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Catalytic Oxidation of Graphite by Platinum and Palladium

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The catalytic influence of small particles of platinum and palladium on the graphite–oxygen reaction has been investigated by controlled atmosphere electron microscopy. Both metals exhibited pitting and channeling modes of attack on the graphite. Addition of water inhibited both the catalyzed and uncatalyzed reactions, but had no significant effect on the activation energies for these processes. Quantitative kinetic analysis indicates that all active particles, irrespective of their size, gasify the same amount of carbon per unit time under given experimental conditions. These effects and other characteristics of these systems are discussed.

INTRODUCTION

Catalytic oxidation of graphite is one of the most interesting and intriguing topics in the field of catalysis. It is well known that extremely small amounts of impurities can have a profound effect on the oxidation rate of graphite and over many years considerable effort has been applied to this topic, but as yet the precise mechanism of how impurities operate is still unknown.

The interaction of platinum and palladium with graphite is of particular importance since these metals are catalysts for numerous reactions and an oxidation step is usually employed to reactivate a carbon contaminated catalyst. The catalytic influence of platinum (*1–6*) and palladium (*5–7*) on the oxidation of graphite has been reported previously. Presland and Hedley (*2*) used electron microscopy to study the Pt/graphite–O_2 reaction at 600–1000°C, and found that the metal particles were only active when they contacted edges or steps on the graphite surface. Some particles produced pits while others generated channels across the surface. L'Homme *et al.* (*3*) investigated the same reaction and suggested that oxygen dissociated on the platinum surface and the atoms produced migrated over the catalyst particle to the carbon.

Fryer (*7*) observed that palladium particles catalyzed the oxidation of graphite at 500°C in air by a channeling mode. He reported that the active particles were at a higher temperature than stationary inactive particles. From bulk measurements, Heintz and Parker (*6*) obtained values of 89.8 and 124.5 kcal $mole^{-1}$, respectively, for the platinum and palladium-catalyzed decompositions of graphite in air.

In this paper we report on the dynamic observations of the catalytic effects of both platinum and palladium on the graphite–oxygen reaction using controlled atmosphere electron microscopy. An attempt has been made to use the quantitative data obtained here to gain a further insight into the mechanism of catalyzed oxidation of graphite.

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METHODS

Technique

The technique of controlled atmosphere electron microscopy (CAEM) has been described previously (*8*); it enables one to follow the changes taking place in the transmission image of a solid while it is undergoing reaction with a gaseous environment at elevated temperatures.

Materials

Natural single crystal graphite from Ticonderoga, New York was used. Cleaved sections of crystals were prepared by the standard technique (*9*). They were mounted on coated platinum heater ribbons (*8*). Platinum was introduced onto the graphite either by evaporation of the metal (99.9% pure) from a tungsten filament at a residual pressure of 5×10^{-6} Torr or as an atomized spray of an aqueous solution of chloroplatinic acid. Palladium was applied either by evaporation of the metal or as an aqueous solution of palladium chloride.

The reactant gas used in this work, oxygen, was >99% pure (B.O.C. Ltd.) and final traces of water were removed by passing the gas through 5A molecular sieve before use. For the experiments using wet oxygen the gas was passed through a bubbler tube containing water at 25°C before entering the gas reaction cell.

Analysis

The video record was transferred to 16 mm film and quantitative analysis was carried out of the projected image frame by frame. In some cases the relative thicknesses of various portions of the graphite surface were determined by optical density measurements from the cine film.

RESULTS

Catalytic Oxidation of Graphite by Platinum

When graphite specimens containing chloroplatinic acid were heated in 5 Torr dry oxygen decomposition of the acid commenced at 250°C. The original dense hexagonal shaped crystals (about 1 μm in size) restructured to form a dense ring of material, which at 350°C split up to form isolated particles (2–20 nm diam). Under the same conditions the evaporated metal film nucleated to produce small particles, 2–5 nm diam at 425°C, and thereafter both platinum species behaved identically.

At 500°C the average particle size had increased and in a few cases particles were penetrating the graphite basal plane to produce pits. The pits were subsequently expanded by edge recession due to uncatalyzed attack and produced hexagonal holes. With continued oxidation the pit increased in depth and the uppermost graphite layers become progressively more circular in shape, as shown in Fig. 1. (It is not possible to see the catalyst particle in this micrograph).

