Catalytic Gasification of Graphite by Bimetallic Particles

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Controlled-atmosphere electron microscopy was used as a microanalytical probe of Pt : Ir (80 : 20 atomic ratio) on single-crystal graphite. The test reaction for this probe was the catalytic gasification in 5 Torr oxygen. Continuous observation of samples prepared by vacuum evaporation of a Pt : Ir alloy wire onto graphite showed the particles propagated shallow channels emanating from edges and steps on the graphite surface for temperatures near 670°C; increasing the temperature up to 950°C led to increased channeling activity; near 1000°C the catalytic gasification ceased; finally, at higher temperatures (ca. 1030°C), channeling recommenced and particle mobility was observed. This behavior is characteristic of Ir particles, and no particles showing Pt behavior were seen. Thus, Pt : Ir on single-crystal graphite forms alloy particles, the surface of which is enriched with Ir in an oxidizing atmosphere. A similar series of experiments performed with a Pt : Rh alloy showed that the Rh component preferentially segregates to the surface of the particles.

INTRODUCTION

Over the past few years there has been increasing interest in the behavior of supported bimetallic systems (*1, 2*). They exhibit unusual selectivity patterns (*3*) and have a high tolerance toward coke buildup (*4*), features which make them very attractive as catalysts for several hydrocarbon conversion processes. One of the most intriguing problems pertaining to bimetallic catalysts is the question of what is the composition of the surface during exposure to the reactant gas. The advent of a number of sophisticated surface chemical tools, together with the more conventional hydrogen chemisorption studies, has heralded a major assault on this aspect.

Capitalizing on the observation that copper does not chemisorb hydrogen very strongly, several workers (*3, 5, 6*) have used this property to determine the amount of copper present in the surface of nickel–copper alloys. This selective chemisorption approach is obviously limited to examination of systems which exhibit widely differ-

ent chemisorption characteristics for a given gaseous adsorbate. Spectroscopic techniques have been used to examine the surface of various alloys. These include Auger spectroscopy (AES) (*7–9*), photoelectron spectroscopy (XPS) (*10*), and secondary ion mass spectroscopy (SIMS) (*11*). Derouane (*12*) reviewed the relative merits of these and other surface tools, which all suffer from a common limitation, namely, that the specimen has to be examined under high-vacuum conditions, nominally 10^{-15} Torr.

In situ measurements can be performed with Mössbauer spectroscopy, and Garten (*13*) has used this approach to demonstrate that bimetallic clusters are formed during reduction of $PdFe/\eta\text{-}Al_2O_3$ catalysts, prepared by conventional procedures. Unfortunately Mössbauer spectroscopy can only be applied to systems which contain certain elements such as Fe, Sn, Co, Ru, or Au and there are difficulties in deconvoluting the spectrum into surface and bulk components (*14*).

Recently Prestridge *et al.* (*15*) performed a very elegant study with high-resolution transmission electron microscopy, demonstrating that in the Cu–Ru/silica system,

small particles (6-nm diam) were in the form of rafts consisting of a layer of Ru atoms covered by a layer of Cu atoms. Scanning transmission electron microscopy (STEM), the latest in the line of electron optical techniques, has the capability of generating crystallographic and chemical information from regions as small as 2 nm. Chen and Schmidt (16) have used STEM to examine the structure, sintering rates, and chemical composition of Pt–Pd crystallites supported on SiO_2 after heating in various gases. With conventional electron microscopy one also encounters limitations in that materials can only be viewed in a vacuum environment, confining observations to the postreaction state, which can give misleading information. This drawback is readily overcome by controlled-atmosphere electron microscopy (CAEM), where it is possible to observe the appearance of the specimen while it is undergoing reaction (17).

In the current investigation CAEM has been used as a microanalytical probe of Pt–Ir and Pt–Rh particles on single-crystal graphite. The test reaction for this probe was the catalytic gasification of graphite in 5 Torr oxygen, a reaction which is extremely sensitive to the nature of the catalyst surface. By comparing the catalytic behavior of the alloys with that of the pure constituents on the graphite–oxygen reaction, it has been possible to determine in the bimetallic systems which component preferentially segregated to the particle surface.

EXPERIMENTAL

This work was conducted in the controlled-atmosphere electron microscope (17).

