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# NOTES

## An Electron Microscopy Study of the Low Temperature Catalyzed Steam Gasification of Graphite

Controlled atmosphere electron microscopy was used to directly observe the catalyzed low temperature gasification of graphite. Potassium hydroxide was used as the catalyst in the reaction between steam and graphite. Catalytic channeling of the graphite was observed in the temperature range of 500–600°C, lower temperatures than previously reported for this mechanism using other catalysts. Kinetic studies of the potassium hydroxide-catalyzed steam–graphite reaction give a constant activation energy of 11 ± 1 Kcal/mole at temperatures of 200–600°C suggesting that one reaction mechanism holds good throughout this range of temperatures.

The use of an environmental cell in a transmission electron microscope in which a gas–solid reaction may be carried out while observing the solid specimen (controlled atmosphere electron microscopy or CAEM) has been employed in the study of a number of carbon gasification reactions (see, for example (*1–12*)). According to Baker (*12*), catalysis of the gasification of graphite crystals may occur by "basal plane penetration in imperfect regions or by altering the rate of reaction at edges or steps. Catalysts operating in the former mode are termed pitting catalysts and those operating by the latter mode are referred to as edge-specific or channeling catalysts." Catalytic gasification by the channeling mode is a reaction that is ideally suited to study by CAEM and observed for a number of metal catalysts. In these studies channels were observed to propagate in the graphite crystals, each channel having a catalyst particle at its head and in all cases the channels were observed to emanate from some step or edge in the crystal. Significant differences in the qualitative characteristics of various metal and metal oxide catalysts for the oxidation reaction of graphite have been found. Thus, lead (*2*) and silver (*4*) were found to be extremely active at relatively low temperatures (~350°C) whereas temperatures of 725°C were required for zinc (*1*). Metals such as molybdenum (*3*), platinum, and palladium (*7*) catalyzed the oxidation of graphite by a pitting mode at lower temperatures and then switched over to channeling attack at higher temperatures. A limited number of CAEM studies focused on the catalytic gasification of graphite with steam have been reported. Baker and Chludzinski (*10*) have examined the catalytic gasification of graphite in oxygen, steam, and hydrogen using copper and chromium as catalysts. They found no evidence of catalytic gasification of the graphite when using steam and concluded that neither metal was an effective agent for dissociation of water molecules, a necessary step in the catalytic process. Baker and Sherwood (*11*) investigated the catalytic gasification of graphite by nickel in steam, hydrogen, and oxygen. Channeling of the graphite by nickel in steam was reported but did not occur until a temperature of 935°C was reached.

Recently we reported (*13, 14*) that methane may be produced from the catalyzed reaction of high density graphite and water vapor at low temperatures (200–300°C) to produce methane and carbon dioxide. The reaction is catalyzed by potassium hydroxide and potassium carbonate as well as by other alkali hydroxides. When this reaction was catalyzed by potassium compounds, an activation energy of 11.9 ± 0.5 kcal/mole (for the $CH_4$ production) was measured in the temperature range 200–300°C.

In the present study, CAEM has been

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used to examine the morphology of the high density graphite during the course of the gasification reaction. Thin specimens of highly oriented pyrolytic graphite were obtained by cleavage from similar specimens to those used in the kinetic studies. Potassium hydroxide was introduced onto the surface of the graphite by dipping the specimens, supported on copper or nickel grids, into a 0.38 *M* solution of the hydroxide and then drying them. Transmission electron microscopy was carried out in a Hitachi 650 keV microscope equipped with a Gatan environmental cell and single-tilt heating stage. Argon, at ~1 atm pressure, was bubbled through water at room temperature, giving an Ar/$H_2O$ ratio of about 40/1, and then introduced into the environmental cell to give a pressure of 50 Torr. The specimens were heated in the flowing gas mixture and periodically observed. At 500°C the potassium hydroxide was dispersed as particles 0.1–0.5 $\mu$m in diameter on the surface of the graphite. Auger electron spectroscopy failed to detect impurities at the surface of the graphite used in these experiments. Only graphite and potassium hydroxide were detected in electron diffraction studies of the samples after mounting on the grids and immersion in KOH. With increasing exposure time, gasification was evident as the particles at the edges of the graphite crystals began moving toward the crystal centers leaving channels in their wake.

