

CONTROLLED ATMOSPHERE ELECTRON MICROSCOPY STUDY OF THE
 K_2CO_3 - CATALYZED GRAPHITE - H_2O REACTION

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Controlled atmosphere electron microscopy has provided unique insight into the details of the mode of catalytic attack of carbons by reactive gases (1). 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 (e.g. Mo (2)) display increased tendency to wet the reactive graphite surface and therefore exhibit a stronger interaction.

Alkali salts are perhaps the best known catalysts for gasification of carbon and have been extensively studied. Several investigators have provided evidence that potassium salts react readily with the carbon substrate to form surface salt complexes (3). We undertook this study in part to see if the morphology of K_2CO_3 - catalyzed attack would reflect this strong surface bonding.

EXPERIMENTAL METHOD

All experiments were performed in the controlled atmosphere microscope (4). Pure, thin specimens of Ticonderoga graphite were mounted on heating stages and impregnated by a fine mist of 0.1% K_2CO_3 solution. Water vapor was admitted to the controlled atmosphere cell from a wet argon stream. The behavior was 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. Several successful runs on different samples make up the data base.

RESULTS

Initial heating cycle in H₂O

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. Up to temperatures of 550°C the only change noticed was the gathering of particles of K₂CO₃ on the edge of the specimen (see Figure 1a). The particles generally had liquid-like shapes with contact angles suggestive of attractive (wetting) interaction. When the temperature was raised above 550°C the particles slowly, or more rapidly at higher temperature, disappeared from the graphite edge. The sequence of photographs in Figure 1 shows this occurrence over the span of approximately 2 minutes at 670°C. That catalyst remained on the specimen after the particles disappeared was shown by the subsequent gasification behavior of the graphite. Therefore we believe that the disappearance of the particles reflects spreading of the salt to a thin film on the graphite surface rather than evaporation.

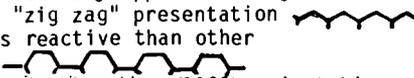
Onset of gasification

Almost simultaneously with the disappearance of the catalyst particles, attack of the edges of the graphite specimen became evident. The edges began receding at many places along the entire edge, at first showing as a series of irregular notches. Soon the notches took on a hexagonally faceted appearance (see Figure 2). The rate of edge recession at 550°C was too slow to be readily apparent in real time but increased with increasing temperature. The rates were much faster than the uncatalyzed rate at the same conditions, reflecting the fact that catalyst had remained on the sample. The edge recession eventually involved the entire specimen edge with hexagonal faceting throughout.

We analyzed films of the experimental runs to derive rates of edge recession. Reactive edges exhibit a reproducible and characteristic recession rate which is general for all features on a given sample. These rates for one run are plotted in Figure 3. Data are shown for both increasing temperature sequence and decreasing temperature sequence. We observed no hysteresis in the rates for a complete cycle of temperature.

DISCUSSION

The morphology of the K₂CO₃ catalyst during gasification is striking confirmation of strong interaction between the catalyst and the edges of the graphite lattice. The interfacial bonding is strong enough to compete with the cohesive bonding within the bulk salt and effectively disperse the catalyst along the active edge. Surface salts groups such as phenoxide analogs have been identified on less ordered carbons impregnated with alkali catalysts and quenched from gasification conditions (3c). These surface salts are thought to be 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.

Hexagonal faceting of the gasifying graphite edge reflects a preferential reaction of one crystallographic orientation over another. J. M. Thomas exploited this feature very elegantly in optical microscopy (5). The facets in this study are aligned parallel to the $\langle 1120 \rangle$ set of crystal directions. This can be determined by noting the orientation of the facets with respect to twin bands along the $\langle 1010 \rangle$ direction which are usually present in graphite specimens. One such twin boundary appears in Figure 2. The K_2CO_3 catalyzed reaction thus exposes the "zig zag" presentation of the surface. This orientation must be less reactive than other orientations, for example the "armchair" or  configuration. This is perhaps not surprising in that the $\langle 1120 \rangle$ orientation presents one uncondensed carbon atom per ring exposed at the edge whereas the $\langle 1010 \rangle$ orientation presents two uncondensed carbons together. The latter might a priori be expected to be the more reactive and would explain the results obtained here. Thomas did see a dependence of the orientation of etch pits in the graphite- O_2 reaction on reaction conditions.

