

Potassium-Catalyzed Gasification of Graphite in Oxygen and Steam

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Controlled atmosphere electron microscopy has been used to study the catalytic influence of potassium salts on the graphite-oxygen and graphite-steam reactions. This investigation showed strong interaction of potassium species with the graphite substrate in both reactant atmospheres. Potassium salt particles in contact with the edges of the graphite layers were observed to wet and spread on the edges at about 500°C. Gasification then proceeded in both atmospheres by recession of the edges of the layer planes, with little or no attack by discrete catalyst particles. This behavior is consistent with previous indications of high catalyst dispersion associated with the formation of alkali surface complexes as active sites in alkali-catalyzed gasification. The technique also revealed other interesting details regarding the mode of catalyzed attack. In steam the edges show hexagonal faceting with the receding edges parallel to the $\langle 11\bar{2}0 \rangle$ set of crystal directions. This indicates a preferential reactivity in removal of the edge atoms. Occasionally portions of actively receding edges suddenly became inactive. No strong crystallographic preference or deactivation was found in the catalyzed graphite-oxygen reaction.

INTRODUCTION

Alkali salts are known to be active catalysts for gasification of carbon particularly in a steam environment (1, 2). Their use in gasification processes were patented over a century ago (3). Recently there has been considerable attention focused on the potassium-catalyzed gasification of carbon (4-11). Several investigators have provided evidence that potassium salts react readily with the carbon substrate to form surface salt complexes (12-16).

In the present work we have used controlled atmosphere electron microscopy to directly observe the gasification of graphite by potassium salts in steam and oxygen. In the past this technique has provided a unique insight into the details of the modes of attack of several catalysts in graphite-gas reactions (17). Many of the systems investigated show graphite gasification to occur at the interfaces between discrete catalyst particles and edges of the graphite

layer planes. Graphite is removed in these cases by the formation of channels through the graphite sheets. Some catalysts such as molybdenum (18) display an increased tendency to wet the reactive graphite surface. The technique also yields intrinsic gasification rates and can give indications of preferential reactivity of certain crystallographic orientations. The objective of the present study was in part to see how the surface bonding between the potassium catalyst and carbon was reflected in the morphological characteristics of the catalytic attack.

EXPERIMENTAL METHOD

A detailed description of the CAEM technique has been presented previously (19). Potassium was introduced onto transmission specimens of single crystal graphite (Ticonderoga, N.Y.) as an atomized spray of either a 0.1% aqueous solution of potassium carbonate or a 0.1% aqueous solution of potassium hydroxide. Sample preparation was performed in air and some KOH undoubtedly reacted with atmospheric CO₂ to form carbonate or bicarbonate. Specimens were mounted on silica-coated plati-

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num heaters, and with this treatment it was possible to prevent diffusion of extraneous metals onto the graphite surface during reaction.

The permanent gases used in this investigation, oxygen, argon, and CO₂ were obtained from Scientific Gas Products, Inc. with stated purities of 99.999% and were used without further purification. In the majority of experiments steam was admitted to the controlled atmosphere cell as a wet argon stream. The argon was saturated by flow through a bubbler containing deionized water maintained at 0°C, producing an argon/water ratio of about 40:1. This resulted in steam partial pressures in the range of 0.1 Torr in the cell at typical operating pressures (2–5 Torr). Occasionally, higher steam pressures (up to 17 Torr) were achieved by connecting a water-containing reservoir directly to the cell inlet.

The changes in appearance of the specimen surface were monitored as the sample was taken by steps through heating and cooling cycles to temperatures as high as 800°C. Higher temperatures than this were avoided to minimize the amount of catalyst vaporization. Eight successful runs on different samples make up the data base. In addition to complete cycles in one reactant gas, experiments were performed wherein the gas phase was switched. For example, specimens which had reacted to some degree in steam were subjected to subsequent reaction in oxygen and then returned to steam. Finally, partially reacted samples were held at high temperature in dry argon to look for particle growth and any continued reaction between the salt and the graphite. We paused for sufficient time (15 min) at each temperature during the initial heating program to detect slow changes in the specimen and catalyst morphology. As will be discussed later, gasification with both sources of potassium catalyst proceeded almost entirely by edge recession rather than channeling by discrete catalyst particles. Analysis of films made from video tapes of the runs provided quantita-

tive measurements of edge recession rates during reaction of the specimen. Tracings were made from the projected image of selected frames in a film. By matching selected reference points which remained stationary during a film sequence, the movement of the edge features could be measured.

