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# Fundamental Differences in the Mechanisms of Carbon Gasification by Steam and by Carbon Dioxide

## INTRODUCTION

Since the work done by the Hinshelwood school, the mechanisms of the C–$H_2O$ reaction (*1*, *2*) and the C–$CO_2$ reaction (*3–5*) have been considered to be essentially the same (*6*). The rates in all these studies as measured by changes of mass or evolved gas analysis were the total rates over all edges and crystallographic faces of graphite. As the active sites were not known, it was not possible to measure the rate as a turnover frequency. Such measurement became possible by the use of electron microscopy (*7*, *8*). Among the electron microscopic techniques, the most useful is etch-decoration transmission electron microscopy (TEM) which has made it possible to study the gas–carbon reactions on a truly atomic scale.

The etch-decoration TEM technique has been used to study the C–$H_2O$ and C–$CO_2$ reactions at 600°C, and fundamental differences in the two reactions are observed.

## EXPERIMENTAL

The experimental technique consists of etch-decoration followed by examination with TEM. The technique, described elsewhere (*7*, *9*), consists of cleaving single crystals (natural graphite from Ticonderoga, N.Y.) to a thickness of a few hundred angstroms, etching the graphite in a gas ($H_2O$ or $CO_2$ in this work) which expands surface vacancies to create pits one atomic layer deep, decorating the edge of the pits with gold nuclei, and examining with TEM. The radius or the size of the pit is proportional to the time of etching. The atoms on the edge of the pit are the active sites. From the pit growth rate, we are able to calculate the turnover frequency in terms of the number of carbon atoms removed per active site per unit time.

In studying the C–$H_2O$ and C–$CO_2$ reactions, precautions must be taken in removing traces of $O_2$ from the "inert" carrier gas. The ratio of the overall rates as measured by TGA or evolved gas analysis (for all crystallographic planes of graphite) for the $O_2/H_2O$ reactions is approximately $10^5/3$ under conditions usually reported in the literature (*6*). Thus the gasification rates by 1 ppm of $O_2$ is approximately the same as the rate by 23 Torr of $H_2O$; and most of the commercial grades of the inert gases, e.g., $N_2$ and Ar, contain more than 1 ppm of $O_2$. In this study an "Oxygen-Free" grade $N_2$ (<0.5 ppm $O_2$, Linde) was used as the carrier gas. The gas was further purified by flowing through a preheater column packed with copper turnings maintained at 550°C to remove the residual $O_2$ in the gas stream. Oxidation of copper turnings by $H_2O$ or $CO_2$ is undetectable at this temperature as concluded from our TGA measurements. Water vapor was introduced by passing the $N_2$ through distilled water, which was outgassed prior to each run. Other details are available elsewhere (*9*).

## RESULTS AND DISCUSSION

All reactions were carried out at 600°C. The reaction with $H_2O$ was at 23 Torr of water vapor in 1 atm of $N_2$ for 14 hr. The $CO_2$ reaction was at 1 atm of $CO_2$ for 2 hr.

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All reactions started from the residual vacancies present on the basal plane of graphite. The density of the natural vacancies can be counted as the density of the etch pits as seen in the electron micrograph.

### *The C–$CO_2$ Reaction*

A typical electron micrograph of the gold decorated basal plane etched by $CO_2$ is shown in Fig. 1. Like the C–$O_2$ reaction, all etch pits are circular. But unlike the C–$O_2$ reaction, the pits are unusually uniform in size (*10, 11*). This result shows that (a) $CO_2$ does not create vacancies on the basal plane at 600°C, and more important, (b) the chemisorption–surface diffusion mechanism is absent in the C–$CO_2$ reaction at 600°C. Thus, all gasification events are