Natural single-crystal graphite was obtained from Ticonderoga, New York. The crystals were released from the pyroxene mineral in which they are embedded by repeated leaching in concentrated hydrochloric acid, followed by treatment in hydrofluoric acid, and finally washing the crystals in distilled water. Prolonged inter-

action with hydrochloric acid is necessary for the complete removal of Ca salts. If this step is not performed proficiently, then on addition of hydrofluoric acid Ca will be left as a residue on the crystals as the fluoride salt and function as a catalyst in subsequent reactions (18). The surface purity of graphite specimens used in this study was checked with XPS, which showed only those peaks attributable to either C or O.

Platinum–iridium and platinum–rhodium, both 80 : 20 atomic ratio, were introduced onto the graphite transmission specimens by evaporation of alloy wires (99.99% pure) from a tungsten filament at a residual pressure of 5×10^{-6} Torr. Subsequent heating of these specimens in the gas reaction cell resulted in nucleation of the deposited alloy films, which would be expected to show significant variations in composition (16).

The reactant gas used in this investigation, oxygen, was 99.99% minimum purity (Scientific Gas Products Inc.) and was used without further purification.

RESULTS

Catalytic Oxidation of Graphite by Platinum–Iridium

When graphite specimens containing approximately a monolayer of platinum–iridium on their surface were heated in 5 Torr oxygen, nucleation of the deposited film commenced at 315°C. The nucleation process was extremely uniform, the film initially transforming into a chainlike network, which collapsed at 465°C to form discrete particles, 4–10 nm diam. As the temperature was raised, the particles appeared to increase in size and become spherical in outline, but remained stationary on the surface. This state of affairs persisted until the temperature reached 670°C when the first signs of catalytic attack were observed. This took the form of very shallow channels created behind some of the particles as they moved across the basal plane of the graphite. Exhaustive

examination of the surfaces of many specimens confirmed that this was the only form of catalytic action, there being no evidence of attack by the pitting mode.

Channeling by particles which came into contact with edges or steps on the graphite surface became more prolific as the temperature was raised; at 850°C, the sizes of active particles ranged from 2.5 to 50 nm. It was noticeable that even with increasing temperature the channels did not get perceptibly deeper, and moreover, they tended to remain parallel sided for relatively long periods of time, indicating that the alloy particles were not wetting the graphite surface. A gradual decrease in channeling velocity was apparent as the reaction temperature approached 950°C and eventually at 1000°C an appreciable fraction of previously active particles lost their catalytic action and remained motionless at the channel tips.

This dormant condition was relatively short-lived, as a tremendous change in appearance of the surface was observed at 1030°C. There was a significant reduction in the amount of material present on the graphite surface, and those particles which remained were quite large (up to 75 nm diam), much denser than those seen at lower temperatures and tended to be spherical in outline. Particles which came into contact with edges, including those which had previously lost their channeling activity, proceeded to cut very deep channels. Figure 1 is a sequence showing the propagation of a channel at 1030°C; the electron-dense catalyst particle is clearly evident at the leading tip of the channel. It was significant to find that these channels had all of the qualitative characteristics of those produced from the iridium/graphite-oxygen system under similar conditions.

The generation of channels lead to the creation of more edges on the graphite surface and a consequent increase in the number of particles which became activated. This condition was accelerated as the temperature reached 1065°C when all

particles became mobile and the probability of a given particle contacting an edge increased dramatically. Observations were continued up to 1200°C, when both the catalyzed and uncatalyzed reactions became so intense that specimens were rapidly oxidized.

The rate of progress of a given catalyst particle was obtained from frame by frame measurements of a cine film taken of the video record of individual experiments. From these measurements, it was apparent that the rate of channel propagation decreased with increasing particle size, provided that the channels were of similar depth (Fig. 2). These data can be expressed in the form of channel propagation rate α $1/(\text{particle size})^{1/2}$.

The variation in rate of channel propagation was also determined as a function of temperature. To allow for the effect of particle size and channel depth on rate, these mesurements were performed for particles of constant size, 25 nm, propagating channels of similar depth, and taken from regions where the channels were being produced in a smooth fashion. When this data is expressed in the form of an Arrhenius plot (Fig. 3), it is possible to evaluate apparent activation energies of 31.4 ± 3.2 kcal mole^{-1} for the catalyzed reaction between 670 and 980°C and 57.3 ± 6.1 kcal mole^{-1} for the system above 1030°C. Each point on these plots is an average of at least three different particle rates and is based on 10 experiments.

