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Deactivation of Copper–Nickel Catalysts Due to Changes in Surface Composition

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A reversible deactivation phenomenon is observed when copper–nickel particles are reacted in ethylene at temperatures in excess of 700°C. Addition of hydrogen to the system is found to extend the active life of the catalyst to higher temperatures. *In situ* electron diffraction analysis performed on a model catalyst system indicates that separation of the alloy into its single constituents occurs at 700°C in ethylene and 800°C in hydrogen. This deactivation phenomenon is extremely complex and involves not only the reactions occurring at the gas/catalyst interface but also modifications in the particle chemistry arising from dissolved carbon and hydrogen species, and also the influence of the deposited graphite in the form of a filament at the rear of the particle. Lowering of the temperature results in a reestablishment of the bimetallic surface and restoration of catalytic activity. By measuring both the gas-phase and solid products of the reaction, we have been able to develop a novel method to continuously follow the changes in composition of the surface as a function of reaction temperature, time, and nature of the reactant gas. These results are discussed in terms of a model, which relates the ethylene adsorption characteristics to the surface composition of the bimetallic system. © 1993 Academic Press, Inc.

INTRODUCTION

For many years one of the goals of workers in the field of heterogeneous catalysis has been to identify the chemical composition of the surface of bimetallic particles under reaction conditions. In this regard, copper–nickel has been one of the most extensively investigated systems, since it provides an ideal tool for segregation studies. In contrast to nickel, copper does not chemisorb hydrogen very strongly, and this aspect has been exploited by several workers in an attempt to determine the fraction of copper which is present in the surface of copper–nickel alloys (*1–4*). The results of this selective chemisorption technique are open to debate, since the measurements are performed on samples which have been cooled to room temperature and removed from their reaction environment. Various surface science techniques have been used to examine the surfaces of copper–nickel films under high-vacuum conditions following heat treatment in a gaseous environment (*5–11*). Cale and Richardson (*12*) were responsible for performing the first *in situ* characterization studies of supported copper–nickel particles. Using a specially designed sample cell, they were able to perform magnetic measurements, which were followed by hydrogen chemisorption and kinetic studies on the same specimens. The results of these studies were discussed in terms of a model in which limited surface enrichment of the particles in copper was postulated.

Perhaps the most precise method of determining the state of the surface is one involving the use of a reaction which is sensitive to the chemical composition. In this context, decomposition of a simple hydrocarbon such as ethylene may provide an ideal probe. It is well known that when cer-

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tain metals are heated in hydrocarbon environments and conditions are reached which favor the rupture of a carbon–carbon bond in the molecule then the resulting species may dissolve in the metal particle, diffuse to the rear faces, and ultimately precipitate to form a filamentous carbon structure. One of the consequences of this process is that although considerable amounts of solid carbon are produced, the surface of catalyst particles exposed to the gas remains free of any deposit. In a previous study from this laboratory it was found that when copper–nickel powders were reacted in ethylene/hydrogen mixtures, then in addition to the formation of carbon filaments, an excessive amount of methane was also produced, which could not be accounted for solely on the basis of hydrogasification of the carbon deposit (*13*). Arguments were put forward which claimed that this product was formed from the decomposition of an "ethylidyne" intermediate. It was significant that when the reaction was performed over a pure nickel catalyst, the amount of methane formed was appreciably smaller and corresponded to that evolved during the hydrogasification step.

In a subsequent investigation, it was found that when the copper–nickel/ethylene system was reacted at temperatures in excess of 740°C, the catalyst exhibited a complete loss of activity. This deactivation step was shown to be reversible in nature, as evidenced by the fact that the activity of the catalyst could be completely restored by lowering the temperature to about 700°C (*14*). It was suggested that this unusual form of catalyst deactivation might be attributable to the tendency of copper to segregate to the metal/gas interface at high temperature, and since this metal does not readily decompose hydrocarbons, the reaction would be suppressed. On cooling to a lower temperature regime, it was proposed that the alloy composition at the surface was reestablished to about its original value and the catalyst regenerated.

In the current study we have endeavored to examine this deactivation phenomenon in greater detail and also to follow the formation of solid carbon and the gaseous products as a function of a number of variables, including the relative amounts of copper and nickel in the catalyst particle surfaces. Flow reactor studies conducted with powdered alloy catalysts have been complemented by *in situ* electron diffraction analysis of model systems consisting of alloy particles dispersed on single crystal graphite. The objective of the present study is to explore the possibility of using a chemical probe reaction as a means of developing a novel method to continuously monitor the composition of the surface during reaction.

EXPERIMENTAL

Materials

Copper–nickel powers of various compositions were prepared by coprecipitation of the metal carbonates from nitrate solutions mixed in the desired ratios using ammonium bicarbonate, according to procedure outlined by Best and Russell (*15*) and Sinfelt *et al.* (*4*). The precipitate was dried overnight at 110°C, and then calcined in air for 4 hr at 400°C followed by reduction in hydrogen at 500°C to form the copper–nickel alloys. The bulk composition of the powders was checked using energy dispersive X-ray spectroscopy (EDS). Nickel powders were prepared using a similar procedure.

The gases used in this work, hydrogen (99.999%), ethylene (99.99%), acetylene (99.6%), helium, (99.99%), nitrogen (99.99%), and argon (99.99%) were obtained from Alphagaz Co. and were used without further purification. Reagent grade nickel nitrate [$Ni(NO_3)_2\,6H_2O$] and Reagent grade cupric nitrate [$Cu(NO_3)_2\,3H_2O$] were obtained from Fisher Scientific for the catalyst preparation.

