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Catalytic Oxidation of Graphite by Iridium and Rhodium

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Controlled atmosphere electron microscopy has been used to investigate the catalytic influence of iridium and rhodium on the graphite–oxygen reaction. Both systems were found to exhibit a similar behavioral pattern. As the temperature was raised, the initial catalytic action was followed by a short period of inactivity before a second, more intense catalytic attack occurred at temperatures >1000°C. It is probable that the two activity regions correspond to the existence of oxides, IrO_2 and Rh_2O_3 at the lower temperatures and the respective metals at temperatures >1000°C. This pattern is quite different than that found for platinum and palladium, which are present in the metallic state throughout the gasification sequence and as a consequence exhibit only a single continuous catalytic action on the graphite–oxygen reaction. Another aspect revealed from these experiments is the manner by which iridium and rhodium particles supported on graphite sinter in an oxidizing environment. Atomic migration accounts for the growth of inactive particles below the Tammann temperature for the metal (1110°C for iridium; 910°C for rhodium); above this temperature the overriding mode of growth is via particle migration. Particle mobility on graphite can occur below the Tammann temperature as the catalytic channeling action induces motion into active particles.

INTRODUCTION

Carbon deposition during hydrocarbon decomposition reactions is one of the major causes of deactivation of supported metal catalysts. Regeneration of a coked catalyst is normally accomplished by heating the system in an oxidizing environment. During such a step the metal particles may have a beneficial effect by catalyzing the gasification of carbon.

Because of their high activity and desired selectivity patterns, the elements of the platinum metal group are particularly suitable for a number of catalytic applications. It is, therefore, of the utmost importance to establish the influence of these metals on the carbon–oxygen reaction. In an earlier paper (*1*) we reported on the dynamic observations of the catalytic effects of platinum and palladium on the graphite–oxygen reaction using controlled atmosphere electron microscopy. Graphite was selected as the carbonaceous material as it can be obtained in a relatively pure form and in a coke deposit it is the most oxidation-resistant component. This type of investigation has been extended to cover the behavior of iridium and rhodium, two noble metals which have been less frequently used, but are becoming of increasing interest in catalytic applications.

Very little information is available on the catalyzed gasification of graphite by either iridium or rhodium. McKee (*2*) examined the effect of a number of noble metals on the graphite–oxygen reaction and found that all were fairly active catalysts for this reaction. Using controlled atmosphere optical microscopy he identified the major catalytic action, in the temperature range 500–900°C, to be the promotion of irregular etch pits on the graphite basal plane. Other workers (*3*) have investigated the catalytic activity of iridium and rhodium in the hydrogenation of graphite. In this case the role of the metal was believed to involve a hydrogen spillover mechanism.

The motivation for the present investigation arose from the idea that differences in characteristics of the oxides of iridium and rhodium compared to that of platinum

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might be manifested in differences in the catalytic action of these metals on the graphite–oxygen reaction. Platinum only forms a surface oxide, which decomposes at temperatures >450°C. On the other hand, both iridium and rhodium form bulk oxides, which are stable up to temperatures ~1000°C at 1 atm of oxygen (*4*).

EXPERIMENTAL METHODS

Two experimental procedures were used in this investigation; controlled atmosphere electron microscopy to continuously follow the changes in appearance of specimens accompanying reaction and high-resolution transmission electron microscopy for detailed postreaction examination of certain samples.

Controlled Atmosphere Electron Microscopy (CAEM)

Details of the CAEM technique have been documented previously (*5*). Transmission specimens, varying in thickness from 15 to 100 nm, were prepared from single crystal graphite (Ticonderoga, New York) by a standard cleaving procedure. Iridium was introduced onto these specimens as an atomized spray from a 0.1% aqueous solution of chloroiridic acid. Rhodium was applied by evaporation of the metal (99.9% purity, Alfa Chemicals) from a cleaned tungsten filament at a residual pressure of 5×10^{-6} Torr to produce a continuous film at least one atom thick.

The reactant gas used in this investigation, oxygen, was 99.999% minimum purity (Scientific Gas Products Inc.) and was used without further purification.

Transmission Electron Microscopy (TEM)

In some experiments rhodium/graphite specimens were heated in 5 Torr oxygen for 15 min at 610, 805, and 910°C. After cooling, they were examined in a Philips EM 400 transmission electron microscope with a resolution of 0.35 nm. Particle size distributions were obtained from measurement of over 1000 particles after each treatment.