Catalytic Oxidation of Graphite by Platinum–Rhodium

The platinum–rhodium film nucleated to form an array of small chains when specimens were exposed to 5-Torr oxygen at 300°C. Transformation of these structures into discrete particles was rather sluggish, but was complete as the temperature was raised to 550°C. With the exception of an increase in the average particle size, no further change in appearance of the surface
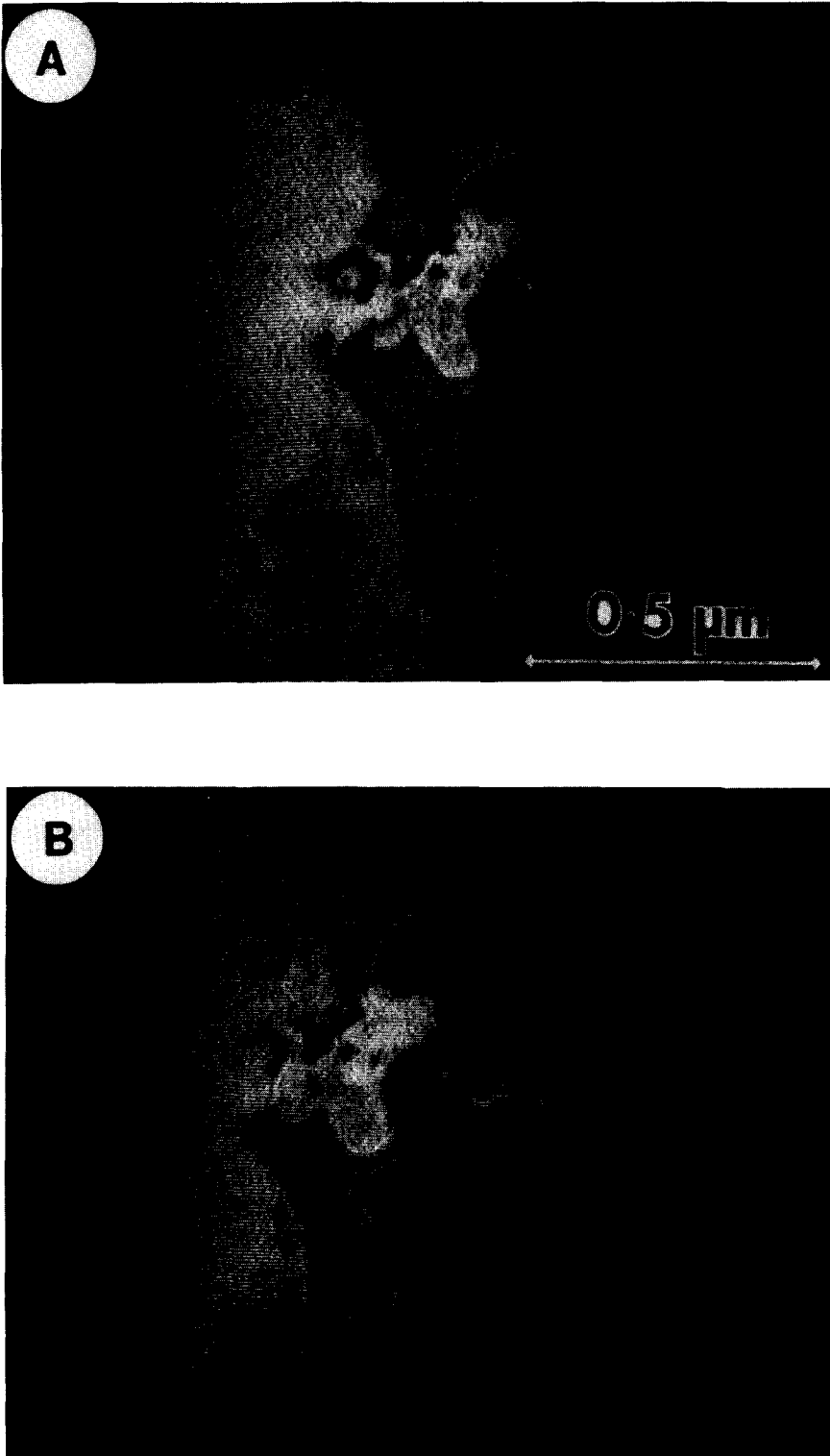
FIG. 1. Sequence (A to D) showing the propagation of deep channels across the graphite surface by Pt–Ir particles at 1030°C in 5 Torr O_2.
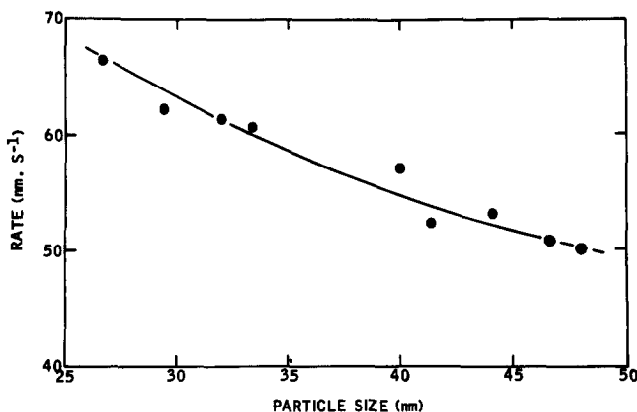
FIG. 1—*Continued*

