JOURNAL OF CATALYSIS 66, 56–64 (1980)

Catalytic Hydrogenation of Graphite by Platinum, Iridium, and Platinum–Iridium

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Received February 8, 1980; revised May 19, 1980

The interaction of Pt, Ir, and Pt–Ir with graphite under 1 Torr of hydrogen has been studied using controlled-atmosphere electron microscopy. As the sample temperature was progressively increased for each of these systems, three predominant phenomena were observed after initial nucleation of metallic particles: (i) spreading (or wetting) of the metallic particles over the graphite surface, (ii) renucleation of smaller, metallic particles on the graphite, and (iii) channeling of these metallic particles across the graphite basal plane due to catalytic hydrogenation of carbon. For platinum, spreading was observed at 755°C followed by renucleation and channeling at 845°C, for iridium, spreading took place at 965°C followed by renucleation and channeling at 1050°C; and for Pt–Ir, spreading was observed at 850°C followed by renucleation and channeling at 970°C. From the temperature dependence of the channel propagation rate for metal particles of constant diameter (25 nm) and channels of constant depth, apparent activation energies for the catalytic hydrogenation of graphite were determined to be approximately 50 kcal mol^{-1} for Pt, Ir, and Pt–Ir. The absolute values of the channel propagation rates for Pt and Pt–Ir were essentially equal, while the corresponding rate for Ir was substantially faster. It is suggested that the surface of Pt–Ir alloy particles is enriched in platinum under the reducing conditions of the present study. The driving force for particle spreading over the graphite surface is discussed in terms of "activation" of the graphite surface by atomic hydrogen produced on the metallic particles.

INTRODUCTION

In a previous paper (*1*) we described the application of the catalyzed oxidation of graphite as a probe reaction to determine which component in a bimetallic system preferentially segregated to the surface of the catalyst particles. We have attempted to extend the concept to cover the behavior of bimetallic particles in a reducing environment. The system selected to test this idea was the platinum- and iridium-catalyzed hydrogenation of graphite.

In order to understand the behavior of the bimetallic system it has been necessary to first establish the characteristics of the pure components, platinum and iridium, on the graphite–hydrogen reaction. Although considerable effort has been devoted to catalytic oxidation of graphite (*2*), a review of the literature reveals that the area of catalytic hydrogenation of graphite has for the most part been neglected. In recent years Tomita and co-workers (*3–5*) have attempted to remedy this situation and have made some major contributions to the understanding of the reaction. These workers along with McKee (*6*) observed that catalyzed hydrogenation of graphite was accompanied by the formation of channels across the basal-plane surface. Both platinum and iridium were found to be active catalysts for this reaction, with the latter exhibiting the higher reactivity (*3*). Rewick *et al.* (*7*) derived an activation energy of 55 ± 3 kcal mol^{-1} for the platinum-catalyzed hydrogenation of several different carbon substrates. They interpreted the catalytic effect according to a mechanism involving hydrogen dissociation on the metal surface, followed by surface diffusion across the metal/carbon interface and finally reaction with carbon. This conclusion was also shared by Tomita and Tamai (*3*), but in the

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0021-9517/80/110056-09$02.00/0

opinion of Russian workers (*8*) the reaction proceeds via dissolution of carbon in the metal, followed by methane formation, according to a solid–solid–gas mechanism. Most recently, the Pt-catalyzed hydrogenation of graphite was studied by Olander and Balooch (*9*) using molecular beam reactive scattering. In particular, the authors suggested that hydrogen is dissociatively adsorbed on platinum, followed by surface diffusion of atomic hydrogen over the graphite surface. Once in contact with the graphite, the atomic hydrogen can (i) attack the carbon leading to methane formation, (ii) recombine to form molecular hydrogen, or (iii) diffuse into the graphite structure.