RESULTS

Catalytic Oxidation of Graphite by Iridium

When heated in 5 Torr oxygen the evaporated film of chloroiridic acid decomposed to form small particles (5 to 10 nm diameter) at 415°C. During this phase of the reaction, it was apparent that many of the particles tended to collect at surface features such as edges and steps. As the temperature was raised to 625°C, a very small number of them were observed to attack the graphite in a direction perpendicular to the basal plane to produce hexagonal pits. This action is believed to result from the interaction of a particle with a vacancy or screw dislocation in the graphite surface. Figure 1 is a fine example of such a pit which has formed at the intersection of three twin bands, a likely location for a vacancy. With continued heating, the pits expanded laterally due to the uncatalyzed reaction and also became progressively deeper.

A change in the mode of catalytic attack occurred at 700°C and this took the form of channels, which were developed behind certain particles as they moved across basal plane surfaces. The characteristic appearance of these channels, which all emanated from edges or steps on the graphite surface, is depicted in Fig. 2. This micrograph was taken after cooling a specimen which had been reacted in 5 Torr oxygen at 750°C. Under these conditions the depth of the channels is relatively shallow and the widths, governed by that of the particle responsible for their formation, are in the range 15 to 25 nm. An example of how a particle becomes deactivated by loss of contact with an edge is indicated by the arrow. It is also apparent from this micrograph that active particles are in general significantly larger than inactive ones, which remained static on the surface under these conditions. This difference is readily explained by the fact that active particles tended to incorporate any material they

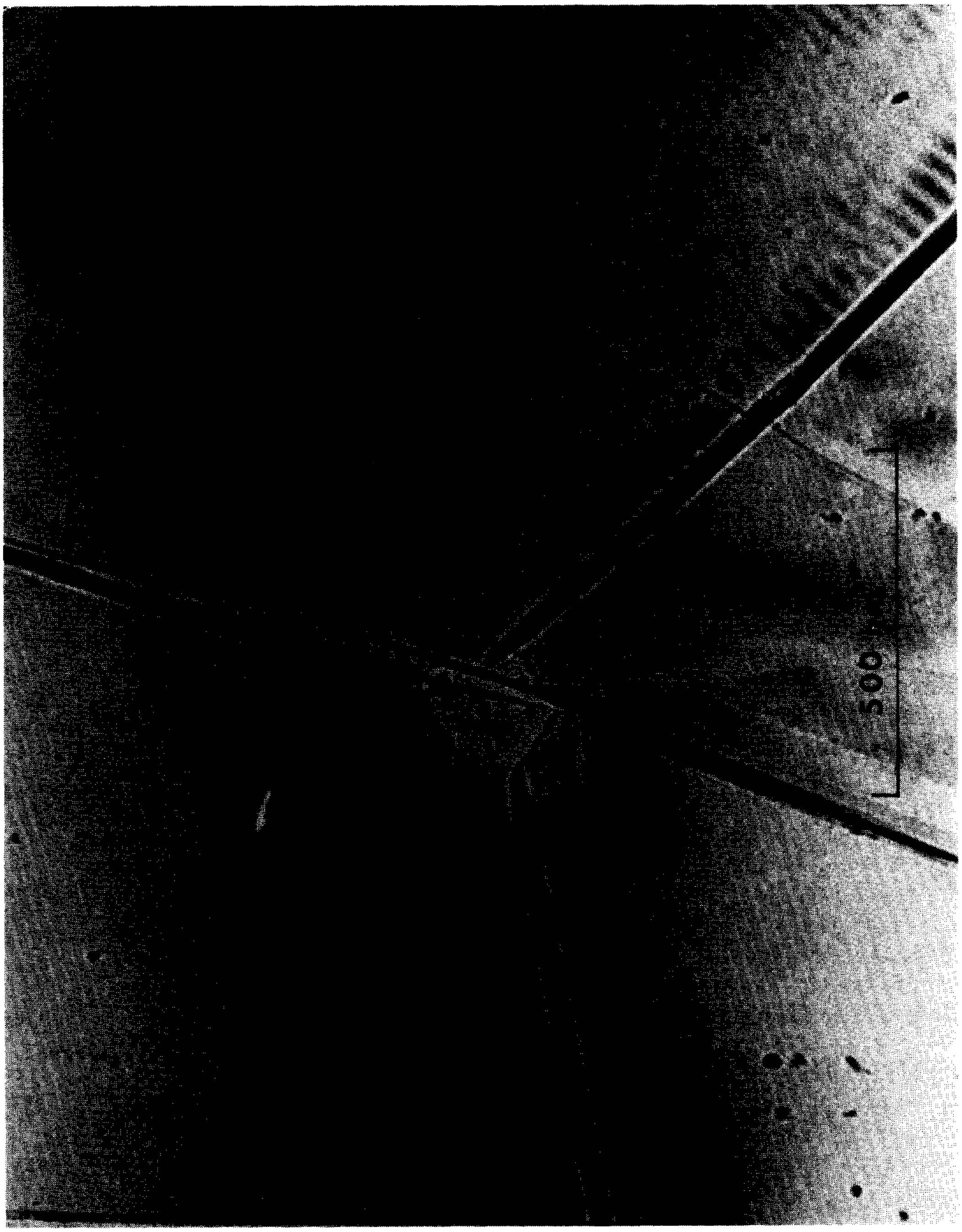

FIG. 1. Transmission micrograph of a pit formed by iridium-catalyzed oxidation of graphite in 5 Torr O_2 at 625°C.