FIG. 2. Relationship between channel propagation rate and Pt–Ir particle width at 900°C.

occurred until 700°C, when the onset of catalytic gasification of the graphite was observed. This took the form of the creation of a multitude of very fine channels along edges of the graphite surface, giving these areas a feathered outline. At this stage, the widths of a few channels were ~25 nm with the majority less than 10 nm. It was also significant that there was no indication of catalytic attack by the pitting mode.
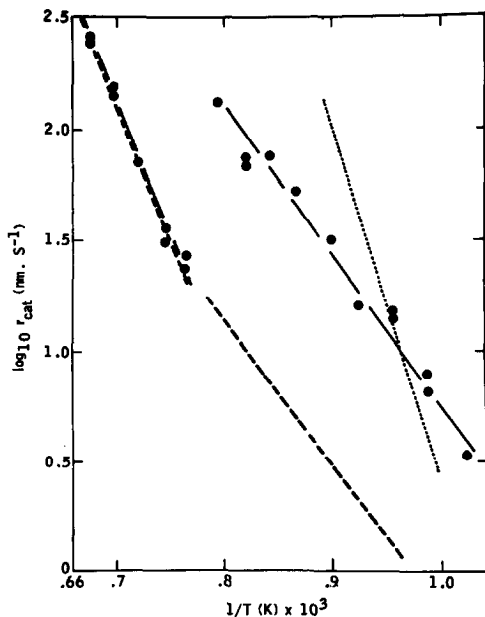
As the temperature was increased, so the

FIG. 3. Arrhenius plots of Pt–Ir-catalyzed rate and its pure constituents: Pt–Ir, ——; Pt, · · · ; and Ir,–––.

number and limiting size of particles which displayed catalytic action also increased and at 870°C the widths of channels were in the range of 5 to 100 nm. A major departure from expected behavior was encountered at 900°C; the rate of channel propagation became perceptibly slower and in some cases channels actually came to a standstill. This state of relative inactivity continued until 940°C despite the fact that all particles became mobile on the surface at 910°C.

The second phase of catalytic attack ensued at 950°C and was very analogous in character to that described for the previous system. Very deep channels, produced by particles up to 200 nm in size, were developed from edges and steps on the graphite substrate. These particles appeared to be quite fluid and frequently spread at the catalyst–graphite interface, causing the channels to follow an erratic path with intermittent straight sections. Observations of this behavior were terminated at 1150°C as the surface appearance of organized chaos made it impossible to follow the progress of individual catalyst particles.

From detailed quantitative analysis, it has been possible to evaluate apparent activation energies for the two regions of catalytic gasification of graphite by Pt–Rh particles. The values, which were obtained from 25-nm particles cutting channels of similar depth, are 27.1 ± 3 kcal mole^{-1} (700–910°C) and 66.7 ± 7 kcal mole^{-1} (940–1035°C),
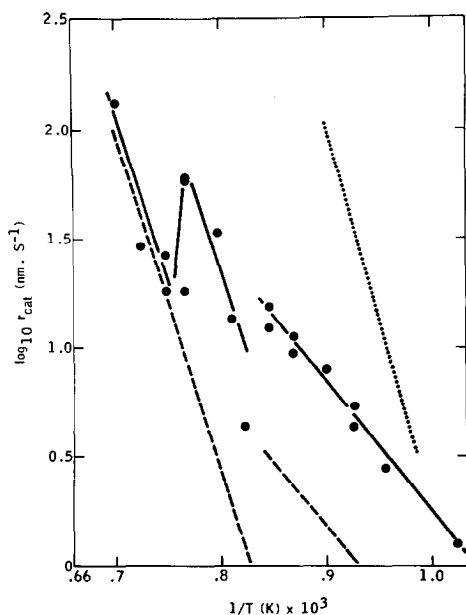
FIG. 4. Arrhenius plots of Pt–Rh-catalyzed rate and its pure constituents: Pt–Rh, ——; Pt, ⋯; and Rh, ---.

being derived from the Arrhenius plot (Fig. 4).