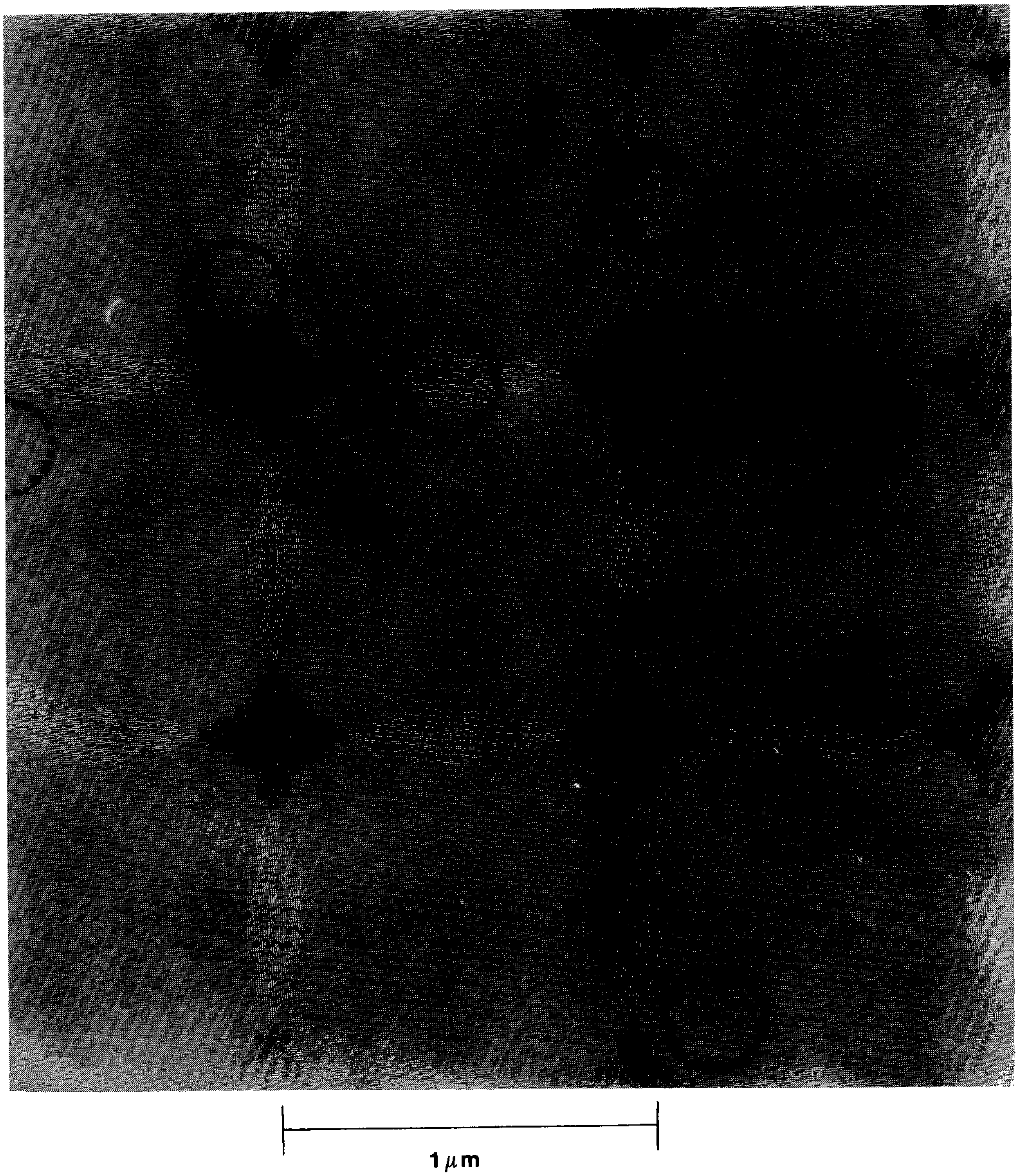

FIG. 1. TEM micrograph of gold-decorated monolayer pits on the basal plane of graphite produced by reaction with 1 atm $CO_2$ at 600°C for 2 hr.

caused by direct collision of $CO_2$ on the active sites, or the edge carbon atoms.

The turnover frequency is 0.112 $sec^{-1}$ for the $C-CO_2$ reaction at 1 atm $CO_2$ and 600°C.

