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In-Situ Electron Microscopy Studies of Surface Segregation in Bimetallic Catalyst Particles

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We have used various techniques including *in-situ* transmission electron microscopy to examine the manner by which the catalytic action of platinum is modified by the introduction of either iron, cobalt, or nickel into the metal. Changes in the behavior of the noble metal have been investigated by the use of the probe reactions, catalytic oxidation, and hydrogenation of single-crystal graphite, which are known to be extremely sensitive to the chemical state of the catalyst surface. *In-situ* electron diffraction measurements showed that in all cases alloys were formed when the mixed system was treated in hydrogen. When such specimens were subsequently heated in oxygen the composition and chemical state of the particles changed significantly, the ferromagnetic metal tending to segregate to the catalyst–gas interface in the form of an oxide leaving platinum and residual alloy at the graphite interface. Under these conditions the catalyst was observed to undergo a spreading action along the graphite edge regions and it was interesting to find that in this bimetallic state there was a significant decrease in the catalytic activity of the noble metal toward graphite oxidation. © 1992 Academic Press, Inc.

INTRODUCTION

The successful application of bimetallic catalysts for a variety of commercial processes, including reforming, has prompted a considerable number of fundamental studies of such catalyst systems (*1, 2*). In addition to the enhanced activities and greater control of selectivities toward desired products which can be achieved with such catalysts, it is also found that bimetallic particles exhibit a higher resistance for longer times toward deactivation by poisoning and carbon deposition (*3, 4*). Probably the most widely studied bimetallic catalysts are those based on platinum (*5–7*).

A complicating factor when attempting to predict the behavior of a given bimetallic catalyst is the fact that one can never be absolutely certain of the surface composition when the system is in the form of small particles. Both experimental and theoretical studies have demonstrated that the surface composition of a bimetallic can be significantly different from the bulk composition due to one of the components preferentially segregating to the surface. Furthermore, the presence of an adjuvant gas can exert a major influence on the segregation process. The topic of surface segregation and the theoretical models which have been developed to explain this phenomena have been reviewed by Kelley and Ponec (*8*).

The manner by which metal particles catalyze the gasification of graphite in various gas environments has been observed directly with controlled atmosphere electron microscopy (CAEM) (*9*). These reactions are found to be extremely sensitive to the chemical nature of the catalyst particle at the graphite interface. Based on the data collected from many systems it has been shown that a given metal can be identified from the characteristic pattern of activity that it exhibits in such reactions. Baker and co-workers (*10–12*) have demonstrated that the concept of using catalyzed gasification of graphite as an *in-situ* microanalytical probe of bimetallic particles appears to be a viable approach. From a comparison of the

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behavior of a bimetallic system with that of its pure constituents, these workers showed that it was possible to determine which component preferentially segregated to the particle surface either under oxidizing or reducing conditions.

In the present work we have used the procedures outlined above to examine the effect of mixing platinum with cobalt, iron, and nickel, respectively. The information obtained about the surfaces of the bimetallic particles from the controlled atmosphere electron microscopy studies has been augmented by *in-situ* electron diffraction analysis which provides data of the bulk composition under the same conditions. In addition, thermogravimetric studies were conducted to ascertain the macroscopic behavior of the bimetallic catalyst on the graphite gasification reactions.

Bardi and co-workers (*13*) studied the interaction of oxygen with a platinum-20% cobalt alloy using XPS and LEED techniques. They found that at temperatures of about 425°C an epitaxial surface layer of CoO was formed and as the temperature was increased the oxide phase changed to that of Co_3O_4. Bartholomew and Boudart (*14*) performed characterization studies of the surface composition of carbon supported platinum alloy particles with both Mössbauer spectroscopy and chemisorption techniques. Treatment of the specimen in hydrogen at room temperature did not appear to introduce any changes in the surface composition compared to that of the bulk. In contrast, when these samples were reacted in air at 300°C, iron enrichment of the surface was found to occur. Dominguez and co-workers (*15*) employed X-ray diffraction and transmission electron microscopy to characterize graphite-supported platinum–nickel particles and reported that homogeneous alloys were formed following reduction in hydrogen at 850°C. Sedlacek and co-workers (*16*) claimed that the surface of clean platinum–nickel alloys is always enriched in platinum, however, this relationship is reversed when the system is treated in oxygen. Surface enrichment in nickel following oxidation was also found by Wielers and co-workers (*17*) from their investigations of silica-supported platinum–nickel catalysts.

Studies of the combination of these metals poses some intriguing questions when one attempts to predict the manner in which the bimetallic particles may operate during the oxidation of graphite. In oxygen, platinum supported on graphite is present in the metallic state at temperatures in excess of 350°C and remains as discrete particles, which facilitate the removal of carbon atoms from the graphite edge regions by a channeling mode (*18*). On the other hand, at temperatures below 880°C, cobalt forms oxides which tend to spread along the graphite prismatic faces in the form of a thin film and catalyze oxidation by the edge recession mode (*19*). Both nickel and iron are readily converted to the highest oxidation state and since the respective oxides are not easily reduced to a lower state the particles cannot perform a redox cycle at the graphite interface, a necessary step in the catalytic oxidation of graphite, and as a consequence, exhibit very little activity for this reaction (*20*).