DISCUSSION

The objective of the present investigation was to establish if it was possible to determine in a bimetallic system which component preferentially segregated to the particle surface by comparing the catalytic behavior of alloys with that of the pure constituents on the graphite–oxygen reaction. The reactions chosen to test this idea were the Pt–Ir and Pt–Rh (both 80 : 20 atomic ratio) catalyzed gasification of graphite in 5 Torr oxygen. A comparison of the events which occurred when these systems (and their pure constituents supported on graphite) were heated in oxygen is given in Tables 1 and 2. The temperatures given here are those of the graphite surface and are accurate to within ± 10°C; the temperature of the active catalyst particle surfaces will be higher than the tabulated values because of heat release from the exothermic carbon gasification reaction. Inspection of this data enables one to draw some fairly

firm qualitative conclusions regarding the behavior of the two bimetallic systems.

(a) While all five systems show channel initiation near 700°C, only Pt/graphite is characterized by very deep channels at this temperature. At higher temperatures (~1000°C) the other systems also produce these deep channels.

(b) Ir/graphite and Pt–Ir graphite, Rh/graphite and Pt–Rh/graphite all show a loss of activity between 900 and 1000°C. This aspect is probably related to the IrO₂ → Ir and Rh₂O₃ → Rh transitions, respectively (21).

(c) Ir/graphite and Pt–Ir/graphite, Rh/graphite and Pt–Rh/graphite exhibit particle mobility at ~1100 and 910°C, respectively. These values correspond to the Tammann temperature for Ir and Rh, calculated from the expression: Tammann temperature = 0.52 (bulk melting point) °K.

(d) No appreciable phase separation takes place in either of the bimetallic systems, i.e., we do not see particles that behave like Pt/graphite. This is in contrast to the work of Sinfelt and Via (22) on silica- and alumina-supported Pt–Ir catalysts. Thus, it must be the case that the Pt–Ir phase separation in oxygen observed by the authors does not take place over carbon-supported Pt–Ir particles, or that the Pt-rich particles after phase separation are still primarily covered with Ir.

TABLE 1

Comparison of the Catalytic Behavior of Pt, Ir, and Pt–Ir (80 : 20 Atomic Ratio) on the Graphite–Oxygen Reaction

Event	Temperature (°C)		
	Pt[a]	Ir[b]	Pt–Ir
1. Onset of pitting attack	500	625	—
2. Onset of channeling I	735	700	670
3. Loss of activity	—	980	1000
4. Particle mobility	850	1100	1065
5. Onset of channeling II	—	1030	1030

[a] Reference (19).
[b] Reference (20).

TABLE 2

Comparison of the Catalytic Behavior of Pt, Rh, and Pt–Rh (80:20 Atomic Ratio) on the Graphite–Oxygen Reaction

Event	Temperature (°C)		
	Pt[a]	Rh[b]	Pt–Rh
1. Onset of pitting attack	500	635	—
2. Onset of channeling I	735	700	700
3. Loss of activity	—	900	900–940
4. Particle mobility	850	910	910
5. Onset of channeling II	—	940	950

[a] Reference (19).
[b] Reference (20).

(e) The surface of the alloy particles in Pt–Ir/graphite resembles Ir/graphite more than Pt/graphite; similarly, Pt–Rh/graphite simulates the behavior of Rh/graphite. This suggests that in an oxidizing environment, at the lower-temperature regimes particles are probably covered with a layer of IrO_2 or Rh_2O_3, respectively, while at higher temperatures, where the oxides are highly volatile (23), the surface enrichment will be metallic in nature, i.e., Ir or Rh, respectively. It should be appreciated that even though the oxides of irridium have the highest volatility of those investigated here, the actual rate of oxidation of iridium is slow (24) and so particles will remain on the surface for appreciable times even at 1200°C.

The observation that neither Pt–Ir nor Pt–Rh particles showed any tendency to catalytically attack the graphite by the pitting mode is somewhat strange and beyond any explanation at this time.