### *The $C-H_2O$ Reaction*

An etch-decoration electron micrograph for the $C-H_2O$ reaction is shown in Fig. 2. All etch pits by $H_2O$ are hexagonal in

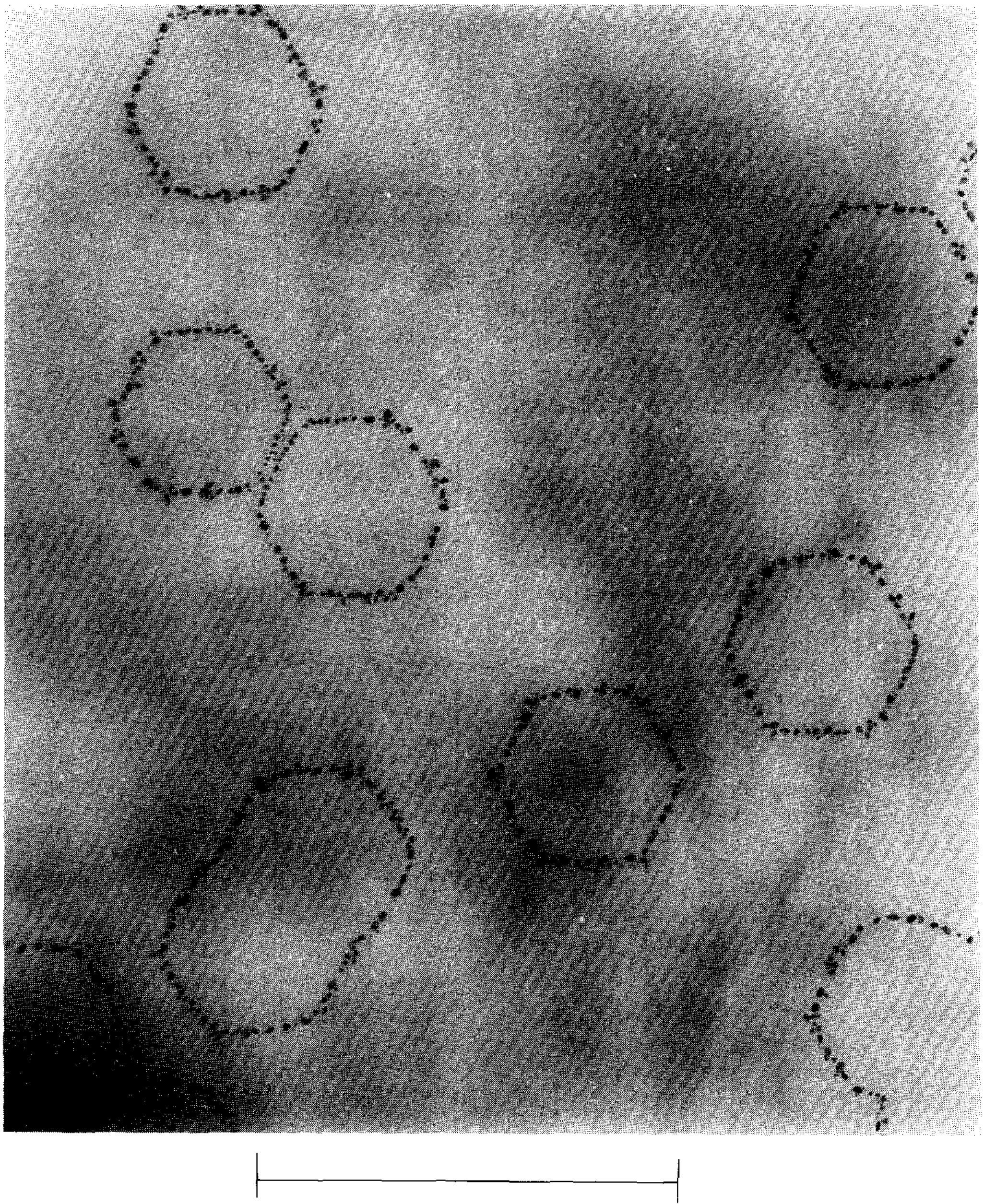

FIG. 2. TEM micrograph of gold-decorated monolayer pits on basal plane etched by 23 Torr $H_2O$ (in 1 atm $N_2$) at 600°C for 14 hr.