RESULTS

Potassium/Graphite–Steam

When graphite specimens containing either potassium carbonate or potassium hydroxide were heated in 2 Torr wet argon (argon/water, 40:1) both sources of potassium appeared to behave identically. Since the majority of our experiments were performed with the carbonate, observations will be presented in terms of this salt.

No distinct morphology was exhibited by the catalyst deposit upon heating in steam at temperatures below 450°C even for periods of 1 h. Up to temperatures of 550°C the only change noticed was the gathering of particles of catalyst on the edge of the specimen (see Fig. 1A). The particles generally had liquid-like characteristics with contact angles suggestive of attractive (wetting) interaction. Even as these particles formed, no particle nucleation or growth was observed on the basal surfaces of the specimen.

When the temperature was raised above 550°C the particles on the graphite edges slowly (or more rapidly at higher temperature) disappeared from these regions. The sequence of photographs in Fig. 1 shows this occurrence over the span of approximately 2 min at 550°C. Evidence that catalytic material remained on the specimen after the particles disappeared was demonstrated by the subsequent gasification behavior of the graphite. In the absence of added potassium species, no change in graphite appearance was observed under the conditions used here.

Almost simultaneously with the disappearance of the catalyst particles, attack of the edges of the graphite specimen became

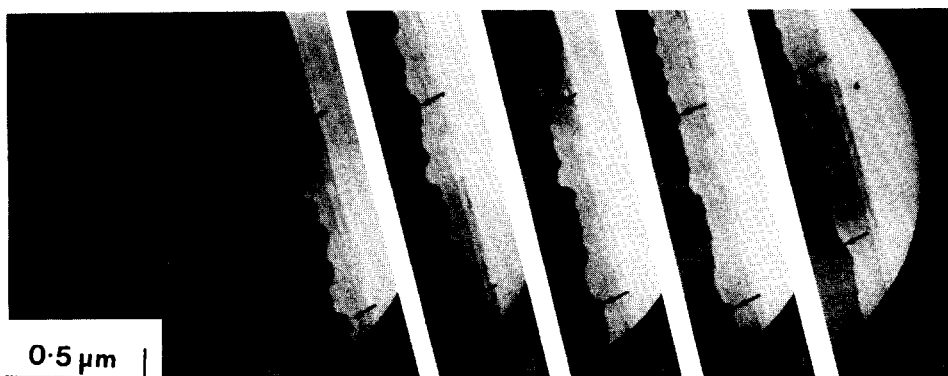


FIG. 1. Sequence of photographs taken from the CAEM video display showing the progressive disappearance of droplet-like particles of K_2CO_3 on the edge of graphite at $550^\circ C$ in steam. Two of the particles are marked by a series of arrows. The sequence spans 120 sec.

evident. Recession occurred at many regions along the entire edge, at first showing as a series of irregular notches. Soon the notches took on a hexagonally faceted appearance (see Fig. 2). The rate of edge recession at $550^\circ C$ was too slow to be readily apparent in real time but increased with increasing temperature. The edge recession eventually involved the entire specimen edge with hexagonal faceting throughout.

All gasification over the temperature range observed was a result of edge recession. This mode of attack still persisted in experiments where 17 Torr steam was used. A very few channels suggestive of impurities were seen at high temperatures during two of the runs. With this exception, no particles greater than 2.5 nm in size (the resolution of the technique) were observed on either the active receding edges or the basal plane during reaction.

The facets produced in steam were aligned parallel to the $\langle 11\bar{2}0 \rangle$ set of crystal directions. This can be determined by noting the orientation of the facets with respect to twin bands which are usually present in graphite specimens and are always oriented parallel to the $\langle 10\bar{1}0 \rangle$ direction. One such twin boundary appears in Fig. 2.