Apparatus and Procedures

The experimental and analytical approaches used in these studies were similar to those described previously (*13*). Powdered catalyst samples (50 mg) contained in a ceramic boat were placed in a quartz tube, brought up to the desired reaction temperature in the presence of a hydrogen–argon (1:10) mixture, and at this stage the reactant ethylene/hydrogen feed was introduced at a total gas velocity of 0.4 cm/sec and allowed to react for various periods of time at temperatures ranging from 550 up to 900°C. Long term experiments were performed in larger reactor vessels to accommodate the excessive amounts of carbon deposit produced under such conditions, and in this case the gas mixture velocity was 0.1 cm/sec for the same flow rate of 100 sccm/min. The amount of carbon deposit produced during these reactions was determined by weight difference. The gas-phase product distributions were determined at various intervals for reaction times of up to 380 min. The filamentous nature of the carbon deposit was established by examination in both the scanning and transmission electron microscopes.

BET surface area measurements were performed with nitrogen at −196°C. A value of 16.0 (Å)^2 was assumed for the area of a nitrogen molecule with a maximum working pressure of 300 Torr. Hydrogen chemisorption experiments were carried out according to the procedures described in Ref. (*4*). Active metal surface was determined from the irreversibly chemisorbed hydrogen at 25°C by assuming that the uptake of hydrogen at zero pressure corresponds to a monolayer coverage of the metal. These values were determined by extrapolation of the high-pressure linear portion of the isotherms. In some experiments catalyst powders were pretreated in either methane or methane–hydrogen mixtures at 750°C for 30 min to induce modifications in surface composition prior to chemisorption measurements. Both physical and chemisorption studies were performed with a Coulter Omnisorp 100CX instrument.

Controlled atmosphere electron microscopy studies (CAEM) were performed in a modified JEM 120 electron microscope which was fitted with an AGI gas reaction cell and details of this technique have been given previously (*14*). The samples used in these experiments were prepared by two methods: (a) nickel/graphite specimens were made by evaporation of the metal in the form of a wire from a tungsten filament at 10^{-6} Torr; (b) copper–nickel/graphite samples were produced by introducing the components mixed in the desired ratio, as an atomized spray from an aqueous solution of the respective metal nitrates. Prior to reaction in acetylene both these systems were pretreated in 1 Torr hydrogen at 400°C for 3 hr.

In situ electron diffraction analysis of copper–nickel/graphite specimens undergoing reactions in 0.2 Torr hydrogen and 0.2 Torr ethylene, respectively, were carried out as a function of temperature in a modified JEOL 200 CX TEM system. This procedure, which was described in detail in a previous paper (*16*), allows for a <2% error between theoretical and experimental values.

RESULTS

Adsorption Studies

The surface area values of the copper–nickel catalyst particles as determined by nitrogen adsorption isotherms were within the range 0.25–0.31 m^2/g and appeared to be independent of catalyst composition. The data presented in Table 1 show the fraction of strongly adsorbed hydrogen as a function of catalyst composition. It can be seen that the addition of as little as 5 wt% copper to nickel results in a dramatic decrease in the ability of the catalyst to chemisorb hydrogen, and this trend continues as the percent of copper in the mixture is increased. This dependence is completely consistent with those reported by Sinfelt *et al.* (*4*). Also included in this table are data obtained from copper–nickel (3:7) powders which were pretreated in methane and methane/hydrogen (1:4) mixtures, respec-

TABLE 1

Metal Surface Area from Hydrogen Chemisorption (25°C) as a Function of Catalyst Composition

Catalyst composition	Metal surface area (m^2/g)
Ni	0.269
Cu–Ni (5:95)	0.021
Cu–Ni (2:8)	0.019
Cu–Ni (2:8)	0.000[a]
Cu–Ni (3:7)	0.013
Cu–Ni (3:7)	0.038[b]
Cu–Ni (5:5)	0.008
Cu	0.000

[a] Pretreated in CH_4 at 750°C for 30 min.

[b] Pretreated in CH_4/H_2 (1:4) at 750°C for 30 min.

tively. These experiments were carried out in an attempt to assess changes that might occur at the surface of the catalyst as a result of treatments in these environments. For this purpose we elected to use methane as the hydrocarbon source, since previous work has demonstrated that it does not undergo catalytic decomposition at these temperatures (*13*).

Effect of Reaction Time on Product Distribution

Table 2 summarizes the changes in the gas phase composition resulting from the interaction of copper-nickel (2:8) with an ethylene/hydrogen (4:1) mixture at 600°C as a function of reaction time. Examination of this data shows that steady state is attained after a period of about 25 min and maximum activity is maintained for up about 1 hr. On continued reaction the catalyst progressively loses activity with respect to the conversion of ethylene, which is reduced from a maximum of 93 to 57% following reaction for 6 hr. Similar reactivity trends were found for other catalyst compositions rich in nickel.