shape, and all have the same orientation. The orientation was identified by matching the electron micrograph with its selected area electron diffraction pattern using TEM. The etch pits are composed of $\{10\bar{1}0\}$ faces, or the zig-zag planes, on the six sides. To understand these results, the discussion must be made in conjunction with the formation of circular pits by $O_2$ and $CO_2$, which was not understood.

The origin of etch pits is largely from single vacancies, as discussed by Dawson and Follett (*12*). The active sites are carbon atoms with one unbonded or free $sp^2$ electron. These atoms are more active than the fully bonded, or "bulk" atoms. Figure 3 illustrates the early development of the etch pit starting from a single vacancy. It is seen that after the first three layers of active sites are removed, the pit is already bonded by the surface atoms which form a hexagon, and the sides of which are the zig-zag or $\{10\bar{1}0\}$ faces. Further removal of the active sites, layer by layer, will simply expand the hexagonal pit. To form a circular pit, on the other hand, will require additional removal of atoms near the middle of each side, or making the hexagon rounded. Once rounded, continued removal will lead to a larger circular pit. Thus, the conformation of etch pits is determined in the early stage of pit expansion. In the early stage, after a few layers removed, the dimension of the pit (a few angstroms) is relatively small compared to the collision diameter of the reactant gas molecules (ca. 4 Å for $O_2$) and, therefore, the probability of removal of the corner atoms in the hexagonal pit is hindered due to steric reasons. A support of this has been obtained in the reaction of the basal plane of graphite by oxygen atoms. It has been shown that O atoms (at room temperature) forms hexagonal pits with $\{10\bar{1}0\}$ faces (*16*), whereas $O_2$ creates circular pits. It is known that the first step in both $H_2O$ and $CO_2$ reactions with carbon is the attack and bonding of the oxygen (in $H_2O$ or $CO_2$) with the carbon active site. The $CO_2$ molecule is a linear one. Thus it is expected that the conformation of the pit produced by $CO_2$ is the same as that by $O_2$, because the two oxygen atoms at the two ends have the same reactivity. The $H_2O$ molecule, however, is a triangular one with oxygen in the middle. Thus it is not surprising that the oxygen may attack the corner carbon atoms in the hexagonal pit unhindered and thereby preserving the hexagonal shape.

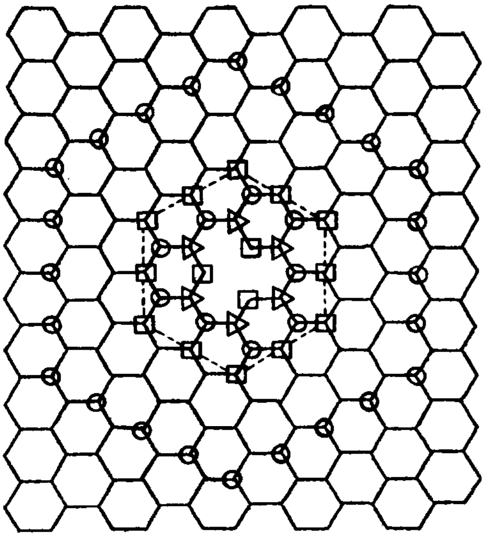

FIG. 3. Conformation of etch pit from a single vacancy in the early development. The symbols denote surface atoms at each step during pit expansion.

The turnover frequency of the C–$H_2O$ reaction is, like the C–$O_2$ reaction, dependent on the density of the pits on the surface. For example, it is 0.037 $sec^{-1}$ at 1 pit/$\mu^2$, and 0.022 $sec^{-1}$ at 3 pit/$\mu^2$.