EXPERIMENTAL

The details of the CAEM technique have already been extensively documented (*21*). For experiments using this approach spectrographic pure metals in an equal atomic ratio were deposited onto transmission specimens of single-crystal graphite to produce a two-monolayer coverage by evaporation from a tungsten filament at a residual pressure of 10^{-6} Torr. *In-situ* electron diffraction experiments were performed in a modified JEOL 200CX TEM/STEM microscope (*22*). The samples used in these experiments were prepared in the same manner as those for the CAEM studies with the exception that heavier metal loadings were used in this case (about 20 Å in total thickness) to achieve better contrast in diffraction patterns which would otherwise be obscured by the strong background pattern of the graphite support.

Temperature programmed gasification reaction studies of larger scale specimens were carried out in a Cahn 2000 microbalance reactor which was fitted with a furnace capable of operating at temperatures up to 1100°C. For thermogravimetric experiments, the catalyst–graphite samples (Ultra "F" purity, Ultracarbon Co.) were prepared by the incipient wetness technique using aqueous solutions of a platinum ammonium complex (Engelhard Co) and nitrates of the ferromagnetic metals (reagent grade, Fisher Co.). The impregnate was dried overnight at 110°C, calcined at 250°C for 4 h reduced in hydrogen at 500°C for 12 h, and finally passivated using a 2% oxygen–helium mixture before removal from the preparation vessel. The ratio of the metals in the bimetallic mixtures introduced onto the graphite was confirmed by Energy Dispersive Spectroscopy.

The reactant gases used in this work, oxygen, hydrogen, and helium, were obtained from Alphagaz Co. with stated purities of 99.999% and were used without further purification.

RESULTS

In-situ Transmission Electron Microscopy Studies

(*a*) *Catalytic hydrogenation of graphite by platinum–cobalt.* When the graphite samples containing about a 2-monolayer coverage of platinum–cobalt (1 : 1) were exposed to 1 Torr hydrogen the deposited film nucleated to form discrete particles of approximately 2.5-nm diameter at 365°C. In order to ensure that the metals were homogeneously mixed, specimens were generally held at this temperature for periods of up to 3 h. On continued heating, particles located at edge and step sides were initially observed to wet and then spread along these regions at about 480°C. As the temperature was gradually raised to 560°C the coated edges started to undergo recession. This form of attack persisted up to 930°C, at which point the rate of edge recession declined as particles started to reform and eventually proceeded to cut channels across the basal plane. At 1175°C a dramatic change in the characteristics of the particles associated with channels was observed. Under these conditions there was a tendency for active particles to become progressively smaller in size, and this behavior produced a stepped appearance to the channels. Eventually, particles completely disappeared from their location at the tips of channels and the catalyzed hydrogasification reaction came to a complete halt. A typical example of this sequence of events is presented in Fig. 1. It was significant that catalytic activity could not be restored by either raising or lowering of the temperature.

Detailed kinetic analysis of many reacting sequences has enabled us to determine values for the apparent activation energy for the edge recession mode of attack (14.8 ± 2 kcal/mole) and for the channeling action (32.5 ± 3 kcal/mole), Fig. 2. This latter data was obtained from 20-nm particles cutting channels of similar depth.

In-situ electron diffraction experiments were performed over the temperature range 20 to 900°C while a platinum–cobalt/graphite specimens was exposed to 0.25 Torr hydrogen. In these experiments an attempt was made to follow changes in the chemical state of the bimetallic catalyst particle supported on graphite at each stage of the hydrogenation reaction. From analysis of the data presented in Table 1 it was found that the two metals formed an alloy, PtCo, at 785°C and the particles remained in this state up to 900°C. In the diffraction pattern analysis the spots of the graphite substrate were used as an internal standard for calibration of the patterns of all other materials.

(*b*) *Catalytic hydrogenation of graphite by platinum–iron.* Nucleation of particles of platinum–iron supported on graphite was extremely sluggish when the system was heated in hydrogen; commencing at 370°C and not being complete until 470°C. With the exception of a slight increase in the average particle size little change in the appearance of the specimen was observed until the tem-