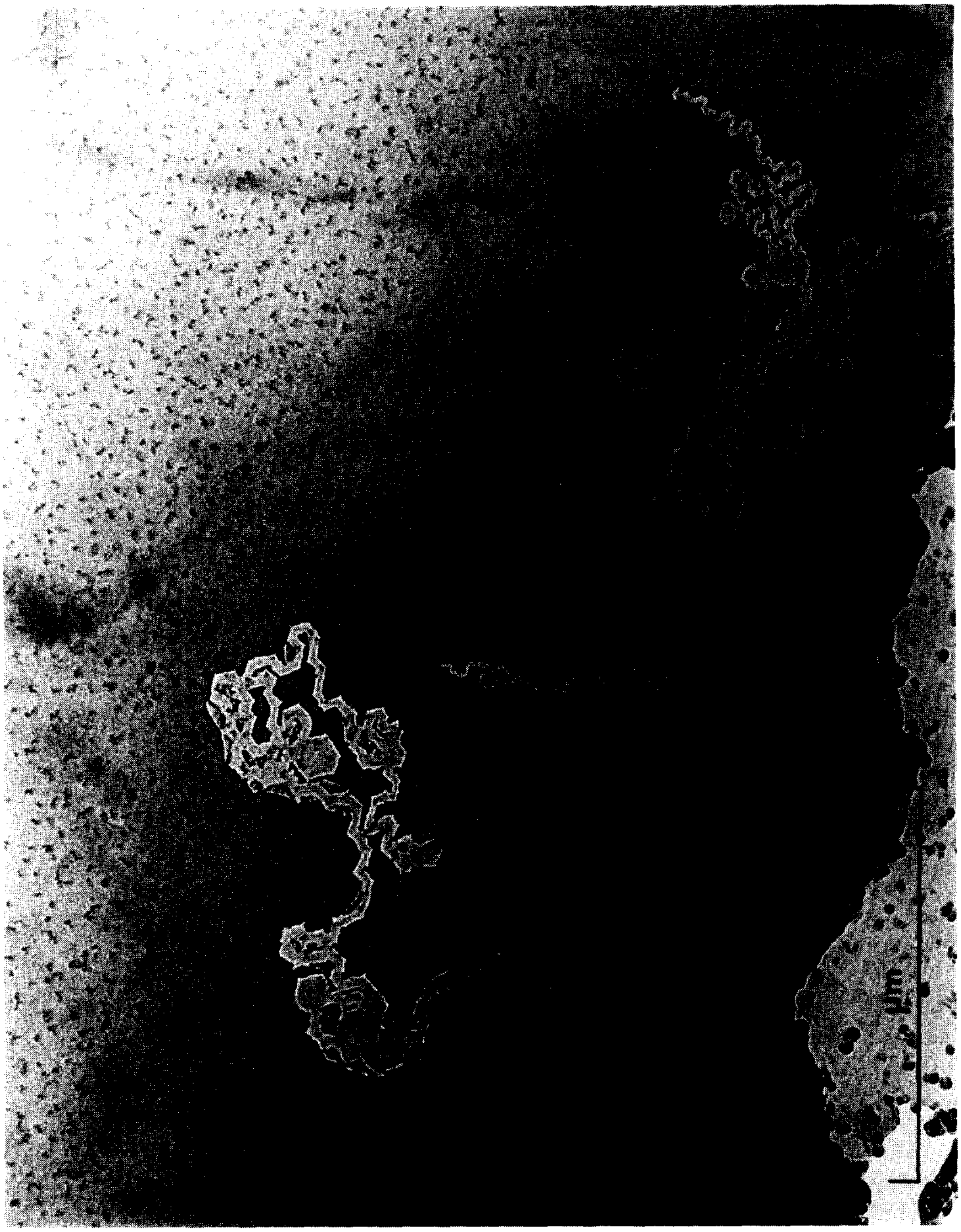

FIG. 2. Catalytic channeling by iridium particles at 750°C in 5 Torr oxygen; the particle X has lost contact with an edge and become deactivated.

collected within their path. Although the fraction of particles propagating channels was small, it was nevertheless at least an order of magnitude higher than that of particles which had previously created pits.