Actively gasifying edges were also seen to stop suddenly on occasion. Figures 3 and 4 demonstrate both of these phenomena. Figure 3 is a trace of features taken from

the projected film of a catalyzed sample gasifying at $715^\circ C$. The solid lines show the positions of the edges as the sequence begins and the dashed lines represent the final positions. The relative positions were fixed by stationary reference features on the specimen. The edge positions were measured along the lettered directions indicated for a series of intermediate times and the results are shown in Fig. 4. When active, all features show a reproducible rate (~ 3 nm/sec in this example). A plot (Fig. 5) of feature (C) from Fig. 3 demonstrated that cessation of edge movement occurred suddenly without a gradual fall off of activity.

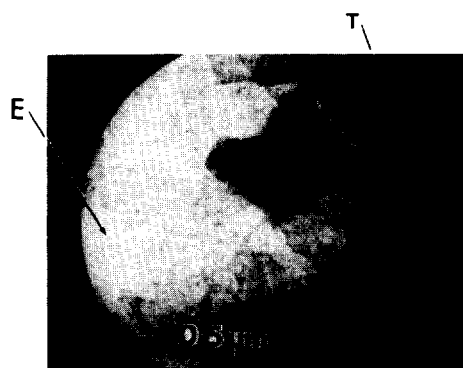


FIG. 2. Photograph of video display showing active edge of graphite while reacting at $715^\circ C$ in steam. General motion of features was from left to right. The remnant of the original edge (E) can be seen as well as a twin band (T).

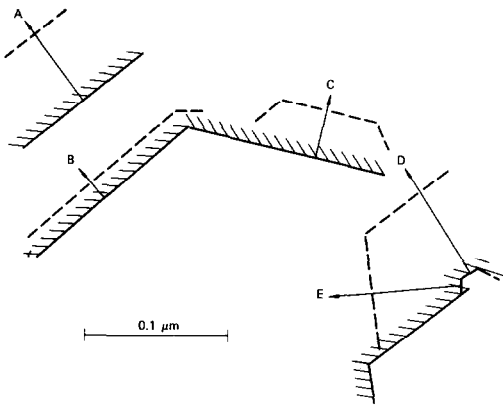


FIG. 3. Sketch of actively receding edge features on graphite at 715°C in steam. Solid lines represent the initial position and the dashed lines represent the final position of the features after approximately 100 sec of reaction. The arrows with letters show the direction along which recession data were measured.

Any residual edge recession was less than one-hundredth of that during the active phase.

When dry argon was substituted for steam, edge recession ceased. This proved that oxygen contamination was not a problem here. When steam was reintroduced, some, but not all of the features which had been receding remained stationary.

Detailed quantitative kinetic analysis of many edge recession sequences showed some interesting aspects regarding the edge

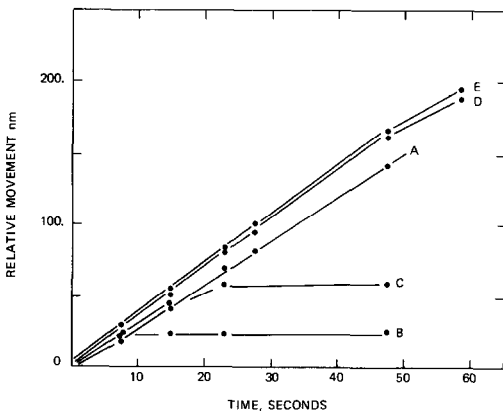


FIG. 4. Relative position of edge features in Fig. 3 as a function of time. Letter labels correspond to similarly labeled directions in Fig. 3.

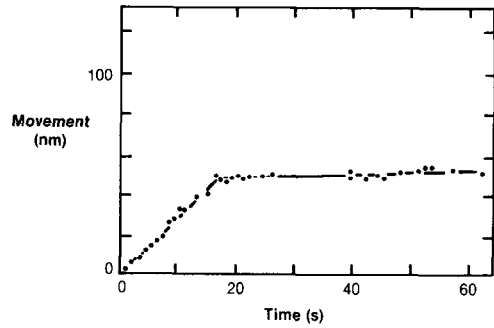


FIG. 5. Relative position of feature (C) (from Fig. 3) at short-time intervals show suddenness of deactivation.

recession mode of catalytic attack. At any given temperature all edges, which were undergoing gasification, appeared to recede at the same rate, within experimental error, regardless of their thickness or length. The variation in edge recession rate was determined as a function of temperature and this data is presented in the form of an Arrhenius plot (Fig. 6). Variation from run to run in the absolute rate values reflects uncer-