The activation energy derived from the edge recession data (35 kcal/mol) is lower than that observed by McKee and Chatterji for K_2CO_3 on graphite (52.2 kcal/mol (6)). Direct comparison is difficult because in neither study is the reactant gas composition (particularly the H_2 partial pressure) well characterized. Furthermore very different pressures were used in the two studies.

CONCLUSIONS

We have seen microscopic evidence of strong interaction between potassium catalyst and the reactive edges of graphite. This interaction is thought to be driven by the formation of surface salt bonds. The spreading of the catalyst which results from this strong interaction provides high dispersion and efficient use of the catalyst. The hexagonal faceting provides additional insight into the reactivity of proposed surface ensembles.

REFERENCES

- 1 R. T. K. Baker, to be published.
- 2 R. T. K. Baker, P. S. Harris, D. J. Kemper and R. J. Waite, Carbon **12**, 179 (1974).
- 3 a. F. J. Long and K. W. Sykes, J. Chem. Phys. **47**, 361 (1950).
b. C. A. Mims, and J. K. Pabst, Proc. Int. Conf. on Coal Sci. 1981 p. 730 (verlag Gluckauf GmbH, Essen).
c. C. A. Mims and J. K. Pabst, J. Am. Chem. Soc. to be published.
- 4 R. T. K. Baker and P. S. Harris, J. Sci. Instrum. **5**, 793 (1973).
- 5 J. M. Thomas in Chemistry and Physics of Carbon (P. L. Walker, ed.) vol. 1 p. 122, Marcel Dekker (NY) (1965).
- 6 D. W. McKee and D. Chatterji Carbon **16**, 53 (1978).

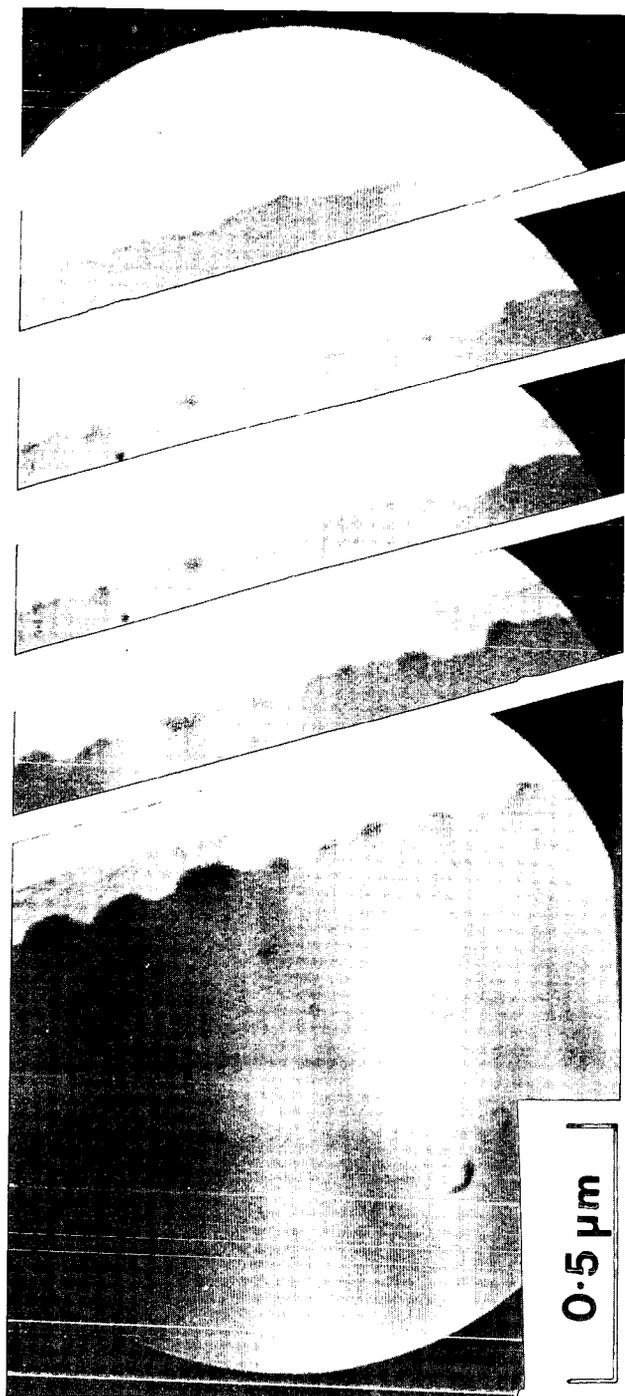


Figure 1. Sequence of photographs taken from the CAEM video display showing the progressive disappearance of droplet-like particles of K_2CO_3 on the edge of graphite at $670^\circ C$ in water vapor. The sequence spans 120 seconds.