A distinct change in the nature of the channels was evident at 780°C, which is depicted in the schematic diagram, Fig. 3. The catalyst particles were diminished in size as material was left as a film on the sides of the channels due to a wetting phenomenon. As a consequence, the width of the channel was reduced and channel sides receded at a much faster rate than uncontaminated edges or steps, causing the channels to acquire a fluted appearance. Eventually when all the material from a given catalyst particle was deposited on the walls, forward progression of that channel ceased. As channel edges receded and lengthened, the adherent film often ruptured leading to the formation of a large number of small particles which then commenced to propagate secondary channels originating from the sides of the primary ones.

Although there was not a marked increase in the number of particles exhibiting channeling activity over the temperature range 780–940°C, it was apparent that the channels were on average wider, 30 to 50 nm, and being produced at a significantly faster rate. This action came to an abrupt termination at 980°C, and detailed examination revealed that most of the iridium had collected on the edges of the graphite as a thin film and appeared to have lost its catalytic influence.

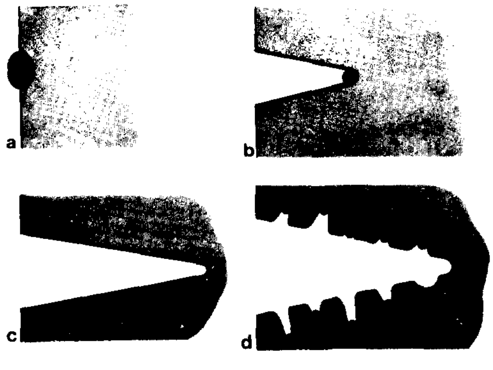

Fig. 3. Schematic diagram showing the effect of iridium/graphite "wetting" on the catalytic channeling mode, at temperatures >780°C.

This period of inactivity persisted until the reaction temperature was raised to 1030°C when a dramatic change in behavior of the system was observed. First, the film restructured to form discrete particles, ranging in size from 5 to 50 nm. These particles tended to be located at graphite edges and steps, making them potentially active catalysts for further channel propagation. After a short period of time many did indeed fulfill this function. It was also evident that the particles had a higher electron scattering density than those formed at the lower temperature region, which could be a reflection of a difference in morphology, i.e., particles at lower temperature wetted the support and became thin; particles at higher temperature assumed a more hemispherical shape. The channels that were created were extremely deep and in general maintained their initial width for considerable distances in contrast to those formed at the lower temperature regime. In many cases a flashing phenomenon was observed in front of an active particle, which was probably caused by buckling of the graphite layers in the immediate vicinity of the moving particle. Channels produced under these conditions showed at least an order of magnitude variation in width and it was clear that those produced by the smaller particles were being propagated at the fastest linear rates. There were also many examples of active particles splitting into two or more smaller particles which continued to produce channels at a faster rate than the parent particle.

It was apparent that only active particles were mobile, a condition which continued until 1108°C. At this temperature all particles started to move on the surface; the motion tending to take the form of vibration about a fixed point rather than a random walk process. The particles still maintained a faceted outline and upon collision with an adjacent one would stick to form an irregular shaped "dumbbell," there being no obvious signs of complete coalescence to form one larger particle. Even in this united state the particles continued to move as a single entity.

The reaction was terminated at 1200°C when the rate of uncatalyzed reaction, seen as the recession of edges and steps, had reached a comparable rate to that of the catalyzed reaction. At this stage there appeared to be less material on the specimen than was present initially, indicating that volatilization had occurred to a significant degree.

Quantitative kinetic analysis of the recorded reaction sequences, a typical example of which is shown in Fig. 4, confirmed what had been suspected from the qualitative observations: that there are two distinct activity regions, separated by a short period of inactivity. From Arrhenius plots of the rate data obtained from 25-nm-diameter particles propagating channels of similar depth it has been possible to evaluate an apparent activation energy of 30.8 (5) ± 3 kcal. mole^{-1} for the catalyzed reaction between 700 and 980°C and a value of 59.0 ± 6 kcal. mole^{-1} for the catalyzed process above 1000°C (Fig. 5). For comparison purposes, the relationship obtained for platinum (from Ref. 1), which exhibits continuous activity over the whole temperature range, is included as the dotted line in Fig. 5.