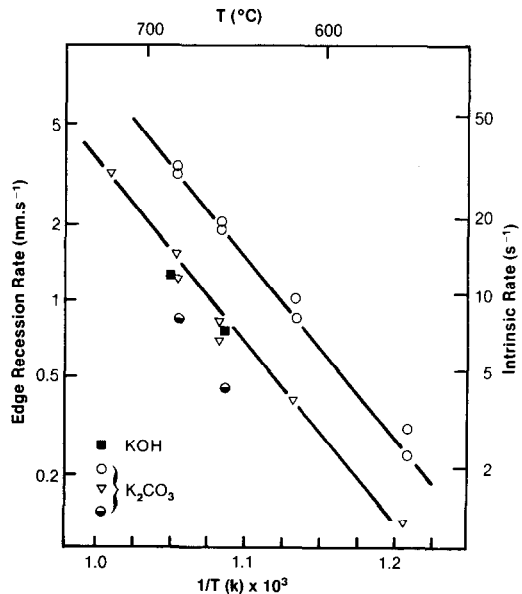


FIG. 6. Arrhenius plot of catalyzed edge recession rates measured on a single graphite sample in 2 Torr wet argon. Data points are the average of many features. Data for ascending and descending temperature sequence are shown at several temperatures.

tainty in the true temperature. Rates were measured from both potassium salts and from increasing and decreasing temperature sequences. We observed no hysteresis in the rates for a complete cycle of temperature. From the slopes of the lines we have derived an apparent activation energy of 35 ± 4 kcal mole⁻¹ for the potassium-catalyzed steam gasification of graphite.

Potassium/Graphite-Oxygen

In these experiments the carbonate was the only source of potassium used. Reaction of these specimens in 5 Torr oxygen showed many similar characteristics to those found in steam. At 500°C particles located on the graphite edges were observed to first wet and then spread along these features. Following this action attack of the graphite was observed via the edge recession mode. No particle formation was detected on either the basal plane or at edge regions above 500°C during the time period of these experiments, about 2 h.

When compared to the behavior in steam two major differences were observed in oxygen: (i) no abrupt deactivation of gasifying edges was noted, and (ii) there was no obvious tendency to develop hexagonal faceting of the edges during the reaction.

When oxygen was introduced to a sample which had been previously treated in steam, the hexagonal outlines which had developed in steam lost their uniformity and gradually became indistinct (see Fig. 7A). These included edges which had lost their activity during reaction in steam. After substantial reaction (several μm of edge recession) the receding edges assumed a smoother outline but still did not exhibit any preferred orientation characteristics (Fig. 7B).

A smaller data base exists for derivation of intrinsic kinetics in oxygen. Figure 8 is an Arrhenius plot of average edge recession rates in oxygen based on one experiment. These rates are derived by following the same procedure as described for the graphite-steam system. However, in this case,

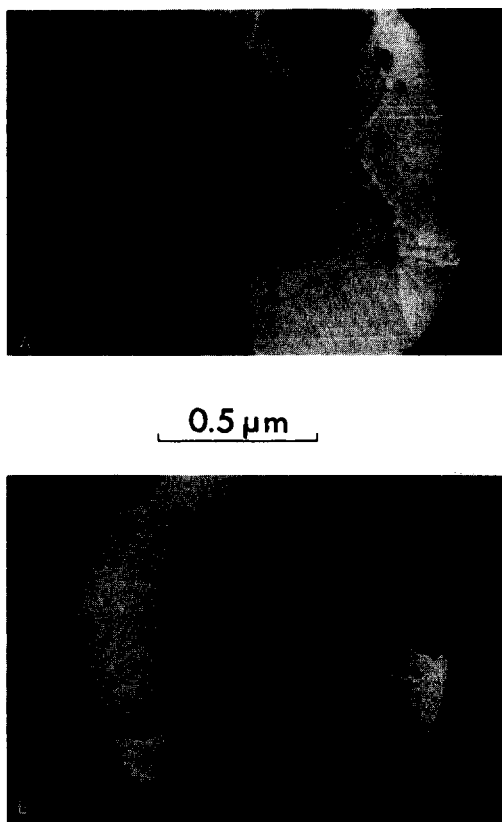


FIG. 7. Photographs of video display showing gasifying edges in oxygen at 686°C.

the irregularity of the edges made the measurements somewhat more uncertain. The edge recession was measured normal to the average edge orientation at each chosen location. The reproducibility of the magnitudes of the rates between runs was no better than a factor of 2. We have derived an apparent activation energy of 30 ± 5 kcal mole⁻¹ from the data presented in Fig. 8.