Figure 1 shows two micrographs recorded 11 min apart taken from a sequence showing the channel growth at 500°C. Channels are evident in two adjacent graphite crystals emanating from the edges of the crystals, each channel with a particle at its head. The interface between the particles in the channels and the graphite shows a hexagonal, faceted morphology. As the reaction continues the particles move and the length of the channels increase, as can be seen by the particles that are indicated by the arrows. The channels remain roughly parallel sided indicating that there is little effect of uncatalyzed reaction at the channel edges, or of wetting of the channel sides by catalytic material. Initially, particles lying on the surface of the graphite crystals do not contribute to the catalytic gasification of the carbon. At a later stage, however, faceted pits in the graphite are evident at the former positions of these particles. The catalyst particles are present within, and at one edge of, the pits. In some cases channeling by these particles away from the original pits is evident.

Similar observations have been noted at 600°C. At this temperature, however, no "incubation" period was noted for the catalytic reaction involving the particles dispersed on the surfaces of the graphite crystals and widespread channeling due to gasification was observed from the outset. Figure 2 shows two micrographs taken from the same area undergoing catalytic gasification at 600°C under the same gas conditions as before. The micrographs were taken 10 min apart and the first was taken after only a 2-min exposure. Some of the catalytic particles are large and form wide channels up to ~1 $\mu$m wide, extending from the edge of the crystal. Channeling is also evident originating at pits, away from the edges of the crystal, again with particles at the heads of the channels. The channels are not straight-sided and there is a general enlarging of the pits. This suggests a wider dispersion of the catalytic phase, possibly as a liquid, forming a thin film along the crystal edges and around the edges of the pits.

Because a pronounced catalytic activity of the KOH in the graphite was observed during these CAEM studies at 500°C and at higher temperatures, it was desirable to extend our kinetic investigations that were carried out in the 200–300°C range, up to 600°C. The purpose was to check whether the same mechanism was responsible for $CH_4$ production at 300°C as well as at 600°C by measuring the rates and activation energies over a wider temperature range. Therefore, a sample of high density graphite simi-