Catalytic Oxidation of Graphite by Rhodium

In many respects the behavior of the rhodium/graphite–oxygen system paralleled that described for iridium. When graphite specimens containing an evaporated film of rhodium were heated in 5 Torr oxygen, particle nucleation (2–3 nm diameter) took place at 325°C. The first sign of catalytic attack was observed at 635°C and this took the form of a pitting action at points where particles were located at surface defects. This behavior, which occurred in a few limited regions of the surface, persisted until the temperature was raised to 700°C when the predominant mode of attack changed to that of channeling. Under these conditions catalytic activity was restricted to particles in the size range 5 to 10 nm diameter even though there were particles of up to 50 nm diameter present on the surface. On continued heating to higher temperatures eventually all particles which came into contact with edges or steps on the graphite exhibited the channeling action. The characteristics of these channels showed many similarities to those produced at the lower temperature region in the previous system. There was, however, one major difference. Here the width of a given channel tended to remain relatively constant throughout the propagation period, there being no evidence of the catalyst particle "wetting" the graphite edges.

As the temperature approached 900°C, the majority of particles appeared to lose their activity. It was during the period of catalytic inactivity that many of the particles were observed to undergo a transformation from a thin faceted form to a quite dense globular shape. At 910°C most of the particles, irrespective of their location, became mobile on the surface and this resulted in a rapid increase in average particle size due to collisions and coalescence between adjacent particles. At this stage in the reaction, it was not uncommon to find particles of up to 150 nm in size; but the majority were in the range 5 to 50 nm diameter.

As the temperature was raised to 940°C, there was a regeneration in catalytic activity and this was seen as the development of very deep channels emanating from graphite edges and steps. Figure 6 is a particularly informative micrograph as it shows all three types of catalytic attack. Continuous observations of the events occurring in this area showed that initially pits were produced at the positions A, fine channels