### *The Surface Diffusion Mechanism in the C–$O_2$ and C–$H_2O$ Reactions*

It has been demonstrated, by several independent experiments, that in the C–$O_2$ reaction at 650°C, the "nonactive" sites can make a substantial contribution to the turnover frequency at the active sites on surfaces with a low density of active sites (*10, 11*). This is probably caused by $O_2$ chemisorbed on the basal plane carbon atoms (as well as on the edge atoms) and the chemisorbed oxygen contributes to the turnover frequency of the edge atoms via a surface diffusion mechanism *(10, 11)*. At slightly higher temperatures, e.g., 700°C, chemisorption of $O_2$ from the gas phase on the basal plane becomes strong enough that new vacancies are created on the perfect plane. The kinetics of the creation of these new vacancies is presently under study in our laboratory. However, the important question on the nature of the bonding and the structure of the chemisorbed oxygen remained unresolved. The chemisorbed oxygen cannot be in the atomic state because O atoms can create new vacancies efficiently at relatively low temperatures, e.g., room temperature.

Figure 4 shows the dependence of the turnover frequency (which is proportional to the pit size) on the density of pits. Such dependency indicates the contribution of the "nonactive" sites (through the surface diffusion mechanism) to the overall turnover frequency. Such a mechanism is clearly important in the $C-H_2O$ reaction at pit densities below ca. 1 $\mu^{-2}$. An interesting comparison may be made between the reactions of carbon with $H_2O$ and $O_2$. As seen in Fig. 4, the dependence is very strong for $C-O_2$ and the dependence extends to a rather high pit density (up to 10 $\mu^{-2}$), whereas it is seen for $C-H_2O$ only at low pit densities (below 1 $\mu^{-2}$). This comparison indicates that a much greater amount of chemisorption for $C-O_2$ (0.2 atm $O_2$ at 650°C) occurs than that for $C-H_2O$ (23 Torr $H_2O$ at 600°C). For the $C-CO_2$ reaction at 600°C