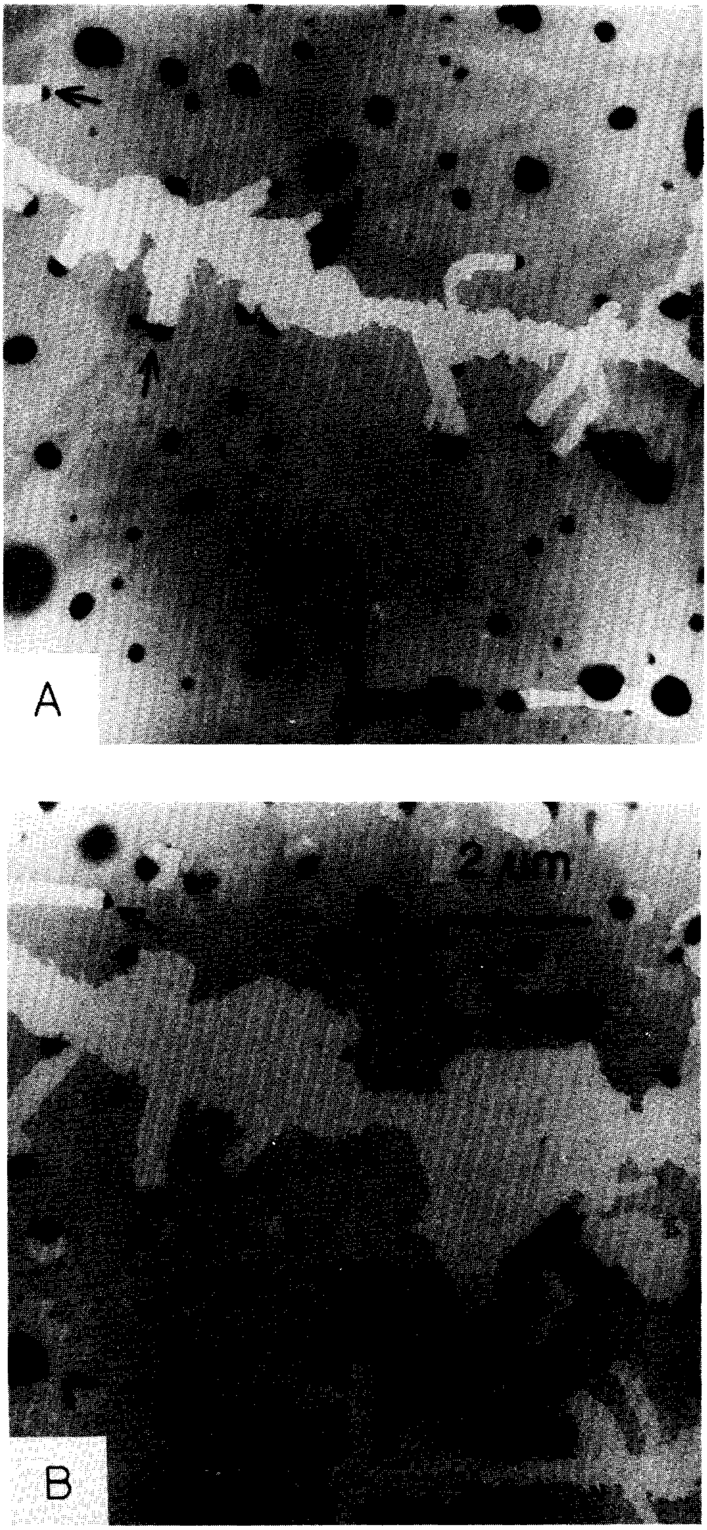

FIG. 1. Catalytic channeling by KOH at 500°C in $H_2O$ + Ar: (A) 22-min exposure, (B) 33-min exposure.

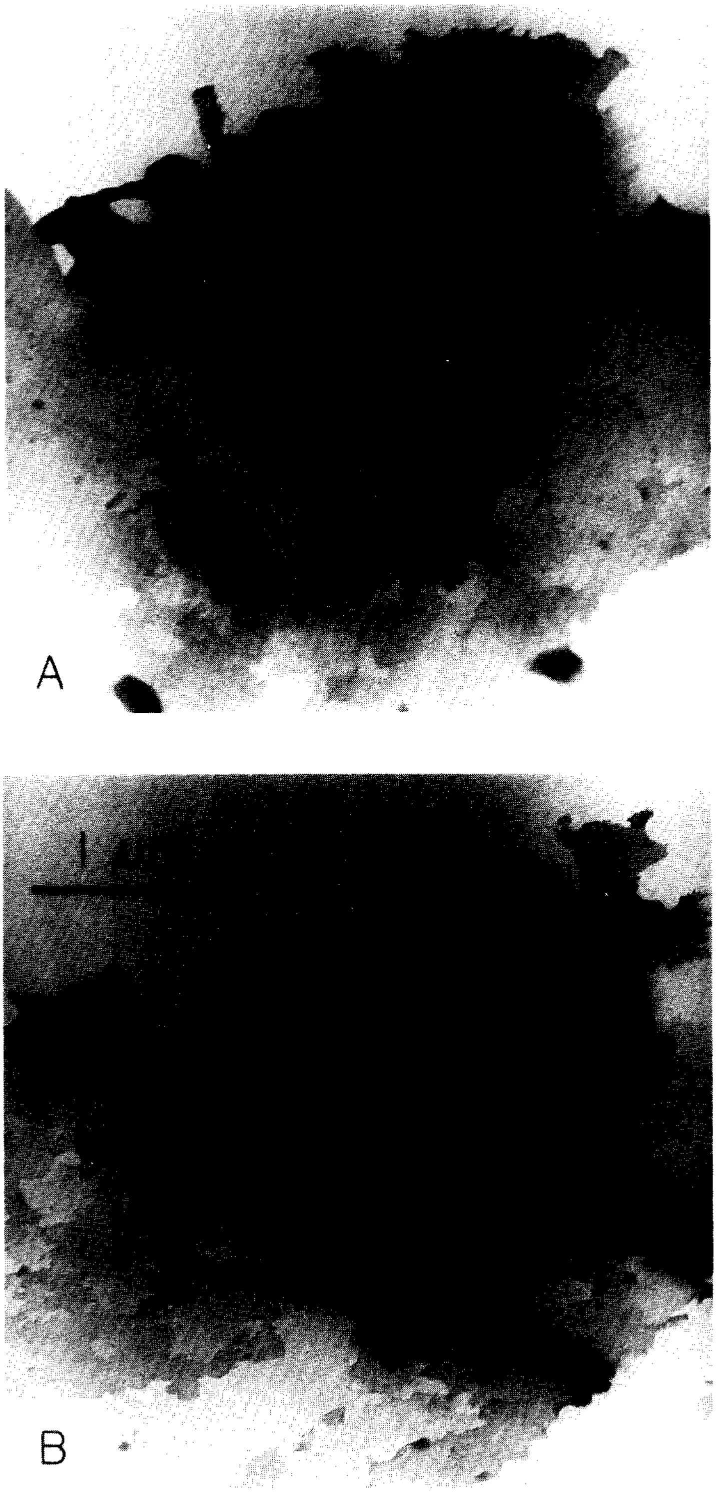

FIG. 2. Catalytic gasification of carbon by KOH at 600°C in $H_2O$ + Ar: (A) 2-min exposure, (B) 12-min exposure.