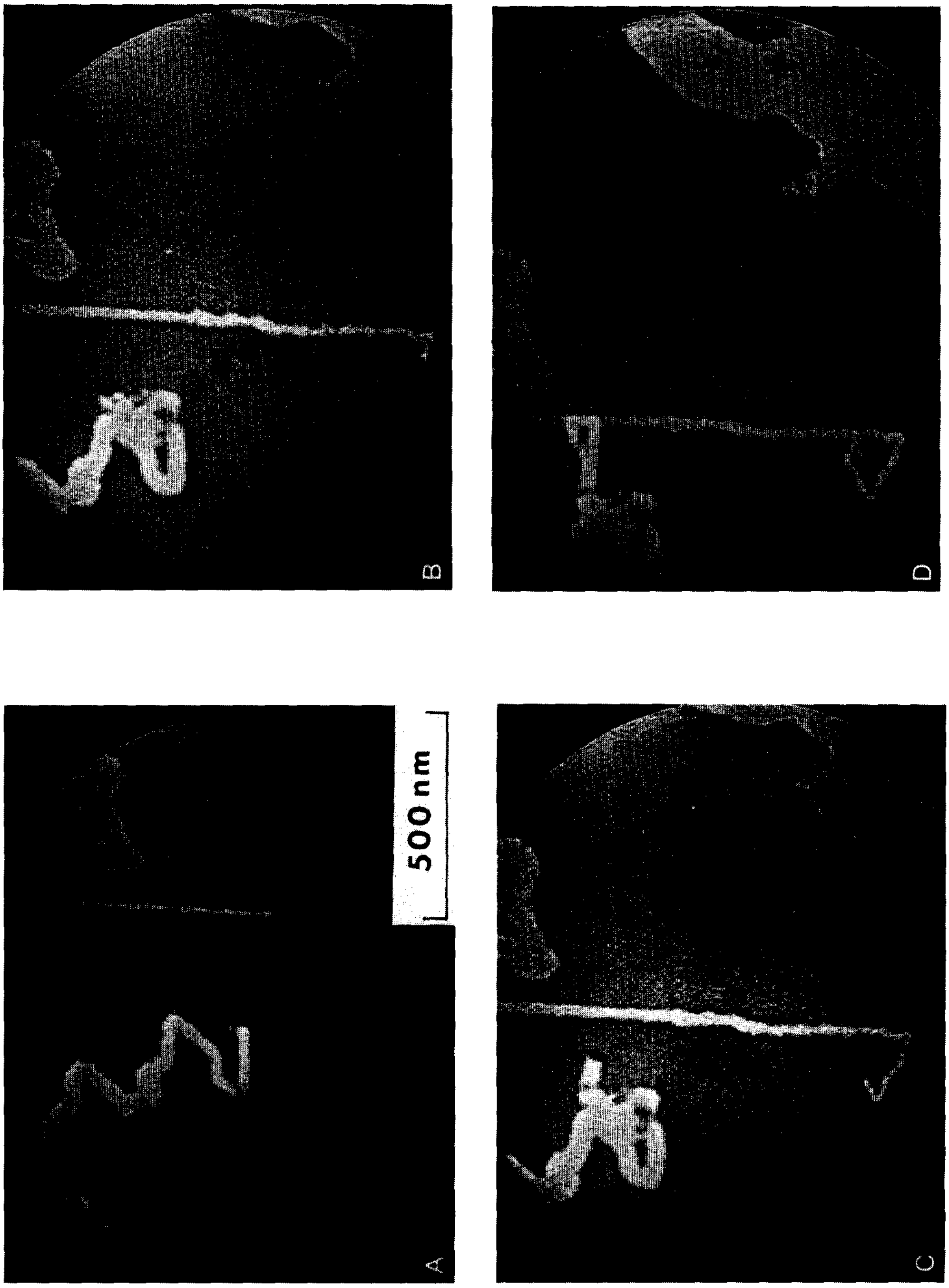

FIG. 4. Sequence (A to D) showing the development of channels across the graphite surface by iridium in 5 Torr O_2 at 1050°C. Time interval between each frame approx. 10 sec.

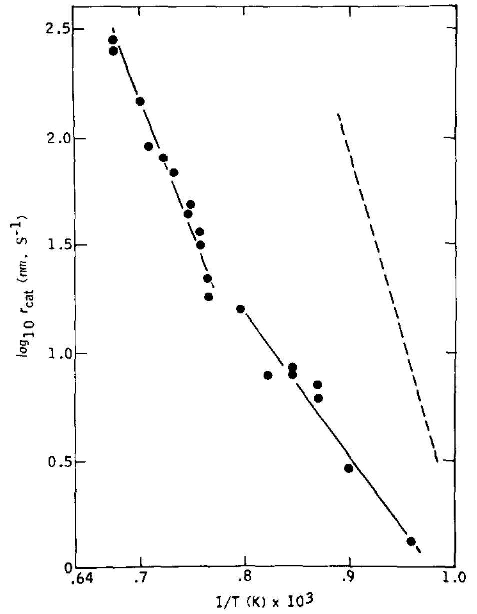

FIG. 5. Arrhenius plots of iridium-catalyzed rate; dotted line is relationship obtained for platinum under identical conditions (from Ref. 1).

were then formed at the edges of the pits B, and finally after heating to 950°C material collected up around the rim of the pit and proceeded to cut the deep channel designated C. This channeling action was followed up to 1200°C when both catalyzed and uncatalyzed reactions became so severe that specimens often disintegrated.

Detailed kinetic analysis of a number of experiments revealed that, like the iridium/graphite-oxygen systems, there were two separate catalytic activity regimes. Arrhenius plots of the results obtained from 25-nm-diameter particles cutting channels of similar depth yielded apparent activation energies of 28.6 ± 3 and 70.7 ± 7 kcal. mole^{-1} for the low- and high-temperature activity regions, respectively (Fig. 7).

Inspection of the particle size distributions at various temperatures (Fig. 8) provides a quantitative appreciation of the growth characteristics of rhodium on graphite. It is evident that the distribution at 610°C is quite narrow and almost symmetrical in shape. Some change is apparent after the treatment at 805°C, a condition where some particles were producing channels and this behavior accounts for the group in the range 20 to 35 nm. Even ignoring this aspect, it is clear we were seeing the development of a bimodal distribution. Continuous observation of the sample heated to 910°C showed that at this temperature the greater majority of particles exhibited mobility. Here, the distribution is extremely broad and nonsymmetrical in shape, displaying a tailing off region in the direction of the larger particles. It is also interesting to find that the size of the smallest particles present has increased from 1 nm, at the lower temperatures, to 6 nm.

DISCUSSION

This investigation has demonstrated that iridium and rhodium exhibit similar behavioral patterns in their catalytic influence on the graphite–oxygen reaction, but show major differences to those of platinum and palladium (*1*). The existence of two distinct activity regions separated by a short period of apparent inactivity in both the present systems can be rationalized according to the notion that the active species at the lower temperatures is an oxide and that at higher temperatures the metal. Although the significance of the period of inactivity is not fully understood, it is possible that a noncatalytic intermediate is being formed in both cases, rather than a gradual transition of oxide to metal. The bulk phase diagrams for these metals in equilibrium with 1 atm oxygen indicates that for iridium/oxygen the stable phase below 1120°C is IrO_2 and the only solid phase above this temperature is Ir metal (*4*). The comparable data for the rhodium/oxygen system show that Rh_2O_3 exists up to 1000°C and Rh metal is the only stable solid phase at higher temperatures (*6*). Newkirk and McKee (*7*) used thermogravimetric analysis to show that the decomposition of chlororidic acid (the source of iridium in the present investigation) to form IrO_2 in 1 atm

air was complete at 680°C, and that the oxide decomposed to Ir at 1025–1070°C, with an indication that some oxide volatilization occurred at about 680°C. The corresponding experiments for the rhodium salt showed that Rh_2O_3 was formed at 755°C and existed up to 1040°C when Rh metal was the stable phase. Schmahl and Minzl