This paper describes the results, based on direct observations, of the catalytic effects of Pt–Ir and the pure constituents, Pt and Ir, on the graphite–hydrogen reaction using controlled-atmosphere electron microscopy. From the quantitative kinetic information derived from this study it has been possible to determine which component in the bimetallic system preferentially segregated to the particle surface in a reducing environment. The data also provide support for a mechanism which involves diffusion of active species over the catalyst particle surface to the metal/carbon interface.

EXPERIMENTAL

All the dynamic studies described in this paper were performed in the controlled-atmosphere electron microscope (*10*). Temperatures reported in this paper are those of the graphite support and were measured by means of a Pt/Pt 13% Rh thermocouple spot-welded to a platinum heater ribbon at a point in close proximity to the position of the specimen. Temperature variations across a given specimen were controlled to within ±10°C of the stated values. It is highly probable that the actual temperature of active particles was much higher than that of the support due to the heat input from exothermic processes occurring at their surfaces. For this reason kinetic parameters, such as activation energies, are quoted in apparent rather than absolute terms. Platinum and platinum–iridium (80 : 20 atomic ratio) were deposited onto single-crystal graphite transmission specimens by evaporation of the respective wires (99.99% pure) from a tungsten filament at a residual pressure of 5×10^{-6} Torr. The conditions were chosen so as to produce metal films at least one atom in average thickness. Iridium was applied as an atomized spray from a 0.01% solution of iridium dicarbonyl acetyl acetonate in acetone, or from a 0.01% aqueous solution of chloroiridic acid.

The reactant gas used in this investigation, hydrogen, had a stated minimum purity of 99.999% (Scientific Gas Products, Inc.) and was used directly.

RESULTS

Catalytic Hydrogenation of Graphite by Platinum

The evaporated platinum film nucleated to form small discrete particles (~2.5-nm diam.) when specimens were treated in 1.0 Torr hydrogen at 500°C. Although the rate of particle growth was rather sluggish, at 700°C some particles had grown to between 25 and 35 nm in size. As the temperature was raised to 755°C particles not only ceased to grow but were also observed to undergo a distinct structural change, schematically illustrated in Fig. 1. This transition, which took place over a period of 10 min, occurred in discrete steps. At first, the original dense particles became progressively lighter in appearance while retaining their lateral dimensions, suggesting that metal was being lost from those surfaces not in contact with the graphite substrate. On continued reaction it was apparent that material was being preferentially removed from the central areas of the particles so that subsequently only skeletal outlines remained and eventually even these residues disappeared, leaving a ghost imprint marking the original location of each particle. These features were highlighted by the apparent increase in electron scattering density of the immedi-

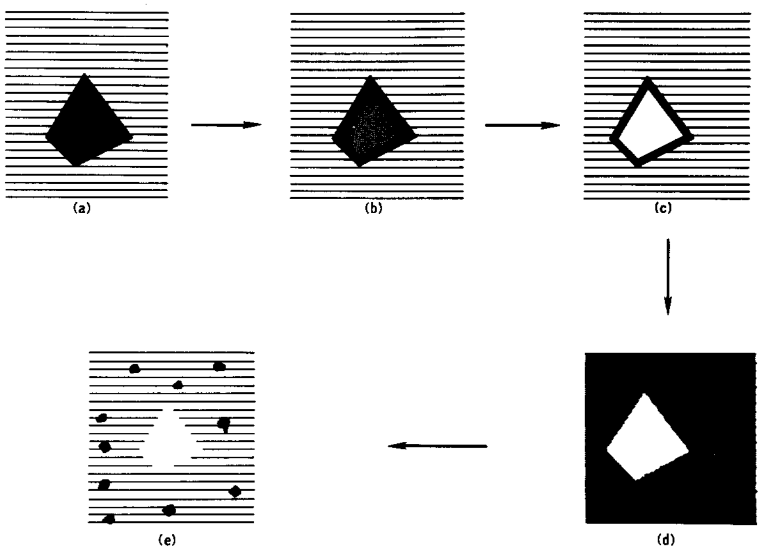

FIG. 1. Schematic representation of the gradual disappearance of platinum particles on graphite in 1 Torr H_2 at 755°C, followed by reformation at 845°C.

ate surrounding areas of the support. It was noticeable that during this process no particle motion was evident. Increasing the temperature to 845°C resulted in the renucleation of small particles, 2.5-nm diam., at positions remote from the sites of the original particles. These fresh particles were quite dense and after 10 min at 845°C many had grown to 10–25 nm in size.