Changes in Reactivity as a Function of Catalyst Composition

The effect of adding increasing amounts of copper to nickel on the catalytic decomposition of ethylene-hydrogen at 600°C is shown in Table 3. Inspection of this data shows that copper–nickel catalysts containing between 10 and 30 wt% copper were

TABLE 2

Percentage Carbon Distribution at 600°C as a Function of Time for a Copper–Nickel (2:8) Catalyst in the Presence of C_2H_4/H_2 (4:1)[a]

	Carbon products				
Time (min)	CH_4	C_2H_4	C_2H_6	C_s	$C_2H_6 + C_s$
8	1.2	15.4	2.2	81.2	83.4
15	2.0	12.5	3.1	82.4	85.5
25	3.0	10.0	4.1	83.0	87.1
40	4.5	8.2	5.4	81.8	87.2
55	6.5	6.8	7.0	79.7	86.7
70	7.1	8.4	7.3	77.3	84.6
85	7.8	9.3	7.9	74.9	82.8
95	8.1	10.4	8.3	73.2	81.5
150	8.5	18.1	9.8	63.6	73.4
160	8.4	19.6	10.1	61.9	72.0
180	8.0	22.6	10.7	58.7	69.4
300	5.2	27.1	12.8	54.9	67.7
320	4.4	31.3	13.5	50.8	64.3
380	3.2	43.0	13.6	40.2	53.8

[a] Experiments performed at a gas velocity of 0.1 cm/sec.

TABLE 3

Percentage Carbon Distribution as a Function of Catalyst Composition when Reacted in C_2H_4/H_2 (4:1) at 600°C for 90 Mins

	Carbon products				
Bulk % Ni	CH_4	C_2H_4	C_2H_6	C_s	$C_2H_6 + C_s$
95	11.3	4.4	18.6	65.6	84.2
90	12.6	2.4	9.1	75.8	84.9
80	14.7	2.5	6.7	76.0	82.7
70	19.8	2.4	5.8	72.0	77.8
50	22.2	10.1	7.2	60.4	67.6
30	10.5	32.3	8.2	48.9	57.1
15	1.3	71.8	9.7	14.5	24.2

[a] Experiments performed at a gas velocity of 0.4 cm/sec.

extremely reactive for the decomposition of ethylene. It is also apparent that the percentage of conversion of ethylene to solid carbon at equilibrium conditions reaches a maximum between 10 and 20 wt% of copper and also the maximum production of methane is attained between 30 and 50 wt% of copper. Addition of further amounts of copper results in a decline of both methane and solid carbon formation, as well as the reactivity of ethylene.

Effect of Gas Composition on the Deactivation of Copper–Nickel

Changes in the reactivity of ethylene as a function of temperature were investigated in a detailed manner and these results are presented in Fig. 1. When ethylene decomposition over copper nickel (3:7) was followed in the absence of added hydrogen, the catalyst lost its activity with regard to solid carbon formation at 700°C. When a

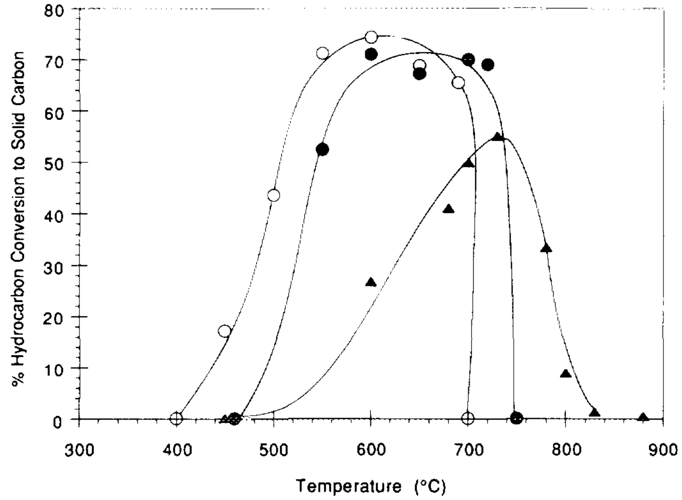


FIG. 1. Effect of temperature and gas composition on the amount of solid carbon produced from the copper–nickel (3:7) catalyzed decomposition of ethylene/hydrogen mixtures: (○) C_2H_4; (●) C_2H_4/H_2 (4:1), and (▲) C_2H_4/H_2 (1:4).

sample of the same catalyst was reacted in a ethylene/hydrogen (4:1) mixture, then activity was maintained up to 750°C. In a final series of reactions the catalyst was treated in an ethylene/hydrogen (1:4) mixture, and under these conditions the activity was sustained up to 850°C.

Effect of Temperature on the Deactivation of Copper–Nickel

When copper–nickel (3:7) powders were reacted in ethylene/hydrogen (4:1), the product distribution changed significantly as the temperature was raised to 750°C (Table 4). Inspection of these data shows that although the catalyst loses its activity to produce solid carbon at 750°C if the temperature is lowered to 700°C not only its activity is restored but the product distribution is comparable to that of a catalyst treated at a maximum temperature of 700°C.

Controlled Atmosphere Electron Microscopy Studies (CAEM)

Major differences in the behavior of nickel/graphite and copper/nickel (3:7)/graphite specimens were observed when the respective systems were heated in the presence of 2 Torr acetylene. With the pure metal, onset of filamentous carbon growth occurred at about 500°C. Under these conditions the filaments were produced in a whisker-like mode, with the catalyst particle being carried away from the support surface and remained at the tip of the growing filament. As the temperature was gradually raised both the number and average size of metal particles creating carbon filaments increased. This action continued in a relatively smooth fashion until about 850°C, when there was a significant decrease in the number of new filaments being formed, and finally at 900°C, growth of this type of deposit ceased. Lowering of the temperature to a previously active regime did not result in reactivation of the spent catalyst particles. Catalytic activity could, however, be restored if the hydrocarbon was replaced by hydrogen and the specimen treated at 750°C for 5 min. When acetylene was reintroduced into the system existing filaments continued to grow and new filaments were formed.