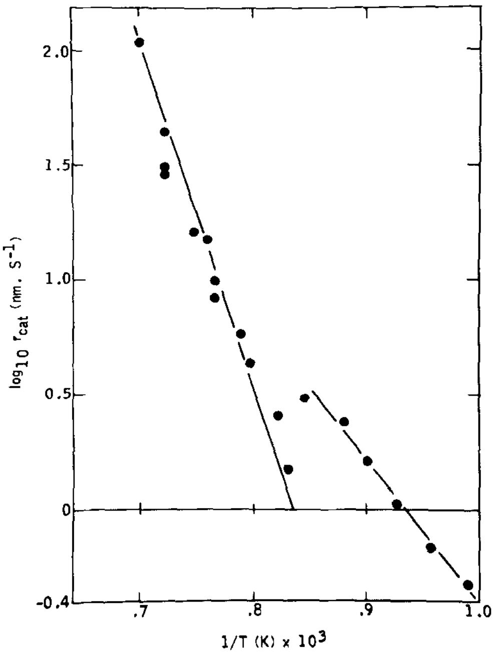

FIG. 7. Arrhenius plots of rhodium-catalyzed rate.

(*8*) found that as the partial pressure of O_2 was reduced so the transition temperature of the oxide to metal was lowered, which accounts for the lower transition temperatures observed in the present study.

It is interesting to find that the bulk phase diagram for the plantinum/oxygen system shows that the dissociation temperature of PtO_2 to Pt metal is at 350°C (*9*), which thus accounts for the finding that platinum exerts a single catalytic action on the graphite–oxygen reaction at temperatures above 500°C (*1*). The data for palladium/oxygen is more uncertain, but it is probable that the metallic state is the stable phase at temperatures greater than 700°C (*6*).

The lack of available information on the behavior of iridium and rhodium for bulk oxidation of graphite makes it difficult to draw comparisons between micro- and macro-systems. It is, however, intriguing to discover that the apparent activation energies determined in this work of 59.0 ± 6.0 kcal. mole^{-1} for iridium, and 70.7 ± 7 kcal. mole^{-1} for rhodium fit on extrapolated curves based on bulk data for other 5d and 4d transition metals, respectively (*10*). Based on a comparison of the rates of channel propagation measured in this study and those obtained from previous work (*1*) at a given temperature, it is possible to derive the following order of catalytic activity for the oxidation of graphite: Pd $\gg$ Pt $>$ Ir $>$ Rh. This sequence shows some deviation from that obtained by McKee (*2*) who studied the bulk behavior in 1 atm dry oxygen and found the following order: Pt $>$ Ir $>$ Rh $>$ Pd. A further comparison can be made with the work of Tomita and Tamai (*3*) who reported the exact reverse of the present order for the catalyzed hydrogenation of an active carbon, viz, Rh $\gtrsim$ Ir $>$ Pt $\gg$ Pd. Although it is highly unlikely that the mechanism of catalytic oxidation is merely the reverse of that of catalyzed reduction, we think that this reverse dependence will be significant to the elucidation of these two mechanisms.

The emphasis in this study has been placed on the action of catalytically active particles, however, the behavior of the greater majority of particles, which remained inactive, should not be ignored. The growth characteristics of these particles provides a direct insight into the mechanisms by which small catalyst particles sinter on a support, an area of considerable controversy at the present time. The two models which have been advanced to account for the sintering phenomenon in supported metal systems differ mainly in what the respective proponents regard as the limiting size of the migrating species. Ruckenstein and Pulvermacher (*11*) believe that particle growth occurs via movement of the particles followed by collision and coalescence to form larger particles. Flynn and

FIG. 6. Transmission micrograph of the situation found on a rhodium/graphite specimen after heating to 950°C in 5 Torr O_2. The pits, marked A, were produced at 650°C; the fine channels, B, were developed at around 750°C; and the deep channel, C, started to form at 950°C.