There was a change in the mode of catalytic attack at 735°C; those particles which had created pits initiated an action parallel to the basal plane to form channels, with the particle at the head of the channel. Channels were also being produced by other particles which had contacted edges or steps on the graphite surface. Channels propagated by small particles (up to 25 nm diam) were relatively straight lines making angles of 60 and 120° to one another, and were usually orientated parallel to $\langle 11\bar{2}0 \rangle$ directions. Particles greater than 100 nm diam propagated irregular channels, which possessed hexagonal facets at the graphite–catalyst interface, the facets being orientated parallel to $\langle 1120 \rangle$ directions. Figure 2 shows the typical appearance of

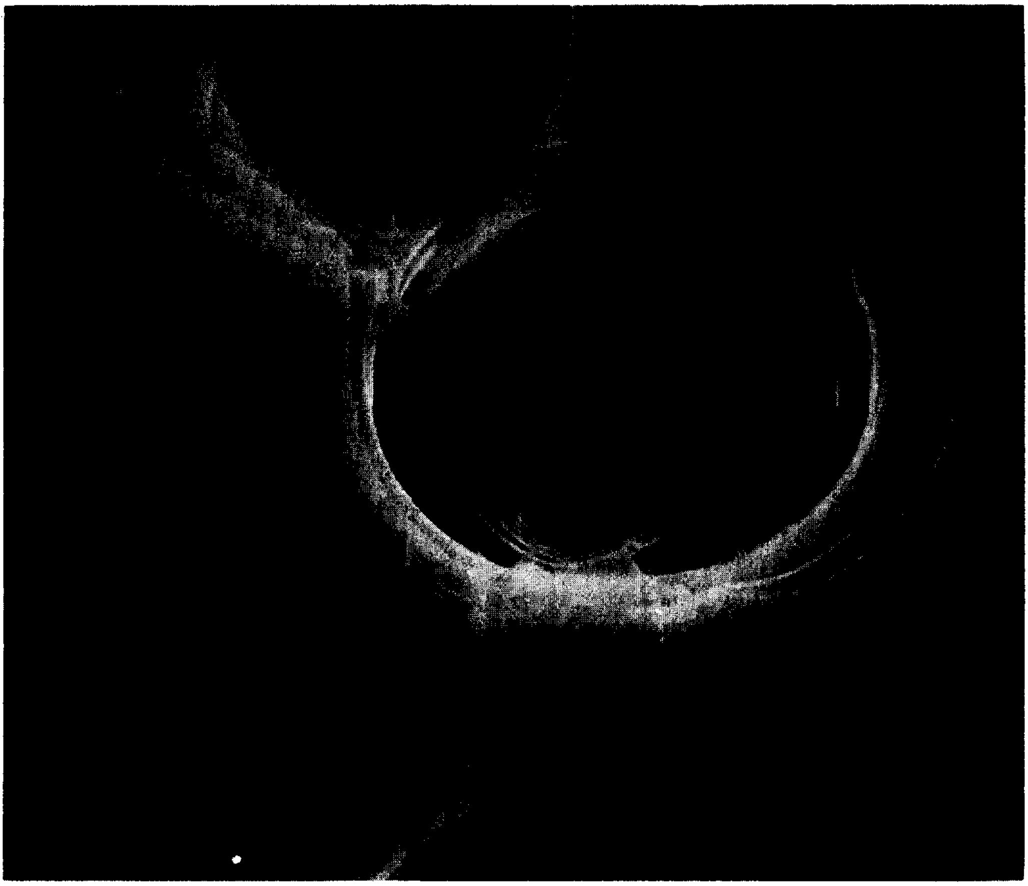


FIG. 1. Scanning micrograph of a pit produced by platinum-catalyzed oxidation of graphite in 5 Torr O_2 at 500°C; ×2070.

channels created by platinum particles on graphite in 5 Torr oxygen at 750°C.

All channeling particles showed many common characteristics:

a. The width of the channel was governed by that of the catalyst particle responsible for its propagation, and often changed as the particle spread or contracted at the graphite–metal interface.

b. Occasionally particles split up and the fragmentary particles continued to channel but at faster linear rates than that of the parent particle. Conversely active particles collided with inactive stationary particles and coalescence occurred; channel propagation was arrested for a short time and finally the new particle accelerated to reach a new but lower constant channel propagation rate.

c. An intermittent density change was often seen in front of particles, particularly with deep channels. This effect is shown in Fig. 3 at the area marked A and was thought to be caused by buckling of the graphite layers in front of the particle, and was observed most easily when the particle was in an imperfect area of graphite where moiré fringes highlighted the flash. The distance over which the flash was apparent increased with increasing particle size.

d. Loss of activity occurred if the particle lost contact with an edge on the graphite surface. At higher temperatures

FIG. 2. Catalytic channeling by platinum particles at 750°C in 5 Torr oxygen; ×25,000.

such particles often contained sufficient kinetic energy to find a fresh edge or step and continued to propagate channels.

e. When particles temporarily lost their activity they took on a spherical form. In contrast, inactive particles which remained stationary were irregularly shaped. At 850°C there was general particle mobility and all particles became spherical in form.