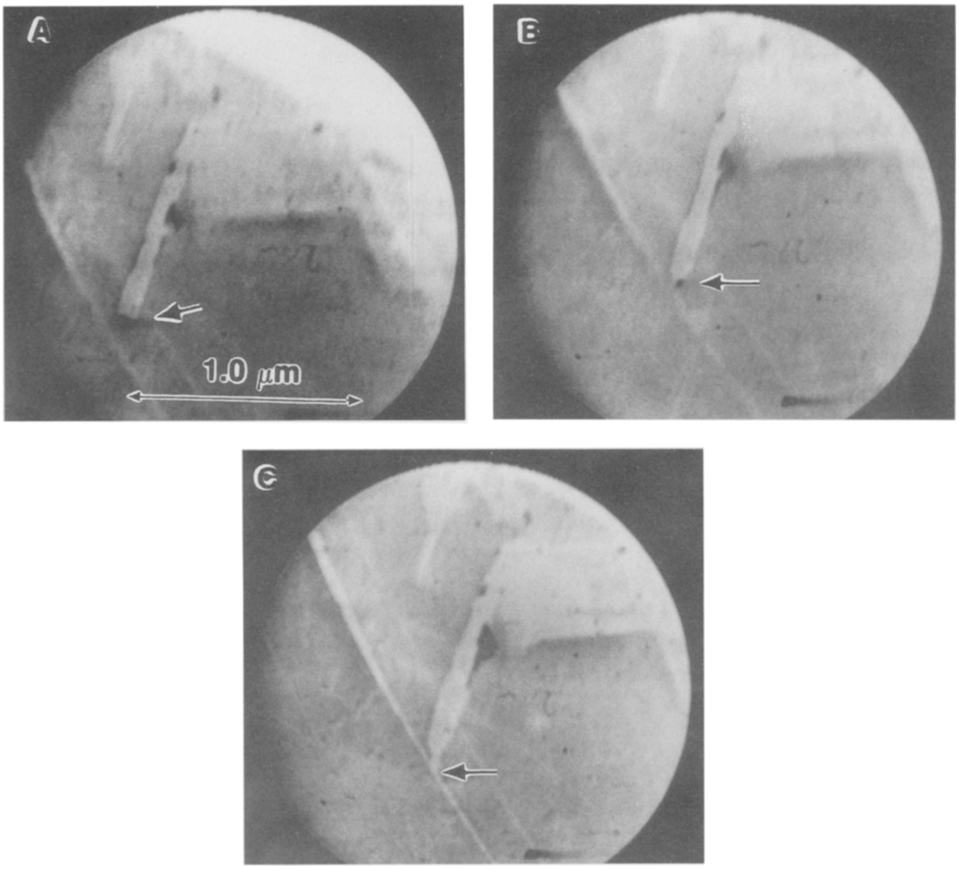

FIG. 1. (A–C) Sequence showing the gradual disappearance of Pt–Co particles located at the tips of channels at 1175°C in 1.0 Torr hydrogen.

perature was raised to 760°C; at this point some of the particles located on the basal plane were observed to exhibit mobility. On continued heating up to 840°C, particles which had accumulated at edge and steps sites were observed to undergo a wetting action and eventually proceeded to cut channels across the graphite surface at a relatively slow rate. Initially, this action was limited to particles of about 25-nm diameter, however, as the temperature was increased, larger particles were observed to propagate channels. In contrast, the majority of particles which were on the graphite basal plane adopted either triangular or rectangular shapes. It was signficant that on continued heating up to 930°C particles which were responsible for creating channels started to spread and eventually disappear. This behavior coincided with a loss in catalytic action. Also, at this time, it was apparent that the majority of particles on the basal plane were undergoing a spreading action which eventually resulted in their complete disappearance. No further changes in appearance of the specimen were observed even when the temperature was raised to 1050°C.

In a complementary series of experiments, *in-situ* electron diffraction experiments were performed as platinum–iron/graphite specimens were progressively heated from room temperature up to 900°C in hydrogen. From analysis of the diffraction data, presented in Table 2, it was possi-

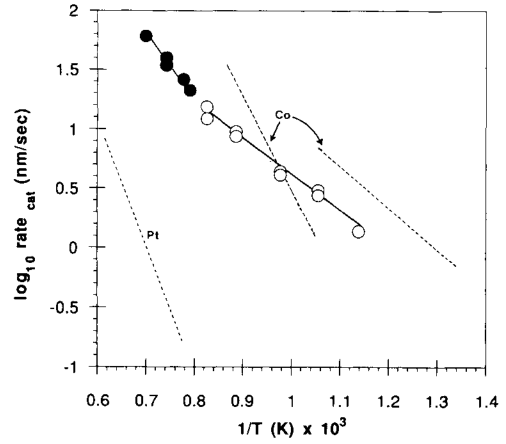

FIG. 2. Arrhenius plot of Pt–Co catalyzed hydrogasification of graphite, ○ = edge recession, ● = channeling action. Shown for comparison purposes is the behavior of the single components.

ble to conclude that platinum–iron alloys were formed in the system and remained stable up to the highest temperatures attained in this study. Furthermore, the alloys preserved their form when the specimens were subsequently cooled to ambient temperature.

(*c*) *Catalytic hydrogenation of graphite by platinum–nickel.* When the platinum-nickel/graphite samples were treated in 1 Torr hydrogen, the mixed metal film ruptured to initially form a network of short fibers and these structures eventually transformed into discrete globular particles at temperatures between 320 and 370°C. In contrast to the previous system the nucleation step occurred in a uniform fashion all over the surface in a relatively short time.

TABLE 1

Electron Diffraction Analysis of Pt–Co/Graphite at 785°C in 0.2 Torr H_2

Calculated *d*-spacings (nm)	*d*-spacings (nm) PtCo
0.213	0.217 (101)
0.187	0.184 (110)
0.133	0.132 (113)

TABLE 2

Electron Diffraction Pattern Analysis of Pt–Fe/Graphite at 810°C in 0.2 Torr H_2

Calculated *d*-spacings (nm)	*d*-spacings (nm)		
	$PtFe_3$	PtFe	Pt_3Fe
0.213	0.217 (111)		
0.183		0.186 (002)	
0.130		0.128 (300)	0.129 (300)

As the temperature was progressively raised, a survey of many areas of the specimen showed that there was little evidence of catalytic attack and the only obvious change in the appearance of the particles was that they exhibited a small increase in average size. Continuous observation of particles located on the edge and step regions showed that they remained in a nonwetting state until 940°C. At this stage of the reaction, all particles irrespective of their location underwent a spreading action and were no longer visible. As with the platinum–iron/graphite–hydrogen system there was insufficient quantitative kinetic data available from the dynamic studies to enable us to evaluate an apparent activation energy from the catalytic effect of either of these alloys on the hydrogasification reaction.