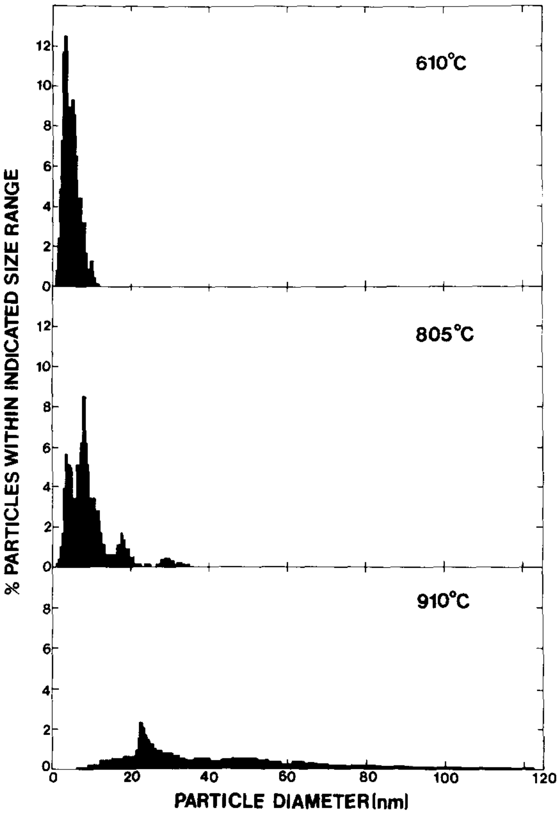

FIG. 8. Variation of PSD with oxidation temperature for Rh on graphite.

Wanke (*12*) argue that particles themselves remain static on the support and that the mobile entities which are responsible for changing particle dimensions are dissociated atomic or molecular species. One of the features of this model is that larger particles grow at the expense of smaller ones.

Particle motion was observed in both systems described here, commencing at 1108°C for iridium and 910°C for rhodium. These mobility temperatures show extremely close agreement with the Tammann temperature of these metals (calculated as 0.52 bulk melting point (°K) which are 1122 and 891°C for iridium and rhodium, respectively). The Tammann point is the temperature of onset of mobility of lattice atoms or ions. In a system where there are relatively weak interactive forces between particle and support one would expect to see particle motion at this temperature. Since this mobility temperature is a characteristic of a particular material, it can be used to some degree as an identification of that material, and, in the present systems, lends further support to the belief that we are dealing with metals rather than oxides at the high temperature regions.

Even though there was no observed general motion of particles >2 nm diameter below the Tammann temperature, particle growth did take place, albeit at a much slower rate compared to the situation where particle growth probably occurred exclusively by the atomic migration mechanism, whereas above the Tammann temperature the overriding mode was via particle migration. These conclusions are supported by the shapes and magnitudes of the particle size distributions obtained at various temperatures.

A further complicating factor in metal/graphite systems which tends to be overlooked is the influence of the catalytic carbon gasification reaction itself on the metal particle size distribution. When this action takes the form of channel propagation, as in the present systems, a certain number of particles will exhibit mobility at temperatures well below that of the Tammann temperature and the channeling action provides a very facile route for a particle to make many collisions. As a consequence, both particle coalescence and splitting can occur and completely alter any particle size distribution map that might be predicted by a theoretical model approach (*13*). It should be appreciated that this type of particle motion is indigenous to a carbonaceous support giving rise to unusual metal particle sintering characteristics, e.g., particle motion due to channeling was observed in the iridium/graphite–oxygen system at 700°C whereas under identical conditions growth of iridium particles on alumina occurred only by the atomic migration mode (*14*).

Finally, a rather intriguing difference was observed in the catalytic behavior of these two metals at the lower temperature region; iridium showed a great tendency to wet the graphite edges, rhodium did not exhibit this effect. Whether this phenomenon was due to a genuine difference in metal behavior or the presence of chloride ions from the iridium salt is not clear. Rather than speculate as to possible reasons for this observed effect we prefer to await the results of experiments specifically designed to answer this question.

CONCLUSIONS

This CAEM study has highlighted the rather unusual activity patterns exhibited by both iridium and rhodium for the catalytic oxidation of graphite. There is little doubt that dual catalytic behavior in these systems is associated with the existence of an oxide at low temperatures and the metal at high temperatures. This feature differentiates the behavior of these metals from that of platinum, an aspect which we have exploited in a further investigation (*15*).

The results also provide a unique insight into the manner by which metal particles sinter on a carbonaceous support in the presence of an oxygen environment. Atomic migration accounts for the growth of inactive particles below the Tammann temperature for the metal; above this temperature the overriding mode of growth is via particle migration. The picture is somewhat obscured due to the fact that the catalytic channeling action provides an alternative route for the migration of a small fraction of particles at temperatures much lower than that of the Tammann temperature.

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