystallographic faces of platinum can chemisorb hydrogen while other faces are incapable of performing this function. This aspect is even more apparent for the results presented here where the active surface for precipitating carbon is in fact encapsulated by the filamentous structure and is therefore unavailable to chemisorb any gas. It is due to these problems, among others, that we believe that the often-cited "turnover frequency" or "turnover number" calculated from chemisorption measurements has little value when studying filamentous carbon formation from metal/hydrocarbon interactions.

Comparison of the Behavior of Cobalt−Silver and Cobalt−Copper. A comparison of the data presented here with those obtained previously for the cobalt−copper-catalyzed decomposition of ethylene to produce filamentous carbon (1) reveals the existence of a number of differences in the behavior of the two bimetallic systems. Cobalt−copper was found to exhibit a high activity for the conversion of pure ethylene to solid carbon, ∼70%, over a wide catalyst composition range. In contrast, under the same conditions the activity of the cobalt−silver system for this reaction was considerably lower, and the maximum conversion of ethylene was obtained over a relatively narrow catalyst composition range (Figure 1). This distinction in the catalytic activity of the two bimetallic powders cannot be accounted for by the selective formation of alloys in one of the systems since both silver and copper exhibit only limited bulk miscibility in cobalt.[15] As previously stated, we believe that in addition to geometric effects electronic interactions between the two components are operative in these systems, and the degree to which these two factors impact on the behavior of the cobalt bimetallics will be a function of the adatom. In this context it is important to consider the models devised by Goodman and co-workers[27] that predict the direction of electron transfer resulting from the mixing of two metals. From this model we would expect that the direction of any electron transfer in either copper−cobalt or silver−cobalt to be from cobalt to the adatom. The result of this electron flow would be a change in the strength of the interaction of ethylene molecules with the surface cobalt atoms, and this aspect may lead to the observed enhancement in carbon deposition activity for both bimetallics.

Methane and ethane, in approximately equal quantities, were found to be the major gaseous products when ethylene/hydrogen mixtures were passed over a selection of cobalt−copper catalysts. These results are to be compared with the highly selective formation of ethane in preference to methane found in the current work under a variety of reaction conditions and cobalt−silver catalyst composition ranges. A synopsis of the total product distribution obtained from the decomposition of an ethylene/hydrogen (1:4) mixture over cobalt doped with 2% copper and 2% silver at 600 °C is shown in Table 3.

TABLE 3: Percent Product Distribution for Ethylene/Hydrogen (1:4) Decomposition over Co/Cu (98:2) and Co/Ag (98:2) after 60 min at 600 °C

catalyst	% yield			
	carbon	ethane	ethylene	methane
Co/Cu	48.47	22.59	5.08	23.84
Co/Ag	71.21	22.74	4.30	1.74

Under these particular reaction conditions, high cobalt content and high hydrogen partial pressure, the activity of the silver-containing catalyst for carbon deposition is actually higher than its copper analogue. It is significant, however, that the total conversion of ethylene and yields of ethane are similar for both catalysts. Surface science studies have shown that the electronic nature of the metal can dictate the mode of adsorption of ethylene on the metal.[28] If the magnitude of the electronic perturbation of cobalt by copper is appreciably different than that induced by silver, this aspect could be reflected in a modification in the ethylene adsorption characteristics on these bimetallic surfaces. As a consequence, one would not be surprised to find variations in the product selectivity pattern. A further feature to be taken into consideration is that when particles are undergoing reaction several crystal faces are generated. Each face can possess an arrangement of atoms that exhibit different adsorption characteristics with respect to the reactant gas. This behavior can lead to the formation of a variety of products, i.e., ethane or methane. The formation of an ethylidyne intermediate may be favored on the exposed faces of copper-modified cobalt, but the atomic arrangement of the cobalt atoms at the surface may be different when silver is present and the formation of this particular reactive intermediate may not be a facile process. This argument could also be extended to the events occurring at the metal/solid carbon interface where the nature of the adatom could induce modifications in the crystallographic orientation of the faces responsible for carbon precipitation. This effect would be manifested in a difference in the structural and conformational characteristics of carbon filaments generated by the respective cobalt bimetallics, as was observed experimentally.

Summary

From this investigation it is evident that the addition of a small amount of silver to cobalt has a profound effect on the catalytic behavior of the host metal toward the formation of filamentous carbon when the bimetallic is heated in the presence of ethylene. While one might rationalize the modification in catalytic action of the system in terms of a geometric effect when significant amounts of silver are present, it is difficult to conceive of how such an explanation can account for the dramatic enhancement in activity when only 1% of the additive is incorporated into the particles. It is possible that this change in behavior is attributable to electronic perturbations in the cobalt lattice brought about by the addition of silver to the system, which results in an improvement in reactivity of the surface toward ethylene decomposition. Similar effects are observed when copper is introduced into cobalt; however, in this case the gas phase selectivity pattern is significantly different than that observed in the present system. In the former system, methane was produced in similar amounts to that of ethane, whereas when ethylene was decomposed over a cobalt−silver catalyst the ratio of ethane to methane formed was between 10 and 30.

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