Examination of edges and steps on the graphite surface showed that particles located at these regions were starting to exhibit catalytic attack by the channeling mode. The channels, which became more prolific as the temperature was increased, showed many similar characterisitcs to those formed under oxidation conditions (*11*, *12*), but there were some major differences. Figure 2 is an example of the typical apearance of channels produced by platinum particles on graphite after reaction with 1 Torr hydrogen at 1230°C. Continuous observation of the catalytic process has enabled a number of the detailed features of the channeling action to be identified, some of which are evident in Fig. 2.

(a) The width of the channel was determined by that of the catalyst particles located at its leading end.

(b) Even at the highest temperatures the channels remained parallel-sided throughout their propagation, indicating that the rate of uncatalyzed attack, which would result in edge recession, was insignificant under the prevailing reaction conditions.

(c) The majority of channels were straight, being orientated predominantly parallel to $(11\bar{2}0)$ directions, and occasionally altered course by executing turns through angles of 60 and 120°.

(d) At 1000°C general particle motion occurred and this behavior facilitated both the growth of particles, due to agglomeration, and their relocation to edges and steps on the graphite surface. The net result was that both the size and the number of particles exhibiting catalytic attack increased appreciably.

(e) At any given temperature it was found that the larger the catalyst particle the faster the rate of catalytic attack for channels of similar depth. This dependence can be seen more clearly from the quantitative kinetic data plotted in Fig. 3, for particles at

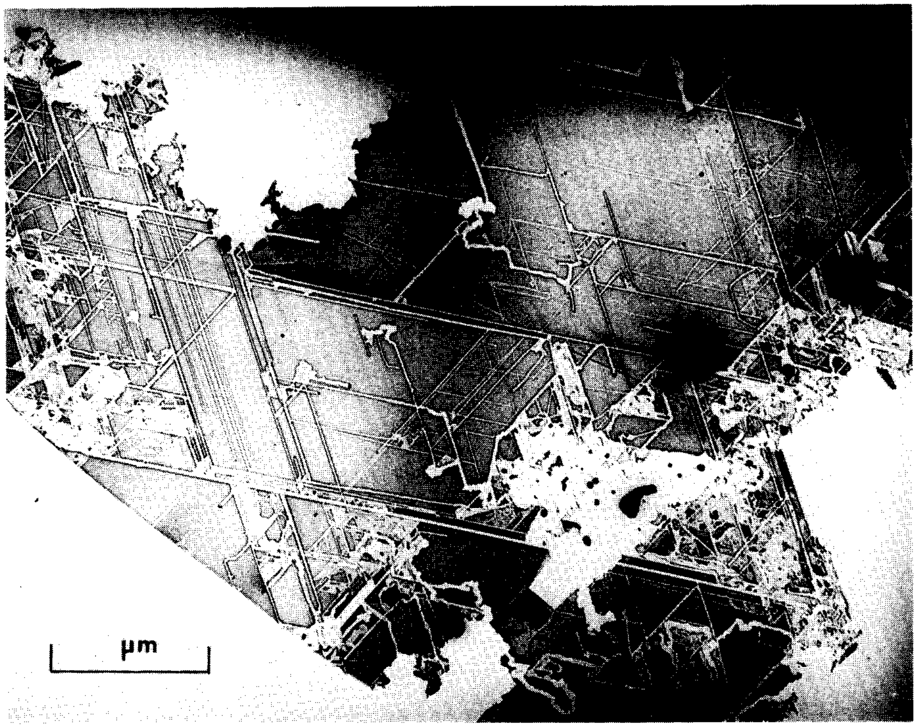

FIG. 2. Typical appearance of channels formed by platinum particles after reaction with graphite in 1 Torr hydrogen at 1230°C.