Potassium/Graphite-CO₂

Although a detailed study of the catalyzed graphite-CO₂ reaction is not part of the present paper, we include preliminary observations which are relevant to the current study. Gasification of catalyzed graphite in 5 Torr of CO₂ proceeded by edge recession in the same manner as in water vapor and oxygen. This edge recession was also preceded by a wetting of the graphite

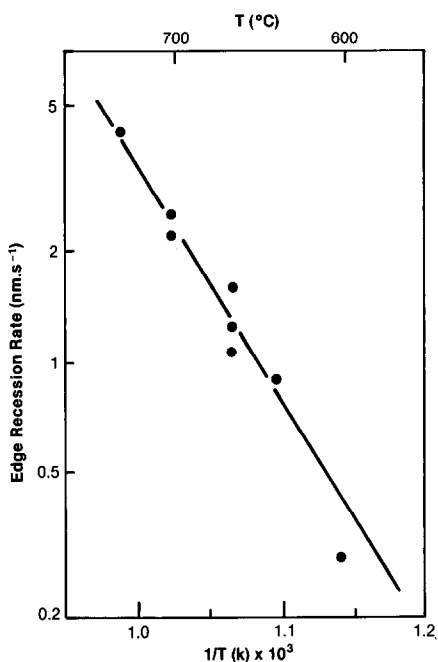


FIG. 8. Arrhenius plot of average edge recession rates in 2 Torr oxygen. These were taken from one area of the specimen during one temperature cycle.

edge by the catalyst. With a higher catalyst loading, particles could be observed on the basal plane during reaction in CO_2 . Even when these particles were visible, edge recession was the sole mode of gasification and no particles could be seen on the edges of the specimen.

DISCUSSION

Potassium/Graphite–Steam

Previous studies of K_2CO_3 catalysis of the gasification of paracrystalline carbons as well as graphite have presented evidence that K_2CO_3 is mobile and wets the carbon surface maintaining the intimate contact necessary for good catalyst dispersion and high carbon conversion. The reproducibility of the catalytic effect with very different impregnation techniques including physical mixing has been attributed to the achievement of a reproducible and high surface coverage (20).

In the CAEM, this self-dispersion is shown by wetting and spreading of the cata-

lyst on the reactive edges and by maintenance of the catalyst in a spread state during reaction. Hydrolysis of K_2CO_3 to form KOH and CO_2 with subsequent evaporation of KOH could contribute to the disappearance of the catalyst particles in Fig. 1. For this to occur however, the $\text{CO}_2/\text{H}_2\text{O}$ ratio must be less than 10^{-7} at 550°C . Under these conditions the Langmuir desorption rate of the hydrolyzing salt would be too slow to explain the changes seen in Fig. 1. More conclusively, the same behavior is seen in 5 Torr CO_2 where the stable bulk phase of the catalyst is K_2CO_3 . For these reasons we believe that the initial disappearance of catalyst particles reflects a wetting and spreading of the catalyst onto the graphite rather than evaporation of the catalyst. From the gasification behavior it is obvious that the catalyst remains on the graphite in a high state of dispersion during reaction and shows no tendency to agglomerate into particles on the reactive edges.

The spreading of a fluid-like phase on another surface occurs when the work of adhesion exceeds the work of cohesion of the fluid phase. In terms of interfacial tensions, γ ,

$$\gamma_{\text{LS}} > \gamma_{\text{GS}} + \gamma_{\text{LG}} \quad (1)$$

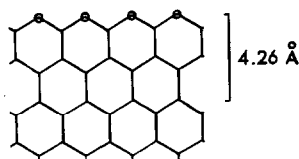
where the subscripts L, S, and G refer to liquid (catalyst), solid (graphite), and the gas atmosphere, respectively. The temperatures here are well above an annealing or mobility temperature for K_2CO_3 (300°C), given by approximately one-half the bulk melting point. The relationship between Tammann temperature and catalyst particle mobility on graphite has been recently discussed (21). Therefore, under the conditions of this study small K_2CO_3 particles can show fluid-like behavior and respond to interfacial forces on an observable time scale. The surface tension of alkali salts is quite low compared to transition metals (22). Surface salt groups on the carbon have been shown to exist on potassium-catalyzed carbons (14) and are thought to con-

tribute to the driving force for spreading of K_2CO_3 on the reactive edge surfaces.