Growth of carbon filaments commenced on the graphite supported copper–nickel particles at between 280 to 300°C, when this system was reacted in 2 Torr acetylene. In this case, the filaments were produced in a bidirectional mode, where the catalyst particle remained confined within the body of the structure throughout the growth process. The characteristics of the filaments

TABLE 4

Percentage Carbon Distribution as a Function of Temperature for a Copper–Nickel (3:7) Catalyst in C_2H_4/H_2 (4:1) at 600°C for 90 mins[a]

	Carbon products				
T (°C)	CH_4	C_2H_4	C_2H_6	C_s	$C_2H_6 + C_s$
550	14.6	9.8	23.2	59.4	82.6
600	19.8	2.4	5.8	72.0	77.8
650	28.7	1.2	3.1	68.3	71.4
700	19.5	1.2	9.1	70.0	79.1
720	15.2	3.0	12.8	69.5	82.3
750	24.4	—[b]	9.1	0.0	9.1
750 → 700	12.1	3.2	11.5	68.3	79.8

[a] Experiments performed at a gas velocity of 0.4 cm/sec.

[b] Ethylene undergoes polymerization reactions.

were identical to those discussed in an earlier paper (*14*). There appeared to be an upper temperature limit of 750°C, above which growth of carbon filaments came to an abrupt halt. If, however, the temperature was reduced to around 650°C, then on holding at this temperature for about 10 min a number of the previously deactivated particles were observed to resume their ability to create carbon filaments, without the need for an intermediate hydrogen regeneration treatment.

In Situ Electron Diffraction Studies

The distribution of chemical species present when the copper–nickel (1:1)/graphite system was heated in 0.2 Torr hydrogen from 400 up to 800°C and then finally cooled to room temperature is presented in Table 5. Inspection of these data shows some very interesting features. In contrast to the powdered alloy samples, it is clear that in the graphite supported catalyst system we are producing a dispersion of alloy particles, some of which have different compositions to that of the precursor solution. It was also apparent that the single components could be present throughout the heating cycle. The most significant finding is at 800°C, where copper appears to be the only constituent present. On cooling to room temperature the original alloy mixture is reestablished.

The corresponding data obtained when similar specimens were reacted in ethylene at temperatures up to 800°C is given in Table 6. In this case, only a Cu–Ni (1:1) alloy is identified which exists only up to about 700°C; above this temperature only the separate elements are present.

DISCUSSION

Catalyst deactivation is a complex phenomenon generally attributable to either carbon deposition, particle sintering, or poisoning by sulfur and heavy metals (*17*).

TABLE 5

Electron Diffraction Pattern Analysis of a Cu–Ni/Graphite Specimen as a Function of Temperature in 0.2 Torr Hydrogen

Temperature (°C)	Calculated *d*-spacings (nm)	*d*-spacings (nm)			
		Cu–Ni (7:3)	Cu–Ni (1:1)	Cu	Ni
500	0.2081	0.2071_{111}		0.2087_{111}	
	0.1800	0.1794_{200}		0.1807_{200}	
	0.1261	0.1268_{220}	0.1262_{220}		0.1246_{220}
	0.1080	0.1082_{311}		0.1090_{311}	
600	0.2068	0.2071_{111}	0.2060_{111}		
	0.1796	0.1794_{200}		0.1807_{200}	
	0.1257	0.1268_{220}			0.1246_{220}
	0.1069		0.1076_{311}		0.1062_{311}
700	0.2065		0.2060_{111}		
	0.1799	0.1794_{200}	0.1785_{200}	0.1807_{200}	
	0.1251				0.1246_{220}
	0.1064		0.1076_{311}		0.1062_{311}
800	0.2098			0.2087_{111}	
	0.1807			0.1807_{200}	
	0.1272			0.1278_{220}	
	0.1093			0.1090_{311}	
Cooled to room temperature	0.2072	0.2071_{111}			
	0.1798	0.1794_{200}			
	0.1257		0.1262_{220}		
	0.1078		0.1076_{311}		

TABLE 6

Electron Diffraction Pattern Analysis of a Cu–Ni/Graphite Specimen as a Function of Temperature in 0.2 Torr Ethylene

Temperature (°C)	Calculated *d*-spacings (nm)	*d*-spacings (nm)		
		Cu–Ni (7:3)	Cu	Ni
600	0.2041	0.2060_{111}		0.2034_{111}
	0.1839		0.1807_{200}	
	0.1263	0.1262_{220}		
700	0.2041	0.2060_{111}		0.2034_{111}
	0.1789	0.1784_{111}		
	0.1291		0.1278_{220}	
	0.1230			0.1246_{111}
	0.1103		0.1090_{311}	
750	0.2074		0.2087_{111}	
	0.2048			0.2034_{111}
	0.1819		0.1807_{200}	
	0.1760			0.1762_{200}
	0.1278		0.1278_{220}	
	0.1227			0.1246_{220}
800	0.2063		0.2087_{111}	
	0.1807		0.1807_{200}	
	0.1776			0.1762_{200}
	0.1248			0.1246_{220}