In a separate series of experiments *in-situ* electron diffraction studies were performed over the temperature range 20 to 900°C in the presence of hydrogen the analytical data obtained from the electron diffractin patterns is presented in Table 3, where it can be seen that with only one exception, the measured *d*-spacings do not correspond to PtNi or either of the pure components. Since there is no crystallographic data available for $PtNi_3$, an alloy which according to the phase diagram will form at temperatures greater than 450°C, we believe that the unmatched *d*-spacings are those associated with the formation of this alloy.

(*d*) *Catalytic oxidation of graphite by platinum–cobalt.* Platinum–cobalt/graphite specimens which had initially been treated

TABLE 3

Electron Diffraction Pattern Analysis of Pt–Ni/Graphite at 800°C in 0.2 Torr H_2

Calculated *d*-spacings (nm)	*d*-spacings (nm)				
	Pt	Ni	Ni_3C	PtNi	$PtNi_3$
0.242					?
0.201					?
0.183					?
0.149				0.150 (112)	?

in hydrogen at 365°C for 1 h were cooled, the hydrogen removed, and then the system reheated in 2 Torr oxygen at 370°C. Particles which had collected at edge regions were observed to undergo a wetting and spreading action and this transformation in morphology was followed by oxidation of the graphite via the catalyzed edge recession mode. The rate of edge recession became appreciable above 650°C and continued to increase in a uniform manner as the temperature was progressively raised to 1050°C. Figure 3 shows a sequence of attack of graphite according to the edge recession mode by a film of platinum–cobalt at 880°C. When other specimens which had been previously reacted in hydrogen to the point where loss of catalytic activity was realized were reheated in oxygen, then in this case, it was necessary to increase the temperature to 750°C in order to induce reaction. At this temperature the fluted channels were observed to undergo recession without any evidence of particle renucleation and in other areas of the specimen attack by the edge recession mode was also observed to occur.

In some cases, following restoration of catalytic activity by the oxidation step, specimens were cooled to room temperature and the oxygen replaced with hydrogen. On subsequent reheating of the specimen, particles were observed to reform along the edges of the previously dormant channels and eventually started to create fresh secondary smaller channels emanating from the sides of the original ones.

From analysis of the video recordings of numerous reaction sequences it has been possible to obtain quantitative kinetic information on the edge recession process, which is represented in the form of an Arrhenius plot in Fig. 4. From the slope of the line, an apparent activation energy of 23.8 ± 3 kcal/mole was determined. It is noticeable that the reaction rate for the oxidation of graphite by the bimetallic catalyst system consisting of platinum on cobalt is significantly lower than that exhibited by either of its pure components. In a separate series of experiments, *in-situ* electron diffraction analysis was conducted on the platinum–cobalt/graphite system to follow changes in the chemical nature of the bimetallic catalyst particles in an oxidizing environment. The data obtained from this study is presented in Table 4 from which it can be seen that the alloy formed in reducing conditions was subsequently transformed to a mixture of cobalt oxides, Pt_3Co and Pt during reaction of the system in oxygen.

(*e*) *Catalytic oxidation of graphite by platinum–iron*. It was necessary to treat the platinum–iron/graphite system at 600°C in hydrogen for 1 h in order to produce bimetallic particles. In some cases experiments were conducted on specimens which had initially been used in the hydrogenation reaction. Identical behavior was observed from both sets of specimens when they were subsequently reacted in 2 Torr oxygen.

As the temperature was slowly raised to 540°C the particles located on the basal plane were observed to gradually disappear and at the same time those which had accumulated at the edge and step regions underwent a wetting and spreading action along the prismatic faces and this behavior led to the onset of gasification which commenced at 600°C. The rate of edge recession became significant when the temperature was increased to 740°C and exhibited a steady enhancement as the temperature was progressively raised to 1100°C. Occasionally, it was observed that when particles came into contact with a receding edge they suddenly