Particles were seen on the basal plane during reaction in CO_2 but not in H_2O and O_2 . This difference could be due in part to different catalyst loadings but the gas composition does affect the surface tensions in Eq. (1). The results in CO_2 show that in this case the adhesive forces are stronger on the edge surface than on the basal plane. No specific functionalities such as surface phenoxides can contribute to catalyst interaction with the basal plane. The interfacial tension in this case is probably dominated by charge/polarizability forces. There are indications that pure KOH does wet the basal plane under vacuum (23).

The morphology of the catalyst seen here differs significantly with that recently reported by Coates *et al.* in a CAEM study of KOH-catalyzed attack of graphite in steam (11). They reported large ($1 \mu m$) particles of catalyst on the basal plane which attack the graphite. There was a marked channeling behavior by these very large catalyst particles although the micrographs also showed evidence of edge recession. No obvious reasons explain the differences seen between this study and the observations reported by Coates *et al.* The sample of graphite used by these workers was polycrystalline (domain size $\sim 2 \mu m$) and attack appeared to take place along domain boundaries. By comparison the graphite used here had very few such defects which could form natural lines of attack. Furthermore, Coates *et al.* appeared to have used much larger quantities of catalyst salts so that the excess salt formed quite large particles. Finally, the H_2O vapor pressure was somewhat higher in Ref. (11) and this can influence the catalyst composition and surface tensions. However, it is worth noting that we did not observe any change in mode of catalytic attack on increasing the partial pressure of water by a factor of 10.

The edge recession rates can be converted to turnover frequencies. Consider the $\{10\bar{1}0\}$ or zigzag orientation.



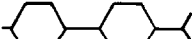
The removal of four carbon atoms for each exposed carbon (O) results in the recession of the edge of the graphitic sheet by 4.26 \AA . Therefore the turnover frequency N (per exposed carbon per second) is related to the edge recession rate R (in nm/sec) by

$$N(\text{sec}^{-1}) = 9.39R. \quad (2)$$

The turnover frequencies calculated this way are indicated on the right-hand ordinate of Fig. 6.

It is interesting to compare these turnover rates which have been measured on microcrystalline char-like carbons, particularly since these can be expressed as turnover rates with respect to surface salt groups. In these systems, near 1 atm at $700^\circ C$ and with $H_2O/H_2 = 1$, the characteristic rate per potassium atom is $\sim 2.5 \times 10^{-3} \text{ sec}^{-1}$ (20). The number of surface salt groups on active specimens is ~ 0.2 per potassium atom (14) therefore the turnover frequency per surface salt is $1.0 \times 10^{-2} \text{ sec}^{-1}$ at these conditions. If one assumes that each exposed carbon atom on the receding graphite edges has a surface salt group with the same reactivity as those on amorphous carbon then the edge recession rate at 1 atm and $H_2O/H_2 = 1$ would be $\sim 10^3$ times slower than that observed. Unfortunately, this comparison is very tenuous because of the very different conditions employed in the two studies and to a lesser degree the uncertainty in temperature measurement of the catalytic event in CAEM. Hydrogen inhibits the alkali-catalyzed steam-carbon reaction (12) and the higher H_2O/H_2 ratio in the CAEM (calculated to be $\sim 10^4$) could contribute to the faster rate seen there. However, extensive extrapolation of rate expressions in the literature (12) to the CAEM conditions does not bring the two rates within an order of magnitude of each other.

Several observations in the steam reaction caution against a simplified "single site" picture that all edge carbons can be treated as equally reactive. The most striking observation is the hexagonal faceting of the reactive edge which leaves edges parallel to the $\{10\bar{1}0\}$ planes. As previously discussed the edges expose the so-called "zigzag" configuration. This faceting of the gasifying graphite edge reflects a preferential reaction of one crystallographic orientation over another. This feature was exploited by Thomas (24) in a very elegant optical microscopy study.