lar to those used in previous studies (*13, 14*) was impregnated with a 0.38 *M* solution of KOH. Then, it was exposed to a mixture of 20 Torr of water vapor and 1 atm of purified helium and heated to the desired temperature. The surface composition was monitored by Auger electron spectroscopy (AES) before and after reaction and the reaction products were measured by means of a high-performance gas chromatograph with a thermal conductivity detector. The apparatus used in these experiments has been described elsewhere (*13, 14*). Since high temperatures (~600°C) were needed in these experiments we switched from our previous method of direct heating of the graphite (resistively heating the graphite by a high current ac power supply) to indirect heating (resistively heating a gold foil that was in contact with one face of the graphite crystal). The steady state rates for $CH_4$ production were measured at different temperatures between 300 and 600°C. In order to obtain a turnover frequency, the rates were divided by the total number of carbon surface atoms exposed (assuming $1 \times 10^{15}$ atoms per 1 $cm^2$). The logarithms of the turnover frequency as a function of the inverse absolute temperature were plotted and are displayed in Fig. 3. From this figure an activation energy of 11 ± 1 kcal/mole is obtained in good agreement with our previous experiments at much lower temperatures.

Pronounced increase in the amount of $CH_4$ produced was observed from one graphite sample to another, when only the thickness of the samples was increased. This indicates that most of the active sites for this reaction are located on the edges of the graphite crystals. It is not surprising then, that scattering in the turnover frequencies is found, since it is very difficult to accurately reproduce the morphology of these edges when the samples are cut from a larger piece of graphite.

At high temperatures (over 500°C) a significant amount of the KOH was desorbed form the graphite basal plane, as revealed by AES and thermal desorption experiments (*14*). This partial loss of the catalyst might be responsible for a lower rate of $CH_4$ production than the rate expected at 600°C.

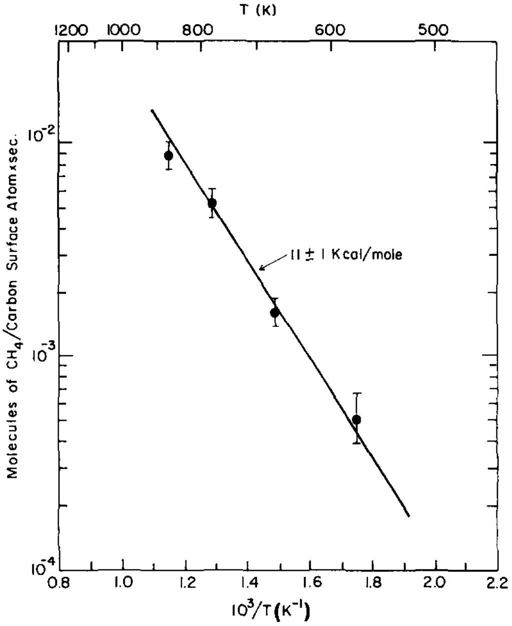

FIG. 3. Logarithm of the $CH_4$ production rate as a function of the inverse absolute temperature for the KOH-catalyzed reaction of graphite and water vapor.

It is evident that a similar mechanism of catalytic gasification of graphite in water vapor by potassium hydroxide occurs at 500 and 600°C, causing channeling of the graphite in contact with the catalyst particles. The identical activation energy that was observed for the reaction at low (300°C) and at high (600°C) temperatures suggests that the mechanism of the reaction is unchanged throughout the temperature range 200–600°C.

This work shows that gasification of graphite with water vapor occurs catalytically and by a channeling mode from the edges inward. The temperatures at which this is observed are much lower than has previously been found using metal catalysts and may have significant implications in the low temperature gasification of coal and other carbonaceous materials. The results of CAEM investigations at lower temperatures which are currently being undertaken will be reported subsequently.

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