As the temperature was raised uncatalyzed oxidation of graphite became appreciable, causing pits and channels to expand, and specimens would rapidly break up and so terminate the experiment.

When experiments were performed in 5 Torr wet oxygen similar qualitative features to those described above were observed, but pitting attacks were more numerous and the onset of uncatalyzed oxidation appeared to be delayed.

Quantitative kinetic analysis showed that for a given temperature the linear rate of channel propagation was inversely proportional to both the catalyst particle size and the channel depth. In all cases small particles cutting shallow channels gave the highest rates. As the temperature was raised so the rate of channel propagation increased. Arrhenius plots of the data obtained from 20 nm diam particles cutting channels of similar depth yielded apparent activation energies of 84.8 ± 8.5 and 81.3 ± 8.2 kcal mole^{-1} for the catalyzed reaction in dry and wet oxygen, respectively (see Fig. 4). From these plots it is evident that the presence of water reduced the catalyzed rate in the same ratio at all temperatures. A similar effect was found for the uncatalyzed reaction.

Catalytic Oxidation of Graphite by Palladium

When graphite containing either palladium chloride or evaporated palladium

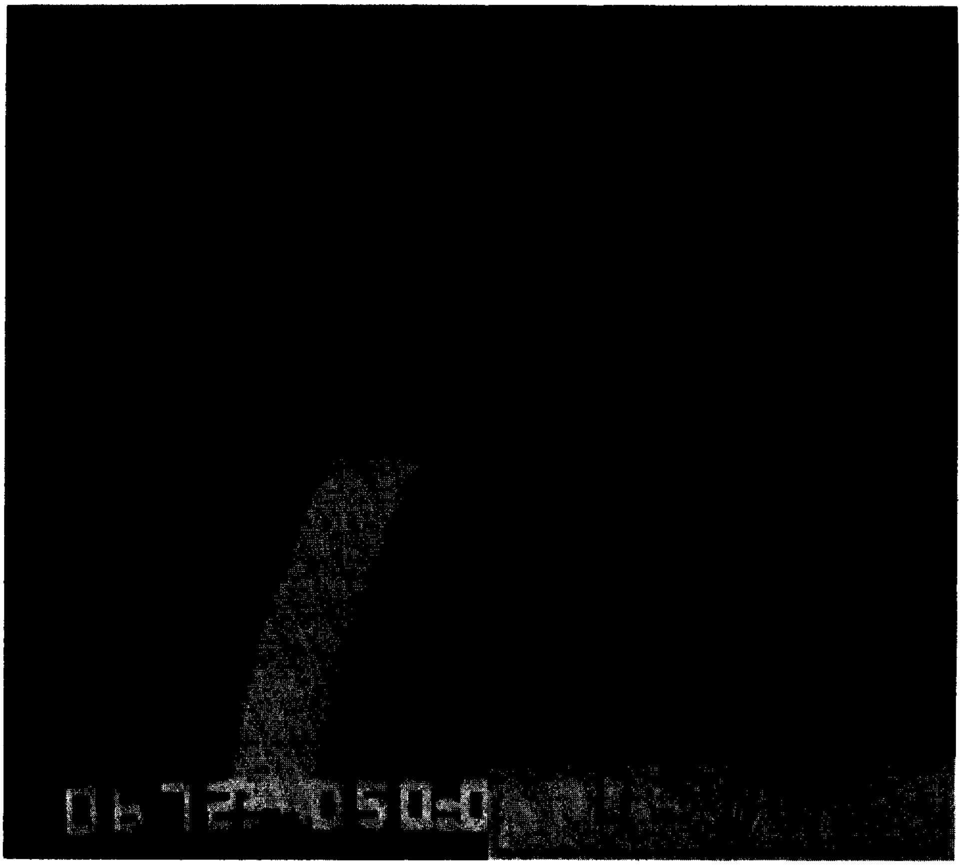


FIG. 3. Buckling of graphite layers by active platinum particle causing flashing at A; ×118,450.