A comparison of the apparent activation energies for the catalytic oxidation of graphite by the two alloys and their appropriate pure components is presented in Table 3. The values confirm the qualitative conclusions that Ir and Rh preferentially segregate to the respective alloy particle surfaces. The results would also seem to imply that the presence of Pt exerts no influence on the catalytic activity of the bimetallic particles. This is a completely

false impression which is readily corrected upon examination of the Arrhenius relationships for the alloys and their pure constituents (Figs. 3 and 4). It is evident that Pt additions to both Ir and Rh have a significant promotional effect on these metals in their catalytic action on graphite oxidation. Over the lower-temperature regime Pt addition to Ir leads to an increase of an order of magnitude in the graphite gasification rate, whereas the rise is somewhat less when Pt is introduced into Rh, being a factor of 6. At the highest reaction temperature there is an eightfold enhancement in the gasification rate with the Pt–Rh alloy, but there is no difference between Pt–Ir and Ir. This enhancement in the gasification rate is maintained with the Pt–Rh alloy until the reaction temperature reaches about 1030°C, when the rate drops to that exhibited by Rh. In contrast, the high-activity region of Pt–Ir does not start until 1030°C and under these conditions the rate measurements display continuous correspondence with those found for Ir.

One can rationalize these findings according to the following model. Consider the state of an active particle at lower temperatures (<900°C). For the monometallic systems, Ir and Rh, the particles are probably surrounded by a thin viscous

TABLE 3

Comparison of Apparent Activation Energies for Catalyzed Oxidation of Graphite

Catalyst	Activation Energy (kcal mole^{-1})	Temperature range (°C)
Platinum	84.8 ± 8.5[a]	735–950
Iridium	30.8 ± 3.0[b]	700–980
	59.0 ± 6.0	1030–1200
Platinum–iridium	31.4 ± 3.2	670–980
	57.3 ± 6.0	1030–1200
Rhodium	28.6 ± 3.0[b]	700–900
	70.7 ± 7.0	940–1150
Platinum–rhodium	27.1 ± 3.0	700–910
	66.7 ± 7.0	940–1150

[a] Reference (19).
[b] Reference (20).

layer of oxide. Such an argument follows from the fact that the metals are below their Tammann temperatures, whereas the corresponding oxides which are formed on their surface are above these critical values. If carbon diffusion through the particles is one of the steps involved in catalytic oxidation of graphite, then such a process would be expected to occur most readily by transport through the viscous layer. The amount of carbon gasified by such a particle is going to be a function of the thickness of the viscous layer. Addition of platinum to both these metals is likely to facilitate the rate of carbon diffusion through the particles since it will also be in the viscous state over most of the low-activity region, its Tammann temperature being about 750°C. At temperatures above 1000°C it is probable that some atomic mobility is present even in the bulk of the Ir and Rh particles so that addition of platinum to either metal under these conditions is unlikely to produce any significant change in the diffusion characteristics of carbon through the particles. This reasoning is consistent with the observations that the channels formed at the lower temperatures are shallow, their rate of propagation being also enhanced by the presence of platinum in the particles. In contrast, the channels produced at higher temperatures are deep and their rate of propagation seem unaffected by addition of platinum.

It is intriguing to find that for a given temperature the rate of channel propagation has an inverse square root dependence with particle size. At this point in time we do not understand the implications of this relationship, since a detailed interpretation of this result would require projections of the particle and channel shapes normal to the channeling direction. In the absence of this information, however, the following qualitative conclusion can be drawn: the catalytic oxidation of graphite does not seem to be limited by the activation of oxygen on the exposed metal surface or at the metal–carbon interface, since this would require that the rate be proportional to the square of the particle radius, which is the case for catalyzed hydrogenation of graphite and where dissociation of hydrogen on the metal surface is believed to be rate determining (25). Instead, the inverse dependence of channel propagation rate on particle size seems to imply that the diffusion of carbon through the particle is one of the slow steps in the gasification process.

CONCLUSIONS

Catalytic gasification of graphite by the channeling mode is extremely sensitive to the nature of the catalyst particle surface. This feature has been exploited in the present work in an attempt to demonstrate that it is possible to determine which component preferentially segregates to the particle surface in a bimetallic system from a comparison of the catalytic behavior of an alloy with that of the pure constituents on the graphite–oxygen reaction. Using this approach we have established that in Pt–Ir and Pt–Rh alloys, the Ir and Rh components, respectively, segregate to the particle surface in an oxidizing atmosphere.

There are major advantages studying this type of problem with CAEM. All the particles (>2 nm diam) are seen and consequently such phenomenon as phase separation is readily detected. Also, differences in behavior for different particles sizes, various locations on the support surface, or different phases can be studied. However, in order to arrive at "typical behavior" for a supported metal or alloy, many samples and different fields of view on each sample must be examined.

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