1170°C, which can be expressed according to the relationship, (channel propagation rate) $\propto$ (particle size)^2. This finding is in direct contrast to catalytic oxidation of graphite where the rate of channel propagation is inversely proportional to the square root of particle size (*1*).

(f) Fragmentation of active catalyst particles into two or more smaller entities was a common occurrence at temperatures in excess of 1150°C. The fragmentary particles continued to create channels but at a slower rate than the parent particle.

From a kinetic analysis of several experiments it has been possible to derive an apparent activation energy of 49.3 ± 5 kcal mol^{-1} for the platinum-catalyzed hydrogenation of graphite (Fig. 4). To allow for the effects of particle size and channel depth on rate, these measurements were obtained from 25-nm-diam. particles cutting channels of similar depth.

Catalytic Hydrogenation of Graphite by Iridium

It proved to be virtually impossible to achieve particle nucleation when graphite specimens containing chloroiridic acid were heated directly in 1 Torr hydrogen. This problem was readily overcome by prenucleating the particles in 5 Torr oxygen at 525°C. Following such a procedure it was found that particles grew to 20–40 nm in diameter when specimens were subsequently treated in hydrogen at 750°C. No nucleation difficulties were experienced when the carbonyl complex was used as the source of iridium; however, since in this case the specimens did not undergo an intermediate oxygen treatment the particles were somewhat smaller, being in the range 5 to 20 nm in diameter at 750°C. With the exception of the difference in average sizes, particles

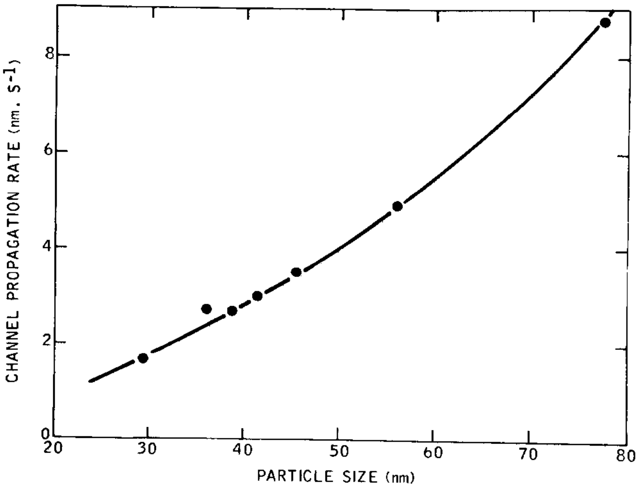

FIG. 3. Relationship between channel propagation rate and platinum particle width at 1170°C.

from both metal sources had identical morphological characteristics, tending to be very dense and having a faceted outline. The particles continued to grow, maintaining the same form until the temperature reached 950°C. At this stage particles tended to become quite smooth in outline; this feature was seen most easily from particles located on edges. Close examination of these particular regions showed that the situation depicted in Fig. 5a existed, where the contact angle, Θ, between particles and the surface was >90°. This geometry underwent a major change at 965°C to create the arrangement in Fig. 5b, the particles now wetting the surface and giving rise to contact angles <90°. On prolonged reaction at this temperature a dramatic change occurred as particles rapidly subsided into the edge so that the original rippled appearance gave way to a smooth profile. Over the same period, the majority of particles located on the basal plane of the graphite behaved in a similar fashion to that described for platinum, disappearing and leaving behind an array of lighter patches on the surface as the only evidence of their previous existence. As with the platinum/graphite system no lateral particle motion was observed during this time. An attempt was made to rejuvenate particle growth by lowering the temperature; however, this operation proved to be fruitless, demonstrating the irreversible nature of the process.