The "zigzag" orientation must in this case be less reactive than other orientations, for example, the "armchair" or  configuration. This is perhaps not surprising in that the $\{10\bar{1}0\}$ orientation presents one uncondensed carbon atom per ring exposed at the edge whereas the $\{11\bar{2}0\}$ orientation presents two uncondensed carbons together. The latter might then be expected to be the more reactive and would explain the results obtained here.

The degree of reaction anisotropy required to produce hexagonal faceting in pits is not necessarily large. Thomas (24) saw an alteration of the orientation of etch pits in the graphite-oxygen reaction with small changes in conditions. Circular as well as hexagonal etch pits in graphite have been seen in TEM and their uncatalyzed expansion rate in oxygen studied. Some modeling is justified to understand the implications of maintenance of regular structures over a significant extent and conversion.

The simplified picture of gasification of graphite as the reaction of a two-dimensional solid is also not necessarily valid. In the uncatalyzed graphite-oxygen reaction it has been reported that growth rates of etch pits in a single graphite layer were much slower than etch pits involving many layers at the same conditions (25, 26). This implies that interlayer cooperation is possi-

ble in the reaction. Many layers are involved in the receding edges observed in this study. It is not easy without modeling to know whether the maintenance of the features requires some interlayer cooperation. A cooperative effect in the catalyzed reaction might explain the possible discrepancy with the rate measurements on less ordered "paracrystalline" carbons. Interlayer cooperation is also less likely with the poor stacking order in these carbons.

The abrupt termination of edge recession during reaction could also be due to interlayer effects. Alternatively, the sudden loss of activity might reflect the loss of a cooperative effect as the catalyst layer becomes "stretched too thin." Loss of catalyst from the region affected is an unlikely explanation for the cessation on two counts. (a) The suddenness of the deactivation and the constant activity until it happens argue against gradual loss of catalyst. It is also inconsistent with a gradual decrease in catalyst surface concentration on the expanding features. Also, areas immediately adjacent to deactivated edges continue to react. (b) The subsequent reactivity in oxygen of "dead" areas indicates that catalyst is still available after deactivation.

The activation energy derived here of 35 kcal mole⁻¹ from the edge recession data is lower than that reported by McKee and Chatterji (27) from TGA studies of K₂CO₃ on graphite of 52.2 kcal mole⁻¹. Again direct comparison is difficult because in neither study is the reactant gas composition (particularly the H₂ partial pressure) well characterized. It is possible that in the present system the activation energy is lowered because of the inhibition by hydrogen produced in the reaction.

Potassium/Graphite-Oxygen

The overall rates of carbon-oxygen reactions, both catalyzed and uncatalyzed, are much faster than the respective reactions in steam. McKee and Chatterji (4, 27) found that the overall rates of the K₂CO₃/graph-

ite-oxygen reaction were >200–1000 times faster than the corresponding values for the K_2CO_3 /graphite-steam system at 600°C. The recession rates in oxygen measured here are on average only a factor of 2 faster than those in steam. This wide variation may be a reflection of the fact that in oxygen more of the edge surface is active and the deactivation phenomenon seen in steam is not operative. Differences in reactant gas compositions also contribute to this variation. Compared to the TGA studies we used a lower oxygen pressure and possibly a higher H_2O/H_2 ratio. Both conditions would tend to bring the rates into closer agreement.

The oxygen reaction is orientationally less selective and does not produce ordered features under our conditions. Oxygen also reacts with the deactivated edges from steam gasification. No reaction with the basal plane in the form of new etch pits was noticed; however, this observation does not preclude the possibility that uniform removal of basal plane carbon atoms or formation of single layer pits occurs, events which would not be manifested in a TEM examination without using decoration techniques.

McKee and Chatterji (4) observed by optical microscopy large particles channeling in the potassium salt-catalyzed graphite in oxygen. These particles were very much larger than the field of view in Fig. 7 and reflect the fact that much larger amounts of catalyst were used. It is possible that these channels also reflect the attack of faults in the graphite specimen by large particles and are more likely to be seen in the optical microscope because of the much larger scale of observation.