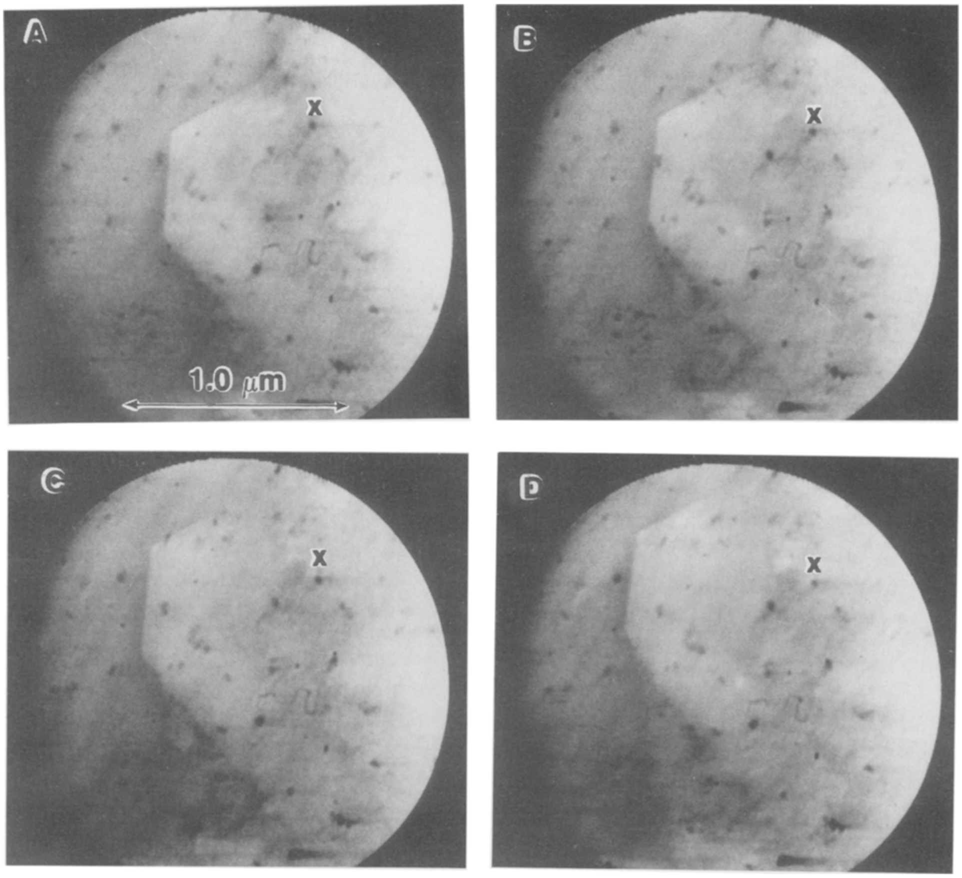

FIG. 3. (A–D) Sequence showing the edge recession mode of attack exhibited by Pt–Co during oxidation of graphite at 880°C in 2.0 Torr oxygen. "x" indicates the location of a static particle on the graphite basal plane.

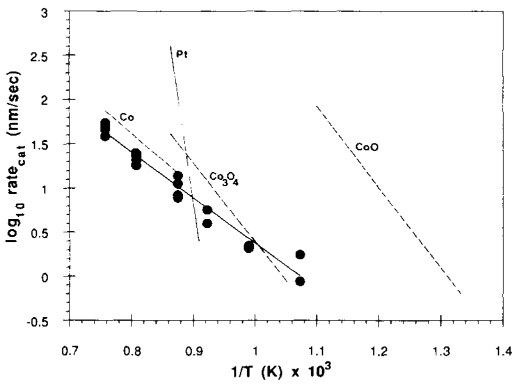

FIG. 4. Arrhenius plot of Pt–Co catalyzed oxidation of graphite. Shown for comparison purposes is the behavior of the single components.

started to cut channels which followed a random path across the surface. It was, however, evident that the major route by which graphite was being gasified was via the edge recession mode.

Quantitative kinetic analysis was carried out on many edge recession sequences and the data obtained from these measurements is presented in the form of an Arrhenius plot in Fig. 5. From the slope of the line, it was possible to evaluate an apparent activation energy of 24.5 ± 3 kcal/mole for the platinum–iron catalyzed oxidation of graphite.

In-situ electron diffraction analysis was conducted on the platinum–iron system to determine the chemical state of the catalyst

TABLE 4

Electron Diffraction Pattern Analysis of Pt–Co/Graphite at 850°C in 0.2 Torr O_2

Calculated d-spacings (nm)	d-spacings (nm)			
	Co_3O_4	CoO	$CoPt_3$	Pt
0.471	0.467 (111)			
0.290	0.286 (220)			
0.249		0.246 (111)		
0.228				0.227 (111)
0.205	0.202 (400)			
0.159			0.157 (211)	
0.146	0.143 (440)			

particles at various stages in the graphite–oxygen reaction. Initially, the specimen was treated in hydrogen to 600°C, a condition where alloy formation occurred and then cooled to room temperature before treating in 0.2 Torr oxygen at temperatures up to 900°C. From the analysis of a series of diffraction patterns it was apparent that the platinum-iron alloy formed under reducing conditions was subsequently transformed to produce a mixture of iron oxides (Fe_2O_3 and Fe_3O_4) in addition to Fe_3Pt, $FePt_3$ and Pt, when the system was heated in oxygen (Table 5). Furthermore, the catalyst remained in this state even after the sample was cooled to room temperature.

(*f*) *Catalytic oxidation of graphite by platinum–nickel.* Prior to treatment of the platinum–nickel/graphite systems in oxygen the specimens were heated in hydrogen at 375°C for 1 h to ensure uniform nucleation of bimetallic particles. When these specimens were reacted in 2 Torr oxygen the original dense globular particles transformed into flat structures which tended to spread on the graphite and on continued heating eventually coalesced to produce an interconnected network.

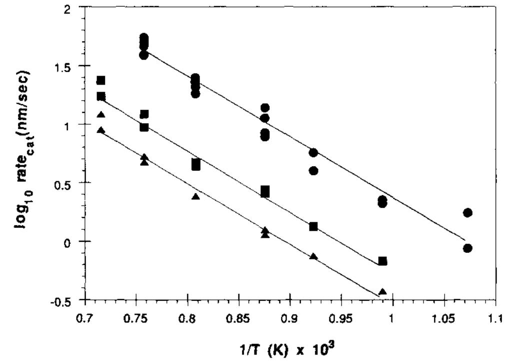

FIG. 5. Arrhenius plots for the catalytic oxidation of graphite in the presence of Pt–Co (●); Pt–Fe (■), and Pt–Ni (▲).