Particles did start to reform at 1050°C, but not in the same regions as they had previously been located. It was at this

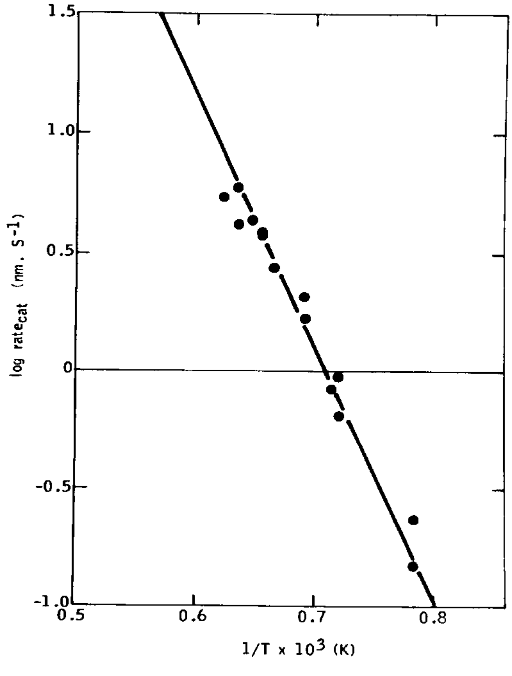

FIG. 4. Arrhenius plot of platinum-catalyzed rate.

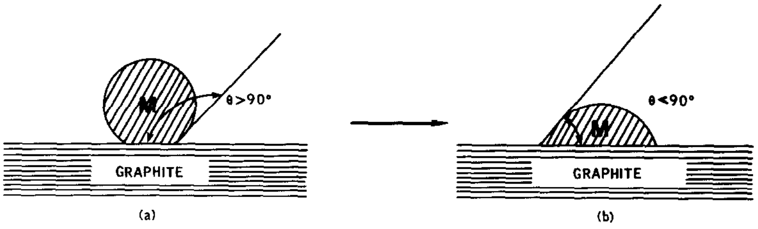

FIG. 5. Schematic diagram of the changes in iridium particle morphology on graphite in 1 Torr hydrogen at 950°C.

temperature that catalytic channeling was quite prominent, even though there had been isolated examples of such attack at lower temperatures. This action was followed continuously up to 1230°C when the rate of attack became so rapid that specimens did not remain intact for long. The characteristics of these channels were identical to those of the former system, the tracks being quite deep and predominantly straight, and at the highest temperatures particle splitting was a common event. Temperatures of 1170°C were required to induce mobility of inactive particles.

An Arrhenius plot of the data obtained from 25-nm particles cutting channels of similar depth yielded an apparent activation energy of 48.5 ± 5 kcal mol^{-1} for the iridium-catalyzed hydrogenation of graphite (Fig. 6).

Catalytic Hydrogenation of Graphite by Platinum–Iridium

When graphite samples containing a monolayer coverage of platinum–iridium were exposed to 1 Torr hydrogen, the deposited film was observed to collect up into a stringy network arrangement, which eventually collapsed to form discrete particles at 605°C. In later experiments more effective nucleation was achieved by preheating the samples in 5 Torr oxygen at 315°C. This treatment did not appear to induce any anomalous effects as in subsequent reaction with hydrogen all samples exhibited similar behavior.

The ensuing reactivity pattern of the alloy duplicated that of its pure components, the only difference being the respective temperatures at which various events occurred. Faceted particles transformed to a spherical outline at 850°C and shortly after started to disintegrate. Reformation of very small particles was observed at 970°C and almost coincidently the development of catalytic channels was detected from the action of particles situated at edges of the graphite. This attack intensified as the temperature was raised and was enhanced at 1050°C by the movement of previously inactive particles, which resulted in an increase in the number of particles making