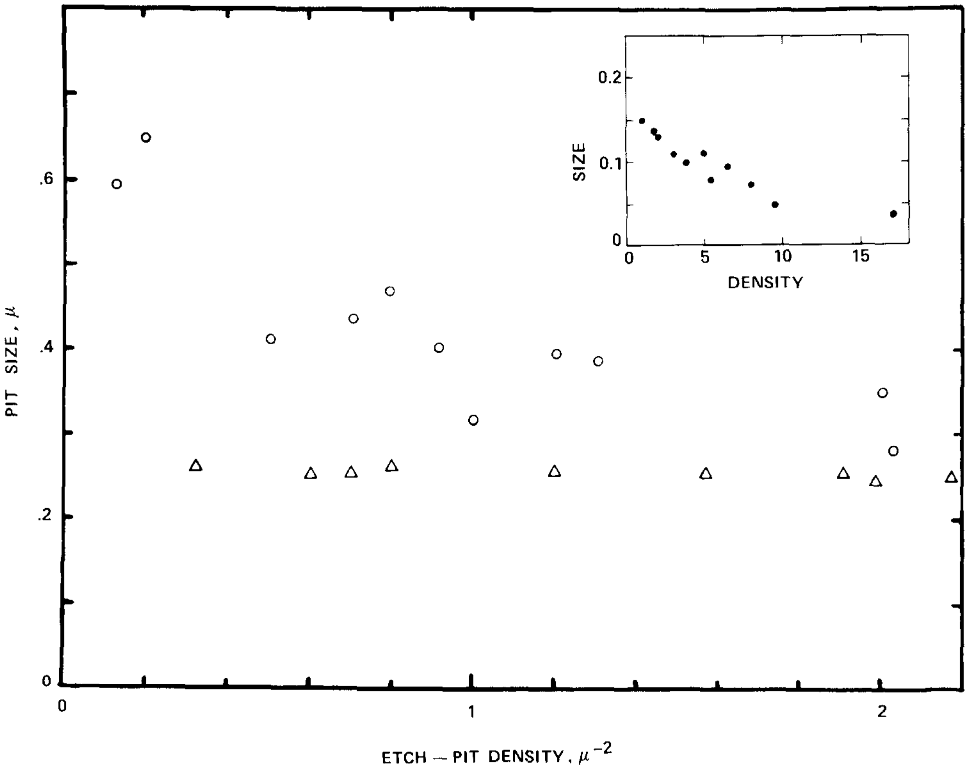

FIG. 4. Dependence of the pit size, which is proportional to the turnover frequency of carbon gasification, on the density of pits, for the $C-H_2O$ reaction (23 Torr $H_2O$, 600°C, 14 hr) (○), the $C-CO_2$ reaction (1 atm $CO_2$, 600°C, 2 hr) (△), and the $C-O_2$ reaction (0.2 atm. $O_2$, 650°C, 20 min) (upper right corner, Ref. *(11)*).

with 1 atm $CO_2$, it is seen that the nonactive sites do not contribute to the rate.

### *Relative Gasification Rates by $O_2$, $H_2O$, and $CO_2$*

The relative rates reported for a polycrystalline graphite at 0.1 atm and 800°C were $10^5$, 3, and 1, for $O_2$, $H_2O$, and $CO_2$, respectively (*6*). The relative turnover frequencies on the edge atoms of monolayer pits, as measured here, are substantially different. The ratios for $O_2/H_2O/CO_2$ at 23 Torr and 600°C are 35/11/1 for a pit density of 1 $\mu^{-2}$, and 22/3.4/1 for high pit densities where the "nonactive" sites do not contribute to the rate (or, the leveled-off rates in Fig. 4). In calculating these ratios, extrapolations were made based on (a) the rate with $O_2$ is proportional to $P_{O_2}{}^{1/2}$ (*7, 8*), (b) the rate with $CO_2$ is proportional to $P_{CO_2}$, and (c) the activation energy for the C–$O_2$ reaction is 35 kcal (*13*).

The rates on the polycrystalline graphite are total rates on all edges and planes. It is known that the multilayer edges are more reactive toward $O_2$ than the single-layer edges (*13, 14*), and the enhancement factor is as high as 100. Taking into account the multilayer effects for $O_2$ and assuming such effects do not exist for $H_2O$ and $CO_2$, one still faces difficulty in correlating the overall rates with the single layer turnover frequencies.

A final note may be added regarding (1) the conformation of etch pits on graphite observed by earlier workers, and (2) the effects of impurities. Almost all earlier observations on the conformation of etch pits were on deep, rather than monolayer, pits. The deep pits were created by $O_2$ at high temperatures (*8*) or by atomic oxygen at near-ambient temperatures (*15, 16*). Deep pits were also observed for catalyzed C–$O_2$ reactions (*8, 17, 18*). Briefly, both hexagonal, e.g., armchair-sided for C–$O_2$ at below 900°C and zigzag-sided at above 1000°C, and conical pits were reported in these studies. For the atomic oxygen reaction, hexagonal monolayer pits with the zigzag orientation have been found (*16*). Montet and Myers (*19*) studied the $H_2O$ reaction with TEM by first reacting the sample with $O_2$ followed by expansion of the pits with $H_2O$, and circular pits were seen. This result is consistent with our interpretation. However, since the $H_2O$ was generated by bubbling helium through a "30% by volume" of $H_2SO_4$ solution, uncertainties remain regarding the sulfur oxides in the reaction. The turnover frequency calculated from the data by Montet and Myers, by extrapolating to our conditions, is about 50% lower than our data. The impurity question has been addressed in detail elsewhere (*7, 9*). In brief, no differences were observed in rates for the samples cleaned by repetitive acid washing and the samples further purified by annealing at 3000°C or by electron bombardment. The freshly cleaved surface usually does not contain impurities. When it does, with few exceptions such as WC and $Cr_2O_3$ (*9*), all impurity particles create channels or deep pits. The results presented here are without such channels or pits. It is believed that the impurity effects on the results are absent or minimal.

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