SUMMARY

In summary, potassium carbonate is the prime example of a catalyst which in its active mode spreads across the reactive graphite surface. It appears from electron microscopy examination that attack of the

graphite at our conditions takes place exclusively by edge recession with no appreciable evidence of channeling action.

The morphology of the K_2CO_3 catalyst during gasification is striking confirmation of strong interaction between the catalyst and the edges of the graphite lattice. The interfacial interaction is strong enough to compete with the cohesive bonding within the bulk salt and effectively disperse the catalyst along the active edge. Surface salt groups such as phenoxide analogs which have been identified on less ordered carbons are thought to be partly responsible for the high dispersion of alkali catalysts on carbons such as coal char and also explain the reproducibility of the catalytic effect of potassium salts on these materials. The detailed microscopic behavior of the edge recession in water vapor however, reveals a more complex reaction than a single site picture would predict.

REFERENCES

1. Walker, P. L., Jr., Shelef, M., and Anderson, R. A., in "Chemistry and Physics of Carbon" (P. L. Walker, Jr., Ed.), Vol. 4, p. 287. Dekker, New York, 1968.
2. McKee, D. W., in "Chemistry and Physics of Carbon" (P. L. Walker, Jr., and P. A. Thrower, Eds.) Vol. 16, p. 1. Dekker, New York, 1981.
3. Tessi du Montay, C. M., and Marechal, C. R., *Brit. Pat.* 2548 (1867).
4. McKee, D. W., and Chatterji, D., *Carbon* **13**, 381 (1975).
5. McKee, D. W., *Carbon* **20**, 59 (1982).
6. McKee, D. W., *Fuel* **62**, 170 (1983).
7. Kapteijn, F., and Moulijn, J. A., *Fuel* **62**, 221 (1983).
8. Wigmans, T., Goebel, J. C., and Moulijn, J. A., *Carbon* **21**, 295 (1983).
9. Cabrera, A. L., Heinemann, H., and Somorjai, G. A., *Chem. Phys. Lett.* **81**, 402 (1981).
10. Cabrera, A. L., Heinemann, H., and Somorjai, G. A., *J. Catal.* **75**, 7 (1982).
11. Coates, D. J., Evans, J. W., Cabrera, A. L., Somorjai, G. A., and Heinemann, H., *J. Catal.* **80**, 215 (1983).
12. Long, F. J., and Sykes, K. W., *J. Chem. Phys.* **47**, 361 (1950).
13. Mims, C. A., and Pabst, J. K., in "Proceedings, International Conference on Coal Science," p. 730. Verlag Gluckauf GmbH, Essen, 1981.

14. Mims, C. A., and Pabst, J. K., *J. Amer. Chem. Soc.* **104**, 6886 (1982).
15. Mims, C. A., and Pabst, J. K., *Fuel* **62**, 176 (1983).
16. Freriks, J. L. G., van Wechem, H. M. H., Stuiver, J. G. M., and Bouwman, R., *Fuel* **60**, 463 (1981).
17. Baker, R. T. K., *Chem. Ind.* 698 (1982).
18. Baker, R. T. K., Harris, R. S., Kemper, D. J., and Waite, R. J., *Carbon* **12**, 179 (1974).
19. Baker, R. T. K., and Harris, P. S., *J. Sci. Instrum.* **5**, 793 (1972).
20. Mims, C. A., and Pabst, J. K., *Amer. Chem. Soc. Div. Fuel Chem., Prepr. Pap.* **25**, No. 3, 258 (1980).
21. Baker, R. T. K., *J. Catal.* **78**, 473 (1983).
22. Moore, W. J., "Physical Chemistry" 3rd., p. 732. Prentice-Hall, Englewood Cliffs, N.J., 1962.
23. Kelemen, S., and Mims, C. A., *Surf. Sci.* **133**, 71 (1983).
24. Thomas, J. M., in "Chemistry and Physics of Carbon" (P. L. Walker, Jr., Ed.), Vol. 1, p. 122. Dekker, New York, 1965.
25. Yang, R. T., and Wong, G., *Carbon* **20**, 253 (1982).
26. Evans, C. L., Griffiths, R. J. M., and Thomas, J. M., *Science* **171**, 174 (1971).
27. McKee, D. W., and Chatterji, *Carbon* **16**, 53 (1978).