Figure 2. Photograph of video display showing active edge of graphite while reacting at 715°C in H_2O . 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).

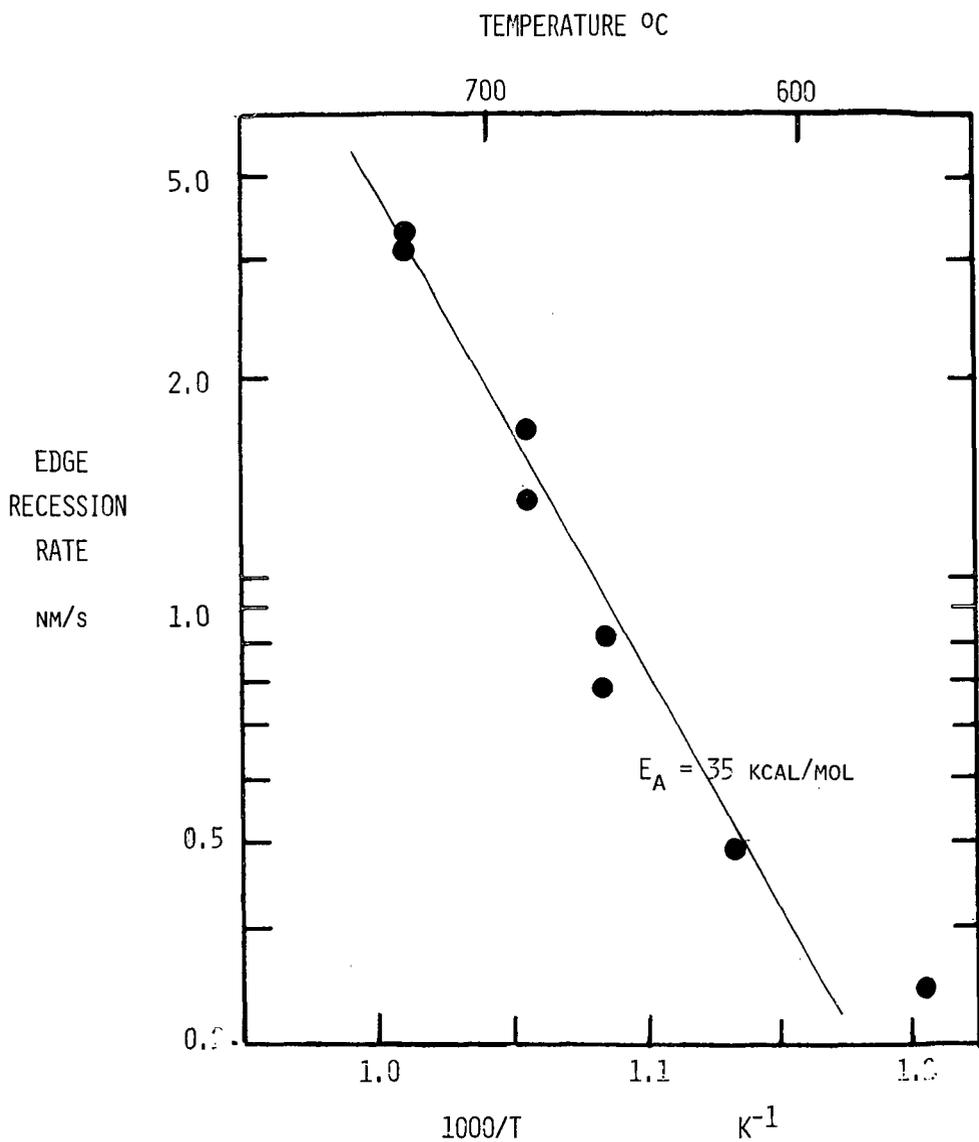


Figure 3. Arrhenius plot of catalyzed edge recession rates measured on a single graphite sample. Data points are the average of many features. Data for ascending and descending temperature sequence are shown at several temperatures