The first signs of attack of graphite were observed along the edges and steps of the specimens when the reaction temperature was raised to 600°C. Particles located at these sites were seen to initially wet and then spread to form a film along these features. Sections of the specimen where this phenomenon occurred immediately proceeded to undergo gasification by the edge recession mode and the rate of this process became appreciable as the temperature reached 750°C. Edge recession remained the exclusive form of catalytic attack up to 1100°C, the highest temperature reached in these experiments.

Form the detailed kinetic analysis of several experiments an apparent activation energy of 23.9 ± 3 kcal/mole was derived for the catalytic oxidation of graphite by platinum–nickel catalysts. For comparison purposes this data is presented along with that determined for platinum–iron and platinum–cobalt bimetallic catalysts in Fig. 5.

After a specimen was heated to 800°C in hydrogen it was cooled and hydrogen replaced with oxygen and reheated to 850°C. From the analysis of *in-situ* electron diffraction patterns it was determined that a mixture of nickel oxide, a platinum–nickel alloy and platinum was present under these conditions, Table 6.

Thermogravimetric Studies

In order to correlate the experimental data obtained from the micro-scale studies of the three bimetallic systems on the graphite oxygen reaction with the macroscale behavior, a series of thermogravimetric reac-

TABLE 5

Electron Diffraction Pattern Analysis of Pt–Fe/Graphite at 850°C in 0.2 Torr O_2

Calculated *d*-spacings (nm)	*d*-spacings (nm)				
	Fe_2O_3	Fe_3O_4	Fe_3Pt	$FePt_3$	Pt
0.463		0.467 (111)			
0.294	0.295 (220)				
0.254	0.252 (110)				
0.228					0.227 (111)
0.213	0.215 (021)		0.217 (111)		
0.160	0.160 (211)			0.158 (211)	
0.148	0.145-0.149				

tion studies of larger scale specimens was performed. Temperature programmed oxidation experiments of graphite specimens containing similar loadings of 50 : 50 mixtures of platinum with the respective ferromagnetic metals was compared with that of pure graphite and graphite impregnated with the pure components cobalt, nickel, iron, and platinum. Figure 6 shows the weight loss curves obtained from the various samples under exactly the same operating conditions in the microbalance. It was found that graphite impregnated with either iron or nickel exhibited identical oxidation behavior to that of uncontaminated graphite indicating that neither of these metals participated in the graphite–oxygen reaction. On the other hand, it is clear that both cobalt and platinum exert a significant catalytic influence on the reaction. Examination of the behavior of the bimetallic system shows that while platinum addition to either nickel or iron increases the catalytic activity of these metals toward graphite oxidation, when the noble metal is mixed with cobalt the behavior of the bimetallic is significantly less than that of either of its pure components.

TABLE 6

Electron Diffraction Pattern Analysis of Pt–Ni/Graphite at 800°C in 0.2 Torr O_2

Calculated *d*-spacings (nm)	*d*-spacings (nm)			
	NiO	NiPt	Ni_3Pt	Pt
0.242	0.241 (111)		?	
0.228			?	0.227 (111)
0.213		0.216 (111)	?	
0.148	0.148 (220)	0.150 (112)	?	

DISCUSSION

Catalytic Hydrogenation of Graphite

The overall qualitative behavior in the catalyzed hydrogenation of graphite by platinum–cobalt catalyst particles appears to parallel that found for cobalt under the same conditions; hydrogenation of graphite is found to take place by the edge recession mode over the low-temperature region, and the catalytic action undergoes a transformation to the channeling mode as particles are reformed at the higher temperature range. Furthermore, a comparison between the apparent activation energies exhibited by the platinum–cobalt system and those obtained with cobalt for this reaction shows that, within experimental error the values are in close agreement. It appears therefore, that the bimetallic system shares a common rate-determining step with cobalt for this reaction. However, the intrinsic catalytic activity exhibited by platinum–cobalt catalysts was between those found for its pure constituents.

The observed behavior of the bimetallic catalyst in the graphite–hydrogen reaction can be rationalized according to the notion that surface segregation of platinum in the

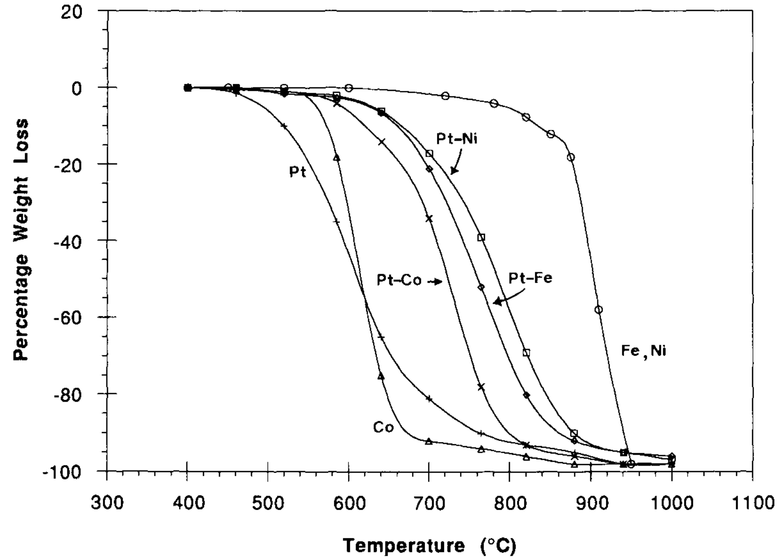

FIG. 6. Temperature programmed oxidation of graphite in the presence of various metallic and bimetallic catalysts.