Regeneration of a spent catalyst can be achieved in some cases by combustion in air, which results in gasification of solid carbon to CO_2 followed by redispersion of agglomerated metal particles in a chlorine/oxygen environment. In the present investigation, we have found an unusual form of catalyst deactivation which appears to be extremely dependent on reaction temperature and the fraction of hydrogen in the hydrocarbon feed as shown in Fig. 1. The reversible nature of this process is evident from the data presented in Table 4, where it can be seen that catalytic activity is restored to about its original value by lowering the temperature to a previously active regime. Furthermore, CAEM studies of the behavior of individual catalyst particles indicates that when copper–nickel (3:7) particles were heated in the presence of acetylene, the observed sequence of events was quite different to that found when pure nickel was reacted under the same conditions. In the latter case, it was not possible to restore the activity of a spent catalyst merely by lowering the reaction temperature. It was necessary to perform an intermediate treatment in hydrogen in order to rejuvenate the particles toward subsequent carbon filament growth, indicating that deactivation was probably caused by encapsulation of the particles by a carbonaceous overlayer. In contrast, with the bimetallic system decreasing the temperature to about 650°C resulted in resumption of the growth of filaments on particles which at higher temperatures had lost their activity. Based on these observations, it is clear that there are subtle differences in the modes by which these two systems undergo deactivation.

From the numerous experimental studies and available thermodynamic data of the behavior of bimetallic systems, certain predictions can be made on the segregation phenomena which occur when copper–nickel surfaces are exposed to mixtures of ethylene and hydrogen. Ponec and co-workers (*18*, *19*) have emphasized the need to take into account the effect of chemisorption-induced surface segregation which can occur in a reactive environment and have cautioned against the dangers of using data obtained under high-vacuum conditions for this purpose. These workers reported that when Pt–Cu allows were heated in the presence of ethylene, then selective chemisorption of the hydrocarbon led to the segregation of platinum to the alloy surface (*18*). In other work, Cu–Ni alloys were treated in CO and under these circumstances gas-induced enrichment of the surface in nickel was observed (*19*). Since the binding energy of ethylene to nickel is very high (*20*) one might reasonably expect that chemisorption-induced segregation of nickel to the surface will take place, overriding the natural tendency of copper to segregate to the surface (*2–4*, *6*). If indeed the surface of the catalyst becomes completely covered with a layer of nickel atoms, then decomposition of surface carbide to precipitate a graphitic overlayer would be possible. As hydrogen is added to the reactant gas one might reasonably expect a moderation in the surface carbon concentration, and as a consequence an increase in the active life of the catalyst. Such a dependence was indeed observed in the present series of reactions.

A closer examination of the experimental data, however, reveals some inconsistencies when this somewhat simplified explanation is applied to the deactivation of the bimetallic system. It is difficult to rationalize the observed reversible deactivation phenomena observed in both macro- and microscale studies of copper–nickel/ethylene systems solely in terms of a mechanism based on formation of an encapsulating graphite overlayer. For the case where a bimetallic catalyst particle is attached to a solid carbon structure, such as a filament, the surface segregation phenomena is even more complex. We now have to consider all the events which are taking place on and in the particle, where a fraction of the surface is exposed to a reactant gas and the remainder is in intimate contact with graphite, and the particle itself contains dissolved carbon and hydrogen. Under these conditions, it is not sufficient to merely consider the events which are occurring at the catalyst/gas interface, since the driving force for segregation may be greater in the opposite direction, i.e., at the catalyst/solid carbon interface. Thus, any scientific rationale based on previous studies performed on model systems must be tempered, in view of the lack of data dealing with the situation encountered in the present work.

From a consideration of both thermodynamics and our experimental results, we suggest the following model. In the absence of added hydrogen, nickel will tend to segregate to the catalyst surface, and the concomitant decrease in carbon solubility resulting from the chemical changes at the surface layers due to phase separation results in the formation of graphite at the particle/gas interface. If the temperature is subsequently lowered to a regime where the alloy composition is reestablished, then the precipitated carbon can be redissolved in the particle and filament growth resumed. Hydrogen is expected to promote the formation of a strong interaction between nickel and the graphite platelets constituting the carbon filament structure produced at the rear of the particle. Indeed, the strength of this latter interaction may well be greater than that between nickel and ethylene, so that in the limit the exposed surface of the particle becomes enriched in copper and since ethylene does not readily dissociate on this metal, further growth of filamentous carbon is suppressed. Lowering of the temperature results in a decrease of the interfacial energy between nickel and graphite due to the high concentration of carbon remaining in the particle (*21*). This allows for restoration of the alloy phase, and once again conditions are established under which carbon filament growth is favored.

Support for some of the steps proposed

in the above rationale can be obtained from a consideration of the data from previous controlled atmosphere electron microscopy studies of the influence of copper–nickel (1:1) particles on the graphite–hydrogen reaction (*22*). One of the major features to emerge from such investigations was the finding of a change in the manner by which the alloy particles underwent reaction with graphite as the temperature was increased above 675°C. Below this temperature, discrete particles were produced, and those located at edge regions proceeded to attack the graphite by a channeling mode. As the temperature was raised to above 675°C, particles underwent a spreading action which resulted in continued gasification via the edge recession mode. This change in particle morphology and consequent pattern of reactivity was directly related to a modification in the wetting characteristics of the catalyst at the graphite interface and was attributed to preferential segregation of one of the components at this region. This behavior is to be contrasted with that of the nickel/graphite–hydrogen system, where the spreading action of active metal particles resulted in the formation of an inactive film along the channels at temperatures of 975°C, and in this case, lowering of the temperature to a previously active regime did not restore catalytic activity (*23*). This irreversible deactivation phenomena associated with pure nickel particles was later attributed to the intermediate formation of nickel carbide which on cooling decomposed to the metal with a graphitic monolayer coating (*24*).