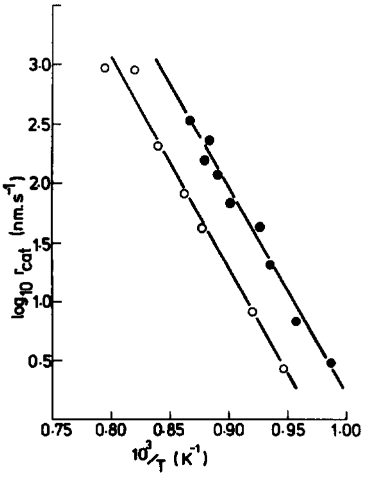


FIG. 4. Arrhenius plots of platinum-catalyzed rate: (●) 5 Torr dry O_2; (○) 5 Torr wet O_2.

metal was exposed to 5 Torr dry oxygen particle nucleation occurred at 350°C. Catalytic attack by the pitting mode commenced at 440°C. The pits often penetrated right through the graphite, nominally

TABLE 1

RELATIONSHIP BETWEEN PALLADIUM PARTICLE WIDTH AND CHANNEL PROPAGATION RATE FOR PARTICLES CUTTING CHANNELS OF SIMILAR DEPTH ON THE SAME AREA OF GRAPHITE IN 5 TORR OXYGEN AT 575°C

Particle width (nm)	Channel propagation rate (nm s^{-1})	Particle width × channeling rate (nm^2 s^{-1})
28	30.6	857
42	20.6	865
52	16.6	863
56	15.5	868
108	7.9	853

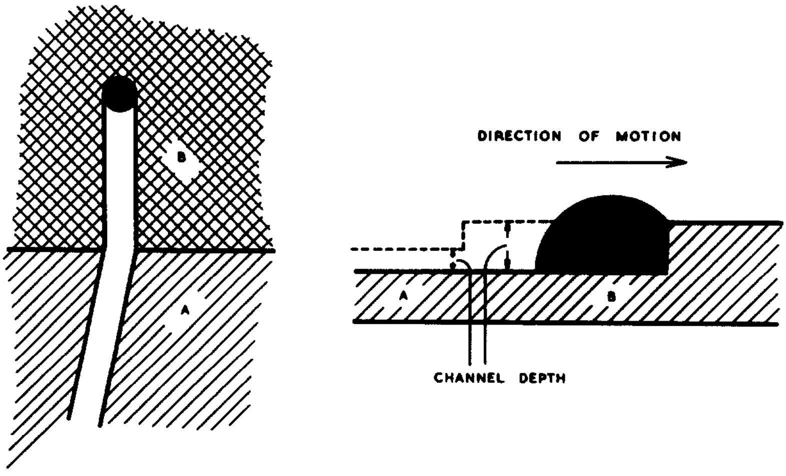
TABLE 2
VARIATION IN CHANNEL PROPAGATION RATE OF PALLADIUM CATALYST PARTICLES MOVING FROM THIN AREAS OF GRAPHITE, "A", TO THICKER AREAS, "B"

Particle width (nm)	Channeling rate ($nm\ s^{-1}$)		Rate on A/rate on B	Thickness ratio area B/area A
	Area A	Area B		
36	2389.0	352.5	6.8	7.1
49	150.8	71.9	2.1	2.0
56	556.5	53.5	10.4	10.8
139	255.1	97.4	2.6	2.8

100 nm thick, but the particles remained attached to the edges of the pits. At 520°C these and other particles in contact with edges or steps on the graphite surface started to propagate channels with similar characteristics to those described for platinum. In general channels were deep and the flashing phenomenon was observed more frequently. Temperatures of 850°C were again necessary to induce mobility of previously inactive particles. No differences in behavior were detected between the two sources of palladium and in this case water did not affect the temperature at which various events took place.

Quantitative kinetic analysis showed that at any given temperature the linear channel propagation rate was inversely proportional to the particle width for particles cutting channels of similar depth. An example of this relationship is given in Table 1 for particles at 575°C.

Table 2 shows the effect of channel depth on the channel propagation rates for various particles at different temperatures. These values have been measured from a situation where a particle has been active on a relatively thin area of graphite, "A", and then encountered a step on the surface causing the depth of the channel to increase as the particle moved through a thicker region of graphite, "B", Fig. 5a. Since channels were never seen to become perceptibly deeper on areas of uniform thickness the particle can be considered as



(a) (b)

FIG. 5. Schematic diagram showing the effect of surface relief of graphite on channel depth.