mixed metal particles occurs in a reducing environment. In this context, it is instructive to examine the possibility of surface segregation of platinum in bimetallic systems consisting of platinum and ferromagnetic metals simply by reference to the following two major theories: "bond breaking" (*23*) and atomic size difference (*24*). According to the former theory, surface segregation of ferromagnetic metals is expected to occur because the heat of sublimation values of ferromagnetic metals are smaller than that of platinum. However, this segregation phenomenon becomes complex when one considers the strain energy effect due to the significant difference in atomic sizes of platinum and ferromagnetic metals. If platinum is in excess, i.e., functioning as a solvent, the theory predicts that surface enrichment of ferromagnetic metals would be further enhanced, however, this condition does not appear to be borne out in practice since Burton and Polizzotti (*25*) reported no segregation of iron or nickel even in diluted systems such as 2% Fe–Pt and 2% Ni–Pt. On the other hand, in cases where the concentration of ferromagnetic metals exceeds that of platinum, then the noble metal atoms will tend to move toward the surface in order to lower the elastic strain energy in the bulk resulting from the lattice mismatch, and this effect will be compensated by the former (bond-breaking) effect. Under such circumstances, one would not expect to observe surface segregation.

Sedlacek and co-workers (*16*) used Auger and photoelectron spectroscopic techniques to demonstrate that clean surfaces of platinum–nickel alloys were enriched in platinum and their surface concentrations tended to increase as that of platinum in the bulk increased. A similar conclusion was reached by Deckers and co-workers (*26*) from their investigation of the (111) faces of a platinum–nickel (50 : 50) single crystal. Thus the preferential surface segregation of platinum in the platinum–ferromagnetic metal mixtures seems to be a distinct possibility.

Based on a comparison of the qualitative and quantitative behavior of platinum–cobalt particles with that of the single components coupled with *in-situ* electron diffraction analysis, it is clear that in the presence of hydrogen, platinum, and cobalt interact to form alloy particles. During the catalytic hydrogenation of graphite it is possible that the surfaces of the catalyst in contact with the gas phase are enriched in platinum, whereas those surfaces in contact with the carbon interface are richer in cobalt. We believe that similar behavior can also account for the results obtained with both platinum–iron and platinum–nickel systems which exhibit very little activity in the graphite–hydrogen reaction.

The observed spreading action of particles located on the basal plane and the concomitant gradual loss of channeling activity in the bimetallic/graphite–hydrogen systems at elevated temperatures is extremely fascinating since only nickel of the single components exhibits this behavior (*27, 28*). There is little doubt that in the deactivated state, the mixed metal species remain in the form a thin film along the walls of the channel, rather then being lost due to volatilization, since the influence of the additive is once again observed following an intermediate treatment in oxygen. It is possible that during the spreading action a reconstruction of the deposited catalyst film occurs and crystallographic faces are created which favor the precipitation of graphite at the metal–gas interface. This action will result in the formation of a graphite overlayer on the mixed-metal surface which is responsible for preventing the access of hydrogen to the metal surface and ultimately leads to loss of catalytic activity. This rationale is consistent with the finding that it was essential to heat the deactivated system in oxygen to 750°C in order to restore catalytic activity, whereas fresh samples exhibited oxidation behavior at significantly lower temperatures. Such a high-temperature treatment will result in gasification of the graphite via the uncatalyzed route, and this action will once again expose the metal to the gas environment.

Catalytic Oxidation of Graphite

The typical events observed during the oxidation of graphite by the platinum-ferromagnetic metal catalysts are compared with those displayed by the constituent pure metals in Table 7. The observation that a platinum–cobalt catalyst attacks graphite exclusively by the edge recession mode in the presence of oxygen is at first sight somewhat surprising, since under these same conditions platinum operates by the channeling mode over the whole temperature range (*18*) and furthermore, cobalt also promotes oxidation of graphite by the channeling mode at temperatures in excess of 880°C (*19*). In addition, the intrinsic reaction rates exhibited by platinum–cobalt catalysts for this reaction were significantly lower than those found for either of the single metals over the whole range of experimental conditions, a result confirmed by the thermogravimetric studies of larger scale specimens. This pattern of behavior would seem to indicate that the observed edge recession is being catalyzed by species containing both components rather than by a single component arising from a phase separation process.