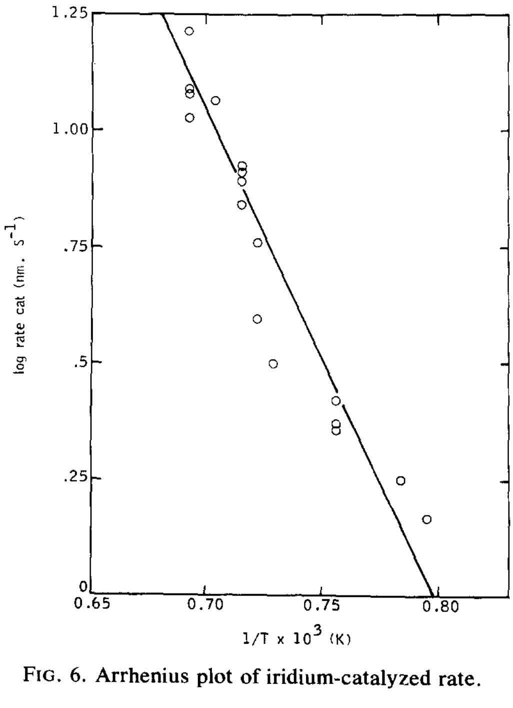

FIG. 6. Arrhenius plot of iridium-catalyzed rate.

contact with steps and edges on the substrate surface. The channels had all the features of those described for the pure metals.

Finally, the channel propagation rates of 25-nm particles operating at a constant depth of graphite have been measured as a function of temperature. These results are expressed in the form of an Arrhenius plot, Fig. 7, from which it has been possible to derive a value of 50.6 ± 5 kcal mol^{-1} for the apparent activation energy of the reaction.

DISCUSSION

The major objective of this work was to use the catalyzed hydrogenation of graphite as a diagnostic test of which component in a bimetallic system preferentially segregated to the particle surface. During the course of the investigation we have also discovered a unique particle redispersion phenomenon. In order to prevent confusion in the minds of readers we have chosen to treat these two aspects separately.

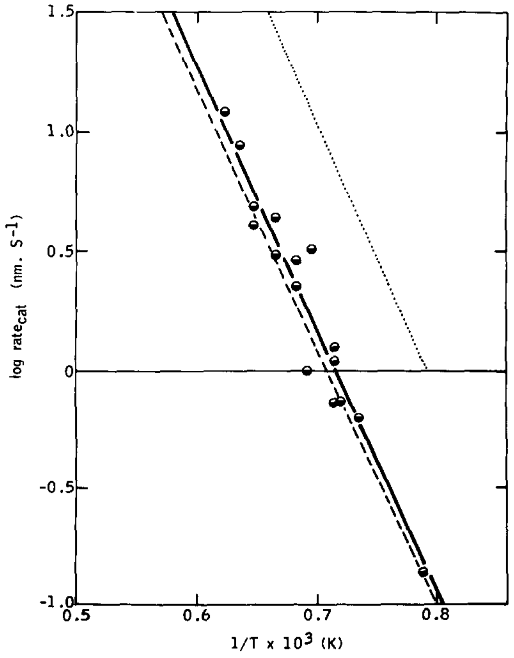

FIG. 7. Arrhenius plot of Pt–Ir catalyzed rate and its pure constituents, Pt (----) and Ir (····).

Catalytic Hydrogenation of Graphite

A comparison of the behavior of Pt, Ir, and Pt–Ir on the graphite–hydrogen reaction (Table 1) shows that there are considerably fewer distinguishing features of this reaction compared to the catalytic oxidation of graphite (*1*). It is impossible to draw any firm conclusions from these data as to which component segregates to the surface of the alloy particles. The temperatures where particle mobility occurs are somewhat higher than the Tammann temperatures for the respective metals (800°C for Pt and 1122°C for Ir), which suggests that the presence of hydrogen increases the strength of the metal-support interaction (*12*).