In situ electron diffraction analysis of model catalyst systems provides one with some insights into the understanding of the chemical changes which are occurring in individual alloy particles as a function of temperature and gas environment. It should be appreciated that although such experiments were performed on model systems, the chemical changes exhibited during the reaction should parallel those of the powdered alloy catalysts used in the flow reactor studies. It is apparent that the gas environment can have a profound effect on the behavior of bimetallic particles. In the presence of hydrogen, two alloy phases were observed, and these persisted up to 800°C, at which point only copper was identified. This situation arises from a combination of factors resulting from separation of the alloy into copper particles and a thin film of nickel, which spreads on the graphite support under these conditions and consequently does not contribute to the diffraction pattern. This transformation in morphology is in agreement with previous controlled atmosphere electron microscopy studies performed on nickel/graphite specimens heated in hydrogen, which showed that the metal particles tended to undergo a spreading action on the substrate at high temperatures (*23*). It is significant that under the same reaction conditions copper did not exhibit a spreading action on the graphite substrate, but instead remained in the form of discrete particles (*25*). In contrast, when the reaction was performed in ethylene only a single alloy phase was detected and at 700°C appeared to separate into its constituent elements. It is significant that in this system, both copper and nickel were detected in the electron diffraction pattern. It is also apparent from these experiments that although metal carbide species were not formed, the presence of dissolved carbon in both the alloy and metal particles caused a slight distortion of the crystal lattices, as seen from the differences between the measured and actual values. Accumulation of carbon on the specimen was observed at the highest temperatures and such occurrence prevented detailed analysis upon cooling.

The results of the present investigation reveal that the product distribution from the decomposition of ethylene and ethylene/hydrogen mixtures over copper–nickel catalysts is extremely sensitive to the chemical nature of the exposed surfaces, a condition which is dictated by a number of factors including the initial composition of the bimetallic, the reaction temperature, nature of the reactant gas and extent of the reaction. Before embarking on a lengthy discourse to account for the various product trends and catalyst activity, it is worthwhile to take into account the events which are occurring at the interface between the catalyst surface and the adsorbed hydrocarbon molecules. Let us consider the situations depicted in Figs. 2A and 2B for the adsorption of ethylene molecules on nickel and copper–nickel surfaces, respectively. On the pure metal surface in the absence of any other gas phase reactant, there will be tendency for ethylene molecules to adsorb in a conformation such that the C=C bond is "parallel" to the solid surface. At saturation coverage there is a high probability that these molecules will interact with each other and eventually lead to the formation of a graphitic overlayer (*26–28*). In contrast, when the hydrocarbon is adsorbed on the bimetallic surface, Fig. 2B, then other conformational molecular arrangements are possible. For the situation where the ethylene molecule encounters two unperturbed adjacent nickel atoms one might expect the hydrocarbon to be adsorbed "parallel" to the surface. In contrast, when adsorption occurs at a nickel atom where the only unoccupied nearest neighbor is a copper atom, then it is possible that ehthylene is linked to the surface in an "end-on" arrangement. During subsequent reaction it is probable that these two adsorbed intermediates will give rise to different products.

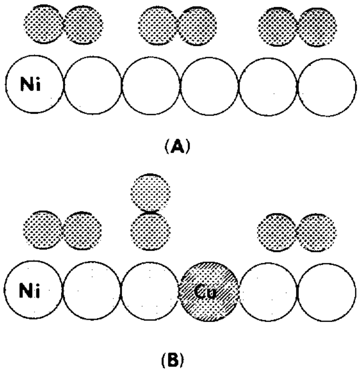
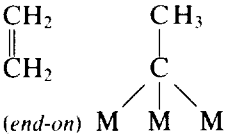


FIG. 2. Possible configurations for adsorption of ethylene molecules on (A) nickel (parallel to the surface) and (B) copper–nickel (parallel and end-on to the surface).

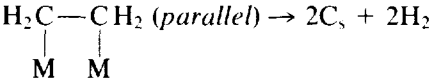
Ethylene adsorbed in the "parallel state" may undergo C=C bond scission leading to carbon dissolution and precipitation to form a filamentous structure. In this state the adsorbed hydrocarbon may also undergo hydrogenation and desorb from the surface as ethane. Ethylene adsorbed in the "end-on" configuration may rapidly rearrange to form an "ethylidyne" intermediate, which in turn would undergo C—C bond scission to produce a methane molecule leaving behind a carbon atom on the surface, which eventually contributes to the formation of the carbon deposit. On this basis, one could argue that as the concentration of nickel atoms in the surface increases, the number of ethylene molecules adsorbed in the "parallel" configuration will also increase, and this condition should be reflected as a build up in the formation of both solid carbon and ethane. Likewise, as the copper concentration is raised the amount of methane generated should climb to a maximum level which will be dictated by the availability of copper–nickel pairs which favor ethylene adsorption in the "end-on" configuration.