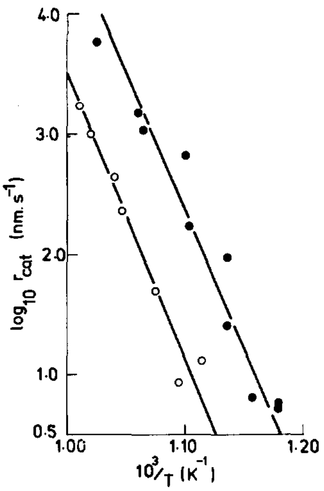


FIG. 6. Arrhenius plots of palladium-catalyzed rate: (●) 5 Torr dry O_2; (○) 5 Torr wet O_2.

operating on a base level and the change in depth is determined by the height of the step, Fig. 5b. There is good agreement between the ratio of channel propagation rates and the relative thicknesses of the graphite when compared to the remaining thickness at the base of the channels, indicating that channel propagation rate is inversely proportional to the channel depth; moreover, this relationship is independent of temperature.

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 measurements were taken from 50 nm diam particles propagating channels of similar depth. From the Arrhenius plots (Fig. 6), it is evident that water has a similar effect on this system to that found for platinum. Apparent activation energies of 104.8 ± 15 kcal mole^{-1} (dry) and 108.9 ± 15 kcal mole^{-1} (wet) were evaluated from the slopes of these lines.

DISCUSSION

From these studies it is evident that there is a striking similarity in the behavior of platinum and palladium in the catalytic oxidation of graphite. It is not clear what causes the metals to change their mode of attack from pitting to channeling, but it could be influenced by the manner in which the metals bond to either oxygen or carbon (*10*).

The presence of water clearly inhibits the rates of both catalyzed and uncatalyzed reactions. A similar effect was reported by McKee (*11*) for the copper-catalyzed oxidation of graphite. The apparent activation energies for these reactions are not significantly altered in wet oxygen indicating that water is only affecting the preexponential factor, A, in the Arrhenius equation, $k = A \exp(-E/RT)$. This factor is composed of two terms, one associated with the influence of entropy changes in the system and the other, a term for the probability that active species will undergo reaction. We cannot be sure at this time which of these two terms is affected by water. It is probable that the competing species arrive at active sites on the graphite by surface diffusion over a substantial distance. Molecular orbital calculations by Hayns (*12*) show that where oxidation is occurring at edge sites on the graphite, water molecules may arrive at these sites much more frequently than oxygen molecules. Water will tend to be firmly bound at such sites while oxygen forms species which are desorbed. For this reason water might be expected to be an effective inhibiting agent for graphite oxidation.

There is ample evidence to suggest that in these catalytic systems active particles were at a higher temperature than those which remained stationary on the surface. In particular, this evidence comprises the observations that active particles were spherical in contrast to inactive ones which remained irregular shaped below 850°C, and also the ability of active particles to fragment and coalesce, behavior usually associated with liquids. This does not mean to imply that such particles were actually liquids, but merely that they possessed "liquid-like" characteristics. Many workers have reported that small particles exhibit mobility at temperatures well below that of the bulk melting point of the metal, and for gold and silver a value of 700°C was quoted for this difference (*13*). Using this value for the cases of palladium and platinum, one could predict particle mobility temperatures of 860 and 1070°C, respectively. Active particles were mobile on graphite surfaces at 520°C (Pd) and 735°C (Pt), which suggests that they could have been approximately 300°C hotter than the surrounding surface. Such an effect would of course induce errors in the measured kinetic parameters. Rather than speculate as to the precise temperature of the metal–graphite interface under any given condition we have based our measurements on the temperature of the graphite and for this reason we have quoted our values as apparent activation energies.

The agreement between the apparent activation energies obtained here for the platinum-catalyzed reaction of 81.3 and 84.8 kcal $mole^{-1}$, and that reported by Heintz and Parker (*6*) of 89.8 kcal $mole^{-1}$ from bulk experiments is excellent. This suggests that the rate controlling step is the same and that any other factors affecting the overall value are also operative in both cases. Although there is a discrepancy between the corresponding values for the palladium-catalyzed reaction this can be accounted for by experimental errors.

Quantitative measurements indicated that the linear rate of channel propagation was inversely proportional to particle radius for channels of similar depth, which confirms earlier data (*14*). Furthermore, for a given sized particle, the channel propagation rate was inversely proportional to the channel depth. These two facts suggest that all active particles, irrespective of their size, gasify the same amount of carbon per unit time under given experimental conditions.

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