Although the values of the apparent activation energies determined for these three systems are the same, within experimental error, there are major differences in the reactivity of the catalysts. Examination of the collective Arrhenius plots, Fig. 7, shows that the reactivity pattern of platinum and the alloy virtually coincide, whereas that of iridium is about an order of magnitude higher. This correlation indicates that in a hydrogen environment the Pt–Ir alloy particles are enriched with platinum. A similar conclusion was reached by Kuijers and Ponec (*13*) who used Auger spectroscopy to demonstrate that platinum preferentially segregated to the surface of Pt–Ir films after heating to 400°C *in vacuo*. This is also the effect predicted from a

TABLE 1

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

Event	Temperature (°C)		
	Pt	Ir	Pt–Ir
1. Onset of catalytic channels	845	1050	970
2. General particle mobility	1000	1170	1050

theoretical approach based on heats of sublimation of the two pure metals (*14*).

The finding that the rate of catalytic attack is dependent on the surface area of the active particle is consistent with the model proposed by Rewick *et al* (*17*). These workers suggest that the role of the catalyst is to provide the reactive atomic hydrogen which is eventually responsible for reacting with carbon to produce methane. In such a situation one would expect larger particles to be more reactive than smaller ones.

Redispersion of Metal Particles

The observed particle redispersion phenomenon can be divided into two separate events, disappearance of large particles at a critical temperature, followed by renucleation of smaller entities at a higher temperature. Particles start to vanish at a temperature close to that of the Tammann point, where the surface atoms become mobile. The gradual reduction in electron density of particles located on the basal planes of the graphite would seem to imply that material is preferentially lost from the upper surfaces. It is tempting to speculate that during this process the particle morphology changes from that of a hemisphere to a flat disk-like structure. Such a transformation is seen in the case of particles situated along edges of the graphite surface. However, the most enlightening feature in this particular sequence is the subtle change in contact angle of the particles to a condition where they wet the surface and facilitate spreading of the metal.

Clearly, the nature of the gas plays an important role in this process. Hydrogen atoms produced by dissociation of molecular hydrogen on the metal surfaces will diffuse onto the support and perform a very efficient cleanup operation by reacting with graphite (*15*) and other adsorbed surface species.

Let us now consider the fate of an isolated metal particle on this highly active surface at a temperature near the Tammann point of the metal. Atomic species will escape from the particle to the graphite surface and migrate along the surface until they come into contact with a reactive surface carbon atom. As a consequence the particle will gradually become depleted in material until eventually no metal remains at the original site, since the area covered by the particle will have been protected from gas-phase attack and will be relatively unreactive. Lowering of the temperature at this stage would not be expected to result in reformation of particles. We intend to deal with this wetting and spreading behavior in more detail in a subsequent paper (*16*).

Metal atoms are expected to remain in a highly dispersed form until conditions are reached which induce rupture of the metal–support interaction. At this point reformation of particles will occur, but at positions remote from those of the original particle locations. Once formed, the particles will now act as hydrogenation catalysts for graphite.

At high metal loadings, such as encountered with solution-derived specimens where metal concentration on the graphite surface is difficult to control, it is likely that there will be insufficient reactive carbon sites available to accommodate all the metal atoms, so some large particles will remain throughout the whole temperature range and be available to perform catalytic hydrogenation of the graphite.

CONCLUSIONS

The concept of using the catalytic gasification of graphite as a probe reaction to determine the nature of an active bimetallic particle has been extended to cover the behavior in a hydrogen environment. In this study we have demonstrated that when Pt–Ir particles are heated in hydrogen, the particle surface is enriched in the Pt component. A combination of the findings from this work with those when the same system was reacted in oxygen (*1*) suggests that it should be possible to interchange Pt and Ir at the surface of an alloy particle merely by switching from O_2 to H_2 and vice versa.

This study has also revealed that Pt and Ir particles supported on graphite can be redispersed by treating specimens in hydrogen at 755 and 965°C, respectively. Unfortunately, any potential benefits afforded by an increase in metal dispersion are quickly lost as on raising the temperature the reformed particles proceed to attack the graphite and facilitate sintering.

ACKNOWLEDGMENT

The authors wish to thank Dr. G. B. McVicker for furnishing the sample of iridium dicarbonyl acetyl acetonate.

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