According to this hypothesis, it should be possible to develop a relationship between the catalyst surface composition and the product distribution according to the following simplified approach. A sequence of reaction steps may be written to account for the formation of the various products as follows:

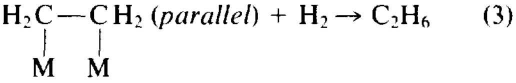


$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \qquad \begin{matrix} CH_3 \\ | \\ C \\ /\,|\,\backslash \\ M\;\;M\;\;M \end{matrix} \quad + H \rightarrow C_s + CH_4. \qquad (1)$$

Reaction (1) which would be dependent on the number of copper–nickel units at the surface is expected to produce methane and an equal amount of solid carbon, C_s:



$$\underset{M}{H_2C}-\underset{M}{CH_2}\ (parallel) \rightarrow 2C_s + 2H_2 \qquad (2)$$



$$\underset{M}{H_2C}-\underset{M}{CH_2}\ (parallel) + H_2 \rightarrow C_2H_6 \qquad (3)$$

The extent of reactions (2) and (3) would depend on the number of nickel–nickel units. By taking into account the relative amounts of all the products formed in the reaction the fraction of nickel atoms present in the surface at any stage can be estimated from the following relation:

$$\text{Rate of Reaction} \sim \text{Density of Ni Surface atoms} \approx \{C_s + C_2H_6\}. \qquad (4)$$

The values of $\{C_s + C_2H_6\}$ have been calculated for all experiments and this product has been included in Tables 2 to 4. From Eq. (4) it is apparent that such values provide one with an assessment of the percent nickel present in the surface of the series of alloy catalysts and these data are plotted as a function of the respective bulk alloy composition in Fig. 3. Based on this relationship it is evident that the concentration of surface nickel atoms is significantly different to that of the bulk composition when the catalyst is reacted in an ethylene/hydrogen environment and is higher for alloys containing more than 20% copper. It is interesting to compare this information, which is derived from the behavior of the catalysts under reaction conditions, with that obtained by hydrogen chemisorption procedures of the same materials at room temperature following a reduction at 300°C, Fig. 4. From this plot it is apparent that all the alloy powders including those consisting of bulk compositions up to 95% Ni exhibit similar very low hydrogen chemisorption capacity. This would indicate that either the surfaces are enriched in copper or the presence of copper has a dramatic influence on the ability of nickel to chemisorb hydrogen. Clearly, this dilemma highlights the dangers of attempting to predict the surface composition of bimetallic particles by a postreaction method.

In addition to verifying that under the prevailing reaction conditions, nickel tends to segregate to the catalyst surface, we can learn more about the manner in which the two types of atoms are arranged with respect to one another by combining this information with the variation in methane

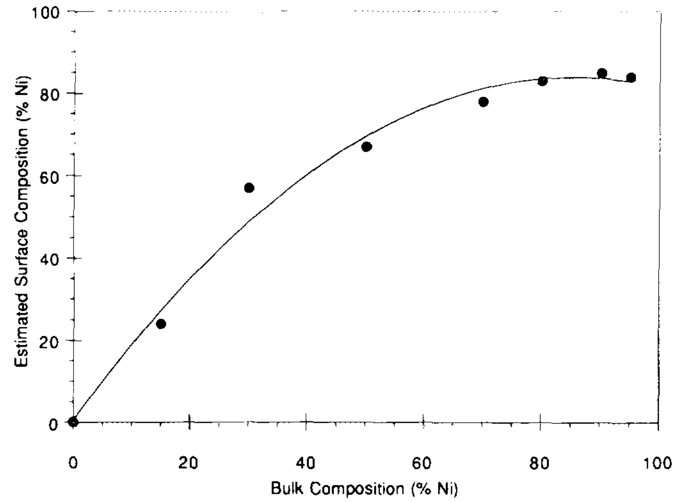


FIG. 3. Variation of estimated nickel composition at the catalyst surface from product distribution analysis, as a function of the bulk composition.

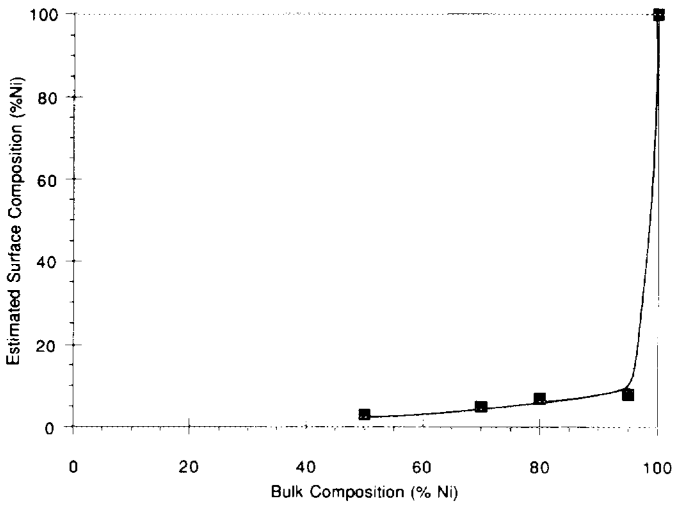


FIG. 4. Variation of estimated nickel composition at the catalyst surface based on hydrogen chemisorption measurements, as a function of bulk composition.

yields as a function of composition, Table 3. The observed increase in methane yield with increasing copper content up to 50% is consistent with an increase in the number of Cu–Ni units which are capable of adsorbing ethylene in the "end-on" configuration, suggesting that the two metals are homogeneously dispersed in the surface. At higher copper concentrations, the methane yields exhibit a dramatic decline, however, the corresponding decrease in overall reactivity is not so severe. One can rationalize these findings according to the notion that the metals now tend to collect up in the form of clusters rather than being uniformly dispersed.