Consideration of the information obtained from the *in-situ* electron diffraction analysis provides some insights into the complex character of the prevailing catalytic species and this data coupled with that derived from the CAEM studies allows us to make some predictions regarding the nature of the chemical states which tend to segregate to the graphite–catalyst and oxygen–catalyst interfaces, respectively. For the case of platinum–cobalt/graphite system *in-situ* electron diffraction analysis indicated that platinum–cobalt alloys formed under reducing conditions underwent transformation into a mixture consisting of cobalt oxides, Pt_3Co and platinum upon subsequent reaction in oxygen. Both the intrinsic measurements of the action of individual catalytic entities and the macro-scale results demonstrate that although the catalytic oxidation of graphite takes place by the most efficient mode, i.e., edge recession, the rate of this process is significantly lower than that displayed either of the single components for the graphite–oxygen reaction. We believe that it is possible to rationalize the experi-

TABLE 7

Comparison of the Catalytic Action of Pt–Co, Pt–Ni, and Pt–Fe with That of the Single Components on the Graphite–Oxygen Reaction

Event	Pt-Co	Pt-Ni	Pt-Fe	Pt (*18*)	Co (*19*)	Ni (*28*)	Fe (*20*)
Onset of edge recession	650°C	740°C	740°C	—	475°C	—	—
Onset of catalytic channeling action	—	—	—	735°C	880°C	1150°C[a]	850°C[a]
Apparent activation energy (kcal/mole)	23.8	23.9	24.5	81.3	42.4 39.5 30.1	—	—

[a] This behavior was only exhibited by few isolated particles.

mental data according to the following arguments:

(i) Under these conditions it is probable that the surface of the catalyst is enriched in cobalt, which is thermodynamically favored to form Co_3O_4, and as a result platinum will tend to segregate to the graphite interface.

(ii) Since oxides are believed to form a strong interaction with the oxygenated graphite surfaces (*9*), it is not unreasonable to expect that the cobalt oxide layer promotes the spreading action of the catalyst at the graphite interface, which subsequently results in attack by the edge recession mode.

(iii) In this configuration, the ability of Co_3O_4 to undergo a redox cycle at the graphite–gas interfaces is hindered since platinum is acting as a barrier toward carbon dissolution, a key step in the process, and hence the catalytic activity of the mixed metal system is significantly decreased over that of the single components.

(iv) At temperatures in excess of 880°C previous studies have shown that cobalt oxides are converted to the metallic state, and this transformation is accompanied by a change in the wetting characteristics of the catalyst on graphite, which results in the reformation of particles at the edge regions and a concomitant modification in the mode of catalytic action from edge recession to channeling (*19*). Clearly the presence of platinum at the graphite interface impedes this transformation and as a result the tendency for the catalyst to undergo the reconstruction mentioned above is prevented.

(v) Unfortunately, the electron diffraction analysis does not allow us to determine definitively whether the Pt_3Co or Pt is the favored chemical entity at the graphite interface.

A comparison of the three mixed platinum–ferromagnetic metal systems shows that they share many common features in their behavior on the graphite–oxygen reaction. In all cases it is seen that they exert a retarding effect on the rate of catalytic oxidation of the graphite by platinum, and *in-situ* electron diffraction analysis shows the presence of a mixture of ferromagnetic metal oxides, alloys and pure platinum. Therefore it is suggested that the concept of preferential surface segregation of ferromagnetic metals postulated for the platinum–cobalt system can also be extended to both platinum–iron and platinum–nickel systems. This argument is consistent with data obtained by many other workers (*13, 14, 16, 17*).

Continuous observations of the catalyzed oxidation reactions shows that these cata-

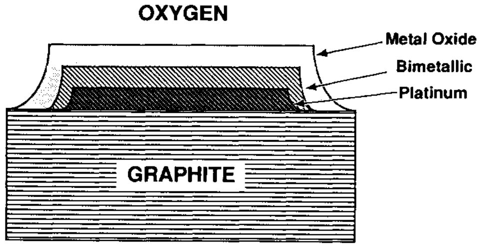

FIG. 7. Schematic representation of the postulated behavior of platinum–ferromagnetic mixtures on graphite when heated in oxygen.

lysts all operate by the same mode of edge recession with identical activation energies (~24 ± 3 kcal/mole). In this context, it should be noted that of the three ferromagnetic metals, only cobalt is found to exhibit a significant catalytic activity for the oxidation of graphite. Both nickel and iron tend to form very stable oxides under these conditions, and as a consequence are unable to undergo the required redox cycle at the graphite interface (*19*). It is clear therefore that the observed activity of these systems, particularly in the case of iron and nickel, is due to the presence of platinum in the mixtures. Furthermore, the finding that these systems have the same activation energy suggests the existence of a common rate-determining step. Based on this information, we speculate that in all cases platinum tends to preferentially segregate to the graphite interface and the rate determining step depends on both carbon solubility and diffusion through this component. It is possible that a redox cycle could occur at the oxide/alloy interface. A somewhat simplified description of the catalyst configuration at graphite edges is presented in the schematic diagram, Fig. 7.

It is apparent that the ability of platinum to catalyze the removal of carbon deposits produced during a hydrocarbon conversion reaction will be seriously hindered if any of the ferromagnetic metals is deliberately or inadvertently introduced into the catalyst. On the other hand, from a consideration of the above concepts coupled with a reasonable understanding of the surface segregation phenomena such a combination could be used for the development of a bimetallic system to control the oxidation characteristics of carbonaceous materials.

SUMMARY

In-situ electron microscopy studies of bimetallic catalysts containing platinum and ferromagnetic metals dispersed on graphite have shown that in reducing environment alloys are formed, and that in this state the wetting properties of the mixed system are significantly changed from those exhibited by the single components. In the presence of oxygen catalytic attack of graphite by the bimetallics took place via the edge recession mode. It was interesting to find that addition of ferromagnetic metals to platinum decreased the catalytic activity of the noble metal toward graphite oxidation, and this retarding effect is believed to be associated with the preferential segregation of the ferromagnetic metals, in the form of oxides, to the surfaces of the bimetallic catalyst particles.

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