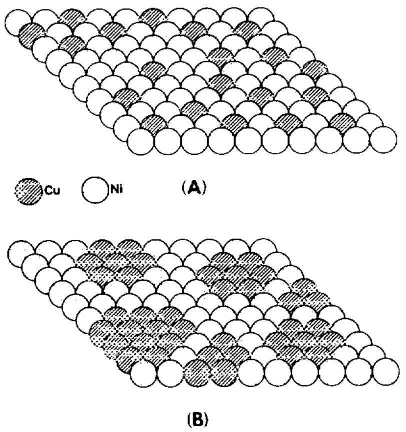


FIG. 5. Postulated arrangements of copper and nickel atoms in the surfaces of (A) copper–nickel (3:7) and (B) copper–nickel (7:3) alloys.

The arguments employed to derive the relationship shown in Fig. 3 can also be used with the experimental data presented in Table 3 to construct models which represent what the actual surfaces of the alloy particles might look like under reaction conditions. For this purpose we have selected the two alloys with bulk compositions of Cu–Ni (3:7) and (7:3), respectively. The postulated arrangements of atoms in the surface of these two alloys are shown in the schematic diagram, Fig. 5.

SUMMARY

The results of the present investigation indicate that deactivation of copper–nickel alloy catalysts during the decomposition of ethylene to produce carbon filaments is extremely complex and involves a number of factors which might contribute to the reversible nature of the process. One must take into consideration not only the events occurring at the gas/catalyst interface, but also changes in the chemistry of the particle resulting from dissolved carbon and hydrogen species and the influence of the deposited graphite at the rear of the particle. If hydrogen is added to the ethylene, then deactivation is shifted to higher temperatures. *In situ* electron diffraction analysis indicates that separation of the alloy occurs much more readily in the presence of ethylene than in hydrogen. Rejuvenation of a deactivated catalyst can be achieved by a lowering of the temperature to a previously active regime where electron diffraction demonstrates that the bulk alloy phase is reestablished. Under these circumstances it is postulated that the surface composition of the catalyst is restored to approximately its initial value. In conclusion, the deactivation phenomena associated with bimetallic systems appears to be dependent not only on the composition of the bimetallic system itself, but also on the gas composition and also on the nature of the metal/support interaction.

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REFERENCES

1. van der Plank, P., and Sachtler, W. M. H., *J. Catal.* **7,** 300 (1967).

2. van der Plank, P., and Sachtler, W. M. H., *J. Catal.* **12,** 35 (1968).

3. Cadenhead, D. A., and Wagner, N. J., *J. Phys. Chem.* **72,** 2775 (1968).

4. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24,** 283 (1972).

5. Sachtler, W. M. H., and Dorgelo, G. J. H., *J. Catal.* **4,** 654 (1965).

6. Helms, C. R., *J. Catal.* **36,** 114 (1975).

7. Watanabe, K., Hashiba, M., and Yamashina, T., *Surf. Sci.* **61,** 483 (1976).

8. Kuijers, F. J., and Ponec, V., *Surf. Sci.* **68,** 294 (1977).

9. Ng, Y. S., McLane, S. B. Jr., and Tsong, T. T., *J. Vac. Sci. Technol.* **17,** 154 (1980).

10. Webber, P. R., Rojas, C. E., Dobson, P. J., and Chadwick, D., *Surf. Sci.* **105,** 20 (1981).

11. Morris, M. A., Webber, P. R., and Zhang, Z. G., *Thin Solid Films* **156,** 65 (1988).

12. Cale, T. S., and Richardson, J. T., *J. Catal.* **79,** 378 (1983).

13. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **131,** 60 (1991).

14. Kim, M. S., Rodriguez, N. M., and Baker, R. T. K., *J. Catal.* **134,** 253 (1992).

15. Best, R. J., and Russell, W. W., *J. Am. Chem. Soc.* **76,** 838 (1954).

16. Oh, S. G., and Baker, R. T. K., *J. Catal.* **128,** 137 (1991).

17. Trimm, D. L., *in* "Progress in Catalyst Deactivation" (J. L. Figueiredo, Ed.), NATO Series A Applies Sciences, No. 54, p. 3. Martinus Nijholf Publishers, London, 1982.

18. van Langeveld, A. D., van Delft, F. C. M. J. M., and Ponec, V., *Surf. Sci.* **134,** 665 (1983).

19. Harberts, J. C. M., Bourgonje, A. F., Stephan, J. J., and Ponec, V. J., *Catal.* **47,** 92 (1977).

20. Rye, R. R., Greenlief, C. M., Goodman, D. W., Hardegree, E. L., and White, J. M., *Surf. Sci.* **203,** 101 (1988).

21. Weisweiler, W., and Mahadevan, V., *High Temp. High Pressures* **4,** 27 (1972).

22. Baker, R. T. K., Chudzinski, J. J., Bernardo, C. A., and Figureiredo, J. L., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1059. Chem. Institute of Canada, Ottawa, 1988.

23. Baker, R. T. K., and Sherwood, R. D., *J. Catal.* **70,** 198 (1981).

24. Simoens, A. J., Derouane, E. G., and Baker, R. T. K., *J. Catal.* **75,** 175 (1982).

25. Baker, R. T. K., and Chludzinski, J. J., *Carbon* **19,** 75 (1981).

26. McCarty, J. G., and Wise, H., J. Catal. **57,** 406 (1979).

27. Goodman, D. W., Kelley, R. D., Madey, T. E., and White, J. M., *J. Catal.* **64,** 479 (1980).

28. Nakamura, J., Hirano, H., Xie, M., Matsuo, I., Yamada, T. and Tanaka, K., *Surf. Sci.* **222,** L809 (1989).